A STUDY OF NEW TYPES OF CARBON BLACKS PRODUCED BY THE ELECTRICAL DISCHARGE

Part B: Evaluation and Economics of the New Battery Black and a Study of Other Electric Discharge Blacks

DISSERTATION

Approved:

[redacted]

Presented to the Faculty of the Graduate School of
The University of Texas in Partial
of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

By

Max Banfield, B.S. and M.S. in Ch.E.

tin, Texas

June, 1948

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Dean of the Graduate School

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PREFACE

Joint Responsibility

Because of the great scope and nature of this work, studies in this field necessitated the work of two persons. Hence the work is divided into two parts. Part A, which bears the name of King Irwin Glass, deals primarily with a survey of the literature on carbon black technology, a discussion of the methods of laboratory investigation used by the authors, a description of the construction and operation of the pilot plant, and a description of the properties of the untreated carbon black produced from methane by means of the electric discharge.

Part B, which bears the name of Max Samfield, deals with the properties of the treated black produced from methane by means of the electric discharge, the possibilities for commersialization of the black, carbon work related directly to the gas discharge pilot plant, and the properties of carbon produced from gasoline by means of the electric discharge.

The entire work was shared equally by the two authors, and hence they jointly assume responsibility for the information contained therein.

Signed:

Max Samfield
Max Samfield

King Irwin Glass
King Irwin Glass

Acknowledgement

A special expression of gratitude is given by the authors to Dr. E. P. Schoch, Director of the Bureau of Industrial Chemistry, who guided and encouraged this work.

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Burgess Battery Company
Columbian Carbon Company
Commercial Solvents Corporation
Monsanto Chemical Company

The authors also wish to express their appreciation to Mr. L. L. Antes of the Electrical Engineering Department, who was kind enough to aid them in taking the electron microscope photographs.

A STUDY OF NEW TYPES OF CARBON BLACKS PRODUCED BY THE ELECTRIC DISCHARGE

Table of Contents

Page No.

Table of Contents (continued)

Table of Contents (continued)

PART A: DEVELOPMENT OF A NEW BATTERY BLACK FROM THE METHANE-TO-ACETYLENE PROCESS

Page No.

PART B: EVALUATION AND ECONOMICS OF THE NEW BATTERY BLACK AND A STUDY OF OTHER ELECTRIC DISCHARGE BLACKS

Table of Contents (continued)

Table of Contents (continued)

Page No.

Table of Contents (continued)

Table of Contents (concluded)

INTRODUCTION

Part A of this work dealt primarily with the following subjects: (1) the history of carbon black and the present methods for producing it, (2) the properties and uses of commercial blacks, (3) a description of all the standard tests on carbon black and the tests used in this research work, (4) a description of the experimental work for evaluating the untreated methane-to-acetylene black for use in rubber, (5) a description of the laboratory work on the purification of methane-to-acetylene black for use in dry cell batteries, (6) the design and construction of a continuous pilot plant for purifying the black for use in dry cell batteries, and (7) the operation and determination of the optimum conditions of the pilot plant.

This part of the research work (Part B) is more or less a continuation of the work outlined in Part A, and includes a study of the following: (1) the chemical and physical properties of the methane-to-acetylene carbon, (2) carbon work related directly to the gas discharge chamber; e.g., material balance on the plant (production rate of carbon black) and rate of electrode wear from carbon ash determinations, (3) cost of purifying methane-to-acetylene carbon black for use in dry cell batteries, (4) purification and properties of kerosene-collected methane-to-acetylene carbon, (5) purification and properties of gas oil-collected methane-to-acetylene carbon, (6) purification and properties of gasoline-to-acetylene carbon, and (7) classification and correlation of the properties of gas discharge carbons.

Since Part A is inseparable from Part B; i.e., since both works must be read for a complete understanding of the problem, the sections and figures are numbered consecutively through both parts. This system is used since it was necessary to refer to figures in Part B in Part A and vice versa. The "Table of Contents" for Part B is given in the "Table of Contents" for Part A, and the Table of Contents" of Part A is repeated in the "Table of Contents" of Part B. Such an arrangement makes it much easier for the reader to locate the desired information.

At the end of each Part, the reader will find a "glossary of Technical Terms" in which the more common terms peculiar to the rubber and carbon black industries are defined.

SECTION IV: CHEMICAL AND PHYSICAL PROPERTIES OF THE PURIFIED BATTERY BLACK AND COMPARISON WITH THE UNPURIFIED BLACK

Burgess Battery Tests

The various tests on dry cells made by the Burgess Battery Company have been discussed in Part A. Burgess' results on purified black made by the batch process were also previously given; however, for the sake of comparison, these results are repeated in Table 25 given below, along with results on the Shawinigan black-ore standard mixtures and on samples submitted to Burgess by Commercial Solvents Corporation. The meanings of the abbreviations used in the column headings are explained in the appendix to the table.

Attention is called to the fact that the batch sample (4/20/43) gave a much lower resistivity in a 90/10 mix than any of the other samples submitted. It is necessary, however, always to compare the sample under observation with the Shawinigan standard tested at the same time. Thus the 4/20/43 sample (batch) shows a mix resistance which is 3/5 of that of the Shawinigan black, whereas the 12/23/43 sample (pilot plant) shows about the same resistivity as Shawinigan, the standard Shawinigan sample giving a greater resistivity in the latter test.

The pilot plant sample shows a greater 10-day amperage and about the same 10-day voltage as the batch-treated carbon for the same mix ratio. The primary drawback to University of Texas carbon produced in the pilot plant was its shorter shelf life. For example, University of Texas carbon gave a light industrial test of only 625 minutes after a 3 months shelf life, whereas

TABLE 26

Summary of Burgess Battery Company Tests

Type Black	Ore Black Ratio	Mix Resistance	Cell Type	Amperes	Volts	4 ohm con. to 0.75 min.	Hy. Ind. min. to 0.9	Lt. Ind. min. to 0.9	Signal Corps Tests		
									BA-2 hrs.	BA-39 hrs.	BA-30 hrs.
				10 days							
Batch	90/10	0.6	A	3.8	1.61	---	---	---	60	42	---
Shaw.	90/10	1.0	A	3.2	1.54	---	---	---	62	45	---
Pilot	90/10	1.45	-	8.0	1.55	---	370	750 721	--	--	13.5 13.8
							(3 mo. = 625 min.)				
Pilot	92.5/ 7.5	1.95	-	5.6	1.56	---	381	730 781	--	--	14.9 15.2
							(3 mo. = 649 min.)				
Shaw.	87.5/ 12.5	1.40	-	7.5	1.59	---	371	760 752	--	--	13.7 13.8
							(3 mo. = 724 min.)				
				24 hrs.							
Com. Solv.	86/14	1.95	D	5.8	1.56	417	254	637	--	--	10.1 10.6
Com. Solv.	90/10	4.40	D	4.4	1.56	386	231	593	--	--	9.7 8.5
Shaw.	87/13	1.50	D	6.2	1.59	629	320	750	--	--	12.7 12.6

APPENDIX TO TABLE 25

Nomenclature for the Table

Hv. Ind. — Heavy Industrial Flashlight Test—4 ohms/cell, 4 min. out of 15 min. for 8 hrs./day or 128 min. discharge/day to 0.9 volts. Capacity given in minutes.

Lt. Ind. — Light Industrial Flashlight Test—4 ohms/cell, 4 min./hr. for 8 hrs./day or 32 min. discharge/day to 0.9 volts. Capacity given in minutes.

Signal Corps Test BA-30 — 6-2/3 ohms/cell, 4 min./0.5 hrs., 10 hrs./day, 5 days/week to 0.935 volts. One day—80 min. Capacity given in days.

Signal Corps Test BA-2 — Capacity test. Continuous discharge through 166-2/3 ohm resistance.

Signal Corps Test BA-39 — Intermittent discharge through 36 ohms for 2 min. followed by standing with open circuit for 4 min.

Shaw. — Shawinigan carbon sample used as standard.

Pilot — Carbon purified with University of Texas pilot plant.

Batch — Carbon purified with University of Texas batch process.

Com. Solv. — Commercial Solvents carbon black.

4 ohm con. to 0.75, min. — Flashlight 4 ohm continuous test. Previously described.

Ore/Black Ratio — The weight ratio of manganese dioxide ore to carbon black.

Mix Resistance — Refers to the resistance of the ore-carbon mixture as measured on the Burgess Battery apparatus previously described.

Shawinigan tested at 724 minutes. The problem of overcoming this difference was later attacked separately and will be discussed in a separate heading. In all other respects, this black was comparable with or better than Shawinigan black, and Burgess was highly pleased with its qualities.

Samples sent from the University of Texas laboratories were either uncompressed or only slightly so. Burgess Battery Company wished to know if compression was likely to affect the quality of the black as the black had to be compressed before it could be handled satisfactorily in the battery plant. This was another question which had to be answered, and the work done in connection with this problem is discussed in a following section.

Compression vs Burgess Resistance

In the section above, it was mentioned that the Burgess Company wished to know if compression of the black for handling was detrimental to the mix resistance. Accordingly, this laboratory compressed a sample of the black purified with the pilot plant to various densities and measured the mix resistances. A sample of Shawinigan black was also compressed to various densities and the mix resistances run for comparative purposes.

The samples were placed in a Heathering and Berner dust press and compressed by the hand-wheel. The densities resulting from a given amount of compression could not be calculated in advance; and, moreover, the amount of compression could not be measured, hence a fairly wide range of densities was obtained by trial and error, and a curve of apparent density vs mix resistance was plotted. The values used in plotting the curve are given in Table 26 and the curve is shown in Figure 20.

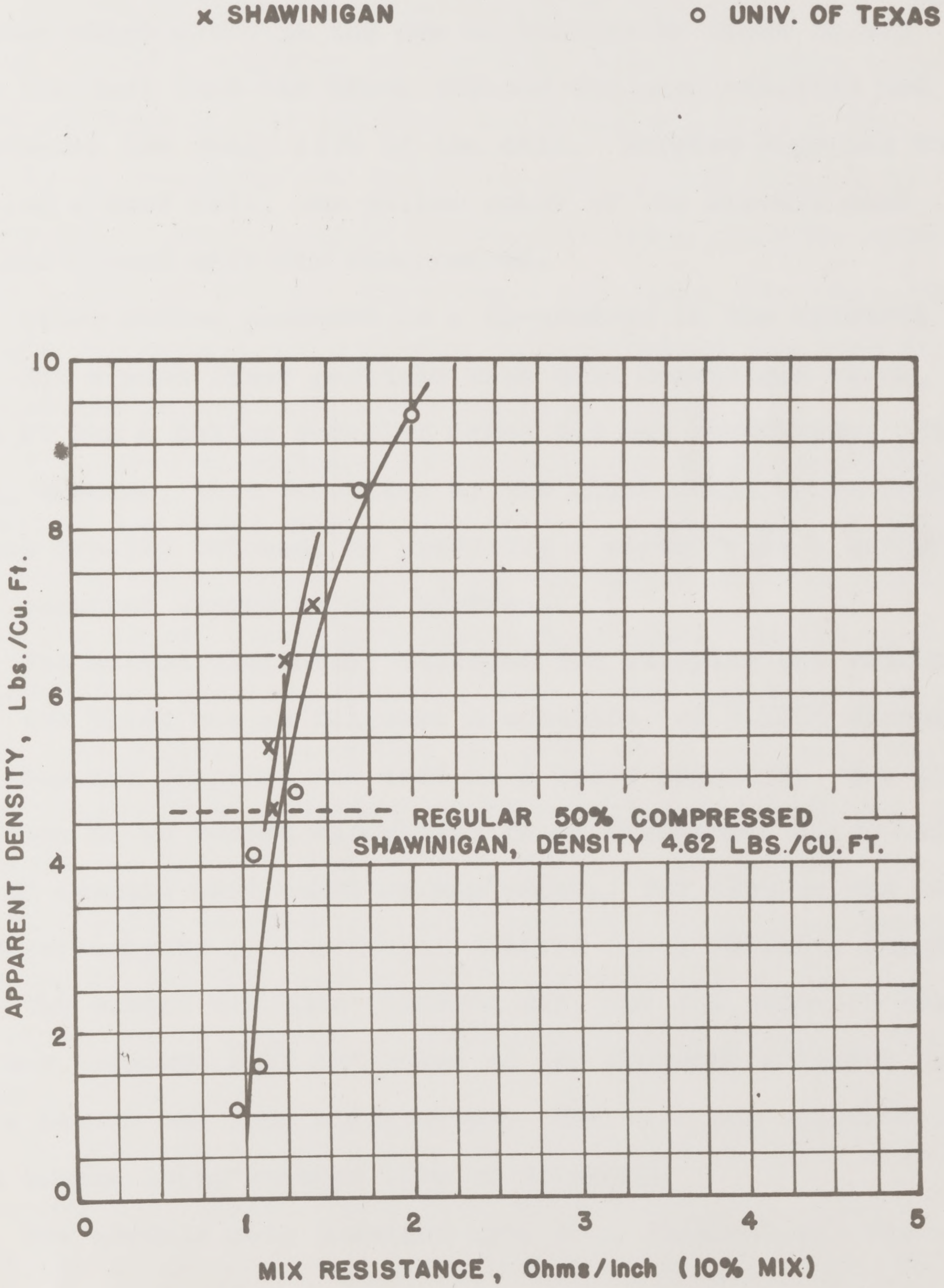
Check results were difficult to obtain with the Burgess apparatus as the values in the table clearly show. The trend of the curve, however, is apparent. The data also show clearly that the curve of Shawinigan black lies definitely to the left of that for University of Texas carbon. Apparently University of Texas carbon approaches Shawinigan carbon in mix resistance at low densities, however, the deviation is too small at low densities to be certain on this point. The data show that 4.62 lbs./cu.ft., the density of regular 50% compressed Shawinigan black, the two curves are for all practical purposes identical. Hence mechanical compression of the carbon should not affect its mix resistance in

TABLE 26

Density-Mix Resistance Values

Type of Carbon	Apparent Density, lbs.cu./ft.	Mix Resistance ohms/column in.
University of Texas Pilot Plant	1.08	0.95
	1.60	1.08
	4.12	1.05 1.10 1.08 average
	4.86	1.29 1.37 1.33 average
	8.42	1.75 1.67 1.71 average
	9.36	2.16 1.87 2.02 average
Shawinigan	4.62	1.18 1.23 1.17 1.19 average
	5.40	1.13 1.21 1.17 average
	6.47	1.24 1.32 1.28 average
	7.11	1.44 1.47 1.46 average

FIGURE 20
APPARENT DENSITY vs MIX RESISTANCE



batteries. A copy of Figure 20 was sent to the Burgess Battery Company, and their views supported the conclusions of the University laboratory.

Chromic Acid Reduction

To prevent polarization of their dry cells, the Burgess Battery Company uses a 0.1% solution of chromic acid. A strip of asbestos paper is wet with this solution, and the paper is then placed next to the zinc electrode inside the cell. One of the difficulties which arose in the use of University black in dry cells was the fact that the black reduced the acid solution and hence shortened the shelf life of the cell. Burgess reported that upon opening a used cell, the yellow color of the chromic acid solution had almost entirely disappeared.

Since carbon produced as a by-product in the electric discharge had a much finer particle size than Shawinigan black, the fact that it was a better reducing agent was not surprising. It was hoped, however, that reduction by the black could be prevented, or at least greatly reduced, by producing a carbon with a larger amount of combined oxygen on the surface.

The method ultimately employed for studying the reducing action of the black was as follows: A solution of 0.125% chromic acid solution was prepared and used as a color standard. One gram of the carbon to be tested was placed in an Erlenmeyer flask and 100 c.c. of chromic acid solution was added. The mixture was then stirred vigorously by an air-driven stirrer for a definite length of time. The carbon was then filtered off, and the color of the filtrate was compared with the color of the standard solution by means of a Bausch and Lomb colorimeter. The test was repeated on the given sample using another time of stirring.

The chromic acid solution used as a standard was run through a filter paper in case the filter paper itself were to possess some reducing power. The results of the tests are reported as per cent color remaining in the solution at a given length of time. The data is presented in Table 27 and the results are illustrated graphically in Figure 21.

Figure 21 shows that the amount of reduction in a given time is not solely a function of the total volatile matter (exclusive of moisture.) For example, the batch sample gave the least amount of reduction and had a volatile matter content of 4.73%. One pilot plant sample (Run No. 18) had a volatile matter content of 5.23% and reduced the chromic acid less than the pilot plant sample having a 4.38% volatile matter content but more than the batch sample having only 4.73% volatile matter.

The above discrepancy is probably due to the fact that in the case of the batch sample,all (or very nearly all) of the volatile matter was combined oxygen on the carbon surface, since the carbon was heated for a longer period of time. In the case of the pilot plant samples, however, part of the volatile matter might have been organic impurities and part of it combined oxygen. The allowable amount of reduction which a carbon may have and still be acceptable for battery use has not yet been determined. However, no difficulty in producing an acceptable black in a commercial plant similar to the one used is anticipated as all of the variables involved may be changed at will with no alteration in the construction of the plant.

In addition to the above considerations, Burgess Battery Company stated very clearly that they would withhold a final opinion of the carbon until at least 100 lbs. was available for

TABLE 27

Reduction of Chromic Acid with Carbon Black

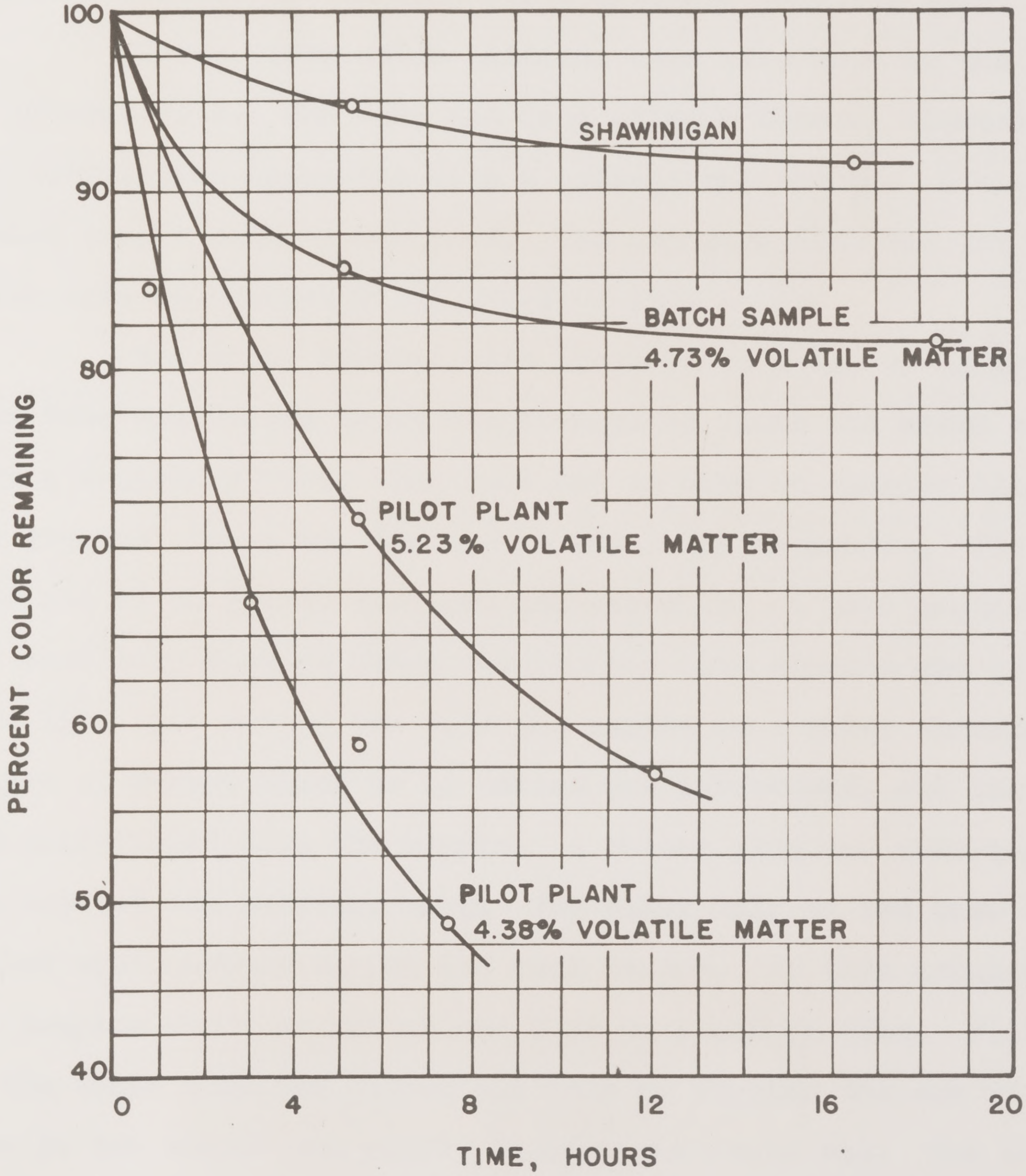
0.125% Chromic Acid Solution
1 Gram Carbon/100 c.c. solution
Zero Colorimeter Reading = 10.0

Sample No.	Time Hrs.	Final Reading	Color Remaining %
	Pilot Plant Sample		
1	0.92	11.8	84.5
2	3.08	15.0	67.0
3	5.50	17.0	58.7
11	7.50	20.5	48.5
	Batch Sample		
12	5.20	11.7	85.5
13	18.30	12.4	80.6
	Shawinigan Black		
14	3.42	10.6	94.4
15	16.50	10.9	91.5

FIGURE 21

PERCENT COLOR REMAINING vs TIME

0.125% CHROMIC ACID SOL. 1 GM. CARBON/100 CC.



testing and that they would have to have at least six months to work with the carbon. Hence a full scale purification unit would have to be built to make the necessary quantities for testing purposes.

X-Ray Diffraction Studies

Monsanto Chemical Company made X-Ray diffraction patterns on treated University black and on Shawinigan black and found that the two blacks were indistinguishable. Both samples showed a slightly graphitic structure, the 002 line being about the same intensity in each and quite diffuse, which was to be expected because of the very small ultimate particle size.

X-Ray diffraction patterns were also made in the University laboratories. The work was done using a General Electric X-Ray diffraction apparatus with a cylindrical camera. A water-cooled copper cathode was used. The exposure time was two hours using Agfa Non-Screen Film, 1-7/8" x 16".

The X-Ray samples were prepared as follows: A Pyrex test tube was heated in an oxygen-methane flame and drawn out to form a capillary tube. The tube had to have an outside diameter not greater than 1 mm. for use in the X-Ray apparatus. The tubes also had to be fairly straight and circular. A good section of the capillary tube so drawn out was cut into lengths not greater than 1½". One end of the tube was sealed in a Meker burner. The sample of carbon black to be tested was introduced, and the tube was half-filled with the sample. A cotton plug was inserted into the tube at the half-way mark. The other half of the tube was filled with another sample and then sealed. By this arrangement, two samples could be run at one time on a single film. Filling of the tubes with the carbon was done by dipping the end of the tube in the sample and gently tapping the lower end. The cotton plug was prepared by rolling a few strands of cotton between the fingers and pushing the roll into the tube with a piece of fine copper wire. The diffraction apparatus had mounted on it a small motor which rotated the sample tube during exposure.

With regard to the oxidized carbon produced in batch operation, the findings of the University laboratory checked the results reported by Monsanto; namely, that Shawinigan black and University black were indistinguishable, both showing slightly graphitic structures. In addition to the two samples mentioned above, patterns were also obtained on pure graphite (for comparative purposes) and on methane-to-acetylene black which had been heated to a high temperature (1100°C). Photographs of the X-Ray patterns obtained on these blacks are shown on the following page. For some unexplained reason, the carbon heated to a high temperature in the presence of steam had a less graphitic structure.

X-Ray data proved to be of little value except for rough comparative purposes. Because of this fact and the fact that X-Ray films were difficult to obtain, this method of analysis was abandoned.

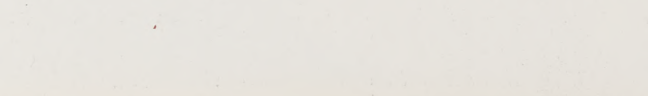
FIGURE 22

X-RAY DIFFRACTION PATTERNS

Graphite

Shawinigan

Batch-Oxidized University Black



Heated in the Presence of Steam to 1100°C

Electron Microscope Observations

Electron microscope photographs of Shawinigan black and treated methane-to-acetylene carbon are shown in the photographs of Figure 23. These photographs were taken in the laboratory of the Monsanto Chemical Company

These photographs show clearly that methane-to-acetylene carbon is different from Shawinigan black in size and shape of the particles. Shawinigan black shows up as "platelets, generally circular in shape." Treated methane-to-acetylene carbon, however, appears as "aggregates of needle-like particles." This is a difference which could not be observed by means of X-Ray diffraction patterns.

Electron microscope pictures of gasoline-to-acetylene carbon and untreated methane-to-acetylene carbon were taken in the University laboratory and are shown later in Figure 39.

FIGURE 23

ELECTRON MICROSCOPE PHOTOGRAPHS
(20,000 x)

University Methane Pilot-Plant Carbon

Shawinigan Black

Dry Compression vs Resistance

At least one investigator[43] has classified carbons according to the slopes of curves obtained when the pressure applied to the carbon is plotted against its resistance. Any cross-section area may be used for the carbon column as long as it is kept constant for all the comparative runs.

The pressure-resistance data were obtained in the University laboratory by using the Burgess resistance apparatus previously described. The weight on the arm of the apparatus was moved to the first notch (15 lbs./sq.in.), and carbon was placed in the porcelain cup. The arm was lowered so that the graphite electrode rested on the carbon column. The height of the column was recorded, and the resistance of the carbon was measured in the conventional manner. Pressures of from 15 to 22 lbs./sq.in. could be obtained.

Tests were run on: (1) unpurified black, (2) black which had been heated at 1100°C in the presence of steam, (3) black which had been purified in the pilot plant (sample sent to Burgess,) and (4) Shawinigan black. The data are given in Table 28 and are shown plotted in Figures 24 and 25.

Shawinigan black is far more incompressible than any of the University blacks. It gives a slope of 0.023 ohms/column in./lb./sq.in. whereas the pilot plant carbon gives a slope of 0.044 or about twice that of Shawinigan black. The untreated carbon is the most compressible with a slope of 0.498. It is interesting to note

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[43] Kaufmann, Charles, <u>Acetylene Carbon Black</u>, Can. Chem. Met., 93 (May 1933.)

TABLE 28

Dry Compression vs Resistance

Pressure lbs/sq.in.	Milli-amperes	Milli-volts	Height in.	Height(corr.) in.	Resistance ohms/in.
		Pilot Plant Sample			
15	1.400	3.83	2.01	1.95	1.40
16	1.400	3.43	1.93	1.87	1.31
17	1.400	3.19	1.88	1.82	1.25
18	1.400	3.04	1.86	1.80	1.21
19	1.401	2.98	1.86	1.80	1.18
20	1.401	2.90	1.84	1.78	1.16
		Steam Treated at 1100°C			
15	1.398	4.12	2.00	1.94	1.52
16	1.398	3.84	1.95	1.89	1.45
17	1.398	3.55	1.91	1.85	1.37
18	1.398	3.55	1.87	1.81	1.32
19	1.398	3.28	1.86	1.80	1.30
20	1.398	3.25	1.85	1.79	1.30
21	1.396	3.15	1.84	1.78	1.27
22	1.396	3.06	1.82	1.76	1.24
		Untreated University Carbon Black			
15	1.000	24.79	2.06	2.00	12.40
16	1.001	23.77	2.03	1.97	12.06
17	1.001	22.79	1.99	1.93	11.80
18	1.002	21.66	1.97	1.91	11.32
19	1.004	20.42	1.93	1.87	10.88
20	1.005	19.39	1.89	1.83	10.54

TABLE 28 (concluded)

Dry Compression vs Resistance

Pressure lbs/sq.in.	Milli-amperes	Milli-volts	Height in.	Height(corr.) in.	Resistance ohms/in.
		Shawinigan Black			
15	1.400	1.68	2.03	1.97	0.61
16	1.400	1.60	1.98	1.92	0.60
17	1.400	1.54	1.96	1.90	0.58
18	1.400	1.49	1.94	1.88	0.56
19	1.400	1.44	1.92	1.86	0.55
20	1.400	1.39	1.89	1.83	0.54
21	1.400	1.35	1.87	1.81	0.53
22	1.400	1.32	1.86	1.80	0.52

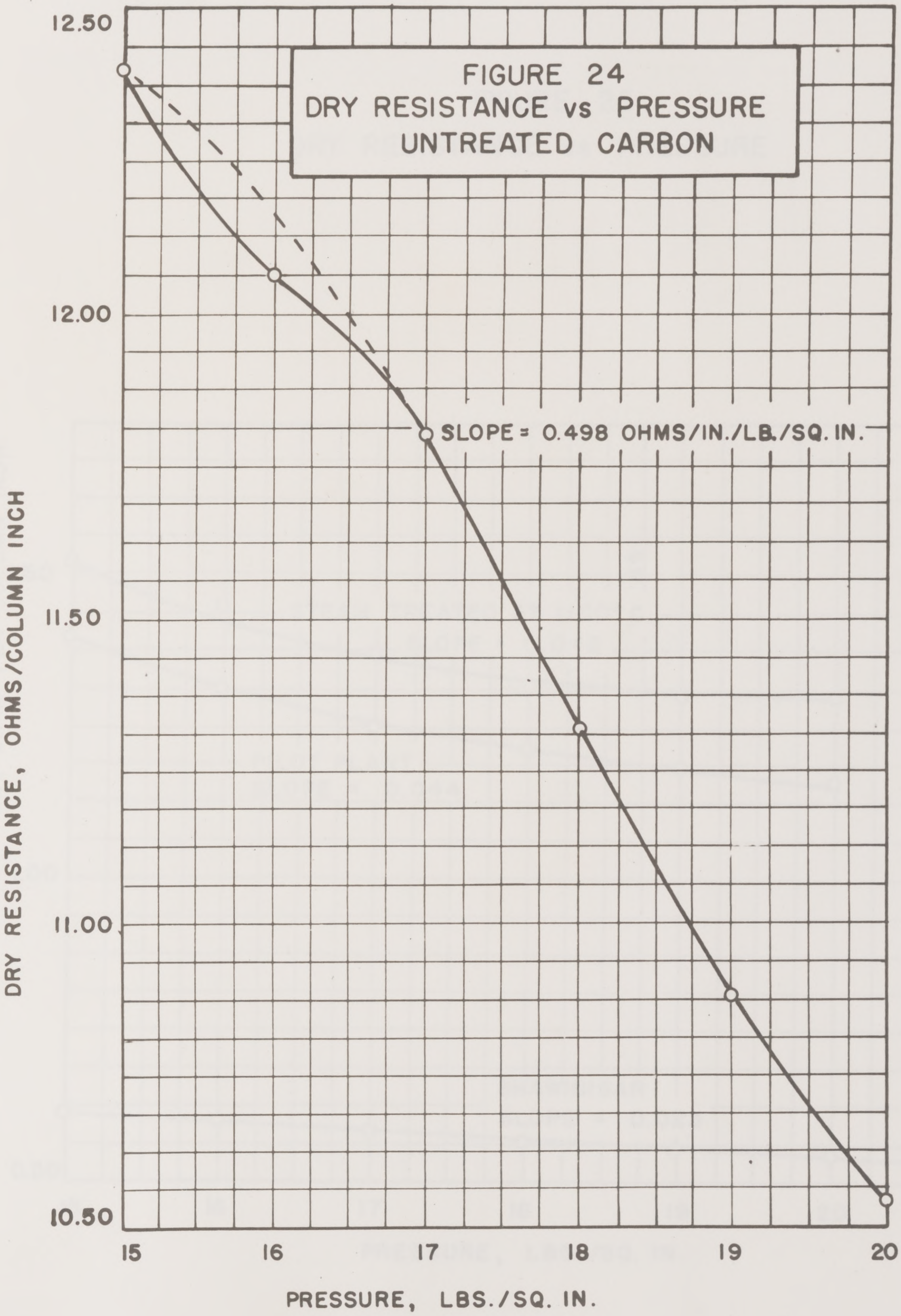
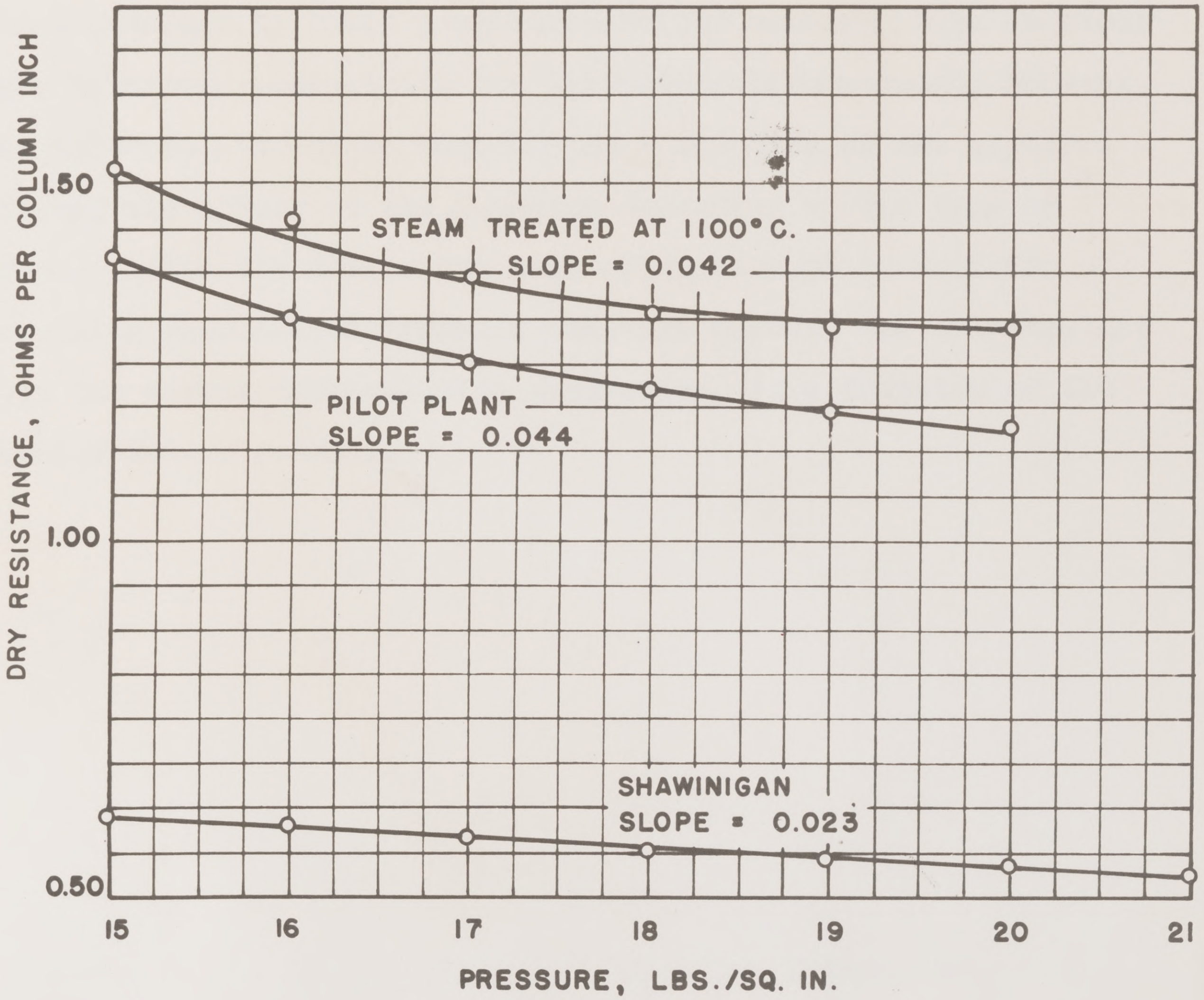


FIGURE 24
DRY RESISTANCE vs PRESSURE
UNTREATED CARBON

FIGURE 25

DRY RESISTANCE vs PRESSURE



that the dry resistance of University treated carbon is much higher than Shawinigan black whereas the two give about the same Burgess mix resistance.

Carbon Tetrachloride and Electrolyte Absorption

An examination of the carbon tetrachloride absorption data of the feed and product carbons listed in Table 23, Section A, shows that the oxidized carbon has an increased absorptive capacity. For example, the feed carbon gave a carbon tetrachloride absorption of 39.1 c.c./5 gms. whereas the product carbon tetrachloride absorptive capacity was 45.0 c.c./5 gms.

Data on carbon tetrachloride absorption values for treated methane-to-acetylene carbon are too scanty to relate the values obtained to other properties of the carbon. Data on other types of carbon produced in the University laboratories, however, show that the absorptive capacity is a function of the apparent density, the nature of the function depending on the type of carbon. Since the data which were obtained were on carbons containing considerable organic volatile matter, the density, and hence the carbon tetrachloride absorption, is a function of the volatile matter content.

pH Value of the Carbon

The method for determining the pH of the carbon sludge has been described in a previous section. Wiegand[44] has related the pH of the carbon sludge and the D.P.G. adsorption to the volatile matter content of the carbon. He has also asserted that carbons may be classified as to type (rubber, high color, etc.) by means of these three properties. (See Figure 48)

The pH value of the pilot plant carbon sent to Burgess Battery Company was determined to be 4.9, corresponding to a volatile content of 4.4%. According to Wiegand's classification, this carbon would fall on the border line between Ultra-Micronex carbons and rubber carbons.

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[44] Wiegand, W. B., pH Properties of Colloidal Carbon, Ind. Eng. Chem., 29, 953 (1937)

Diphenylguanidine Adsorption

The diphenylguanidine adsorption index of the treated carbon was found to be 36.4. This places the carbon in the general classification of rubber carbons, but the D.P.G. adsorption index and per cent volatile matter does not place the carbon on the D.P.G.-volatile matter curves of Wiegand, the D.P.G. adsorption index being much higher than normal for purified methane-to-acetylene carbon. (See Figure 40)

Also according to Wiegand, deactive heat treatment; i.e., heating the carbon to a high temperature in the absence of oxygen, tends to raise the pH and lower the D.P.G. adsorption of the heated carbon slurry. This was found to be the case; for carbon which had been heated in the presence of methane to 1100°C for four hours, gave an adsorption index of 4.8 as compared with 36.4 for the oxidized black.

A complete discussion of the relation between all of the chemical properties of the different carbon blacks will be given in the last two sections of this work.

Discussion and Conclusions

The continuous pilot plant for purifying methane-to-acetylene black for use in dry cell batteries gives a battery black with excellent properties. The product obtained from the pilot plant was almost identical with that previously obtained under batch-purification conditions. The only difference between the batch sample and the pilot plant sample was that the latter gave a slightly shorter battery shelf life than Shawinigan black. This was said to be caused by reduction of the chromic acid inhibitor. A method for measuring the amount of reduction has been designed and described, and a method for correcting this deficiency has been suggested.

It has been shown that mechanical compression of the purified carbon black has little if any effect on the Burgess Battery mix resistance.

X-Ray diffraction patterns have shown that the purified black is indistinguishable from Shawinigan black as far as crystal structure is concerned.

Electron microscope observations, however, have shown that methane-to-acetylene black is very different from Shawinigan black. The former appears as needle-like aggregates whereas the latter appears as platelets.

Dry-compression-resistance tests have shown that Shawinigan black is far more incompressible than either purified or unpurified methane-to-acetylene black, but the unpurified black is far more compressible than the purified black.

Purification of the black by oxidation raises the carbon tetrachloride absorption by about 15%.

The pH of the purified carbon was determined to be 5.9 which, together with the measured volatile content of 4.4%, places the carbon on the border line between Ultra-Micronex and rubber carbons.

Purification of the black raises the D.P.G. adsorption index from about 19%/gm. to about 36%/gm.

SECTION V: CARBON WORK RELATED TO THE GAS DISCHARGE CHAMBER AND THE COST OF PURIFYING METHANE-TO-ACETYLENE CARBON BLACK

Carbon Work Related to Gas Discharge Chamber

Introduction: A description of the gas discharge pilot plant has been amply given in previous works on the electric discharge.[45] One major discrepancy between experimental and calculated results obtained with the pilot plant was in the amount of carbon produced as by-product. By podbielniak analysis of inlet and outlet gas and a material balance, the calculated amount of carbon formed did not agree with the experimental results obtained by actually weighing the carbon collected in the filters. This discrepancy was at first believed to be due to polymer formation. It was thought that the polymers either collected in the discharge chamber, being absorbed on the carbon, or else were condensed on the carbon in the main body of the gas and were carried out to the filters. However, calculations were later made taking into account the amount of polymer contained on the filter carbon, but even this failed to account for the difference between calculated and experimental amounts of carbon formed.

A better explanation was found to lie in the probable amount of carbon held up within the discharge chamber. A portion of this section will deal with the method of estimating the carbon hold-up in the chamber, the calculations involved in a material balance, and a comparison between calculated and experimental results.

The determination of ash in the filter carbon will later

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[45] Kasperik, A. S., Dissertation, University of Texas, 1943.

be shown to be a useful tool in the estimation of electrode wear. The calculations will be presented, and the calculated values of wheel wear will be compared with experimental measurements.

Experimental Determination of Carbon Production in the Gas Discharge Chamber: The actual experimental procedure was extremely simple. The plant was run for a considerable length of time so that the amount of time necessary for the plant to come to equilibrium would be negligible. The plant was then shut down, and the carbon filters were then flushed with air for 2-3 hrs. Three cardboard boxes were covered with canvas attached to the boxes with bailing wire. A hole the size of the filter outlet was cut in the center of the canvas, and an arm-hole was cut in one corner of the canvas. The latter was necessary in order to be able to reach through the top of the box up into the filter so that the carbon could be loosened from the walls with a length of stiff wire. The boxes, together with the canvas and bailing wire, were weighed empty. Then the carbon was collected from each of the three filters in the three boxes. The boxes were then weighed again. This procedure could be carried out with very little, if any, loss of carbon.

From the above data, the length of time the plant was run, the power input, and the cubic feet per hour of inlet gas, the pounds of carbon produced per hour per kilowatt-hour per cubic foot of inlet gas could be calculated. The data on the carbon production of the gas discharge pilot plant are given in the table on the following page. Note that the power input is given as 0.0563 KWH/cu.ft. inlet gas at S.T.P. Data in previous works have reduced the gas measurements to 20°C and 760 mm.

TABLE 29[a]

Experimental Values in the Determination of Carbon Production in the Gas Discharge Pilot Plant

Time of Plant Operation Hrs.	Total Carbon Produced lbs.	Rate of Production lbs/hr.	Relative Resistivity of Carbon	Volatile Matter of Carbon %
23.50	12.99	0.552	22.10	----
23.50	11.11	0.473	23.87	9.80
20.24	9.25	0.457	----	----
46.73	25.98	0.556	24.98	9.85
39.17	19.95	0.510	26.62	10.28
20.00	10.30	0.515	20.95	9.43
Average Value	=	0.511	23.70	9.84

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[a] Conditions of Plant Operation: 24 KW, 426 cu.ft./hr. inlet gas (S.T.P.) or 0.0563 KWH/cu.ft. (S.T.P.) (8 cu.ft./min. at 30°C and 750 mm.)

The above value would be 0.061 KWH/cu.ft. inlet gas at these conditions.

Material Balance On Gas Discharge Chamber: The purpose of the following discussion is: (1) to show that the discrepancy between observed and calculated outlet-to-inlet gas ratios or between observed and calculated amounts of carbon formation is primarily due to the hold-up of carbon within the reaction chamber rather than to polymer formation and condensation. (2) to show that even after 100 plant operating hours, carbon deposition equilibrium within the reaction chamber may not be established, and (3) to arrive at a reasonable figure for the extent of carbon formation for the given plant operating conditions.

The pilot plant operating conditions for the calculations which follow are as follows: 24 KW, 8 cu.ft./min. of inlet gas measured at 30°C and 750 mm. Quantitative measurements on the amount of carbon collected in the filters have already been shown to be 0.811 lbs/hr. for a plant operating at the above conditions. The average amount of volatile matter on the carbon is about 9.84% as determined from three sets of analyses. The experimentally determined ratio of outlet to inlet gas was 1.337:1.

In order to see if the amount of polymer on the carbon varied at different points within the pilot plant discharge lines, samples of carbon were removed at different points in the plant and analyzed. Samples were taken in the carbon filters, the heat exchanger outlet, the heat exchanger inlet, and in the main discharge chamber. The results are shown below:

Location	Volatile Matter,%	Relative Resistivity
Filters	9.85	24.98
Exchanger Inlet	----	54.20
Exchanger Outlet	11.01	44.90
Discharge Chamber	20.26	2437

The above data show that, as might be expected, the amount of polymer on the carbon increases as the reaction chamber is approached from the outlet side. Just what per cent of the total polymer the amount in the discharge chamber represented could not be determined until the hold-up in the chamber was estimated.

The Dow Chemical Company has reported the following Podbielniak analysis on the pilot plant gas:

TABLE 30

Podbielniak Analysis of Discharge Pilot Plant Gas

Constituent	Feed, %	Product, %
CO_2	1.1	0.6
CO	0.0	0.6
CH_4	91.6	45.2
C_2H_2	0.0	9.1
C_2H_4	0.0	0.5
C_2H_6	4.1	2.9
C_3H_8	1.6	0.5
I-C_4H_{10}	0.3	0.0
N-C_4H_{10}	0.3	0.2
C_5H_{12}	0.3	0.3
C_6+ (considered as C_7H_{16})	0.3	0.4
H_2	0.0	39.2
N_2	0.4	0.5
Total	100.0	100.0

To calculate the amount of chamber hold-up, one can proceed as follows: Take the basis for calculation, 100 cu.ft. of inlet gas at S.T.P. The amount of inlet material will then be:

Cu.ft. CH_4 = 91.6 = 0.25515 mols = 4.091 lbs.
" " CO_2 = 1.1 = 0.00306 mols = 0.135 lbs.
" " CO = 0.0 = 0.00000 mols = 0.000 lbs.
" " C_2H_2 = 0.0 = 0.00000 mols = 0.000 lbs.
" " C_2H_4 = 0.0 = 0.00000 mols = 0.000 lbs.
" " C_2H_6 = 4.1 = 0.01142 mols = 0.343 lbs.
" " C_3H_8 = 1.6 = 0.00446 mols = 0.196 lbs.
" " C_4H_{10} = 0.6 = 0.00167 mols = 0.097 lbs.
" " C_5H_{12} = 0.3 = 0.00084 mols = 0.061 lbs.
" " C_6+ = 0.3 = 0.00084 mols = 0.084 lbs.
(considered as C_7H_{16})
" " H_2 = 0.0 = 0.00000 mols = 0.000 lbs.
" " N_2 = 0.4 = 0.00111 mols = <u>0.031</u> lbs.
Total lbs./100 cu.ft. gas = 5.038

Now let y = cu.ft. outlet gas/cu.ft. of inlet gas. Experimentally, the value of y was found to be 1.337, but for the moment it will be assumed that this quantity is unknown in order that an equation may be derived with both y and x, the amount of the chamber hold-up, plus amount collected in the filters as unknowns.

The amount of outlet material will then be:

Cu.ft. CH_4 = 45.2y = 0.12591y mols = 2.019y lbs.

" " CO_2 = 0.6y = 0.00167y mols = 0.074y lbs.

" " CO = 0.6y = 0.00167y mols = 0.047y lbs.

" " C_2H_2 = 9.1y = 0.02535y mols = 0.660y lbs.

" " C_2H_4 = 0.5y = 0.00139y mols = 0.039y lbs.

" " C_2H_6 = 2.9y = 0.00808y mols = 0.243y lbs.

" " C_3H_8 = 0.5y = 0.00139y mols = 0.061y lbs.

" " C_4H_{10} = 0.2y = 0.00056y mols = 0.033y lbs.

" " C_5H_{12} = 0.3y = 0.00084y mols = 0.061y lbs.

" " C_6+ = 0.4y = 0.00111y mols = 0.111y lbs.
(considered as C_7H_{16})

" " N_2 = 0.5y = 0.00139y mols = 0.039y lbs.

" " H_2 = 39.2y = 0.10919y mols = 0.220y lbs.

Total lbs./100 cu.ft. outlet gas = 3.604y lbs.

Equating the inlet and outlet material:

$$3.604y + x = 5.038$$

If first it is assumed that the experimental ratio of inlet to outlet gas, 1.337, is correct, then:

$$(3.604)(1.337) - 5.038 = x$$

or x = 0.220 lbs. of polymer plus carbon formed per 100 cu.ft. of inlet gas measured at S.T.P. Reducing the inlet gas rate to standard conditions:

$$\text{Cu.ft./min.} = \frac{(492)(750)(8)}{(546)(760)} = 7.11 \text{ at S.T.P.}$$

$$7.11 \text{ cu.ft./min.} = (7.11)(60) = 426.6 \text{ cu.ft./hr.}$$

$$\text{The lbs. of carbon + polymer/hr.} = \frac{(426.6)(0.220)}{100} = 0.939$$

The amount of carbon + polymer recovered from the filters = 0.511 lbs./hr.

The holdup in the chamber will then be:

0.939 - 0.511 = 0.428 lbs. carbon + polymer/hr.

The dimensions of the inside of the reaction chamber were measured as follows:

Overall Dimensions = 88" x 96" x 19½"

$$\text{Area of the sides} = \frac{(2)(8)(88)}{(12)} = \qquad 117.0 \text{ sq.ft.}$$

$$\text{Area of top and bottom} = \frac{(2)(19.5)(88)}{(12)(12)} = 23.8 \text{ sq.ft.}$$

$$\text{Area of the ends} = \frac{(2)(19.5)(8)}{(12)} = \qquad 26.0 \text{ sq.ft.}$$

$$\text{Total area of angle irons} = \qquad \underline{10.0} \text{ sq.ft.}$$

$$\text{Total inside area} = \qquad 176.8 \text{ sq.ft.}$$

The average density of the reaction chamber carbon was 2 lbs./cu.ft. Measurement showed it to have an average thickness of about 1/2" on the walls. The amount present in the reaction chamber would then be:

$$\frac{(176.8)(2)}{(2)(12)} = 14.7 \text{ lbs.}$$

Hence the holdup would be 0.147 lbs. carbon + polymer per hour assuming uniform build-up. Since 0.511 lbs. carbon + polymer per hour were removed from the filters, the total amount formed per hour would be:

0.511 + 0.147 = 0.658 lbs. carbon + polymer/hr.

This represents 0.1548 lbs./100 cu.ft. inlet gas.

$$3.604y + 0.1548 = 5.038 \qquad \text{or}$$

$$y = 1.350$$

The experimental ratio was found to be 1.337:1, hence an error of only 0.96% is involved. An error in the gas analysis could very easily make up this difference since some of the constituents were reported to only one significant figure.

The chamber carbon was found to contain 20.26% volatile matter. The actual carbon held up in the chamber is, then:

$$(0.147)(0.7974) = 0.118 \text{ lbs./hr.}$$

The average volatile content of the filter carbon is 9.84%. The actual carbon collected in the filters will then be:

$$(0.511)(0.9016) = 0.460 \text{ lbs./hr.}$$

The total actual carbon formed per hour in the discharge will be:

$$0.460 + 0.118 = 0.578 \text{ lbs./hr.}$$

The total polymer formation will be:

$$0.029 + 0.051 = 0.080 \text{ lbs./hr.}$$

Although the chamber carbon is high in volatile matter content, 64% of the polymer goes out with the filter carbon. It was assumed in the calculations above that chamber holdup continued uniformly over the period of time that the plant was run. This was probably very nearly true, for the amount of carbon recovered from the filters showed no uniform increase for the successive determinations on carbon formation. At any rate, it is very likely that at the time the ratio of outlet to inlet gas was determined, the hold-up in the chamber had not reached equilibrium.

The fact that the total material deposited as calculated by a material balance on the plant was 0.939 whereas the amount deposited as calculated by hold-up measurements was 0.658 shows that a fairly large error in the carbon balance has little effect on the gas ratio. A carbon balance on the plant gives a much closer check: 0.725 lbs./hr. Since the polymer on the carbon is most likely composed of hydrocarbons, the above value checks fairly closely with the 0.658 lbs./hr. of carbon ≠ polymer found by measuring the chamber holdup. The error involved in this case is about 10% in the amount of carbon formation. Tentatively the 0.511 figure will be used, primarily because this amount of carbon was actually recovered, on the average, from the filters, and it is not certain to what extent hold-up within the chamber will continue. The carbon in the chamber has a tendency to pack considerably due to the larger amount of polymer present on its surface.

The above discussion has served to show: (1) Fairly large errors in carbon formation result in relatively small errors in the outlet to inlet gas ratio (2) The discrepancy between observed and calculated outlet to inlet gas ratio could very easily be due to chamber hold-up, and (3) Errors in gas analysis could make up the difference after allowance is made for (2) above, and (4) Although the amount of polymer on the chamber carbon is much higher than on the filter carbon, it represents only about 35% of the total formed.

The results of the calculations may be summarized as follows for a gas discharge unit operating at 24 KW and utilizing 8 cu. ft./min. of methane measured at 30°C and 750 mm.: (1) The gas discharge chamber after 100 operating hours had a hold-up of approximately 0.118 lbs. of carbon plus polymer per hour, the carbon containing 20.3% volatile matter; (2) The best estimate for the amount of actual carbon formed per hour is 0.578 lbs./hr. although the production rate of 0.400 lbs./hr. (0.511 lbs. carbon and polymer/hr.) is to be used in the calculations which follow; (3) The total rate of polymer formation is approximately 0.080 lbs./hr.

Estimation of Electrode Wear from Carbon Ash Determinations: When a gas discharge plant has been run for some length of time, the entire inside surfaces of the plant becomes covered with a layer of carbon black, and hence there can be no contact between the gas in the chamber and the chamber walls. It is logical to assume then, that any iron found in the filter carbon must come from vaporization of the surfaces of the electrodes. No accurate measurements have been made on wheel-wear in the gas discharge pilot plant. Holcomb[46] and co-workers have, however, measured the wheel-wear in the gasoline discharge pilot plant. They found that the average decrease in radius of the high potential blower wheel was 0.0152"/1000 KWH. The above value was determined by integration of their point values over the surface of the wheel.

Ash determinations on the filter carbon showed that wheel wear was approximately constant and did not decrease with time as had previously been supposed. Four different ash determinations at widely different times on the gas pilot plant filter carbon gave analyses of 0.43%, 0.54%, 0.41% and 0.43% in the order named. The average of these results is 0.45% ash. The method for making ash determinations was given in an earlier section. The residue was heated in an oxidizing atmosphere to be certain the iron was converted to the oxide. The ash was completely soluble in HCl and the solution gave the characteristic red precipitate of the iron hydroxide with ammonium hydroxide. The iron was not quantitatively determined in solution.

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[46] Holcomb, R. A., Dissertation, University of Texas, 1943

If we assume that all of the ash is Fe_2O_3, we can calculate the amount of electrode wear as follows:

% Fe in Fe_2O_3 = (111.70/159.70)(100) = 70.0%

Using the figure of 0.511 lbs./hr. for carbon formation (plus polymer), the amount of iron oxide formed from the electrodes per hour will be:

Lbs. Fe_2O_3/hr. = (0.511)(0.0045) = 23.0×10^{-4}

The lbs. of Fe vaporized from the electrodes per hour will be: $(23.0 \times 10^{-4})(0.70) = 16.1 \times 10^{-4}$ lbs. Fe/hr.

Using 7.8 for the specific gravity of steel, the cu.ft. of iron vaporized per hour can be calculated:

$$\text{Cu.ft. Fe/hr.} = \frac{(16.1 \times 10^{-4})}{(7.8)(62.4)} = 3.30 \times 10^{-6} \text{ cu.ft./hr.}$$

The blower electrode was 36" in diameter with 3/4" x 3/4" openings. It contained three webs of 12 gauge steel (0.081"). The area of the vertical webs will then be:

(3)(0.081)(3.14)(36) = 22.5 sq. in.

The area of the cross pieces will be:

$$\frac{(0.081)(1.5)(3.14)(36)(4)}{(3)} = 27.5 \text{ sq. in.}$$

The factor 1.5 comes in the above expression because there are two 3/4" webs across the face of the wheel spaced 3/4" apart around the periphery.

The total surface area will then be $22.5 + 27.5 = 50.0$ sq.in.

The cubic inches of Fe vaporized per hour will be:

$$(3.30 \times 10^{-6})(1728) = 5.69 \times 10^{-3} \text{ cu.in.Fe/hr.}$$

The average electrode wear will be:

$$5.69 \times 10^{-3}/50.0 = 1.14 \times 10^{-4} \text{ in./hr.}$$

The above figure is the decrease in radius of the blower wheel per 24 KWH.

The figure obtained on the gasoline discharge was for 1000 KWH. The wheel wear for 24 KWH will be:

$$(0.024)(0.0152) = 3.65 \times 10^{-4} \text{ in./hr. decrease in radius/24 KWH.}$$

A power input of 24 KW was used and the blower size was 36", hence the figures are entirely comparable.

Nothing can be stated as to the accuracy of the above method for several reasons: (1) The gas pilot plant may not have been run long enough to determine if carbon hold-up has reached equilibrium (2) The record of how long the gasoline plant had been run was not too accurate, and (3) Wear in the gasoline chamber may conceivably be different from that in the gas plant.

The calculated value of wheel wear from ash determinations gives results in the same order of magnitude as the experimental results, and hence this method for keeping a check on wheel wear presents possibilities. The low potential rotors of course receive some wear, but it is much smaller than the blower wheel wear.

Cost of Purifying Methane-to-Acetylene Black

Basis for Calculations: Before proceeding with the calculations, it is necessary to decide upon reasonable cost figures for the raw materials involved. The following figures were chosen because they represent average costs in Texas:

(1) Natural Gas = 5¢/1000 cu.ft.
(2) Steam = 20¢/1000 lbs.
(3) Power = 2¢/KWH

The cost figures for purifying the black will be figured exclusive of labor, since labor costs are subject to wide variations. Labor costs would include plant operation and packaging. Transportation costs will also not be figured.

In the cost estimates which follow, a purification plant for each acetylene plant was assumed. This increases the cost figures for units of small size. If a central purification plant were built to purify carbon from, say, three or four 500-KW units, the costs would be reduced considerably, particularly labor costs. Another possibility would be to ship the raw carbon directly to the consumer, and it could be purified at the point of use. In this latter case, of course, the decrease in cost to the manufacturer would be reflected in a decrease in price for the carbon.

In all of the calculations it is assumed that the carbon is merely a by-product, and hence the cost of operating the acetylene plant cannot be chalked up as cost of carbon production.

The design of the purification plant will be based on the operating characteristics of the pilot plant.

Size of Commercial Units: Operating at 0.51 RPM, the conveyor used in the pilot plant had a feed capacity of 0.28 lbs. carbon/hr. (50% loading). Other capacities may be figured approximately proportional to the screw speed.

The sizes of commercial carbon purification equipment can be calculated for acetylene plants of various sizes. A sample set of calculations for a 500 KW unit follows:

Let: L = length of heated section

M = mass rate of carbon flow, lbs./hr.

t = time of contact, hrs., in the heated section .

D = diameter of the screw, inches.

S = screw speed, RPM.

c = subscript, refers to commercial plant.

p = subscript, refers to pilot plant.

An expression for the mass rate of carbon flow for the commercial plant in terms of the conveyor diamter and screw speed will be:

$$M_c = (D_c/D_p)^2(S_c/S_p)(M_p)$$

This is equivalent to saying that for a given screw speed, the capacity of the unit is proportional to the square of the diameter (50% screw loading); and, for a given diameter, the capacity is directly proportional to the screw speed (50% loading.) D_p, S_p, and M_p are known and may be combined in the form of constants:

$$M_c = (D_c/4)^2(S_c/0.51)(0.28) = 0.0342D_c{}^2S_c$$

Also t_c is given by the expression:

$$t_c = t_p \ (L_c/L_p)(S_p/S_c)$$

But $t_c = t_p$, hence:

$$L_p/L_c = S_p/S_c \text{ or } L_c = (L_p/S_p)(S_c)$$

However, L_p and S_p are known and hence may be combined in the form of a constant:

$$L_c = (6/0.51)(S_c) = 11.75S_c$$

The derivation of the latter equation is obvious. Of course it is assumed that the same per cent screw loading is to be used.

The velocity of the gas in the conveyor is not critical except insofar as entrainment of the carbon in the gas is concerned. The maximum allowable velocity in the pilot plant was found to be that corresponding to a gas flow of 150 cu.ft./hr. (0°C and 760 mm.). Based on the free-flow area, this rate corresponds to a velocity of 0.685 ft./sec. At the operating conditions of the conveyor (about 450°C), the velocity would be 1.81 ft./sec.

This limiting velocity does not affect the size of the conveyor used since enough free-flow area can be provided by building up the sides as done in the pilot plant.

The lbs. of oxygen/lb. of carbon is, of course, critical; but this factor is taken care of by merely increasing the gas rate to correspond to the carbon feed rate. In the pilot plant, the ratio of oxygen to carbon was found to be 0.535 lbs. of oxygen per lb. of carbon when operating at optimum conditions.

It was necessary to decide upon a reasonable set of cost figures for screw conveyors in order to determine the most economical conveyor diameter. The cost data were taken both from Perry's Handbook (p. 2233) and from the Link-Belt catalogue. Because of the temperatures used, it was assumed that the maximum shaft diameter furnished with a given size screw is to be used and that the flights to be used are 1/4" thick. For trough and cover costs, it is assumed that malleable flange connections are to be furnished. The costs per foot of length for screw, trough-and-cover, and total are shown plotted against the conveyor diameter in Figure 26.

Sample calculations for a 500 KW acetylene plant are given below:

The amount of carbon plus polymer produced in a 500KW acetylene plant operating at 0.05 KWH/cu.ft. inlet gas will be:

$$(500/24)(0.511) = 10.61 \text{ lbs./hr.}$$

Assume that a 12" diameter conveyor is to be used:

$$S_c = 10.61/(0.0342)(64) = 4.85 \text{ RPM}$$

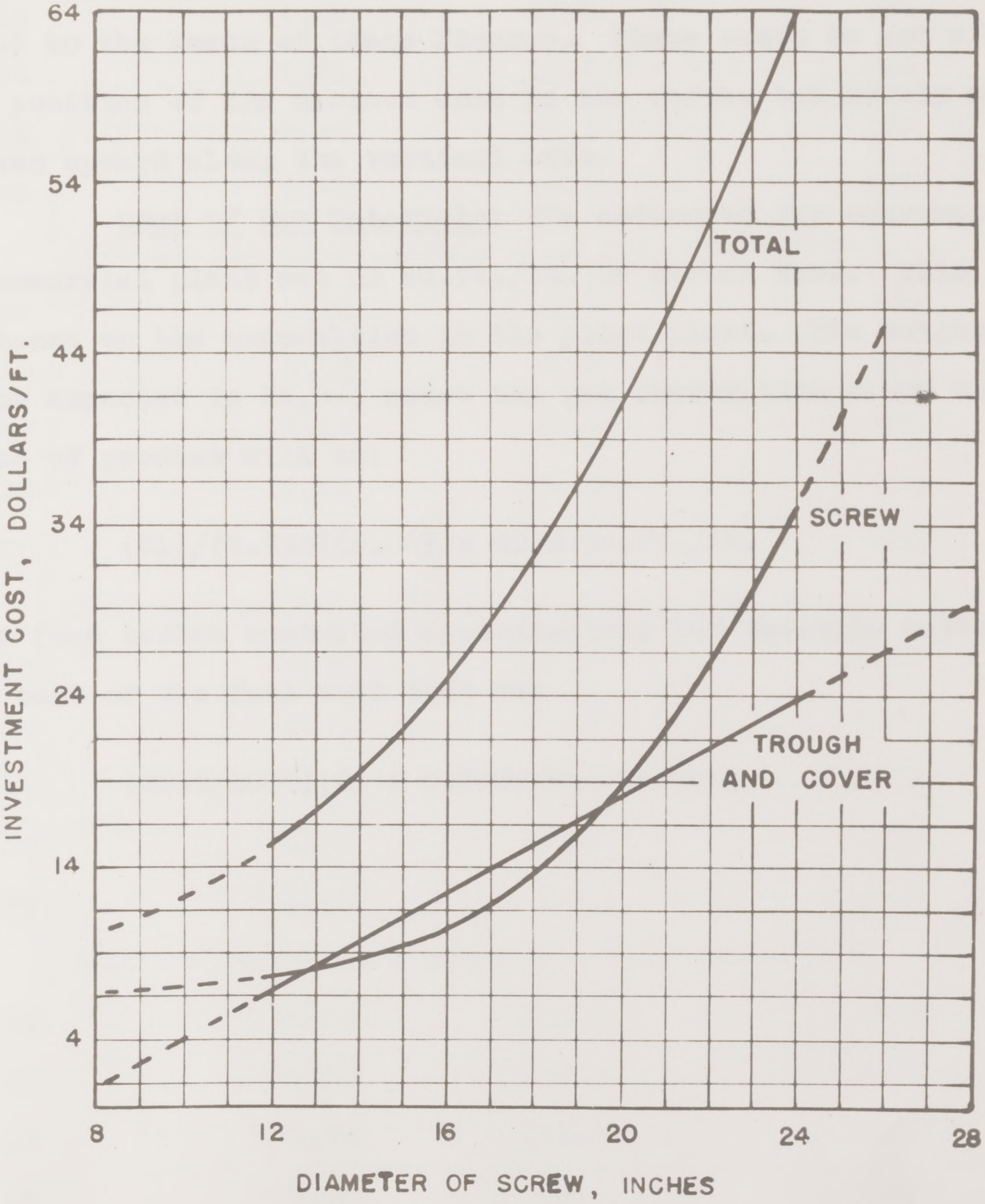
$$L_c = (11.75)(4.85) = 56.9 \text{ ft.}$$

From Figure 26 the total cost/ft. of length for a 12" diameter conveyor is $13.50.

Total cost = (56.9)(13.50) = $768

Similar calculations were made for conveyors of 14", 16", 18", and 20" diameters. Another complete set of calculations were made for acetylene units of 1000, 2000, and 4000 KW. All of

FIGURE 26
INVESTMENT COST vs DIAMETER
FOR SCREW AND TROUGH-AND-COVER
1/4" FLIGHTS, TROUGHS WITH MALLEABLE
FLANGE CONNECTIONS



the curves naturally had their minima at the same conveyor diameter. The complete set of calculated data is presented in Table 31. The data of Table 31 are shown plotted in Figure 27. It should be remembered that the investment cost figures of Figures 26 and 27 do not include the cost of accessory equipment such as drive mechanism, and flanges, hanger bearings, etc. The cost of the accessory equipment represents the major investment and must be added to the costs of these Figures. These costs do not affect the position of the minimum cost on the curves but merely move the curves upward along the vertical axis.

<u>Cost of Raw Materials</u>: The estimated gas consumption for a commercial plant was 61 cu.ft./lb. of carbon feed. This figure is based on the consumption in the pilot plant. The weight loss to be expected is 24.5%, hence the gas consumption based on a pound of product will be:

$$(61)/(0.755)(0.90) = 89.9 \text{ cu.ft./lb.}$$

(The feed carbon contained approximately 10% volatile matter.) The cost of the fuel will then be:

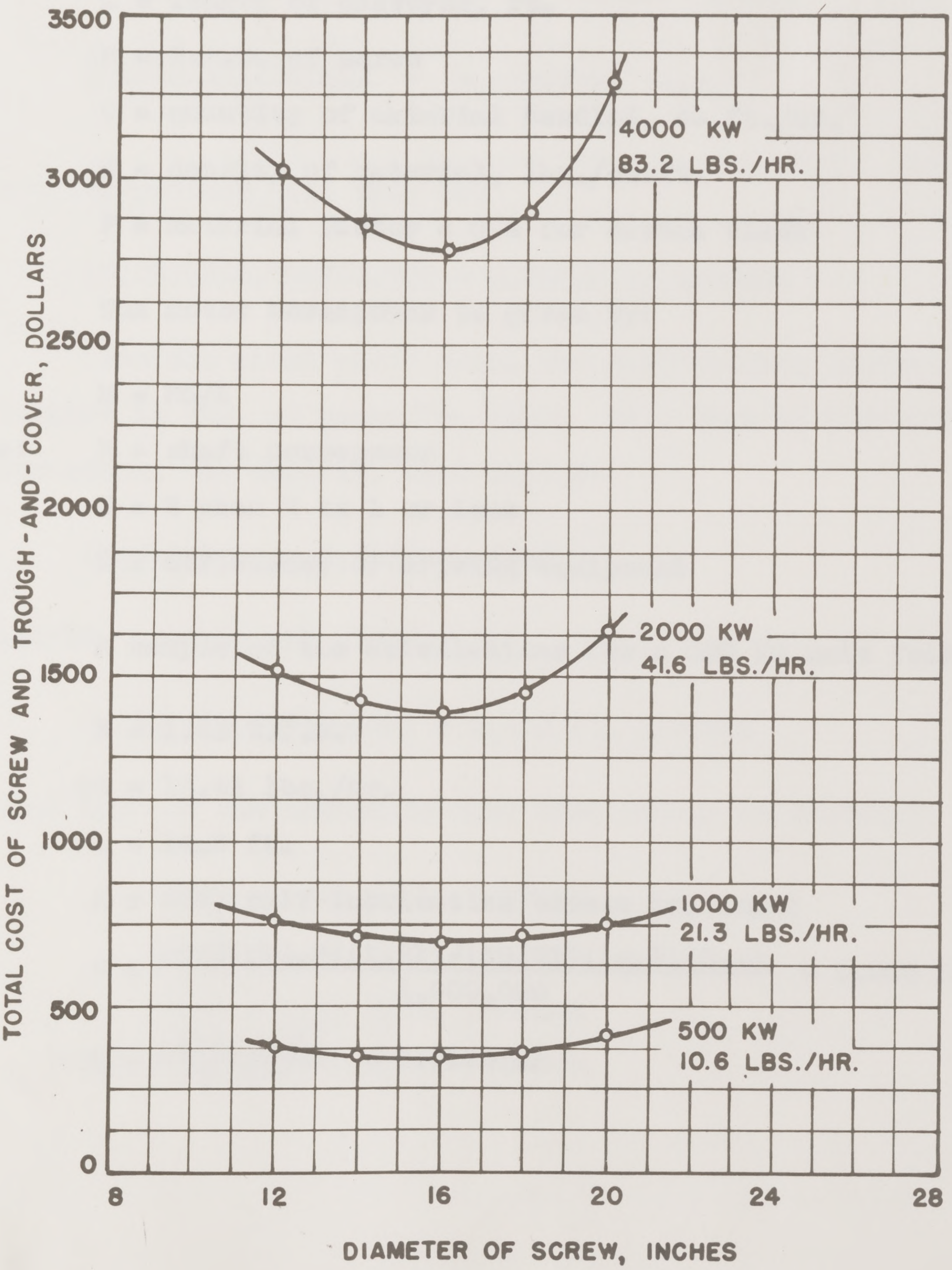
$$(89.9/1000)(6) = 0.554¢\text{/lb. product}$$

TABLE 31

Sizes of Purification Plants and Investment Costs

Diameter of Conveyor in.	Speed of Rotation RPM	Length of Conveyor ft.	Cost of Trough, Cover & Screw Dollars
500 KW Acetylene Plant--10.61 lbs. carbon/hr.			
12	2.15	25.3	379
14	1.59	18.6	359
16	1.21	14.2	348
18	0.96	11.3	361
20	0.85	10.0	410
1000 KW Acetylene Plant--21.3 lbs. carbon/hr.			
12	4.30	50.4	763
14	3.17	37.3	718
16	2.44	28.4	703
18	1.92	22.6	722
20	1.56	18.3	750
2000 KW Acetylene Plant--41.6 lbs. carbon/hr.			
12	8.60	101.2	1520
14	6.34	74.4	1430
16	4.88	56.8	1390
18	3.84	45.2	1440
20	3.12	40.0	1640
4000 Kw Acetylene Plant--83.2 lbs. carbon/hr.			
12	17.20	202.4	3030
14	12.68	148.8	2860
16	9.76	113.6	2790
18	7.68	90.4	2900
20	6.24	80.0	3280

FIGURE 27
TOTAL COST OF SCREW AND TROUGH-AND-COVER vs DIAMETER OF SCREW



The power required to turn the conveyor was calculated by means of the Link-Belt formula (p.934 Link-Belt Catalog 800).

$$H = \frac{ALN + CWLF}{1,000,000}$$

where: A = size factor (given in tables)

L = length of conveyor, ft.

N = R.P.M. of screw

C = quantity of material handled, cu.ft./hr.

W = density of material, lbs./cu.ft.

F = material factor = 0.4 for carbon black

The motor horsepower is given by:

$M = HG/E$

where: H = shaft horsepower

G = 2 when H is 1 or less

E = efficiency of driving equipment

A sample of the calculations for a 500 KW unit follows:

N = 1.21 R.P.M.

CW = 10.61 lbs./hr.

L = 14.2 ft.

A = 336 (self-lubricating bronze bearings)

$$H = \frac{(336)(14.2)(1.21) + (10.61)(14.2)(0.4)}{1,000,000} = 0.006 \text{ HP}$$

$$M = \frac{(2)(0.006)}{(0.96)} = 0.0125 \text{ HP}$$

The extremely low horsepower given by the above formula is due to the very low speed of rotation and the relatively short length of conveyor and small amount of material handled. Because of possible rusting of parts, it has been found that at least 1/6 HP should be used. The cost of the power required will then be:

$$\frac{(0.166)(0.746)(2)}{10.61} = 0.023¢/\text{lb. feed.}$$

The cost/lb. product will then be:

$$(0.023)/(0.755)(0.90) = 0.034¢/\text{lb. product}$$

From the pilot plant data, the purification process will require 14 lbs. of steam/lb. feed. At a cost of 20¢/1000 lbs. for steam, the cost/lb. feed will be:

$$(0.014)(20) = 0.28¢/\text{lb. feed.}$$

The cost/lb. product will be:

$$(0.28)/(0.755)(0.90) = 0.41¢/\text{lb. product}$$

The total cost of raw materials will then add up as follows:

Fuel = 0.53 ¢/lb. product
Steam = 0.41 ¢/lb. product
Power = <u>0.03</u> ¢/lb. product
Total Cost = 0.97 ¢/lb. product

The depreciation cost of the equipment per pound of carbon will be roughly the same regardless of the size of the unit. The cost of raw materials (gas and steam) per pound of carbon will be about the same regardless of the size of the unit; i.e., about 1¢/lb. product.

No attempt has been made to figure the cost of depreciation, labor, transportation, taxes, etc. as these costs are variable, depending on plant location, time at which the plant is built, etc. A complete plant has not yet been designed. Such a plant would require very little attention, and a portion of the labor cost could conceivably be chalked up to production of the acetylene.

Discussion and Conclusions

The rate of carbon production for the pilot plant gas discharge chamber has been experimentally determined to be 0.51 lbs./hr. of carbon plus polymer when operating at 0.0563 KWH/cu.ft. inlet gas (S.T.P.) or 0.460 lbs. of net carbon/hr. (Total power = 24 KWH and gas rate = 8 cu.ft./min. at 30°C and 750 mm.)

The volatile content and relative resistivity of the carbon produced in the gas pilot plant was found to increase as the discharge chamber is approached from the outlet end. It was shown that it is possible to account for discrepancies between observed and calculated values for the amount of carbon produced by an estimation of the amount of chamber hold-up. The probable chamber hold-up was estimated to be 0.147 lbs. carbon plus polymer per hour. From this value, the estimated rate of production was determined to be 0.658 lbs. carbon plus polymer/hr. or 0.578 lbs. of net carbon/hr.

It has been shown that electrode wear may be estimated from carbon ash determinations. The wear in the gas discharge pilot plant was estimated to be 1.14 x 10^{-4} in./hr./24 KWH decrease in radius. This is a fairly close check on the value 3.65 x 10^{-4} in./hr./24 KWH decrease in radius found for the gasoline chamber electrodes by experimental measurements.

The cost of raw materials for purifying methane-to-acetylene black for use in dry cell batteries was found to be 0.97¢/lb. This figure does not include labor, transportation, depreciation, or taxes. The method used for determining the optimum conveyor diameter was presented as well as the calculations involved in determining the length of the conveyor and the screw speed. The sizes of conveyors necessary for various sizes of discharge units were calculated and tabulated.

The title of this section deserves an explanation. The term "kerosene-collected methane-to-acetylene carbon" refers to methane-to-acetylene carbon which has been wet with kerosene or suspended in it and then filtered. A study of the properties of such carbon became necessary because of the work of Claasen[47] and Burks. Their work is described in the thesis indicated in the footnote but will be briefly discussed here. One of the bad features of the gas pilot plant described in the works of Kasperik[48] and Howard[49] was the fairly large pressure drop encountered in the recycle gas heat exchanger. The heat exchanger used provided for cooling the gas on the tube side with water on the shell side. It was necessary to maintain a high velocity in the tubes in order to keep them free of carbon.

To circumvent the large pressure drop of a standard heat exchanger, a new method for cooling the gas was proposed. This was by means of a specially designed cooler consisting of sheet metal plates hung vertically from a common overflow weir. A liquid such as kerosene or gas oil was allowed to flow down the sheets in a thin film counter to the flow of gas. The pressure drop with this apparatus was only a small fraction of the drop which had previously been encountered in the heat-exchanger. The liquid removed a considerable portion of the carbon in the gas.

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[47] Claasen, Jack, Thesis, University of Texas, 1944

[48] Kasperik, A. S., Dissertation, University of Texas, 1948

[49] Howard, W. B., Dissertation, University of Texas, 1948

SECTION VI: KEROSENE-COLLECTED METHANE -TO-ACETYLENE CARBON

Introduction

The title of this section deserves an explanation. The term "kerosene-collected methane-to-acetylene carbon" refers to methane-to-acetylene carbon which has been wet with kerosene or suspended in it and then filtered. A study of the properties of such carbon became necessary because of the work of Claasen[47] and Burks. Their work is described in the thesis indicated in the footnote but will be briefly discussed here. One of the bad features of the gas pilot plant described in the works of Kasperik[48] and Howard[49] was the fairly large pressure drop encountered in the recycle gas heat exchanger. The heat exchanger used provided for cooling the gas on the tube side with water on the shell side. It was necessary to maintain a high velocity in the tubes in order to keep them free of carbon.

To circumvent the large pressure drop of a standard heat exchanger, a new method for cooling the gas was proposed. This was by means of a specially designed cooler consisting of sheet metal plates hung vertically from a common overflow weir. A liquid such as kerosene or gas oil was allowed to flow down the sheets in a thin film counter to the flow of gas. The pressure drop with this apparatus was only a small fraction of the drop which had previously been encountered in the heat-exchanger. The liquid removed a considerable portion of the carbon in the gas.

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[47] Claasen, Jack, Thesis, University of Texas, 1944

[48] Kasperik, A. S., Dissertation, University of Texas, 1943

[49] Howard, W. B., Dissertation, University of Texas, 1943

It had been hoped that the liquid would remove all of the carbon. As it was, however, not enough carbon was removed and the damp carbon tended to clog up the transfer lines.

Experiments with kerosene-collected carbon paralleled the work on the cooler, since it was necessary to determine if kerosene-wetting altered the properties of the carbon and to see if the purification plant could also be used as a means for recovering the kerosene on the carbon. Wetting the carbon with a solvent was also being considered as a means of preliminary treatment in order to increase the capacity of the conveyor, and to increase the density of the product so that additional mechanical compression would be unnecessary.

Along with the general purposes of the work as outlined above, it was necessary to obtain filtration data on carbon sludges in order to determine the advisability of using this as a preliminary means of carbon-kerosene separation.

Experimental Work

Outline: The laboratory work can be divided into the following subjects: (1) preparation of the feed stock, (2) operation of the pilot plant, (3) operating data and material balance, (4) analyses and properties of the product carbon, and (5) filtration studies of carbon sludges.

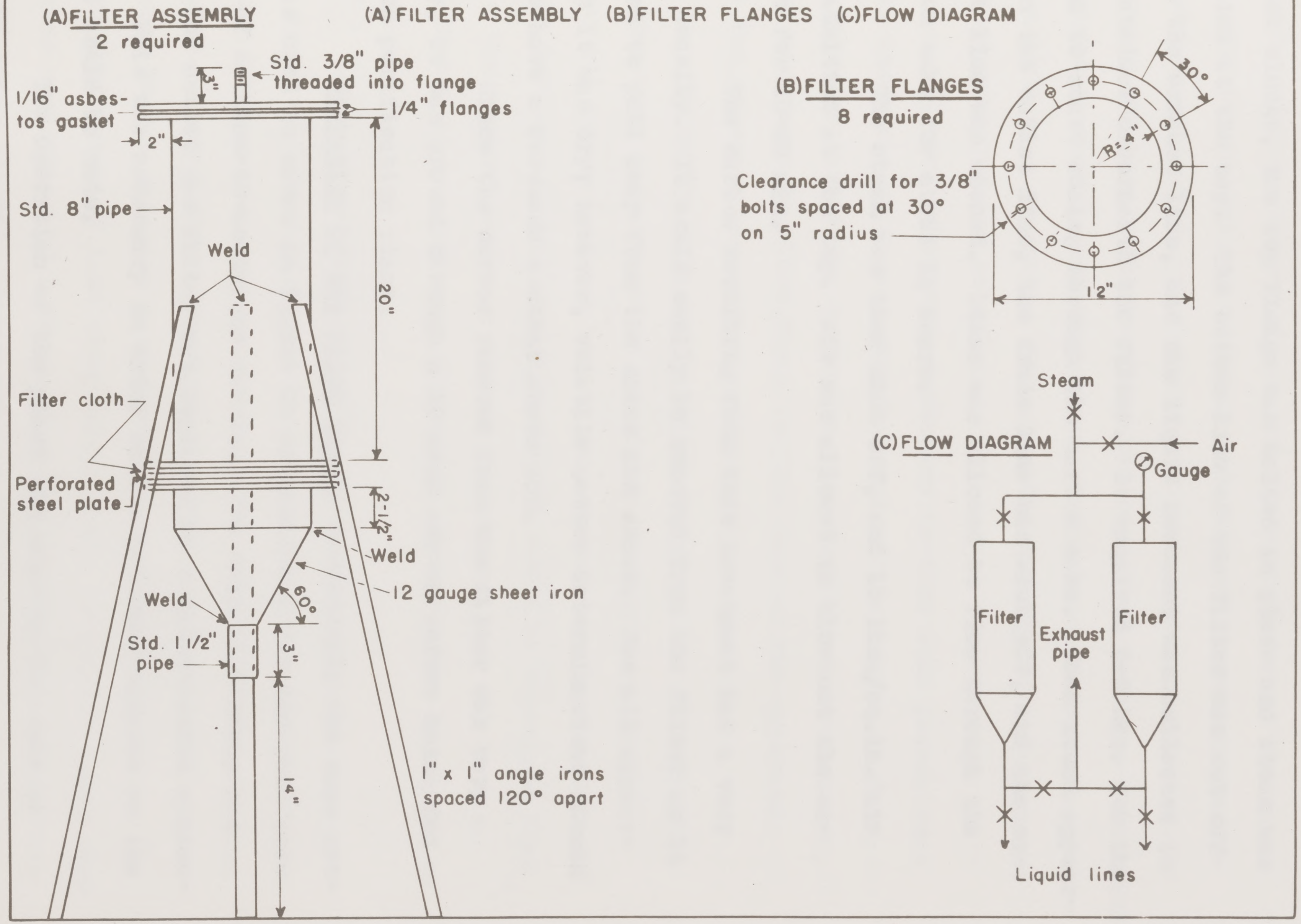
Preparation of the Feed Stocks: The stock was prepared by mixing up kerosene with carbon black until a thick, viscous sludge was formed. The sludge was then poured into a batch filter. A diagram of the filter construction is shown in Figure 28 along with a sketch of the flow system.

The filter consisted of a 20" section of standard 8" pipe flanged at both ends. Between the bottom flange of the pipe and another similar flange was inserted a canvas filter cloth, and between the latter flange and still another flange was inserted a perforated steel plate about 1/8" thick. This plate was drilled with 1/4" holes spaced on approximately 1/2" equilateral centers. The purpose of the plate was to support the filter cloth under pressure.

Welded to the last flange was a 60 degree cone rolled from 12 gauge sheet iron, and welded to the bottom of the cone was a 3" nipple of 1½" standard pipe. Two such filters were connected in parallel as shown in the flow diagram. With this arrangement, one filter could always be in operation. The piping was such that either air or steam could be admitted to the top of the filter. The pressure in the filters was read with a Bourdon gauge. The two filters terminated in a common exhaust pipe.

FIGURE 28

(A) FILTER ASSEMBLY (B) FILTER FLANGES (C) FLOW DIAGRAM



After the 20" section of 8" pipe was filled with the carbon sludge, the top flange was bolted in place and steam was applied at the top. The bottom line of the filter was cut off from the exhaust line, and the liquid kerosene was collected in a container underneath the filter. It required 2-8 hrs. for the steam to start coming through the carbon cake. When steam appeared in the outlet line, the drain line was shut off, and the exhaust line was opened. Steam was allowed to flow through the carbon cake for about 1½ hours.

The steam was then shut off, and 15 lbs./sq.in. air was admitted at the top. Air was allowed to blow out the exhaust for 20-30 min.

The carbon resulting from this treatment had a very high density. It could easily be removed from the filter as it tended to pull away from the sides and crack. For all appearances it was dry; however, volatile matter determinations showed it to have a kerosene content above 40%.

Since the carbon removed from the filter was very lumpy, it was ground through a 10 mesh screen before being fed to the purification plant.

<u>Operation</u> <u>of</u> <u>the</u> <u>Pilot</u> <u>Plant</u>: Essentially the same setup was used as shown in Figure 14 of Section A for the purification of methane-to-acetylene carbon. The only difference was that the outlet gas filter was replaced by a water-cooled condenser. This was necessary in order that a material balance on the plant could be made.

The operation of the plant was exactly the same as described in a previous section except that it was necessary to run the carbon through the plant twice: once using steam only and once using a mixture of air and steam as before. The same data were taken; but, in addition, the amount of condensate recovered was recorded. The condensate contained a mixture of water and kerosene. The kerosene was separated from the water with a separatory funnel, and the volume of the kerosene was measured with a 1000 c.c. graduate. The specific gravity of the kerosene was also measured and recorded.

It was, of course, necessary to take more precautions in the treatment of this carbon because of the danger of fire. In particular, after the burner to the plant had been shut off, it was necessary to allow steam to flow through the apparatus until the conveyor had cooled sufficiently.

Operating Data and Material Balance: Two primary difficulties were encountered in purifying the kerosene-wetted carbon: (1) The use of too high a temperature resulted in cracking the kerosene on the carbon before it could be vaporized thus giving the product carbon a higher resistance, and (2) It was found that a higher per cent oxygen and slower screw speed had to be used.

At a temperature of 450°C, it was necessary to use a screw speed of 0.21 R.P.M. and 15% oxygen in the gas stream. The relation between relative resistivity and Burgess resistance was, of course, changed since the type of carbon was different. It was found that a relative resistivity of 0.47 corresponded to a Burgess resistance of 1.34 ohms/column inch. A product which gave a Burgess resistance of 1.34 could be produced with a weight loss of 30.1%, only slightly higher than that obtained with methane-to-acetylene carbon (27.4%.)

Not a great many runs were made, since it was desired to produce a sample as quickly as possible to send to Burgess Battery Company for testing. Temperatures of 450 and 550°C were used with screw speeds of 0.51 R.P.M. One run was made with a screw speed of 0.21 R.P.M.

A summary of the data from several runs is given in Table 32. This table shows that when operating the pilot plant for recovery of the kerosene, a screw speed of 0.51 R.P.M. may be used and recovery is almost 100%. At this speed the plant has a capacity of 0.84 lbs. carbon/hr. When oxidizing the carbon, the screw speed must be reduced to 0.21 R.P.M., giving a capacity of 0.35 lbs./hr.

TABLE 32

Summary of Pilot Plant Operating Data

Run No.	Temperature °C	Steam Rate gms./min.	Oxygen %	Weight Loss %	Relative Resistivity
52	550	46.0	---	7.70	3.66
53	450	29.8	8.23	2.58	2.29
54 (Re-run of carbon from run no. 53)	550	19.2	13.0	25.60	1.21
65-66	550	48.8	---	1.58	2.89
67	550	19.2	13.9	40.6	0.78
69-70	450	46.0	---	0.0	2.74
71-72	450	19.2	13.0	30.1	0.47

In the above table, the different runs should be examined in pairs. For example, in runs 65-66 the carbon was steamed only for recovery of the kerosene, and run 67 represents treatment of the product carbon from runs 65-66. The same is true of runs 69-70 and 71-72. Runs 52 and 53 were also made in this sequence but because of the high resistivity of the carbon from run 53, this carbon was re-run in an oxidizing atmosphere (run 54).

The results from run 67 show that a temperature of 550°C is too high for the weight loss is 40.6%. Also the resistivity of 0.78 corresponded to a Burgess resistance of 2.55 which was much too high. The kerosene probably cracked at this temperature. Runs 69-70 and 71-72 were the ones used in preparation of the Burgess Sample. The resistivity 0.47 corresponded to a Burgess resistance of 1.34 which fell within the allowable limits.

The following tables give the operating data for this series of runs:

TABLE 33

Preparation of Burgess Sample: Runs 69-70, Kerosene Vaporization
Screw Speed = 0.51 R.P.M. Steam Orifice No. 43

Time	Steam "Hg	Shell Temperature, °C 1	2	3	Avg.	Inlet Gas Temperature °C	Outlet gas Temperature °C	Carbon Feed gms.
1:00 PM	13.2	456	462	390	450	292	100	1723
2:00	13.0	470	468	420	458	294	176	1185
3:30	12.9	462	462	411	452	297	209	896
4:30	12.9	470	462	422	452	297	308	398
10:30 AM	13.1	438	450	403	436	277	208	1471
11:30	13.1	470	472	425	462	300	132	1009
1:00 PM	13.1	464	470	428	460	303	202	950
2:30	13.0	465	469	420	458	302	215	---
2:50	13.0	440	450	410	443	296	213	1835
4:45	12.9	445	469	413	453	295	174	---
10:45 AM	13.0	430	474	443	469	313	146	1046
11:45	13.1	460	448	420	445	303	207	1159
12:45 PM	13.1	461	455	420	450	304	207	1367
2:10	13.3	460	448	420	444	304	207	1376
4:30	13.5	462	461	427	450	248	308	---

TABLE 33 (concluded)

Preparation of Burgess Sample: Runs 69-70, Kerosene Vaporization
Screw Speed = 0.61 R.P.M. Steam Orifice No. 43

Time	Steam "Hg	Shell Temperature, °C 1	2	3	Avg.	Inlet Gas Temperature °C	Outlet Gas Temperature °C	Carbon Feed gms.
10:05 AM	13.0	480	478	434	465	258	176	1400
11:45	13.0	470	473	430	460	287	198	1341
12:35 PM	13.1	470	475	425	455	262	203	860

Total Feed = 18,135 gm.

Total Weight of Product = 8703 gms.

TABLE 34

Average Conditions of Plant Operation for Runs 69-70

Average Shell Temperature, °C	453
Average Inlet Gas Temperature, °C	290
Average Outlet Gas Temperature, °C	188
Average Feed Rate, lbs./hr.	1.05
Average Steam Rate, lbs./hr.	6.1
Total Weight of Product, lbs.	19.40
Total Weight of Feed, lbs.	40.04
Total Volume Kerosene Recovered, c.c.	8905
[a]Specific Gravity of Kerosene at 29°C	0.821
Volatile Content of Feed, %	53.6
Volatile Content of Product, %	2.59
Average Relative Resistivity of Product	2.74
Average Relative Resistivity of Feed	8.64
Average CCl_4 Absorption of Feed, c.c./5 gms.	10.2
Average CCl_4 Absorption of Product, c.c./5 gms.	19.7
Average Moisture Content of Product, %	0.05
Apparent Density of Feed, lbs./cu.ft.	21.6
Apparent Density of Product, lbs./cu.ft.	11.3

---

[a] The specific gravity was measured at the temperature at which the kerosene was collected.

From the information in Table 34, a material balance can be run on the pilot plant. The net amount of carbon fed into the plant will be:

$$(40.04)(0.464) = 18.58 \text{ lbs. net carbon in.}$$

The net amount of carbon recovered will be:

$$(19.40)(0.974) = 18.90 \text{ lbs. net carbon out.}$$

The above material balance checks to about 1.7%.

Some kerosene was lost as shown by the following balance: The kerosene in the feed will be:

$$40.04 - 18.58 = 21.46 \text{ lbs. kerosene in}$$

The kerosene in the product will be:

$$19.40 - 18.90 = 0.50 \text{ lbs. out in product}$$

The kerosene recovered as distillate will be:

$$\frac{(8905)(0.821)}{(453)} = 16.13 \text{ lbs. out as distillate}$$

Total kerosene in = 21.46 lbs.

Total kerosene out = 16.13 + 0.50 = 16.63 lbs.

Percent kerosene lost = $\frac{(21.46 - 16.63)(100)}{21.46} = 22.6\%$

The high kerosene lost was caused by leaks in the apparatus. The per cent removal of the kerosene from the carbon, however, was high:

lbs.kerosene/lb. carbon in = 21.46/18.58 = 1.16

lbs.kerosene/lb. carbon out = 0.50/18.90 = 0.0264

$$\% \text{ kerosene removal} = \frac{(1.16 - 0.03)}{1.16}(100) = 97.5\%$$

On the following page are given the data for runs 71-72 in which the carbon from runs 69-70 was re-run in an oxidizing atmosphere.

TABLE 28

Preparation of Burgess Sample: Runs 71-72, Oxidation

Screw Speed = 0.21 R.P.M., Air Orifice No. 2

Time	Steam #/Hr	Air Cu.Ft	Shell Temperature, °C 1	2	3	Ave.	Inlet Gas Temperature °C	Outlet Gas Temperature °C	Carbon Feed gms.
11:00 AM	5.1	11.0	468	460	428	452	270	127	613
12:10 PM	5.0	10.5	480	475	440	470	290	242	---
1:25	4.9	11.2	474	471	426	463	280	243	---
2:50	4.9	11.0	473	460	442	466	304	243	---
4:10	5.0	9.6	482	460	440	463	308	243	---
4:25	Shut Down								
12:10 PM	5.0	11.0	479	441	400	450	280	137	503
12:30	4.9	11.2	498	460	437	471	310	203	---
1:25	5.2	10.7	491	458	440	468	312	241	---
4:40	4.9	10.6	494	454	447	470	315	242	---
4:55	Shut Down								
10:00 AM	5.0	11.0	478	465	440	460	280	130	748
11:40	4.9	10.7	473	470	434	463	285	228	---
4:15	4.8	11.2	470	456	428	460	296	233	---
4:45	Shut Down								

TABLE 36 (continued)

Preparation of Burgess Sample: Runs 71-72, Oxidation

Screw Speed = 0.21 R.P.M., Air Orifice No. 2

Time	Steam "Hg	Air Cm.Hg	Shell Temperature, °C 1	2	3	Avg.	Inlet Gas Temperature °C	Outlet Gas Temperature °C	Carbon Feed gms.
10:00 AM	5.0	10.7	485	470	450	470	306	176	606
11:45	6.0	10.5	469	470	450	472	305	227	----
2:20	4.8	10.5	479	475	442	470	301	225	413
4:55	6.0	12.0	468	462	440	460	295	Shut Down	
9:00 AM	5.0	10.9	480	458	443	462	320	107	----
10:35	5.0	11.0	479	467	450	469	310	231	369
1:25 PM	5.0	10.6	478	475	448	470	304	238	350
4:40	5.4	11.0	475	471	442	460	305	Shut Down	
10:45 AM	5.0	11.0	474	471	410	468	297	127	562
2:15 PM	5.1	10.7	468	468	400	460	299	230	----
3:20	6.0	11.0	469	470	440	462	304	233	456
4:30	Shut Down								
9:40 AM	6.0	11.0	470	464	443	459	274	99	----
11:45	5.0	11.0	475	480	455	470	302	223	457
10:40 AM	5.0	10.9	490	472	450	474	359	217	510

TABLE 35 (concluded)

Preparation of Burgess Sample: Runs 71-72, Oxidation

Screw Speed = 0.21 R.P.M., Air Orifice No. 2

Time	Steam "Hg	Air Cm.Hg	Shell Temperature, °C 1	2	3	Avg.	Inlet Gas Temperature °C	Outlet Gas Temperature °C	Carbon Feed gms.
2:10 PM	5.5	11.0	480	470	445	467	328	235	643
10:00 AM	5.0	10.9	475	460	440	458	309	123	----
1:05 PM	5.0	10.9	470	479	461	470	322	236	252
4:35	5.0	11.6	478	490	452	473	327	Shut Down	
9:35 AM	5.0	11.0	462	458	444	456	328	117	----
12:30 PM	5.0	10.6	466	463	432	450	342	221	----
2:35	5.0	9.0	460	459	432	455	341	223	----

Total Feed = 7890 gms

Total Weight of Product = 5371 gms.

TABLE 36

Average Conditions of Plant Operation for Runs 71-72

Average Shell Temperature, °C	484
Average Inlet Gas Temperature, °C	307
Average Outlet Gas Temperature, °C	200
Average Feed Rate, lbs./hr.	0.347
Average Steam Rate, lbs./hr.	2.64
Total Weight of Product, lbs.	11.83
Total Weight of Feed, lbs.	17.40
Volatile Content of Feed, %	2.59
Volatile Content of Product, %	7.68
Average Relative Resistivity of Product	0.47
Average Relative Resistivity of Feed	2.80
Average CCl_4 Absorption of Feed c.c./5 gms.	19.7
Average CCl_4 Absorption of Product, c.c./5 gms.	29.9
Average Moisture Content of Product, %	1.28
Apparent Density of Feed, lbs./cu.ft.	11.3
Apparent Density of Product, lbs./cu.ft.	7.7
Burgess Resistance of Product, ohms/column inch	1.34
Steam Consumption, lbs.steam/lb.carbon	7.61

From the data of Table 36 the weight loss of carbon during oxidation can be calculated:

Net carbon in feed = (17.40)(0.9741) = 16.95 lbs.

Net carbon in product = (11.83)(0.9872) = 11.68 lbs.

% carbon lost = (100)(16.95 - 11.68)/16.95 = 31.1%

In calculating the per cent loss, as before, the amount of oxygen adsorbed on the surface of the carbon was considered to be saleable product. Allowance was made, however, for the moisture content of the product.

In removal of the kerosene from the carbon with steam, the steam rate had to be kept high enough so that the kerosene vapors would not diffuse to the outlet end of the plant. It was also necessary to maintain a high steam rate in order to lower the partial pressure of the kerosene. The amount of steam used corresponded to 5.8 lbs. of steam per lb. of carbon feed. The volume ratio of the distillate was 2.65 volumes of water to 1 volume of distillate. The vaporization temperature would, of course, be the temperature of the gas stream rather than the temperature of the conveyor trough, flash vaporization primarily occurring in the downspout from the feeder to the trough.

In oxidation of the carbon, the amount of steam used corresponded to 7.6 lbs. of steam per lb. of carbon feed, although the hourly steam consumption was lower than in the distillate run.

As seen from the tables, each successive throughput resulted in a lowering of the apparent density. The final apparent density (7.7 lbs./cu.ft.) would be sufficiently high to permit the carbon to be shipped without further compression. If carbon treated in this manner could be used for batteries, other advantages would be: (1) an increased equipment capacity, and (2) lower moisture content of the product.

Analyses and Properties of the Product Carbon

Introduction: An examination of the data from Table 36 of this section and Table 23 of section A shows that the kerosene-wetted methane-to-acetylene carbon differs in several respects from carbon obtained directly from the filters: (1) The initial relative resistivity is considerably lower than that of untreated carbon obtained from the gas filters although it possesses a much higher volatile matter content. This is caused by the fact that it is effectively "packed" under considerable pressure by being wet with the kerosene. (2) For the same Burgess resistance, the relative resistivity is much lower than treated methane-to-acetylene gas filter carbon. (3) The carbon tetrachloride absorption of the wetted black is much lower than the unwetted raw methane-to-acetylene carbon. Although oxidation improved the absorption properties, the finished product still has a lower absorption than the treated gas filter carbon, and (4) The apparent density of the product is much higher than that of the treated gas filter carbon.

Various pilot plant runs gave products whose analyses did not differ by any great extent in spite of the wide variation in Burgess resistances. A summary of the analyses of the product and feed carbon for various runs is given in Table 37. The Burgess resistance is evidently dependent upon a multitude of factors: (1) the presence of a different type of carbon deposited from a foreign source; i.e., as a result of cracking the kerosene, (2) the presence of organic volatile matter caused by incomplete oxidation of the carbon, (3) the amount of oxygen adsorbed on the surface, and (4) the apparent density.

TABLE 37

Summary Analyses of Feed and Product Carbon

Run No.	52		53		54	
	Feed	Product	Feed	Product	Feed	Product
Volatile Matter, %	60.0	2.94	2.94	4.70	4.70	3.81
Moisture, %	-	-	-	0.98	0.96	0.93
Ash, %	0.06	0.41	-	1.36	1.36	1.46
Apparent Density, lbs./cu.ft.	24.9	9.7	9.7	9.4	9.4	7.6
CCl_4 Absorption, c.c./5 gms.	8.3	23.0	23.0	25.6	25.6	32.5
Relative Resistivity	6.71	3.66	3.66	2.29	2.29	1.21
Burgess Resistance, ohms/column in.	-	-	-	4.98	4.98	2.20

TABLE 37 (concluded)

Summary Analyses of Feed and Product Carbon

Run No.	65-66		67		69-70		71-72	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Volatile Matter, %	53.5	3.66	3.66	4.70	63.6	2.63	2.63	6.40
Moisture, %	-	0.32	0.32	1.17	-	0.05	0.05	1.29
Ash, %	-	-	-	0.49	-	-	-	0.65
Apparent Density lbs./cu.ft.	20.8	11.7	11.7	8.4	21.6	11.3	11.3	7.74
CCl_4 Absorption c.c./5 gms.	-	22.0	22.0	28.5	10.2	19.7	19.7	29.9
Relative Resistivity	6.06	2.89	2.89	0.74	8.64	2.80	2.80	0.47
Burgess Resistance ohms/column in.	-	-	-	2.55	2.55	-	-	1.34

Carbon Tetrachloride Absorption: The data of Table 37 show that a relationship exists between the apparent density and the carbon tetrachloride absorption. The data are plotted in Figure 29 in order to show the relationship more clearly. The lower curve represents data taken on "gas filter carbon." The term is perhaps a misnomer for the data were taken from samples of carbon taken from various points in the discharge system (chamber, heat exchanger, and filters), and these samples contained varying amounts of volatile matter.

The two curves of Figure 29 apparently have no relationship to each other--at least none has been found. The curves have little value except perhaps as an easy method for determining the apparent density for a given type of carbon. An equation may be used as well, for a plot of log (apparent density) vs. log (CCl_4 absorption) gives a straight line showing that a relationship of the type:

$$\log A = a + b\ (\log B)$$

exists where A is the apparent density and B is the carbon tetrachloride absorption.

Properties of the Distillate: The distillate obtained from the pilot plant runs had a somewhat higher specific gravity than the original kerosene, indicating that some of the lighter fractions had been lost through incomplete condensation. The original kerosene used to prepare the feed stock for runs 52-54 had a specific gravity of 0.798 (27°C). The distillate had a specific gravity of 0.817 (27°C). The following Table gives the distillation data of the original kerosene and the distillate for runs 52-54. For purposes of comparison, the data are shown plotted in Figure 30.

FIGURE 29
CARBON TETRACHLORIDE ABSORPTION VS APPARENT DENSITY

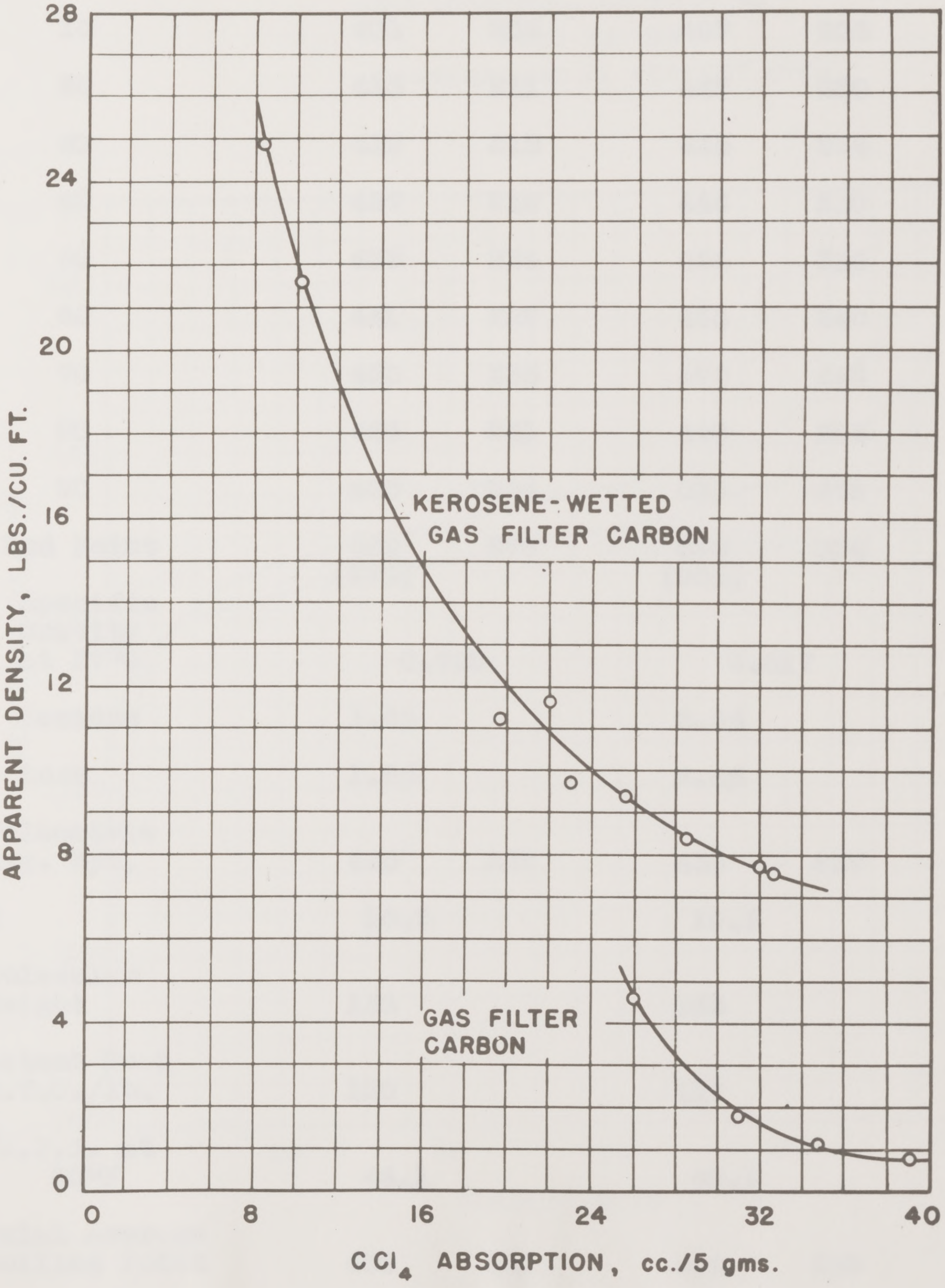
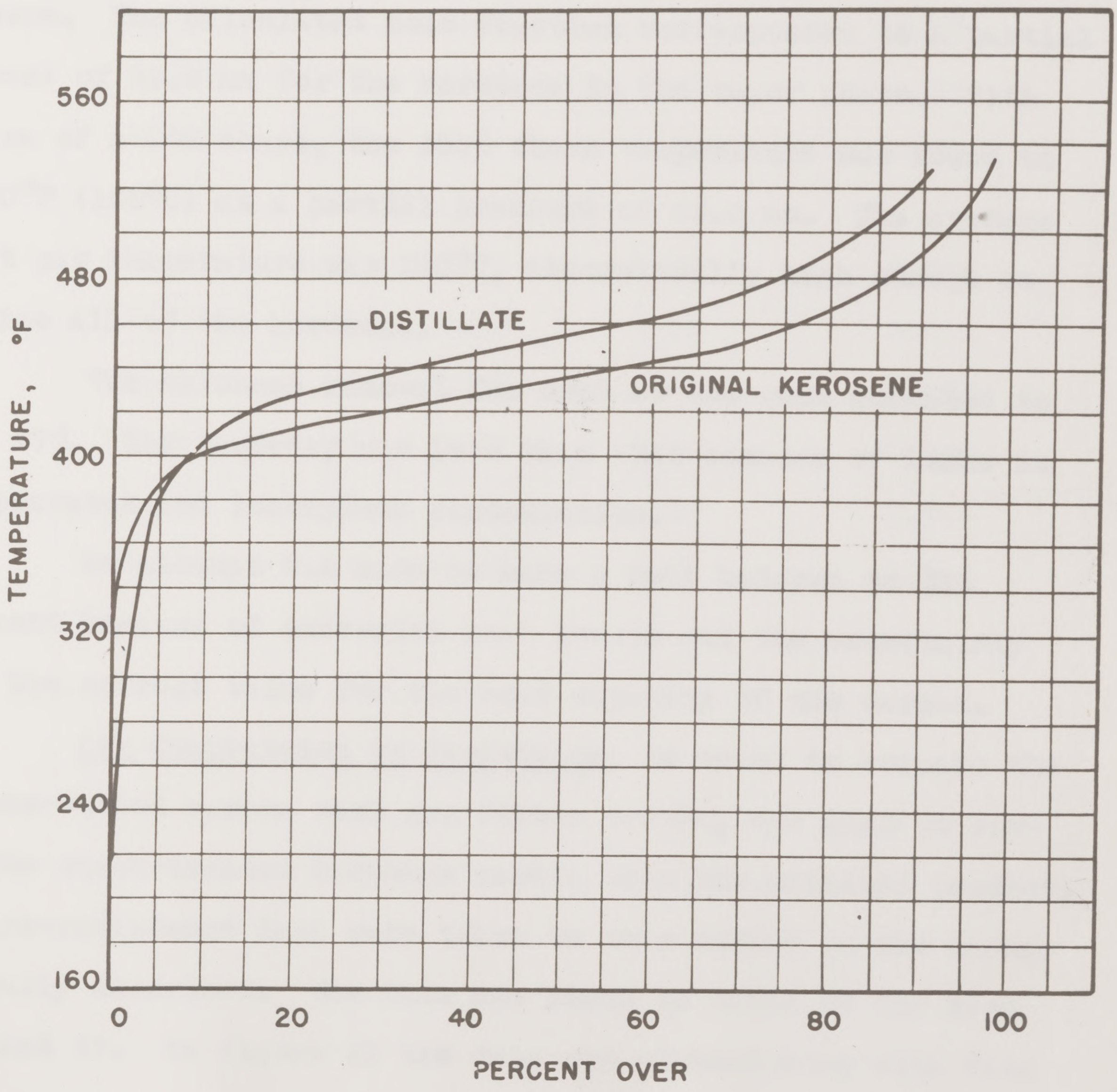


TABLE 38

Distillation Data for Original Kerosene and Distillate, Runs 52-54

Percent Off	Original Kerosene Temperature °F	Original Kerosene Temperature °C	Distillate Temperature °F	Distillate Temperature °C
Over Point	328	171	218	103
10	401	205	407	208
20	413	211	427	220
30	419	215	435	224
40	427	219	446	230
50	435	224	454	236
60	441	227	463	240
70	453	235	475	246
80	466	241	490	254
90	490	254	522	272
End Point	529 (97%)	276	578 (95%)	304
Specific Gravity at 27°C	0.798		0.817	
Residue	1.2%		2.6%	
Loss	1.8%		2.4%	
Volumetric Avg. Bpt.	440	227	459	237
K	10.5		10.5	
Molecular Weight	156		165	
Latent Heat B.T.U./lb.	120		117	
°A.P.I. at 60°F	44.1		40.1	
Molal Average Boiling Point	430	221	449	232

FIGURE 30
ENGLER DISTILLATION OF DISTILLATE
AND ORIGINAL KEROSENE
RUNS 52 - 54
TEMPERATURE vs PERCENT OVER



In Table 38 the values for the volumetric and molal average boiling points, the characterization factor (K), the molecular weight, and the latent heat were read from standard Piromoov curves. Also from the curves, the equilibrium flash curve for atmospheric pressure was calculated. Since the volume ratio of water to kerosene in the distillate was known, the mole fraction of kerosene in the vapor could be calculated from the specific gravity and molecular weight of the water and kerosene. The calculated mole fraction corresponded to a partial pressure of 25.6 mm for the kerosene in the vapor phase. With the use of a Cox chart, the 100% flash temperature was found to be 280°F (138°C) at a partial pressure of 25.6 mm. The average outlet gas temperature was 200°C, theoretically high enough to vaporize all of the kerosene.

The kerosene removal for most of the runs amounted to about 97%. The recovery was less than this because of leaks in the apparatus and incomplete condensation.

No attempt was made to make a heat balance on the equipment because of excessive heat losses and the uncertainty as to the correct value for the heat capacity of the carbon.

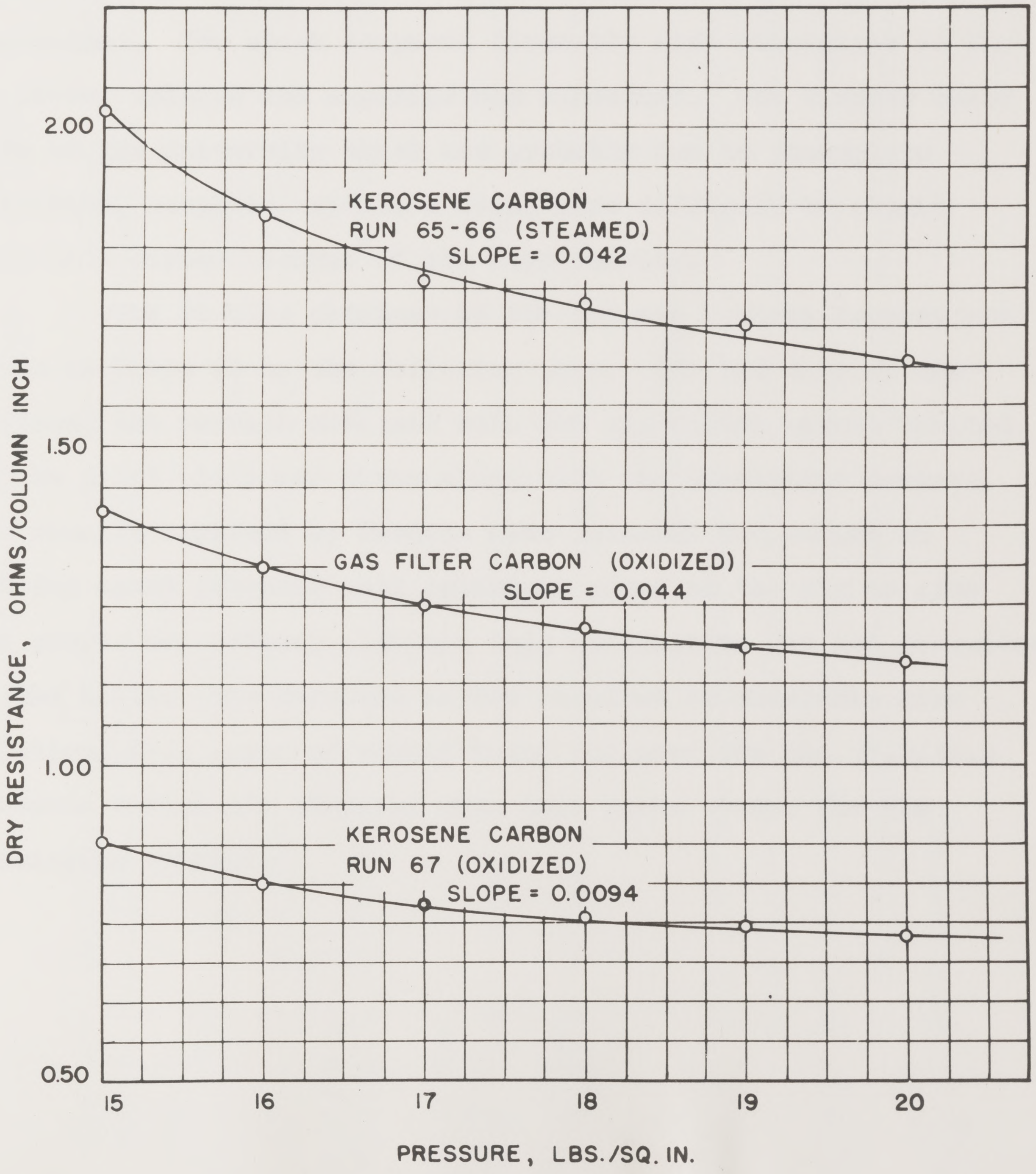
Dry Compression vs Resistance: In order to compare the kerosene-wetted carbon with gas filter carbon, and also to compare the steam-treated kerosene carbon with the oxidized product, pressure-resistance data were taken on this carbon in the manner previously described. The data are shown in Table 39 for runs 65-66 and 67. In Figure 31 the data are plotted along with data taken on the treated gas filter carbon for the sake of comparison.

TABLE 39

Dry Compression vs Resistance

Pressure lbs/sq.in.	Milli-amperes	Milli-volts	Height in.	Height(corr.) in.	Resistance ohms/in.
		Run 65-66 (Steamed)			
15	1.005	4.59	2.32	2.26	2.02
16	1.005	4.21	2.31	2.25	1.86
17	1.007	3.94	2.28	2.22	1.76
18	1.007	3.83	2.28	2.22	1.72
19	1.007	3.77	2.27	2.21	1.69
20	1.008	3.60	2.26	2.20	1.62
		Run 67 (Oxidized)			
15	1.400	2.70	2.27	2.21	0.873
16	1.401	2.49	2.25	2.19	0.811
17	1.401	2.37	2.22	2.16	0.783
18	1.401	2.28	2.20	2.14	0.760
19	1.401	2.22	2.19	2.13	0.744
20	1.401	2.15	2.17	2.11	0.727

FIGURE 31
DRY RESISTANCE vs PRESSURE



An examination of the curves shows that oxidation greatly reduces the compressibility of the carbon, the compressibility of the oxidized carbon being even less than that of Shawinigan.

Burgess Battery Tests on Pilot Plant Product: Data on the preparation of the sample sent to Burgess Battery Company have already been given. The results reported by them were disappointing. The mix resistance of the black was unusually high and did not check the results of the University laboratory; the shelf life of cells made from the black was also lower than Shawinigan. The black compared favorably with Shawinigan as far as 10-day voltage and amperage was concerned. The shorter shelf life of the University black was probably due to incomplete oxidation, complete oxidation being more difficult to obtain with this carbon because of its high density.

The results obtained by the Burgess Battery Company are given in Table 40 on the following page. For the sake of comparison, the results obtained with the gas filter carbon treated in the pilot plant are given along with the Shawinigan control. The results reported by Burgess also included the amount of wetting agent (chromic acid solution) added to the mix to give the proper consistency although this information was not presented in the table. The kerosene carbon required considerably more solution, 47.4 parts of wetter being required for the 87.5/12.5 kerosene carbon mix compared with 34.3 parts wetter for the Shawinigan control.

TABLE 40

Burgess Battery Company Tests; Run 71-72

Type of Carbon	Ore/Black Ratio	Mix Resistance ohms/in.	Ten Day Volts	Ten Day Amperes	Hy.Ind. min. to 0.9	Lt.Ind. min. to 0.9	Signal Corps Fr. (days)
Kerosene Pilot Plant Run 71-72	90/10	2.7	1.56	6.2	309(Fr.)	639	12.7
"	87.5/12.5	1.9	1.55	6.0	285(Fr.)	632	11.0
Shawinigan (Control)	87.5/12.5	1.4	1.59	6.0	330(Fr.)	680	11.8
Gas Filter Carbon Pilot Plant	90/10	1.45	1.55	8.0	370	736	13.6
Shawinigan (Control)	87.5/12.5	1.40	1.59	7.5	371	756	13.7

Nomenclature

Hy.Ind.: Heavy Industrial Flashlight Test—4 ohms/cell, 4 min. out of 15 min. for 8 hours/day or 128 min. discharge/day to 0.9 volts. Capacity given in minutes.

Lt.Ind.: Light Industrial Flashlight Test—4 ohms/cell, 4 min./hr. for 8 hrs/day or 32 min. discharge/day to 0.9 volts. Capacity given in minutes.

Fr.: Fresh Capacity.

<u>Compression vs. Mix Resistance</u>: The fact that the kerosene carbon had such a high density and gave a high battery mix resistance led the Burgess Battery Company to suspect that mechanical compression affected the mix resistance adversely. It has already been shown that laboratory tests showed this conclusion to be incorrect in the case of treated gas filter carbon.

Tests run on the kerosene carbon were, perhaps, unfair since the samples tested were from different runs. The samples, therefore, probably differed in density by virtue of their difference in volatile content and manner of treatment rather than by any amount of mechanical compression. The variation in the mix resistances obtained indicated that the mix resistance is probably a function of the apparent density, but the results are inconclusive. The data obtained are given in the table below:

TABLE 41

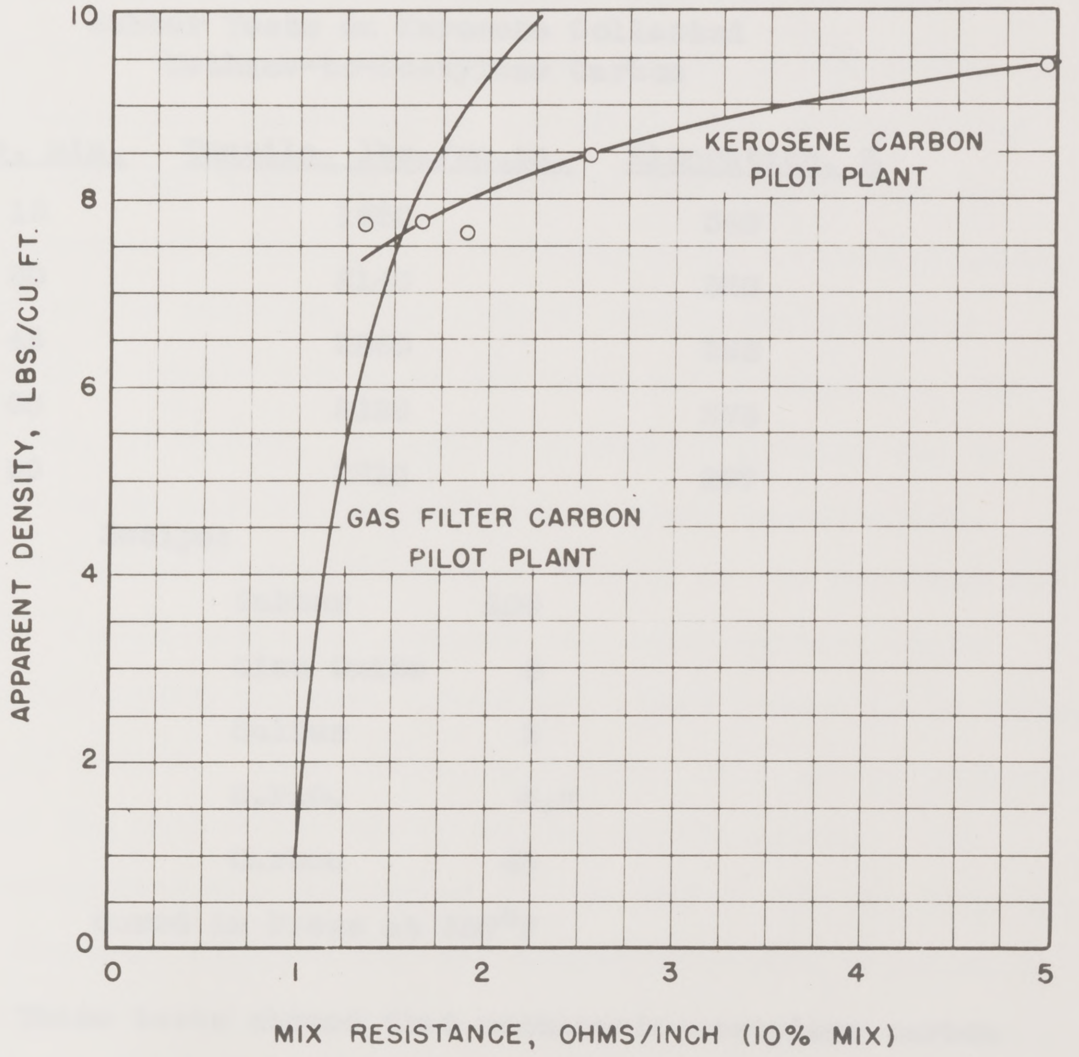
Compression vs Burgess Resistance

Apparent Density lbs./cu.ft.	Mix Resistance ohms/column in.
7.74	1.34
7.74	1.66
7.63	1.80
8.44	2.56
9.40	4.96

The data of Table 41 are shown plotted in Figure 32. It is evident that small changes in density cause large changes in the mix resistance. The data for the gas filter carbon are plotted in the same figure for the sake of comparison.

FIGURE 32

APPARENT DENSITY vs MIX RESISTANCE



<u>Rubber Reinforcement</u>: The analyses of the feed and product carbon for run 67 were given in Table 37. The product of this run was sent to Commercial Solvents for testing its value as a rubber reinforcing agent. The pH of the carbon sludge was found to be 4.6, about the same as Micronex.

The results of the rubber tests are presented in the table below:

TABLE 42

Rubber Tests on Kerosene Collected
Methane-to-Acetylene Carbon

Time, min.	Tensile, lbs./sq.in.	Elongation, %
15	1860	340
30	2140	320
45	2260	293
60	2190	273
90	2210	277

Recipe:

Rubber	100
Zinc Oxide	5
Sulfur	3
D.P.G.	0.7
Carbon	40

Cured in Press at 267°F

These tests showed that methane-to-acetylene carbon which had been collected in kerosene gave a lower tensile strength and lower per cent elongation in the same rubber mix recipe than either thermal acetylene black or electro-black made by the

Jakowsky process. Previous tests run by Commercial Solvents on untreated methane gas filter carbon or extracted methane gas filter carbon cannot readily be compared with the above tests because a different test recipe was used.

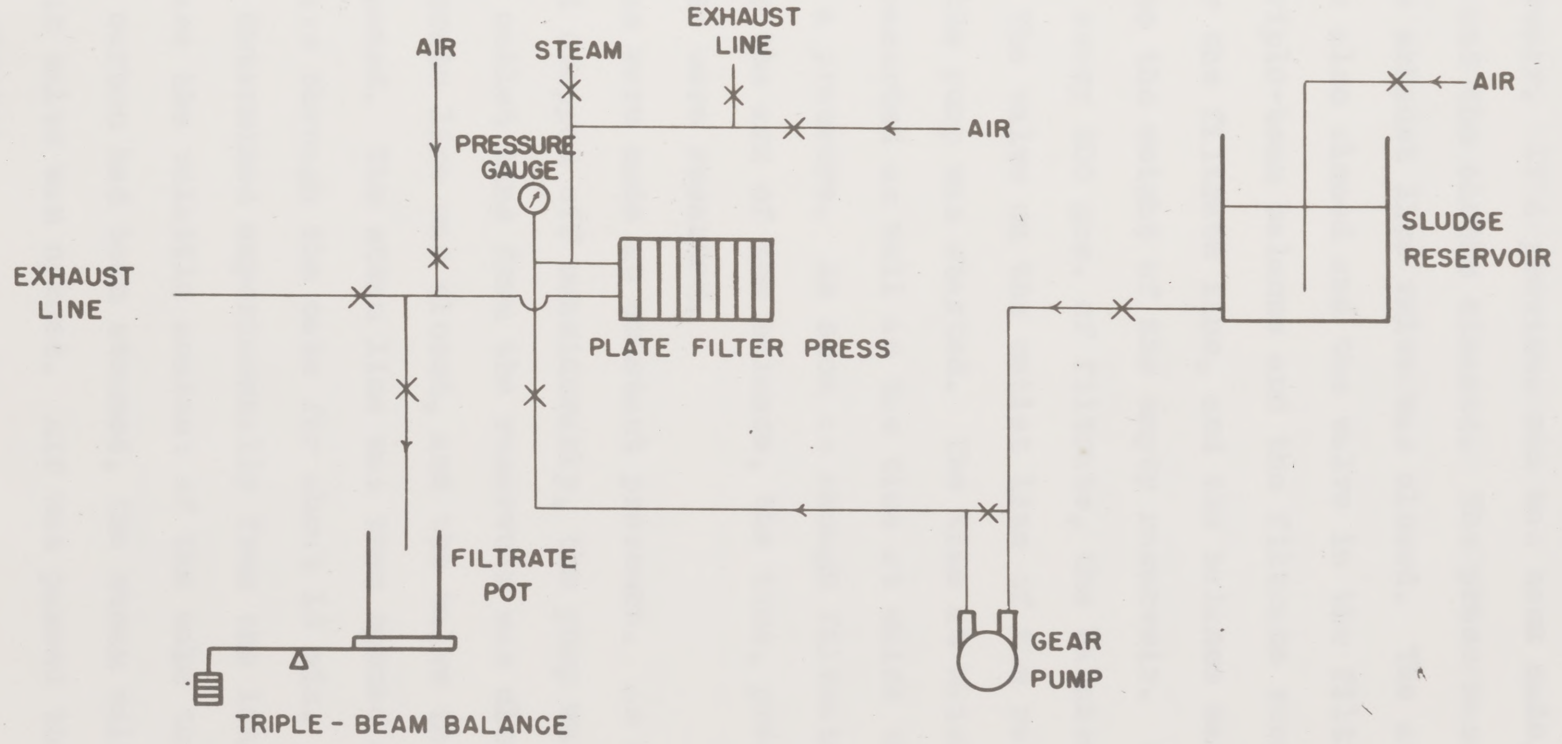
Filtration of Carbon-Kerosene Sludge

The necessity for obtaining filtration data on carbon-kerosene sludge has already been discussed. The laboratory set-up for obtaining the necessary data is shown in Figure 33. The carbon sludge was pumped from a reservoir by means of a rotary gear pump into a center-feed type of recessed plate filter press. The filtrate line emptied into a pot mounted on a triple beam balance. Also connected to the filtrate line was an exhaust line which was used during the steaming period of the cycle. Air and steam lines were connected to the inlet side of the filter press. An air line was also connected to the outlet line so that counter-current drying of the carbon could be accomplished. The sludge in the reservoir was stirred continuously during filtration by a gentle stream of air bubbling through it. The reservoir was, of course, covered by a loosely-fitting top to prevent excessive loss of the kerosene through vaporization.

The proper concentration of carbon in the kerosene was selected by consideration of the maximum concentration which could be pumped with the pump available. This proved to be about 2% carbon by weight. This concentration was made up approximately by weighing the carbon and the kerosene, before mixing. The exact concentration was determined at the end of the run from the amount of kerosene filtrate and the amount of carbon retained on the filter cloth. Volatile matter determinations had to be made on the filtered carbon to determine the net amount of carbon collected.

FIGURE 33

KEROSENE-CARBON FILTRATION FLOW DIAGRAM



Filtration runs were made as follows: The reservoir was filled with the sludge after closing the valve on the outlet line of the reservoir. If a previous run had been made, the press was opened and the cloths cleaned. The press was reassembled and the exhaust line valve was closed. The air and steam valves were also closed and the valve in the filtrate line was opened. A triple-beam balance and the filtrate reservoir were placed under the filtrate line, and the balance was tared by an amount equal to the weight of the empty reservoir. Since data were taken after every 200 gms. of filtrate, the balance arm was set at 200 gms. The valve on the outlet line of the reservoir was opened, and the pump was started. The time at which the pump was started was recorded as well as the time at which the gauge first registered a pressure. As soon as enough filtrate had been collected to trip the arm of the balance, the time, pressure, and weight of filtrate were recorded.

All runs were made at constant pressure. As soon as the filtrate rate had dropped off considerably, the pump was stopped, the valve in the outlet line from the reservoir was closed, the valve in the filtrate line was closed, and the valve in the exhaust line was opened. The steam line was then opened and steam was allowed to pass through the cake for about 15 min. The time for steaming was determined experimentally from the length of time necessary to reduce the volatile content of the cake to 60% or less. After the carbon had been steamed, the steam valve was closed and the air valve was opened. Air was passed through the cake for about 5 minutes.

The filter press was then opened, and the cake was scraped off the cloth and weighed. A sample of the cake was removed for a volatile matter determination.

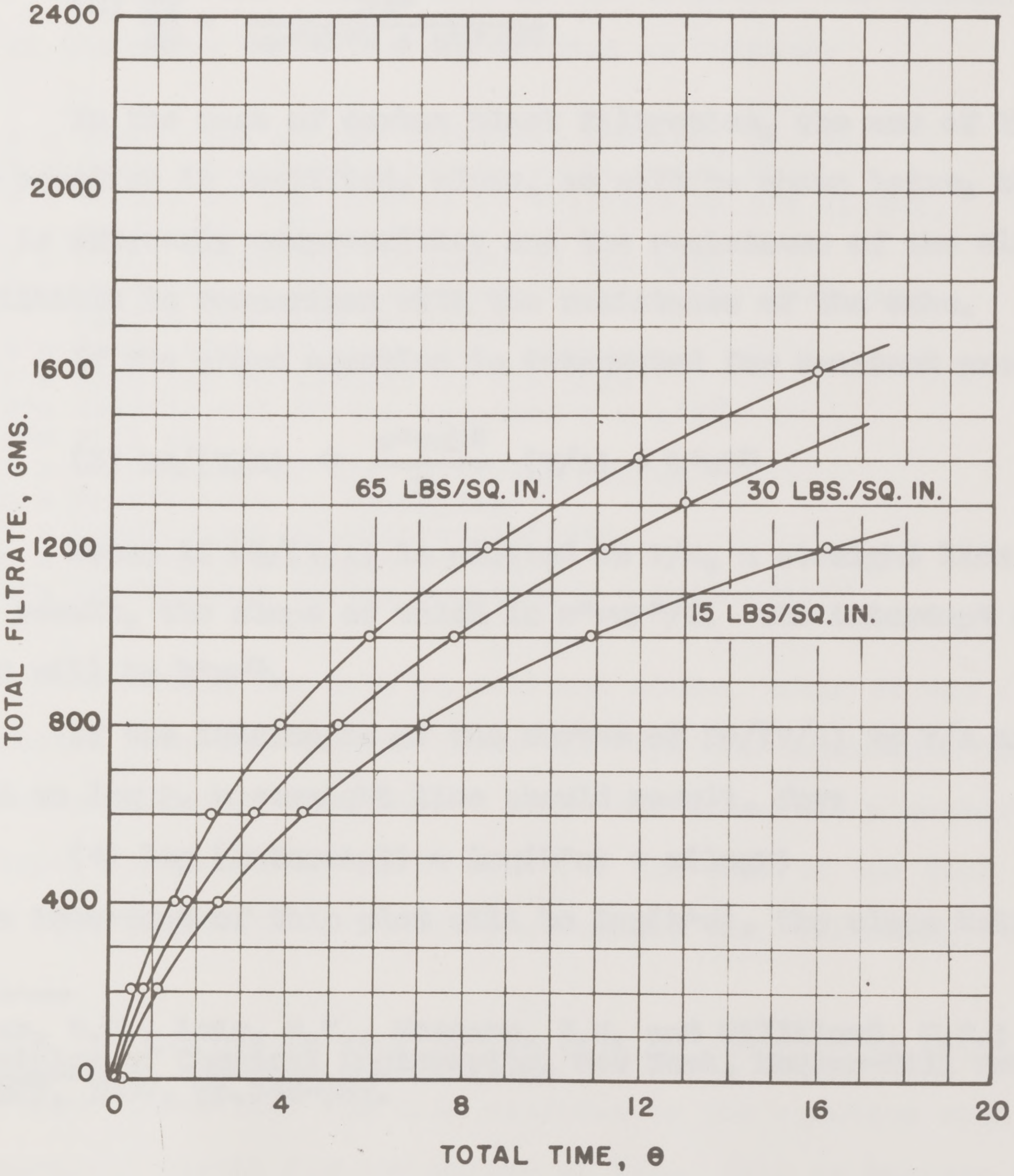
The experimental data are given in Table 43 and the results are shown plotted in Figure 34.

TABLE 43

Constant Pressure Filtration of Carbon-Kerosene Sludge
Average Concentration of Carbon = 1.69%

Time, θ min.	Total Filtrate, gms.	Pressure, Lb./sq.in.ga.	
0	0	15	Steam rate = 97 gms./min.
0.83	200		Steaming time = 21.0 min.
2.23	400		Air drying time = 1.2 min.
4.10	600		Volatile content of cake = 76.7%
6.86	800		Total Weight of cake = 119.0 gms.
10.65	1000		
15.95	1200		
0	0	30	Steam rate = 488 gms./min.
0.53	200		Steaming time = 10.8 min.
1.58	400		Air drying time = 1.0 min.
3.00	600		Volatile content of cake = 40.3%
4.95	800		Total weight of cake = 47.0 gms.
7.58	1000		
10.92	1200		
12.83	1300		
0	0	65	Steam rate = 46 gms./min.
0.58	200		Steaming time = 15.3 min.
1.33	400		Air drying time = 1.3 min.
2.33	600		Volatile content of cake = 75.6%
3.90	800		Total weight of cake = 122.5 gms.
5.90	1000		
8.57	1200		
11.93	1400		
15.95	1600		

FIGURE 34
TOTAL FILTRATE vs TOTAL TIME
CARBON - KEROSENE SLUDGE
AVERAGE CARBON CONCENTRATION = 1.69%



It was decided to treat the filtration data after the method of Walker, Lewis, McAdams, and Gilliland[50] using the generally applicable equation:

$$(1)\quad \frac{dV}{d\theta} = \frac{P}{\dfrac{ur''vV(1 - P_1/P)P^s}{A^2(1-(P_1/P)^{1-s})} + \dfrac{ub'(1-P_1/P)^m P^m}{A}}$$

If P_1/P is small, the equation reduces to:

$$(2)\quad \frac{dV}{d\theta} = \frac{PA^2}{ur''vP^sV + ub'AP^m}$$

In the case of carbon black filtration, the use of the latter equation is justified, since, as will be shown later, the sludge is extremely compressible; and the resistance of the cloth is neglibible in comparison with the resistance of the cake.

If the above equation is integrated for constant pressure:

$$(3)\quad P\theta/(V/A) = \frac{r''vuP^s}{2}\,(V/A) + b'uP^m$$

Hence if $P\theta/(V/A)$ is plotted vs V/A, a straight line should result, the slope of which is $r''vuP^s/2$. The intercept at $V/A = 0$ will be $b'uP^m$.

If the intercepts of the curves of $P\theta/(V/A)$ vs V/A are plotted vs log P, a straight line should result, for:

$$(4)\quad \text{Log (intercept)} = \log(b'u) + m(\log P)$$

and the intercept of this plot will be log(b'u), the slope being m.

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[50] Walker, W.H., Lewis, W.K., McAdams, W.H. and Gilliland, E.R.; Principles of Chemical Engineering, New York, McGraw-Hill Book Company, 1937, pp.345-367.

If the slopes of the curves of $P\theta/(V/A)$ vs V/A are plotted vs log P, a straight line should result, for:

$$(5) \log (\text{slope}) = \log(r''vu/2) + s(\log P)$$

and the intercept of this plot will be $\log(r''vu/2)$, the slope being s.

From this calculated data, the equation representing the constant pressure filtration can be derived. The symbols used in the above equations are defined as follows:

A = Total area of the filtering surface, sq. in.
V = Total weight of filtrate up to time, θ
v = Volume of the cake as it collects on the filter, cu.in./lb. filtrate
P = Total filtering pressure on the cake
P_1 = Pressure at the interface between the filtering medium and cake channels
θ = Total time of operation, minutes
r = Specific resistance of the cake
r' = Coefficient in the equation $r = r'P^s$
r'' = $r'(1 - s)$
b = Resistance of the filtering medium
m = Coefficient of "plugging"
s = Coefficient of compressibility
u = Viscosity relative to water
b' = Coefficient in the equation $b = b'(P - P_1)^m$

Treating the data as outlined above, Table 44 was first constructed from the data of Table 43. V/A was calculated from the measured area of the press. Since the press was a center-feed type, allowance had to be made for the area of the feed holes. The calculated area was 71.2 sq.in. (two filtering surfaces).

A plot of the data of Table 44 is shown in Figure 35. This figure shows that the data conforms to the equation with fair accuracy except for low values of V/A. This is because of the inaccuracy involved in the measurement of short time intervals.

TABLE 44

Calculated Values of Pθ/(V/A) and V/A

Time, θ min.	Pθ/(V/A) min.	V lbs.	V/A lbs./sq.in.
	15 lbs./sq.in. gauge		
0.83	2000	0.441	0.00622
2.23	2590	0.882	0.0124
4.10	3310	1.323	0.0186
6.86	4150	1.764	0.0248
10.65	5150	2.205	0.0310
15.95	6430	2.646	0.0372
	30 lbs./sq.in. gauge		
0.53	2560	0.441	0.00622
1.52	3660	0.882	0.0124
3.00	4840	1.323	0.0186
4.93	6000	1.764	0.0248
7.56	7330	2.205	0.0310
10.92	8840	2.646	0.0372
12.83	9620	2.870	0.0402
	65 lbs./sq.in. gauge		
0.38	6060	0.441	0.00622
1.33	6950	0.882	0.0124
2.33	8150	1.323	0.0186
3.90	10,200	1.764	0.0248
5.90	12,350	2.205	0.0310
8.57	15,100	2.646	0.0372
11.93	17,900	3.087	0.0434
15.95	20,900	3.528	0.0495

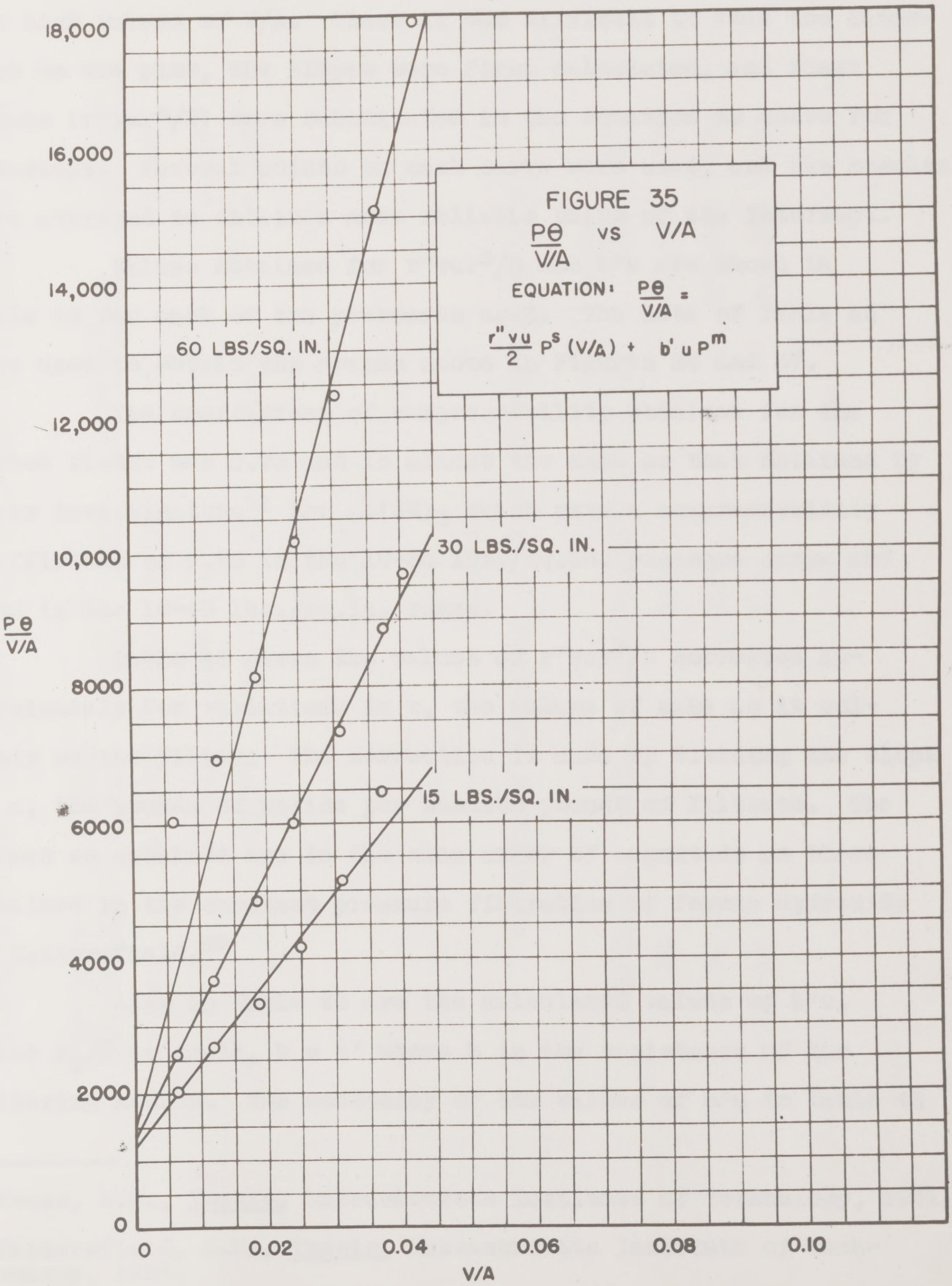

FIGURE 35

$\frac{P\theta}{V/A}$ VS V/A

EQUATION: $\frac{P\theta}{V/A} = \frac{r''vu}{2} P^{s} (V/A) + b' u P^{m}$

This error is not serious, for the time of operation was sufficiently long for initial errors in time to become minimized for high values of V/A. Since it was difficult to read the intercept on the plot, the slopes were first calculated, and these values ($r''vuP^s/2$) were substituted in the equation to solve for intercept. Several points on each curve were used, and the results were averaged to obtain a more reliable value of the intercept.

Values obtained for $r''vuP^s/2$ and b'u are shown in Table 45 for each of the pressures used. The data of Table 45 were used to obtain the graphs shown in Figures 36 and 37.

The coefficient of compressibility obtained for the carbon sludge was 0.73 and is almost the same as that obtained by other investigators[51] for $Al(OH)_3$ which gave a compressibility coefficient of 0.75 in the 10-60 lbs./sq.in. pressure range and 0.88 in the 10-40 lbs./sq.in. range.

Table 46 gives the values of $r''vuP^s/2$ corrected approximately for variations in v, the volume of cake as it collects on the filter. The correction is made by dividing the slope by a, the pounds of solids per hundred pounds of filtrate. The values so obtained are in the same order of magnitude as those obtained in the constant pressure filtration of ferric hydroxide by Tattersfield.[52]

Also in Table 46 are the calculated values of b'u. Since P_1/P is small, b = b' where b is the resistance of the filtering medium. The constancy of the values of b'u in Table 46

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[51] Evans, S.B., Thesis, Massachusetts Institute of Technology, 1921.

[52] Tattersfield, S.M., Thesis, Massachusetts Institute of Technology, 1922.

TABLE 45

Calculated Values for $r''vuP^s/2$ and $b'u^n$ and Calculation of n and s

Pressure lbs./sq.in.	$\frac{r''vuP^s}{2}$	$b'u^n$	Log P	Log($r''vuP^s/2$)	Log($b'u^n$)
15	125,800	1200	1.177	5.100	3.080
30	199,000	1310	1.478	5.300	3.118
65	360,000	1430	1.813	5.556	3.156

n = 0.12

s = 0.73

TABLE 46

Approximate Correction of Slope for Variations in v

lbs./sq.in.	a (lbs. solids/lb. filtrate) x 100	$\frac{r''vuP^s}{2a}$	b'u
15	1.70	73,500	870
30	1.84	108,000	874
65	1.45	248,000	867

FIGURE 36

$\text{Log } \frac{r'' \gamma u P^{S}}{2}$ vs Log P

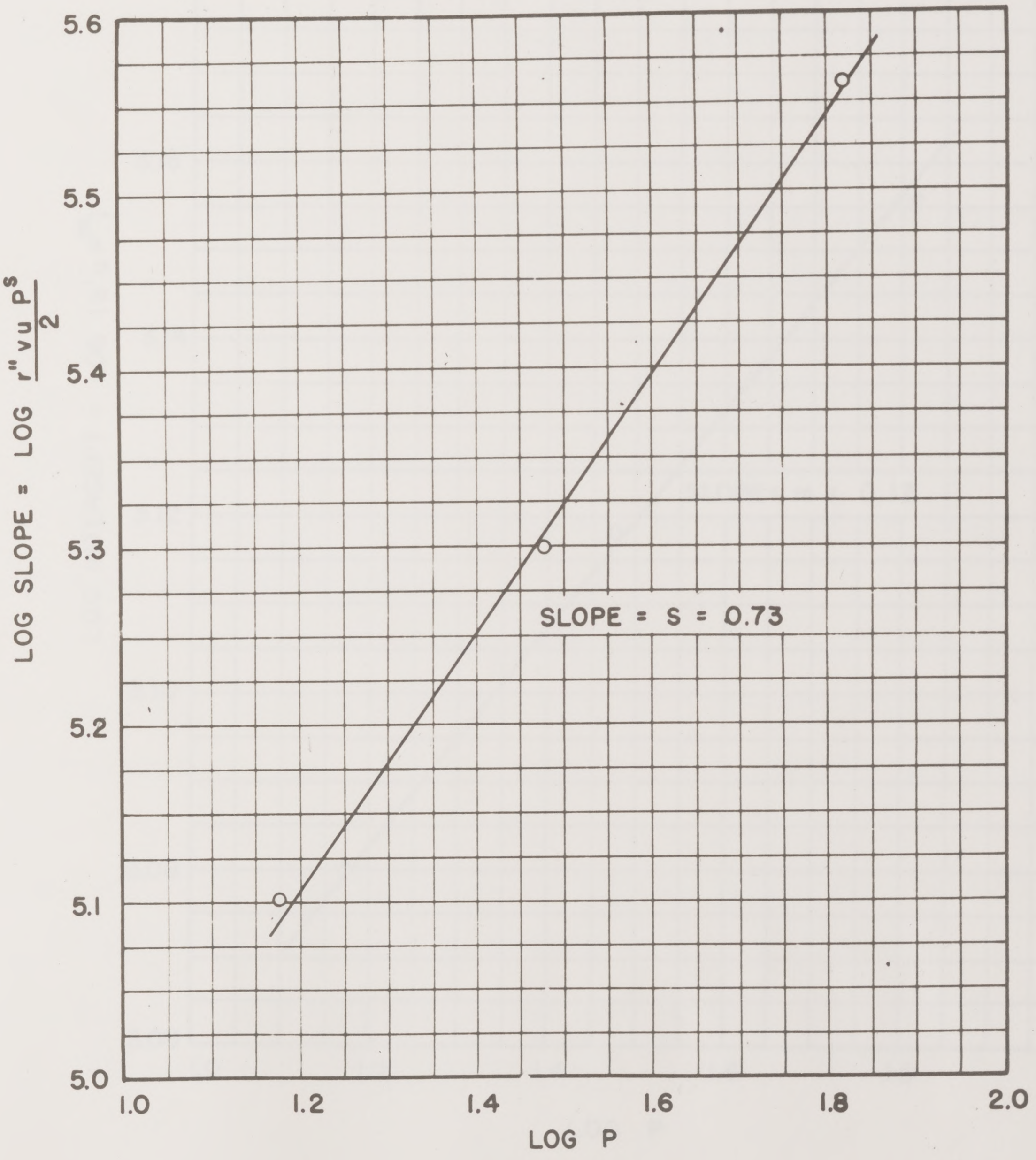
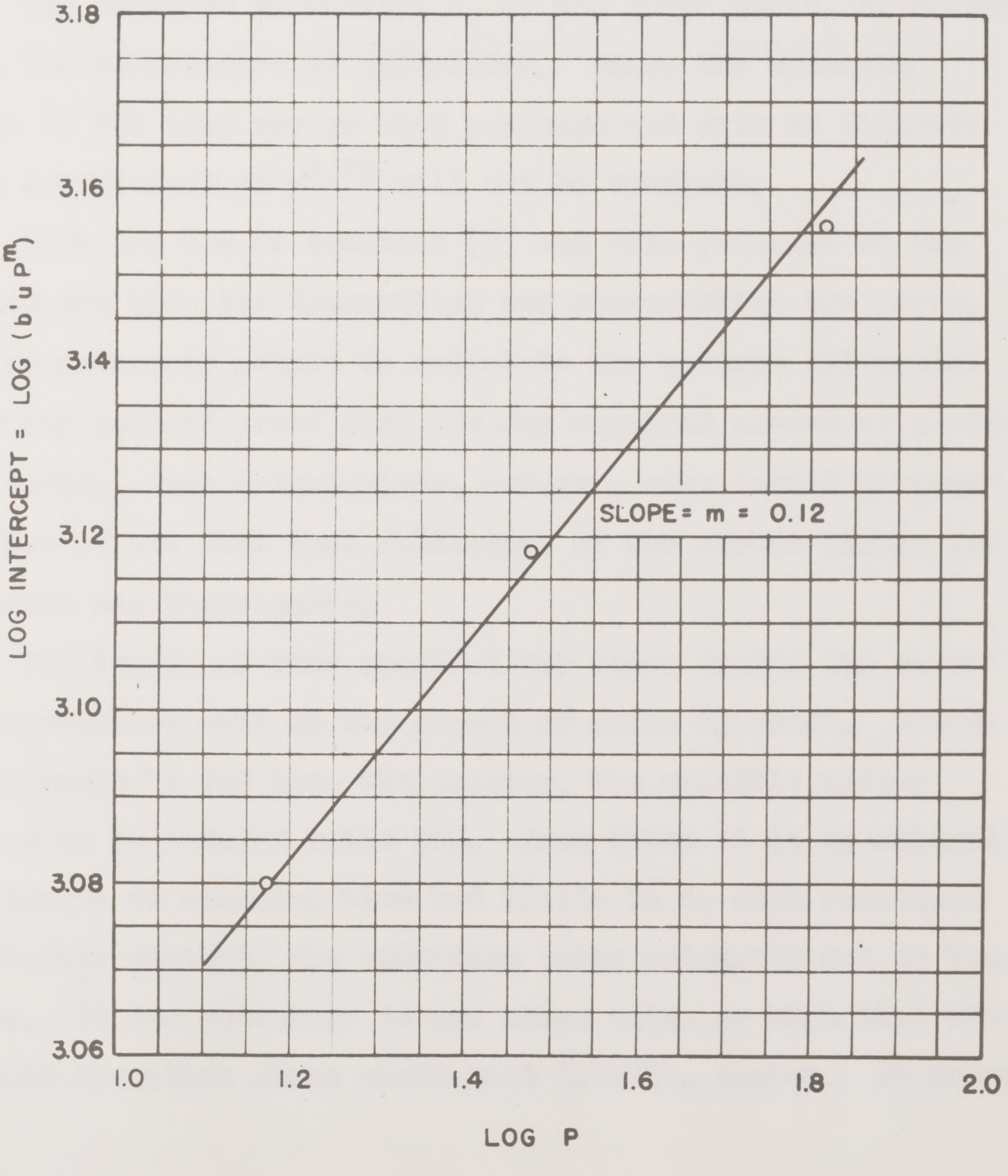


FIGURE 37

Log $(b'u P^m)$ vs Log P



indicates that the resistance of the filtering medium was essentially constant and varied little with rate of flow.

From the calculated data previously given, substitution may be made in the constant pressure filtration equation previously given, to obtain a general equation for constant pressure filtration of a carbon-kerosene sludge:

$$(6)\ P\theta/(V/A) = r''vuP^{0.73}(V/A) + b'uP^{0.12}$$

The relative viscosity, u, of the fluid would, of course, vary with the temperature of filtration. Since the specific resistance of the cake varies with pressure and rate of filtrate flow, the coefficient of $P^{0.73}$ will not be constant.

With the use of equation (6) and data obtained on the drying time and time for dismantling and reassembling the press, it would be extremely simple to calculate the optimum filtration cycle for any assumed press size and any required amount of sludge to be filtered. Such calculations, however, were deemed unnecessary in view of the fact that filtration of the carbon sludge for present needs was inadvisable.

The length of time required for steam drying the carbon was one drawback as well as the amount of steam consumed. Before the carbon could be fed into the treater, the volatile matter content had to be reduced below 50%. From Table 43 it is evident that the length of steaming time had little to do with reduction of the volatile content, the reduction being primarily due to the steam rate. It was necessary to use steam rates so high that the cost of this operation alone would cost 2.7¢/lb. carbon. To reduce the volatile content of the carbon to 70% required far less steam and less time for the operation, hence the use of the filter press as a means of separating carbon from a hydrocarbon liquid such as gasoline or kerosene might be economical if the carbon is to be discarded. If such a means of spearation is ever considered, the filtration data presented in this section should prove of value and were presented for this reason. To complete the data, constant rate runs would have to be made; however, for homogeneous compressible sludges, filtration at constant pressure is usually advisable.

Discussion and Conclusions

The preparation of the kerosene-collected methane-to-acetylene carbon feed stocks has been described, and a description of the construction and operation of the apparatus used for the preparation has been presented.

The operation of the pilot plant for purification of the carbon has been described, and a summary of the operating data and analyses of feed and product carbon have been given.

It was found that purification of this carbon entailed a slightly higher weight loss than that incurred in purification of methane-to-acetylene carbon when producing carbon of the same Burgess mix resistance.

For this type of carbon, the carbon tetrachloride absorption was found to be a function of the apparent density. The carbon tetrachloride absorption was, in general, lower for this carbon than for purified methane-to-acetylene carbon.

The characteristics of the kerosene used in preparation of the feed stocks were given. The pilot plant was found to be a very efficient continuous means for recovering absorbed hydrocarbons on the black. Ninety-seven per cent of the kerosene was removed when operating with an outlet gas temperature of 200°C using a screw speed of 0.21 R.P.M. corresponding to a feed rate of 0.35 lbs./hr.

Dry compression - resistance curves showed that this type of carbon is even less compressible than Shawinigan black.

Battery tests on the purified black showed that the black gave the cells a much shorter shelf life than Shawinigan black. The mix resistance was also somewhat higher, and the 10-day voltage and amperage were lower.

Experimental tests showed that as the apparent density of the black increased, the Burgess mix resistance increased tremendously. The difference in apparent density may, however, have been caused by absorbed impurities rather than by mechanical compression.

Rubber tests showed that this black gave the rubber a much lower tensile strength and lower per cent elongation than unpurified methane-to-acetylene black; however, the results in regard to this point are not conclusive as the two samples were run in different test recipes. The carbon was also poorer in these two respects than thermal acetylene black or electro-black made by the Jakowsky process.

Filtration data were taken on a 1.69% by weight kerosene-carbon sludge, and the compressibility coefficient in the equation of Walker, Lewis, McAdams, and Gilliland was evaluated. The carbon was found to give an extremely compressible cake, the compressibility coefficient being 0.73, in the same order of magnitude as that for $Al(OH)_3$ determined by other investigators.

SECTION VII: GAS OIL-COLLECTED METHANE-TO-ACETYLENE CARBON

Laboratory Work

The special gas cooler designed by Claasen[53] and Burks has previously been described. The use of kerosene in the cooler was abandoned in favor of a narrow boiling range gas oil. This step was taken because an inordinately large amount of the kerosene was vaporized by the hot gases of the cooler. The vapors passed into the discharge and were decomposed by the action of the electric discharge. In addition, the vapors condensed in the gas lines thus wetting the carbon to such an extent that it tended to cause clogging of the pipes.

Removal of the gas oil from the carbon black and subsequent purification of the black constituted the same problem as that in the case of the kerosene. The following table shows roughly the properties of the gas oil:

TABLE 47

Properties of the Gas Oil

Distillation

I.B.P.	330°F (approximate)
10%	450
90%	620
E.P.	650

°A.P.I. = 39

Specific Heat = 0.455 B.T.U./lb.-°F

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[53] Claasen, Jack, Op. Cit.

Removal of the gas oil by means of the pilot plant carbon treater proved to no more difficult than removal of the kerosene. Ninety-five per cent of the gas oil was removed when operating at 450°C using a screw speed of 0.21 R.P.M. and a steam rate of 46 gms./min. The same volumetric ratio of water to gas oil was maintained as in the case of kerosene. In operating under the above conditions, a feed containing 36.79% volatile matter was used. A product containing 2.52% volatile matter was obtained.

Mix resistance tests on gas oil carbon which had first been steamed and then oxidized showed the carbon to be of poor quality. The lowest mix resistance which was obtained was 3.23 ohms per column inch which was far above the allowable limit. The relative resistivity corresponding to a Burgess resistance of 3.23 was 1.22. The above mix resistance was obtained using a screw speed of 0.19 R.P.M., a temperature of 450°C, and an oxygen concentration of 13.1%.

A brief summary of some of the results obtained using gas oil is given in Table 48 on the following page.

TABLE 40

Pilot Plant Purification of Gas Oil Carbon

Run No.	Screw Speed R.P.M.	Screw Temperature °C	Steam Rate gms/min.	Oxygen %	Relative Resistivity	Mix Resistance ohms/column in.
73	0.21	480	46.0	0	4.75	---
74	0.41	480	19.2	13.1	2.29	7.55
	0.19	480	19.2	13.1	1.22	3.23
75	0.75[a]	320	46.0	0	---	---

[a] 15.67% volatile matter left in product.

Average volatile content of feed for stripping runs = 34.0%

The carbon from run 73 which had been only steam stripped was sent to Commercial Solvents for testing in rubber. The pH of the carbon sludge was also measured and found to be 3.7. The volatile content of the product as determined in the University laboratory was 2.58%.

The results of the rubber tests are presented in the Table below:

TABLE 49

Rubber Tests on Gas Oil Collected Methane-to-Acetylene Carbon

Time, min.	Tensile, lbs./sq.in.	Elongation, %
15	3280	420
30	3190	390
45	3530	387
60	3410	370
90	3190	345

Recipe:

Rubber	100
Zinc Oxide	5
Sulfur	3
D.P.G.	0.7
Carbon	40

Cured in Press at 287°F

The tensile strength and per cent elongation were much greater with this carbon than the kerosene collected carbon, although both properties were too poor to allow the carbon to be used as a rubber reinforcing agent.

Discussion and Conclusions

The approximate properties of the gas oil were given, and the method for removing it from the carbon was briefly described. In view of the failure to produce a successful battery black from kerosene-collected methane-to-acetylene carbon, no battery tests were run on the gas oil carbon.

From the standpoint of hydrocarbon removal, the pilot plant was as efficient in removing gas oil as it was in removing kerosene, 95% removal being accomplished in the former case and 97% in the latter.

Results of rubber tests using the gas oil-collected carbon have been presented and discussed. The tensile strength of this carbon was considerably higher than that of kerosene-collected carbon. The per cent elongation was also somewhat higher; however, the carbon gave a hard, stiff, cured rubber sheet, and this property made it too poor for direct use as a rubber reinforcing agent.

SECTION VIII: GASOLINE-TO-ACETYLENE CARBON

Introduction

The purpose of this work was (1) to study the properties of gasoline-to-acetylene carbon, (2) to devise a method for recovery of the gasoline from the carbon, and (3) to discover if the carbon could be treated to make it commercially usable.

The construction and operation of the gasoline discharge unit has been amply discussed in the work of Holcomb,[54] however, a brief discussion relative to the production of carbon black will not be out of place here.

The general flow scheme of the gasoline unit has been altered several times in the course of experimentation. Carbon black was the cause of most of the difficulties encountered in operation of the unit. In the final flow plan, carbon black was removed from the system in three places: (1) from the bottom of the reaction chamber, (2) from the bottom of a cyclone separator placed between the vertical-tube spray cooler and the discharge chamber, and (3) from the liquid gasoline filters. It was later decided that it was unnecessary to remove carbon black from three places in the system so it was planned to remove the cyclone separator upon improved design of the spray cooler.

No data have been taken on the production of carbon black in the discharge chamber. Such data would be practically impossible to obtain with the present method for operation of the unit. This is because liquid gasoline is fed to the insulators, and it is difficult to determine the actual amount acted on by the discharge.

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[54] Holcomb, H.A., _op. cit._

A large amount of carbon also collects on the chamber walls, and the portion which falls to the bottom is contaminated with unvaporized gasoline which flows down the chamber walls from the insulators.

On the assumption that one-fourth as much carbon black as acetylene is formed (based on the amount of carbon produced in the gas discharge pilot plant), 1.7 lbs. of carbon/hr. are formed when operating at 0.29 KWH/lb. gasoline.

Chemical and Physical Properties of the Gasoline-to-Acetylene Carbon

Preliminary Tests: Experimental work on gasoline-to-acetylene carbon was begun at about the same time that work was started on the methane-to-acetylene carbon. All attempts to purify the black for use in dry cell batteries failed, although the recovery system which was devised worked quite well. The first attempt at purification consisted of extracting the gasoline black with acetone. Samples of the black which had been extracted four times with fresh acetone were sent to Burgess Battery Company for testing. Since the black would not wet with water, battery tests could not be run. The gasoline carbon which was sent had been removed from the bottom of the reaction chamber.

Further small-scale tests were run on the carbon merely as a preliminary means of examination. Water-wetting and relative resistivity were the only tests used for effectiveness of treatment during these preliminary experiments.

A sample of the gasoline chamber carbon was heated in a tube over a Meker burner, and a large amount of yellow vapor was emitted. The carbon was heated to a dull red glow. After the carbon had cooled, water was added, and it was found the carbon could not be wet with water.

A similar test was run on carbon from the cyclone separator. This carbon after treatment wet with water rather slowly but more rapidly than Shawinigan carbon.

Another sample of the gasoline cyclone separator carbon was vacuum distilled at 2 mm Hg pressure for three hours at 280°C, and the relative resistivity of the carbon was measured. The resulting resistivity was 1854--far too high to be useful for batteries.

Carbon from the discharge chamber was extracted with acetone four times and dried. The resistance of the carbon was too high to measure. Similar experiments with gasoline filter carbon were tried and the same results were obtained.

Steam distillation of the carbon was conducted on a small scale and combined with dry distillation. The carbon was steam distilled for three hours at 200°C and dried. The resulting relative resistivity was 8422. Heating the carbon in air at 300°C for 10 minutes brought the resistivity down to 2150. A second heating at the same temperature for 1/2 hour brought the relative resistivity down to 539.

Gasoline chamber carbon heated first for 2 hours and then extracted with acetone 4 times gave a relative resistivity of 807.

Further tests were conducted heating the carbon in air at 450°C for 1-1/2 hours. The relative resistivity dropped to 69. Heating for an additional 2-1/2 hours brought the relative resistivity down to 44.

Gasoline cyclone separator carbon was acetone extracted and centrifuged 7 times and dried. The relative resistivity was 1310.

Skellysolve B was tried as a solvent and the filtered carbon was dried. A relative resistivity of 1231 resulted. Ethyl acetate was also tried as a solvent and about the same results were obtained.

Heating the gasoline carbon in an electric furnace in natural current of air for three hours at an average temperature of 300°C brought the relative resistivity down to 61. On putting the carbon back in the furnace and heating for an additional hour at 460°C, the resistivity was brought down to 50.

In view of the failure of the above tests to produce a carbon of low enough relative resistivity, high temperature heating in the presence of methane was tried. The carbon was heated to 1100°C for 1 hour which produced a relative resistivity of 3.4, the lowest ever obtained. However, the carbon showed strong evidence of graphitization.

On the average, the carbon tetrachloride absorption on untreated gasoline black was about 14 c.c./5 gms., and removal of volatile matter did not improve the absorption properties a great deal.

A summary of the results of the tests discussed above is given in Table 50.

TABLE 50

Results of Preliminary Treatment of Gasoline-to-Acetylene Carbon Black

Type of Carbon	Method of Treatment	Relative Resistivity
Cyclone Separator (Old)	None	6220
Cyclone Separator (Fresh)	None	3201
Cyclone Separator	Vacuum Distilled 3 hrs. at 260°C	1054
Cyclone Separator	Steam Distilled 3 hrs. at 200°C	2422
Cyclone Separator	Vacuum Distilled 3 hrs. at 260°C & Heated 10 min. at 400°C	2150
Cyclone Separator	Same as Above but Heated for 30 min.	539
Cyclone Separator	Heated 90 min. at 400°C	69
Cyclone Separator	Acetone Extracted & Centrifuged 7 Times	1310
Cyclone Separator	Heated 3½ hours at 400°C	25
Gasoline Filters	Acetone Extracted 4 Times & Heated to 400°C for 10 min.	669
Gasoline Filters	Heated 3 hrs. at 300°C	65

TABLE 80 (concluded)

Results of Preliminary Treatment of Gasoline-to-Acetylene Carbon Black

Type of Carbon	Method of Treatment	Relative Resistivity
Gasoline Filters	Heated 4 hours at 460°C	50
Gasoline Filters	Steam Distilled at 400°C for 2 hrs.	54
Discharge Chamber	Acetone Extracted Four Times	Too High to Measure
Discharge Chamber	Acetone Extracted 4 Times & Heated at 400°C 2 hrs.	807

There was not a great deal of difference between the effects of the same treatment on carbon collected from different places in the flow system. Cyclone separator carbon naturally had a smaller volatile content than the filter or discharge chamber carbon. Cyclone carbon was also fluffier and had a lower density than chamber or filter carbon.

The steam distillation tests were conducted in the apparatus with the rotary stirrer described in Section A and shown in Figure 8 of that section. Vacuum distillation was done in a glass tube about 1" in diameter and about 8" long, the tube being inserted in a Hoskins round electric furnace. The tube was closed at one end and a Duo-Seal vacuum pump was attached to the other. A condenser was placed between the pump and the tube.

The heating of the carbon in the presence of air was conducted in a Hoskins electric furnace, the temperatures being measured with a calibrated chromel-alumel thermocouple.

The results of these preliminary tests were not encouraging from the viewpoint of production of a satisfactory battery black.

<u>High Temperature Treatment</u>: As far as relative resistivity was concerned, preliminary experiments showed that high temperature heating produced the best results. A sample of gasoline carbon black was placed in a Hoskins electric furnace and heated to 1000°C in the presence of hydrogen. The time of heating was about two hours. The resulting carbon was lumpy, graphitic in nature, and non-uniform. The top 1" layer of carbon gave a relative resistivity of 1.38 whereas the bottom 3/4" gave a relative resistivity of 0.79. The carbon would wet with water

but would not disperse uniformly. The carbon tetrachloride absorption of the untreated carbon was rather low, 14 c.c./5 gms. The upper layer of the treated carbon gave a carbon tetrachloride absorption value of 19 c.c./5 gms., the lower layer giving an absorption value of 15 c.c./5 gms.

Another high temperature run was made in a small Hoskins electric furnace. This run was made to determine the weight loss of carbon incurred at the high temperature. A sample of gasoline cyclone carbon was heated to 1000°C for 4½ hours. The weight loss was determined to be 47%. A considerable amount of carbon may have been actually formed on the original carbon by thermal cracking of the hydrocarbon impurities. The resulting relative resistivity of the carbon was 3.54. The corresponding Burgess resistance was determined to be 2.92.

Tests were also run on cyclone carbon at high temperatures using a covered container so that the carbon did not have access to the atmosphere. In one such test, the carbon was heated for four hours at a temperature of 800°F. The relative resistivity of the carbon was 6.52 and the carbon tetrachloride absorption was 27.0 c.c./5 gms. The original carbon had an absorption value of 9.9 c.c./5 gms.

<u>Volatile Content of Raw Carbon</u>: The volatile content of the gasoline-to-acetylene carbon varied depending on the operating conditions of the plant and the point of removal of the carbon. Carbon from the reaction chamber had, on the average, about 55% volatile matter. The nature of the adsorbed material also depended on the operating conditions as well as the nature of the gasoline fed to the discharge.

A sample of the absorbed impurities on the gasoline cyclone carbon was obtained by running the carbon through the carbon purification pilot plant in the presence of steam and collecting the condensate. The plant was operated at about 500°C and the outlet gas temperature was 215°C. The feed carbon contained 53.9% volatile matter as determined by vacuum distillation at 1000°F.

The material collected as condensate was dried over calcium chloride, and a distillation was made. A sample of the volatile matter contained on the gasoline chamber carbon was collected in the same manner. The distillation data are shown plotted in Figure 38. For the sake of comparison, the distillation curves of original and recycle gasoline from the discharge chamber are also plotted.

The properties of the distillates are listed in Table 51 on a following page. From the curves and the table, it may readily be seen that the cyclone carbon distillate was by far the heaviest. This is not surprising in view of the fact that the gasoline unit was run with the cyclone maintained at a temperature of 300°F by means of hot oil flowing in a jacket around the separator. The original gasoline had a volumetric average boiling point of 263°F whereas the volumetric average boiling point of the recycle gasoline was 312°F. Holcomb[55] has found that successive recycles did not change the specific gravity of the gasoline. As might be expected, the end-point of both gasolines were essentially

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[55] Holcomb, H.A., op. cit.

FIGURE 38
GASOLINE DISTILLATION

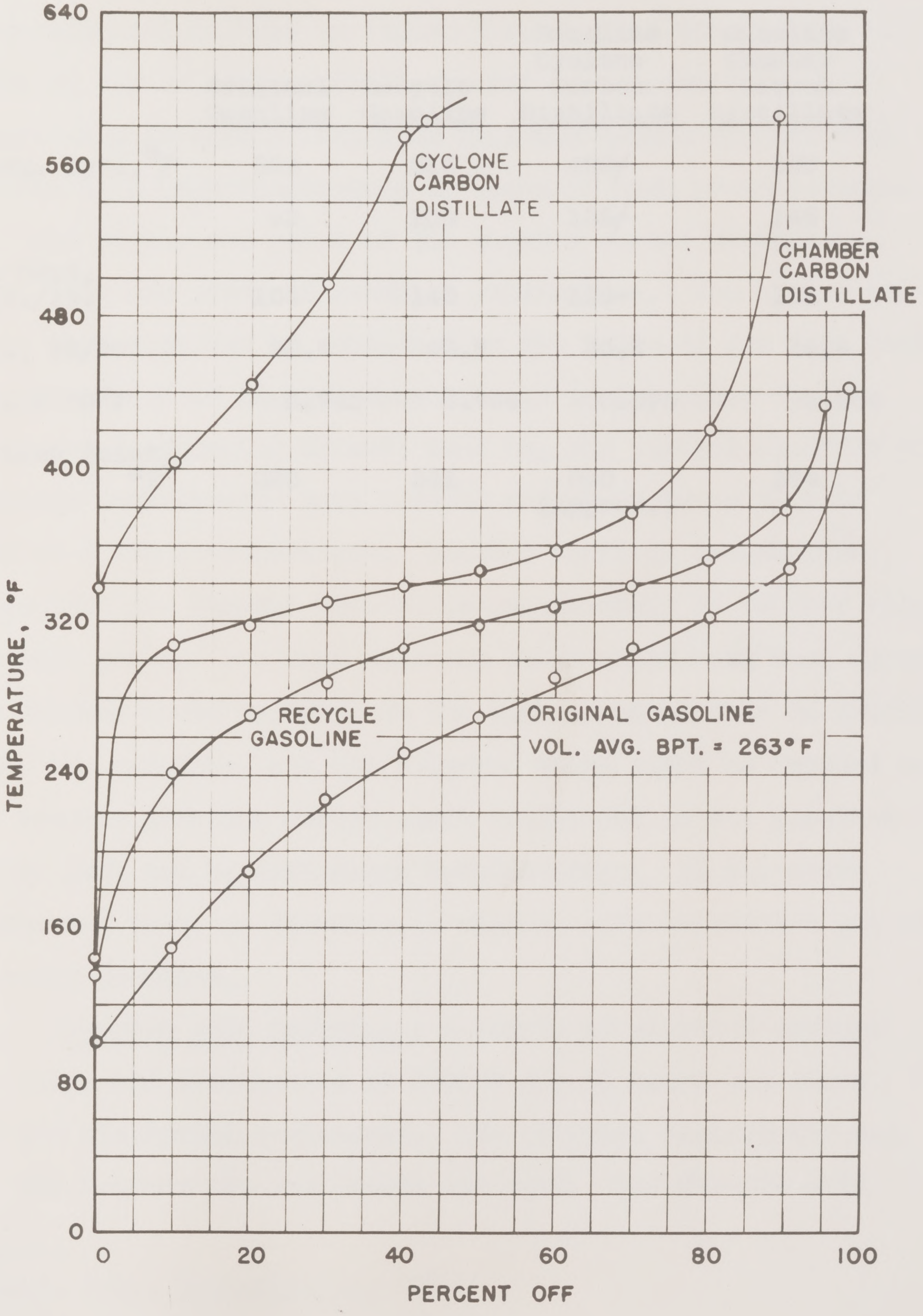

TABLE 51

Properties of the Distillates

	Original Gasoline	Recycle Gasoline	Gasoline Cyclone Carbon Distillate	Gasoline Chamber Carbon Distillate
Vol. Avg. Bpt., °F	263	312	498+	369
M. Wt.	93	108	155+	146
Latent Heat, B.T.U./lb.	154	145	119-	121
°A.P.I., 60/60	58.9	43.7	30.2	44.4
Sp. Gr. @ 60°F	0.743	0.764	0.875	0.804
100% Flash Point, °F	320	361	600 (Approx.)	374

the same. Another investigator[86] has found that the distillation curves of the gasoline did not change a great deal with successive recycles through the discharge. The fact that the chamber carbon distillate is higher than that of the recycle gasoline as far as average boiling point is concerned is also not surprising in view of the fact that the carbon box was also maintained at a high temperature by means of high pressure steam coils. The higher end point of the chamber carbon distillate, however, does not offer as ready an explanation. The higher end-point in this case may be explained on the basis of the fact that the larger amount of lighter constituents in the other distillates caused a stripping effect; that is, the partial pressure of the heavier constituents were reduced enough to cause them to distill at a lower temperature. Another possible explanation might be that the chamber carbon was continuously in contact with the chamber gases. Any high polymers which might have been formed in the chamber would condense on the carbon rather than be carried out with the gasoline, and any polymers which might be carried out in the recycle gasoline stream would settle out in the gasoline reservoir tank and be left there by decantation. It has often been observed that, on standing, a viscous polymer settles out of the recycle gasoline.

<u>Chromic Acid Reduction</u>: A sample of gasoline cyclone carbon which had been heated at 1700°F for 4½ hours was first tested for electrical resistance. The relative resistivity was 3.54. The Burgess mix resistance was 2.92. The chromic acid

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[86] Metcalf, J.D., <u>Dissertation</u>, 1930.

reduction was then measured in the manner described in Section IV of this part. It was found that 91.5% of the color was removed (8.5% remaining) in 18.2 hours, which was a much more rapid reduction than that encountered with any of the other samples tested.

In heating the carbon in the manner described above, 47.1% loss was encountered.

Pilot Plant Purification

Operating Data: No attempts were made to purify the black for use in dry cell batteries in view of the negative results obtained in the laboratory work. It was decided to remove the major portion of the volatile matter from the carbon by steam stripping in the pilot plant and to remove the remainder by selective oxidation. It was believed that carbon treated in this manner might have some value for use in rubber reinforcement even if not of use for dry cell batteries.

Steam stripping was carried out at a screw temperature of 400°C and an outlet gas temperature of 200°C. In the oxidation run, 13% oxygen was used in the gas stream using a screw temperature of 400°C. The outlet gas temperature was 180°C.

Analytical Data: The sample of carbon purified as described above was sent to Commercial Solvents Corporation for evaluation as a rubber reinforcing agent. The analyses of the feed and product are presented in Table 52.:

TABLE 52

Analyses of Feed and Product Carbon: Steam Stripping

	Feed	Steamed Product	Oxidized Product
Volatile Content, %	53.4	10.0	10.8
Apparent Density, lbs./cu.ft.	24.1	14.5	12.0
Relative Resistivity	7884	3470	572

The relative resistivity of the product of the oxidation run was 572. Commercial Solvents determined the pH of the carbon sludge to be 6.1. The CCl_4 absorption of the oxidized product was 18.8 c.c./5 gms.

Evaluation for Rubber Reinforcement: The results of Commercial Solvents showed that the gasoline carbon gave a lower tensile strength and lower per cent elongation in natural rubber than either kerosene or gas oil collected methane-to-acetylene carbon.

The gasoline carbon gave considerable odor on the mill, indicating that the carbon contained considerable impurities. This carbon gave cured sheets which were very soft, and the carbon would not disperse satisfactorily. The cured sheets were lumpy when stretched, and remilling for better dispersion did not improve this quality. The results of the tests are given in the table on the following page.

TABLE 53

Rubber Tests on Gasoline Carbon

Rubber	100	100 (Remilled)
Zinc Oxide	5	5
Sulfur	3	3
D.P.G.	0.7	0.7
Carbon	40	40

Cured in Press at 287°F

Time, Min.	Tensile Strength, lbs./sq.in.	
15	500	690
30	670	690
45	610	730
60	580	660
90	710	820

Elongation in Percent

15	150	330
30	197	300
45	170	295
60	163	245
90	166	230

Electron Microscope photographs of the gasoline cyclone carbon were made in the University laboratory and compared with untreated methane-to-acetylene carbon. The photographs are shown in Figure 39a on the following page. Both samples were dispersed in carbon tetrachloride and deposited on supporting screens. Magnification up to 10,000 x was accomplished with the microscope. The additional magnification up to 20,000 times was performed optically.

The photographs show that the untreated methane-to-acetylene black disperses slightly more than gasoline carbon. The gasoline carbon particles are also slightly different in shape, being generally spherical whereas the methane-to-acetylene carbon seems to be composed of platelets, similar to the treated carbon as shown in a previous photograph.

Measurements of particle size show that the particles of gasoline carbon are somewhat smaller. The measured particle diameter of the gasoline carbon was about 20 mu as compared with 30 mu for the untreated methane-to-acetylene carbon. Columbian Carbon Company had estimated the particle size of the untreated methane-to-acetylene carbon to be 17.5 mu. They did not state how the particle size was determined. Measurements from the photograph taken by Monsanto Chemical Company show the particle size to be about 25 mu, in better agreement with this laboratory's results. The poor dispersion obtained with the samples tested makes measurements difficult.

FIGURE 39a

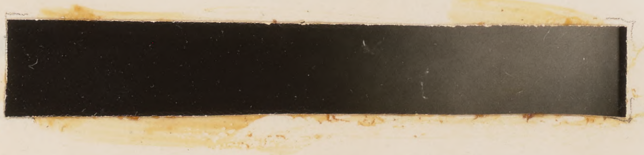
ELECTRON MICROSCOPE PHOTOGRAPHS
(20,000 x)

Untreated Gasoline-to-Acetylene Carbon

Untreated Methane-to-Acetylene Carbon

FIGURE 39b

X-RAY DIFFRACTION PHOTOGRAPHS



Untreated Gasoline-to-Acetylene Carbon

Batch Treated Methane-to-Acetylene Carbon

X-Ray diffraction patterns showed that gasoline carbon was less graphitic in nature than treated methane-to-acetylene carbon. A comparison of these two blacks is shown in Figure 39b.

The results of the X-Ray analysis bear out the findings of the electron microscope observations (Figure 39a) which show the gasoline particles to be generally spherical in shape whereas the methane-to-acetylene carbon particles are semi-crystalline, needle-like particles.

Construction and Operation of a Carbon Removal Valve:

The removal of carbon from the gasoline discharge unit presented a problem different from that encountered with the methane discharge unit. The methane-to-acetylene carbon was a "dry" carbon, having approximately 10% volatile matter, and it could be filtered from the gaseous mixture by ordinary sock filters. The gasoline-to-acetylene carbon could not be removed in the same manner, because of the high temperature of the gases, and because of the liquids present on the carbon. The gasoline-to-acetylene carbon was found to have a volatile content amounting to 50% or more, a large percentage of this being gasoline, which has to be returned to the discharge system to improve the efficiency. Also, the removal of the carbon had to be accomplished in order to make the operation of the gasoline discharge unit continuous.

The rotary air lock, or "star" valve was first thought to be the solution to the problem. This type of valve was tried by Commercial Solvents Corporation on their gasoline discharge unit, and reports on the valve said that it leaked quite badly. With the chance of the mixture of gasoline vapor, acetylene, and hydrogen leaking out, and of air leaking in, it did not seem advisable to use the rotary air lock.

The valve decided upon is the one illustrated in the assembly view of Figure 40, a valve of the ball and seat type. The completed valve will consist of two of the units of Figure 40 in series, the valves being actuated alternately by an automatic cam mechanism, which introduces and releases air to the diaphragms. The upper valve will have a funnel in its lower portion to reduce the diameter to the same size as the ball valve.

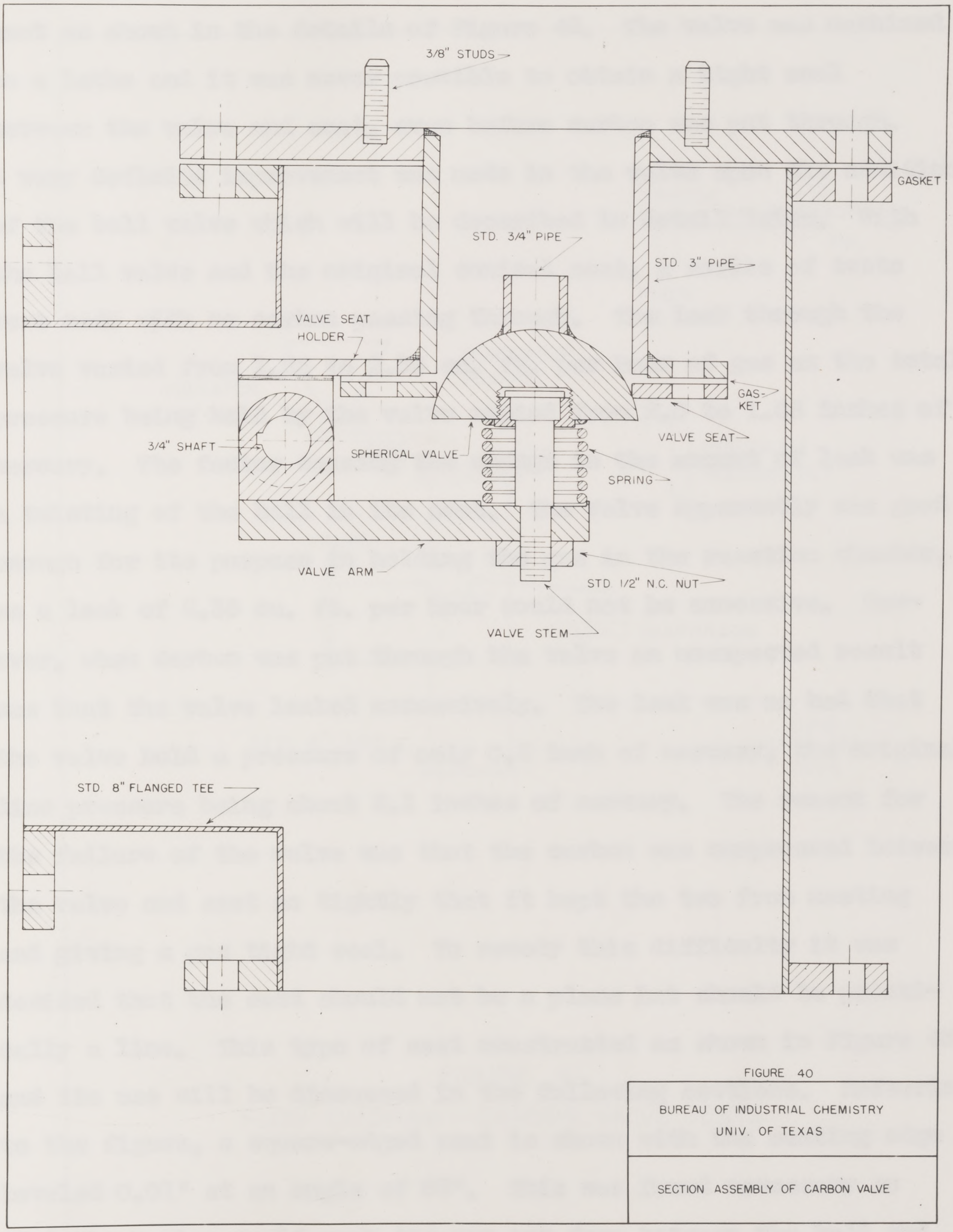


FIGURE 40

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SECTION ASSEMBLY OF CARBON VALVE

The first valve mechanism constructed had a valve and seat as shown in the details of Figure 42. The valve was machined on a lathe and it was never possible to obtain a tight seal between the valve and seat, even before carbon was put through. A very definite improvement was made in the valve upon the addition of the ball valve which will be described in detail later. With the ball valve and the original conical seat, a series of tests were made with no carbon passing through. The leak through the valve varied from 1.25 to 2.35 cu. ft. per hour of gas as the total pressure being held by the valve varied from 2.0 to 1.65 inches of mercury. The factor causing the change in the amount of leak was a twisting of the ball in its seat. The valve apparently was good enough for its purpose in holding the gas in the reaction chamber, as a leak of 2.35 cu. ft. per hour would not be excessive. However, when carbon was put through the valve an unexpected result was that the valve leaked excessively. The leak was so bad that the valve held a pressure of only 0.2 inch of mercury, the original line pressure being about 2.1 inches of mercury. The reason for the failure of the valve was that the carbon was compressed between the valve and seat so tightly that it kept the two from meeting and giving a gas tight seal. To remedy this difficulty it was decided that the seat should not be a plane but should be practically a line. This type of seat constructed as shown in Figure 43 and its use will be discussed in the following sections. Referring to the figure, a square-edged seat is shown with the seating edge beveled 0.01" at an angle of 52°. This was found necessary so that the carbon could work its way out from between the ball and the seat.

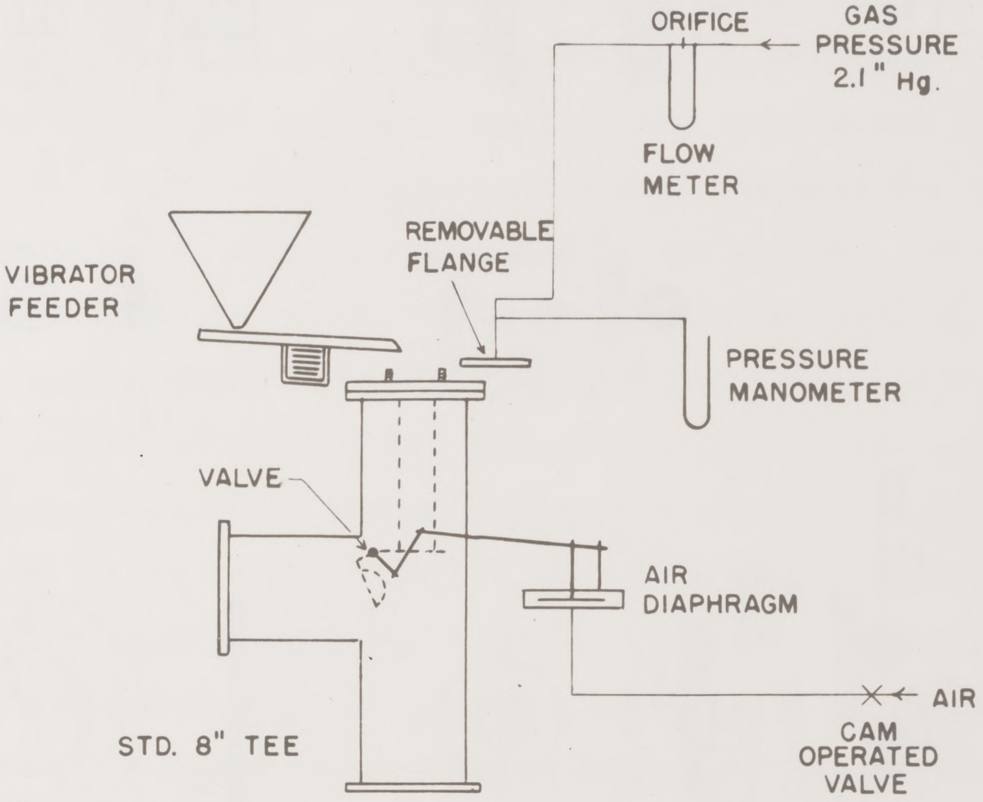

FIGURE 41

FLOW DIAGRAM — CARBON VALVE TESTS

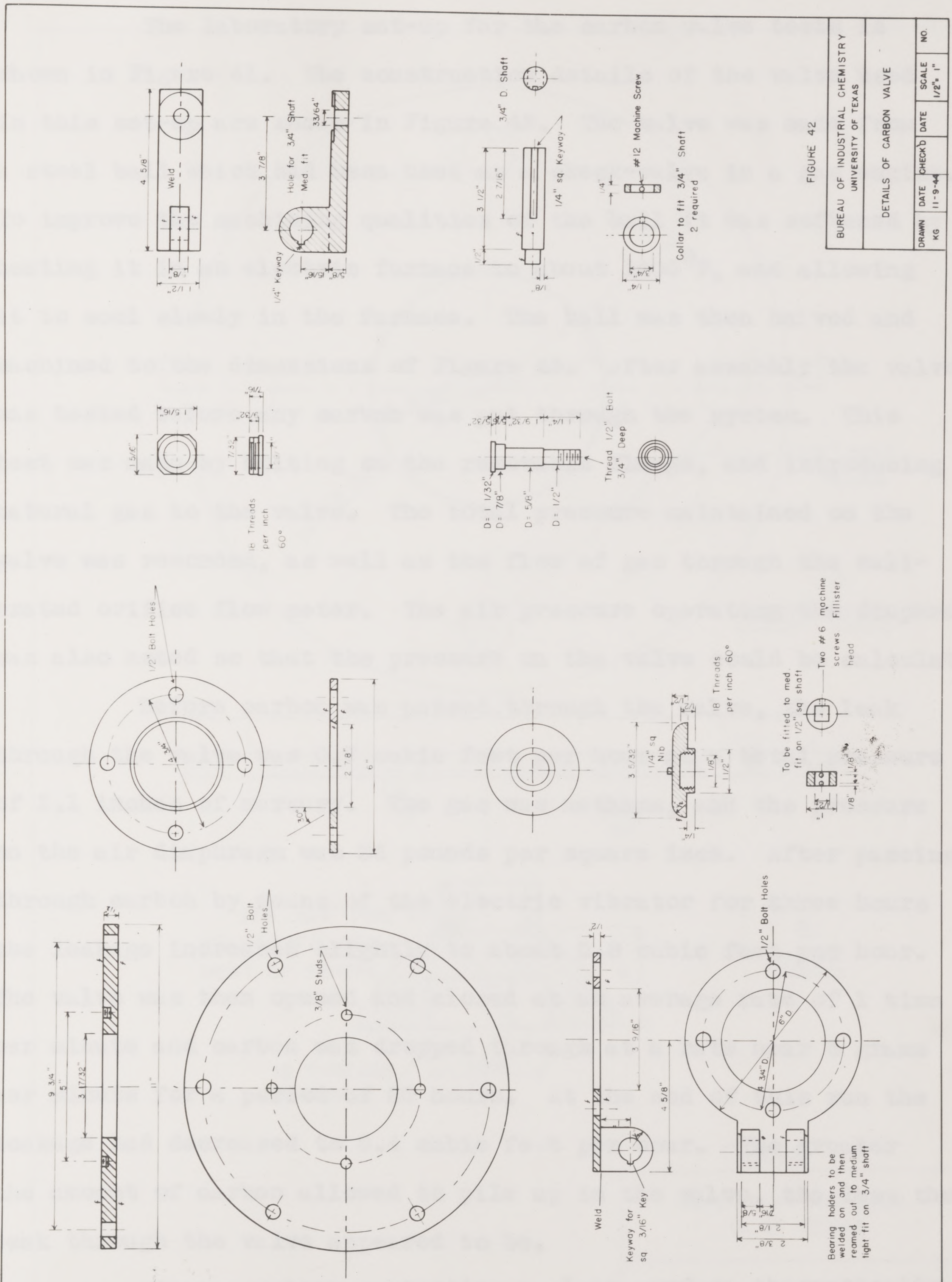

FIGURE 42

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DETAILS OF CARBON VALVE
DRAWN KG
DATE 11-9-44
CHECK'D
DATE
SCALE 1/2" = 1"
NO.
4 5/8"
Weld
1/8"
1 1/2"
Hole for 3/4" Shaft
Med fit
3 7/8"
33/64"
1/4" Keyway
15/16"
5/8"
3/4" D Shaft
3 1/2"
2 7/16"
1/4" sq Keyway
#12 Machine Screw
1/2"
1/8"
1/4"
3/4"
Collar to fit 3/4" Shaft
2 required
1 5/16"
1 5/16"
7/16"
3/32"
1 7/32"
18 Threads
per inch
60°
D = 1 1/32"
D = 7/8"
D = 5/8"
D = 1/2"
Thread 1/2" Bolt
3/4" Deep
1/2" Bolt Holes
4 3/4"
2 7/8"
6"
30°
3 5/32"
1/4" sq
Nib
1 1/8"
1 1/2"
18 Threads
per inch 60°
To be fitted to med.
fit on 1/2" sq shaft
Two #6 machine
screws Fillister
head
1/8"
1/2" Bolt
Holes
3/8" Studs
9 3/4"
5"
3 17/32"
11"
3 9/16"
4 5/8"
Weld
Keyway for
sq 3/16" Key
1/2" Bolt Holes
6" D
4 3/4" D
7/16"
2 1/8"
2 3/8"
Bearing holders to be
welded on and then
reamed out to medium
tight fit on 3/4" shaft

The laboratory set-up for the carbon valve tests is shown in Figure 41. The construction details of the valve used in this set-up are shown in Figure 42. The valve was made from a steel ball which had been used as a check-valve in a gas engine. To improve the machining qualities of the ball it was softened by heating it in an electric furnace to about 1400°F, and allowing it to cool slowly in the furnace. The ball was then halved and machined to the dimensions of Figure 43. After assembly the valve was tested before any carbon was put through the system. This test was made by bolting on the removable flange, and introducing natural gas to the valve. The total pressure maintained on the valve was recorded, as well as the flow of gas through the calibrated orifice flow meter. The air pressure operating the diaphragm was also noted so that the pressure on the valve could be calculated.

Before carbon was passed through the valve, the leak through the valve was 0.7 cubic feet per hour at a total pressure of 2.1 inches of mercury. The gas was methane, and the pressure on the air diaphragm was 36 pounds per square inch. After passing through carbon by means of the electric vibrator for three hours the leakage increased slightly to about 0.8 cubic feet per hour. The valve was then opened and closed at an average rate of 1 time per minute and carbon was dropped through at a rate near 5 grams per minute for a period of 20 hours. At the end of this run the leakage had decreased to 0.4 cubic feet per hour. The greater the amount of carbon allowed to pile up in the valve, the less the leak through the valve appeared to be.

Since a sphere contacting a plane surface theoretically gives a thin line of contact, it seemed best to calculate the

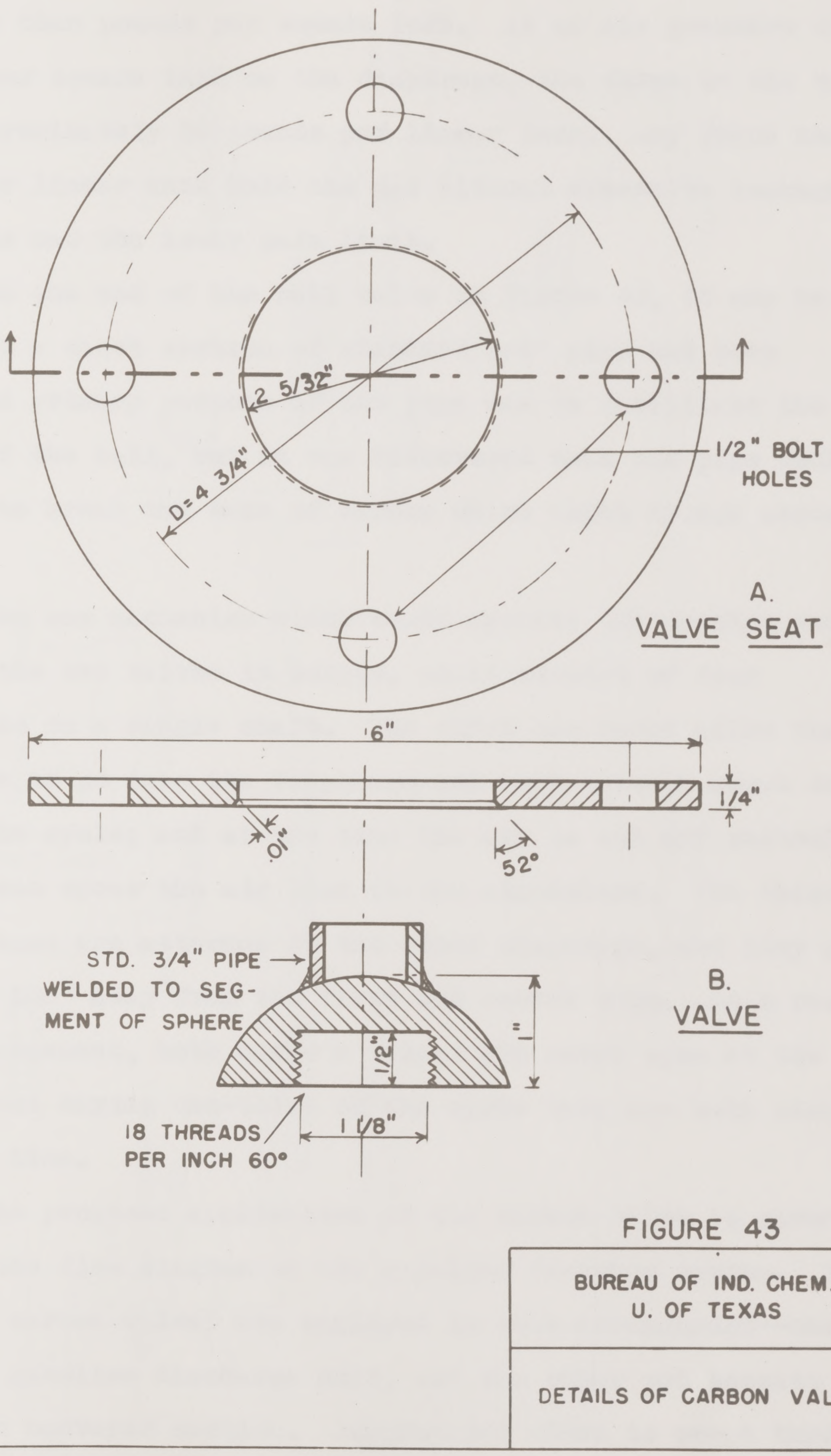

FIGURE 43

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U. OF TEXAS

DETAILS OF CARBON VALVE

force of the valve against the seat in terms of pounds per linear inch rather than pounds per square inch. At an air pressure of 36 pounds per square inch on the diaphragm, the force on the valve seat is approximately 19 pounds per linear inch. Any force above 7 pounds per linear inch held the gas without excessive leakage, but 7 pounds was the lower safe limit.

On the end of the ball valve in Figure 43, it may be noticed that a short section of standard 3/4" pipe has been welded. The primary purpose of the pipe was to facilitate the machining of the ball, but it was discovered that the pipe would also serve to break the cake of carbon which might bridge across the valve.

The cam mechanism which would operate the opening and closing of the two valves in series, would consist of four separate cams on a single shaft. The first cam would allow the air pressure to go into the diaphragm and hold through about two-thirds of the cycle; and at the time the air is cut off suddenly, the second cam opens the air line to the atmosphere. The third and fourth cams are attached to the other diaphragm, and they are set exactly 180° away from the first and second cams. As a result of this arrangement, both carbon valves are never open at the same time, but during one-third of the cycle they are both closed at the same time.

The proposed application of the carbon valve is given in Figure 44, the flow diagram of the gasoline recovery system. Two sets of the carbon valves are employed in this arrangement--one beneath the gasoline discharge unit, and the other set beneath the heated screw conveyor section. Superheated steam is swept through

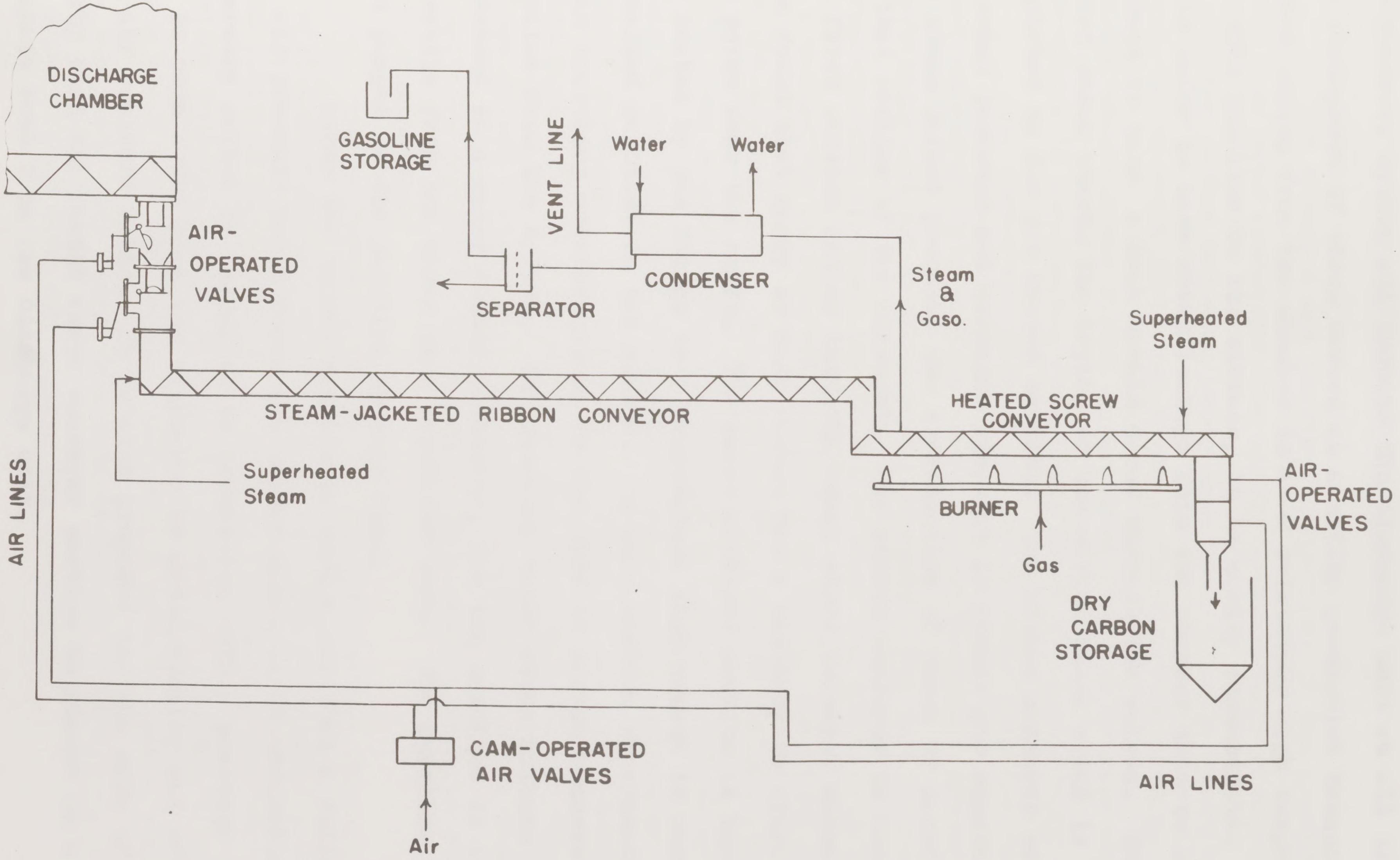

FIGURE 44

FLOW DIAGRAM – GASOLINE RECOVERY SYSTEM

the recovery system and beneath the discharge unit at all times.

The atmosphere of steam serves as a safety precaution because the carbon coming from the chamber is at a relatively high temperature, and with gasoline on its surface, it is easily combustible. Also, it is safer to have steam leakage into the chamber than to have air leakage in case a leak should occur through the valves. The superheated steam starts the drying of the carbon black which is later completed in the gas heated section. The ribbon conveyor section is steam jacketed and contains steam at 15 pounds per square inch. The steam jacket prevents the condensation of steam or gasoline in that section of the conveyor. The ribbon conveyor is used in the first section rather than the usual screw conveyor since it has been found that gummy or damp carbon has a tendency to stick to the screw near the shaft. The screw conveyor section is insulated, and heated by gas flames to a temperature high enough to remove the entrained gasoline in the carbon. In this section superheated steam traveling countercurrent to the flow of carbon removes the gasoline from the system. The gasoline vapor-steam mixture is condensed in a water cooled condenser, and the gasoline is allowed to settle from the water in a separator tank. The gasoline is then pumped to the gasoline storage tank.

Since the valves operate in such a way that a failure in the air pressure would leave all valves open, it is advisable that a mercury switch be installed in connection with a pressure indicator in such a way that the discharge be automatically cut off when the air pressure fails. It is also proposed for the sake of safety that the heated screw conveyor section be placed in a separate room from the discharge unit.

Discussion and Conclusions

The chemical and physical properties of the gasoline carbon have been discussed: The carbon tetrachloride absorption of gasoline carbon was much lower than that of methane-to-acetylene carbon, being about 10-14 c.c./5 gms. The apparent density of the gasoline-to-acetylene carbon as received from the chamber was very high--about 24 lbs./cuft., containing about 50% gasoline by weight.

The characteristics of the distillates obtained from carbon collected from various places in the discharge system were investigated and the results were presented: The distillation characteristics differed considerably; when the original gasoline had a volumetric average boiling point of 263°F, the distillate from the cyclone carbon had a volumetric average boiling point of 498/$^{\circ}$F. The chamber carbon distillate was also considerably higher in boiling point than either the recycle gasoline or original gasoline. The specific gravities of the distillates varied from 0.743 for the original gasoline to 0.875 for the cyclone carbon distillate. Successive recycles does not change the specific gravity of the gasoline feed after a certain value has been reached.

All attempts to purify the gasoline carbon for use in dry cell batteries were without success. The continuous pilot plant purifier can, however, be used as a means for recovering the gasoline from the carbon black. For continuous removal of the carbon black from the gasoline chamber, a special carbon valve has been designed. The design has been described in detail as well as the experimental work for testing its operation.

Purification of the gasoline-to-acetylene carbon for use as a rubber reinforcing agent was described in detail. The carbon was tested in natural rubber (Hevea) by Commercial Solvents Corporation, and the results of the tests have been presented. The carbon is unsatisfactory for use as a rubber reinforcing agent when purified as described. It was evident that all of the organic impurities had not been removed.

A proposed flow system for a commercial gasoline unit for continuous removal of gasoline from the carbon black has been illustrated and described.

The physical characteristics of the gasoline-to-acetylene carbon have been studied by means of x-ray diffraction patterns and electron microscope photographs. The gasoline carbon was compared with untreated methane-to-acetylene carbon.

Gasoline-to-acetylene carbon is composed of finer particles (ca. 20 mu) than the methane-to-acetylene carbon (ca. 30 mu). Gasoline carbon is also less graphitic and is composed of spherical particles, whereas methane-to-acetylene carbon particles appear as irregularly shaped platelets.

SECTION IX: EFFECT OF THE PROPERTIES OF CARBON BLACK ON RUBBER REINFORCEMENT AND CORRELATION OF EXPERIMENTAL DATA

Introduction

A brief description of the tests used for evaluating carbons for use in rubber was given in Part A, Section II of this work, and a general survey of the properties of rubber blacks was given in Part A., Section I. But in order to decide upon the course of future experimental work designed to improve the electric discharge carbon for use as a rubber reinforcing agent, a more detailed study of the inter-relation of the different properties of the blacks, and the effect of these properties on rubber reinforcement is necessary.

The data on the reinforcing properties of the electric discharge carbon are incomplete. A few conclusions may be drawn from the data which have been obtained, however, and these may serve as a possible quide for future work. The purpose of this section is to review the work which has been done on the reinforcing properties of carbon black, to correlate the data which have been obtained in this laboratory, and to suggest means for improving carbon black produced in the electric discharge for use in rubber.

Value of Analytical Tests on Carbon Black as a Means of Evaluating Rubber Reinforcing Properties

General: The value of laboratory analytical tests as a means of predicting the behavior of blacks in rubber has long been a subject for debate. The properties of carbon black which have generally been held to be of primary importance by a great number of investigators are: (1) particle size or surface area, (2) pH of the heated carbon sludge, (3) dephenylguanidine absorption index (D.P.G.), (4) structure, and (5) nature and amount of absorbed impurities on the surface of the black, and the effect of impurities on the surface of the black. The effect of impurities in the form of hydrocarbons and in the form of moisture has been separately investigated.

Very few, if any, of the investigators have considered all of the above properties in evaluating blacks for rubber. Consequently, such investigations must be viewed with reservation as too much emphasis is often placed on the effect of a single property without an attempt to discuss the possible effects of other variables.

In addition to the properties of the carbon itself, the rubber mix used has a great effect on the reinforcing ability of the carbon. The properties of the mix would be determined by: (1) the nature of the latex, (2) the type of accelerator, (3) the per cent loading of the black in the rubber, (4) the degree of dispersion of the black, and (5) the conditions of curing the rubber (time, temperature, etc.).

Effect of pH: In 1937 Wiegand[57] published an article on the pH properties of carbon. In this work, he attempted to classify carbons as to type by means of the volatile content, pH of the heated carbon sludge, and diphenylguanidine (D.P.G.) adsorption. By studying a large number of carbons covering a wide range of

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[57] Wiegand, W.B., pH Properties of Colloidal Carbon, Ind. Eng. Chem., 29, 953 (1937).

particle sizes, he arrived at the following conclusions:

(1) Deactivating carbon by heating in the absence of air to high temperatures (above 400 - 500°C) raises the pH of the heated carbon sludge.

(2) There is a definite relation between per cent volatile matter and pH, and the lower the volatile content, the higher the pH.

(3) There is a definite relation between D.P.G. adsorption and pH, and the lower the D.P.G. adsorption, the higher the pH.

(4) By combining the relations of (2) and (3), carbon may be classified ("rubber", "ink", "thermal", etc.).

(5) Low pH retards vulcanization of rubber but increases dispersibility. In selecting a rubber carbon, it is necessary to compromise between higher pH with diminished dispersibility and low pH with excessive retardation of cure.

From the above conclusions, he formulated the following theory: pH is explained on the basis of the amount of C_xO_y complex associated with the carbon surface. Removal of oxygen decreases the adsorptive activity of the carbon toward alkaline substances and increases adsorption toward acidic materials. A minimum possible pH of 2.6 suggests saturation of the surface with C_xO_y radicals.

In a later paper[58] Wiegand relates the CO_2 content of the carbon to pH and obtains a much better correlation. He also changes over from total D.P.G. adsorption to "chemi-sorption D.P.G. index" and obtains a better correlation with pH using this index. By chemi-sorption index is meant the factor $Z - Z_0$, where Z is the total D.P.G. adsorption value and Z_0 is the value determined on the same carbon sample after complete devolatilization

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[58] Wiegand, W.B., Recent Developments in Colloidal Carbon, Can. Chem. Proc. Ind., 151, March 1944.

by heating. The chemi-sorption index is reported in moles D.P.G./gm. carbon. The question as to whether the high temperature necessary for complete devolatilization of the carbon causes a change in structure has been raised.

In regard to rubber reinforcement, Wiegand states that pH governs the time for optimum cure: the lower the pH, the greater the time of cure.

Also in regard to pH: (1) The high pH carbons cure faster than low pH carbons in Hevea, but high pH coarse carbons cure slower than low pH fine carbons, (2) High carbon surface is as valuable as high pH as a cure promoter, and (3) Satisfactory cures cannot be obtained with low loadings of coarse, low pH carbons. The above conclusions were stated by Wiegand who used Captax as an accelerator, but the same general trends have been observed when using other accelerators except either pH or surface may become dominant.

Zapp[59] relates tear, modulus, tensile, and energy (heat generated when using a flexometer) to pH (volatile content). In general, as the pH decreases the tensile strength increases, but in many cases tensile reaches a maximum value. As a result of his experimental work, Zapp arrives at the conclusion that a large particle carbon with a low pH is slightly superior to a finer particle carbon with a high pH and that the effect of oxidizing the carbon surface is to "temper" vulcanization so that physical properties are more constant over the curing range.

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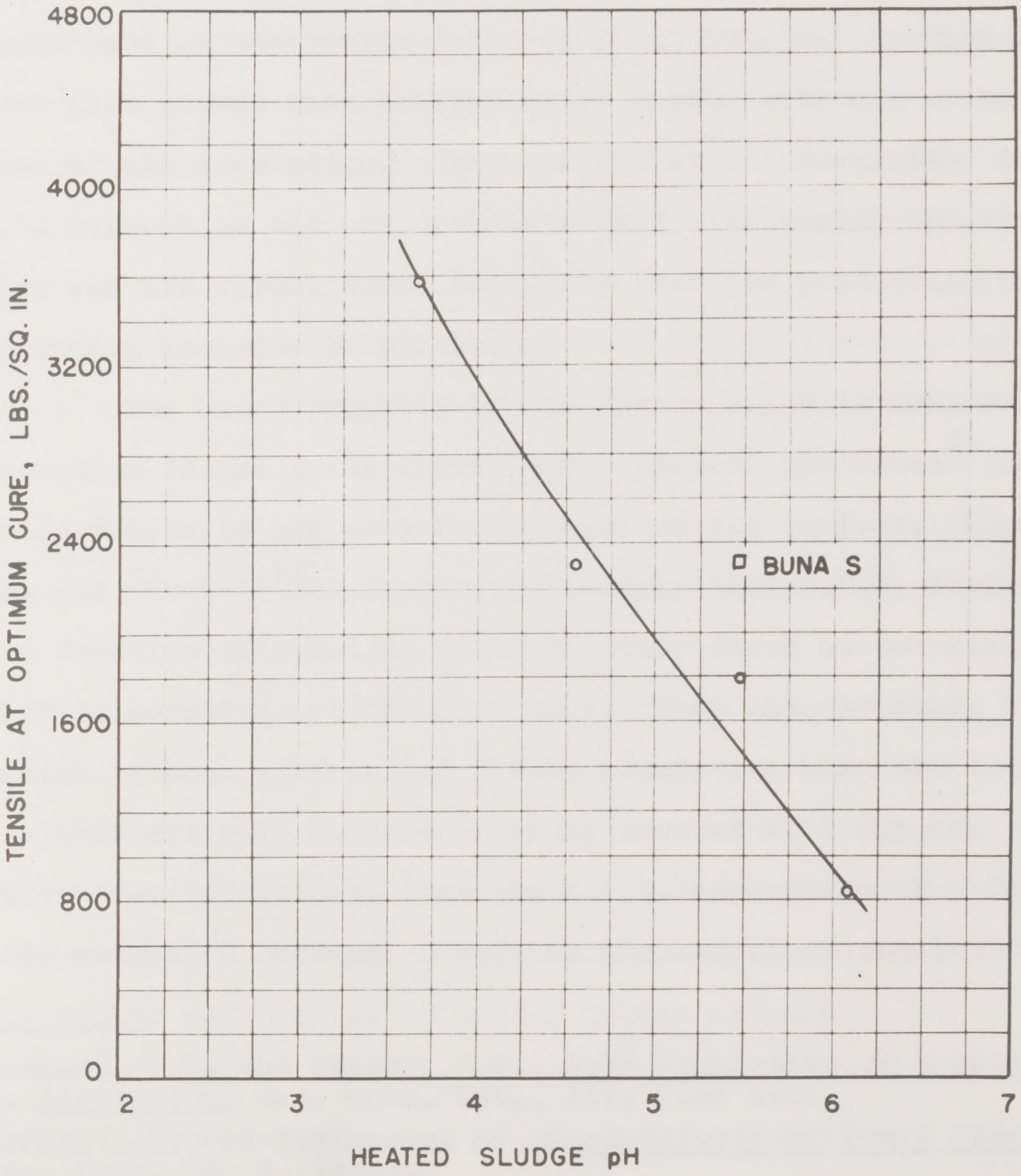
[59] Zapp, R.L., op. cit.

The data obtained in this laboratory on electric discharge carbons substantiate the conclusions of Lapp. A curve of tensile strength vs pH of the heated carbon sludge is shown in Figure 45. Five points are shown, four of which were obtained using natural rubber (Hevea) and one using Buna S. Since some of the carbons received slightly different treatments, the results are not necessarily conclusive. The general trend with pH, however, is evident.

FIGURE 45
HEATED SLUDGE pH vs TENSILE AT OPTIMUM CURE —
DISCHARGE CARBON
NATURAL RUBBER, 40 PARTS CARBON



Diphenylguanidine Adsorption: This property is generally held to be a relatively more important gauge of the reinforcing ability of a black in rubber than pH. The relation between this property and pH as shown by Wiegand has already been discussed.

Wiegand and Snyder[60] in 1931 correlated D.P.G. adsorption with the tensile strength of the rubber; the less the D.P.G. adsorption the greater the tensile strength. In general, rubber carbons have an adsorption index of about 10%/gm. Wiegand and Snyder also showed that activation of carbon with air or steam increased the adsorption. They arrived at the conclusion that D.P.G. Adsorption did not correlate well with curing behavior of rubber and the D.P.G. index cannot be used for predicting the rubber compounding behavior of blacks.

The exact property of the carbon which is measured by D.P.G. adsorption is not fully understood. Wiegand and Cohan[61] attribute the adsorption to the oxygen complexes on the surface. However, Smith and Thornhill[62] state very definitely that D.P.G. adsorption is not a function of volatile content. They found no correlation between D.P.G. adsorption and total surface. They did, however, find a relation between surface and D.P.G. adsorption when the total surface was either entirely bare or entirely covered with oxygen. These results seem to indicate that the D.P.G. adsorption is a function of the extent of surface as well as the amount of chemi-sorbed

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[60] Wiegand, W.B. and Snyder, J.W., *Some Properties of Carbon Black--I. Adsorption*, Can. Chem. Met., 157, June 1931.

[61] Cohan, L.H. and Steinberg, M., *Conductivity of Tread Stocks*, Ind. Eng. Chem. *36*, 7 (1944).

[62] Smith, W.R. and Thornhill, F.S., and Bray, R.I., *Surface Area and Properties of Carbon Black*, Ind. Eng. Chem., *33*, 1303 (1941).

oxygen present.

An attempt was made to classify the various types of carbon produced in the electric discharge and subjected to varying degrees of treatment. The method of Wiegand was used. In Figure 46 the heated sludge pH is shown plotted vs per cent volatile matter. The solid line curve is that of Wiegand whereas the dotted curve represents the data obtained on discharge carbon. The individual experimental points are labeled. Note that the curve obtained for discharge carbons is reversed from that of Wiegand. The difference is readily explained on the basis of the conclusions of Smith and Thornhill; i.e., that the D.P.G. adsorption (and hence pH) is related to volatile content only if the surface is entirely bare or entirely covered with oxygen. The above statement applies to a wide range of types of carbons with varying surface areas. In this case, however, removal of organic impurities is, at the same time, accompanied by an addition of oxygen to the bared surface. The volatile matter is, then, determined not only by the amount of chemi-sorbed oxygen but also by the amount of organic impurities removed. It is quite conceivable that oxidation of the hydrocarbons on the surface produces compounds which give an appreciable pH to the carbon sludge.

Figure 47 shows only two experimental points on the Wiegand curve of pH vs D.P.G. adsorption. These points fall on the extension of the high color carbon curve in agreement with Nigrometer values reported by Columbian Carbon Company.

Figure 48 is a reproduction of Wiegand's curves for classifying carbons by means of pH, D.P.G. adsorption, and volatile content. From this curve, it can be seen that the untreated

FIGURE 46
HEATED SLUDGE pH vs % VOLATILE MATTER
(WIEGAND, W.B., IND. ENG. CHEM., 29, 953 (1937))

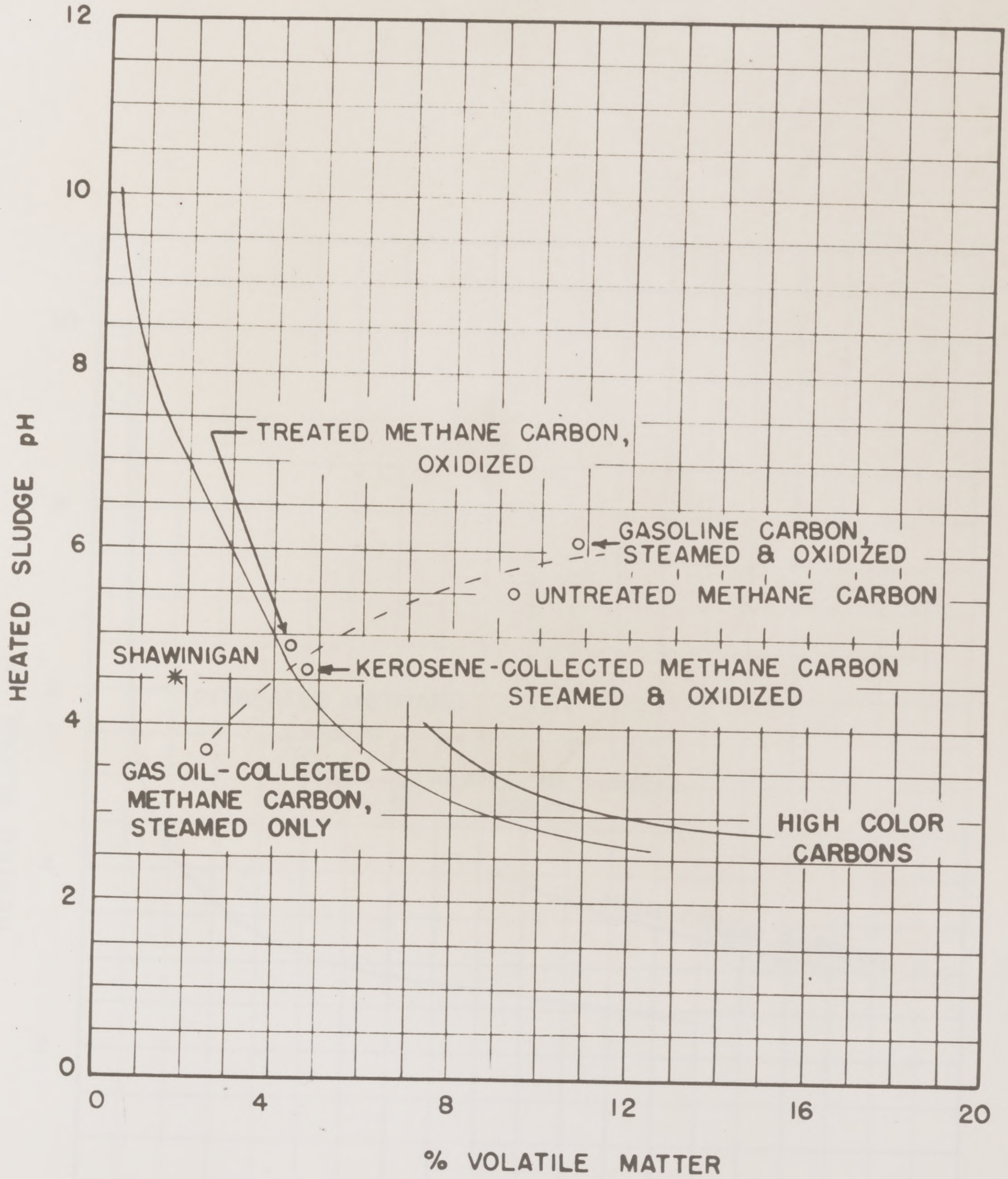


FIGURE 47

HEATED SLUDGE pH vs D.P.G. ADSORPTION INDEX

(WIEGAND, W.B., IND. ENG. CHEM., 29, 953 (1937))

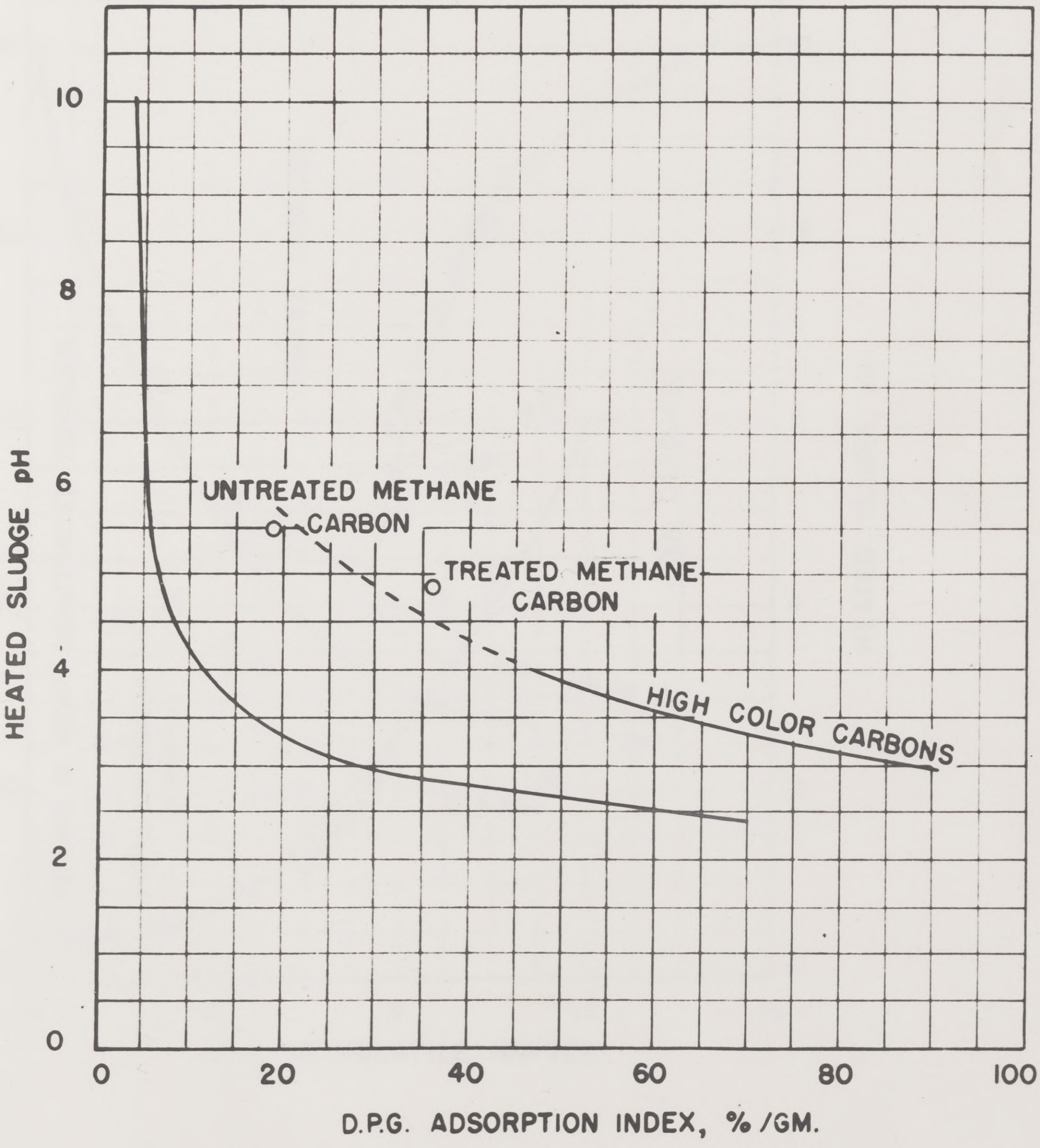
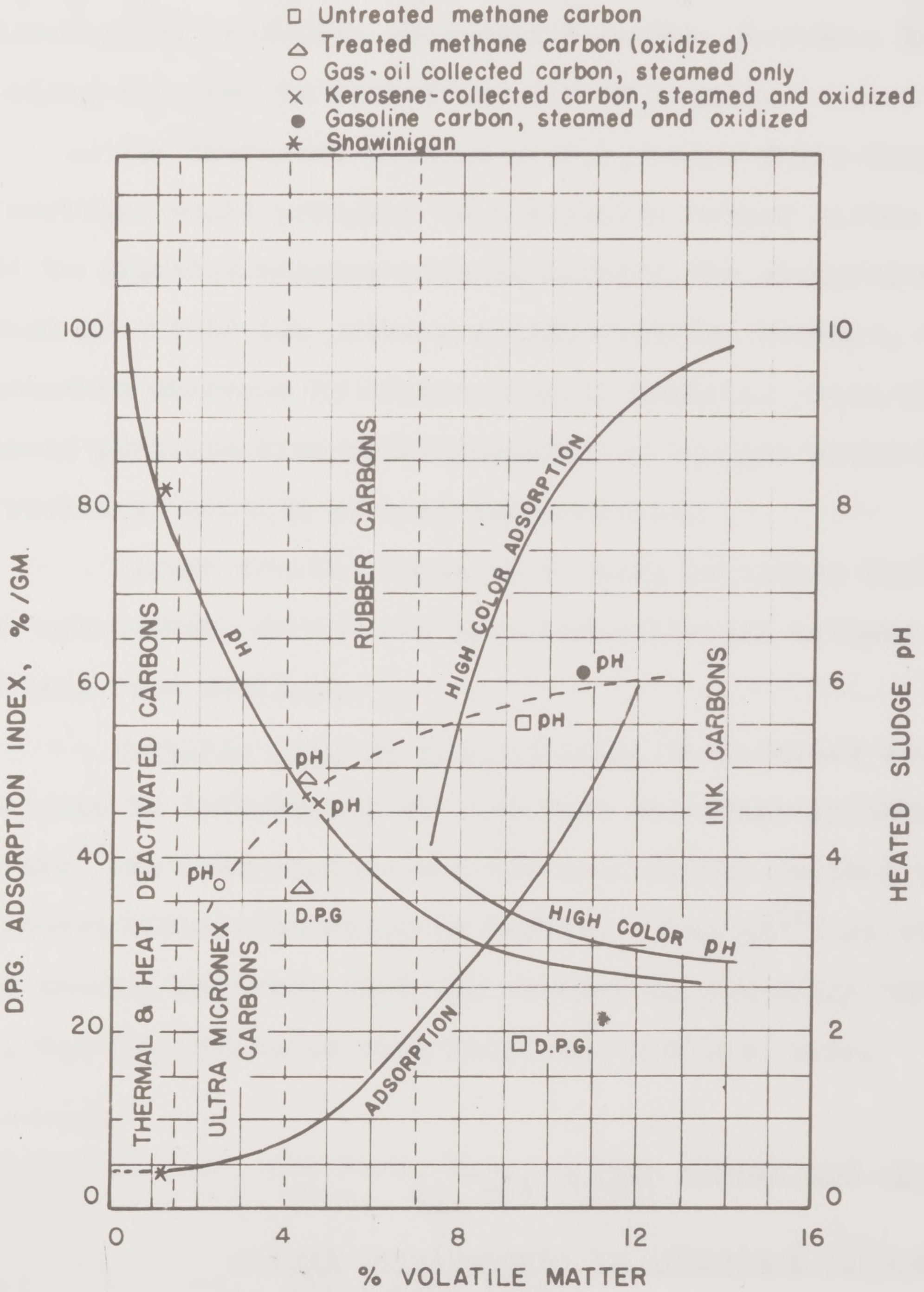


FIGURE 48

CLASSIFICATION OF CARBONS ACCORDING TO pH, D.P.G. INDEX, AND VOLATILE MATTER

(WIEGAND, W.B., IND. ENG. CHEM., 29, 953 (1937))



methane carbon falls in the high color carbon range. Oxidation of the carbon raises the adsorption and lowers the pH, shifting the carbon to the extreme left edge of the rubber carbon region.

As might be expected, the gas oil carbon with lowest pH gave the greatest tensile in rubber. However, the per cent elongation was poor. The high pH gasoline carbon gave very low tensile and elongation and is definitely out of bounds.

The untreated methane carbon, which falls in the range of ink carbons, would probably be a suitable rubber carbon if the pH could be slightly reduced without harming the elongation. The rebound is one of the primary considerations, however, and this can be somewhat overcome by higher pigment loading. Some alteration in ultimate particle size could possibly be brought about by agitation and prolonged heating at high temperatures.

Figure 48 also shows that there is little difference between raw methane carbon and kerosene-collected methane carbon when both have been oxidized.

<u>Particle Size or Surface Area</u>: This factor is of prime importance in influencing the behavior of blacks in rubber. Goodwin and Park[63] in 1928 stated that the most finely divided blacks had the lowest tensile strength in rubber. Wiegand[64] and others have since showed, however, that the reverse is generally the case; i.e., tensile increases with decreased particle size.

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[63] Goodwin, Morris, and Park, C.R., <u>Carbon Blacks and Their Use in Rubber</u>, Ind. Eng. Chem., <u>20</u>, 706 (1928).

[64] Wiegand, W.B., <u>Recent Developments in Colloidal Carbon</u>, Can. Chem. Proc. Ind., 151 (March 1944).

Cohan and Steinberg[65] have recently found that the relation between particle size (surface area) and tensile strength depends on the type of rubber used in the mix. They found that in natural, reclaim, and Buna S rubbers, the modulus and tensile were constant for large particle size blacks but decreases with decreasing particle size for finer blacks. However, in Thiokol N tensile decreased with decreased particle size whereas in Butyl (GRI) stocks, the tensile reached a maximum for a certain particle size.

These investigators claim that fine particle blacks (ca. 10 mu) retard cure and are difficult to disperse; however, increased dosages of stearic acid and accelerator overcome these difficulties. When acetylene black is used, the amount of stearic acid added has little effect on the properties of the rubber.

Another very important factor governed by particle size is the power consumed in milling the rubber and the heat generated on flexing the finished product.

Drogin, Grote, and Dillingham[66] extensively investigated this property and found that the exact relation between particle size and power consumed in milling depended on the type of latex used, but that blacks with the smallest particle size (largest surface) increased the power required for milling. Increasing the per cent loading also increases power consumption.

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[65] Cohan, L.H. and Steinberg, M. op. cit.

[66] Drogin, I., Grote, H.W., and Dillingham, F.W., Behavior of Blacks in Rubber, Ind. Eng. Chem., 36,124(1944).

Goodwin and Park[67] found that the smaller the particle size, the greater the hardness of the rubber product.

The specific resistance of rubber stocks is determined primarily by particle size. Cohan and Mackey[68] found that the specific resistance, R_s, of a rubber stock varies exponentially with the diameter of the ultimate carbon particles; i.e., log(R_s) vs particle diameter is a linear function. The presence of volatile matter increases the resistance but is of less importance than particle size.

<u>Iodine Adsorption</u>: One of the earliest attempts to predict the reinforcing properties of carbon black was by means of iodine adsorption. The cause of the adsorption and the properties of the carbon which influence the extent of the adsorption are not clear. Johnson[69] in 1929 found no correlation between volatile matter and iodine adsorption. He also found that blacks heated to high temperatures (500 - 900°C) in the absence of oxygen showed high iodine adsorption and low accelerator (diphenylguanidine) adsorption. He made no attempt to explain this phenomenon.

Carson and Sebrell[70] claimed that the iodine adsorption capacity of a black is a measure of the rate of cure of the rubber mix. They found that low adsorptive blacks gave a faster cure than the high adsorptive blacks. The same phenomenon found by

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[67] Goodwin, Norris, and Park, C.R., <u>op. cit.</u>

[68] Cohan, L.H., and Mackey, J.F., <u>Conductivity of Rubber Tread Stocks</u>, Ind. Eng. Chem., <u>35</u>, 806 (1943).

[69] Johnson, C.R., <u>Carbon Black—II. Role of Oxygen</u>. Ind. Eng. Chem. <u>21</u>, 1288 (1929).

[70] Carson, C.M., and Sebrell, L.B., <u>op. cit.</u>

Johnson was encountered: heating blacks to high temperatures in the absence of air increased the iodine adsorption, but the treated blacks gave greater rates of cure and were difficult to disperse.

Wiegand and Snyder[71] bore out the findings of Carson, Sebrell, and Johnson. They found that heating carbon black to a high temperature in the absence of air decreased the per cent volatile matter but increased the adsorption of iodine.

Smith and Thornhill[72] have recently explained satisfactorily the phenomenon encountered by the previous investigators by showing that iodine adsorption is independent of the nature of the surface and dependent only on the extent. Cohan and Steinberg[73] also hold the view that iodine adsorption is a measure of the bare surface.

Structure: Crystal structure determines to a large extent the electrical conductivity of the black in rubber goods. Cohan and Mackey[74] have shown that, in general, the more crystalline the black, the better the conductivity; however, acetylene black has a greater conductivity than can be explained on the basis of crystal structure alone; for graphon, with the same degree of graphitization and smaller particle size is less conducting than Shawinigan black.

Wiegand has shown that some carbons have an abnormally high oil absorption. These carbons he calls "structure carbons"

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[71] Wiegand, W.B., and Snyder, J.W., op. cit.

[72] Smith, W.R. and Thornhill, F.S., and Bray, R.I., op. cit.

[73] Cohan, L.H. and Steinberg, M.S., op. cit.

[74] Cohan, L.H. and Mackey, J.F., op.cit.

because they are said to form carbon-to-carbon chains in rubber mixes. These carbon chains have less strength than rubber-to-carbon chains and hence lower the tensile strength of the rubber. These carbon chains, however, increase the electrical conductivity of the rubber. It has already been shown that other factors govern tensile strength and conductivity so this method of classification should not be taken too literally.

Moisture: Little work has been done on the effect of the moisture content of carbon blacks on their reinforcing ability in rubber. Wiegand and Snyder[75] found that a moisture content up to 5% in the black did not affect the stress strain characteristics of the rubber. Their work was with a rubber mix containing diphenylguanidine as an accelerator, and they state that other accelerators might possibly be more sensitive to moisture.

Cohan and Johnson[76] also found that tensile at break is not affected by moisture content; however, they claim that the modulus at 400%, abrasion resistance, and age resistance of the rubber decrease as the moisture content of the black increases. The extrusion time of uncured tread stocks was found to be decreased by the presence of moisture. The moisture content of a black however, does not affect its dispersibility.

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[75] Wiegand, W.B., and Snyder, J.N., Some Properties of Carbon Black--II. Moisture, Can. Chem. Met., 285, October 1931.

[76] Cohan, L.H., and Johnson, C.R., Influence of Moisture Content of Carbon Black on Rubber Properties. Ind. Eng. Chem., 33, 1183 (1941).

Other Factors Determining the Properties of A Rubber Mix

Per cent Loading: Garvey and Freese[77] investigated the effect of the per cent loading of the black on the properties of the rubber mix. They do not state the type of latex used, but all tests were conducted with the same mix. Their results may be summarized as follows: (1) The slope of the per cent loading - per cent elongation curve depends on the type of black used. Some of the curves show a minimum and some a maximum. For acetylene black, the greater the loading the greater the tensile and the less the per cent elongation, (2) The greater the loading the greater the hardness, (3) The greater the loading the less the rebound, (4) The greater the loading the less the hysteresis, (5) The greater the loading the greater the brittleness, (6) The greater the loading the greater the tear resistance, (7) The greater the loading, the greater the milling time, and (8) The greater the per cent loading the less the plasticity.

Type of Accelerator: Goodwin and Park[78] studied the reinforcing properties of different blacks using four different accelerators: (1) mercaptobenzothiazole (2)ethylidene-aniline, (3) diphenylguanidine, and (4) litharge. The first three named gave identical results regardless of the type of black used. When litharge was used; however, the order of the reinforcing ability of the carbons was reversed when stearic acid was added.

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[77] Garvey, B.S. and Freese, J.A., Jr., Effect of Carbon Black in Synthetic Tire Compounds, Ind. Eng. Chem. 34, 1277 (1942).

[78] Goodwin, Norris and Park, C.R., Op. cit.

Type of Rubber Latex: The work of Cohan and Steinberg regarding the effect of the type of rubber on tensile and modulus has already been discussed in regard to the effect of the particle size of the black.

Wiegand[79] has shown that the variation of tensile strength and energy with particle size is more pronounced in GRS rubber than in Hevea. In Hevea rubber, the specific surface has been shown to have little effect on modulus, but a great effect is observed in the case of GRS. The trend of elongation with surface is about the same in GRS as in Hevea.

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[79] Wiegand, W.B., Recent Developments in Colloidal Carbon, Can. Chem. Proc. Ind., 131, March 1944.

SECTION X: EFFECT OF THE PROPERTIES OF A BLACK ON BATTERY PERFORMANCE AND CORRELATION OF EXPERIMENTAL DATA

Introduction

The invention of the electron microscope has made it possible to study the changes in physical properties of the constituents of a dry cell battery after it has been in operation. It is hoped that future research along these lines may make it possible to predict battery performance by studying the properties of the materials which go into its manufacture.

One such study was recently conducted by H.F. McMurdie[80] on the changes in the manganese dioxide depolarizer of the battery. This study has shown that the manganese dioxide changes from an active, less crystalline form to an inactive, more crystalline form after the battery has been in use. Five distinct crystal varieties of the manganese ore have been found, and each type varies in size and shape of the particles (and hence available surface), solubility, and potential. It is recognized that all of these factors affect the conductivity of the cell, and each type of ore requires a different kind and different amounts of carbon black.

No method for predicting which type of ore is best for a given battery has been worked out.

The carbon black which goes into a battery is as important as the ore. The properties which gvern the suitability of a black for use in batteries are not fully known or understood. A few general criteria are available; however, it must be remembered

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[80] McMurdie, H.F., Microscopic and Diffraction Studies on Dry Cells and Their Raw Materials, Electrochem. Soc., Preprint 86-15, July 1944.

that these criteria constitute the minimum requirements for a black and are not the only properties which govern its worth as a battery black.

X-Ray and Electron Microscope Evaluation

A great deal of effort has recently been directed toward finding a suitable substitute for Shawinigan black. In view of the length of time required for evaluating a battery black by actually making a battery, attempts have been made to devise a method for quick testing of the carbon samples. Mrgudich and Clock[81] have studied various types of battery blacks with X-Rays and the electron microscope. They have concluded that a battery black must possess these three prerequisites: " (1) it must yield an X-Ray diffraction pattern exhibiting definite evidence of partial graphitization; (2) when shaken with tertiary butyl alcohol and subjected to subsequent electron microscope analysis, the black must not show pronounced tendency for clumping into large aggregates, and (3) the ultimate particle size as observed in the electron microscope should be comparable to that of acetylene black, approximately 40 mu in diameter."

Electric discharge black (methane gas filter carbon) meets all of these requirements except, perhaps, with regard to dispersibility. The above authors indicate that lack of graphitization may be somewhat compensated for by reduced particle size.

The above criteria, as pointed out before, are by no means adequate for evaluating a black, but can possibly be used to

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[81] Mrgudich, J.N., and Clock, R.C., X-Ray and Electron-microscope Evaluation of Carbon Blacks, Electrochem. Soc. Preprint 86-29, July 1944.

eliminate obviously undesirable blacks without recourse to the usual tedious laboratory battery tests. Other black properties which the authors mention as important factors in battery performance are: (1) water absorption and water retention, (2) mix compressibility and elasticity, (3) density, (4) surface films, and (5) possible reactivity of the black with manganese dioxide. The authors point out that the three factors established as prerequisites favor the "conducting chain theory" of the function of carbon black in batteries.

Further work on battery carbon has been reported by V.F. Payne.[82] This investigator states that electrical conductivity and electrolyte absorption tests indicate merely which carbon samples are worth testing but give no indication of battery performance.

Not enough data have been obtained in the University laboratories to work out a definite correlation between the properties of the carbon and battery performance for a given carbon because of the manner in which the Burgess Battery Company reported the tests. In some cases, the tests were run on size A cells and in some cases on size D cells; some of the amperages were reported as 10-day values and others as 24-hour values; and quite frequently, the results were reported using different ore/black ratios.

However, examination of their results, coupled with University tests, seem to indicate: (1) The degree of oxidation;

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[82] Payne, V.F., The Development of Substitutes for Shawinigan Black in Dry Batteries, Electrochem. Soc., Preprint 86-21, July 1944.

i.e., the degree of saturation of the carbon surface with C_xO_y complexes has a great effect on the shelf life of a cell. The amount of organic matter retained on the surface of the carbon, however, is probably more important than the amount of C_xO_y complexes as evidenced by the success of Shawinigan black (1.0 - 0.6% volatile matter). Organic matter on the carbon is probably the cause of chromic acid inhibitor reduction and shortened battery shelf life. This has been more or less proved by chromic acid reduction tests in the University laboratory, (2) The presence of organic matter also has a great effect on mix resistance and hence on amperage and voltage characteristics of the cell, and (3) The pH of the carbon evidently has little to do with battery performance except perhaps in some cases to serve as a guide to the amount of volatile (organic) matter associated with the carbon. Shawinigan black has a high pH of about 8 whereas University treated black has a low pH of about 5 and yet excells Shawinigan black. Kerosene-collected carbon with as low a pH as the treated gas filter carbon gave a much higher mix resistance but the same 10-day voltage and a higher amperage.

SUMMARY OF PART B

A discussion of the chemical and physical properties of the purified methane filter carbon black has been given, and the purified black has been compared with the unpurified black. The discussion has included: (1) battery tests on the purified black, (2) effect of compression of the black on the mix resistance, (3) effect of compression of the black on the dry relative resistivity, (4) chromic acid reduction test and its value in evaluating a battery black, (5) x-ray diffraction and electron microscope studies, (6) effect of purification on carbon tetrachloride and electrolyte absorption, and (7) effect of purification on diphenylguanidine adsorption.

The carbon work relative to the gas discharge chamber has been presented: (1) The method for estimating probable chamber holdup and for estimating the amount of total carbon production has been given, and (2) It has been shown that carbon ash determinations may be used for estimating electrode wear.

The cost of raw materials for purifying the gas discharge filter carbon has been calculated, and the sizes of conveyors for commercial units have been tabulated.

The properties of the kerosene-collected methane-to-acetylene carbon have been discussed, and these properties have been compared with gas filter carbon. The properties discussed were: (1) analyses of feed and product carbons, (2) battery tests on the black, (3) effect of compression on mix resistance and comparison with other blacks, (4) effect of dry compression on relative resistivity and comparison with other blacks, (5) properties of the black in rubber, and (6) determination of filtration constants and characteristics of carbon-kerosene sludge.

A similar discussion of gas-oil collected methane-to-acetylene carbon was given. Its behavior in rubber was also discussed.

The properties of gasoline carbon black were compared with those of other carbons. The different properties of the distillates obtained from gasoline carbon taken from various parts of the plant were presented and discussed. The properties of the gasoline carbon which were given particular attention were: (1) carbon tetrachloride absorption of purified and raw black, (2) volatile content and properties of the distillates, (3) chromic acid reduction, (4) evaluation of the carbon for rubber reinforcement, and (5) electron microscope studies.

The construction and operation of a new type of carbon valve was described, and a flow diagram was proposed for continuous removal and distillation of carbon from a commercial gasoline-to-acetylene plant.

The effect of the properties of carbon blacks on rubber reinforcement has been reviewed, and the laboratory data on rubber reinforcement have been correlated. The various discharge blacks have been classified according to the method of Wiegand.

The effect of the properties of a black on battery performance has been reviewed, and the conclusions drawn from the results of the laboratory tests have been listed.

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GLOSSARY OF TECHNICAL TERMS

1. Accelerator:	Compounds added to the rubber mix to decrease the time of cure.
2. Antioxidants:	Substance added to a rubber mix to inhibit oxidation. Now used synonymously with "age resistor" to denote any substance which protects the vulcanizate against aging of any kind, such as oxidation, flex-cracking, heat deterioriation, etc.
3. Bardol:	A rubber dispersing agent.
4. Captax:	Mercaptobenzothiazole. A fast accelerator and antioxidant used for rubber compounding.
5. Conditioning:	Keeping a rubber sample under certain specified conditions of temperature and humidity for a definite period of time after curing.
6. Crystallites:	A definite arrangement of molecules which produces a definite x-ray diffraction pattern.
7. Curing:	Keeping the rubber mix under specified conditions until the reactions have come to equilibrium.
8. D.P.G. Index:	Diphenylguanidine adsorption expressed as percent adsorbed per gram of black.
9. Energy:	The temperature rise of a rubber sample on flexing as measured by any of several standard test instruments.
10. Fillers:	Substances added to the rubber mix to increase the tensile strength and age resistance of the rubber product.
11. Gas Oil Carbon:	Methane carbon wetted with or suspended in gas oil and then filtered and steam-stripped or steam-stripped and then oxidized.
12. Gasoline Carbon:	Carbon black produced as a by-product in the production of acetylene from gasoline by means of the electric discharge.
13. GRS:	Means "government rubber--styrene." A copolymer of butadiene and styrene.
14. Hevea Rubber:	Natural rubber.

15. Kerosene Carbon:	Methane carbon wetted with or suspended in kerosene and then filtered and steam-stripped or steam-stripped and then oxidized.
16. Methane Carbon:	Carbon produced as a by-product in the production of acetylene from methane by means of the electric discharge.
17. Milling:	Running the rubber batch through the rolls of a mill until all the ingredients are mixed and uniformly incorporated into the rubber. This term also means "mixing" as by means of a Banbury mixer.
18. Mix Resistance:	The electrical resistance in ohms/column inch of a standard mixture of manganese ore, sal ammoniac, carbon black, and chromic acid as measured on the Burgess Battery Company resistometer.
19. Nerve:	Term applied to a rubber stock to designate toughness and elasticity.
20. Nigrometer:	Instrument used for determining the degree of blackness of carbons by measuring the percentage of light transmitted by a standard oil-carbon mixture.
21. Ore/Black Ratio:	The weight ratio of manganese ore to carbon black as used in the preparation of a sample for a mix resistance test.
22. Plasticizers:	Compounds used to soften or plasticize the raw rubber so that milling time is shortened. Examples are Plastogen and Reogen.
23. Reclaimed Rubber:	The product resulting from the processing of vulcanized rubber scrap.
24. Relative Resistivity:	Ratio of the resistivity of the black in question to that of Shawinigan black as measured by a special device described in the report.
25. Spectrum:	The classification of carbons according to particle size and surface area.
26. Structure:	Structure carbons are those possessing a certain degree of graphitization or crystal structure.