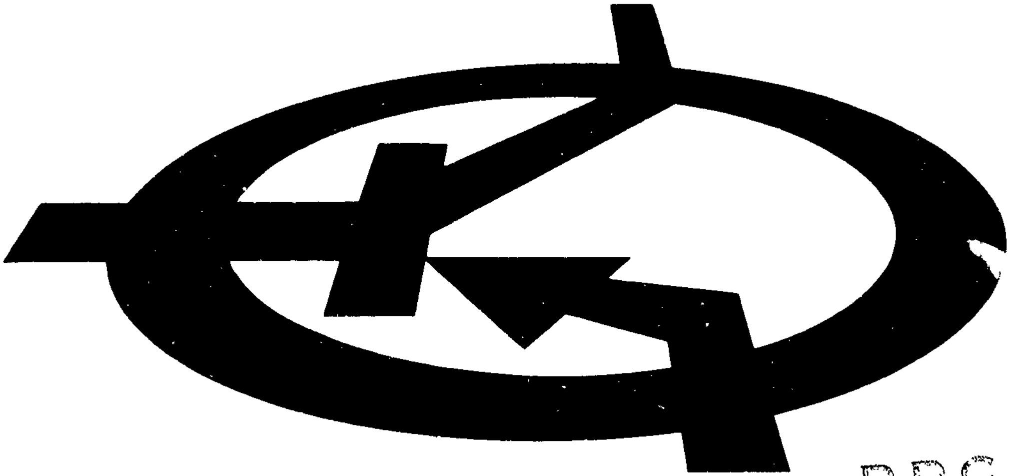

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ORGANIC DEPOLARIZED PRIMARY BATTERIES
SIGNAL CORPS CONTRACT NO.
DA-36-039-SC-87243
DEPARTMENT OF THE ARMY
PROJECT NO. 3A99-09-002

FINAL REPORT
15 June 1961 through 14 December 1962

Prepared for

U.S. ARMY ELECTRONICS RESEARCH AND DEVELOPMENT LABORATORY
Fort Monmouth, New Jersey

Submitted by
RADIO CORPORATION OF AMERICA
Semiconductor and Materials Division
Somerville, New Jersey

ORGANIC DEPOLARIZED PRIMARY BATTERIES

SIGNAL CORPS CONTRACT NO. DA-36-039-SC-87243

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FINAL REPORT

15 June 1961 through 14 December 1962

The objective of this research and development project is the development of primary batteries utilizing organic compounds as the active electrode components.

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Electrochemical Systems,
Semiconductor and Materials
Division.

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ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

TABLES

1. PURPOSE

The purpose of this research and development contract was to:

1. Establish the role of carbon black in the nitro-organic-carbon cathode.
2. Determine the mechanism of the nitro reduction reaction.
3. Extend the development of the magnesium-m-dinitrobenzene cell to establish properties and reliability on shelf.

2. ABSTRACT

A survey was made of experimental and commercial carbon blacks for use with m-dinitrobenzene in magnesium cells. The specification evolved listed low density, large surface area, high electrical conductivity and a maximum volume of voids in the compressed carbon black. These conditions demand a fluffy carbon black which, in the presence of electrolyte, retains a measure of structure adequate for massive material transfer and diffusion processes. No commercial carbon black was found ideally suited for this cathode system. One available pure acetylene carbon black can be adapted, however, by means of an intensive mechanical "opening" process, especially with simultaneous introduction of a small quantity of V_2O_5.

3. EXPERIMENTAL AND FACTUAL DATA

3.1 HISTORY OF PROGRAM

Work prior to this contract was conducted in part under Signal Corps Contract No. DA-36-039-SC-78048 from 15 June, 1958, to 20, September, 1960. The program consisted of two major areas of effort; a Research Phase and a Developmental Phase. The results are summarized briefly in the following sections.

3.1.1 Research Phase

During the course of the previous contract, many classes of organic cathode materials were studied. The work on organic-nitro compounds as cathode materials was extended to various heterocyclic compounds, such as: (1) nitropyridines; (2) nitropyrimidines; (3) nitrofurans; and (4) nitrothiophenes. These materials, as predicted by theory, offer promise for the development of cathode materials with half-cell potentials 0.05 to 0.20 volt higher than are now obtained from m-dinitrobenzene (m-DNB). A higher operating voltage is very desirable for the design of batteries that require a 1.0 v per cell or higher cut-off voltage.

The theory concerning the effect of substituent groups on the operating voltage was developed so compounds could be selected for synthesis with the best balance between capacity and operating voltage.

The general role of carbon and water in a magnesium-nitro organic cell was determined. The capacity of a practical cell is a function of the anode efficiency and the ability of the cathode to store water while maintaining a high ampere-hour efficiency. This latter property sets some broad requirements for the carbon used in the cathode mix. These are:

a. high surface area

b. high electrolyte retention while maintaining good electrical conductivity

c. high affinity for the reactant nitro compound

3.1.2 Development Phase

A detailed study was made of the performance of some organic cathode materials in practical cells. Of the many classes of organic cathode materials, nitro organic compounds were selected because of their high theoretical and experimental capacity. These organic materials, when coupled with a magnesium anode, produce dry cells with a flat discharge curve, and can operate over a wide range of current drains within the voltage limits of conventional dry cells.

Summarized in Figure 3-1 are the watt-hour capacities of the $Mg/Mg(ClO_4)_2/$ mDNB (Columbian carbon 1100 series) system compared with $Mg/MgBr_2/$mDNB (Darco-G-60) June (1958), $Mg/MgBr_2/MnO_2$ (Type M), $Mg/MgBr_2/MnO_2$ (African), and $Zn/NH_4Cl-ZnCl_2/$ electrolytic-MnO_2 systems as a function of discharge rate. The data for the Mg-mDNB system represent over 50% improvement since the start of the previous contract. These data show the excellent watt-hour capacities attained by the use of organic compounds. Capacities in excess of 90 w-hr/lb were obtained at practical discharge rates.

It can be seen that for batteries of the same capacity, a Mg-m-dinitrobenzene battery will weigh 25% less than a Mg-MnO_2 (Syn), and 50% less than Leclanche batteries with the best formulations.

Shelf studies show that Mg-mDNB cells with either a $MgBr_2$ or $Mg(ClO_4)_2$ electrolyte have a favorable shelf life.

To characterize the Mg-mDNB system more fully, its temperature dependence, impedance, and delayed action (time to reach operating voltage) were determined. The latter two properties were studied because of the unusual impedance and delayed action characteristics of magnesium cells.

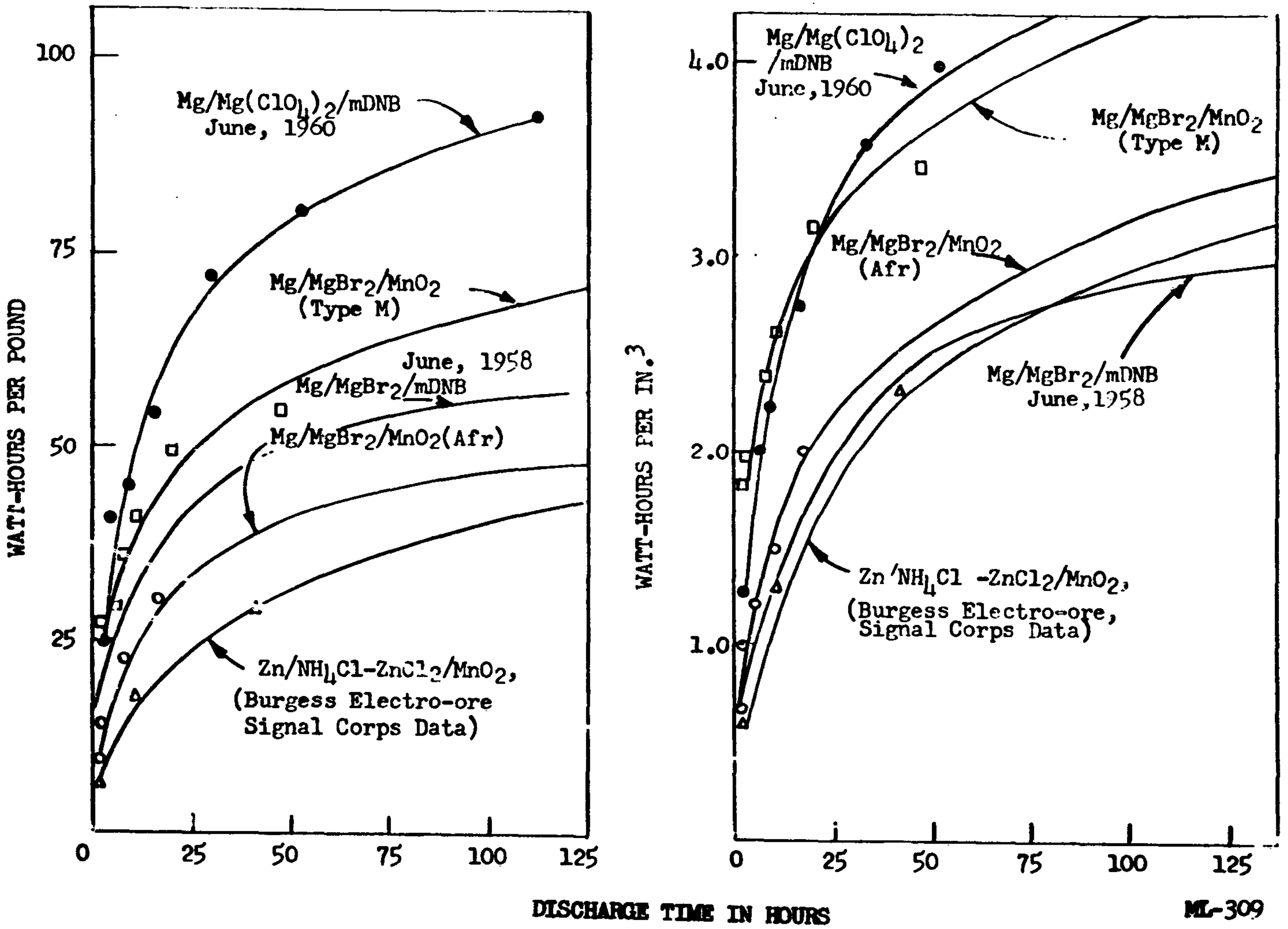

FIGURE 3-1. CAPACITY DATA FOR VARIOUS ELECTROCHEMICAL SYSTEMS.

The temperature dependance over the temperature range +40°C to -30°C of the operating voltage and capacity of $Mg/MgBr_2/mDNB$ (Darco G-60) A-cells discharged through a 20-ohm resistance was also determined. The capacity varied linearly with temperature over the same temperature range. The $\frac{d(cap)}{dt}$ was 0.87 watt-hours per pound per °C. Expressed as capacity retention with the capacity at 20°C taken as 100%, the $\frac{d(cap.\ retention)}{dt}$ was 1.75%. It should be emphasized that this low-temperature performance was achieved with the normal electrolyte (2N).

The impedance of $Mg/MgBr_2/mDNB$ A-cells was measured by a technique previously described. The impedance of comparable-size $Mg/MgBr_2/mDNB$ cells was measured under similar conditions and found to be the same as that noted for $Mg/MgBr_2/MnO_2$ cells. This shows that the high impedance characteristic of the organic system is due to the magnesium anode and should not be any more serious a problem than it is for other magnesium cells.

The delayed action of $Mg(AZ\text{-}10A)/MgBr_2/mDNB$ and $Mg(AZ\text{-}10A)/Mg(ClO_4)_2/mDNB$ cells was measured on tests simulating transceiver operation. Preliminary results have shown that the delayed action of m-DNB cells with magnesium perchlorate electrolyte is considerably less than that of cells with a magnesium bromide electrolyte, and is similar to the delayed action shown by $Mg/MgBr_2/MnO_2$ cells of comparable size.

Formulations and fabrication techniques for magnesium cells with m-DNB and similar nitro-organic cathode materials were established. The important properties of the carbon, and the need for a high anode efficiency were also studied. It was found that the Columbian carbon 1100 series, which has a high percentage of electrolyte retention, gave the best performance.

3.2 TECHNICAL APPROACH TO PRESENT CONTRACT

The work program was planned in two sections, a research phase, and a development phase.

3.2.1 Introduction

The Research phase extended the scope of the m-DNB-carbon studies previously completed (Contract DA-36-039-SC-78048) to determine the fundamental properties of the carbon affecting cell performance, since the development of a practical magnesium cell depended upon gaining a thorough understanding of the function of carbon in the nitro-organic cathode. It was expected that improvements in cathode efficiency and operating voltage would result from a better understanding of the nitro reduction.

The Development phase was planned to characterize the magnesium-m-DNB cell with the best commercial carbon black. This program of application studies was also to explore delayed action and intermittent service.

Unexpected results and problems with carbon black revealed the crucial relation of this material to efficient use of m-DNB in dry cells. The most recent evidence on trace impurities in carbon black, together with alternative methods of cathode-mix preparation, now promises the optimal use of the organic depolarizer.

3.2.2 Experimental and Factual Data

3.2.2.1 The Role of Carbon in m-DNB Cells

Prior work under contract DA-36-039-SC-78048 established the importance of carbon in the performance of the m-DNB cell. The greater improvement in cell capacity was achieved by the use of a more efficient carbon. Since cell capacity is mainly dependent on characteristics of the carbon, the major emphasis of research studies was placed on gaining an understanding of the carbon function.

The energy producing reactions in the magnesium m-DNB cell are given by the following:

(1)

$$6\ Mg + 12(OH)^- \longrightarrow 6\ Mg(OH)_2 + 12e^- \qquad (2)$$

Since it is a non-conductor, m-DNB must be in contact with the carbon in order for reduction to take place. Also, it is seen from equation (1) that water is essential at the reaction site. Since m-DNB has a room-temperature water solubility of 0.057% (Beilstein) and of about 0.1% in 2N $Mg(ClO_4)_2$, it is plausible that the critical step of putting the m-DNB into electrical contact with an active carbon site must be dissolution of solid m-DNB, followed by its diffusion to the carbon surface. High surface area alone, as measured by the standard gas-adsorption technique and size distribution, is not a criterion for a good carbon in the m-DNB system. Surface area values do not correlate to the activity with m-DNB, as evidenced by the wide variation in performance with high-surface-area carbons.

Neither does a high wettability-to-electrolyte characteristic in a carbon correlate to efficient cell performance. Significantly, the phenomenon of wetting of carbons can be observed as diverse sequences of distinct steps, ranging from lyophobic to lyophilic, resulting in a persistent fractionation of a seemingly homogeneous carbon powder. Some carbons acquire a water structure which can persist or decay on aging, depending on temperature, pressure, or agitation.

Initial investigation showed that the preliminary requirements of a carbon for use in the m-DNB cathode are:

a. high active-surface area and good electrical conductivity

b. high affinity for the reactant nitro compound

c. high electrolyte retention

(a) and (b) can be considered as that fraction of the carbon surface having a high activity toward the reduction of m-DNB. Carbon adsorption was studied as one method of determining this activity among the various carbons.

3.2.2.2 m-DNB Adsorption Studies

Various methods were investigated to measure the specific affinity of carbons for m-DNB in the presence of 2N $Mg(ClO_4)_2$ electrolyte. These methods were examined:

a. adsorption of m-DNB by known amount of carbon from 2N $Mg(ClO_4)_2$ containing excess m-DNB, avoiding direct contact of solid m-DNB and carbon. The quantity of m-DNB absorbed is determined by coulometric analysis.

b. agitation of carbon in electrolyte saturated with m-DNB and aliquot analysis of the exhausted electrolyte.

c. centrifuge tests of carbon and electrolyte saturated with m-DNB to measure volume effects upon the carbon-wetting variables. The degree of m-DNB adsorption can be measured by analysis of exhausted electrolyte.

d. coulometric analysis of various carbon electrodes in the presence of excess m-DNB electrolyte. These studies determine the rate of m-DNB adsorption or activation on the carbon surface under discharge conditions.

These studies were made to determine the role of the carbon in the m-DNB cell and the carbon properties associated with efficient cell performance. The suitability of a particular carbon was examined through extensive cell testing over a range of cathode mix compositions in the development phase of the contract.

3.2.2.3 Adsorption of m-DNB by Carbon Black

Adsorption studies were conducted with various Columbian and commercially available carbon blacks in a 2N $Mg(ClO_4)_2$ electrolyte saturated with m-DNB. The initial investigations evaluated the ability of various carbon blacks to adsorb m-DNB.

Adsorption Test

The choice of a test method was guided by:

a. the low solubility of m-DNB in the 2N $Mg(ClO_4)_2$ electrolyte (1.0 gram per liter)

b. the time required to reach equilibrium following the introduction of the carbon-black sample into the solution, and

c. the ease of quantitative transfer of the carbon-black sample into the wet-test cell.

The apparatus is shown in Figure 3-2.

The carbon blacks tested showed wide variations in dry and wet bulk, and in wettability. For this reason, prolonged dispersion of the carbon black in the electrolyte was necessary. Various ratios of carbon/m-DNB were used during initial testing. It was determined that the optimum carbon black-electrolyte mixture consisted of 0.5 gram of carbon black dispersed in 250 ml of 2N $Mg(ClO_4)_2$ saturated with m-DNB. This ratio adequately meets the requirements for the m-DNB-adsorption range, and provides a cathode of suitable size for the wet-cell test.

Operational details and analytical procedure of the adsorption test were given in our Second Quarterly Report, pp. 4-4 and 5-1.

Evaluation of Carbon Black Adsorption

The ability of various carbon blacks to adsorb m-DNB from a 2N $Mg(ClO_4)_2$ electrolyte saturated with m-DNB ranges from zero removal to almost total removal. The lowest degree of adsorption occurred with carbon blacks supplied by Atlas (Darco), Cabot, and Shawinigan. In this property, these carbon blacks are similar to the Columbian (CBN) 10867 series. Higher adsorption values were recorded for the CBN P-1100 series. The highest adsorption values were found with carbon blacks

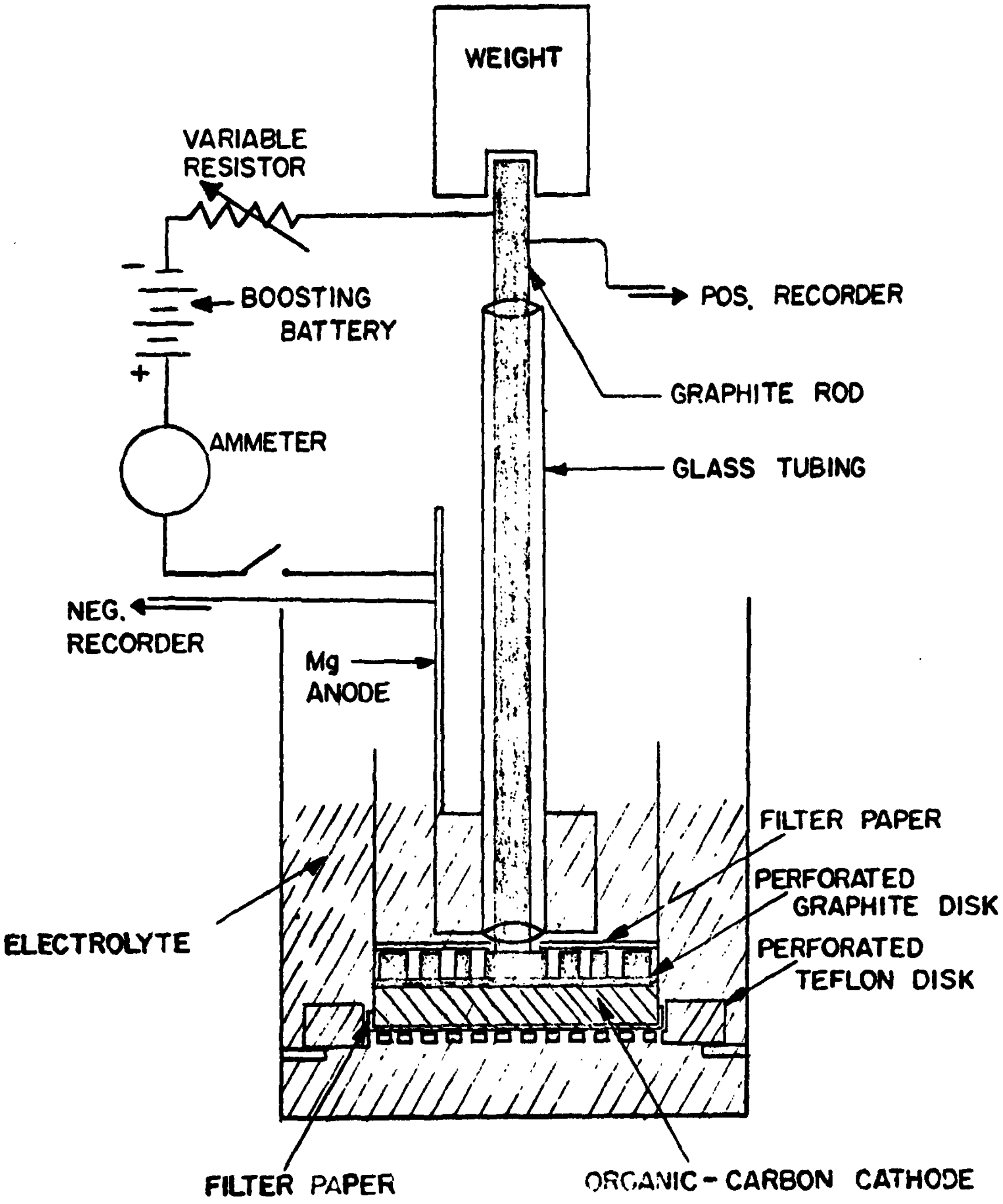

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FIGURE 3-2. WET-CELL CAPACITY TEST APPARATUS.

of the CBN HR-1670 series. Table 3-1 gives m-DNB-adsorption and capacity data for various Columbian and commercially available carbon blacks. A correlation of adsorption with capacity data for AZ-10 magnesium A-Cells is shown in Table 3-1. Manufacturers' data for several carbon blacks are given in the Appendix, 2nd Quarterly Report.

Figure 3-3 presents a comparison of data obtained from testing three types of Columbian carbon blacks and several other carbon blacks commercially available from other suppliers. The samples of carbon black with adsorbed m-DNB were discharged at 50-ma constant current. The curves show that m-DNB adsorbed on CBN P-1100-series and HR 1670-series carbon blacks is utilized more efficiently than it is with CBN 10S67 carbon blacks. The Columbian (CBN) samples are superior to the Darco, Cabot, and Shawinigan carbon blacks in this respect. The voltage decline was lowest for the CBN HR 1670-3386 sample.

The voltage data presented in Figure 3-3 are lower than the true polarization data because the values include an internal resistance drop. This drop is characteristic of the electrolyte, apparatus, and test procedure. Voltage levels are important in the evaluation of the activation and polarization characteristics of carbon blacks.

In the studies conducted, the time required to reach the sharp-break point on the voltage-time curve yields the coulombic capacity used in comparisons of the adsorption and efficiency of m-DNB with various carbon blacks.

The adsorption data show that CBN HR 1670-3386 carbon black has the greatest affinity for m-DNB under these test conditions. This carbon black also was superior to the others tested for capacity with the 50-ma discharge current. Additional 0.5-gram samples of CBN P-1100-CL 20212 and CBN HR 1670-3386 carbon black were tested by exposing the samples to 500 ml of m-DNB-saturated 2N $Mg(ClO_4)_2$, and discharging at a 50-ma current. The results showed an increase in m-DNB adsorption for CBN HR 1670-3386 carbon black with no loss in efficiency.

CARBON TYPE	ADSORPTION TEST NO.	BULK	WETTING	SEDIMENTATION OR FLOAT	FILTRATION	mg m-DNB ON 0.5 g CARBON BLACK	MINUTES AT 50 MA	EFFICIENCY (%)	A-CELL TEST TIME (hours) TO 0.9 VOLT		ABSORPTION OF WATER g H_2O/g CARBON BLACK
									AT 4 OHMS	AT 16-2/3 OHMS	
COLUMBIAN											
P-1100-											
-2142	36	Fluffy	Slow	50/50	Fast	174	300	75	4	29	5.0
-2142 #1	37	Dense	Fast	Total		172	270	68			
-2142 HT 3232	35	↓	↓	↓ Partial		178	360	88	3-5	30	4.1-4.6
-2142 HT 3232	49	↓	↓			179	380	93			
-8417-1	50	Fluffy	Slow			153	285	81	3.5	26.5	4.42
-8417-2	51					167	390	100	4	28	5.13
-8417-3	52					171	300	76	3	29.5	4.23
-8417-4	82	↓	↓	↓		151	300	86	3.5	29	4.23
-CL 20212	8	Very Fluffy	Partial	Total		184	340	80	5	33	4.32
	9					167	340	88			
	27					166	350	92			
	33					165	360	94			
	34					169	390	100			
	45					171	400	100			
	47					170	360	92			
	11*	↓	↓	↓	↓	174	420	100			
	32**					164	320	85			
10567											
-Control	25		Slow	Partial	Fair	0	30	-	1.75	23	2.56
-Control	26		↓		↓	0	30	-			
-3387	19		Fast	↓	Fast	117	205	76	2.75	24	3.97
-3398	20		Slow	Flocculent		23	33	-	3	23.5	4.03
-3399	24	↓	Partial	↓		133	280	92	2.25	24	4.54
-3522	15	Nodules	Fast	Not Dispersed	↓	17	20	-	1.75	22.5	2.88
-3553	54	Fluffy	Slow	Partial		140	300	93	3	25.5	4.10

* Exposed to 500 ml of Electrolyte.
** In N_2 Atmosphere.

TABLE 3-1. ADSORPTION AND WET-CELL CAPACITY FOR m-DINITROBENZENE ON VARIOUS CARBON BLACKS.
(Sheet 1 of 2)

CARBON TYPE	ADSORPTION TEST NO.	BULK	WETTING	SEDIMENTATION OR FLOAT	FILTRATION	mg m-DNB ON 0.5 g CARBON BLACK	MINUTES AT 50 MA	EFFICIENCY (%)	A-CELL TEST TIME (hours) TO 0.9 VOLT AT 4 OHMS	AT 16-2/3 OHMS	ABSORPTION OF WATER g H_2O/g CARBON BLACK
COLUMBIAN											
HR 1670											
-Control	17	Fluffy	Fast	Total	Fast	211	400	83	3.3	27	2.43
-3379	16	↓		↓	↓	195	370	83	1.75	23.5	2.43
-3380	18	Dense				83	120	62	0	14	2.05
-3381	21			Partial	Fair	111	240	93	0	0	1.47
-3382	22			Total		160	240	65	1	15	1.54
-3383	23			↓		209	360	75	2.25	23.5	2.30
-3383	48	↓	↓	Partial	↓	214	405	82			
-3386	13	Fluffy	Slow ↓	Slow Complete	Slow	234	420	78	3	25.5	4.48
-3386	34		Fractional	Slow		233	420	78			
-3386	44					235	360	67			
-3386	46					234	380	70			
-3386**	10					233	400	75			
-3386**	12	↓	↓	↓	↓	231	440	83			
-3523	14		Fast	Total	Fast	232	370	69	1.75	24	4.16
CABOT											
XC 72 F	6	Fluffy	Fast	Partial	Fast	52	100	83	3	22	2.95
Monarch 74	60	Dense		↓	Fair	65	120	80			
Carbolac	61	↓	↓	Very Mobile	↓	109	270	100			
DARCO											
G-60	4	Dense	Fast	Total	Fast	99	145	63	3	20	1.36
G-60	5	↓	↓	↓	↓	96	120	55			
SHAWINIGAN											
50% Compressed	39	Fluffy	Fractional	Partial	Fair	25	35	-	2	18	3.60

* Exposed to 500 ml of Electrolyte.

** In N_2 Atmosphere.

TABLE 3-1. ADSORPTION AND WET-CELL CAPACITY DATA FOR M-DINITROBENZENE ON VARIOUS CARBONS BLACKS.
(Sheet 2 of 2)

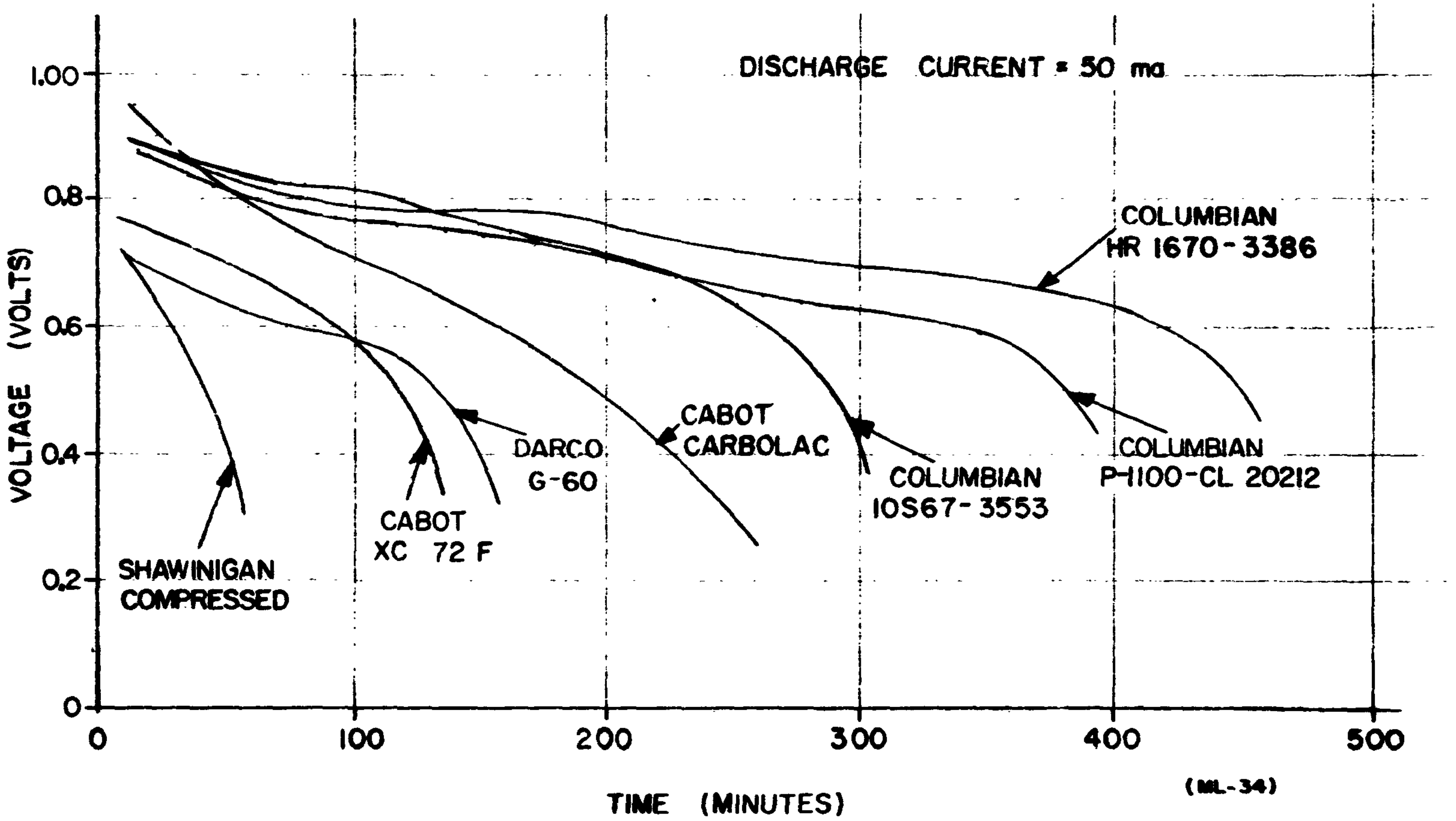

FIGURE 3-3. CAPACITY OF M-DINITROBENZENE WHEN ADSORBED BY VARIOUS CARBON BLACKS.

No significant increase in adsorption was found with the CBW P-1100-CL-20212 carbon black. The data are summarized as follows for 0.5-gram samples of carbon black.

CARBON EXPOSED TO:	0.5 gm COLUMBIAN CARBON BLACKS	
	HR 1670-3386	P-1100-CL 20212
250 ml Electrolyte		
amount of m-DNB adsorbed (mg)	233	167
discharge time at 50 ma (min)	420	390
cathode efficiency (%)	78	100
500 ml Electrolyte		
amount of m-DNB adsorbed (mg)	335	174
discharge time at 50 ma (min)	670	420
cathode efficiency	87	100

The data show general correlation between the adsorbed quantity of m-DNB and its 50-ma discharge capacity. The discrepancy between the adsorbed quantity of m-DNB and the 50-ma discharge capacity may be due to any of the following reasons:

a. The active sites on the carbon black are capable of desorbing the discharge products, and are thus available for adsorbing additional m-DNB. This can permit a carbon black having an initially poor adsorption to give better results in a cell than a carbon black with a very high initial m-DNB-adsorption value.

b. An optimum ratio of H_2O/m-DNB is not maintained during the life of the carbon black.

c. Structure breakdown of the carbon black occurs by mass transport during discharge.

d. Desorption of a quantity of m-DNB into the electrolyte occurs during the wet-cell test.

The m-DNB adsorption test also provides data on the dry bulk of the carbon black, wettability in the electrolyte, sedimentation, and behavior of the carbon black on filtration. As a general rule, the dense or nodular carbon blacks adsorbed less m-DNB than did the ultrafine, fluffy carbon blacks. Slow or partial wetting suggests a heterogeneous surface condition. In the dense carbon blacks, this characteristic may inhibit dispersion and, possibly, the access of electrolyte. The degree of flocculation and sedimentation of carbon black dispersed in excess electrolyte may illustrate the persistence, development, or change of a heterogeneous surface condition. Considerable variation was observed in the speed of filtration with different carbon blacks. CBN HR 1670-3386 is particularly slow.

Effect of Reaction Products

The effect of reaction products was evaluated by the following two general methods:

a. determining the effect of the major reaction products on adsorption of m-DNB by carbon black.

b. regenerating the carbon blacks, after discharge, by further treatment with 2N $Mg(ClO_4)_2$ electrolyte saturated with m-DNB.

Adsorption of Reaction Products: The first method provides information concerning the preferred species adsorbed on carbon black. Studies were conducted on the adsorption of m-DNB from 2N $Mg(ClO_4)_2$ by carbon blacks in the presence of reaction products. Two samples of Columbian carbon blacks, CBN P-1100-CL 20212 and HR 1670-3386, were examined. In one study, m-phenylenediamine was present; in the other, both m-phenylenediamine and m-nitroaniline were present.

Results showed that the capacity obtained from the testing of these carbon blacks in the wet cell was influenced by a reduced adsorption of m-DNB. Higher cell capacity was obtained from testing of HR 1670-3386 carbon black. Capacity data are presented in Figures 3-4 and 3-5.

The adsorption of m-DNB by 0.5 gm of Columbian carbon black in the presence of reaction products is tabulated below. The quantities m-DNB listed in the last two columns were adsorbed upon exposure of the carbon blacks to 250 ml of 2N $Mg(ClO_4)_2$ containing the compounds listed in column 1.

REFER TO CURVE OF FIGURES 3-4 and 3-5:	250 ML OF 2N $Mg(ClO_4)_2$ CONTAINING	m-DNB (grams) ADSORBED BY 0.5 GRAM OF:	
		HR 1670-P3386	P-1100-CL 20212
A	0.25 gm m-DNB	0.235	0.170
B	0.25 gm m-DNB and 0.325 gm m-phenylenediamine	0.197	0.124
C	0.25 gm m-DNB, 0.325 gm m-phenylenediamine, and 0.041 gm m-nitroaniline	0.179	0.112

Carbon Black Regeneration: The second method is directed toward determining the ability of the carbon black to desorb the reaction products formed during discharge. The effect of additional adsorption of m-DNB was studied by discharging the initially adsorbed m-DNB and exposing the carbon sample to a second 250-ml portion of electrolyte saturated with m-DNB by simple percolation through the packed test cell. Test results showed a definite decline of capacity on the second discharge with the same carbon black sample. For the third exposure the sample of carbon black was fully redispersed in 250 ml

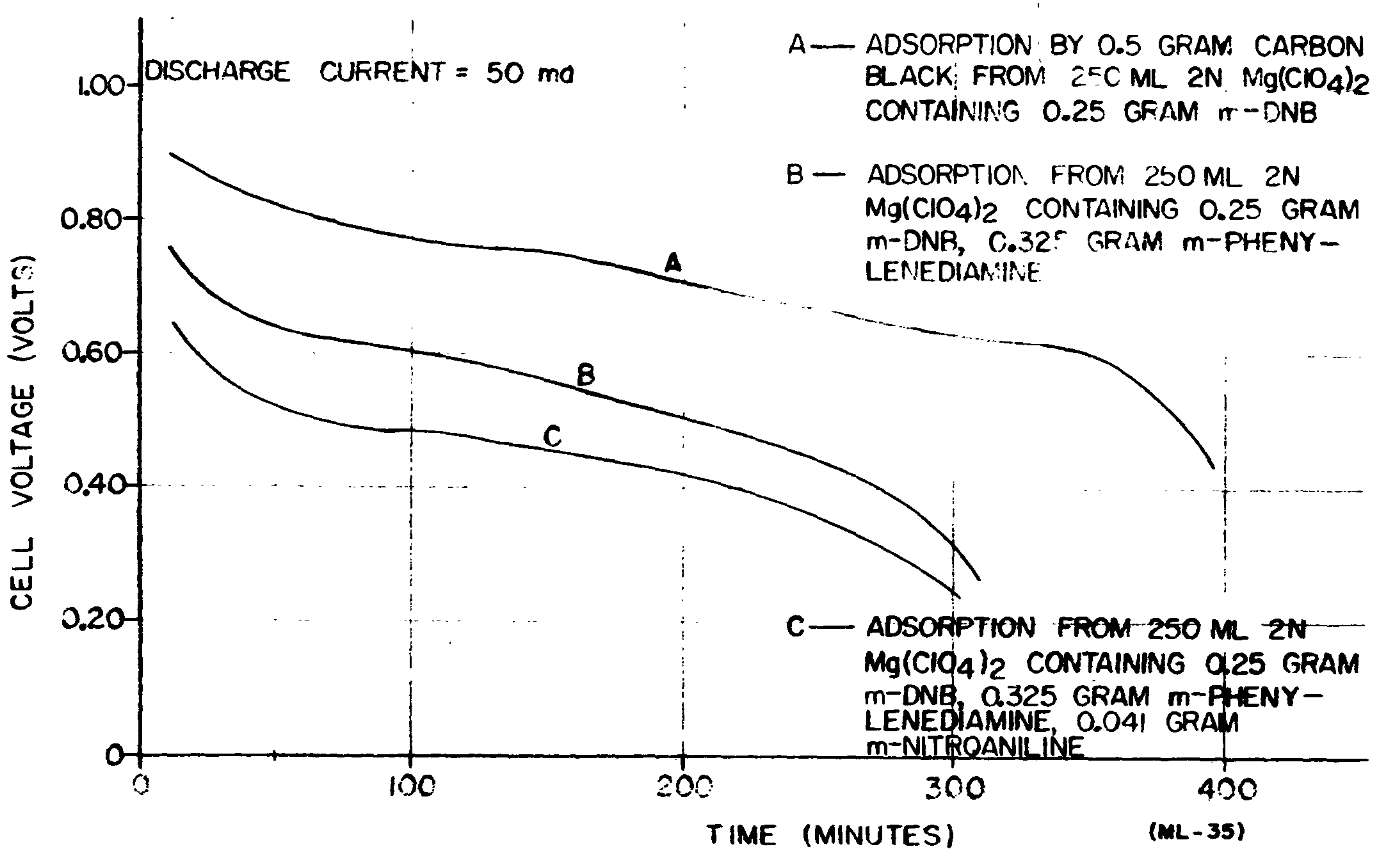

FIGURE 3-4. CAPACITY OF m-DINITROBENZENE ADSORBED BY COLUMBIAN P-1100-CL 20212 CARBON BLACK IN THE PRESENCE OF SELECTED REACTION PRODUCTS.

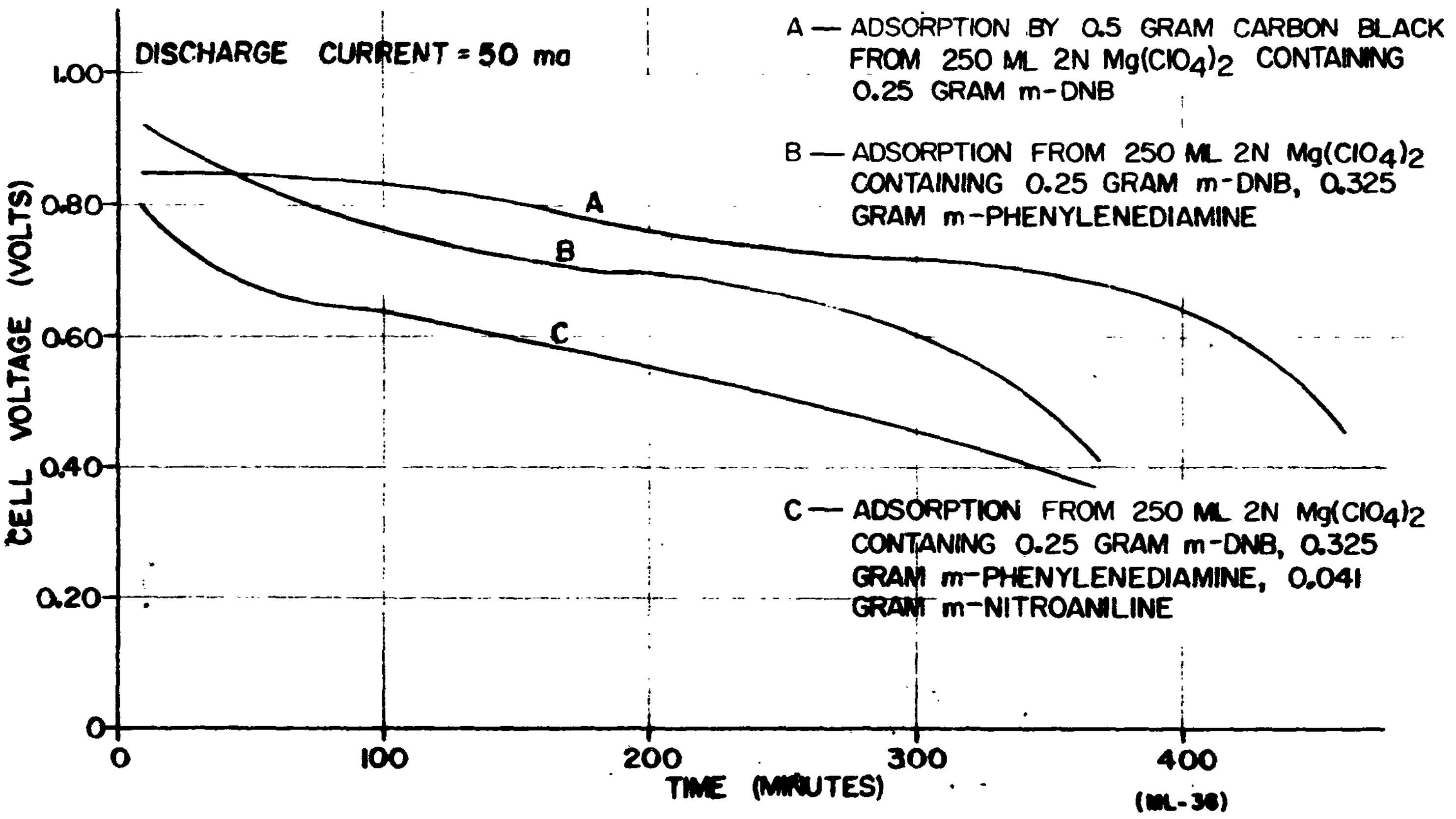

FIGURE 3-5. CAPACITY OF M-DINITROBENZENE ADSORBED BY COLUMBIAN HR 1670-3386 CARBON BLACK IN THE PRESENCE OF SELECTED REACTION PRODUCTS.

of electrolyte saturated with m-DNB, and formed into a wet cell. Performance decreased again. The data are presented in Figures 3-6 and 3-7. The data obtained from the two methods show that the active sites on the carbon blacks are blocked by reaction products. It can not be determined at this point if there is a desorption of reaction products followed by adsorption of more m-DNB, or if new active sites become available.

The present data suggest partial desorption of some sites. An attempt will be made to determine the number of times active sites become available for reaction by adding the total ampere-minutes for a given carbon black sample. This should provide a reasonable approximation of the actual cell.

Effect of Other Cathode-Mix Components

Comparison of the adsorption and wet-cell test data shows that CBN HR 1670-3386 carbon black adsorbs more m-DNB and has greater capacity than CBN P-1100-CL 20212. These advantages, however, do not hold for A-cell tests, where the CBN P-1100-CL 20212 is superior. An examination of both carbon blacks was made by studying the effect of A-cell cathode-mix components on the wet-cell capacity. The transition from the wet cell to the composition of the A-cell mix was tested in this sequence:

MATERIALS	COMPOSITION (grams)			
	I	II	III	IV
carbon black	0.5	0.5	0.5	0.5
m-DNB	1.	1.	1.	1.
$BaCrO_4$	none	.09	.09	none
$Mg(OH)_2$	none	none	.03	.03

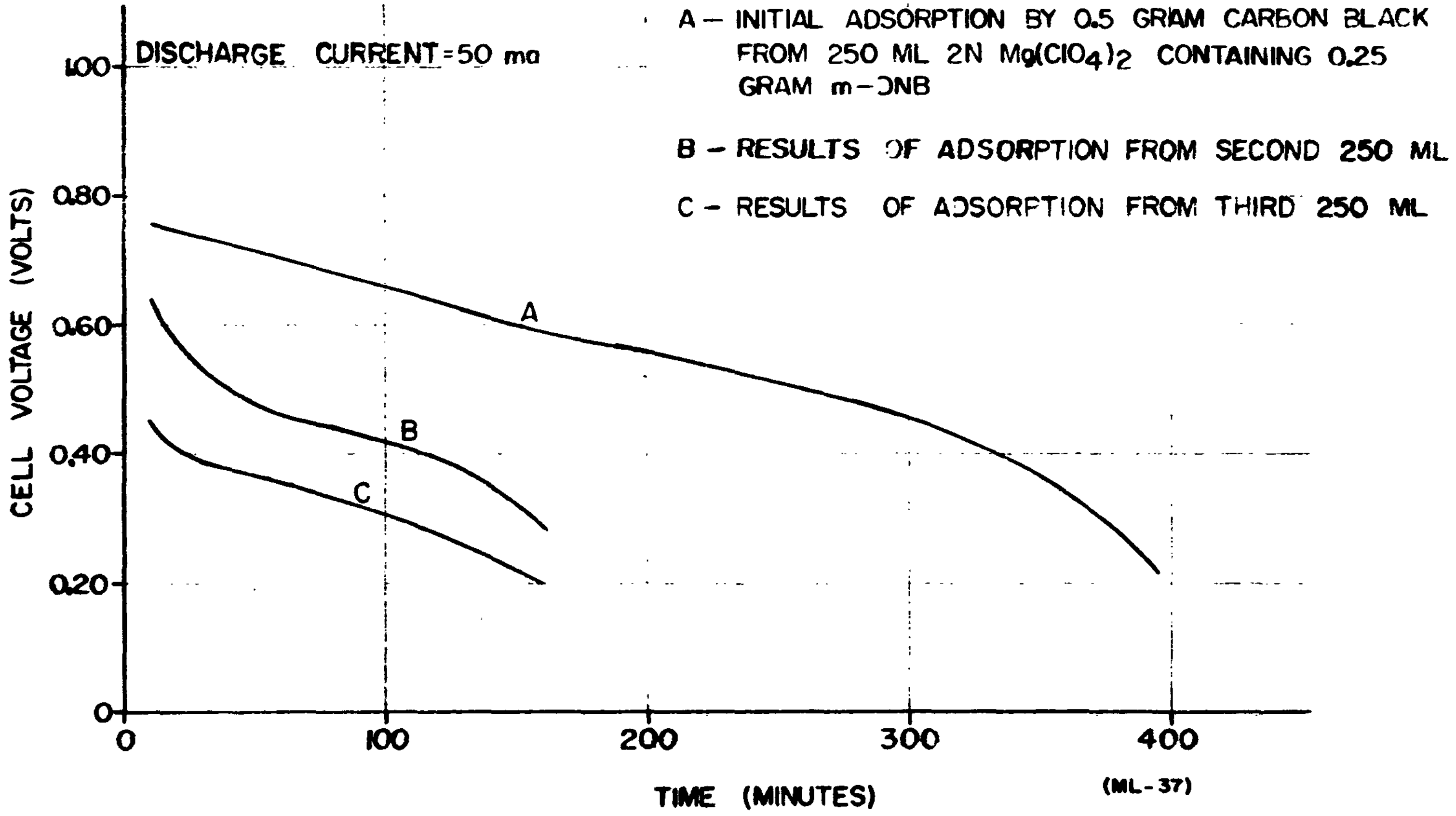

FIGURE 3-6. EFFECT OF THE PROGRESSIVE ADSORPTION OF m-DINITROBENZENE BY COLUMBIAN P-1100-CL 20212 CARBON BLACK UPON WET-CELL CAPACITY.

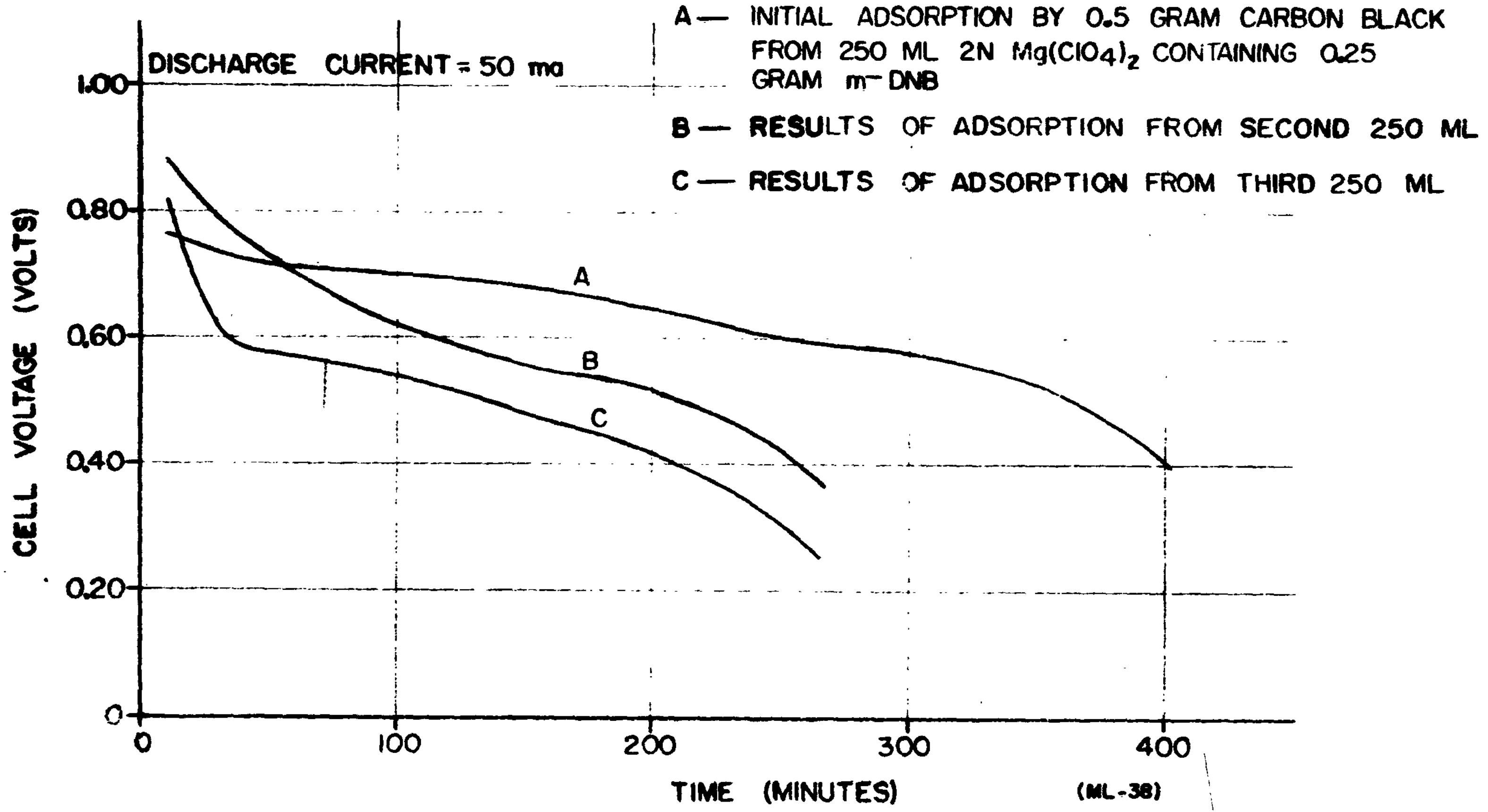

FIGURE 3-7. EFFECT OF THE PROGRESSIVE ADSORPTION OF m-DINITROBENZENE BY COLUMBIAN HR 1670-3386 CARBON BLACK UPON WET-CELL CAPACITY.

These components were milled gently for one hour, transferred in a level layer into the wet-cell assembly previously described, saturated in 2N $Mg(ClO_4)_2$, and discharged at 50 ma. The discharge times were found to be as follows:

CARBON TYPE	COMPOSITION (hours)			
	I	II	III	IV
CBN HR 1670-3386	11	8	12	21
CBN P-1100-CL 20212	9	11	16	21

Examination of the discharged wet cells showed extreme hardening of the CBN HR 1670-3386 cathode with $BaCrO_4$. The advantage of composition IV, which contained no $BaCrO_4$, did not materialize in A-cells.

Discussion of Test Results

A comparison of wet-cell capacities from adsorbed m-DNB, along with information on A-cell performance, is presented in Table 3-2. Variations noted in the performance of different carbon blacks make general conclusions difficult. The CBN 10S67 control sample and several CBN HR 1670 samples, although very fluffy, absorb less water than needed for the 2:1 m-DNB/carbon black cathode mix. For example, the CBN HR 1670 control sample shows 27 hours for the 16-2/3-ohm test, which represents complete utilization of the water content. Simultaneous high values in water absorption and m-DNB adsorption are not unfailing criteria for superior A-cell capacity, as shown for CBN HR 1670-3386 and -3523 carbon blacks. It is reasonable, though, to expect poor A-cell performance from a combined low rating in both properties.

Carbon blacks of apparently "ideal" sorption properties often give relatively poorer 4-ohm A-cell test results than would be expected

CARBON TYPE	WET-CELL TEST Mg of m-DNB on 0.5 g CARBON BLACK	MINUTES AT 50 MA	DRY-CELL TEST HOURS TO 0.90 VOLT	
			AT 4 OHMS	AT 16-2/3 OHMS
<u>COLUMBIAN</u>				
P-1100-2142	174	300	4	29
P-1100-2142 HT 3232	178	360	4	30
P-1100-8417-1	153	285	3.5	26.5
-2	167	390	4	28
-3	171	300	3	29.5
-4	151	300	3.5	29
P-1100-CL 20212	170	360	5.0	33
10S67-Control	0	30	1.75	23
-3387	117	205	2.75	24
-3398	23	33	3	23.5
-3399	133	280	2.25	24
-3522	17	20	1.75	22.5
-3553	140	300	3	25.5
HR 1670-Control	211	400	3	27
-3379	195	370	1.75	23.5
-3380	83	120	0	14
-3381	111	240	0	0
-3382	160	240	1	15
-3383	209	360	2.25	23.5
-3386	234	420	3	25.5
-3523	232	370	1.75	24.0
<u>CABOT</u>				
XC 72 F	52	100	3	22
<u>DARCO</u>				
G-60	99	145	3	20
<u>SHAWINIGAN</u>				
50% Compressed	25	35	2	18

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TABLE 3-2. COMPARISON OF WET-CELL CAPACITY FOR m-DINITROBENZENE ADSORBED BY VARIOUS CARBONS WITH A-CELL DATA.

from the 16-2/3-ohm results. These results may be related to the apparent discrepancies noted above. Failure at the higher current density may be due to poor diffusion resulting from immobility of the electrolyte. The hard-setting mix cake, obtained in the CBN HR 1670-3386 carbon black with $BaCrO_4$, is not conducive to the rapid exchange between reaction products and m-DNB that is necessary to sustain a high-current discharge.

Variations in data obtained from the 4-ohm A-cell tests with carbon blacks of the CBN 10S67 and HR 1670 types emphasize that the adsorption of m-DNB on carbon black is not the rate-controlling property. The data reveal that m-DNB can be discharged efficiently in a tightly packed A-cell with a carbon black which does not adsorb m-DNB from its electrolyte solution. Another factor which must be considered in the deviations between the wet-cell test and the dry-cell results is a structure breakdown within the cathode. During the discharge of a dry cell, two physical changes occur to alter the physical structure of the cathode. These changes are:

a. movement of the free water from the cathode mix through the separator to the anode.

b. transport of m-DNB to carbon black. This action is probably preceded by a dissolution process.

In a typical m-DNB (2:1 ratio) cathode, water comprises approximately 60% of the total cathode volume. During the discharge of an A-cell with a 16-2/3-ohm load for 27 hours, approximately 50% of the water must be transferred out of the cathode mix through the separator to the magnesium anode. Magnesium consumes water in the formation of its hydroxide and hydrogen, and the carbon black cathode structure must, therefore, withstand a 30% volume change during discharge.

The solid m-DNB must dissolve before it can reach the carbon black. This process will also remove substance from the original cathode mix structure and, thus, inevitably alter it.

3.2.2.4 Differences Produced by Mix Variations

Cathode Mix "Pebbling"

The P-1100-CL 20212 carbon black differed strikingly from all the other Columbian carbon blacks in its characteristic "pebbling" tendency. The mix structure made with this carbon black was examined with the objective of matching the mix structure by substituting a blend of two other carbon blacks.

"Pebbling" is the property of forming discrete pebbles of cathode mix when mill-blended dry-cathode-mix components are tumbled with the optimum volume of electrolyte. This phenomenon is tentatively interpreted to be a state of aggregation which firmly holds the electrolyte so that only syneresis supplies a minimum liquid phase. In true "pebbling", this liquid phase carries no carbon. The surfaces of the glass jar remain perfectly clean during tumbling. Other carbon blacks produced smearing on the glass during this operation. The pebbling of CBN P-1100-Cl 20212 has been observed with both $MgBr_2$ and $Mg(ClO_4)_2$ electrolytes.

The selection of two other Columbian carbon blacks which might duplicate the pebbling effect and give superior A-cell performance was based upon color, m-DNB adsorption, dry bulk, absorption of electrolyte, and A-cell data. On these bases of selection, CBN HR 1670 Control II was blended in two different ratios with CBN 10S67-3553 in the following two cathode-mix formulations:

	LOT NO. 432		LOT NO. 433	
	WEIGHT		WEIGHT	
	GRAMS	PERCENT	GRAMS	PERCENT
Columbian HR 1670 Control II	6.25	11.05	8.33	10.95
Columbian 10S67-3553	6.25		4.17	
m-DNB	25.0	22.1	25.0	21.85
$BaCrO_4$	2.3	2.0	2.3	2.0
$Mg(OH)_2$	0.8	0.7	0.8	0.7
2N $Mg(ClO_4)_2$	72.4	64.15	73.9	64.5
TOTALS	113.0	100.00	114.5	100.0

Upon addition of electrolyte to the dry blends of both these formulations, a degree of pebbling was observed, but it did not progress to the same clean system characteristic of CBN P-1100-CL 20212. The parent carbons of the blends gave 3.0 hours of continuous drain at 4 ohms to 0.9 volt in A-cells, whereas both blends improved this drain to 3.5 hours. The A-cell performance in the 16-2/3-ohm tests remained in the 27-to-28-hour range for the blends, and was not significantly improved over the parent carbons.

Electrolyte with Solvent for m-DNB

The low solubility of m-DNB in 2N $Mg(ClO_4)_2$, which is 1 mg/ml, limits high-rate A-cell performance with some carbon blacks. Increasing the solubility of m-DNB may lead to improved capacity if the increased m-DNB concentration does not react with the magnesium anode.

A study was made of the use of small amounts of a mutual solvent, such as acetone or acetonitrile, for m-DNB in 2N $Mg(ClO_4)_2$ to increase the solubility of m-DNB. Columbian P-1100 8417-3 was chosen for this test because, in A-cells, it gave 29.5 hours to a 0.9-volt end-point at 16-2/3 ohms, but only three hours in the 4-ohm test. A modified cathode mix has the following composition:

	LOT 434
P-1100-8417-3	12.5 grams
m-DNB	25.
$BaCrO_4$	2.3
$Mg(OH)_2$	0.8
Electrolyte:	
60 ml 2N $Mg(ClO_4)_2$	
10 ml CH_3CN	75.9
	116.5 grams

The dry mix was blended by rolling with ZrO_2 balls for one hour. When the dry mix was blended with the modified electrolyte, the cathode mix showed a marked degree of pebbling not observed in standard 2N $Mg(ClO_4)_2$ mixes. The solvent-modified mix could be extruded and handled normally in the A-cell preparation.

Capacity tests were run at 4 ohms, and the results were compared with standard mixes. The results show that the discharge time was reduced from 3 hours to 2.5 hours for the solvent mix. Evidence of the ample reserve of m-DNB in the cell discharged at 4 ohms was obtained when the same cell gave 70 hours capacity to a 0.9 cutoff voltage at a drain of 50 ohms.

A similar test using acetone as a mutual solvent resulted in a further reduction from 3 hours to 1.25 hours at 4 ohms. The acetone-treated Columbian HR 1670-3386 lost much of its ability to absorb electrolyte.

It is evident that the increase in concentration of m-DNB by use of a mutual solvent does not make possible a sufficient supply of m-DNB at the carbon reaction site at high discharge rates. Therefore, the use of a mutual solvent does not offer any advantages.

3.2.2.5 Electrical Conductivity and Residual Voids of Compressed Carbon Blacks

Carbon black in intimate contact with m-DNB may become oriented in different ways, and, thereby, exhibit different values of electrical conductivity and of residual volumes of voids. The simple apparatus shown in Figure 3-8 serves both measurements.

Suitable quantities of carbon black, or dry blend, are compressed to a measured volume within a polystyrene cylinder confined by an insulated stainless-steel mold. The voltage across the compressed carbon black is measured at a constant current on the high-sensitivity scale of a Type G11-A Varian recorder. The electrical resistance is determined by Ohm's Law. From the apparent volume of the compressed carbon black, or mix blend, and the absolute volumes of materials, the volume of residual voids is calculated.

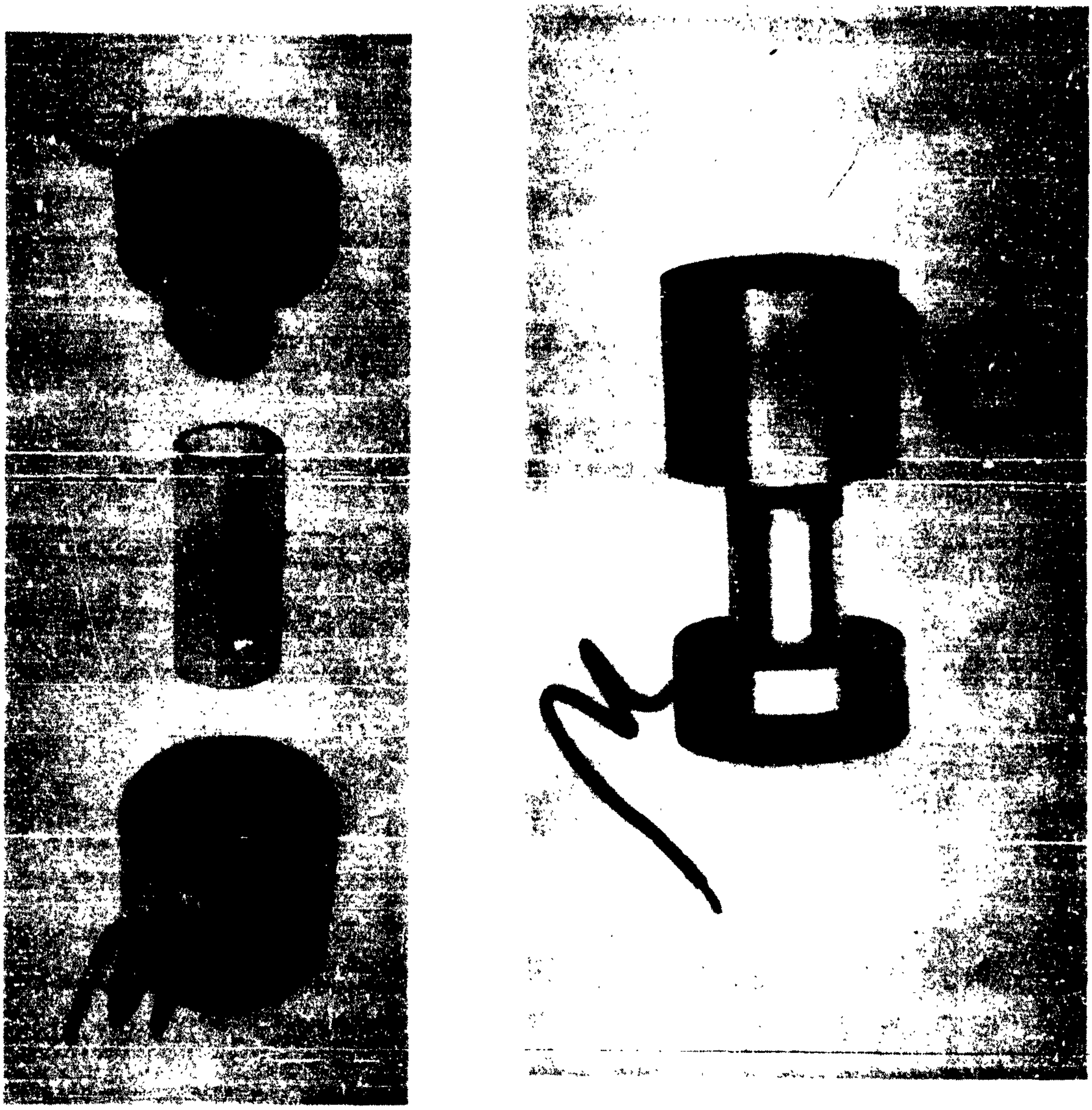

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Figure 3-8. Exploded View and Assembly of the Resistivity Test Fixture for Powdered Material.

The volume of residual voids in a compressed carbon black is of primary importance because the electrochemical reduction of m-DNB consumes much water. The measurement of electrolyte absorption in a cathode mix is subject to several errors. Therefore, a reliable measurement is needed to determine the amount of free space available for the electrolyte in a carbon black. The preliminary survey of volume changes was made with seven experimental Columbian carbon blacks and their blends which contain the usual cathode-mix components.

The theory, experimental procedure, and calculations of a standardized method for electrical conductivity and residual voids are described in our Fourth Quarterly Report.

Discussion of Results

At the end of each of Tables 3-3 through 3-7, a variety of qualitative observations are noted on the seven carbon blacks. A remarkable distinction of P-1100-CL 20212 from the other six carbon blacks is found. This unique material exhibits self-cohesion forces in excess of adhesive tendencies for other surfaces, such as glass, steel, polystyrene, $Mg(OH)_2$, and ZrO_2. Although it packs together more uniformly under pressure than all other carbon blacks, it still remains friable, without the "graphitic-smear effect" of other ultrafine blacks. Another sharp distinction of P-1100-CL 20212 is its persistent resiliency under compression, and exfoliation on release of the pressure.

Figure 3-9 compares the electrical conductivity with the void volumes in seven carbon blacks which were tested in five different dry states. The two most significant states of the carbons are represented in the figure by: (1) the small solid circles for the carbon black as received. (2) the large solid circles for cathode mix milled for 40 minutes. The curves indicated by the solid lines show the changes of the carbon black from its "as received" state to its 1:2 m-DNB-cathode-mix blend. As each carbon black is diluted with two weights of the non-conducting m-DNB, the electrical conductivity decreases

DESCRIPTION	SYMBOLS	UNITS	MATERIAL						
			P-1100 CL20212	HR1670 50#LOT	6R215 P9393	6R216 P9394	6R219 P9396	6R221 P9397	6R223 P9398
Apparent Air-floated Volume		cc	45.	32.	21.5	31.4	23.5	20.3	20.
Tapped to Minimum Reference Volume	(a)	cc	34.5	23.2	14.3	20.0	14.0	11.3	12.5
Apparent Dry Density			0.029	0.043	0.07	0.05	0.07	0.089	0.08
Vise-Compressed to Volume	(b)	cc	3.10	2.30	2.20	2.27	2.264	2.316	2.316
Compression Ratio = a/b	(c)		11.13	10.1	6.25	8.80	6.19	4.88	5.40
Assuming Absolute Volume of 1 gram Carbon Black = 0.455cc: Volume of Voids in Compressed Carbon Black = $(b - v_o)$	(d)	cc	2.645	1.845	1.835	1.815	1.809	1.861	1.861
Volume of Voids at Compression Ratio of 10 = c/10 x d	(e)	cc	2.94	1.87	1.15	1.60	1.12	0.91	1.00
Electrical Conductance at 0.1 ampere	(f)	volts	.075	.082	0.15	0.231	0.11	0.108	0.096
Conductance in mho-cm at Compression Ratio of 10 = $\frac{(b) \times 0.1 \times 10}{(f) \times (c)} = \frac{(b)^2}{(a) \times (f)}$	(g)	mho-cm	3.72	2.78	2.44	1.11	3.32	4.38	4.47
Observations During Above Tests									
Ease of Gathering Carbon Black into Test Cylinder			Good	Difficult	Difficult	Difficult	Difficult	Difficult	Difficult
Elastic Reversal of Piston in Vise		mm	4.	2.	2.	2.	2.	2.	2.
Extrusion at Base of Test Cylinder		mm	1.5	0.4	0.4	0.4	0.1	0.4	0.5
Adhesion to Steel and Polystyrene ZrO_2, Glass			none	severe	severe	severe	severe	severe	severe
Packing Gradient			little	extreme	extreme	extreme	extreme	extreme	extreme
Consistency of Compressed Carbon Black			friable	graphitic	graphitic smear	graphitic smear	graphitic smear	graphitic smear	graphitic smear

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TABLE 3-3. ELECTRICAL CONDUCTANCE AND VOLUME OF RESIDUAL VOIDS IN COLUMBIAN CARBON BLACKS.
ONE-GRAM SAMPLE: NO MILLING.

DESCRIPTION	SYMBOLS	UNITS	MATERIAL						
			P-1100 CL20212	HR1670 50#LOT	6R215 P9393	6R216 P9394	6R219 P9396	6R221 P9397	6R223 P9398
Tapped Minimum Reference Volume	(a)	cc	34.5	23.2	14.3	20.0	14.0	11.3	12.5
Vise-Compressed to volume	(b)	cc	3.5	2.2	2.2	2.2	2.2	2.2	2.2
Compression Ration = a/b	(c)		9.85	10.55	6.5	9.1	6.37	5.14	5.68
Assuming Absolute Volume of 1 Gram Carbon Black, V_o, = 0.455cc, the Volume of Voids on Compressed Carbon Black is equal to	(d)	cc	3.045	1.745	1.745	1.745	1.745	1.745	1.745
Volume of Voids at Compression Ration of 10	(e)	cc	3.00	1.84	1.14	1.59	1.11	0.90	0.99
Electrical Conductance at 0.1 ampere	(f)	volts	0.08	0.08	0.12	0.21	0.07	0.08	0.07
Conductance at Compression Ratio of 10 $= \frac{(b)^2}{(a) \times (f)}$ = Specific Electrical Conductivity	(g)	mho-cm	4.44	2.62	2.82	1.15	4.94	5.35	5.54
Percent gain in Conductivity over Original Carbon Black			19.4	-5.8	15.6	3.6	48.8	22.2	24.0
<u>Observations During Above Tests:</u>									
Adhesion to Glass, ZrO_2, Stainless Steel, Polystyrene			traces	severe	severe	severe	severe	severe	severe
Elastic Reversal of Piston in Vise		mm	3	2	1.5	1	1	1.5	1
Extrusion at Base of Test Cylinder		mm	3	0.5	0.1	0.05	trace	0.5	trace
Packing Gradient			some	distinct	distinct	distinct	distinct	extreme	distinct
Consistency of Compressed Carbon Black			friable	crumbly	crumbly	v.crumbly	crumbly	crumbly	fairly loose
Fracture of Compressed Carbon Black			dull	glossy	glossy	glossy	glossy	glossy	glossy

TABLE 3-4. ELECTRICAL CONDUCTANCE AND VOLUME OF RESIDUAL VOIDS IN COLUMBIAN CARBON BLACKS. ONE-GRAM SAMPLE: MILLED 30 MIN. IN GLASS JAR WITH $3ZrO_2$ BALLS.

DESCRIPTION	SYM-BOLS	UNITS	MATERIAL						
			P-1100 CI20212	HR1670 50#LOT	6R215 P9393	6R216 P9394	6R219 P9396	6R221 P9397	6R223 P9398
MATERIALS — WEIGHT (grams) — ABSOLUTE VOLUME (cc)									
Carbon Black 1.0 0.455									
m-DNB 2.0 1.27									
$Mg(OH)_2$ 0.06 0.025									
$BaCrO_4$ 0.18 0.04									
3.24 g 1.79 cc									
Reference Volume of Dry Cathode Mix I (tapped carbon vol.+absolute vol. of other materials)	(a)	cc	35.84	24.54	15.64	21.34	15.34	12.64	13.84
Vise-Compressed to volume	(b)	cc	4.34	2.94	3.42	3.75	3.80	4.05	3.70
Compression Ratio = a/b	(c)		8.25	8.35	4.58	5.69	4.04	3.12	3.74
Volume of Voids = (b) - 1.79 cc =	(d)	cc	2.55	1.15	1.63	1.96	2.01	2.26	1.91
Volume of Voids at Compression Ratio of 10 less 0.11 cc constant voids in non-carbon ingredients	(e)	cc	2.04	0.85	0.64	1.00	0.70	0.60	0.61
Electrical Conductance at 0.1 ampere	(f)	volts	0.224	0.22	0.47	1.20	0.43	0.59	0.36
Conductance at Compression Ratio of 10 $= \frac{(b)^2}{(a) \times (f)}$	(g)	mho-cm	2.35	1.60	1.59	0.55	2.19	2.20	2.75
<u>Observations During Above Tests</u>									
Elastic Reversal of Piston in Vise		mm	4	2	0.5	0	1.	1.	1.
Extrusion at Base of Test Cylinder		mm	1	0.5	0	0	0	0.1	trace
Packing Gradient			slight	distinct	distinct	distinct	distinct	distinct	extreme
Adhesion to Glass, Stainless Steel, ZrO_2, Polystyrene			none	severe	severe	severe	severe	severe	severe

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TABLE 3-5. ELECTRICAL CONDUCTANCE AND VOLUME OF RESIDUAL VOIDS IN CATHODE MIX I WITH CARBON BLACKS. CATHODE MIX I, MILLED 30 MIN WITH 3 7-OZ BALLS.

DESCRIPTION	SYMBOLS	UNITS	MATERIAL						
			P-1100 C120212	HR1670 50#LOT	6R215 P9393	6R216 P9394	6R219 P9396	6R221 P9397	6R223 P9398
Reference Volume of Dry Cathode Mix II(tapped volume 2 g Carbon + Absolute vol. of other materials)	(a)	cc	70.34	47.74	29.94	41.34	29.34	23.94	26.34
2.5 Grams Mix-Vise-Compressed to volume	(b)	cc	3.9	2.45	2.33	2.24	2.85	2.26	2.28
4.24 Grams would occupy	(b^1)	cc	6.62	4.16	3.96	3.80	4.83	3.84	3.87
Compression Ration = a/b'	(c)		10.6	11.5	7.6	10.9	6.1	6.2	6.8
Volume of Voids - (b') -2.25 (for 2 grams Carbon Black)	(d)	cc	4.37	1.91	1.71	1.55	2.58	1.59	1.62
Volume of Voids at Compression Ratio of 10 (2 g Carbon Black): = c/10xd		cc	4.63	2.20	1.30	1.68	1.56	1.00	1.10
Volume of voids per gram carbon black less 0.11 cc constant voids in non-carbon ingredients	(e)	cc	2.21	0.99	0.54	0.73	0.67	0.39	0.44
Electrical Conductance at 0.1 ampere (on 2.5 g sample)	(f)	volts	0.13	0.08	0.105	0.245	0.145	0.065	0.075
Conductance of Mix II (2:2 m-DNB: Carbon Black) at Compression Ratio of 10 $= \frac{(b)\,(b')}{(a) \times (f)}$ = Specific Electrical Conductivity	(g)	mho-cm	2.82	2.67	2.94	0.84	3.24	5.57	5.15
Observations During Above Tests									
Adhesion to Glass, Steel, ZrO_2, Polystyrene			trace	severe	severe	severe	severe	less	severe
Elastic reversal of piston in vise		mm	3	1	0.2	0	0.5	0.5	0.5
Extrusion at base of test cylinder		mm	0.3	trace	0	0	trace	trace	trace
Packing Gradient			some	some	some	distinct	little	little	little
Consistency of compressed mix			friable	smear	smear	smear	smear	smear	smear

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TABLE 3-6. ELECTRICAL CONDUCTANCE AND VOLUME OF RESIDUAL VOIDS IN CATHODE MIX II WITH COLUMBIAN CARBON BLACKS. CATHODE MIX II = CATHODE MIX I + 1 G CARBON OF TABLE 4-2 MILLED ADDITIONAL 110 MINUTES. TOTAL WEIGHT = 4.2.4 G; ABSOLUTE VOLUME = 2.25 CC.

DESCRIPTION		ABSORPTION ml 2N $Mg(ClO_4)_2$ PER GRAM OF CARBON BLACK	HOURS CONTINUOUS DISCHARGE TO 0.9 V Mg AZ10 A-Cells		DRY MIX TUMBLED FOR 30 MINUTES (DATA CALCULATED TO COMPRESSION RATIO OF 10)			
					ELECTRICAL CONDUCTIVITY (Mho-cm)		RESIDUAL VOIDS (cc/gram carbon black)	
CARBON BLACK	DENSITY grams/cc		4 ohms	16-2/3 ohms	CARBON BLACK	DRY MIX	CARBON BLACK	DRY MIX
Factorial 1	0.235	2.15	1. 1.25 -	11. 11.75 -	22.4	3.48	0.311	0.39
(Columbian) 2	0.227	2.2	1.25 1.25 -	10.5 11. -	15.0	4.07	0.34	0.36
3	0.066	4.2	3. 3. 3.	25.75 26.25 27.25	6.85	3.68	1.23	0.78
4	0.062	4.75	3.5 3.5 3.5	26. 26. 26.	6.26	4.00	1.335	0.83
5	0.444	1.2	0.15 - -	0.5 - -	24.5	1.66	0.276	0.03
6	0.227	2.3	1. 1.25 -	12.5 13. 13.5	17.5	4.90	0.33	0.16
7	0.059	4.4	3. 3. 3.	25. 25.25 23.5	7.06	3.95	1.40	0.84
8	0.066	4.1	2.75 3. 3.	23.5 24.25 24.75	6.07	3.43	1.25	0.64
9	0.063	5.1	3. 3.5 3.5	23.5 23.5 25.25	7.53	4.80	1.29	0.73
10	0.476	1.3	(.5 to .65 v)	2.5 5.25	21.9	1.76	0.13	0.03
11	0.063	4.8	3.5 3.5 3.5	24.75 24.75 24.75	7.50	4.83	1.28	0.74
6 R 215	0.070	3.5	2. 2.25 2.25	21.25 22. 22.	2.44	1.49	1.15	0.78
21[illegible]	0.050	4.5	(1.5 to .8 v)	23.25 23.25 24.5	1.116	0.66	1.61	1.03
219	0.071	4.4	2.75 2.75 3.	25.5 25.5 25.5	3.32	2.55	1.125	0.70
221	0.089	3.7	2.5 2.5 2.75	18.25 22.75 25.25	4.41	2.80	0.915	0.56
223	0.080	3.9	2.5 2.75 2.75	23.5 24.5 25.	4.47	3.02	1.01	0.62
P-1100 2142	0.080	6.0	4. (average)	29. (average)	16.2	5.65	1.05	0.67
8417-3	0.042	5.2	3.+ (average)	29. (average)	5.45	3.45	1.97	1.24
CL 20212	0.029	4.75	5. (average)	34.+ (average)	3.70	3.15	2.95	1.80
ER-1670(50F)	0.043	3.85	3. (average)	27. (average)	2.80	1.78	1.865	1.17
3386 (II)	0.055	5.7	3. (average)	26. (average)	4.03	3.06	1.60	.95
CABOT XC 72F	0.100	4.2	3. (average)	20. (average)	19.2	9.13	0.73	.39
DARCO G-60	0.417-	2.0	0.5 (average)	13.5 (average)	14.9	1.55	0.16	.04
in 2:1 m-DNB mix		1.6	2. (average)	17.5 (average)		7.6		
SHAWINIGAN Uncompressed	0.021	5.5	2 to 3	22	2.68	1.66	3.79	2.39
UNITED 65 SPF	0.333	1.4	-	-	8.1	-	0.24	-

TABLE 3-7. DATA FOR THE EVALUATION OF CARBON BLACKS SUITABLE IN DRY CELLS WITH WATER-CONSUMING DEPOLARIZER. CARBON BLACK TAPPED.

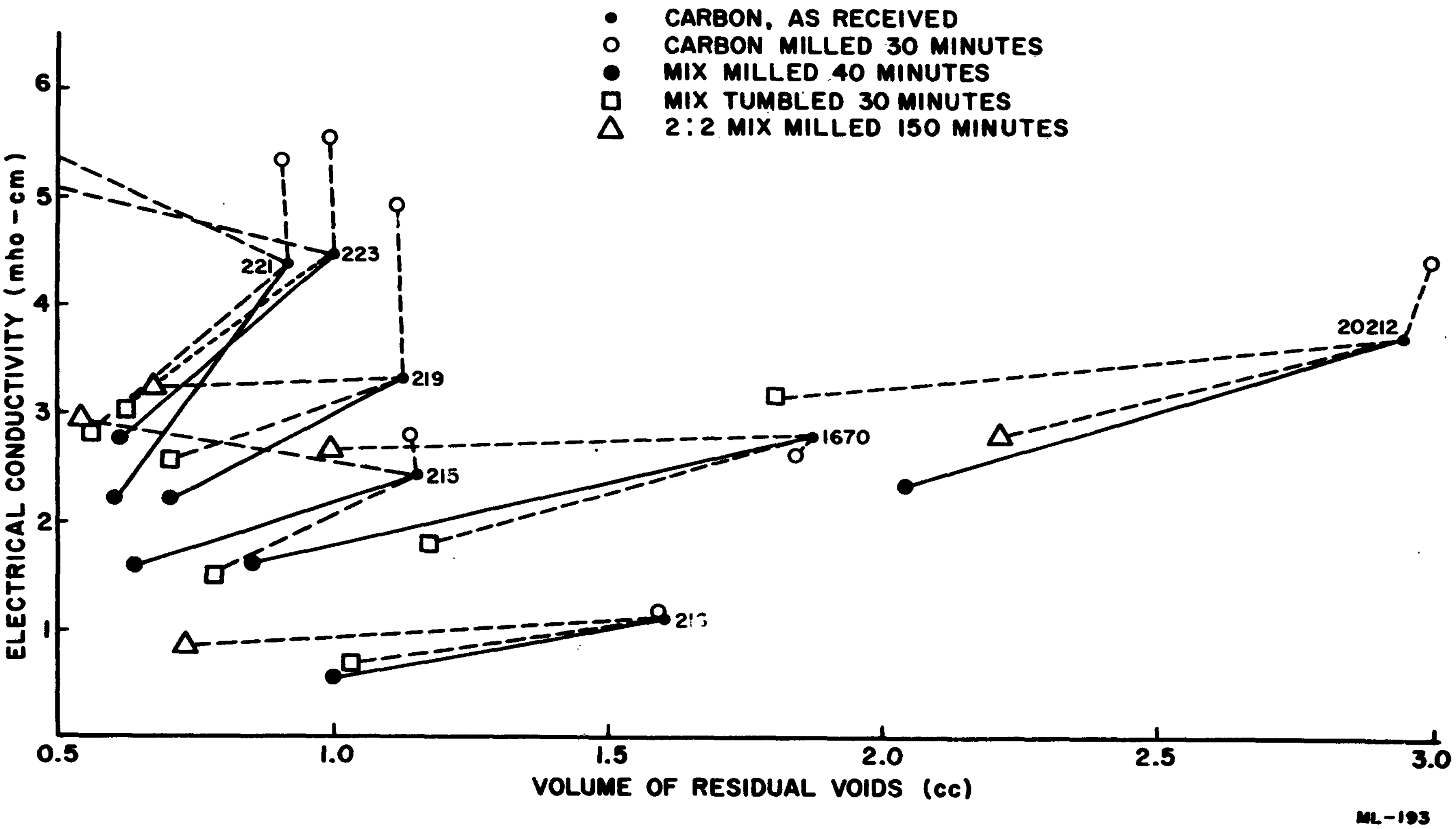


FIGURE 3-9. VARIATION OF ELECTRICAL CONDUCTIVITY AND RESIDUAL VOIDS IN CARBON BLACK AT FIVE DIFFERENT STATES.

as expected. The conductivity increases again upon the addition of more carbon black. The changes in electrical conductivity of different carbon blacks are more irregular when they are milled for 30 minutes with ZrO_2 balls. A comparison of these carbon blacks (represented by the circles) with their milled mix blends (large solid circles) shows that the loss of voids is primarily due to the m-DNB, a rather wax-like material under compression.

The relative positions of the triangles (representing dilution of a standard 1:2 milled mix with an excess of pre-milled carbon black) illustrate the divergent behavior of the seven carbon blacks. Only P-1100-Cl 20212 retains its favored position; HR-1670 is slightly superior to the five 6R samples, where the residual void volumes have decreased below the standard-milled mix (large solid circles), and, these five carbon blacks were condensed into better conducting systems at the expense of their residual void volumes. The results of the mix-blend tumbled for 30 minutes (squares) corroborate the experience that normal mechanical handling of a carbon black is not a critical determinant for cell performance. The very low electrical conductivity of 6R 216 was reflected by the failure of this carbon black in A-cell tests at 4 ohms.

Correlation of Cell Performance with Electrical Conductivity and Residual Voids

From the seven test samples shown in Figure 3-9 it appeared that a comparison of the electrical conductivity and residual voids volume at only two of the five states defined the probable behavior of a carbon black in A-cells. Therefore, in a broader survey of carbon blacks, the measurements were limited to the original carbon black as received, and its 1:2 m-DNB mix-blend tumbled for 30 minutes. The study of the milled mix-blends was abandoned to simplify the procedure, and because severe milling was not necessary for the preparation of cathode mixes.

Data of this type are shown in Table 3-7 for 24 carbon blacks. The table is arranged to show a direct comparison of the apparent density and the absorption of electrolyte in experimental cathode mix formulations, along with data on the performance of magnesium A-cells containing the different carbon blacks.

Figure 3-10 shows the qualitative rating of the 24 carbon blacks with the data presented in columns 3 to 8 of Table 3-7. The distribution of the test samples indicates that both a fair electrical conductivity and the largest possible volume of residual voids are needed for optimum cell performance. However, a definite prediction of cell performance is not assured from the data on the carbon blacks in the intermediate quality range. It is plausible that the unique 5-hour A-cell service at 4 ohms in P-1100-CL 20212 depends upon electrical conductivity, while the 35-hour service at 16-2/3 ohms requires a large volume of residual voids. The simultaneous occurrence of these two optimum characteristics in the same carbon black is rarely found.

Carbon blacks with a very low volume of residual voids contribute little to this study because m-DNB cannot be efficiently reduced if the cathode mix carries insufficient water. Their enormous loss of electrical conductivity, in passing from the carbon black to a dry-mix blend, is interpreted as an envelopment of the large particles by the poorly conducting m-DNB.

There is a direct correlation between the initial tapped density of a carbon black and its loss of electrical conductivity in the cathode mix environment. Figure 3-11, is a log-log relationship of the variation in A-cell services, with the initial tapped density plotted as a function of the volume of voids maintained per unit of electrical conductivity. At any particular ratio of voids to specific electrical conductivity the carbon blacks improve in A-cell capacity from the more dense to the fluffier varieties.

When a set of mutual reciprocals of electrical conductivity and residual voids is plotted on a log-log chart, all points lie on a straight line. The data of Figure 3-11 are re-plotted in this manner in Figure 3-12. Here, the relative importance of the two major variables is coordinated with:

a. the initial tapped density of the carbon blacks.

b. the A-cell performance.

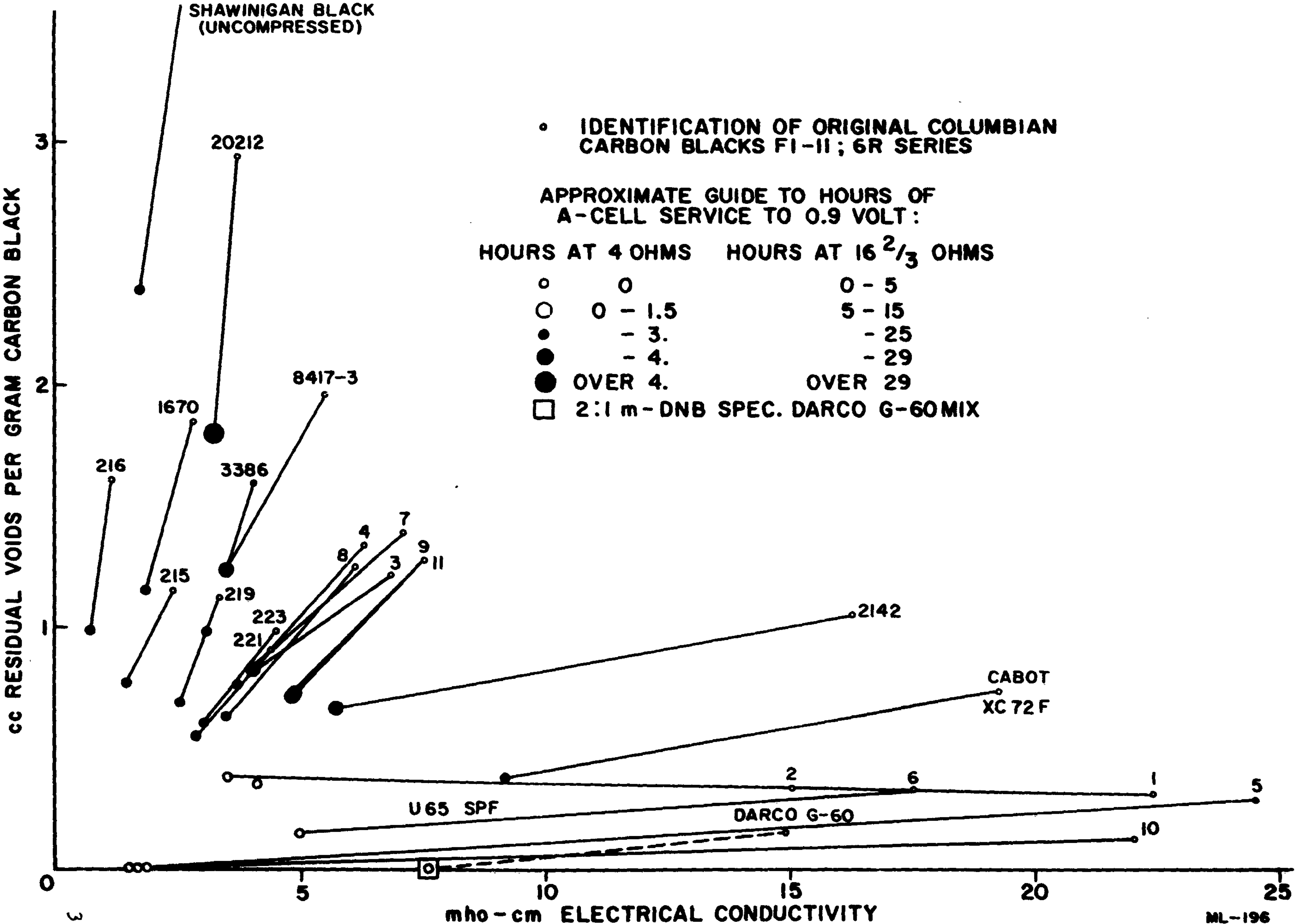
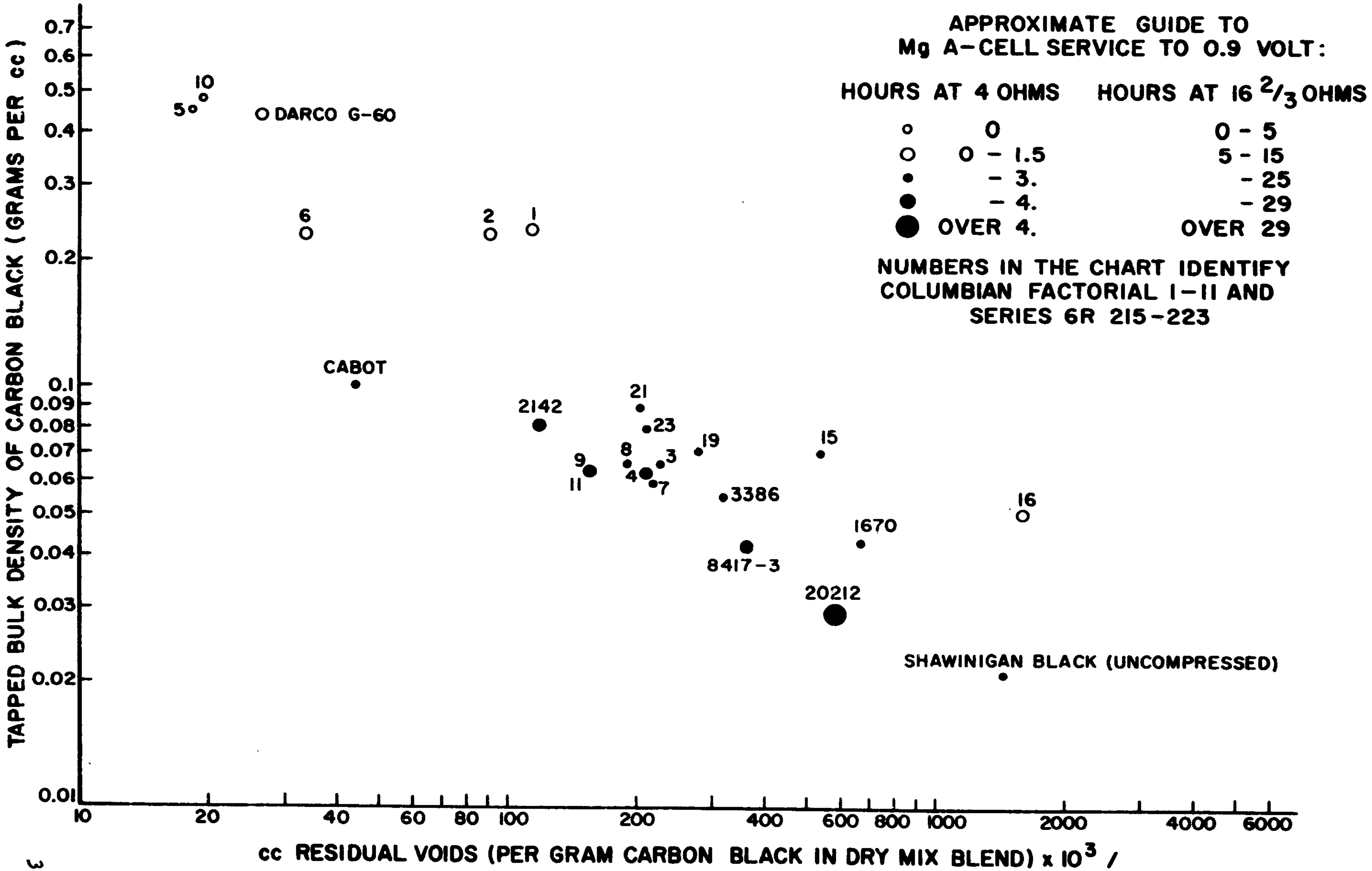


FIGURE 3-10. MAGNESIUM A-CELL PERFORMANCE IN RELATION TO VOLUMES OF RESIDUAL VOIDS AND TO SPECIFIC ELECTRICAL CONDUCTIVITY.



ML-195

FIGURE 3-11. THE RELATION OF THE DENSITY OF CARBON BLACKS TO THE RATIO OF RESIDUAL VOIDS/ELECTRICAL CONDUCTIVITY AND TO THE A-CELL PERFORMANCE.

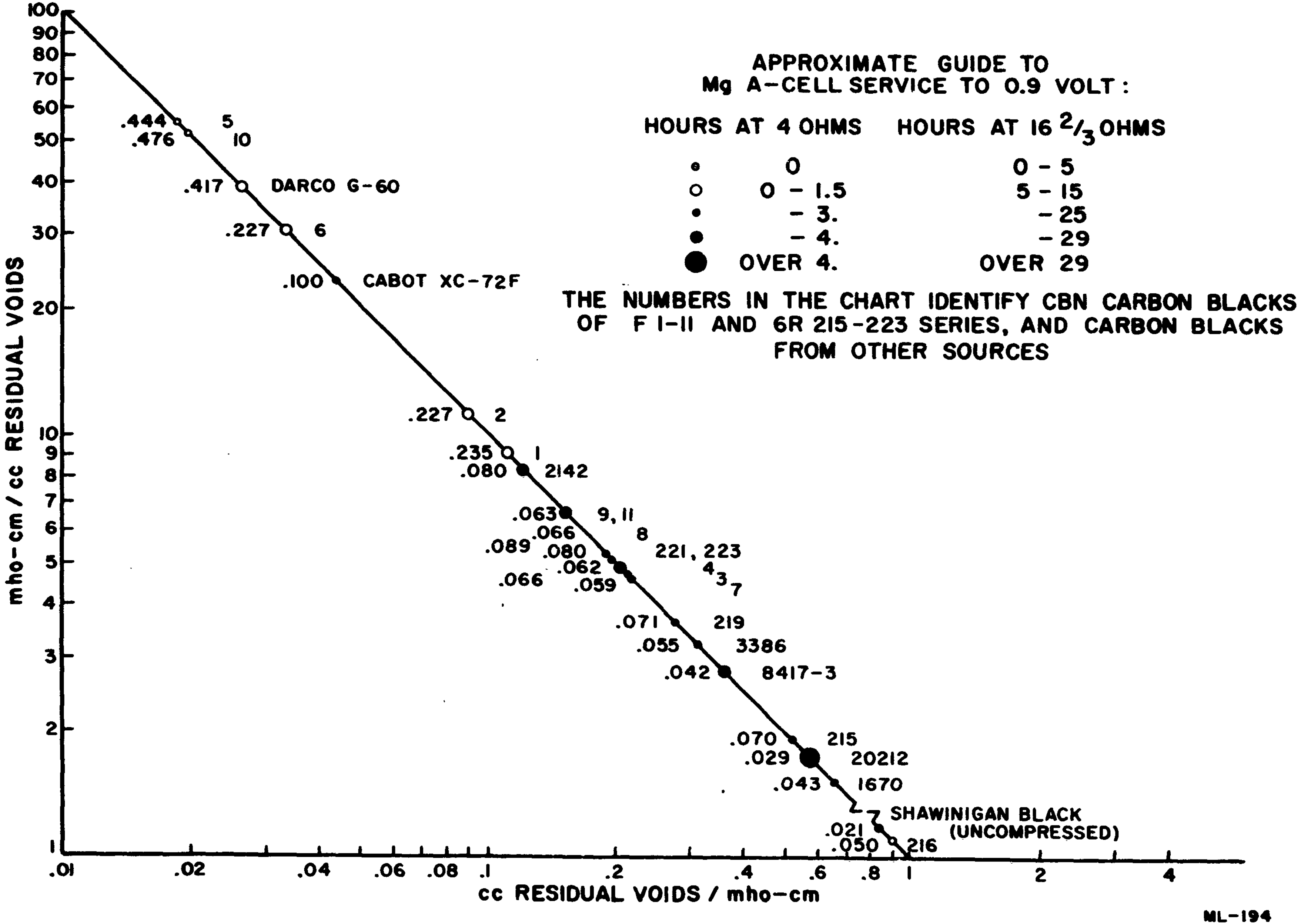


FIGURE 3-12. ORDER OF CARBON BLACKS BY RECIPROCAL RATIOS OF RESIDUAL VOIDS AND ELECTRICAL CONDUCTIVITY.

The distribution of A-cell data confirms the dominant role of residual voids. Non-structural variables, such as trace impurities in carbon blacks, may also affect A-cell performance.

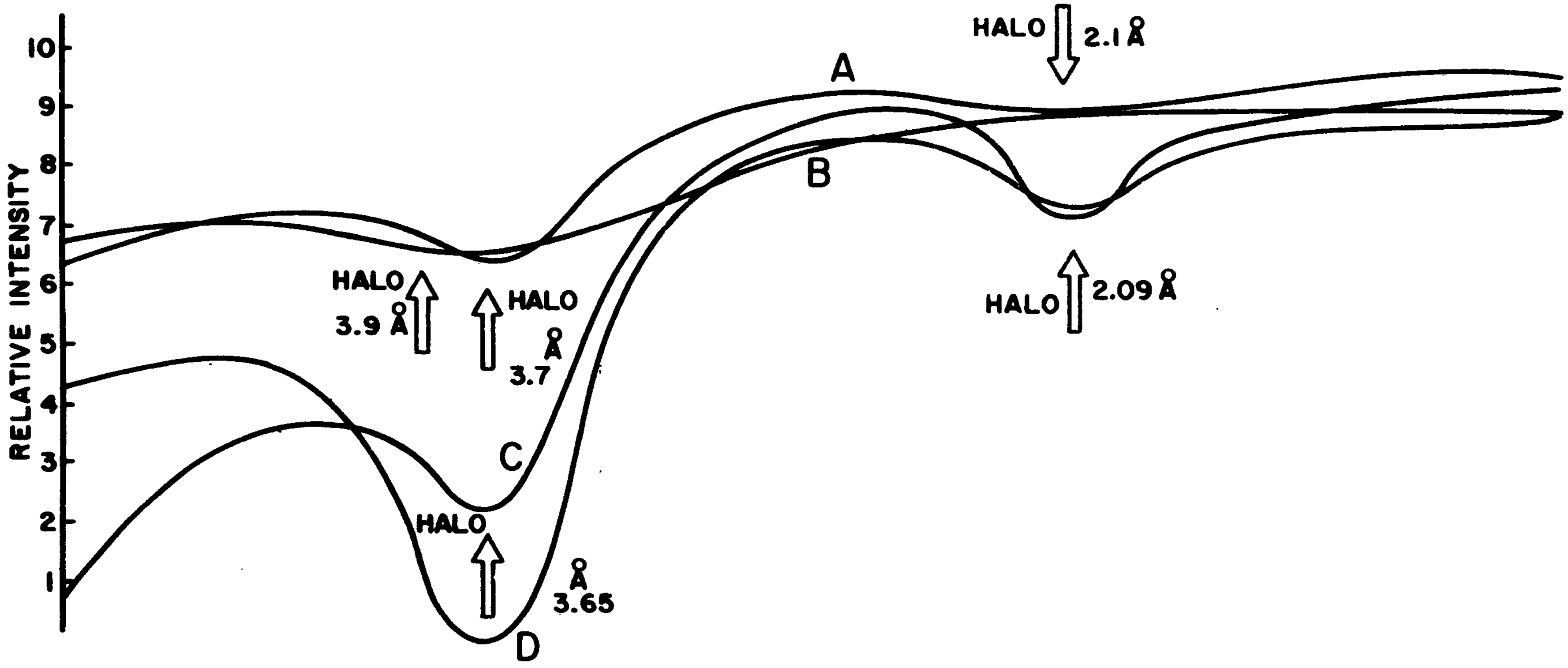
Other Data on Carbon Blacks

The variable residue of void space in different carbon blacks after compression and mechanical abuse is indicated by the degree of resiliency. This property is readily discerned in some carbon blacks but virtually absent in others. The unique and persistent resiliency of P-1100-CL 20212, in contrast with HR 1670, is attributed to its fundamental interatomic arrangement, or lattice. This belief, suggested by work on "pyrolitic graphites" at the Raytheon Company and elsewhere, shows that the thermal history of carbon determines the anisotropic properties associated with a lattice order in the third dimension (c-axis).

X-Ray Diffraction Patterns

The lattice spacings in P-1100-CL 20212 and HR 1670 carbon blacks are compared in curves A and B of Figure 3-13. This figure is a reduced plot of the relative intensity versus the angle of incidence taken from the original scanning traces on X-ray diffraction patterns. Carbon black P-1100-Cl 20212 has diffuse halos at 3.7Å and 2.1Å (as shown on curve A of Figure 3-13). The only diffuse halo in HR 1670 is observed at 3.9Å (curve C of Figure 3-13) which shifts to 3.65Å for a carbon black baked in an induction furnace for five minutes at 2500°C in argon. During this heat treatment, HR 1670 also developed a distinct halo at a lattice spacing of 2.09Å. From these effects it was concluded that P-1100-CL 20212 differs indeed from HR 1670 in a property dependent upon the thermal history.

The scanning trace for United 65 SPF (curve D) has been added in Figure 3-13 because of its approximation to that of the heat-treated HR 1670. The United carbon black is very dense and gritty and wholly unsuited for a cathode mix with m-DNB. This degree of condensation is also evident in the heat-treated HR 1670.



REPRODUCED FROM X-RAY DIFFRACTION PATTERNS ON CARBON BLACKS

A COLUMBIAN P-1100 CL-20212

B HR-1670 (50 # LOT)

C HR-1670 (50 # LOT) 5 MINUTES 2500° C (ARGON) IN RF FURNACE

D UNITED 65 SPF

° 2θ (Cu-K RADIATION) 2°/INCH IN THE ORIGINAL SCANNING TRACE

FIGURE 3-13. RELATIVE INTENSITY VS. ANGLE OF INCIDENCE PLOT REPRODUCED FROM X-RAY DIFFRACTION PATTERNS ON CARBON BLACKS.

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Figure 3-14 presents the scanning traces from X-ray diffraction patterns of two other carbon blacks of the P-1100 series: -8417-3 in curve F, and -2142 in curve G.

A close relationship with P-1100-CL 20212 is clearly evident in curves F and G through the comparable lattice spacings at 3.65Å and 3.7Å. No explanation is available for the other lines in curve F (P-1100-8417-3) at 7.25Å and 2.97Å. In curve E derived from the X-ray diagram of Shawinigan Carbon Black (uncompressed), the 2.09Å halo is present, but the larger spacing has shifted to a halo at 3.52Å.

Spectrographic Evidence

In view of the catalytic potency of structurally oriented trace impurities found in many solids, e.g., boron-doped graphites, two possibilities exist: (a) The thermal genesis of the petroleum-base furnace black (similar to P-1100-CL 20212) could be influenced by impurities and the material could have its structure directed by certain chemical impurities; (b) The chemical impurities could be catalyzing the efficient reduction of m-dinitrobenzene.

With this thought, a spectrographic trace analysis was performed on selected samples of carbon blacks, which resulted in the data of Table 3-8.

3.2.2.6 Modification of Shawinigan Carbon Black

Spectroscopic data of the preceding section on Columbian carbon blacks suggest the improvement of a pure carbon black by the addition of certain elements.

It was assumed that the additive would not only have to be most thoroughly dispersed in a fluffy black, but that it would have to be thermally reacted with the carbon.

Reference values for the cell performance of Shawinigan carbon black are represented by Lot 477 in Table 3-9. The heat treatment itself,

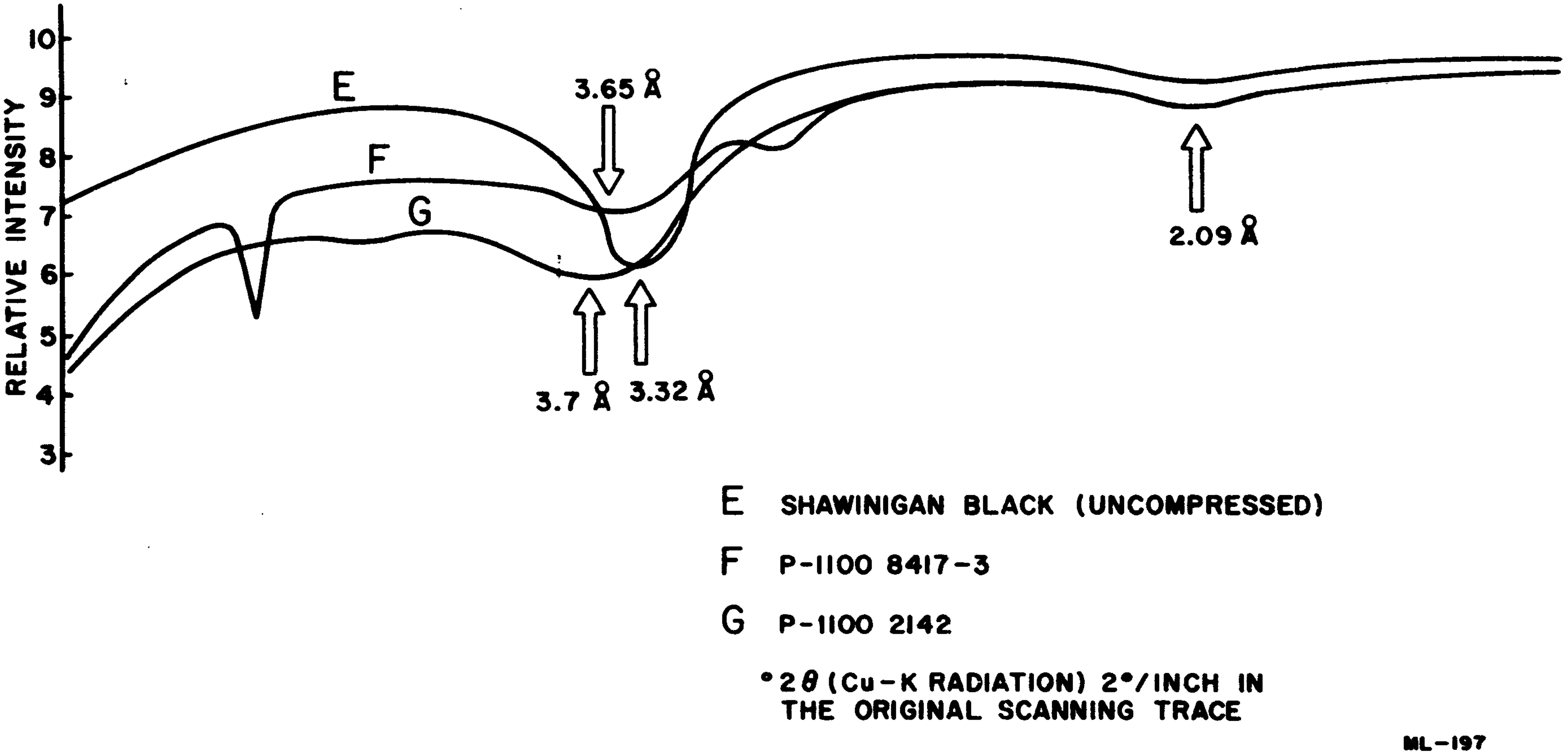

FIGURE 3-14. RELATIVE INTENSITY VS. ANGLE OF INCIDENCE PLOT REPRODUCED FROM X-RAY DIFFRACTION PATTERNS ON COLUMBIAN CARBON BLACKS COMPARED WITH SHAWINIGAN UNCOMPRESSED CARBON BLACK.

MATERIAL	B	Mg	Al	Si	V	Mn	Fe	Ni	Cu	Zn	Ag
Columbian HR 1670	-10	10	-	100	-	10	50	-	25	-	25
P-1100-CL 20212	-10	25	500	200	500	-10	500	100	100+	-	-
P-1100-8417-3	-	25	300	200	500+	10	50	100	100+	-	-
Shawinigan 50% Compressed	-	10	-	-10	-	-	-	-	-	-	-
Suzac 1947 B (Monsanto)	-	-10	-	25	-	-	100	-	100+	-	-

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TABLE 3-8. SPECTROSCOPIC QUANTITATIVE ESTIMATE OF IMPURITIES IN CARBON BLACKS.
(Parts Per Million)

CARBON BLACK				ADDITIVE	HOW	HEAT		A-CELL DATA HOURS TO 0.9V	
CELL LOT	50% C.	-80 MESH	P.K MACHINE	% OXIDE	ADDED	°C	HRS.	4 Ohms	16-2/3 Oms
476	X			2 ea. of Ni,V,Al	Tumbled	590	1	3	26
477	↓			NONE	-	590	15	3	21
478	↓			10 Ni Formate	Tumbled	590	15	3	21
479	↓			4 V_2O_5	↓	590	15	3.25	28
480	↓			5 Baymal (AlOOH)	↓	590	15	2.5	22
481	↓			4 Ni Form. 2V_2O_5, 3 Baymal	↓	590	15	3	29
482	↓			10 Pruss. Blue	↓	590	15	2.5	22.5
483	↓	-40		5 Ni Form. 5 Boric	↓	600	3	1.5	-
484	↓	-40		10 Boric	↓	600	3	1.5	-
485				1 V_2O_5	P.K.	570	5	4	28
486			X	1 Li_2CO_3		570	5	2.5	20
487				1 CoMo		570	5	3.5	22
488				1 Didym.		570	5	3.5	23
489				1 Co_2O_3		570	5	3.5	22
490	X			2 V_2O_5		NONE		3.25	29.5
491		-80		4 Ni_3O_4	Tumbled	600	4.5	3.5	23.5
492		-80		4 MnO_2		570	5	3.25	23
493		-80		4 Fe_3O_4		570	5	3.75	23
494	X			2 Cr_2O_3	P.K.	565	6	4	23
495	↓			2 Co_2O_3	↓	565	6	4	23
496	↓			4 Fe_3O_4	↓	NONE		3.5	25
497	↓			4 V_2O_5	↓	↓		3.75	31
498	↓			4 Cr_2O_3	↓	↓		3.7	25
499	↓			4 Co_2O_3	↓	↓		3.75	25
500	↓			4 MoO_3	↓	↓		3.6	26
501	↓			NONE	↓	↓		3.9	25

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TABLE 3-9. MAGNESIUM AZ-10 CELLS WITH MODIFIED SHAWINIGAN CARBON BLACKS.

(15 hours at 590°C in an atmosphere of 0.1 hydrogen and 0.9 nitrogen) produces no significant improvement in cell performance over the commercial Shawinigan (50% compressed) carbon black. Lots 476, 479, and 481 show distinct improvement in 16-2/3-ohms tests, but none in the 4-ohms tests. In comparison with lots 478 (Ni) and 480 (Al) the most effective additive is V_2O_5. Subsequent test lots (485, 490, and 497) support this conclusion. Additions of boric acid or of lithium carbonate depress the cell performance, as shown in lots 483, 484, and 486.

In several experiments, the commercial Shawinigan carbon black was partially "opened" by screening through 40 or 80-mesh sieves prior to dispersion of the additive. This variation produced minor improvement of cell performance in lots 491-493, which at the same time indicated little improvement from the additions of Ni, Mn, and Fe. Lots 487, 488, 489, 494, and 495 extend the survey to the oxides of Co, Ni, didymium, Ce, Cr, and Co, with rather indifferent results.

Lots 496 to 501 were prepared by the following method:

The commercial Shawinigan carbon black was blended at 20 rpm for two minutes in a 4-gallon Patterson-Kelly Twin-Shell Dry Blender with the stated percentage of additive, then the 3450 rpm intensifier was run for five minutes. The dust was permitted to settle for five minutes, and the necessary non-carbon cathode components (44.8 g to 20 g carbon black) was added, and agitated two minutes with the P-K intensifier. The non-carbon components had previously been milled with Zirconia balls to an extremely fine powder. The blend was tumbled another two minutes, settled five minutes, and discharged for addition of the electrolyte. The "blank" of this set, Lot 501, illustrates the effect of the P-K intensifier action upon Shawinigan carbon black. Its original tapped density of 0.083 was reduced to 0.026, while the cell performance at both drains was 20% greater than the original Shawinigan carbon black.

The cell data of Lots 496-501 show that the P.K. processing augments both the 4 and 16-2/3-ohm performance, even without heat treatment. Lot 497 used a Shawinigan carbon black modified with 4% V_2O_5, in contrast to spectroscopic evidence of about 0.05% vanadium in Columbian P-1100-CL-20212. Since this small quantity of vanadium is probably bound in the carbon substance as an ash residue, it is impossible to predict the optimum quantity or mode of addition of V_2O_5 to Shawinigan carbon black. The vanadium content in CL-20212 is accompanied by similar quantities of Al and Fe, and their contributions to cell performance, if any, also demand further study.

Canvass of Domestic Producers of Carbon Black

Samples of carbon black were requested by letter from the producers listed below. Our letter stated a tentative specification, as follows:

a. a tapped density below 0.05

b. B.E.T. (nitrogen) surface area of not less than 500 square meters per gram.

c. evidence of resiliency upon repeated compression.

d. self-cohesion in excess of adhesion to glass, steel, and zirconia.

e. a dry blend of carbon black with two weights of m-dinitrobenzene at a compression ratio of 10 should retain voids of at least 2 cc per gram of carbon black, and an electrical conductivity of 2 mho-cm.

No fluffy blacks are available from these producers:

Barnebey Cheney Co.
Atlas Powder Co.
Godfrey L. Cabot, Inc.
Great Lakes Carbon Co.
L.M. Huber Corp.
Speer Carbon Co.
*United Carbon Co.
*Continental Carbon Co. (Witco Chem. Co.)
Monsanto Chem. Co.
National Carbon Co.
Ohio Carbon Co.
*Pittsburgh Coke & Chem. Co.
Stackpole Carbon Co.
*R.T. Vanderbilt Co. (Thermatomic)

*Offered eleven samples of dense carbon blacks.

The A-cell data with 1:2 m-DNB cathode mix of these materials are summarized in Table 3-10.

The dense carbon blacks uniformly gave low A-cell capacities. All of these carbon blacks exhibited good electrical conductivity, but showed insufficient residual void space for the absorption of electrolyte.

3.2.3 Development Studies

3.2.3.1 Evaluation of Columbian Carbon Blacks Used in Flat Cells

Studies of flat-cell construction were started because the flat-cell geometry offers greater experimental flexibility in the study of cell parameters. Prior experiments with flat cells under Contract No. DA-36-039-SC-78048 were restricted to the use of $MgBr_2$ with the less efficient carbon blacks. Since the completion of that work, improvements in m-DNB cells and the availability of better carbon blacks indicated that better cell performance would be achieved with the perchlorate electrolyte.

The initial cells constructed under the present study used a copper foil covered with Condulon conductive plastic as the cathode grid. Inspection of these cells after discharge showed that the Condulon plastic absorbs m-DNB from the perchlorate electrolyte with a resultant increase in electrical resistance. Because the Condulon plastic breaks down, a study was made of various grid materials for use in the m-DNB cell with a perchlorate electrolyte. Lead and titanium sheet in direct contact with the perchlorate mix corroded badly, and resulted in poor cell performance. Amalgamated copper and plain copper foil, however, showed no adverse effects, and gave excellent cell performance. Subsequent flat-cell tests were performed with 0.002-inch-thick copper-foil and with expanded copper screen (Exmet 5 Cu5-4/0). In previous flat-cell studies, the copper-foil grid reacted with the $MgBr_2$ electrolyte and could not be used in direct contact with the mix.

	LOT NO.	TAPPED DENSITY	RESIDUAL VOIDS cc/gC	ELEC. CONDUCTIVITY MHO-CM	HOURS TO 0.9V		Ml 2N $Mg(ClO_4)_2$ ABSORBED BY 1 GRAM BLACK
					4-OHMS	16-2/3 OHMS	
Pittsburgh Coke & Chem. Co.							
BL Pulverized	471	0.588	0.11	37.4	0	0	1.1
C "	470	0.571	0.12	32.0	0	1	1.2
RB "	463	0.455	0.16	32.5	0	1-10	1.4
RC "	469	0.513	0.14	30.3	0	13	1.1
United Carbon Co.							
65 SPF	464	0.333	0.24	8.1	2	20-1/2	2.5
R.T. Vanderbilt Co.							
P-33	462	0.462	0.10	5.9	0	0	1.5
Thermix	466	0.642	0.07	13.3	0	0	1.1
Witco Chem. Co.							
F-1	468	0.350	0.17	22.4	0	5 min.	2.4
F-4	461	0.255	0.27	28.1	2	20	2.2
Continex HAF	465	0.423	0.16	27.4	2-1/2	17-1/2	1.9
Continex SRF	467	0.516	0.12	36.5	5 min	13-1/2	1.4

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TABLE 3-10. COMPARATIVE TESTS OF VARIOUS CARBON BLACKS. CATHODE MIX USED 1:2 CARBON BLACK/m-DNB.

In initial experiments, a shallow, adjustable box of clear plastic was fabricated in a flat-cell design. The structure permitted the cell geometry to be varied and the applied pressure to be controlled during discharge. It was found that the external pressure necessary for maximum discharge voltage reached 5 psi. At this pressure the organic cathode mix yielded and showed plastic flow and exudation of electrolyte. This irreversible alteration of cathode-mix structure caused local dry areas in the cathode, and resulted in uneven utilization of the anode surface. The lowered and often erratic discharge voltage with such a flat-cell design was reflected in cell capacities lower than those achieved with earlier designs.

Consequently, the study was continued with a flat cell firmly packed within a heat-sealed plastic (Krene, 0.0035-inch thick) envelope similar to that described on Page IV-86 in the November 1, 1960, Final Report of Contract DA-36-039-SC-78048. Cells with Magnesium AZ-31 anodes, 0.050-inch or 0.071-inch thick and with an active surface area of 18.6 cm^2 (3.8 x 4.9 cm) and seven grams of cathode mix were used to make a direct comparison with A-cell data. The cells were firmly clamped between 0.5-inch-thick plastic plates and discharged at 100 ma (5.4 ma/cm^2), which corresponded to a 10-ohm test with A-cell.

Cathode mix formulations used were as follows:

	COLUMBIAN CARBON BLACK					
	P-1100-CL 20212		P-1100-8417 CONTROL		HR 1670 CONTROL II	
	(grams)	(percent)	(grams)	(percent)	(grams)	(percent)
Carbon Black	6.0	9.65	6.0	9.5	6.0	10.75
m-DNB	12.0	19.3	12.0	19.0	12.0	21.5
$BaCrO_4$	1.1	1.8	1.1	1.7	1.1	2.0
$Mg(OH)_2$	0.4	0.6	0.4	0.6	0.4	0.7
2N $Mg(ClO_4)_2$	42.6	68.6	43.6	69.2	36.3	65.0
Total Mix Weight	62.1		63.1		55.8	
% Water in Mix	58.5		49.0		45.8	
THEORETICAL AMPERE-MINUTES/7g MIX	155		153		173	

The discharge voltage of the freshly prepared flat cells was recorded on a Varian G11A recorder. The data are shown in Figures 3-15, 3-16, and 3-17. Figure 3-15 shows that amalgamation of the copper-cathode conductor is unnecessary. The comparatively superior cell performance with HR 1670 carbon black at the 100-ma discharge rate is encouraging.

Figure 3-16 shows that the expanded copper screen is equivalent to copper foil as a cathode grid contact. The copper screen provides a strong cell structure and is preferred in flat cells.

The following performance characteristics have been derived from the discharge data for the three Columbian carbon blacks in flat cells:

	CONTINUOUS DISCHARGE TO 0.9 VOLTS AT 5.4 ma/cm^2					
	P-1100-CL 20212		P-1100-8417 CONTROL		HR 1670 CONTROL II	
	AMPERE-MINUTES	EFFICIENCY (%)	AMPERE-MINUTES	EFFICIENCY (%)	AMPERE-MINUTES	EFFICIENCY (%)
Hg-Cu Conductor (Figure 3-12)			86	56	83	48
Cu-Foil Cathode Conductor (Figure 3-12)	70	45			93	53
Cu-Screen Cathode Conductor (Figure 3-13)					90	52
	CONTINUOUS DISCHARGE OF INNER CATHODE CELL WITH 12 GRAMS CATHODE MIX AND 36 cm^2 Mg AZ-21 SURFACE AT 2.8 ma/cm^2					
To: 1.1 Volt					96	32
0.9 Volt					164	55

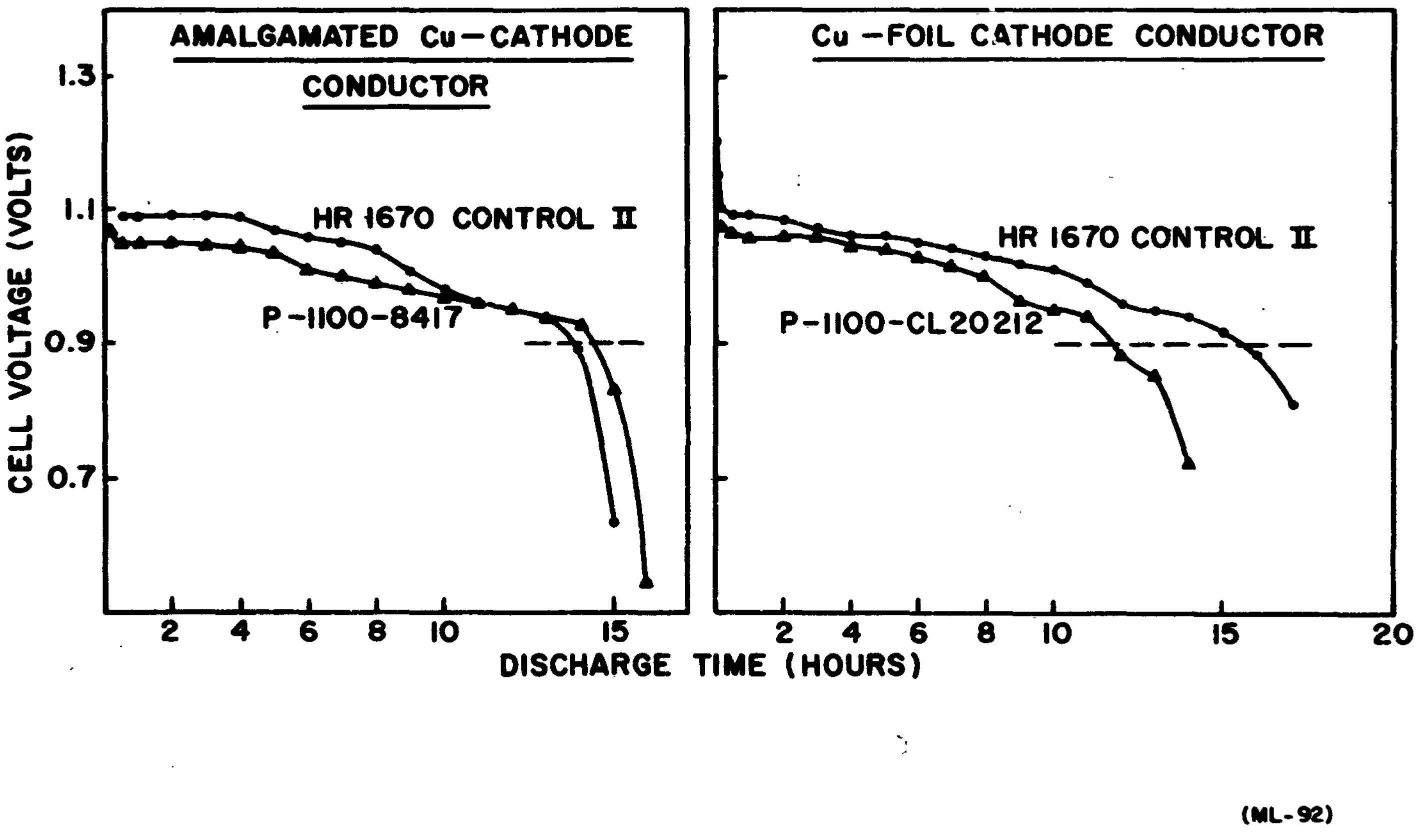
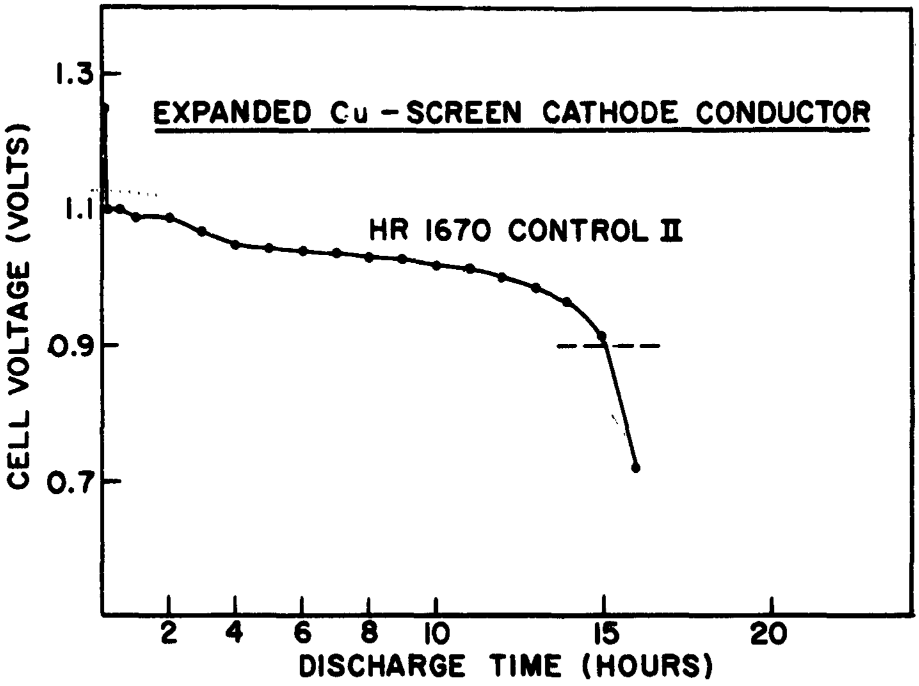
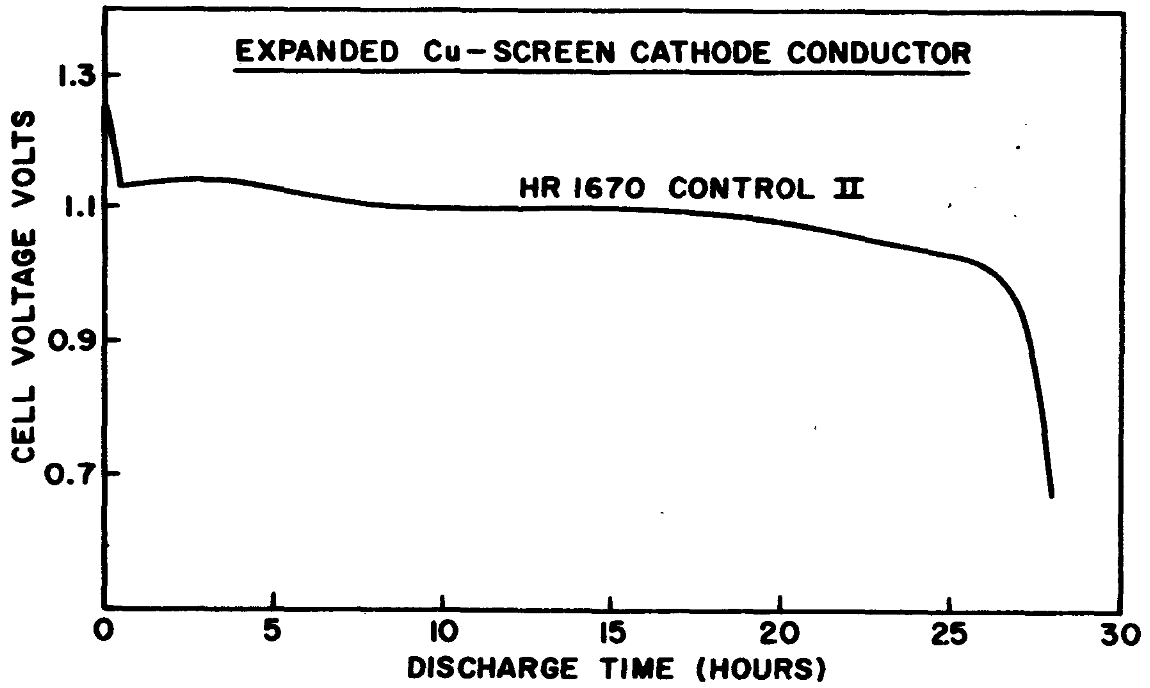


FIGURE 3-15. COMPARISON OF FLAT CELLS DISCHARGED CONTINUOUSLY AT 0.1 AMPERE (5.4 MA/CM^2).



(ML-93)

FIGURE 3-16. CHARACTERISTICS OF A FLAT CELL DISCHARGED CONTINUOUSLY AT 0.1 AMPERE (5.4 MA/CM^2).



(ML-94)

FIGURE 3-17. CHARACTERISTICS OF Mg AZ-21 INNER-CATHODE FLAT CELL DISCHARGED CONTINOUSLY AT 0.1 AMPERE (2.8 MA/CM^2).

Figure 3-17 shows the discharge behavior of the larger flat cell of the inner cathode design at a 100-ma drain and a current density of 2.8 ma/cm^2. The cell was constructed with two 0.020-inch-thick AZ-21 magnesium anode plates and 12 grams of cathode mix (containing carbon black HR 1670 Control II) on an expanded copper screen grid. The cell weight was 18.5 grams and delivered 44 watt-hours per pound to a 1.1 volt cut-off point, and 72 watt-hours per pound to a 0.9 volt cut-off point. It should be noted that this capacity is equivalent to the best capacity obtained in previous tests with P-1100-CL 20212 carbon black. Further improvement can be obtained through optimization of volume and weight in flat cells of this construction.

3.2.4 Shelf Studies

Magnesium AZ-10 A-cells made with two different Columbian carbon blacks were stored at 113°F and 95% R.H. for various periods before discharge at 16-2/3 ohms. The cathode mixes had been prepared in a 2:1 ratio of m-DNB to carbon black with 2N $Mg(ClO_4)_2$ electrolyte. The following results were obtained:

LOT NUMBER	LOT 377		LOT 378	
TYPE OF COLUMBIAN CARBON BLACK	P-1100-P2142 HT 3232		HR 1670-P-3317	
	Hours to 0.9 Volt	Percent Retention	Hours to 0.9 Volt	Percent Retention
Average of Three Cells, Aged 2 Days	30.5	--	26.5	--
Average of Three Cells, Aged 3 Months	29.0	95	26.5	100
Average of Three Cells, Aged 6 Months	29.0	95	23.0	87

4. CONCLUSIONS

4.1 GENERAL

The role of the carbon black in the nitro-organic cathode was shown to fall into three general categories. The carbon black serves to:

a. provide an open structure for the diffusion of reactants and reaction products,

b. provide a surface area for the catalyst used to enhance the nitro reduction reaction, and

c. provide a reservoir for the water volume requirements of the cell reactions.

These conclusions are based on an integrated evaluation of the following parameters:

a. the relation between m-DNB adsorption from solution and carbon blacks.

b. the relation between the electrical conductivity and residual voids.

c. spectrographic studies of experimental carbons which give enhanced performance of Mg/m-DNB cells.

d. successful modification of Shawinigan acetylene carbon black by structure modification and addition of certain catalysts (e.g, V_2O_5).

e. known water requirements of anode and cathode reactions.

The general properties of the carbon required for utilization in nitro organic cathode were established.

No commercial carbon black has been found which is ideally suited to the full exploitation of m-DNB in magnesium cells.

The evaluation of carbon blacks for this purpose rests on objective tests which define a disperse and persistent structure. This property is sensitive to the method of blending the dry cathode mixture.

The addition of V_2O_5 to Shawinigan carbon black significantly improves the cell performance.

It is concluded that in the nitro reduction diffusion of the m-DNB to the carbon surface and electron transfer are important. The former conclusion is based on behavior of carbons with large void volumes and open structures; the latter conclusion is based on the improvement of cathode efficiencies through the use of catalysts.

4.2 RECOMMENDATIONS FOR FUTURE WORK

The present contract has demonstrated the basic requirements of the carbon black required for the development of a practical dry cell with a nitro organic cathode.

The future development of Mg/m-DNB should logically proceed as follows:

a. Develop a suitable source of a carbon black as defined.

b. Select several promising nitro organic compounds for service-test program.

c. Upon demonstration of a suitable carbon black, perform a service-test program to characterize the Mg/m-DNB system.

d. Exploit the system in flat cells.

5. PUBLICATIONS, REPORTS, CONFERENCES

5.1 PUBLICATIONS

The following publication was developed during the course of this contract:

"Magnesium Primary Cells", by G.S. Lozier, R.J. Ryan. Proceedings of the 16th Annual Power Conferece, 1962, Publication Number ST-2298.

5.2 REPORTS

Five quarterly progress reports were prepared and distributed, dated as follows:

September 14, 1961
December 14, 1961
March 15, 1962
June 15, 1962
September 15, 1962

5.3 CONFERENCES

The following conferences were held between representatives of the U.S. Army Signal Research and Development Laboratory and the Radio Corporation of America to discuss the program and progress of this contract:

Date	Location	Representing USASRDL	Representing RCA
7-10-61	Ft. Monmouth	S. Bartosh, F. John D. Linden, J. Pawlak	G.S. Lozier, R.J. Ryan
9-26-61	RCA, Somerville	S. Bartosh, J. Pawlak	G.S. Lozier, R.J. Ryan, J.B. Eisen

Date	Location	Representing USASRDL	Representing RCA
12-5-61	Ft. Monmouth	S. Bartosh, J. Hovendon, J. Pawlak	R.J. Ryan, J.J. Meehan, J. B. Eisen
1-25-62	RCA, Somerville	J. Pawlak	G.S. Lozier, R.J. Ryan, J.B. Eisen
4-1-62	RCA, Somerville	J. Pawlak	G.S. Lozier, R.J. Ryan, J.B. Eisen
6-25-62	Ft. Monmouth	A.F. Daniel, J.M. Hovendon, J.N. Mrgudich, J.J. Murphy, W.F. Nye, J. Pawlak	G.S. Lozier, J.B. Eisen
from Columbian Carbon Co.:		K.A. Burgess, J.M. Ross, C.A. Stokes, C.W. Sweitzer	
9-13-62	Ft. Monmouth	S. Bartosh, J.J. Murphy J. Pawlak	G.S. Lozier, J.B. Eisen

On August 31, 1961, Dr. G.S. Lozier and Mr. R.J. Ryan visited the Columbian Carbon Co. in Princeton, New Jersey, to discuss the status and availability of carbon for use with m-DNB. Present at the meeting were Dr. C.W. Sweitzer, Messrs. K. Burgess, F. Eckert, and L. Ross of the Columbian Carbon Co.

AD__________ ACCESSION NO.__________

Radio Corporation of America, Somerville, New Jersey
ORGANIC DEPOLARIZED PRIMARY BATTERIES
J.B. Eisen, G.S. Lozier, R.J. Ryan

Final Report
69 pages, including 17 illustrations and 10 tables.

Signal Corps Contract DA-36-039-SC-87243
Project No. 3A99-09-002, Unclassified

A survey is presented of experimental and commercial carbon blacks as used with m-dinitrobenzene in magnesium cells. The specification evolved lists low density, large surface area, high electrical conductivity and a maximum volume of voids in the compressed carbon black. This demands a fluffy carbon black which, in the presence of electrolyte, retains a measure of structure adequate for massive material transfer and diffusion processes.

No commercial carbon black was found ideally suited for this cathode system. One available pure acetylene carbon black can be adapted, however, by means of an intensive mechanical "opening" process, especially with simultaneous introduction of a small quantity of V_2O_5.

Experimental flat cells with modified Shawinigan carbon blacks delivered 85 w-h/lb when discharged at the 18-hr. rate.

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