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NATIONAL BUREAU OF STANDARDS REPORT

2447

REPORT ON BATTERY ADDITIVES

by the

NATIONAL BUREAU OF STANDARDS

April 16, 1953

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U. S. DEPARTMENT OF COMMERCE
Sinclair Weeks, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section is engaged in specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant reports and publications, appears on the inside of the back cover of this report.

Electricity. Resistance Measurements. Inductance and Capacitance. Electrical Instruments. Magnetic Measurements. Applied Electricity. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Gage.

Heat and Power. Temperature Measurements. Thermodynamics. Cryogenics. Engines and Lubrication. Engine Fuels. Cryogenic Engineering.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Measurements. Infrared Spectroscopy. Nuclear Physics. Radioactivity. X-Rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. Atomic Energy Commission Instruments Branch.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Gas Chemistry. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Aerodynamics. Engineering Mechanics. Hydraulics. Mass. Capacity, Density, and Fluid Meters.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Organic Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion.

Mineral Products. Porcelain and Pottery. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure. Chemistry of Mineral Products.

Building Technology. Structural Engineering. Fire Protection. Heating and Air Conditioning. Floor, Roof, and Wall Coverings. Codes and Specifications.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Machine Development.

Electronics. Engineering Electronics. Electron Tubes. Electronic Computers. Electronic Instrumentation.

Radio Propagation. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Frequency Utilization Research. Tropospheric Propagation Research. High Frequency Standards. Microwave Standards.

Ordnance Development.
Electromechanical Ordnance.
Ordnance Electronics.
These three divisions are engaged in a broad program of research and development in advanced ordnance. Activities include basic and applied research, engineering, pilot production, field testing, and evaluation of a wide variety of ordnance matériel. Special skills and facilities of other NBS divisions also contribute to this program. The activity is sponsored by the Department of Defense.

Missile Development. Missile research and development: engineering, dynamics, intelligence, instrumentation, evaluation. Combustion in jet engines. These activities are sponsored by the Department of Defense.

- Office of Basic Instrumentation
- Office of Weights and Measures.

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NBS PROJECT
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Contents

I. INTRODUCTION (p. 1.0).

II. TESTS OF BATTERY AD-X2: SUMMARY AND CONCLUSIONS (p. 2.0)

III. BATTERY TESTS OF AD-X2 (p. 3.0).

1. The June 1952 Test (p. 3.1)
2. Tests of Discarded Automotive Batteries (p. 3.43).
3. Tests on New Batteries (p. 3.50).
4. The January 1953 Tests of Batteries Drained and Filled with 1.100 Acid or with Distilled Water (p. 3.53).

IV. IMPORTANT PROPERTIES OF THE COMPONENTS OF LEAD ACID STORAGE BATTERIES (p. 4.0).

1. Determination of solubility of lead sulfate (p. 4.1).
2. The charging process and the rate of conversion of lead sulfate to lead and sulfuric acid (p. 4.2).
3. Tests of prevention of "Sulfation" (4.3).
4. Sediment (p. 4.7).
5. The Discharge Process at Various Rates and for Electrolyte of Various Specific Gravities (p.4.8).
6. Viscosity (p. 4.10).
7. Resistivity (p. 4.11).
8. Cell Voltages and Plate Potentials During Discharge of Automotive Cells Containing Treated or Untreated Electrolyte at Various Specific Gravities (p. 4.11).

V. CHEMICAL AND PHYSICAL PROPERTIES OF AD-X2 (p. 5.0).

1. Summary and conclusions (p. 5.1).
2. Chemical Analyses of Battery AD-X2 (p. 5.2).
3. Spectrochemical Analysis of Battery Electrolytes and Technical Sulfuric Acid (p. 5.6).

VI. SUPPLEMENTARY INFORMATION (p. 6.0).

1. Changes in the Specific Gravity of the Electrolyte of Untreated and Treated Cells during Charge (p. 6.1).
2. Inspection of Discarded Batteries Turned in for Purchase of New Batteries (p. 6.7).
3. Rebuilding and Repair of Batteries (p. 6.10).

Contents (Continued)

VII. APPENDICES

1. Correspondence (p. 7.1).
2. June 1952 Test (p. 7.13).
3. Laboratory Data Pertaining to Tests of Discarded Automotive Batteries (p. 7.327).
4. New Batteries (p. 7.413).
5. The January 1953 Tests of Batteries Drained and Filled with 1.100 Acid or With Distilled Water (p. 7.434).
6. Data Relating to Important Properties of the Components of Lead-Acid Storage Batteries (p. 7.585).
7. Data Relating to Inspection of Discarded Batteries. Turned in for Purchase of New Batteries (7.610).

Part I

INTRODUCTION

I. INTRODUCTION

The purpose of this report is to summarize in one document data on battery additives obtained at the National Bureau of Standards since 1951 when the Bureau's Circular 504 "Battery Additives" was issued. The majority of the data are concerned with the properties of a proprietary product, Battery AD-X2, manufactured by Pioneers, Inc., of Oakland, California. Other data are on mixtures of sodium and magnesium sulfates of proportions similar to those found in Battery AD-X2.

NBS Testing Activities.

The basic functions and responsibilities of the National Bureau of Standards are set forth in the Act of March 3, 1901, as amended by Public Law 619 of the 81st Congress. These functions include:

(1) The determination of the properties of materials when such data are of great importance to scientific or manufacturing interests and are not to be obtained with sufficient accuracy elsewhere;

(2) The development of methods of testing materials, mechanisms and structures and the testing of materials, supplies and equipment, including items purchased for use of government departments and independent establishments;

(3) The rendering of advisory service to government agencies on scientific and technical problems;

(4) The compilation and publication of scientific and technical data resulting from the performance of its functions when such data are of importance to scientific or manufacturing interests or to the general public and are not available elsewhere.

The Bureau's testing of proprietary or brand name products has, with rare exception, been confined to fulfilling requests of other government agencies. Laboratory services performed directly for the public consist almost entirely of the calibration of instruments with reference to the basic standards of science maintained by the Bureau.

The major functions of the National Bureau of Standards involve pure and applied research, development, and engineering. These activities are conducted in the following fields of science and engineering: physics, mathematics, chemistry, metallurgy, electronic engineering, electrical engineering, structural engineering, hydraulic engineering, mechanical engineering, and ceramic engineering. Of the total program, 85 per cent of the work is concerned

with defense research and development, primarily for the Department of Defense and the Atomic Energy Commission. The remaining 15 per cent, constituting that portion of the program supported by direct appropriations from Congress, is largely concerned with research and development relating to the fundamental standards of science (e.g., national standards of mass, length, frequency, electrical resistance, etc.), instrumentation and measurement methods, and determination of the properties of matter (including physical constants).

Growing out of the latter portion of the program--that comprising the 15 per cent--are the calibration, testing and related services, which constitute 4 per cent of the total activity. The bulk of this activity--approximately 3 per cent--has to do with calibration services. These are services characterized by the comparison of master standards in commerce and industry with the national standards (e.g., gage blocks from industry are periodically submitted for calibration, by optical means, in order to ensure that the gage blocks provide uniform and accurate measurements).

The testing done by the Bureau comprises approximately 1 per cent of the activity. Most of this testing is concerned with checking for compliance of materials purchased by the Government with the specification in the purchase contract. The Federal system of purchasing, in order to give all businesses a fair and equal opportunity to compete for Government contracts, involves the issuance of bid documents specifying what the Government wishes to purchase. These bid documents contain data describing the item to be supplied, and the data must be technically adequate wherever possible in order that the proper type of item be purchased and that the competing firms be, in fact, bidding to supply the same, desired item. Responsibility for specifications and the general procedures rest with the General Services Administration. The largest item--totalling more than half of this 1 per cent of testing done by the Bureau--is cement.

A small part of this relatively small testing program, wherein the Bureau acts as a service laboratory for other Government agencies, is concerned with tests for agencies having regulatory authorities--e.g., the Federal Trade Commission and the Post Office Department. The total of all testing done for these agencies, at their initiation and request, is less than $25,000 per year. <u>In short, testing of this kind done by the Bureau comprises less than a twentieth of one per cent of the total NBS program.</u>

The above details are provided only because there appears to be some confusion as to the nature of the Bureau's functions and activities. Insofar as the testing activity is concerned, it should be noted also that the Bureau has no regulatory responsi-

bilities or authority. The Bureau does not either endorse or condemn proprietary products. The results of the small amount of testing done as a service for other Government agencies are not released to the public by the Bureau. Moreover, the fact that the Bureau has tested some material for such an agency is not revealed by the Bureau. In this connection, it is pertinent that public knowledge of the fact that the Bureau had tested AD-X2 resulted not from action by the Bureau but from action by the manufacturer: in a campaign conducted by the manufacturer and his distributors, involving some 28 Senators and the National Better Business Bureau, it was claimed that the Bureau had not tested this product; confronted with inquiries as to the truth of this assertion, the Bureau had no recourse but to tell the truth to the Senators and the National Better Business Bureau. Even then, the Bureau made every effort to avoid future references to the product and did not reveal its test data in an identifiable form until the Senate Small Business Committee issued its release of December 18, 1952, in which the Bureau's tests were discussed with explicit reference to AD-X2.

Background of Battery Additive Work

Almost from the advent of the lead-acid storage battery, numerous materials have been offered for use in batteries to improve their performance and extend their life. For the most part, these materials are supplied in liquid or powder form and the treatment consists essentially of their addition to each cell of the battery.

For the past 30 years the scientific services of the National Bureau of Standards have been requested by the Federal Trade Commission, the Post Office Department, and members of Congress in regard to the merits of these materials, commonly called "rejuvenators" or "additives". Also, the National Bureau of Standards has studied several "additives" for other Government agencies. During the course of the past 30 years, scientists at the National Bureau of Standards have investigated over 100 such materials and have issued 47 reports to the above agencies on 35 different additives.

On February 10, 1925 the National Bureau of Standards published in their Technical News Bulletin No. 94 a brief statement pointing out that solutions do not charge storage batteries, that batteries are charged by the application of electric current, and that many solutions may in fact be detrimental to the performance of lead-acid storage batteries. This latter statement resulted from studies performed by the National Bureau of Standards from 1922 to 1925, inclusive. In 1922 scientists at the National Bureau of Standards developed an accurate method for the determination of the rate of sul-

fation of storage battery plates. In 1922 they applied the method to the determination of the effects of impurities in storage battery electrolytes. It was shown that copper, platinum, iron and manganese in small amounts cause deleterious effects. In 1925, they gave the results of studies of various other impurities. Magnesium sulfate and sodium sulfate were included in these studies because these materials had been suggested as chemicals that would appreciably curtail the rate at which plates would be sulfated.

The agreement between the control solutions and those containing magnesium or sodium sulfate were within the experimental error, and the results, therefore, indicated that magnesium and sodium sulfates are without benefit on the rate of sulfation of plates in lead-acid storage batteries. From 1925 to 1931, six other "additives" were tested for such agencies as the Federal Trade Commission, the Post Office Department and the Navy Yard. During this interval numerous requests for information on "additives" were received by the National Bureau of Standards from the general public. In 1931 a mimeographed leaflet was prepared in order to reduce the cost of replying to these inquiries. No proprietary or "brand name" materials were mentioned in accord with the policy of the National Bureau of Standards. This leaflet was issued May 15, 1931 as Letter Circular 302 entitled "Battery Compounds and Solutions." It gave general information on battery additives and was used in replies to incoming letters.

From 1931 to the start of World War II nine other proprietary "additive" materials were investigated for the Federal Trade Commission, Post Office Department, or the Congress. One was essentially water, another consisted of alum and K_2SO_4 and the rest contained sodium or magnesium sulfates, commonly known respectively as Glauber's Salt and Epsom Salts.

During World War II and since, 15 new additives were tested by NBS, some for a second time, for the Federal Trade Commission, the Post Office Department, the Defense Agencies, or the Congress. Most of these consisted of mixtures of magnesium and sodium sulfates. The National Bureau of Standards also investigated a large number of materials considered as possible "corrosion inhibitors" to see if any of them would curtail the sulfation of lead-acid storage batteries that ensues on storage. This latter study was undertaken to determine the best means to "recondition" or store lead-acid batteries that were in surplus at the termination of World War II. Included in this latter test were sodium and magnesium sulfates; they were not found to be beneficial.

After World War II a number of "additives" were sent to NBS for test by the FTC. One of these was a material known first as "Protecto-Charge" which later became known as "AD-X2". "AD-X2" was first brought to the attention of the National Bureau of Standards early in 1948 by a chemical consultant of the manufacturer. He stated that it was a powder mixture of anhydrous sodium sulfate and slightly basic nearly anhydrous magnesium sulfate.

Among the claims for this product were:

(1) Reduces harmful effects of "sulfation,"
(2) Ordinarily increases the capacity of mechanically sound "sulfated" batteries.
(3) Helps prevent freezing.
(4) Restores to active service, approximately 70 percent of discarded "sulfated" batteries.
(5) Lessens the chance of buckled plates and slowly decreases battery mud.
(6) "Battery AD-X2" will restore your DEAD battery, providing there is no mechanical defect.
(7) "Battery AD-X2" lengthens the life expectancy of new batteries.

The National Bureau of Standards replied to the consultant of the manufacturer to the effect that the NBS does not test proprietary materials for private individuals or concerns. Also it was stated that the Bureau's tests on sodium and magnesium sulfates had not shown them to be of benefit to the operation of lead-acid storage batteries. Later in 1948 the Better Business Bureau of Metropolitan Oakland, Inc., California wrote to the National Bureau of Standards requesting tests on AD-X2 and forwarded samples. The National Bureau of Standards replied to the Better Business Bureau of Oakland, California to the effect that tests were being conducted at other government laboratories (Department of Defense) and additional tests at the National Bureau of Standards were not deemed advisable. The Bureau also stated that the samples submitted were being retained for further reference. The National Better Business Bureau also wrote to the National Bureau of Standards stating that "additives" were again becoming abundant and inquiring whether Letter Circular 302, which had been written in 1931, gave an up-to-date account of the present knowledge on additives.

Early in 1949, partly as a result of inquiries from members of Congress, the National Bureau of Standards started tests on "AD-X2". The samples used were those submitted to NBS by the Better Business Bureau of Metropolitan Oakland. At this same time the Bureau was also engaged in studying another "additive" for the Post Office Department. In view of these increased demands the Bureau initiated a series of tests on

mixtures of sodium and magnesium sulfates, and included "AD-X2" and the other additive then under test in this new series of tests.

On March 22, 1950 the Federal Trade Commission requested tests on "AD-X2". A NBS report was sent to them on May 11, 1950 in which results on tests of "AD-X2" mentioned above were given. Late in 1951 NBS gave testimony at a Federal Trade Commission hearing on still another additive, and at that time the Federal Trade Commission stated that they wanted further tests on "AD-X2" since we had used samples submitted by the Better Business Bureau of Metropolitan Oakland, California and not by their agency. The FTC formally requested the additional tests on February 26, 1952 and NBS accordingly proceeded with them. A report was submitted to the Federal Trade Commission on July 21, 1952.

On September 6, 1951 the Post Office Department requested tests of "AD-X2". The National Bureau of Standards submitted a report to the Post Office Department on December 12, 1951, based on tests obtained on samples submitted by the Better Business Bureau of Oakland, California. The Post Office Department also requested additional tests on samples submitted by them. Accordingly, the National Bureau of Standards initiated still another series of tests of "AD-X2". Specifically, the National Bureau of Standards was asked to provide technical advice on the following claims for "AD-X2":

(1) Reduces harmful effects of "sulfation."
(2) Ordinarily increases the capacity of mechanically sound sulfated batteries.
(3) Restores to active service, approximately 70% of discarded sulfated batteries.
(4) Lessens the chance of buckled plates and slowly decreases battery mud.
(5) Will restore dead battery, providing there is no mechanical defect.
(6) Extends life of mechanically sound old batteries usually discarded because of "sulfation".
(7) Extends the life of batteries two and one-half times their normal life.

and to examine and comment on the claims set forth in literature of the manufacturer, forwarded to the National Bureau of Standards by the above agencies in their requests for tests.

The results of the tests were sent in brief form to the Post Office Department and the Federal Trade Commission. When other government agencies request and finance tests at the National Bureau of Standards, the results and reports become the

property of the requesting agency and the National Bureau of Standards does not provide the results or reports to others without permission of the agencies concerned. The reports to the Post Office Department and Federal Trade Commission were of a summary nature: detailed information is given by the Bureau at hearings if so desired by the agencies requesting the tests.

During these tests the manufacturer repeatedly asked for detailed information on his product. The National Bureau of Standards could not divulge the details of their test for the reasons stated above. However, in view of inquiries from the Congress, the National Bureau of Standards did agree to conduct experiments by a procedure outlined by the manufacturer and mutually agreeable to him and the scientific staff of the National Bureau of Standards. This test was conducted in June, 1952. Throughout the test the manufacturer's representative was present. The manufacturer at no time asked for termination of the test on the grounds that it had been modified or was not being conducted in a satisfactory manner. He participated in the inspection part of the test with eight others and seemed quite content with how it was conducted. Results of the tests were made known to him after completion of a statistical analysis of the results.

The Post Office Department first had called hearings for April 25, 1952; these were postponed or continued at the request of the manufacturer in view of the new tests outlined by the manufacturer and which the National Bureau of Standards had agreed to do. On October 14, 1952 the Post Office Department again called hearings at which time members of the NBS staff testified, presenting the work that had previously been done for the Post Office Department as well as the results obtained in June, 1952 on the test outlined by the manufacturer.

Following the preliminary distribution of the NBS report of the June, 1952, tests, Mr. Blake O'Connor, professional staff member of the Senate Select Committee on Small Business, asked the Bureau if it would conduct additional tests suggested to him by Mr. Jess M. Ritchie, President of Pioneers, Inc., Dr. Keith J. Laidler of Catholic University, and Dr. Harold C. Weber of the Massachusetts Institute of Technology. The Bureau agreed to conduct such tests if batteries "which would not take a charge" were furnished by Mr. Ritchie. Mr. Ritchie was apparently either unable or unwilling to furnish such batteries. The reason for asking for batteries which would not take a charge was based on the fact that nearly all of the proponents of battery additives claim to have had batteries which would not take a charge and which later took a charge after introduction of the additive. This is an experience which the Bureau has been unable to confirm.

At Mr. Connor's request a conference was held on September 29, 1952, at the National Bureau of Standards; attendance included Mr. O'Connor, Dr. Laidler, Dr. Weber, Mr. Ritchie, several members of the Post Office Department and several members of the Bureau's staff. At this meeting, Dr. Weber described some preliminary tests he had carried out in which he claimed to have observed a difference in the performance between batteries treated with AD-X2 and those untreated. The Bureau agreed to attempt to check Dr. Weber's observations if he would furnish a brief description of his testing and his preliminary results. Although the Bureau made several attempts to obtain this information, it was not furnished until the MIT report became available late in December, 1952.

Approximately two weeks after the September 29 conference, Mr. O'Connor informed the Bureau that MIT was planning to carry out a more extensive series of tests to check further Dr. Weber's preliminary observations. The Bureau was invited to participate in these. This invitation was declined primarily because it was believed that any findings unfavorable to the material would have been more acceptable to the proponents of the additive if the tests were conducted without NBS participation.

The MIT Report

On December 18, 1952, the Select Committee on Small Business of the U.S. Senate issued a statement (SSB No. 109, 12/18/52) on battery additives which provided an endorsement of a battery additive known as Battery AD-X2, manufactured by Pioneers Inc. of Oakland, California.

The Senate Small Business Committee release was based primarily on a report by the Massachusetts Institute of Technology and on an analysis made by Dr. Keith J. Laidler, a consultant to the Committee. Although the Senate Committee release claimed that the MIT results were "in sharp contrast to the results of tests conducted on battery additives over a long period of years by the National Bureau of Standards", the MIT test results themselves were not necessarily in conflict because the experimental conditions of the MIT tests and the immediate objectives of the tests were appreciably different from those employed at the Bureau. Furthermore, the MIT report contained a statement to the effect that the correlation of their results "with a beneficial action from the standpoint of normal use of such a battery" was not established.

Immediately after the release of the MIT report the Bureau initiated a laboratory program with the following objectives:

(1) To check the conclusions presented in the MIT report;
(2) To determine whether the phenomena reported, if they are

reproducible, have any significance with respect to a beneficial action on normal storage battery operation; and

(3) To modify or amend the Bureau's prior statements on battery additives if the new results should so warrant.

On February 10, 1953, the National Bureau of Standards provided a summary statement on its work to that date at the request of and for the House Committee on Interstate and Foreign Commerce. In the introduction of this report it was stated: "it is possible on the basis of present data to make certain general statements as of the present time:

"1. There exist as of this date no valid technical data for believing that battery additives have any beneficial action on normal storage battery operation.

"2. Moreover, as a result of recent NBS studies, there is evidence for believing that additives of the type under test have a small but measurable detrimental effect on at least one important phase of normal battery operation--namely, the capability of a battery to start an automobile (or similar) engine.

"3. Some of the MIT observations appear to be contrary to results obtained consistently in reproducible controlled experiments by the National Bureau of Standards. Other phenomena reported by MIT are consistently reproducible under a very limited range of operating conditions; but these phenomena are observed only under conditions which are not encountered in the normal use or operation of automobile storage batteries; and, furthermore, these phenomena are obtained just as readily with a simple mixture of sodium and magnesium sulfates as they are with the proprietary product AD-X2."

The studies reported on to the House Committee on Interstate and Foreign Commerce were continued, and the remainder of this report is largely a presentation of these findings (as well as summation of other work on sodium and magnesium sulfate additives). A summary of these findings is presented in the next part of this report (II. Tests of Battery AD-X2: Summary and Conclusions). These studies indicate conclusively that the material has no measurable beneficial effect in normal battery operation, that what slight effect is observed under non-operating (and therefore meaningless in any practical sense) conditions is insignificant, and that there is actually a small but demonstrable detrimental effect of the material in normal battery operation.

II. TESTS OF BATTERY AD-X2: SUMMARY AND CONCLUSIONS

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Summary

In this report the results of an extensive investigation of AD-X2 are presented. These investigations included: (1) tests of 86 batteries; of this number the behavior of 162 cells and 32 batteries was studied, (2) tests of the charging and discharging characteristics of old sulfated negative plates at various rates, in treated and untreated electrolytes of various specific gravities, (3) determinations of the effect of additions of "AD-X2" on the solubility of lead sulfate in sulfuric acid and battery electrolyte and on the prevention of the "sulfation" of battery plates at various temperatures, (4) determinations of the properties of sulfuric acid solutions with or without "AD-X2" including measurements of viscosity and electrical resistivity, (5) determinations of the effect of AD-X2 during the charging process on the efficiency of the conversion of lead sulfate to lead and sulfuric acid and (6) correlations between battery performance and the effect of AD-X2 on important properties of the components of lead-acid storage batteries. These are all given in detail in Parts III, IV, and V of this report.

Conclusions: The studies summarized above lead to the following general conclusion:

Under ordinary operating conditions there is no benefit to be obtained from Battery AD-X2 or other battery additives of similar composition.

The additive does not increase the solubility of lead sulfate, does not prevent "sulfation" of batteries, does not restore "sulfated" batteries. In fact, the additive is slightly detrimental to batteries in heavy duty service.

The additive Battery AD-X2, or an equivalent mixture of magnesium and sodium sulfates, was found to increase slightly the available discharge from experimental batteries provided both the following exceptional, non-operating conditions prevailed: (a) when the specific gravity of the electrolyte was less than 1.100; and (b) when the battery was discharged at a low rate. The apparent and trivial advantage disappeared when the battery was: (a) given battery acid of standard specific gravity, or (b) repeatedly charged and discharged, or (c) discharged at high rates. In short, this effect is not only trivial but does not appear in normal battery operation and is therefore totally irrelevant in normal battery operation.

Ordinary battery operation involves repeated cycles of charging and discharging; requires sufficiently high specific gravity (above 1.100) to provide electrical capacity; and calls for 300 or more amperes to start automobile motors.

It is, therefore, concluded that there is no benefit to be obtained from the use of Battery AD-X2.

Supporting statements and explanations are given in the following 19 conclusions which refer to various tests covering the operation and behavior of batteries with and without additive.

1. "AD-X2" does not increase the ampere-hour or the watt-hour capacities of old batteries.

   Outputs after full charge: The average ampere hours and average watt hours for 11 shelf-sulfated truck and tractor batteries treated with "AD-X2" were 53.81 and 208.32, respectively, as compared with 51.75 and 205.93, respectively, for 11 similar batteries not treated with "AD-X2". These differences in output are not statistically significant.
   The average total ampere-hour and average total watt-hour outputs for 3 discharges of 27 cells of discarded "sulfated" automotive batteries treated with "AD-X2" were 135.1 and 171.8, respectively, as compared with 145.2 and 185.2, respectively, for 27 cells not treated with "AD-X2".

   Outputs after short charges in low specific gravities: The average ampere-hour and watt-hour outputs of 11 cells of discarded "sulfated" automobile batteries dumped of electrolyte and filled with sulfuric acid of specific gravity of 1.100 and treated with "AD-X2" were 5.67 and 9.69, respectively, as compared with 5.32 and 9.33, respectively, for 11 untreated cells and with 5.45 and 9.42, respectively, for 11 cells treated with a mixture of magnesium and sodium sulfates in composition comparable to "AD-X2". These differences in output are not statistically significant.

The average ampere-hour and watt-hour outputs of 10 cells of discarded "sulfated" automobile batteries dumped of electrolyte and filled with distilled water and treated with "AD-X2" were 4.33 and 7.29 respectively, as compared with 4.11 and 7.21, respectively, for 10 untreated cells and with 4.75 and 8.53, respectively, for 10 cells treated with a mixture of magnesium and sodium sulfates in composition comparable to "AD-X2". These differences in output are not statistically significant.

2. "AD-X2" does not increase the ampere-hour or the watt-hour capacities of new batteries.

   The average ampere-hour and average watt-hour outputs of 9 new cells of automotive batteries when treated with "AD-X2" were 153.5 and 195.2, respectively, for all 3 cycles of successive high-rate discharges, as compared with 173.7 and 247.4 respectively, for 9 similar new cells not treated with "AD-X2". The differences in watt hours between treated and untreated cells suggest that "AD-X2" is detrimental at high-rate discharges for new batteries.

3. "AD-X2" does not remove the detrimental effects generally associated with prolonged overcharges.

   Twenty-seven automotive cells treated with "AD-X2" gave on the average 32.4 ampere hours and 44.0 watt hours after a 7-day overcharge at 20 amperes; 27 similar cells not treated with "AD-X2" gave 38.3 ampere hours and 51.0 watt hours under the same conditions.

4. "AD-X2" does not improve the ability of a partially discharged battery to recuperate or regain charge on an overnight stand without additional charging.

   Twenty-seven old automotive cells treated with "AD-X2" gave on the average 6.1 ampere hours and 7.0 watt hours on high-rate discharges following an overnight stand; 27 similar old automotive cells not treated with "AD-X2" gave 7.5 ampere hours and 8.1 watt hours under the same conditions. Nine new automotive cells treated with "AD-X2 gave on the average 4.2 ampere hours and 5.4 watt hours, respectively, on high-rate discharges following an overnight stand; 9 similar new cells not treated with "AD-X2" gave 4.5 ampere hours and 5.8 watt hours under the same conditions.

5. On high-rate discharges such as are encountered in the cranking of an automotive (or similar) engine, "AD-X2" introduces a small but detectable detrimental effect.

   For 27 treated discarded automotive cells, the average watt hours were 102.4 on a 300-ampere discharge as compared to 106.2 watt hours obtained for 27 untreated cells.

   For 11 treated truck and tractor batteries, the average watt hours were 126.0 on a 300-ampere discharge as compared to 132.5 watt hours obtained for 11 untreated batteries.

6. Adding "AD-X2" is detrimental in the charging process in early stages of charge when the acid electrolyte is low in concentration or percent of acid. Hard sulfated negative plates are redeveloped more efficiently in the absence of AD-X2 in the electrolyte.

   More acid and lead are formed in the charging process per ampere hour in the absence of "AD-X2".

7. There is no difference of any consequence in the amounts of water lost by treated and untreated batteries.

   The total water loss of 18 treated truck and tractor cells throughout a series of charges and discharges was 9002 ml; for 18 untreated truck and tractor cells under the same conditions the total loss was 9110 ml. On cells overcharged with caps removed for 29 hours at 5 amperes the total loss for 18 treated cells was 1128 ml; for 18 untreated cells, 1064 ml.

   Both "AD-X2" and a mixture of magnesium and sodium sulfates were observed to give rise to finer and more numerous bubbles during charge in dilute solutions. There seems to be no connection between this phenomenon and battery performance, or in the amounts of water lost. Some preliminary measurements indicate that the greater number of bubbles in the treated batteries were from greater dissipation of the charging current in electrolysis of water. More evidence would be needed to determine whether or not this is the explanation.

8. No evidence has been obtained that shows that batteries treated with "AD-X2" operate at a cooler temperature on charge or discharge.

9. "AD-X2" does not increase the solubility of lead sulfate in sulfuric acid solutions or in battery electrolyte.

Determinations by the dithizone method show that "AD-X2" decreases the solubility of lead sulfate in sulfuric acid solutions by an exceedingly small amount.

10. "AD-X2" does not prevent "sulfation" of batteries at room temperatures or of batteries subjected to cycles of fluctuating temperatures (25°C to 50°C to 25°C).

Over a period of 5 months at room temperature the internal resistance of an untreated battery increased 0.010 ohm whereas the internal resistance of a battery treated with "AD-X2" increased 0.026 ohm.
Over a period of 5 months under conditions of fluctuating temperatures the average internal resistance of 2 untreated batteries increased 0.045 ohm whereas the internal resistance of 2 treated batteries increased 0.066 ohm.
Over a period of 4 months under conditions of fluctuating temperatures the average internal resistance of 4 additional untreated batteries increased 0.086 ohm whereas the internal resistance of 4 treated batteries increased 0.102 ohm.

11. "AD-X2" does not increase the rate at which lead sulfate is converted to lead and sulfuric acid during charge; instead it is detrimental to this conversion.

Titrations of acid in battery electrolyte prior to and after charge for known ampere-minute inputs show that more acid is formed on charge when "AD-X2" is absent.
Plates charged in solutions to which the "additive" is added give less output than plates charged in untreated electrolyte as judged when the plates are discharged in the same electrolyte.

12. As "AD-X2" neither increases the solubility of lead sulfate in sulfuric acid nor the rate of conversion of lead sulfate to lead and sulfuric acid, it cannot lead to the diminution or disappearance of sediment or "battery mud" at the bottom of the electrolyte.

Sediments removed from 18 untreated and 18 treated cells after several cycles of charge and discharge and an overcharge show no significant difference in the amount of sediment between treated and untreated cells. What small difference was observed was in favor of the untreated cells.

13. "AD-X2" increases the electrical resistivity of sulfuric acid solutions in the specific gravity range of 1.006 to 1.300. This is a detrimental effect.

    The increase is about 5 percent.

14. "AD-X2" increases the viscosity of sulfuric acid solutions in the specific gravity range extending from extremely dilute solutions to 1.300. This is a detrimental effect.

    The increase is about 7 percent.

15. "AD-X2" does not improve the ability of a battery to retain charge on storage.

    After approximately one month of storage at ambient room temperature, 5 treated and 5 untreated batteries were discharged at 50 amperes to 1 volt and then at 10 amperes to one volt. The difference in total watt hours delivered by the treated and untreated batteries was not statistically significant.

16. "AD-X2" is detrimental at high discharge rates over a specific gravity range from 1.020 to the specific gravity of normal operating conditions.

    The detrimental effect becomes less marked as the concentration of battery electrolyte increases.

17. The specific gravities of cells treated with "AD-X2" at the start of charge are higher than the specific gravities of untreated cells. This difference is accounted for by the addition of the additive. As charge proceeds, however, the difference in specific gravities between treated and untreated cells becomes less marked, showing that the untreated cells are taking the charge better. This approach toward a common value is less marked if the additive is added later in the charge or if added to batteries that have considerable residual charge or high specific gravity.

    For 10 treated and 10 untreated batteries the average difference in specific gravity at start of charge was 0.019, at end of charge, 0.003; the average change for treated cells was 0.198; for untreated cells 0.214.

18. Inspection of plates from treated and untreated batteries after full charge showed conclusively that there are no significant differences in the appearances or physical properties of the plates of treated and untreated batteries.

19, No changes in the physical properties of the components of lead-acid storage batteries when "AD-X2" is added have been found which would lead to predictions of greater life expectancy for treated batteries as compared to untreated ones.

The watt hours obtained for 10 treated and 10 untreated truck and tractor batteries after an 8-month storage, followed by seven subsequent charges and discharges were less than those obtained for each 8 months previously. However, the difference in the decrease for treated and untreated batteries is not statistically significant, the decrease being 15 watt hours for the treated and 16 for the untreated batteries.

(When the observed difference between treated and control was in favor of the treated, a statistical evaluation of the difference was made. When the difference was in favor of the control a statistical evaluation of the difference was not required because the data obviously do not support the claims for the product.)

Part III

BATTERY TESTS OF AD-X2

1. The June 1952 Test

   1.1 Introduction
   1.2 Conclusions
   1.3 Summary of Particulars and Procedure
   1.4 Change in Specific Gravity During Charging
   1.5 Comparison of Temperatures During Charging
   1.6 Watt-hour Output
   1.7 Further Tests on Batteries Used in June 1952 Test
   1.8 The Visual and Manual Inspection

2. Tests of Discarded Automotive Batteries

3. Tests on New Batteries

4. The January 1953 Tests of Batteries Drained and Filled with 1.100 Acid or with Distilled Water

   4.1 Outline of Experiment
   4.2 Analysis of Results
   4.3 Details of Analysis of Variance and Covariance

1. THE JUNE 1952 TEST

1.1 Introduction

As noted in detail in Part I, the National Bureau of Standards has investigated the effect of various additives on storage battery operation at the request of various Federal agencies during the past 25 years. Here the results obtained recently by the Bureau in a further series of tests on Battery AD-X2 are given and discussed.

The basic test procedure was established by the manufacturer, whose contention it had been that the Bureau's prior investigations did not constitute adequate testing of his product. The general characteristics of this test were as follows (see Section 1.3 for details): shelf-sulphated batteries in good mechanical condition were to be used; half were to be treated with the manufacturer's battery additive while half were to remain untreated, serving as controls; a prescribed charging procedure was to be used, uniformly charging both treated and untreated sets; a prescribed discharge procedure was to be used, uniformly discharging both treated and untreated sets. The manufacturer claimed that this test would show the following: (1) mechanical differences between the treated and untreated batteries at the conclusion of the test and (2) electrical differences between treated and untreated batteries at the end of the test.

Sulphated batteries were secured by the National Bureau of Standards. Only those approved by the manufacturer as acceptable for the test were used. The batteries were coded into groups of cells to be treated and groups of cells to remain untreated, serving as controls. The code was not known to the people carrying out the electrical tests.

The manufacturer supplied an ample quantity of his additive. His instructions were followed in introducing the additive to those cells which were to be treated.

The tests were conducted by members of the Bureau's staff and were witnessed by experts from other agencies of the Government and a representative of the manufacturer.

Comparisons of treated and untreated batteries with respect to mechanical characteristics were conducted by a group of Bureau scientists, a group of battery experts from other Government agencies, and representatives of the manufactuere (including the manufacturer himself). The detailed results of this aspect of the investigation are presented in Section 1.8.

The data taken during the electrical tests (temperature, specific gravity, voltage, amperage, time, etc.), relevant to effect of the additive on the batteries, are presented in full in Appendix 2 and discussed in Section 1.4ff. These data have been carefully analyzed by the Bureau's Statistical Engineering Laboratory. Careful statistical analysis of such data is necessary if proper conclusions are to be drawn, for batteries under test inevitably show variations reflecting their varying backgrounds and life histories.

Chemical analysis of the additive was conducted by the Bureau's Chemistry Division. The results are presented in Part V.

1.2 Conclusions

(a) The increase in specific gravity during charging was greater for the untreated batteries than for the treated batteries by a small but statistically significant amount: this difference in increase (untreated minus treated) was 0.016 per cell in the case of the trays of lines 1 and 2, and 0.019 per cell in the case of the paired batteries on line 3.

(b) No statistically significant indication of a real temperature difference between treated and untreated batteries during charging was found.

(c) No statistically significant difference in total watt-hour output between treated and untreated batteries was found: the treated trays yielded 5.08* watt hours per battery more than the untreated trays, but the treated batteries on line 3 yielded 0.84** watt hours per battery less than the untreated batteries with which they were paired.

(d) The untreated trays delivered 5.91 watt hours more per battery at the 300 amp discharge rate than did the treated trays; and the untreated batteries, 7.20 watt hours per battery more than the treated batteries with which they were paired. The foregoing is statistically significant, and this statistical significance is more marked when the effects are expressed in terms of fractions of total watt-hour output delivered at the 300 amp rate.

(e) No statistically significant difference between treated and untreated batteries was found in the watt hours delivered on a recovery discharge after standing for one month.

(f) No statistically significant differences between treated and untreated batteries were found with respect to either total watt-hour output or watt-hour output at 300 amp, in 7 charge-discharge cycles after standing in discharged condition for 8 months.

(g) In the inspection test no statistically significant differences between treated and untreated batteries were detected with respect to

softness of positive plate	adherence
softness of negative plate	peroxidation
general condition	

by the 9 judges, either individually or collectively. All 5 of the Government battery experts (2 from the NBS, and 3 from other Government agencies) rated untreated batteries higher than treated batteries, but their leanings in this respect were not sufficiently pronounced to be statistically significant at the 0.05-probability level.

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* Estimated standard error = 12 watt hours

** Estimated standard error = 1.5 watt hours

1.3 Summary of Particulars and Procedures.

Details are given here on the following: (1) steps taken to determine the initial condition of 25 six-cell storage batteries procured from the Naval Aviation Supply Depot, Philadelphia, for use in testing Battery AD-X2 supplied by Jess M. Ritchie, (hereinafter referred to as "the manufacturer") President of Pioneers, Inc., manufacturers of the additive, (2) the procedure followed in readying the batteries for the electrical and inspection tests, and (3) the procedure followed in making the electrical tests on the batteries after some of them had been treated with the additive.

(a) Description of the batteries. The batteries were of the heavy duty type commonly used in buses. The batteries had been in storage in the wet condition for about 4 years and were received at NBS May 20, 1952. Each battery contained 6 cells assembled in a hard rubber tray. The cells were connected in series parallel to provide high capacity at 6 volts.

(b) Initial condition of the batteries. On May 27, all 25 batteries were delivered by NBS truck to a commercial battery shop of the manufacturer's selection and acceptable to the Bureau, where the batteries were dismantled and inspected. One packing crate containing a single battery was opened at the NBS when the shipment was received. Six additional crates containing 4 batteries each were opened in the presence of the manufacturer upon their delivery to the battery shop.

A preliminary inspection of the batteries revealed raised positive terminals in 3 batteries. Raised terminals indicate expanded and unsound positive plates; therefore, these batteries were rejected. The remaining 22 batteries passed the preliminary inspection. Upon removing the elements from these batteries, the positive and negative plates were found to be sulfated and the negative plates were very hard. The positive plates in 6 batteries were expanded excessively and the grid frames of some of the plates in each element were cracked. These 6 batteries were rejected. The plates in the 16 which remained were in sound mechanical condition and the manufacturer approved these batteries for use in the test.

The separators in all elements were in good condition with the exception of two separators which were split, probably during inspection. The split separators were replaced with new ones and the elements were approved.

There was evidence of all batteries having been charged 3 times at different periods as indicated (1) by 3 small holes in the terminals where connectors had been attached and (2) by 3 distinct laminae of lead peroxide on the positive plate straps.

The manufacturer of the additive claimed that the laminae on the plate straps indicated that the batteries had resisted charging and, in view of this and the hardened condition of the negative plates, he concluded that the batteries were in suitable condition (1) for test and (2) to establish the merit of his additive. The proprietor of the commercial battery shop concurred in the manufacturer's conclusions.

The 16 batteries approved by the manufacturer were reassembled and the cells were connected to provide 2 six-volt batteries in each tray. This made a total of 32 six-volt batteries approved by the manufacturer for the test.

During the aforementioned inspection, the elements were placed over the cell compartments and allowed to drain so that no electrolyte was lost. No adjustment of the electrolyte levels was made at the battery shop. The batteries were sealed and returned to the NBS by the battery shop proprietor on May 29.

The manufacturer was granted permission to make experiments on 2 rejected batteries (12 cells) for his own information. The remaining rejected batteries were returned to NBS by the battery shop proprietor on June 2.

(c) Positions and identification of the batteries for test. The 32 individual six-volt batteries were coupled together in pairs to form "trays", and were numbered serially for identification. The trays were divided into 3 groups which were placed on separate test tables for charging on separate lines, as follows:

Line 1

Battery	1,2	3,4	5,6	7,8	9,10
Status	T,T	U,U	U,U	T,T	U,U

Line 2

Battery	11,12	13,14	15,16	17,18	19,20
Status	T,T	T,T	U,U	U,U	T,T

Line 3

Battery	21,22	23,24	25,26	27,28	29,30	31,32
Status	T,U	T,U	U,T	T,U	U,T	U,T

Note: For procedure followed in choosing the batteries that were treated (T) and those left untreated (U) as controls, see Sections 1.4 and 1.5 hereinafter.

The batteries on a single table were connected in series for charging from 110-volt d-c power with a rheostat in each circuit for current control.

(d) Outline and details of test procedure. The test consisted of the following steps; (1) Treating selected batteries according to code. (2) Charging all batteries. (3) Dismantling and inspecting the plates in selected batteries after charge. (4) Discharging batteries which were not dismantled.

Details of the test procedure, in general, followed the procedures established by the manufacturer of the additive,* with certain modifications upon which some agreements were reached in correspondence** and others in subsequent verbal discussions, as follows: (1) Both batteries in any tray on lines 1 and 2 will be either treated or left untreated. (2) The trays to be treated in lines 1 and 2 will be selected at random***. (3) In line 3 one battery in each tray will be selected at random*** for treatment. (4) The charging procedure

* The manufacturer's original specification of procedure for such a test, entitled "Procedure for Testing Battery AD-X2 (Suicide Test)," and dated June 1, 1951, is given in Appendix 1 (See Part VII).

** Copies of letters between the Bureau and the manufacturer on modification of the original proposal are also given in Appendix 1.

*** "The use of controls does not suffice to ensure correct results." To avoid bias "two steps should be taken. The first is the careful matching of specimens [i.e., batteries] to form a subject-control pair [i.e., treated-untreated pair or group] as nearly alike in all pertinent features as possible. The efficiency and sensitivity of the experiment are very dependent on the success of this matching."

No such matching was possible in this test since one of the manufacturer's conditions was that no attempt be made to charge any of the batteries that were to be treated prior to their actual treatment. Consequently a pre-test on which to rate electrical performance of the batteries for matching purposes was impossible.

"The second step ... is the use of the principle of randomization in choosing which member of a pair is to be the subject and which the control [i.e., which batteries were to be treated and which untreated]. A coin should be tossed to decide this question; it most emphatically should not be left to human judgement. It is also unsafe to base it on a supposedly, but not certainly, accidental order. ....the use of coin tossing (or tables of random numbers) permits the probability of unfortunate choices to be predicted with accuracy, whereas any nonrandom

(SEE TOP OF NEXT PAGE)

method of choice is not amenable to such a calculation." [The quotations above are from pages 42-43 of E. Bright Wilson, Jr., An Introduction to Scientific Research, McGraw-Hill Book Company, Inc., New York, 1952.]

Since modern techniques of statistical analysis based on the mathematical theory of probability assume randomness of uncontrolled factors, the validity of any conclusions drawn from an experiment by the use of such techniques is always in doubt unless randomness has been deliberately introduced at appropriate stages in the design and execution of the experiment. (For an elaboration of this point, see, for example, Chapter 7, "Randomization", and Chapter 8, "The Validity of Analyses of Randomized Experiments" in Oscar Kempthorne, The Design and Analysis of Experiments, John Wiley and Sons, New York, 1952.)

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for batteries in line 3 may be altered at the discretion of the NBS. (5) No adjustment of the specific gravity will be made except in the event that the specific gravities of any 5 cells in lines 1 or 2, or any 6 cells in line 3 exceed 1.325, in which event the specific gravity will be reduced 10 points in all cells in the affected line. (This condition did not arise.) (6) If the temperature of any cell in a battery reaches 120°F, 49°C (± 1°C), the battery will be pulled from the charging line until it cools to 110°F, put back on charge (at prevailing rate) and continued until the battery has the total charge of the others. (This condition did not arise.) (7) The bend and twist test will not be used to determine the soundness of the positive plates. (8) The schedule for charging was formulated by the manufacturer to be as follows: (a) 5 amperes for 24 hours, (b) 14 amperes for 8 hours (day period), (c) 10 amperes for 16 hours (night period), (d) repeat (b) and (c) in order until charge is complete. (9) Termination of charge was modified as follows: terminate charge when more than 2/3 of the cells in any line show specific gravity increase in a 16-hour period of less than 10 points, however, all will be charged at least 4 days and none more than 5 days. (This condition was fulfilled in 4 days). (10) Batteries selected for discharge will be discharged at 300 amperes to 3.0 volts, at 200 amperes to 3.0 volts and at 100 amperes to 1.0 volt or lower.

(e) Addition of the Battery Additive. The manufacturer, accompanied by an "observer", delivered 2 cartons (72 envelopes) of the battery additive on June 3, 1952, and demonstrated how the material should be added. He specified that 1½ envelopes be added to each cell to be treated. The manufacturer's observer assisted in dividing the envelopes into the required number of halves after he and a member of the NBS staff had finished adjusting the level of the electrolyte by adding distilled water to the level guide plates as directed by the

manufacturer. The manufacturer himself then inspected the charging circuits and testing equipment and left the laboratory. The charge was then started, at 11:00 AM on June 3, 1952, and after adjusting the charging currents to 5 amperes, the laboratoy personnel left the laboratory.

The batteries to be treated were selected at random subject to the restrictions of (1), (2), and (3) in the second paragraph of Section I.3(d) above, using a table of random numbers. The resulting setup is shown in Section 1 above: Line 1 contained three trays bearing untreated pairs and two bearing treated pairs; the converse was the case for Line 2; and on Line 3, the six trays were made up of one treated battery and one untreated battery.

The random selection of the batteries that were to be treated, their treatment with the additive, and the arrangement of the batteries in the lines as shown above, were performed by the Director, assisted by an individual not connected with the Bureau's Battery Laboratory with no one else present. Which of the batteries had been treated, and which had not, was known only to the Director himself; and was not known to any one of the persons participating in, or present during the carrying out of, either the electrical or the inspection tests.*

(f) The charge. No readings were taken on the batteries prior to beginning the charge because differences between such readings and later readings might have indicated which batteries had been treated. The progress of the charge for each battery was indicated by recorded readings of specific gravities and voltages. To avoid the exchange of electrolyte between treated and untreated cells, each tray, lines 1 and 2, and each bettery in line 3 was supplied with its own hydrometer and thermometer. About 2 hours were required to take and record a round of readings.**

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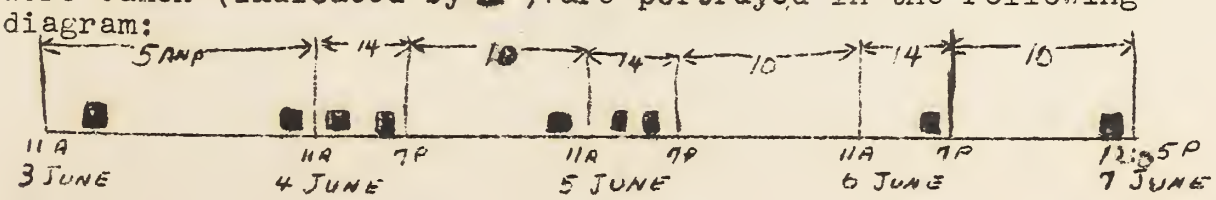
*"In the best experimental designs, the person making comparisons, measurements, or records is kept ignorant of the identity of the subjects and controls. ...No human being is even approximately free from ... subjective influences; the honest and enlightened investigator devises the experiment so that his own prejudices cannot influence the result. Only the naive or dishonest claim that their own objectivity is a sufficient safeguard." [From page 44 of E. Bright Wilson, Jr., An Introduction to Scientific Research, McGraw-Hill Book Company, Inc., New York, 1952.]

**For lines 1 and 2 the seven charging periods involved and the nine periods during which specific gravity and temperature readings were taken (indicated by ■) are portrayed in the following diagram:



The levels of the electrolyte increased to the point of flooding in a number of cells during the first 21 hours of charging. Therefore, to prevent flooding as the charge proceeded, 50 ml of electrolyte were removed from each cell. This electrolyte was stored in measuring cylinders marked with the battery identification numbers and returned to the respective cells after the levels had declined sufficiently. The time that the electrolyte was returned was noted on the data sheets. Water was added to all cells at a later period and again about 2 hours before terminating the charge in order to have the final levels the same as the initial levels. The amounts of water added in each instance are recorded on the data sheet together with the time.

Cadmium readings taken on all cells in line 3 after 46 hours (372 ampere hours) of charging indicated that the charge had been practically completed. Following these cadmium readings, the batteries in line 3 were charged at the scheduled rate of 14 amperes for 8 hours. Then the charging rate was reduced and maintained at 10 amperes until the charge was terminated. The charge on lines 1 and 2 was terminated after a total uninterrupted charge of 4 days, 1 hour. By this time the batteries had received the charge provided by modification (9) of the test procedure. The charge on line 3 was terminated after continuous charging for 3 days and 23-1/4 hours.*

Because of hot weather and heat liberated from the charging resistors, the laboratory temperature reached 85°F during the afternoons. Because of this, a measure of artificial cooling was used in order to avoid exceeding specified temperature limits while the batteries were charging at 14 amperes. Portable electric fans were used to circulate air through the laboratory during the second afternoon. Thereafter dry ice was distributed in the lanes between batteries to reduce the ambient temperature during the period of charging at the 14-ampere rate. Since the temperature and humidity may have been affected to slightly different extents in different parts of the test area any critical comparison of battery temperatures should be based on the charging temperatures at the 10-amperes rate for which no artificial cooling was used.

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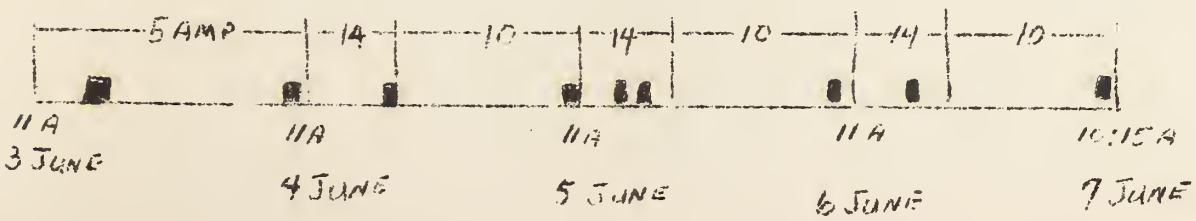
* For line 3, the seven charging periods and the ten periods in which specific gravity and temperature readings were taken are portrayed below:



(g) Discharges. Trays designated to be dismantled for inspection of the plates were set aside after terminating the charge. The others were discharged in accordance with the test procedure to voltages shown in modification (10) of the procedure.

The discharges were begun June 9 about 1:00 PM, 49 hours after terminating the charge. The batteries in trays 11, 12, and 14 from line 3 were discharged during the afternoon. Those in trays 1, 2, and 3 from line 1 were discharged the next morning, June 10. Those in trays 6, 7, 8 from line 2 and 15 from line 3 were discharged during the afternoon. Batteries in tray 16 (line 3) were discharged in the morning of June 11.

The batteries were discharged at 300, 200, and 100 amperes without interrupting the discharge while changing the rate. Voltage, temperature and specific gravity readings were taken prior to discharge. Closed-circuit voltages were read at 30 second intervals and temperatures at less frequent intervals during the discharges. All readings were recorded together with the observed time.

The ampere-hour and watt-hour capacities of each battery to the specified cut-off voltage for each rate were computed and totalized.

(h) Inspection of plates after charge. On June 11, the elements were removed from the trays set aside after the charge and inspected by a group of inspectors under the supervision of the Chief of the Bureau's Statistical Engineering Laboratory. Each element inspected was identified by a code letter. The inspectors compared 2 elements at a time without knowing which had been treated.

1.4 Change in Specific Gravity During Charging.

The increase in specific gravity during charging was greater for the untreated batteries than for the treated batteries to an extent statistically significant at the .003-probability level.

(a) Treated vs Untreated Trays. The average increase in specific gravity per battery from the 1st to the 9th reading was 0.214 for the untreated trays and 0.198 for the treated trays, on lines 1 and 2. This difference, 0.016, is itself statistically significant at the (two-sided) 0.06-probability level.

The basic specific gravity readings are given in Appendix 2. Table 1 hereinafter gives for each tray, the average of the first readings for the two batteries comprising the tray, and the corresponding (average) increase in specific gravity from the 1st to each of the eight succeeding readings.

Only the increases from the 1st to the last (9th) reading are capable of unambiguous interpretation. (See second paragraph of Section 1.1(f) above.) These are as follows:

Untreated Trays

Tray	Total increase in Sp. Gr.
2	0.219
3	0.225
5	0.198
8	0.214
9	0.215
Sum	1.071
Average	0.214

Treated Trays

Tray	Total increase in Sp. Gr.
1	0.181
4	0.203
6	0.212
7	0.198
10	0.198
Sum	0.992
Average	0.198

There are exactly $C_5^{10} = 252$ different ways in which the 10 trays in the above table could be partitioned into two groups of 5 trays each, nominally labelled "treated" and "untreated", respectively; and of these, one finds by direct enumeration that for only 7 of these partitions will the sum of the total increase in specific gravity for the "untreated" group equal or exceed 1.071. If we assume that the differences among the above 10 results reflect tray (or battery) differences only, i.e. if we assume that the treatment had no effect, then the probability

TABLE 1 Increase in Specific Gravity During Charge: Treated vs Untreated Trays (Lines 1 and 2)

	Tray	Battery	First Reading*	2	3	4	5	6	7	8	9
TREATED	1	1,2	1.134	.104	.124	.147	.174	.178	.178	.176	.181
	4	7,8	1.094	.130	.140	.166	.195	.194	.197	.203	.203
	6	11,12	1.090	.128	.143	.166	.197	.198	.199	.207	.212
	7	13,14	1.118	.114	.129	.146	.184	.189	.190	.199	.198
	10	19,20	1.112	.111	.127	.154	.185	.186	.190	.196	.198
	AVERAGE		1.110	.117	.133	.156	.187	.189	.191	.196	.198
UNTREATED	2	3,4	1.086	.138	.141	.172	.211	.214	.214	.214	.219
	3	5,6	1.090	.136	.149	.168	.203	.207	.212	.218	.225
	5	9.10	1.113	.119	.133	.153	.184	.189	.192	.194	.198
	8	15,16	1.084	.132	.146	.168	.203	.203	.204	.213	.214
	9	17,18	1.083	.137	.160	.181	.210	.210	.215	.207	.215
	AVERAGE		1.091	.132	.146	.168	.202	.205	.207	.209	.214
Difference in averages (Treated minus untreated)				-.015	-.013	-.012	-.015	-.016	-.016	-.013	-.016

*Average for the two batteries concerned.

is 7/252 = 0.0278 of obtaining as a result of random assignment a total (or average) for the "untreated" group that exceeds the total (or average) of the "treated" group by an amount equal to or greater than the observed difference. On the other hand, the observed difference between the two groups may reflect a real treatment effect superimposed on whatever tray differences may be present.

Since there is no way of knowing for certain which of these explanations is the correct one, the observed difference in favor of the untreated would be regarded as "statistically significant at the 0.0278-probability level", if a priori the only admissible alternative to "treatment has no effect" is "treatment retards increase in specific gravity." If, on the other hand, the sign of the treatment effect, if any, is not taken as known a priori, so that "treatment enhances increase in specific gravity" is also considered to be admissible a priori and a large effect in either direction would be regarded as "significant" evidence of a real treatment effect, then the observed result would be regarded as "statistically significant at 0.0556-probability level" (2 x 0.0278 = 0.0556) and "in favor of the alternative 'treatment retards increase in specific gravity'."* This is the viewpoint adopted in the present instance.

(b) Treated vs Untreated Batteries. The average increase in specific gravity per battery from the 1st to the 10th reading was 0.194 for the untreated batteries and 0.175 for the treated batteries on line 3. This difference, 0.019, is itself statistically significant at the (rather liberal) 0.10-probability level.

The basic specific gravity readings are given in Appendix 2. Table 2 hereinafter gives, for each battery, the 1st reading of specific gravity and the corresponding increases in specific gravity from the 1st to each of the nine succeeding readings. Only the total increases, from the 1st to the last (10th) reading, are capable of clear-cut interpretation. These values, which are paired in terms of the trays involved, are as follows:

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* The foregoing is an application of the principles and arithmetic involved in performing a randomization test of an hypothesis. For a further discussion of this technique, see, for example, Chapter 7 (especially p.128ff) in Oscar Kempthorne, The Design and Analysis of Experiments, John Wiley and Sons, Inc., New York, 1952.)

Tray	Untreated Battery	Untreated Total increase in Sp. Gr.	Treated Battery	Treated Total increase in Sp. Gr.	Difference
11	22	0.212	21	0.170	0.042
12	24	0.189	23	0.185	0.004
13	25	0.178	26	0.155	0.023
14	28	0.212	27	0.171	0.041
15	29	0.202	30	0.195	0.007
16	31	0.170	32	0.175	-0.005
Average		0.194		0.175	0.0187

There are exactly $2^6 = 64$ different ways in which the 12 individual batteries of the foregoing 6 pairs of batteries could be allocated to one or the other of two distinct groups nominally labelled "treated" and "untreated", respectively. By direct enumeration it may be verified that for only 3 of these splits will the average of the differences, "untreated" minus "treated", exceed 0.0187. Therefore, by reasoning analogous to that given in subsection (a) above, it may be concluded that the observed mean difference is statistically significant at the 0.09375-probability level (6/64 = 0.09375) and favors the conclusion that "treatment retards increase in specific gravity".

(c) Combining the evidence. In (a) it was shown that the probability is 7/252 of obtaining a total for the untreated group as large or larger than that observed, as a result of purely random assignment of the trays. In (b), the probability of obtaining purely as a result of random allocation of the batteries within pairs an average difference (untreated - treated) as large or larger than that actually obtained, was shown to be 3/64. Since the two randomizations were independently performed, the probability P_u of simultaneously experiencing these outcomes as a result of the randomizations alone is (7/252)x(3/64) = 0.001302. The significance probability associated with the product can be calculated by W. Allen Wallis' extension of a technique due to R. A, Fisher and Karl Pearson (W. Allen Wallis,"Compounding probabilities from independent tests of significance", Econometrica, 10, 229-248 (1942)). It is sufficient, however, to note that this significance probability cannot exceed (loc. cit, p.248)

$$P_u[1 - \log_e P_u]$$

which works out to be 0.0013. Had the data been as actually occurred but with the roles of treated and untreated interchanged, we would have reached instead a product P_T equal to the P_u above, and the significance probability associated with

TABLE 2 INCREASE IN SPECIFIC GRAVITY DURING CHARGING: TREATED VS UNTREATED BATTERIES
(Line 3)

	Battery	First Reading	Increase at Reading 2	3	4	5	6	7	8	9	10
Treated	21	1.120	.113	.130	.148	.175	.175	.178	.200	.167	.170
	23	1.122	.130	.146	.163	.190	.190	.190	.208	.171	.185
	26	1.153	.094	.104	.119	.149	.154	.159	.174	.150	.155
	27	1.122	.110	.126	.145	.171	.178	.178	.195	.165	.171
	30	1.100	.150	.170	.183	.205	.205	.208	.222	.193	.195
	32	1.125	.112	.128	.145	.172	.173	.178	.198	.172	.175
	Average	1.124	.118	.134	.150	.177	.179	.182	.200	.170	.175
Untreated	22	1.073	.135	.157	.182	.212	.214	.215	.242	.205	.212
	24	1.103	.139	.155	.169	.194	.195	.197	.217	.180	.189
	25	1.125	.115	.133	.148	.178	.185	.183	.203	.177	.178
	28	1.073	.137	.164	.185	.210	.214	.219	.237	.212	.212
	29	1.080	.152	.173	.185	.208	.208	.213	.240	.195	.202
	31	1.128	.102	.115	.130	.162	.165	.169	.190	.165	.170
	Average	1.097	.130	.150	.166	.194	.197	.199	.222	.189	.194
Difference in averages (Treated minus untreated)			-.012	-.016	-.016	-.017	-.018	-.017	-.022	-.019	-.019

this P_T would likewise be ≤ 0.0013. It follows that the probability of obtaining by randomization alone two <u>consistent</u> results as pronounced or more pronounced than those actually observed is less than $2(0.0013) = 0.0026$. Hence the observed results jointly are regarded as "statistically significant at the 0.0026-probability level" and suggest the conclusion that "treatment retards increase in specific gravity".

1.5 Comparison of Temperatures During Charging.

No statistically significant indication of any real difference between treated and untreated batteries with respect to temperature during charging was found on Lines 1 and 2, where both of the batteries in a tray were treated or both untreated; nor on Line 3, where one of the batteries in a tray was treated and the other left untreated as a control.

(a) Treated vs Untreated Trays. For the reason given in the last paragraph of Section 1.3(f), comparison of average cell temperatures for treated vs untreated trays on lines 1 and 2 is clear-cut only for the data of the 1st, 2nd, 5th, and 9th, temperature readings. These averages are:

	Average cell temperature (°C) at reading			
	1	2	5	9
Treated trays	28.27	32.18	38.72	44.91
Untreated trays	28.32	32.15	39.36	44.19
Difference (T-U)	-.05	+0.03	-0.64	+0.72

There is clearly no evidence here of any consistent tendency.

The basic temperature readings for each of the 3 cells of each of the 10 treated and 10 untreated batteries on lines 1 and 2 are given in Appendix 2. The tray averages for each of the 9 temperature readings are given in Table 3 hereinafter. There is clearly no statistically significant evidence of a temperature difference between treated and untreated trays at the 1st reading ("onset"), nor at the 2nd, 5th, or 9th readings — considered individually.

(b) Treated vs Untreated Batteries. The basic temperature data for the 6 trays of line 3 in which one battery was treated and the other untreated are given in Appendix 2. The average cell temperatures of each of the 2 batteries comprising a tray are given in Table 4 hereinafter, for each of the 10 temperature readings.

For the reason given in the last paragraph of Section 1.3(f) comparisons of average cell temperatures for treated and untreated batteries on line 3 are clear-cut only for the data of the 1st, 2nd, 5th, 8th, and 10th temperature readings. The difference between the average temperature of the 3 cells of the treated battery and the average temperature of the 3 cells of the untreated battery in a tray is given in Table 5 for each of the 6 trays on line 3 at each of the aforementioned temperature readings. Since the 1st and 2nd readings both lie within the initial 5 amp charging period, the difference "(2)-(1)", which equals $(T_2-U_2)-(T_1-U_1)=(T_2-T_1)-(U_2-U_1)$, expresses the difference in rate of

TABLE 3: AVERAGE TEMPERATURE (°C) OF TRAYS AT EACH TEMPERATURE READING (Lines 1 and 2)

	Tray	Battery	Reading 1	2	3	4	5	6	7	8	9
TREATED	1	1,2	27.87	31.77	38.07	45.90	37.78	44.17	46.23	46.68	45.07
	4	7,8	27.98	31.75	39.53	46.67	39.00	45.15	47.80	47.17	44.02
	6	11,12	28.33	32.35	40.07	44.22	39.18	43.40	46.28	47.60	45.72
	7	13,14	28.83	32.45	40.77	45.47	40.00	43.48	46.10	47.48	45.80
	10	19,20	28.32	32.58	41.38	43.72	37.65	42.38	44.65	46.52	43.93
	Average		28.27	32.18	39.96	45.20	38.72	43.72	46.21	47.09	44.91
UNTREATED	2	3,4	28.27	31.68	38.30	45.77	39.12	44.47	46.70	46.17	44.03
	3	5,6	28.67	32.25	39.27	46.73	40.57	45.40	47.23	45.70	42.93
	5	9,10	28.50	32.68	40.98	45.43	38.77	45.03	47.72	46.38	45.48
	8	15,16	27.97	32.05	40.47	45.63	38.93	43.42	46.45	48.42	44.15
	9	17,18	28.17	32.07	40.82	45.32	39.42	44.07	46.87	47.98	44.35
	Average		28.32	32.15	39.97	45.78	39.36	44.48	46.99	46.93	44.19
Differences in averages (Treated minus Untreated)			-.05	.03	-.01	-.58	-.64	-.76	-.78	.16	.72

TABLE 4: AVERAGE TEMPERATURE (°C) OF INDIVIDUAL BATTERIES AT EACH TEMPERATURE READING (Line 3)

Tray	Battery	Average Cell Temperature at Period Indicated									
		1	2	3	4	5	6	7	8	9	10
11	T21	28.0	31.9	42.8	47.5	38.8	44.5	47.3	35.7	42.3	44.2
	U22	28.0	31.7	42.1	46.2	37.8	44.3	46.9	36.1	43.0	42.8
12	T23	27.3	31.7	42.5	46.3	38.5	45.0	47.5	36.6	43.3	42.9
	U24	27.7	31.9	43.0	47.5	39.5	45.7	47.7	36.5	44.4	42.9
13	T26	28.5	32.3	42.9	47.0	40.4	44.5	46.8	37.8	44.0	41.4
	U25	28.1	32.2	42.8	46.5	39.4	44.9	47.3	36.2	43.3	41.2
14	T27	28.1	31.9	42.5	47.1	41.3	45.0	47.6	39.5	44.3	42.6
	U28	28.2	31.9	42.5	47.0	40.7	46.0	48.2	36.8	43.1	42.6
15	T30	27.8	31.8	43.9	47.3	39.0	45.9	47.3	35.7	42.3	44.3
	U29	27.7	31.9	44.4	48.5	40.3	46.3	48.2	35.0	43.5	43.2
16	T32	28.3	30.8	42.9	46.5	37.8	44.5	46.7	36.9	42.3	43.5
	U31	28.9	31.7	43.3	46.8	38.5	44.4	46.4	35.8	41.7	43.6

temperature rise for the treated and untreated during this initial charging period. Apparently the untreated tended to warm up a tiny bit more rapidly than the treated in this initial period, but the observed mean difference of 0.05°C is far from being statistically significant. Indeed, the averages shown in Table 5 are not statistically significant either individually or collectively, at any reasonable probability level.

TABLE 5: COMPARISON OF TEMPERATURES OF TREATED AND UNTREATED BATTERIES WITHIN TRAYS (line 3)

Difference in Average Cell Temperatures of Untreated and Treated Batteries (T-U) at Period Indicated.

	5 amp Charging Rate		Diff.	10 Amp. Charging Rate		
Tray	1	2	(2)-(1)	5	8	10
11	0.0	+0.2	+0.2	+1.0	-0.4	+1.4
12	-0.4	-0.2	+0.2	-1.0	+0.1	0.0
13	+0.4	+0.1	-0.3	+1.0	+1.6	+0.2
14	-0.1	0.0	+0.1	+0.6	+2.7	0.0
15	+0.1	-0.1	-0.2	-1.3	+0.7	+1.1
16	-0.6	-0.9	-0.3	-0.7	+1.1	-0.1
Sum			-0.3	-0.4	+5.8	+2.6
Average			-0.05	-0.07	+0.97	+0.43
Probability*			$\frac{49}{64}$=.766	$\frac{31}{64}$=.484	$\frac{3}{64}$=.047	$\frac{2}{16}$=.125

*Probability of a sum greater than or equal to that observed.

1.6 Watt-hour Output

Six batteries on lines 1 and 2, and ten batteries on line 3 were individually discharged at 300 amps. to 3 volts, then at 200 amps. to 3 volts, and then at 100 amps. to 1 volt. The complete discharge data are given in Appendix 2.

There was no statistical significance between the total watt-hour output of the treated and untreated batteries: the 3 treated trays yielded on the average 5.08 watt hours per battery more than the 3 untreated trays, whereas in the case of the trays containing a treated battery and an untreated battery, the untreated yielded on the average 0.85 watt-hours less. (The standard deviation of the first-mentioned result, which is based on 6 batteries of each kind, is estimated to be approximately 10 watt-hours, and of the latter result based on 5 batteries of each kind is about 1.6 watt-hours, which shows the over-riding influence of tray-to-tray variation and the importance of using matched treated-untreated battery pairs for precise work.)

The watt-hour output at 300 amp. discharge rate of the untreated trays exceeded those of the treated trays by 5.91 watt-hours per battery, and in the case of the treated-untreated pairs of batteries, the 300 amp. output of the untreated batteries exceeded that of the treated batteries by 7.20 watt-hours. There is an indication here, which is statistically significant at the 0.05-probability level, that treatment retarded energy output at the 300 amp. discharge rate by about 6.6 watt-hours per battery. If the analysis is conducted in terms of the fraction (of the total output) that is delivered at the 300 amp. rate, then the foregoing indication is reaffirmed, and measured this way is statistically significant at the 0.02-probability level.

(a) Total Watt-hour Output: Treated vs Untreated Trays. After charging, two of the trays on Line 1 and two of the trays on Line 2 were set aside for use in the inspection test, leaving only three treated trays and three untreated trays (See Section 1.3(c)).

The watt-hours delivered by each tray (the sum of the watt-hours delivered by the two batteries of the tray) were as follows:

Treated		Untreated	
Tray 1	403.17	Tray 2	421.44
Tray 6	435.06	Tray 3	402.42
Tray 7	395.79	Tray 8	379.64
Average	411.34	Average	401.17

The difference between the average for treated and untreated is 411.34 - 401.17 = 10.17 watt-hours per tray = 5.08 watt-hours

per battery. This difference must be judged by the variation among trays. In order that this difference in average be regarded as statistically significant it must be large in comparison with the differences among trays within sets.

There are exactly $C_3^6 = 20$ different ways in which the above 6 trays could be partitioned into two groups of 3 trays each, nominally labelled "treated" and "untreated"; and for 6 of these will the average for "treated" equal or exceed 411.34. Since the trays were actually assigned to the treated and untreated groups at random (See Section 1.3(e)) the probability is 2x6/20 = 0.6 of obtaining by a difference in either direction greater than that actually observed. It is therefore concluded in the present instance that there is no statistically significant evidence of an improvement due to the treatment.

(b) Total Watt-hour Output: Treated vs Untreated Batteries. After charging, one of the trays on Line 3 (tray 13) was set aside for use in the inspection test, leaving five trays each consisting of one treated and one untreated battery.

	Treated		Untreated	
Tray	Battery	Watt Hrs.	Battery	Watt Hrs.
11	21	207.06	22	213.07
12	23	228.63	24	230.10
14	27	238.18	28	238.95
15	30	213.68	29	211.94
16	32	169.91	31	167.62
Average		211.492		212.336

The untreated batteries averaged (212.336 - 211.492) = 0.844 Watt hours more than the treated batteries. The differences between untreated and treated [6.01, 1.47, .77 -1.74, -2.29] are not consistent enough for this slight difference in average Watt hours to be regarded as significant from a statistical point of view. (The probability of a random arrangement yielding an equal or greater average difference in the direction observed is 0.375 .)

Note: The effectiveness of the battery fairing technique is illustrated by the fact that although tray 16 yields extremely low Watt hour values relative to the other trays, the comparison of treated and untreated batteries is not upset by this departure since both the treated and untreated batteries simultaneously reflect this departure. (Tray 16 was not abnormal with regard to temperature or specific gravity.) The precision of the comparisons would be severly reduced if this variability among trays had not been balanced out.

(c) Watt-hour Output at 300 amp Discharge Rate: Treated vs Untreated Trays. The total watt-hour outputs at 300 amp discharge rate for each of the 6 trays (12 batteries) on lines 1 and 2 (for which discharge data were obtained) were as follows:

Treated			Untreated		
Tray	Batteries	Total watt hours at 300 amp.	Tray	Batteries	Total watt hours at 300 amp.
1	1,2	219.88	2	3,4	282.04
6	11,12	287.89	3	5,6	266.21
7	13,14	255.80	8	15,16	250.76
Average		254.52	Average		266.34

Difference (untreated minus treated) = 11.82 watt hours per tray = 5.91 watt hours per battery. This result standing alone is not statistically significant (probability of an equal or larger average for untreated arising from randomization alone is 7/20 = 0.35).

(d) Watt-hour Output at 300 amp Discharge Rate: Treated vs Untreated Batteries. The watt-hour output at 300 amp discharge rate for each of the 5 pairs of batteries on line 3 (for which discharge data were obtained) were as follows:

Tray	Battery		Watt-Hours Output at 300 amp	Difference Untreated-Treated
11	22	Untreated	149.28	7.64
	21	Treated	141.64	
12	24	Untreated	142.35	11.41
	23	Treated	130.94	
14	28	Untreated	162.38	12.87
	27	Treated	149.51	
15	29	Untreated	123.57	2.27
	30	Treated	121.30	
16	31	Untreated	80.70	1.80
	32	Treated	78.90	
			Average difference	7.198 watt hours per battery

The observed mean difference (untreated minus treated) of 7.198 watt hours per battery is by itself statistically significant

at 0.0625-probability level (probability of an equal or larger average excess of untreated over treated as a result of randomization alone = 1/32 = 0.03125), and suggests that watt-hour output at 300 amps. is larger for untreated than for treated batteries.

The results of the immediately preceding and of the present subsection are in the same direction and of approximately the same magnitude. Taken jointly they suggest that treatment retarded watt-hour output at 300 amp discharge rate by approximately (5.91+7.20)/2 = 6.6 watt hours per battery. Moreover this result is statistically significant at the .05-probability level.*

(e) Fraction of Total Watt hours Delivered at 300 Ampere Discharge Rate. The indication of sub-sections (c) and (d) that treatment retards energy output at the high discharge rates is more marked, and its statistical significance more pronounced, when the analysis is conducted in terms of the fractions of the total output delivered at the 300 amp discharge rate.

For the treated and untreated trays considered in sub-sections (a) and (c) above, the fractions are:

Treated		Untreated	
Tray	Fraction delivered at 300 amps.	Tray	Fraction delivered at 300 amps.
1	.5454	2	.6692
6	.6617	3	.6615
7	.6463	8	.6605
Sum	1.8534		1.9912
Average	.6178		.6637

The probability of a greater sum for untreated as a result of randomization is 3/20 = 0.15 (whereas the corresponding probability found in (c) was 7/20 = 0.35).

For treated-untreated battery pairs considered in (b) and (d) above, the corresponding fractions are:

Fraction of total output delivered at 300 amps.

Tray	Treated	Untreated	Difference
11	.6841	.7006	.0165
12	.5727	.6186	.0459
14	.6277	.6796	.0519
15	.5677	.5830	.0153
16	.4644	.4814	.0170
Average	.5833	.6126	.0293

* The procedure followed in reaching this value was as in Section 1.4 (c), except that the one-sided significance probability was calculated directly by Wallis' exact method (ibid.p.244) and yielded 0.02496 which is somewhat less than the approximate value (i.e.upper band) calculated thus: $Pu(1-\log_e Pu)=0.06034$ where $Pu=0.35 \times 0.03125=0.01094$.

It may be noted that all of the fractions for untreated exceed the corresponding fractions for treated. The probability of this occurring as a result of randomization is 1/32 (which is the same as the corresponding probability found in (d)).

The product of these two probabilities is $(3/20)\cdot(1/32)=.00468$ the associated one-sided significance probability is 0.00780; so that the combined evidence is statistically significant (from the two-direction viewpoint adopted in this study) at the 0.0156-probability level.

1.7 Further Tests on the Batteries Used in the June 1952 Test.

After storage for a month the 10 batteries from line 3 remaining from the June 1952 test were given a recovery discharge. There was no statistically significant evidence of a difference between the treated and the untreated batteries with respect to total watt hours delivered.

In March 1953, after 8 months' storage, all 22 batteries remaining from the June 1952 test were put through 7 charge-discharge cycles. The total watt hours produced in these 7 cycles by the treated batteries differed from that produced by the untreated batteries by less than .2 per cent, and which is clearly not statistically significant evidence of an improvement due to the additive upon repeated cycling.

On these 7 cycles the watt hour output delivered by the treated batteries at the 300 amp discharge rate was less than the corresponding output of the untreated batteries by a small (2.8 per cent) and not statistically significant amount.

(a) Recovery discharge after one month's storage. On July 7, 1952 the batteries from line 3 of the June 1952 test were brought out of storage and discharged at 50 amp to 1 volt and then at 10 amp to 1 volt. The full discharge data are given in Appendix 2 Table 3. The following table gives the watt hours delivered by the batteries at the two discharging rates.

Table 6 - Watt hours delivered on recovery discharge* by batteries used in June 1952 test after one month storage.

Tray	Treated	Untreated	Treated minus Untreated
	57.674	47.028	
11	44.943	33.894	
	102.617	80.922	21.695
	67.289	71.812	
12	57.567	57.558	
	124.856	129.370	-4.514
	63.296	59.862	
14	48.047	56.052	
	111.343	115.914	-4.571
	84.434	81.489	
15	76.255	81.199	
	160.689	162.688	-1.999
	21.193	18.466	
16	17.557	14.227	
	38.750	32.693	6.057

Average difference = 3.334 per battery

*- Discharged at 50 amps to 1 volt and 10 amps to 1 volt on July 7, 1952.

The differences in the total watt hours delivered by the treated and by the untreated batteries cannot be regarded as statistically significant evidence of any real difference due to the presence of the additive.

(b) Tests after 8 months of storage: 7 charge-discharge cycles.

(1) Procedure

The 22 batteries of the June 1952 test were stored in a discharged condition for 8 months. In March 1953 they were brought out of storage and a 100 amp discharge was attempted. None of the batteries had any capacity at this discharge rate.

These batteries were then put through the aforementioned 7 cycles of charge and discharge to determine if the additive produces improved performance on cycling.

The 7 cycles of charge and discharge were:

cycle	charge	discharge	date
1	5 amp for 10	300 amp to 3v; 200 amp to 3v; 100 amp to 3v	3/5/53
2	5 amp for 17	300 amp to 3v; 200 amp to 3v; 100 amp to 3v	3/6/53
3	5 amp for 18	300 amp to 3v; 200 amp to 3v; 100 amp to 3v	3/10/53
4	5 amp for 24	300 amp to 3v; 200 amp to 3v; 100 amp to 3v	3/12/53
5	5 amp for 38	300 amp to 3 v; 200 amp to 3v; 100 amp to 3v*	3/17/53
6	5 amp for 4	300 amp to 3v; 200 amp to 3v; 100 amp to 3v*	3/20/53
7	50 amp for 42	300 amp to 3v; 200 amp to 3v; 100 amp to 3v*	3/25/53

* - Also subsequently discharged at 5 amp to 4.5 volts.

These tests involve (a) 3 treated trays containing two batteries each and 3 untreated trays containing two batteries each and (b) 4 treated and 4 untreated batteries from 4 trays each containing one treated and one untreated battery.

Battery 22 of tray 11 was treated with $MgSO_4$ and Na_2SO_4. Hence, the data from tray 11 has not been used in what follows. (The full charge and discharge are given in Appendix 2 Table 4.)

(2) Total watt hour output. The total watt hour output at the 300, 200, and 100 amp discharge rates summed over all 7 cycles gave

Total for Treated : 7,467.9 watt hours
Total for Untreated: 7,456.5 watt hours

Table 7 gives the total of the output at the 300, 200 and 100 amp discharge rates for each battery. The observed difference in the total output between the treated and untreated batteries is neither persistent enough nor of sufficient size to be regarded as statistically significant.

Table 7: Total Watt-hours Delivered by June 1952 Test Batteries at 300, 200, and 100 Amperes Discharge Rate on 7 Charge-Discharge Cycles.

Date of Discharge*

Battery	Mar. 5	Mar. 6	Mar. 10	Mar. 12	Mar. 17	Mar. 20	Mar. 25	Total
				TRAY COMPARISONS				
1T	28.030	105.766	141.601	171.646	164.088	20.242	38.025	669.398
2T	30.558	110.665	141.636	192.769	201.485	25.036	39.553	741.702
11T	31.528	119.123	153.636	188.347	173.458	19.845	36.440	722.377
12T	33.507	125.698	165.244	206.840	218.713	21.565	39.839	811.406
13T	23.193	102.942	146.633	180.492	195.649	24.130	41.714	714.753
14T	24.410	108.043	147.373	182.177	197.380	24.650	41.784	725.817
3U	25.538	114.806	154.726	194.703	207.413	26.031	40.918	764.135
4U	24.187	112.038	150.493	182.451	189.052	22.465	35.915	716.601
5U	22.848	103.763	134.290	169.574	174.825	22.610	38.642	666.552
6U	22.205	104.152	139.268	176.410	189.307	26.264	41.309	698.915
15U	24.640	112.372	162.553	184.617	194.103	36.559	65.774	780.618
16U	25.194	113.043	164.530	199.983	195.130	27.670	48.450	774.000
Totals:								
T	171.226	672.237	896.123	1122.271	1150.773	135.468	237.355	4385.453
U	144.612	660.174	905.860	1107.738	1149.830	161.599	271.008	4400.821
				BATTERY COMPARISONS				
23T	11.866	135.019	175.230	203.662	206.137	22.777	44.527	799.218
24U	11.832	138.718	179.183	210.111	208.563	26.808	49.022	824.237
27T	35.209	132.286	172.645	204.296	208.450	22.190	38.445	813.521
28U	28.663	135.055	170.288	202.021	206.258	28.735	47.820	818.840
30T	49.848	152.237	182.978	209.552	210.491	21.288	43.045	869.439
29U	46.129	150.255	180.921	193.768	189.587	26.598	55.647	842.905
32T	31.957	93.603	113.245	133.353	160.293	25.588	42.269	600.308
31U	27.834	98.464	114.887	132.271	136.733	21.622	37.925	569.736
Totals:								
T	128.880	513.145	644.098	750.863	785.371	91.843	168.286	3082.486
U	114.458	522.492	645.279	738.171	741.141	103.763	190.414	3055.718
Grand Totals:								
T	300.106	1185.382	1540.221	1873.134	1936.144	227.311	405.641	7467.939
U	259.070	1182.666	1551.139	1845.909	1890.971	265.362	461.422	7456.539

*for charge-discharge schedule see text page 3.28.

(3) Watt hour output at 300 amp discharge rate

Table 8 gives the watt hour output of each battery at the 300 amp discharge rate. The total output summed over all 7 cycles is

for treated : 4231.565.
for untreated: 4352.943.

This phenomena of a reduction in output at the 300 amp rate when the additive is present was observed on the June 1952. test. The variability of the results is so great that the observed difference cannot be regarded as statistically significant.

Table 8: Watt Hours Delivered by June 1952 Test Batteries at 300 Ampere Discharge Rate on 7 Charge-Discharge Cycles after 8 Months Storage.

Battery	Date of Discharge: Mar. 5	Mar. 6	Mar. 10	Mar. 12	Mar. 17	Mar. 20	Mar. 25	Total
TRAY COMPARISONS								
1T	5.190	32.555	57.490	76.165	75.355	4.885	10.685	262.325
2T	7.995	49.250	68.970	102.055	110.815	5.740	13.790	358.615
11T	11.825	64.620	79.380	94.300	82.900	3.400	8.230	344.655
12T	15.550	69.525	106.705	145.760	156.370	7.460	18.600	519.970
13T	3.950	45.935	86.015	122.030	138.235	8.365	19.675	424.205
14T	5.990	49.665	89.295	126.805	141.690	7.915	19.535	440.895
3U	9.175	56.840	99.220	140.010	148.415	13.225	21.935	488.820
4U	6.535	45.705	71.250	98.635	102.565	6.450	11.650	342.790
5U	2.995	38.430	66.900	95.030	85.240	6.150	12.870	307.615
6U	2.835	38.775	72.650	108.520	123.640	11.180	19.840	377.440
15U	11.240	69.820	118.775	143.715	152.280	19.105	36.275	551.210
16U	12.735	72.240	122.780	156.055	154.365	16.755	29.545	564.475
Totals:								
T	50.500	311.550	487.855	667.115	705.365	37.765	90.515	2350.665
U	45.515	321.810	551.575	741.965	766.505	72.865	132.115	2632.350
BATTERY COMPARISONS								
23T	2.445	84.820	117.540	139.460	143.235	6.790	20.995	515.285
24U	2.343	86.095	121.160	143.545	144.985	12.235	24.705	535.068
27T	14.655	86.660	123.720	152.640	151.605	8.720	20.220	558.220
28U	12.940	96.555	123.290	157.200	159.325	17.065	28.455	594.830
30T	20.580	95.480	127.950	149.175	151.245	4.580	19.180	568.190
29U	19.010	92.795	84.475	86.055	85.440	9.805	20.465	398.045
32T	9.395	32.480	44.555	61.155	74.700	4.550	12.370	239.205
31U	5.520	27.375	35.970	49.890	57.745	4.560	11.590	192.650
Totals:								
T	47.075	299.440	413.765	502.430	520.785	24.640	72.765	1880.900
U	39.813	302.820	364.895	436.690	447.495	43.665	85.215	1720.593
Grand Totals:								
T	97.575	610.990	901.620	1169.545	1226.150	62.405	163.280	4231.565
U	85.328	624.630	916.470	1178.655	1214.000	116.530	217.330	4352.943

1.8 The Visual and Manual Inspection.

As indicated in Section 1.3(c), four batteries (Nos. 7, 8, 9, 10) were set aside from line 1 after charge, for visual and manual inspection; also four batteries (Nos. 17, 18, 19, 20) from line 2, and two batteries (Nos. 25, 26) from line 3, for the same purpose. These batteries, along with those used in the electrical tests, were approved by the manufacturer himself as acceptable for these tests, on the basis of inspection prior to charging. (See Section 1.1 and 1.3(b)).

On June 11, 1952, in Building 49, NBS, the aforementioned ten batteries were intercompared by visual and manual inspection with respect to the following six characteristics:

(a) softness of positive plate
(b) softness of negative plate
(c) adherence
(d) warping*
(e) peroxidation
(f) general condition.

The manufacturer had claimed that:

"If truly sulphated batteries were used in the beginning the following results will be noted:

"Treated Batteries. The paste will be found to be soft and porous and the active material in both the positive and negative plates will be found to be in firm contact with the grids. There will be little peroxidation of the grids in the positive plates. There will be no warping or buckling of the plates and little shedding. The overall appearance of these batteries will indicate many months of useful service.

"Untreated Batteries. It will be noted that the positive grids are largely, if not entirely peroxided out in the positive plates and that the plates will disintegrate under pressure and twisting, ... The active material in the negative plates will be found to be pried loose from the grid which will cause it to be chunky and sandy. (The plates may or may not be warped.) Shedding of the active material from the plates will be considerably heavier than in the treated batteries. The condition of these batteries, if they were truly sulphated at the beginning, will show that they have little, if any, life expectancy, or they may be inert." (Quotations from manufacturer's discussion of test procedure. See Appendix 1).

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* In no instance was there any warping. Consequently all batteries were "=" in this respect, and this characteristic has been omitted from further consideration in the analysis.

A total of 9 judges completed the full inspection program, as follows: the manufacturer himself and an assistant, 2 NBS battery experts, 3 battery experts from other Government agencies, and 2 NBS scientists without previous battery test experience.*

No statistically significant indication of any real difference was found between the five batteries that were treated and the five untreated controls. The manufacturer and his assistant, who conferred with each other from time to time during the inspection, each so ranked the batteries that there was a perfect balance between the treated and untreated batteries: the probability is exactly 1/2 of obtaining a ranking equal to or more favorable to treated by purely random "blindfold" sorting. The 5 Government experts, on the other hand, all gave to untreated a slight edge over the treated, but their leanings were not sufficiently pronounced to be statistically significant at the (two-sided) 0.05-probability level.

(a) Experiment Design and Procedure. Each battery was compared with every one of the other nine batteries by each of the nine judges who completed the program — a total of 45 direct comparisons by each judge.**

The batteries were presented in nine groups of five pairs each, as shown in the first column of the Raw Data Tally Sheets given in Appendix 2 , where the battery numbers have been replaced by the letters A to J.*** These groups form a balanced incomplete block design (see W. G. Cochran and Gertrude M. Cox, Experimental Designs [John Wiley and Sons, Inc., New York, 1950] Chapter 11, and especially Plan 11.14 on page 331.)

The comparisons called for in the first five groups were carried out in every case in terms of the middle cells of the batteries concerned — e.g. in the case of batteries A and E, which were in the same tray, the 2nd and 5th cell counting

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* Two additional NBS scientists without previous battery testing experience participated in the early stages of the inspection program but were obliged to leave before they had completed their inspection, on account of previously arranged conflicting engagements. Their judgments have been excluded in the analysis.

** Since 5 treated and 5 untreated batteries were involved, there were in all $C_2^{10} = 10 \cdot 9/2 = 45$ different paired comparisons, of which $5 \cdot 5 = 25$ instances involved unlike batteries (treated vs untreated) and 20 involved like batteries (treated vs treated, 10 instances; untreated vs untreated, 10 instances).

*** The key is:

Letter	A	B	C	D	E	F	G	H	I	J
	25	9	8	10	26	17	7	20	19	18

The battery numbers corresponding to treated batteries are underscored here and in the remainder of this section, as an aid to the comprehension of the results portrayed.

from one end of the tray; and in the last four comparisons the cells corresponding to central tray positions — e.g. in the case of batteries A and E, the 3rd and 4th from the end.

Prior to the first group of comparisons, the top (say, the "0th") negative plates of the (middle) cells of each of the ten batteries were removed, and the battery pairs arranged in pans on three tables. Thus, in the 1st group, battery pairs A,B and C,D were on one table; pairs E,F and G,H on another; and I,J on a third.

By visual and manual (e.g. tactual) examination, each judge in turn then compared the top (the 1st) positive plate of (the middle cell of) battery A, say, with the top positive plate of (the middle cell of) battery B; and the next negative plate (say, the "1st") on battery A with the corresponding negative plate of battery B; and so forth for the other comparisons in this first group. All nine of these (middle) cells were then returned to the base point, where they were reorganized into the pairs called for in the second group of comparisons, e.g. A was now paired with C, B with G, and so forth.

Before re-presentation for examination and comparison the positive and negative plates that had been examined were stripped from the cell units. Thus, the second group of comparisons was carried out in terms of the 2nd positive and "2nd" negative plates of the (middle) cells of the respective batteries. Similarly for the 3rd, 4th, and 5th groups of comparison, the 5th expending the bottommost positive and negative plates of these middle cells of the respective batteries. Consequently, the 6th group of comparisons was carried out in terms of the 1st positive and "1st" negative plates of tray-wise central cells from each of the ten batteries; and so forth, for the 7th, 8th, and 9th groups of comparisons.

Between each group of comparisons the cell units were carried back to the "base point" where they were readied for the next group of comparisons. Removal of the plate groups (i.e. positive plate, separator, and negative plate) from the batteries at the "base point" was performed by personnel of the Electrochemical Section, NBS. The pairing of the plate groups at each successive stage of the inspection program, and their arrangement on the tables was supervised by a representative of the Statistical Engineering Laboratory, NBS, who assisted with carrying the pans to and from the "base point." None of the judges was permitted to visit the "base point" prior to, during, or immediately following the inspection test — so that no judge could note which cell units were from a single tray, and which were from different trays, or gain any other ancillary information that might possibly help him in his decisions. As was stated previously: Which of the batteries

had been treated, and which had not, was not known to any one of the persons participating in, or present during the carrying out of, either the electrical or the inspection tests.

(b) Tallies and Scoring. For each comparison each judge indicated on his tally sheet by the appropriate letter which battery, if either, was in his opinion superior in regard to each of the six characteristics, respectively, recording an "=" in the case(s) of characteristics on which neither battery was superior to the other. Thus in the case of the tallies of judge D (See Appendix 2 , Table 5), it is seen that A and B were judged to be equal on the first three characteristics, with A superior to B in respect to peroxidation and general condition. On the other hand, A was judged to be superior to C in respect to softness of both positive and negative plates, but was considered equal to C in all other respects, including general condition.

These symbolic tallies were subsequently converted to scores in the Statistical Engineering Laboratory, NBS, by assigning in each instance a "+1" to the battery favored on a particular characteristic and a "-1" to the other battery; or a "0" to each battery in the case of equality in respect to the characteristics concerned. These individual scores are given in Appendix 2, Tables 6.A - 6.I. Thus, on the basis of judge D's decisions Battery "A's" (i.e. Battery 25's) total scores on the five characteristics were +1, -2, 0, +1, and +1, respectively. The scores obtained by each battery on each characteristic are tabulated, by judges, in Appendix 2, Table 7.

(c) Over-all Ranking of the Batteries. Summing the scores a particular battery received on each characteristic, over all characteristics and all judges, and then ranking the resultant sums from lowest (1) to highest (10), yields the following:

Over-all Ranking of Batteries on Basis of Scores Summed Over All Characteristics and All Judges.

Rank	1	2	3	4	5	6	7	8	9	10
Battery	9	20	25	26	19	8	17	10	18	7

Sum of Ranks: Treated 27, Untreated 28.

Since the sum of all ten ranks must equal 55 in any case, it is evident that the partition (27.28), and its opposite (28.27) are the most nearly equal divisions possible. In the present instance, the untreated received the larger of the two rank sums; but no importance can be attached to this event, since the probability is exactly 1/2 of obtaining by chance a ranking as favorable or more favorable to the untreated.

The scores that the respective batteries received on a given characteristic as the result of the tallies of a particular judge are given for each characteristic, by judges, in Table 7 of Appendix 2.

The differences in spread (i.e., range) of the scores assigned to the batteries by the respective judges are considerable. Thus, on the basis of judge B's tallies, his "winner" (7) received a total score of +45; and 9 and 20 tied for "worst" with scores of -25, making the total spread 70 units. Judge A's scores ran similarly from +34 (for 7) to -24 (for 20), giving a spread of 58 units. On the other hand, D's scores ran from +4 (for 17) to -8 (for 7), a spread of only 12 units; and F's scores ran from +4 (for 10) to -6 (for 7), a spread of only 10 units. It may, therefore, be correctly argued that the top ranking for 7 given above is due in large part to the fact that A and B, who happened to favor 7 (which three other judges considered to be "worst"), by avoiding "=" tallies almost entirely, succeeded in achieving wide spreads to their scores; and their scores tend, therefore, to dominate the situation.

The influence (on the over-all ranking of the batteries) of the difference in the spreads of the scores assigned by the individual judges can be effectively reduced by first ranking the batteries on each characteristic as determined by a particular judge's scores, summing these ranks for a given battery, over all characteristics and all judges, and then ranking the resultant sums. This yields the following:

Over-all Ranking of Batteries on Basis of Ranks on Each Characteristic by Each Judge, Summed over All Characteristics and All Judges.

Rank	1	2	3	4	5	6	7	8	9	10
Battery	25	9	20	26	19	8	17	18	7	10

Sum of Ranks: Treated, 27; Untreated, 28.

Although these over-all rankings differ a bit from those given previously the rank sums for treated and untreated are exactly the same. Clearly the panel of 9 judges was unable to discriminate between the treated and untreated batteries, taking all characteristics into account.

(d) Rankings by the Individual Judges. The rankings of the respective batteries in terms of the total scores received on the basis of the tallies of each individual judge is as shown in Table 9 hereinafter. In only three of the nine instances is the rank sum for the treated larger than the rank sum for the untreated; and the corresponding probabilities of obtaining

TABLE 9. Judges' Rankings of the Batteries on Basis of Scores Summed Over All Characteristics

Group and Judge	Rank 1	2	3	4	5	6	7	8	9	10	Sum of Ranks Treated	Untreated	P**
I*													
A	20	9	25	19	26	17	10	8	18	7	28	27	.500
B	20	9	25 26			8 10 17 19			18	7	28	27	.500#
II													
C	20	19	17	26		8 10 18		25	9	7	23	32	.845
D	7		8 18 19			9 25 26		10 20		17	21.5	33.5	.907#
III													
E	26	9	7 25		8	19	17 20		18	10	23	32	.845
F	7		9 19 25		17 20		8	18 26		10	25	30	.726
G	7		9 20 25		26	8 18		19	10	17	23.5	31.5	.817
IV													
H	25	26	7	18		20	8	9 10		17	22.5	32.5	.867
I	19 25 1		10 17 1	19	9	26	8	1 7 18 1		20	33	22	.155

* I. The Manufacturer and his Assistant; II. NBS Battery Experts; III. Battery Experts from other Government Agencies; IV. NBS Scientists without previous battery testing experience.

** P = probability of obtaining by chance a rank sum equal to or exceeding that observed for "treated."

\# See Section 1-8(f), hereinafter.

by chance a ranking equally or more favorable to the treated are 0.5, 0.5, and 0.2, as indicated in the last column of the table. Clearly there is no significant evidence here in favor of the treated; nor in favor of the untreated. It may be noted, however, that all 5 of the Government battery experts tended to favor untreated over the treated, although in each case the tendency was only slight — and collectively is not statistically significant.

If ranks on each characteristic, rather than scores, are summed over all characteristics for each judge, the judges' rankings given in Table 10 result. Although there are some changes in individual rankings, the picture here is essentially the same as before.

(e) Rankings of the Batteries on Individual Characteristics. The rankings of the respective batteries on each of the five characteristics showing variation, based on the total scores obtained on the respective characteristics from the tallies of all nine judges, are given in Table 11 ; and Table 12 gives the corresponding rankings based on sums of the judges' rankings on the respective characteristics, to reduce the effect to score spreads on the final result. From a comparison of these two tables it is evident that the rankings are somewhat sensitive to the method of derivation. In no case, however, is the evidence significantly in favor of either the treated or the untreated.

(f) Statistical Significance of Results. The technique employed above for judging statistical significance is due to Dr. Frank Wilcoxon, "Individual comparisons by ranking methods," Biometrics Bulletin, vol. 1, no. 6 (December 1945), pp.80-83; and has been considered somewhat more fully by H. B. Mann and D. R. Whitney, "On a test of whether one of two random variables is stochastically larger than the other," Annals of Mathematical Statistics, Vol. 18, no. 1 (March 1947), pp.50-60. The probabilities given in connection with Tables 9-12 were taken directly from Table I of Mann and Whitney in the case of integer rank sums, and in the case of fractional rank sums were calculated by linear interpolation between the adjacent integer values. For 5 items of each kind, these probabilities are:

Probability of Obtaining by Chance a Rank Sum Equal to or Greater Than T When 5 Items of Each of Two Kinds are Ranked at Random.

T	15	16	17	18	19	20	21	22	23	24	25	26	27
Prob.	1	.996	.992	.984	.972	.952	.925	.889	.845	.790	.726	.655	.579

T	28	29	30	31	32	33	34	35	36	37	38	39	40
Prob.	.500	.421	.345	.274	.210	.155	.111	.075	.048	.028	.016	.008	.004

Taken directly from Table I in H. B. Mann and D. R. Whitney, "On a test whether one of two random variables is stochastically larger than the other ", Annals of Mathematical Statistics, 18, 50-60 (1947). Their table gives the "probability of obtaining a U not larger than that tabulated in comparing samples of [size] n and m", and for n=m=5, T = 4-U.

TABLE 10. Judges' Rankings of the Batteries on Basis of Ranks
Summed over all characteristics

Group and Judge		Rank 1	2	3	4	5	6	7	8	9	10	Sum of Ranks Treated	Untreated	P**
I*	A	20	9	25	19	26	17	10	8	18	7	28	27	.500
	B	9 20		25 26				8 10 17 19		18		28	27	.500
II	C	17 19		20	8	18	26	10	25	9	7	24.5	30.5	.758
	D	7	8	18		9 26	19	20	25	10 17		20.5	34.5	.938
III	E	26	25	7	9		8 19	17	18	20	10	24	31	.790
	F	19			8 7 17 20			7 9	26	18	10	23.5	31.5	.817
	G	25	9	20	7	26	18	8	17	19	10	28	27	.500
IV	H	25	26	18		7	20	8	10	9	17	23.5	31.5	.817
	I	25	17	10	19 9	19		8 18 26		7	20	38	17	.016

* I. The manufacturer and his assistant; II. NBS Battery Experts; III. Battery Experts from other Government Agencies; IV. NBS Scientists without previous battery testing experience.

** P = probability of obtaining by chance a rank sum equal to or exceeding that observed for "treated."

TABLE 11 Rankings of the Batteries on Individual Characteristics, on the Basis of Total Scores

Characteristics	Rank 1	2	3	4	5	6	7	8	9	10	Sum of Ranks Treated	Untreated	P**
Softness of Positive Plate	9	26	20	25	17	8	19	18	10	7	28	27	.500
Softness of Negative Plate	26	9 25		19	20	10	17	8	18	7	28	27	.500#
Adherence	25	20	9 19		26	17	8	18	10	7	27.5	27.5	.500
Peroxidation	20	9	25	8 26		18	19	7	17	10	25	30	.726
General Condition	9	25	20	26	19	7	18	8 17		10	26.5	28.5	.617

**P = probability of obtaining by chance a rank sum equal to or exceeding that observed for "treated."

See Section 1.8 (F), hereinafter

TABLE 12. Rankings of the Batteries on Individual Characteristics, on Basis of Sums of Judges' Rankings

Characteristics	Rank										Sum of Ranks		P**
	1	2	3	4	5	6	7	8	9	10	Treated	Untreated	
Softness of Positive Plate	26	17 25		9	8	20	18	7	19	10	29	26	.421
Softness of Negative Plate	25 26		19	9	10	20	17	8	18	7	28.5	26.5	.460
Adherence	25	19	20	8	26	17	9	18	7	10	23	32	.845
Peroxidation	20	8	9	25	7 18		19	26	10	17	23.5	31.5	.817
General Condition	9	25	7	20	26	18	19	17	8	10	28	27	.500

** P = probability of obtaining by chance a rank sum equal to or exceeding that observed for "treated."

As a check on the accuracy of the "interpolation method" when ties are present, the exact probabilities of obtaining a rank sum greater than or equal to T were calculated by direct enumeration, for the following cases.

Observed Ranks	T	P exact	P approx.
$1\frac{1}{2}$, $1\frac{1}{2}$, $3\frac{1}{2}$, $3\frac{1}{2}$; $6\frac{1}{2}$, $6\frac{1}{2}$, $6\frac{1}{2}$, $6\frac{1}{2}$, 9, 10	28	.492	.500
1, 3, 3, 3, 6, 6, 6, $8\frac{1}{2}$, $8\frac{1}{2}$, 10	21.5	.929	.907
1, $2\frac{1}{2}$, $2\frac{1}{2}$, 4, 5, 6, 7, 8, 9, 10	28	.476	.500

The "interpolation method" seems to be quite satisfactory for practical purposes.

For an analysis of the preferences expressed in the 25 direct comparisons between treated and untreated (i.e. neglecting the 10+10=20 comparisons between like batteries) see Table 9 in Appendix 2.

Water Losses of Treated and Untreated Cells

The batteries listed in Table A are part of a group used in a test carried out in June 1952 and used in further tests in March 1953. The cells in these batteries were of the truck and tractor type, and are described elsewhere in this report. The batteries were assembled in trays and each tray contained two three-cell batteries. Prior to the tests in June 1952 five of ten trays were selected at random and each cell in those five trays was treated with the contents of 1½ envelopes of "AD-X2". The cells in the remaining five trays were not treated and served as controls throughout the tests. At the end of the tests in June 1952 the batteries in two treated trays and in two untreated trays, selected at random, were opened for inspection and the remaining six trays, three with treated cells and three with untreated cells were stored under identical ambient conditions until March 1953. At that time further capacity tests of these batteries were started.

Prior to the start of the charge on June 3, 1952 the electrolyte in each cell was raised to a fixed level by the addition of water and the quantity of water added to each cell thereafter is shown in Table A. Since the additive was added after the initial leveling of the electrolyte in June 1952, the volume increase of the electrolyte caused by the addition of the additive must be added to the measured water losses for the treated cells. Taking the volume of the electrolyte in each cell as 1000 ml the increase in volume of the electrolyte caused by the addition of the additive is 14 ml per cell. The increase in the total volume of the electrolyte produced by the additive in the 18 treated cells is, therefore, 252 ml. It is seen by the table that a total of 8,750 ml of water was added to the treated cells. This volume together with the 252 ml increase in volume caused by the addition of the additive gives 9,002 ml as the total loss in water for the treated cells, whereas the total loss in water for the untreated cells, as given in the table, is 9,110 ml. Therefore, the loss in water for the untreated cells was 108 ml greater than the loss for the treated cells. This difference, 1.2 per cent, even if real does not constitute a significant difference in normal battery operation.

After adding water to the cells on April 3, 1953 they were given an overcharge for 29 hours at 5 amperes. During this overcharge period the caps were not on the cells. The amounts of water required to bring the electrolyte to the reference level at the end of this period are shown in Table B. Since the cells were fully charged during this over-charge period the water required to bring the electrolyte to reference level on April 4th is a measure of the loss of water by electrolysis and the loss by spray. Each value given in the table for water loss is affected by the uncertainty in adjusting the electrolyte in each cell on April 3 and also on April 4. However, the precision of the measurement is sufficient to show that no significant difference exists between water and spray losses of treated and untreated cells even with the caps off.

Table A: Water Losses in Treated and Untreated Cells

TREATED CELLS

Batt. No.	Cell No.	Date of adding water 6/6 52 ml	6/7 52 ml	3/16 53 ml	3/31 53 ml	4/3 53 ml
1	1	166	70	160	54	100
	2	152	50	173	64	63
	3	132	45	150	50	73
2	1	132	65	186	46	78
	2	174	70	145	50	102
	3	150	70	145	49	94
11	1	122	85	143	49	93
	2	112	55	174	65	64
	3	139	80	145	34	100
12	1	125	75	147	54	88
	2	70	90	152	50	84
	3	122	75	120	53	85
13	1	135	65	134	54	87
	2	108	85	149	50	88
	3	125	60	158	47	95
14	1	121	60	134	34	100
	2	150	50	142	48	87
	3	131	65	145	61	74
Total ml		2366	1215	2702	912	1555

UNTREATED CELLS

Batt. No.	Cell No.	Date of adding water 6/6 52 ml	6/7 52 ml	3/16 53 ml	3/31 53 ml	4/3 53 ml
3	1	156	60	165	75	78
	2	142	80	157	70	65
	3	141	90	162	37	100
4	1	149	90	150	76	69
	2	130	90	160	52	82
	3	149	75	160	59	76
5	1	147	70	163	55	82
	2	135	80	158	82	59
	3	148	85	150	51	81
6	1	120	95	159	62	75
	2	148	60	158	67	69
	3	140	95	165	38	69
15	1	95	85	142	57	85
	2	116	95	148	54	95
	3	126	90	144	39	95
16	1	141	80	138	58	78
	2	106	80	148	46	100
	3	111	75	134	54	84
		2400	1475	2761	1032	1442

Total ml, Treated cells	8750
Vol. increased by additive	252
Water losses, ml	9002

Total ml, Untreated Cells	9110
Water losses, ml	9110

Difference 108 ml
Difference 1.2%

TABLE B WATER AND SPRAY LOSSES OF TREATED AND UNTREATED BATTERIES WITH CAPS OFF THE CELLS DURING AN OVERCHARGE-PERIOD OF 29 HOURS.
CHARGING RATE 5.0 AMPERES

	Treated Cells			Untreated Cells	
Battery	Cell	Loss ml	Battery	Cell	Loss ml
1	1	76	3	1	37
	2	84		2	57
	3	63		3	54
2	1	77	4	1	62
	2	64		2	72
	3	53		3	43
11	1	56	5	1	56
	2	82		2	63
	3	48		3	55
12	1	61	6	1	60
	2	74		2	71
	3	66		3	71
13	1	50	15	1	54
	2	67		2	57
	3	58		3	76
14	1	48	16	1	51
	2	56		2	65
	3	45		3	60
Total ml		1128			1064

Difference 64 ml
Difference 5.7 %

2. TESTS OF DISCARDED AUTOMOTIVE BATTERIES

In the preceding section, data were presented on 32 batteries of the truck or tractor type. These batteries were shelf-sulfated and on full charge reached a specific gravity of about 1.300. Contrary to the usual procedure, no preliminary determinations of the characteristics of the batteries prior to treatment with "AD-X2" were made; that is, their capacities and their full-charge specific gravities prior to treatment were not measured. These determinations were eliminated at the request of the manufacturer of "AD-X2" who stated that preliminary charging or cycling prior to treatment was to be avoided.

In this section, tests of 18 discarded automotive batteries are described. (These tests actually predated the ones described in the preceding section.) The characteristics of the batteries were determined prior to treatment with "AD-X2" and their specific gravities for the most part were below 1.280. The batteries were subjected to the so-called Randall "standard test for storage batteries". The "Randall test" is stated to be a severe one and one by which the beneficial effects of "AD-X2" may be shown. It consists of two parts: (A) Pre-test period and (B) Test after treatment. The 18 batteries used in this test were various sizes: six group 1, six group 2, four group 3, and two group 4, All 18 batteries were subjected to the "Randall test" as outlined below:

(A) <u>Pre-test Period</u>

(1) Fill each cell with water to proper level.
(2) Give an equalizing charge of 5 amperes, for at least 8 hours, recording the amperage, and individual cell voltages at intervals.
(3) Record open voltage and gravity of each cell.
(4) Discharge the battery at 300 amperes and record voltage of each cell at 30-second intervals until the voltage of highest cell has reached 1.7 volts. (<u>NBS note</u>: This cut-off is not realistic; many batteries will give an initial voltage less than 1.7 volts on a 300-amperes discharge. The initial voltage depends also on the size of battery. Even small new batteries will give an initial voltage less than 1.7; see Appendix 4).
(5) Discontinue discharge and record recovery of each cell at 30-second intervals. After 20 minutes take gravity of acid in each cell.
(6) (a) Leave positive cell untreated.
    (b) Treat middle cell with any product as desired.
    (c) Treat negative cell with "AD-X2" as directed on package. (<u>Note</u>: In this work only "AD-X2" was used. This was added to every alternate cell; i.e., "AD-X2" was added to the end cells of half of the batteries of each size and to center cell of the remaining batteries. Accordingly, 27 cells were treated with "AD-X2" and 27 cells were not treated. "AD-X2" was added during the first test charge.)

(B) Test After Treatment

(7) Charge at any rate up to 20 amperes, recording the time, amperage and voltage at regular intervals until hourly readings with hydrometer indicate full charge. Record voltage and hydrometer readings. (In this work the charge was terminated when the specific gravities, on the average, didn't show a change over a 2-hour period; on first cycle, charge of some was cut short of full charge so that those which had received a full charge were not overcharged. On second cycle, some batteries took the charge inefficiently; they were also cut short of full charge so that all batteries would receive the same input.)

(8)*Discharge at 300 amperes recording voltage at end of each 30-second interval until voltage of highest cell reaches 1.7; then continue discharge as long as rate can be held at 300 amperes. (Record voltage at 1-minute intervals. (See NBS note under A(4) above.)

(9)*Continue discharge at 200 amperes as long as possible and record voltage at 1-minute intervals.

(10)*Continue discharge at 100 amperes as long as possible and record voltage at 1-minute intervals.

(11)*Continue discharge at 50 amperes as long as possible and record voltage at 1-minute intervals.

(12) Discontinue discharge and record voltage recovery at 30-second intervals. (Note: Although these recovery voltages were recorded during test, they are not recorded in this report because they showed no significant difference between treated and untreated cells and were comparable to recovery voltages given in this report for the pre-test recoveries.)

(13) Repeat steps 7 to 12 as often as desired. (Repeated once in this test.)

(14) Allow the completely discharged battery step 11 to stand overnight and then repeat steps 8 to 12.

(15) Allow battery to stand overnight after step 12 and again put through discharge without charging (step 7).

(16) Charge up to 20 amperes and allow to overcharge at 20 amperes for 7 days.

(17) Make discharge as per steps 8 to 12.

(18) Observe level of water and gravity of each cell.

(19) Tear down battery and observe condition of plates in the three cells. Glass cell need not be torn down.

* Note that discharges are continued as long as rate can be held; in tests of preceding section terminal voltages were specified.

Detailed data on the pre-test and tests are given in Appendices 3a, 3b and 3c. It will be noted that nearly all of the cells of this group of batteries gave initial closed-circuit voltages lower than the 1.7-volt cutoff specified in the Randall pre-test. As stated on page 3.43 under (A)(4) this cutoff is not realistic; many batteries on the market will give an initial voltage less than 1.7 volts on a 300-ampere discharge. If, for example, the internal resistance of a battery were only 0.001 ohm, the IR drop would be 0.3 on a 300-ampere drain and if the open-circuit voltage (emf) were 2.0 volts the initial closed-circuit voltage would be 1.7 volts. In this work, for comparison purposes all cells, regardless of the initial closed-circuit voltage, were discharged for 90 seconds at 300 amperes in the pre-test.

Ampere hours and watt hours obtained at each stage of the discharge and for each cycle for each cell are given in tables in Appendix 3d. Cycle 3 refers to the discharge after the 7-day overcharge at 20 amperes. Appendix 3d also gives the total ampere hours and watt hours obtained for each cycle for each cell. The total ampere hours and total watt hours for all cells at a given discharge rate are given in table 15 for treated and untreated cells. The treated cells gave about 7 percent less ampere hours and watt hours than the untreated cells.

The specific gravities of the untreated and treated cells during the test charges are given in Appendix 3. Average values for treated and untreated cells are given in figures D1 to D5B, inclusive. Inspections of the figures do not indicate any significant difference in the rate of increase in specific gravity or temperature between treated and untreated cells during charge (the untreated cells, on the average, show a somewhat greater rate of increase in specific gravity indicating that the untreated cells receive the charge more efficiently). The almost constant difference in specific gravity between treated and untreated cells as shown in the figures is that produced when "AD-X2" is added to the battery electrolyte (see table 13 for the effect of addition of one envelope of "AD-X2" to one liter of sulfuric acid solutions of different specific gravities).

The magnitude of the ampere hours and watt hours obtained after the overnight stand (step 14) was small for both treated and untreated cells and step 15, therefore, was not done. Step 14 showed no beneficial effect from the additive (see table 14), in other words treated cells do not recuperate or retain charge more effectively than untreated cells.

The ampere hours and watt hours obtained for the treated cells after the 7-day overcharge were 16.7% and 14.8%, respectively, lower than the ampere hours and watt hours obtained for the untreated cells. One must conclude, therefore, that "AD-X2" does not have a beneficial effect on batteries during overcharge periods (see table 14), nor remove the detrimental effects generally associated with prolonged overcharging.

The results of this complete test which was proposed by Dr. Merle Randall, a consultant to the manufacturer of "AD-X2", are in favor of untreated batteries and have revealed no beneficial effect of "AD-X2" on battery performance.

A summary of total ampere hours and total watt hours obtained at various drain rates for 27 treated cells and 27 untreated cells are given in table 15. A summary giving the total ampere hours and total watt hours obtained at all drain rates are given in table 14.

After termination of the tests all batteries, excepting batteries 31 to 36 inclusive were opened and inspected. The plates of treated and untreated cells had a similar appearance. The sediment was completely removed from the cells of all inspected batteries, washed in water and introduced into similar test tubes. Photographs of these are shown as figures bearing the battery numbers. It can be seen that there is no significant difference in the amount of sediment in treated or untreated cells, and what small difference there is favors the untreated cells,

Table 13 . Effect of Addition of AD-X2 on the Specific Gravity of Solutions of Sulfuric Acid

Specific gravity of acid without Ad-X2		Specific gravity of acid with AD-X2		Difference
1.300	(25.3°C)	1.314	(21.8 g)	0.014
1.297	(26.1°C)	1.311	(23.0 g)	.014
1.201	(25.8°C)	1.216	(22.7 g)	.015
1.197	(24.2°C)	1.211	(22.5 g)	.014
1.104	(24.0°C)	1.118	(21.4 g)	.014
1.102	(25.4°C)	1.118	(25.8 g)	.016
1.050	(23.5°C)	1.068	(26.7 g)	.018
1.049	(22.8°C)	1.065	(23.1 g)	.016
1.009	(23°C)	1.030	(25.3 g)	.021
1.0025	(22°C)	1.0215	(22.8 g)	.019
1.000**	(23.1°C)	1.019***	(23.9 g)	.019

*Grams AD-X2 added to one liter of sulfuric acid of specific gravity given in first column; amount of AD-X2 varies from one envelope to another.

**Pure water.

***This solution has a pH of 8.1 at 23°C; additive, therefore contains an alkaline ingredient which would be neutralized by the sulfuric acid electrolyte. Solution was made with water having a resistivity of 1,700,000 ohm-centimeters.

TABLE 14: Summary data on ampere-hour and watt-hour capacities of treated (AD-X2) and untreated discarded batteries.

Batteries	Treated (Sum of 27 cells)	Untreated (Sum of 27 cells)	$\% = \frac{T-U}{(T+U)/2}$
		Ampere Hours*	
1,3,4,5,6,7	1023.2	999.0	+ 2.4
10,12,13,17,18,19	1324.0	1487.0	-11.6
31,32,33,34,35,36	1301.3	1435.1	- 9.8
Total	3648.5	3921.1	- 7.2
		Watt Hours*	
1,3,4,5,6,7	1495.5	1419.3	+ 5.2
10,12,13,17,18,19	1540.6	1765.2	-13.6
31,32,33,34,35,36	1603.7	1816.2	-12.4
Total	4639.8	5000.7	- 7.5
		Ampere Hours (overnight stand)*	
1,3,4,5,6,7	43.2	52.3	-19.1
10,12,13,17,18,19	79.3	100.9	-23.9
31,32,33,34,35,36	43.2	49.5	-13.6
Total	165.7	202.7	-20.1
		Watt Hours (overnight stand)*	
1,3,4,5,6,7	56.1	61.0	- 8.3
10,12,13,17,18,19	82.3	99.0	-18.4
31,32,33,34,35,36	50.9	59.8	-16.0
Total	189.3	219.8	-14.9
		Ampere Hours (overcharge)*	
1,3,4,5,6,7	374.7	298.2	+22.7
10,12,13,17,18,19	116.4	195.7	-50.8
31,32,33,34,35,36	383.6	540.1	-33.9
Total	874.7	1034.0	-16.7
		Watt Hours (overcharge)*	
1,3,4,5,6,7	583.6	452.7	+25.2
10,12,13,17,18,19	143.8	240.6	-50.4
31,32,33,34,35,36	460.6	684.3	-39.0
Total	1188.0	1377.6	-14.8

*Sums of outputs at all rates of discharge.

TABLE 15

Summary Table Giving Total Ampere Hours and Total Watt Hours for All Discharges At Various Drain Rates For 27 Treated (AD-X2) and 27 Untreated Cells.

Ampere Rate	300			200			100			50		
				Ampere Hours								
Batteries	T	U	%	T	U	%	T	U	%	T	U	%
1,3,4,5,6,7	536.1	497.7	7.4	108.4	126.0	-15.0	213.3	211.6	0.8	165.4	163.7	1.0
10,12,13,17,18,19	689.2	762.1	-10.2	147.5	208.6	-34.3	245.4	263.9	- 7.3	241.9	252.4	- 4.2
31,32,33,34,35,36	668.7	687.9	- 2.8	98.0	133.0	-30.3	237.1	272.7	-14.0	297.5	341.5	-13.8
Total for 27 Cells	1894.0	1947.7	- 2.8	353.9	467.6	-27.7	695.8	748.2	- 7.3	704.8	757.6	- 7.2

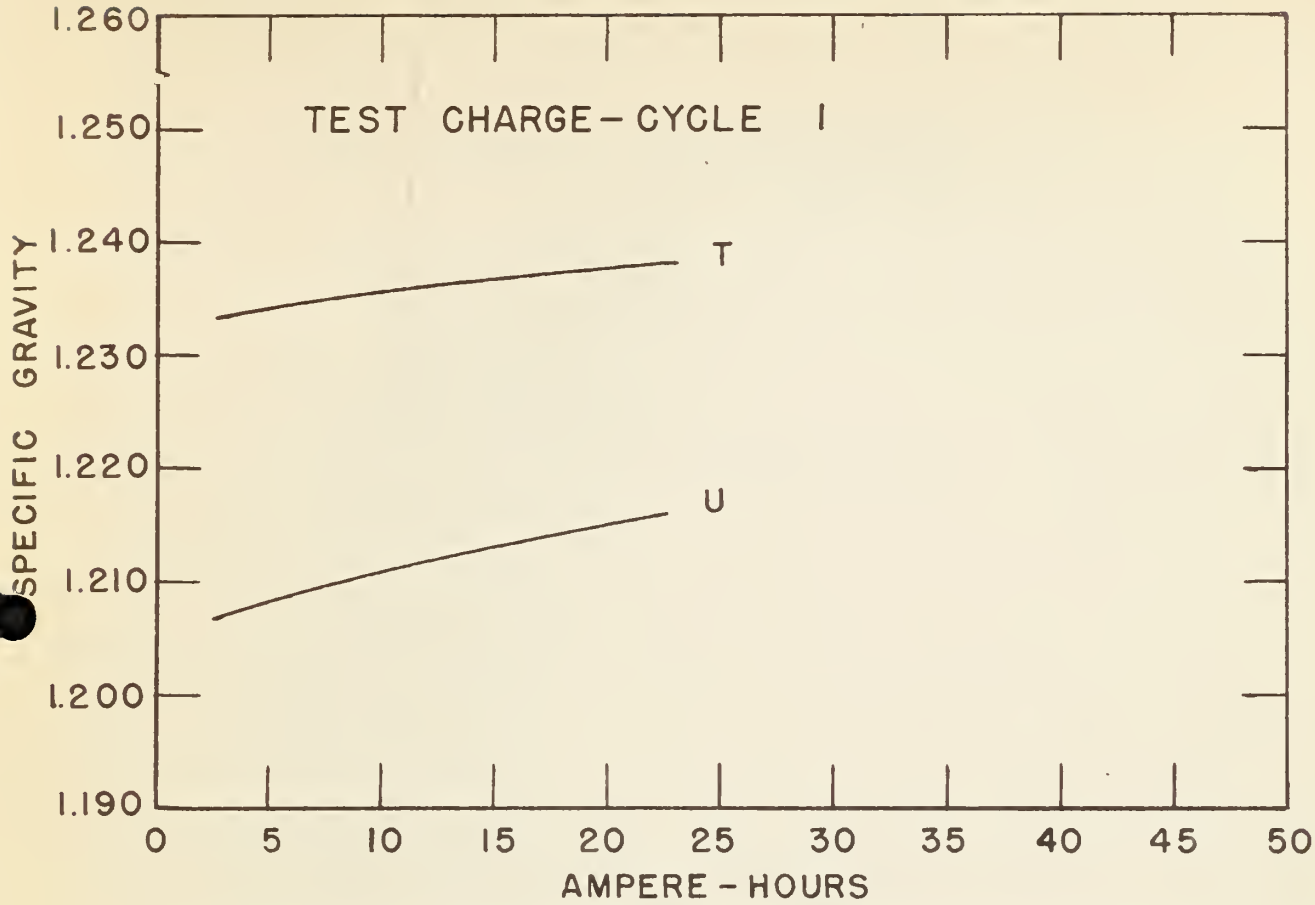
NOTE: $\% = \dfrac{A.H._{T.} - A.H._{U.}}{(A.H._{T.} + A.H._{U.})/2}$

				Watt Hours								
1,3,4,5,6,7	865.6	790.1	9.1	166.6	154.9	7.3	294.4	281.7	4.4	168.9	192.6	-13.1
10,12,13,17,18,19	941.1	1080.5	-13.8	151.4	210.4	-32.6	256.6	255.9	0.2	191.5	218.4	-13.1
31,32,33,34,35,36	957.2	996.2	- 4.0	112.5	165.0	-37.8	249.1	324.0	-26.1	284.9	331.0	-15.0
Total for 27 Cells	2763.9	2866.8	- 3.7	430.5	530.3	-20.8	800.1	861.6	- 7.4	645.3	742.0	-13.9

NOTE: $\% = \dfrac{W.H._{T.} - W.H._{U.}}{(W.H._{T.} + W.H._{U.})/2}$

FIGURE D1

AVERAGE OF CELLS IN BATTERIES 1,3,4,5,6 & 7



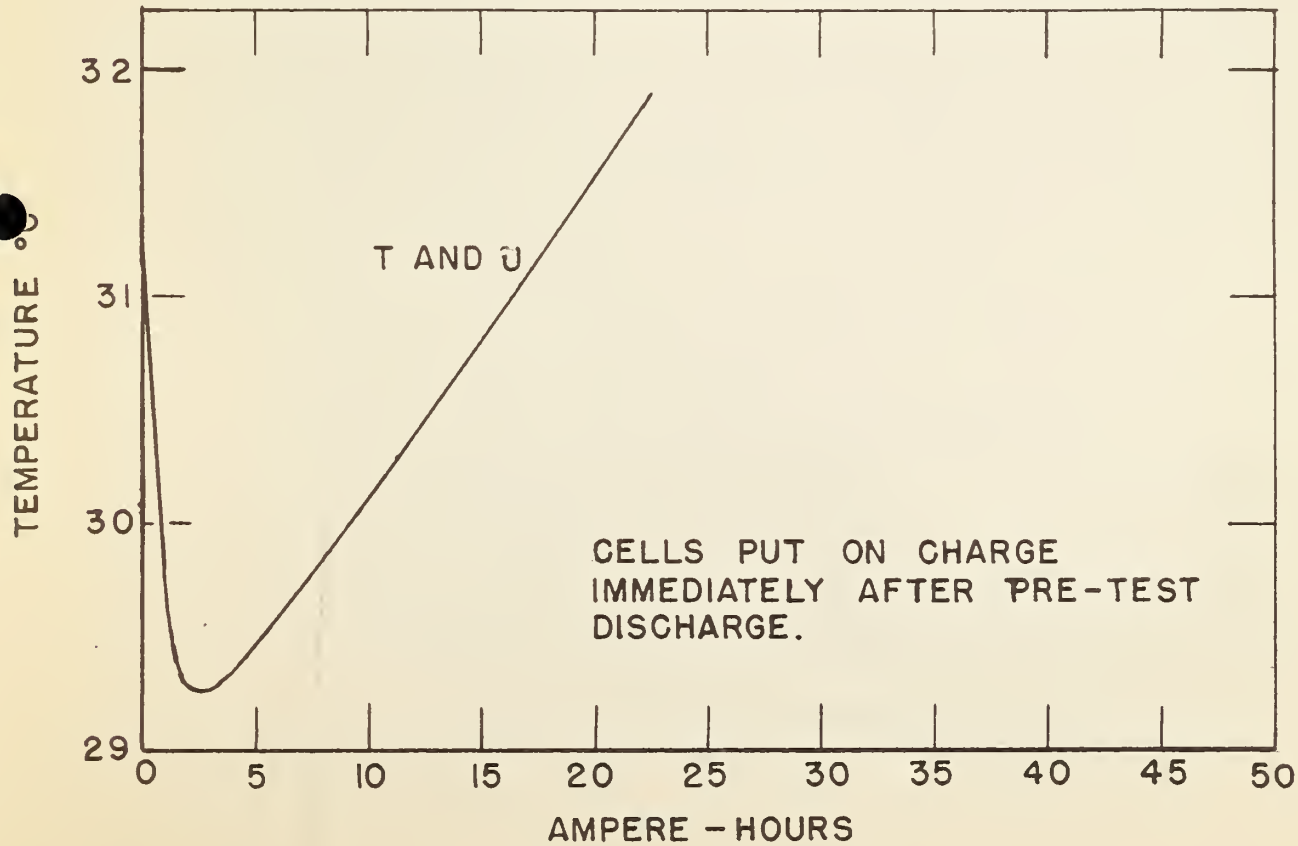
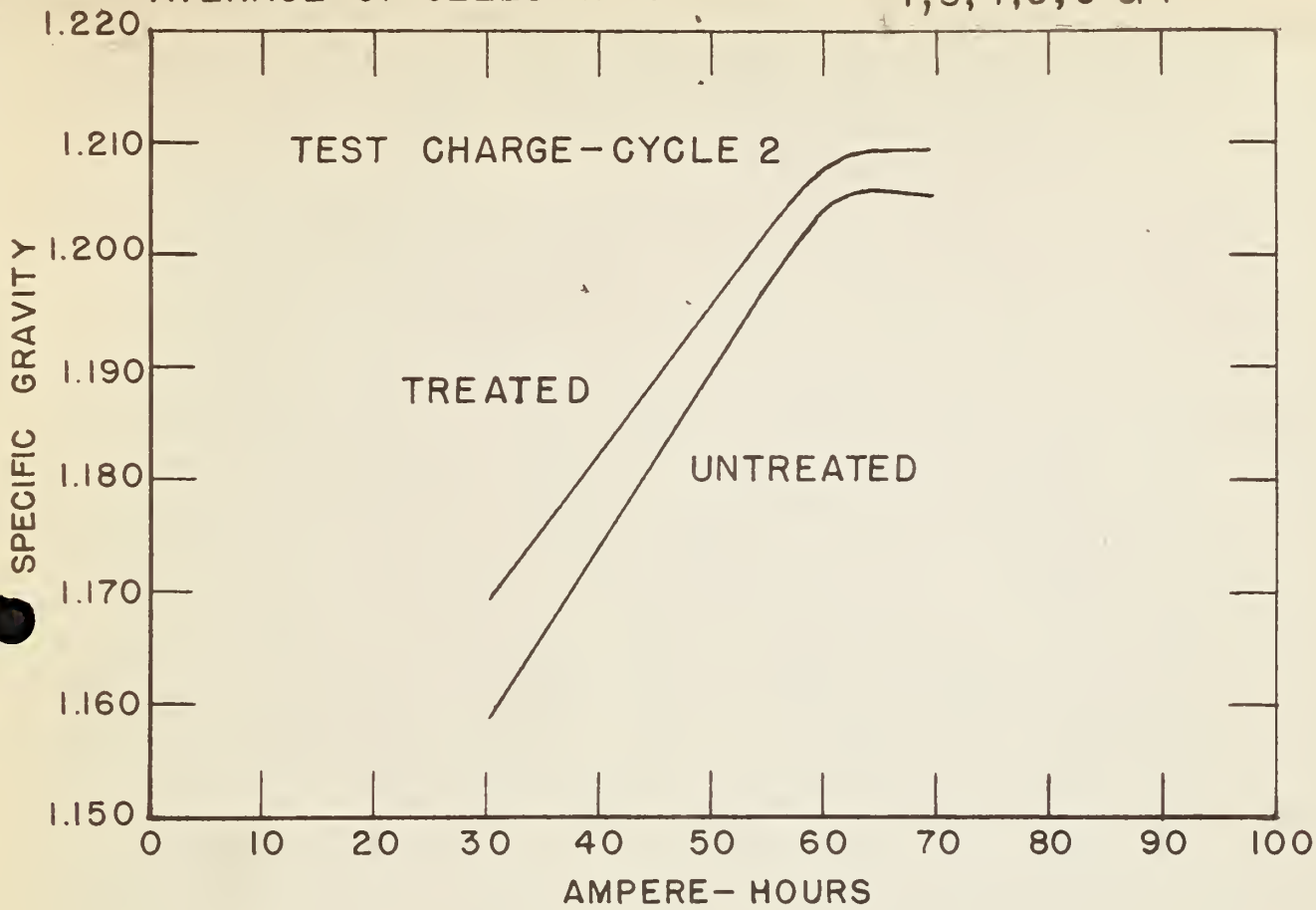
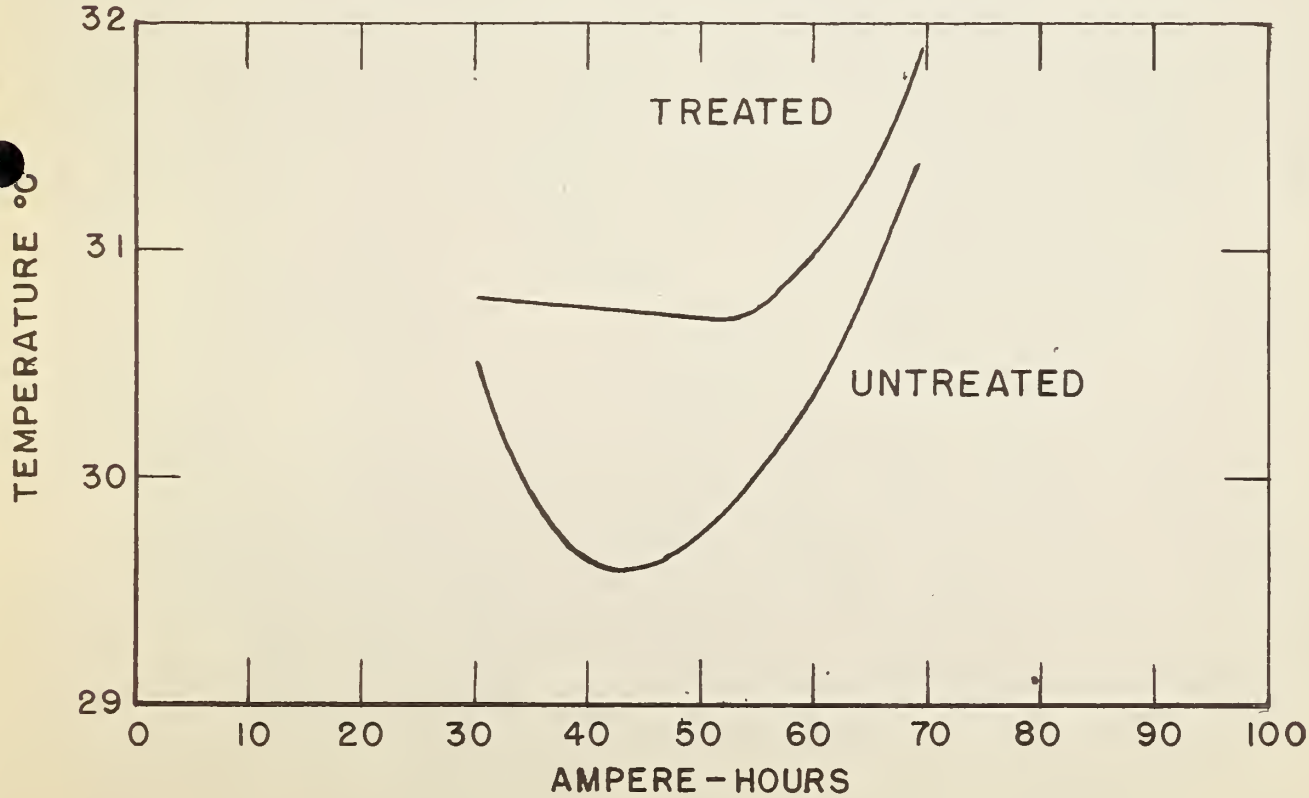


FIGURE D2

AVERAGE OF CELLS IN BATTERIES 1,3,4,5,6 & 7





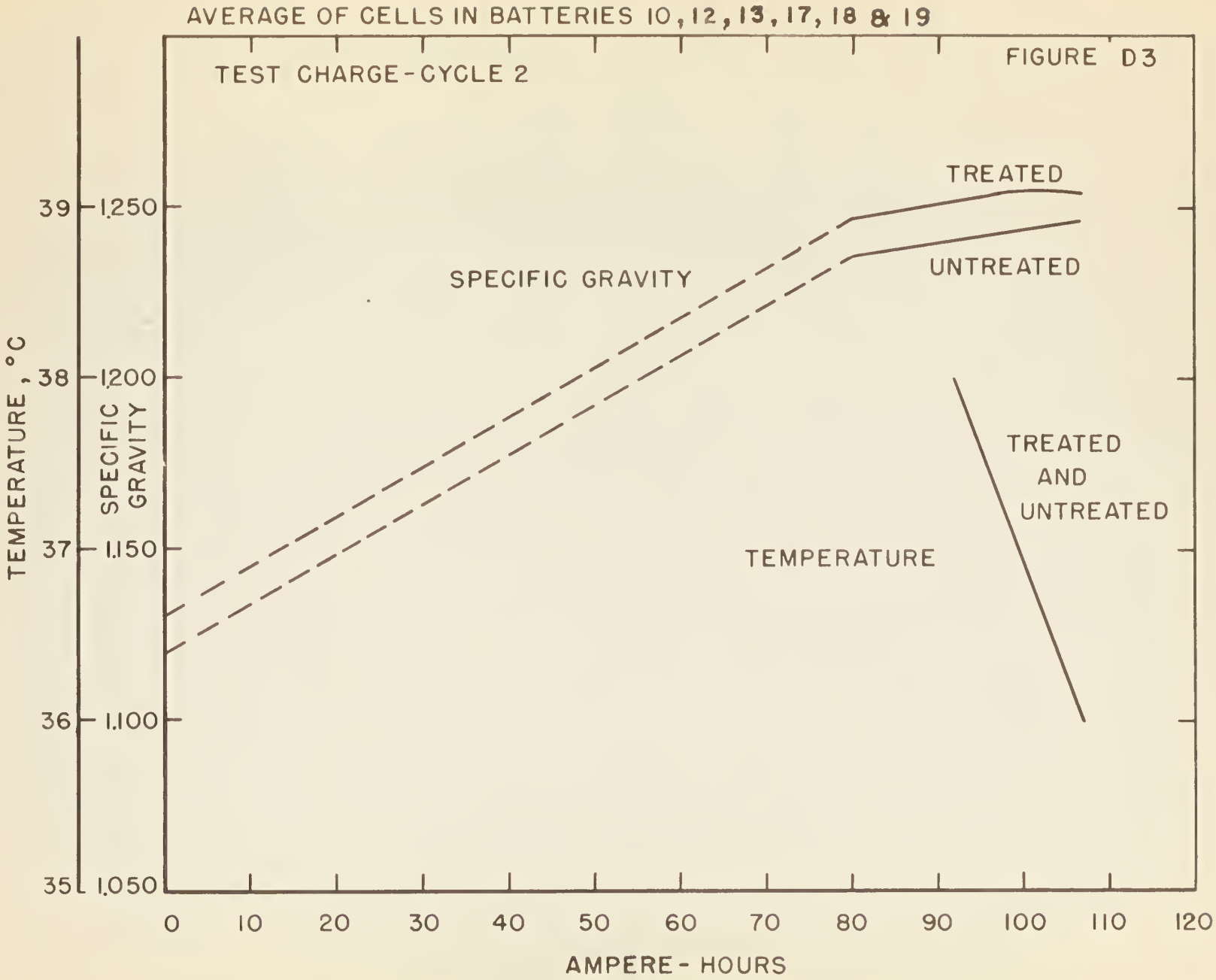
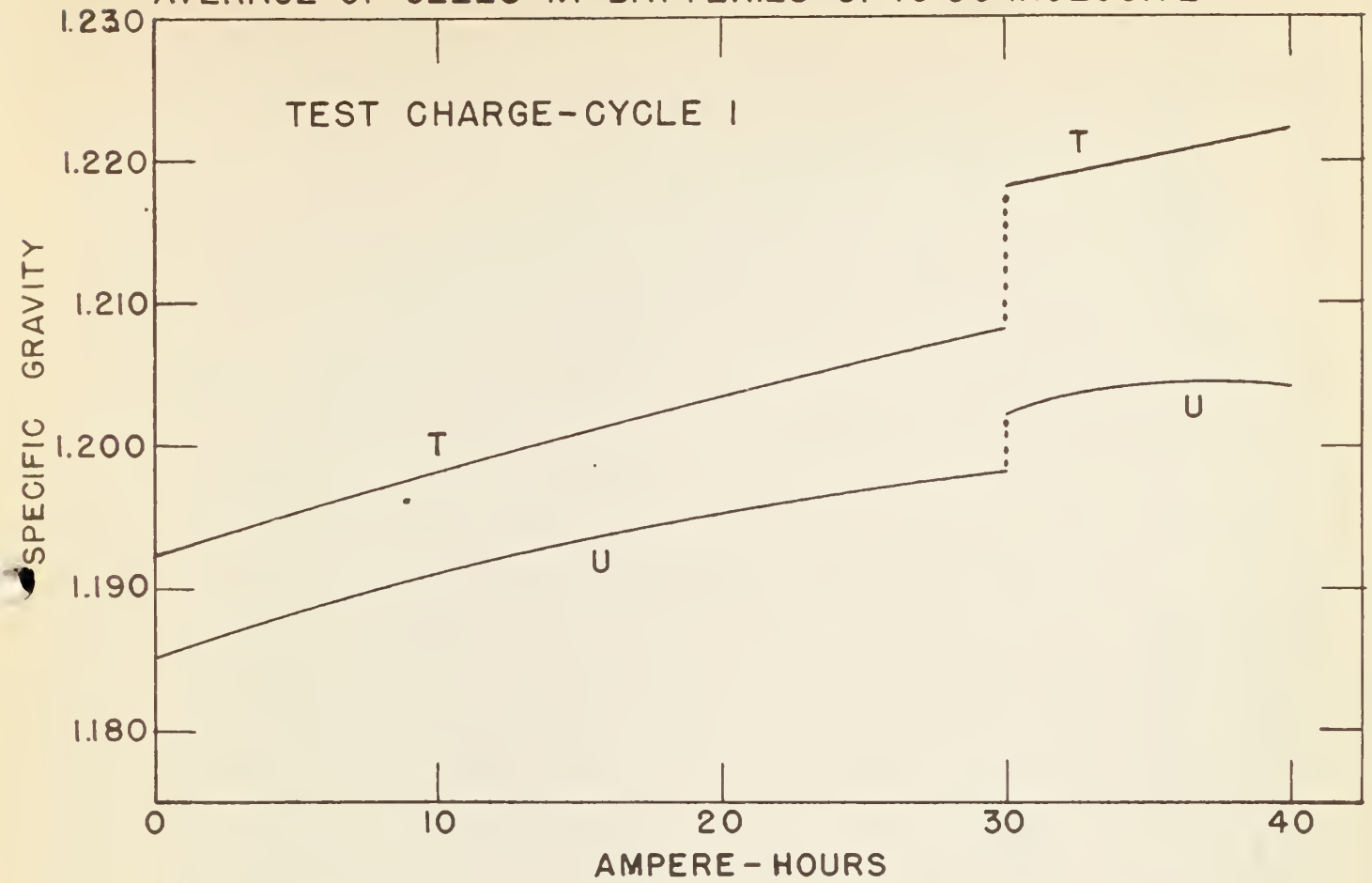
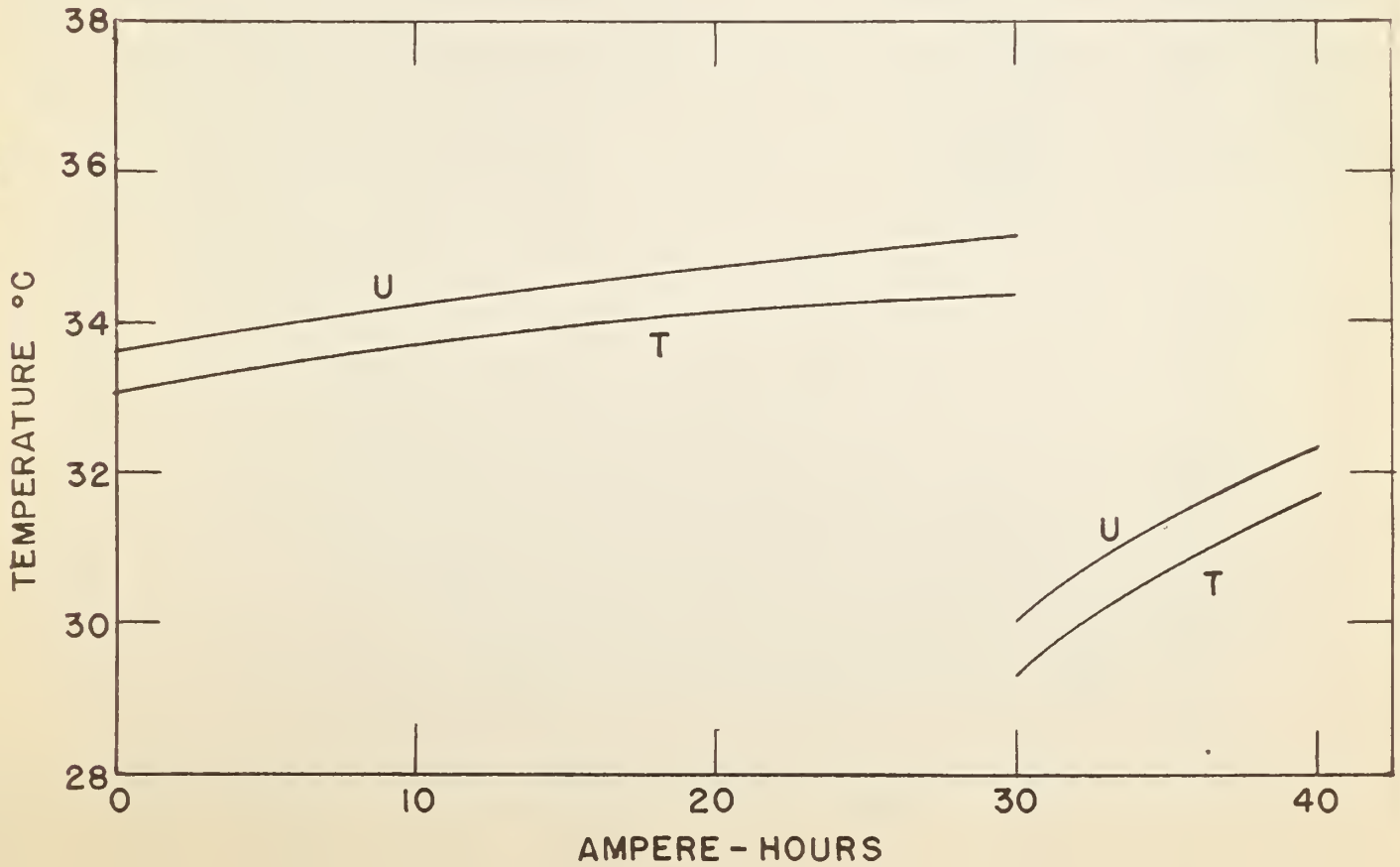

AVERAGE OF CELLS IN BATTERIES 10, 12, 13, 17, 18 & 19
TEST CHARGE-CYCLE 2
FIGURE D3
TREATED
UNTREATED
SPECIFIC GRAVITY
TREATED AND UNTREATED
TEMPERATURE
TEMPERATURE, °C
SPECIFIC GRAVITY
39
38
37
36
35
1.250
1.200
1.150
1.100
1.050
0
10
20
30
40
50
60
70
80
90
100
110
120
AMPERE-HOURS

FIGURE D4

AVERAGE OF CELLS IN BATTERIES 31 TO 36 INCLUSIVE





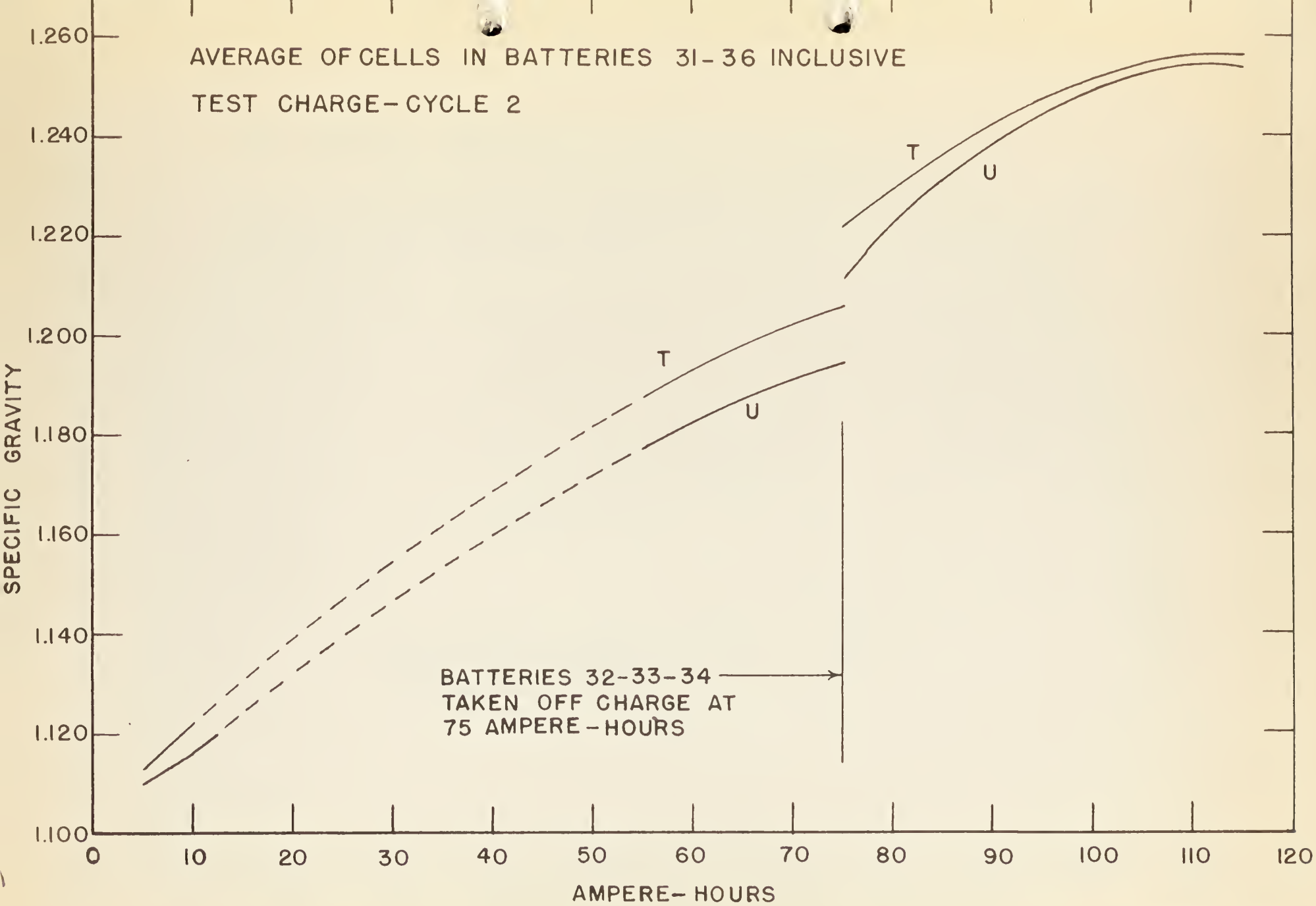

AVERAGE OF CELLS IN BATTERIES 31-36 INCLUSIVE
TEST CHARGE-CYCLE 2
SPECIFIC GRAVITY
1.260
1.240
1.220
1.200
1.180
1.160
1.140
1.120
1.100
T
U
T
U
BATTERIES 32-33-34
TAKEN OFF CHARGE AT
75 AMPERE-HOURS
0
10
20
30
40
50
60
70
80
90
100
110
120
AMPERE-HOURS

FIGURE D5A

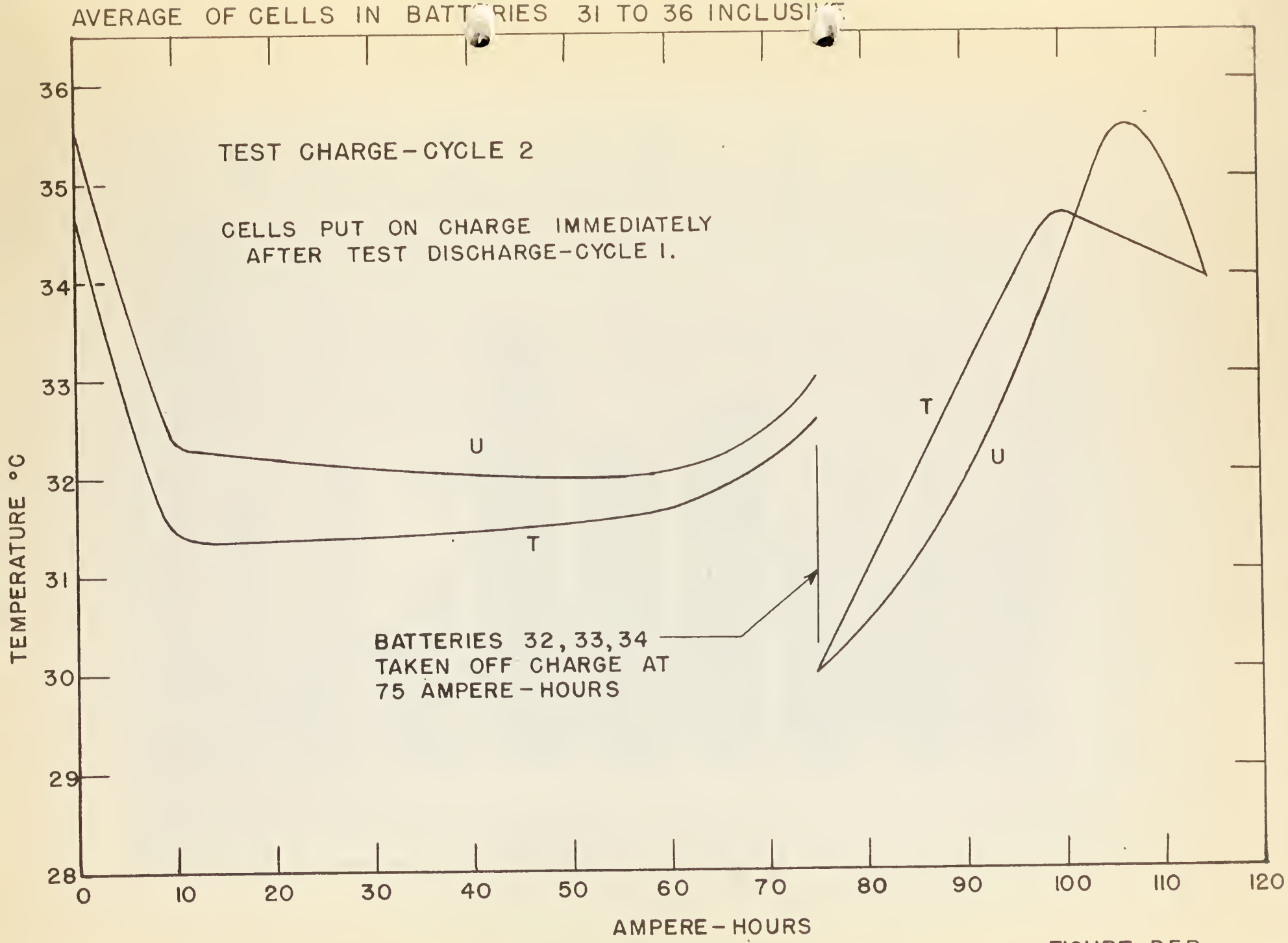
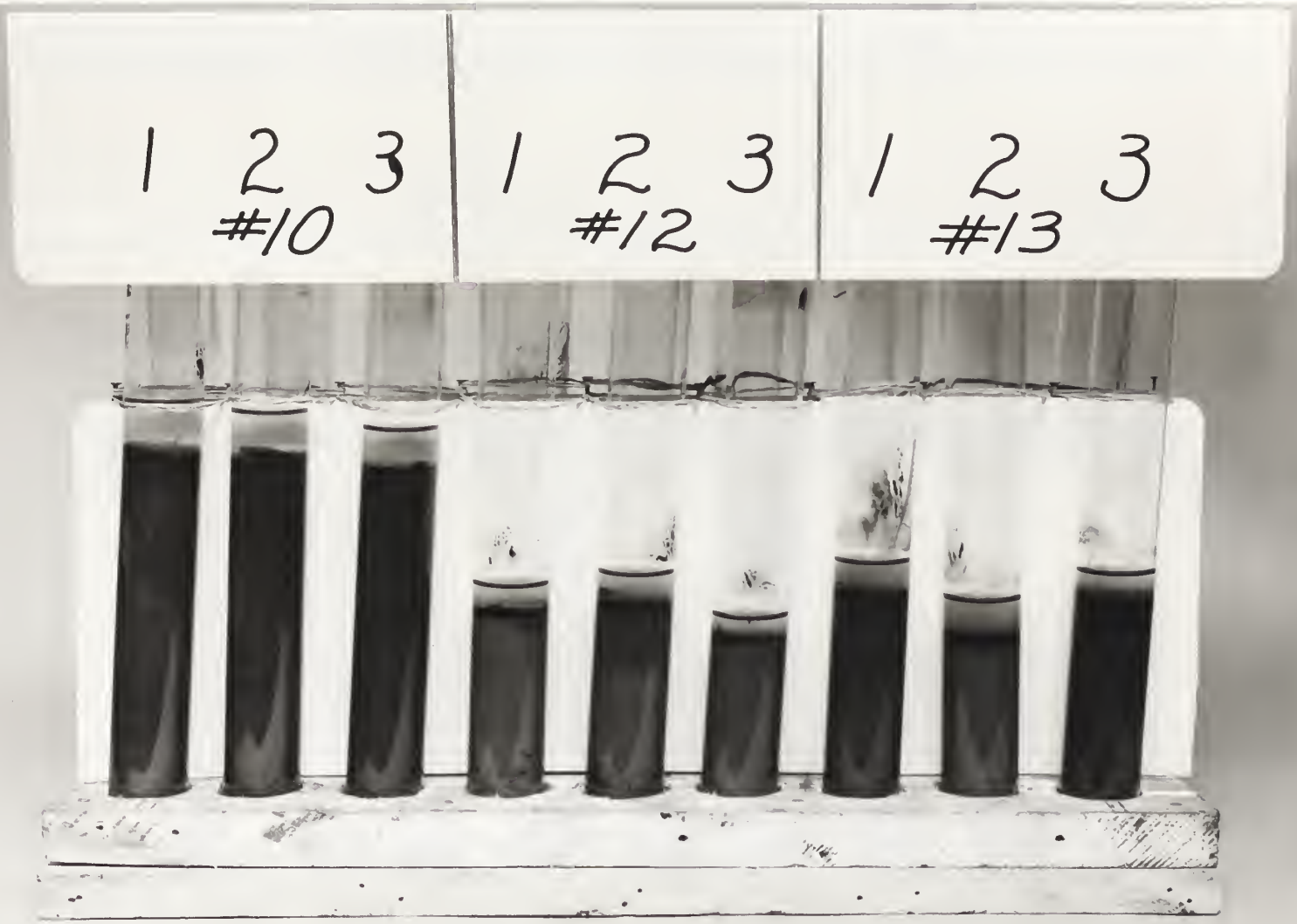
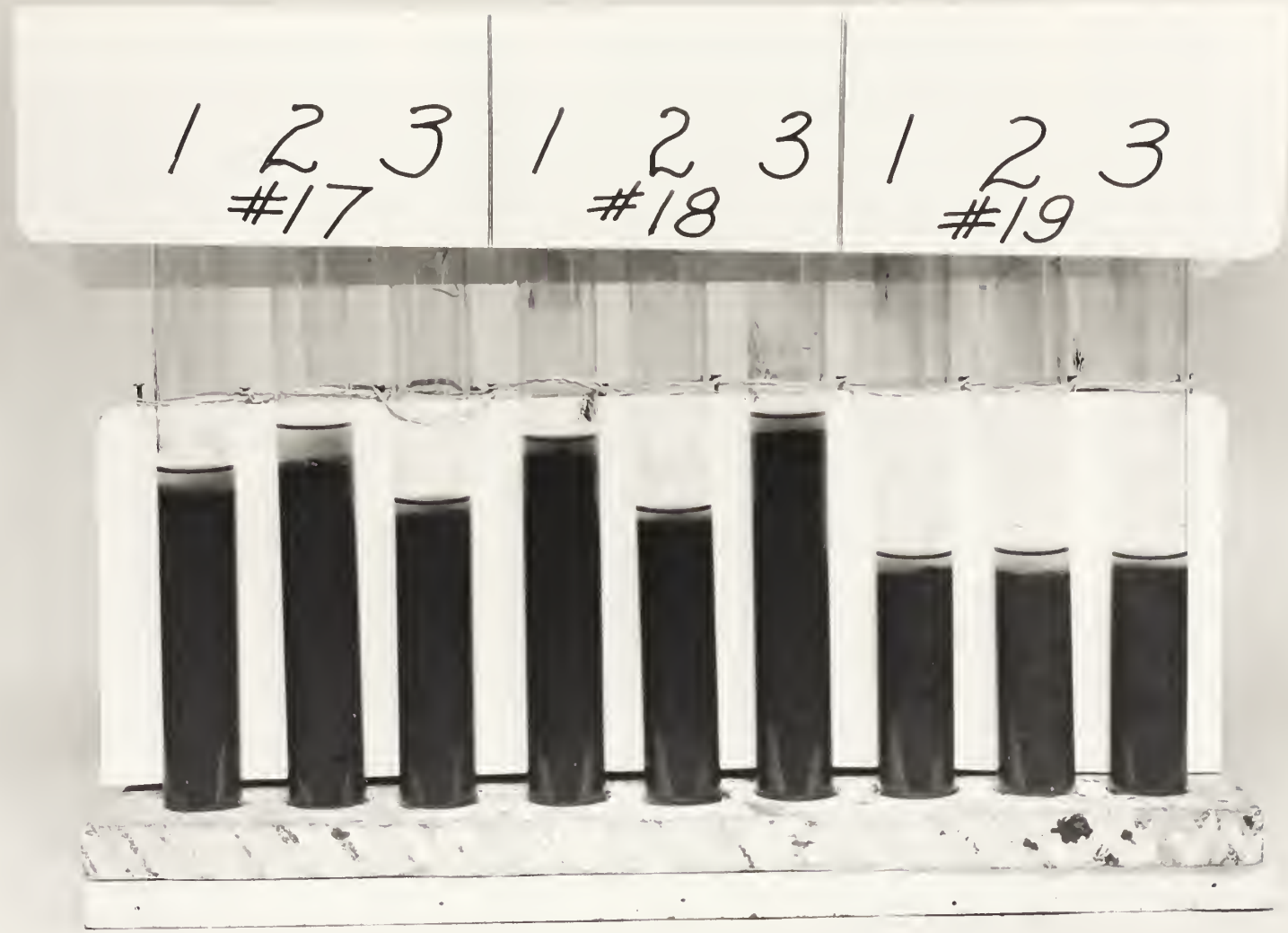

AVERAGE OF CELLS IN BATTERIES 31 TO 36 INCLUSIVE
TEST CHARGE-CYCLE 2
CELLS PUT ON CHARGE IMMEDIATELY AFTER TEST DISCHARGE-CYCLE 1.
U
T
T
U
BATTERIES 32, 33, 34 TAKEN OFF CHARGE AT 75 AMPERE-HOURS
TEMPERATURE °C
36
35
34
33
32
31
30
29
28
0
10
20
30
40
50
60
70
80
90
100
110
120
AMPERE-HOURS

FIGURE D5B


#1
#3
#4
1 2 3
1 2 3
1 2 3


#5
#6
#7
1 2 3
1 2 3
1 2 3


1 2 3
#10
1 2 3
#12
1 2 3
#13


1 2 3
#17
1 2 3
#18
1 2 3
#19

3. TESTS ON NEW BATTERIES

Six new batteries, Group 1, of 100 ampere-hour capacity were obtained and submitted to the Randall test, except that they were not given a 7-day overcharge and were not opened for inspection. Data obtained on the pre-test and test periods are given in Appendix 4a. Three test cycles were run on these batteries and were followed by a discharge test after an overnight stand.

The average total ampere hours and average total watt hours obtained for the untreated cells on the 4 discharges exceeded that obtained for the treated cells by 12.3 and 23.6, respectively. The percentage difference in ampere hours is within the usual variation observed for batteries but the percentage difference in watt hours is somewhat surprising; the magnitude of the difference suggests that "AD-X2" produces an adverse effect on new batteries. However, rather than draw this conclusion we may say that "AD-X2" does not improve the performance of new batteries. At these high discharge rates, the diffusion of ions and the resistivity of the electrolyte would have more pronounced effects and since AD-X2 increases the resistivity and increases the viscosity of the electrolyte (see Part IV, Section 6) the lower watt hours obtained at all the drain rates (300, 200, 100, and 50 amperes) may be rationalized on this basis.

The data of Table 16 for the ampere hours and watt hours obtained after an overnight stand do not indicate that AD-X2 improves the ability of new batteries to retain their charge or to recuperate on standing.

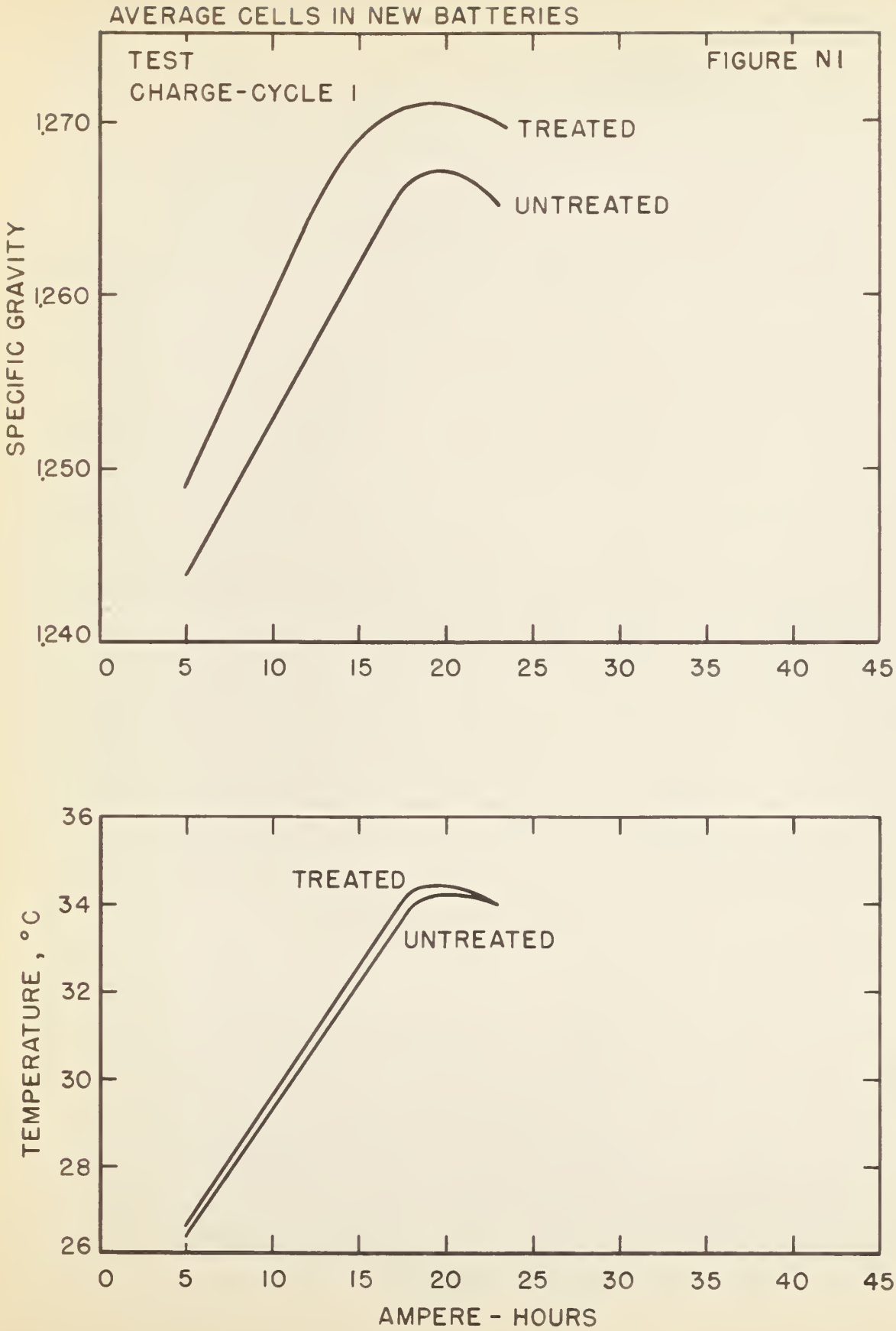
The specific gravities recorded in the tables for various stages of the tests do not indicate any significant differences between treated and untreated cells. Average values of the specific gravities of the 9 treated and the 9 untreated cells at various ampere-hour inputs are shown in figures N1, N2, and N3 for cycles 1, 2 and 3. A glance shows that no significant trend in the difference between treated and untreated cells is produced during charge. The difference, however, is less than that produced by the mere addition of the "additives"; therefore, the untreated cells receive the charge more efficiently. Also Figures N1, N2, and N3 do not show any significant difference in the rate of temperature increase between treated and untreated cells with charge for any cycle. The ampere-hour and watt-hour capacity of each cell for all discharges at all rates is given in Appendix 4b.

In summary, therefore, we have obtained no evidence that AD-X2 improves the performance of new batteries on high-rate discharges such as are required to crank an automobile engine; in fact, the data suggest that AD-X2 has a small but detectable detrimental effect.

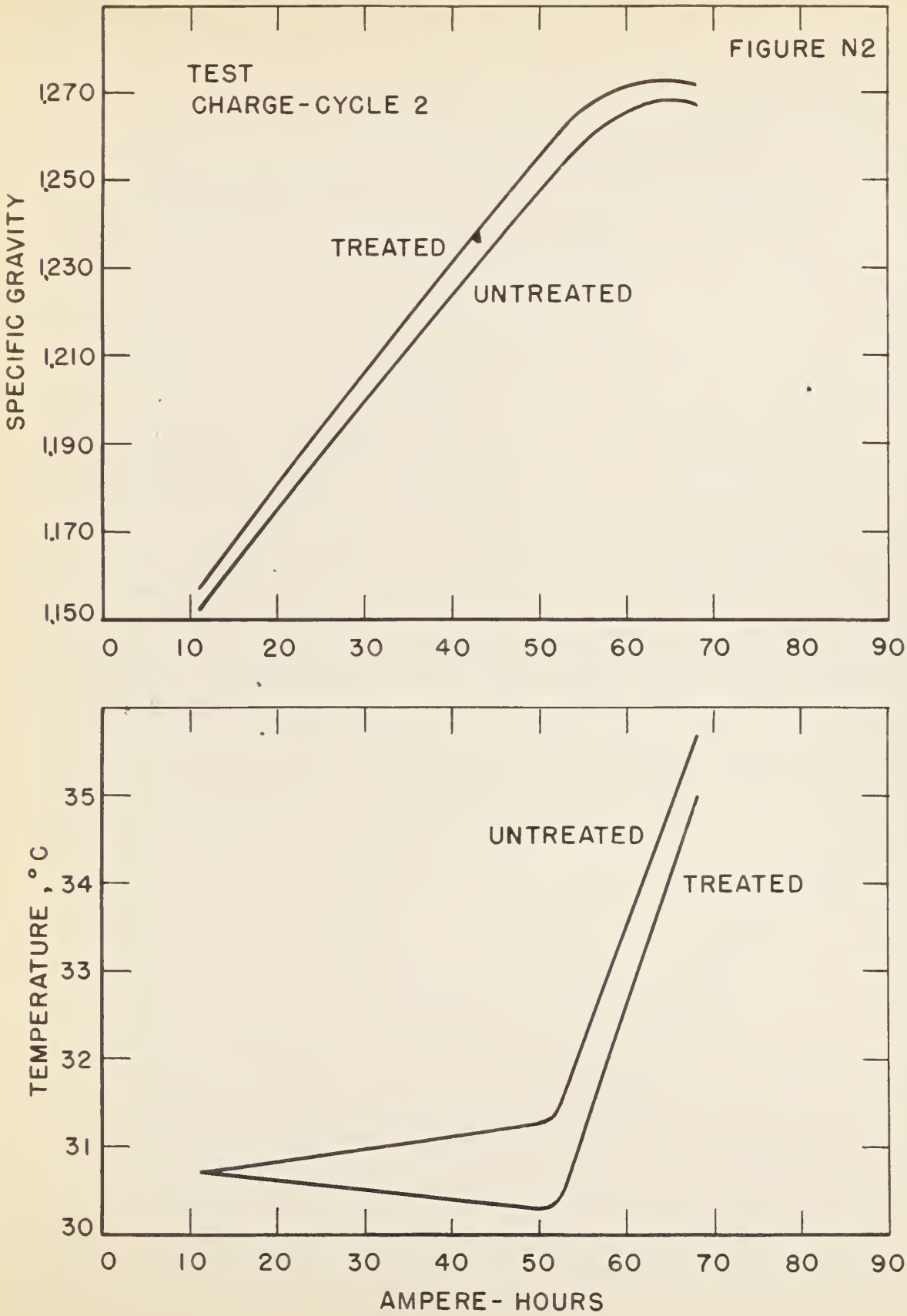
A summary of the ampere hours and watt hours obtained at each discharge rate and the total ampere hours and watt hours obtained for treated and untreated cells at all rates is given in table 16. This table also gives the total ampere hours and total watt hours obtained for all the treated and untreated cells.

Table 16 Summary data on ampere-hour and watt-hour outputs of treated (AD-Y2) and untreated new batteries for all discharges.

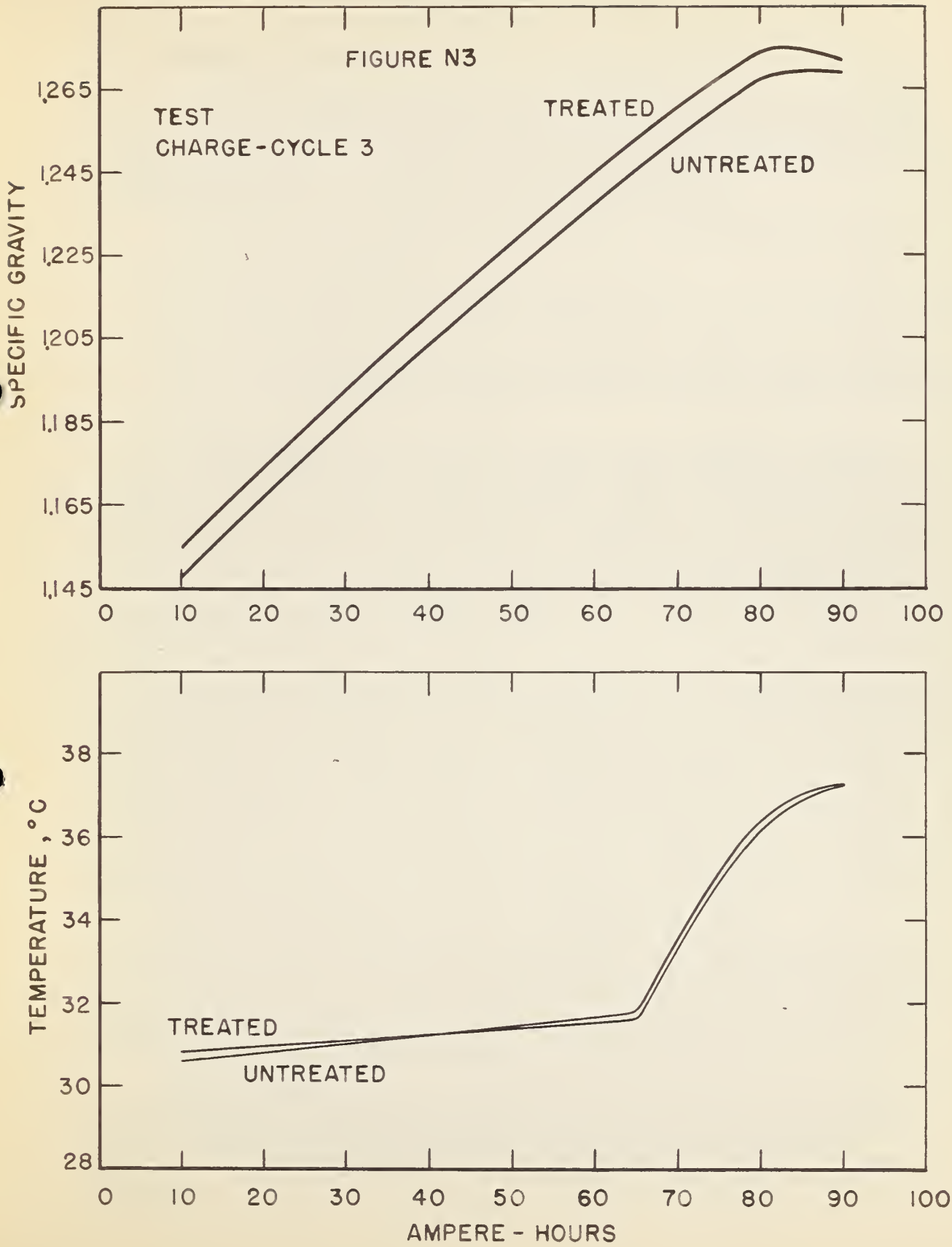
Current Drain (Rate) Amperes	Treated Cells (Sum of 9 cells)	Untreated Cells (Sum of 9 cells)	$\% = \frac{T - U}{(T + U)/2}$
		Ampere Hours	
300	927.3	980.7	- 5.6
200	72.8	56.4	+25.4
100	154.5	215.0	-32.8
50	227.3	311.6	-31.3
TOTAL	1381.9	1563.7	-12.3
		Watt Hours	
300	1386.1	1477.6	- 6.4
200	72.7	76.0	- 4.4
100	122.6	299.1	-83.7
50	175.1	374.2	-72.5
TOTAL	1756.5	2226.9	-23.6
		Ampere Hours (After overnight stand)	
300, 200 100, 50 Total	38.1	40.2	- 5.4
		Watt Hours (After overnight stand)	
300, 200 100, 50 Total	48.7	52.2	- 6.9


AVERAGE CELLS IN NEW BATTERIES
TEST
CHARGE-CYCLE I
FIGURE N1
TREATED
UNTREATED
SPECIFIC GRAVITY
1.270
1.260
1.250
1.240
0
5
10
15
20
25
30
35
40
45
TREATED
UNTREATED
TEMPERATURE, °C
36
34
32
30
28
26
AMPERE - HOURS

AVERAGE CELLS IN NEW BATTERIES



AVERAGE CELLS IN NEW BATTERIES



4. The January 1953 Tests of Batteries Drained And Filled With 1.100 Acid or With Distilled Water

4.1 Outline of Experiment

Thirty discarded lead storage automobile batteries, containing three cells each, were procured for these tests; eighteen of these were drained and filled with an acid electrolyte having a specific gravity of 1.100; the remaining twelve were drained and filled with distilled water. Within each battery the three cells were designated as

(a) control cell to which nothing would be added during the test

(b) AD-X2 cell to which AD-X2 was to be added during the test

(c) Mg-Na cell to which a mixture of $MgSO_4$-Na_2SO_4 (of composition comparable to AD-X2) was to be added during the test

The assigning of the cells to the three treatments (control, AD-X2, Mg-Na) within each battery was made using well known randomization[1/] principles with the restriction that each of the designated cells occur equally often in each of the three positions within the batteries. This latter restriction insures that the existence of any uncontrolled variation due to the position of the cell in the battery would effect the cells for the three treatments equally. A schematic diagram for the two experiments appears in figure a [2/].

1/ Some experimentalists might be tempted not to randomly assign the treatments to the cells, but to "lean over backwards" and assign one of the treatments, say AD-X2, to the cells which show up poorest on the pre-test. Then if these cells exhibit a better performance in the actual tests as compared to the pre-tests performance, one might "infer" that AD-X2 was beneficial to the battery cells. However, the possibility still exists that poorer pre-tested cells may respond better on the test regardless of treatment. If this is true, then the above type of inference is invalid because it will be impossible to differentiate between the effects of additive and selection on the performance.

As an illustration of such a situation, if a battery gave high efficiency, that is, had nearly the same output (in ampere-minutes) as input, there would be very little latitude for an increase in performance and no possibility of a large increase. Alternatively if a battery gave poor efficiency, the opportunity for a battery to show improvement is greater and a large improvement may be a possibility.

2/ The positions for the distilled water experiment on the twelve batteries were not distributed equally among the different treatments due to a mistake in the assigning of the positions to battery 29. However, it is felt that this did not effect the final results of the analysis.

1.100 Acid Experiment

1	2	3
M C T	C T M	T M C
4	5	6
M C T	C T M	T M C
7	8	9
M C T	C T M	T M C
10	11	12
M C T	T M C	C T M
13	14	15
M C T	T M C	C T M
16	17	18
M C T	T M C	C T M

Distilled Water Experiment

19	20	21
M C T	C T M	T M C
22	23	24
M C T	C T M	T M C
25	26	27
M C T	C T M	T M C
28	29	30
M C T	M C T	T M C

Figure a

Schematic Outline of Experiment

(C = Control, T = AD-X2, M = Mg-Na)

After the cells had been designated as to the type of additive each would receive during the actual test, every battery was pre-tested in order to estimate the condition of the cells prior to the tests.

During the pre-test each battery was charged at 5 amperes for 1 hour, then each of its cells was discharged individually and independently at 5 amperes until a cut-off voltage of 1 volt was reached.

For the actual test, each cell received its designated treatment during the charging period (5 to 10 minutes after start of charge). Then every battery was charged at 5 amperes for 2 hours, and each of its three cells was discharged individually and independently at 10 amperes until a cut-off voltage of 1 volt was reached.

The measured variables for each cell in both the pre-test and the actual test which are analyzed in this section are:

(a) Time (in minutes and seconds) to reach cut-off voltage of 1 volt.

(b) Watt hours discharged.

(c) Temperature change while charging

(d) Output on recovery discharge

4.2 Analysis of Results

It is reasonable to infer that if AD-X2 does affect battery cells in a different manner than adding a mixture of $MgSO_4$-Na_2SO_4, or compared to adding nothing at all to the cells, then

(a) the averages for cells having AD-X2 should be significantly* different from the averages for either the control or Mg-Na cells;

(b) the AD-X2 cell within a battery should respond significantly better than the other two cells within the same battery.

In statistical comparison of averages, care must be taken to use statistical techniques which do not allow the inherent variability of the battery cells to obscure the presence of statistically significant differences among the three treatments when present. The

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* The term "significantly different or better" is used here in the statistical sense that a difference is declared significant when that difference has a small probability of being attributed to pure chance, and a greater probability (perhaps less easily calculated) under some admissible alternative to chance (e.g., "treatment" tends to increase (or decrease) the magnitude in question). A result is said to be significant in this section if the result could have occurred by chance 5 times out of 100 or less.

analysis of variance is a technique which accomplishes this by taking advantage of the fact that cells within the same battery tend to be more alike than cells in different batteries. In cases where a measure of the prior condition of each battery cell is known, it is possible to utilize an analysis of covariance, which in effect makes the detection of differences between the averages more sensitive by partly correcting for the inherent variation between cells in different batteries.

The analysis of variance was used in this section to search for differences between the treatment averages of the temperature changes during charging. Covariance analyses were used in comparing the test averages for (a) time to reach cut-off voltages and (b) watt hours discharged, using the pre-test values as estimates of the prior condition of the battery cells. In addition, all recovery data were analyzed by the analysis of variance.

(a) Time on discharge to reach cut-off voltage

Comparison of averages

Tables 23 and 24 summarize the experimental data and figures b and c depict the pre-test values plotted against thetest results for the 1.100 acid and distilled water batteries respectively. The averages and standard deviations on tables 23 and 24 were computed omitting those batteries where the pre-tests indicated a particular cell within a battery. Batteries 4, 10, 12, 13, 14, 16,17 were omitted from these calculations for the 1.100 acid batteries, and 22, 27 were omitted from the calculations for the distilled water batteries.

Linear covariance analyses were made on the data which partly corrected for the inherent variation of the cells. The results of both analyses indicate that there are no significant differences between the averages of cells treated with AD-X2, and Mg-Na mixture, and cells not treated at all.

Section 4.3 contains the computations for these analyses.

Compsrison of cells within the same battery

Tables 25, 26, and 27, 28 give breakdowns of the number of cells treated with AD-X2 which performed better or poorer than the other cells within the same battery for 1.100 acid and distilled water battery cells respectively. None of these tables is significantly different from what one would expect if the ingredients added to the cells had no effect whatsoever.

(b) Watt hours

Tables 29 and 30 summarize the experimental data and figures d and e depict plots of the pre-test results plotted against the test results for the 1.100 acid and distilled water battery cells respectively.

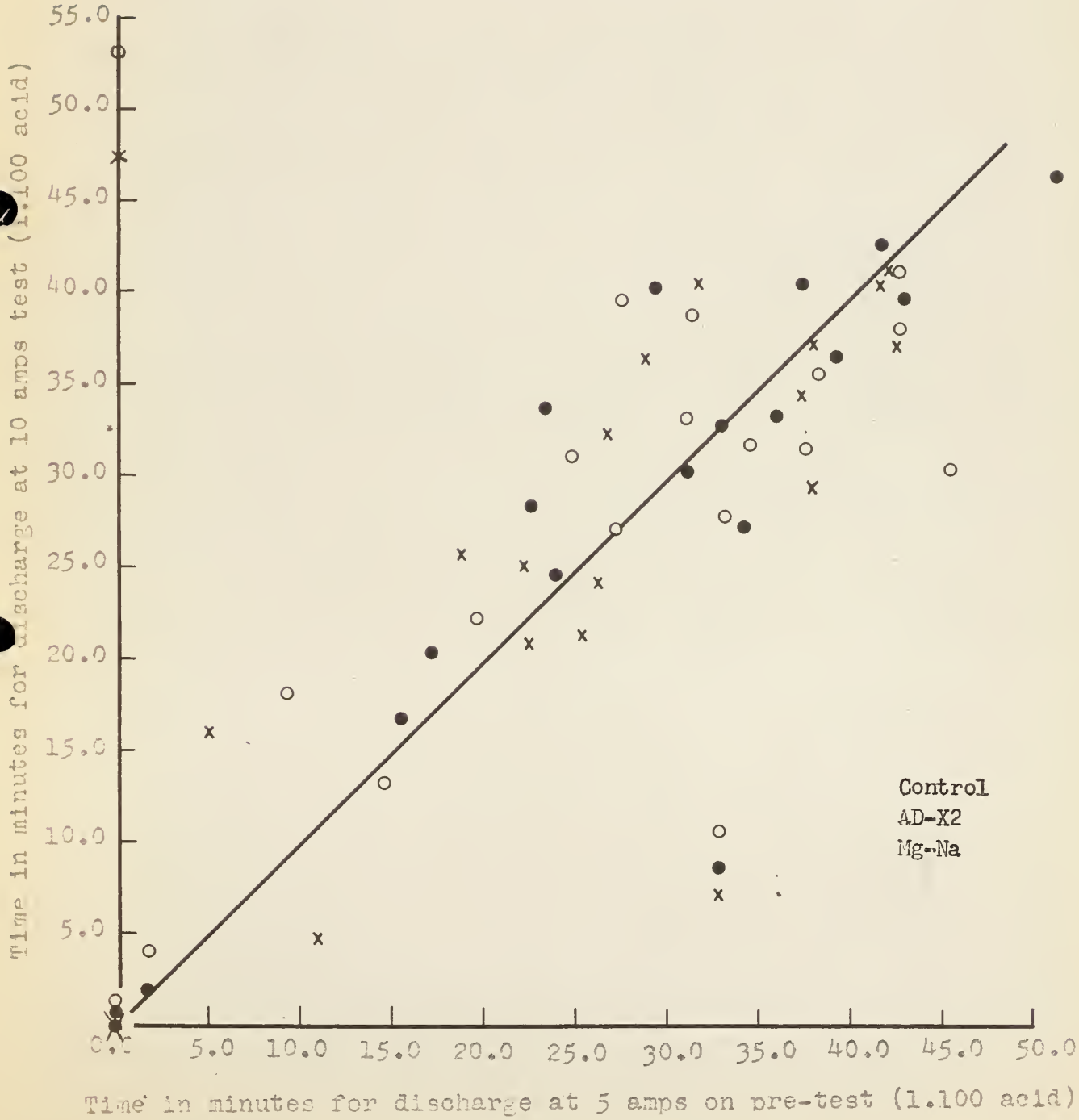

55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
Time in minutes for discharge at 10 amps test (1.100 acid)
Time in minutes for discharge at 5 amps on pre-test (1.100 acid)
Control
AD-X2
Mg-Na

Figure b

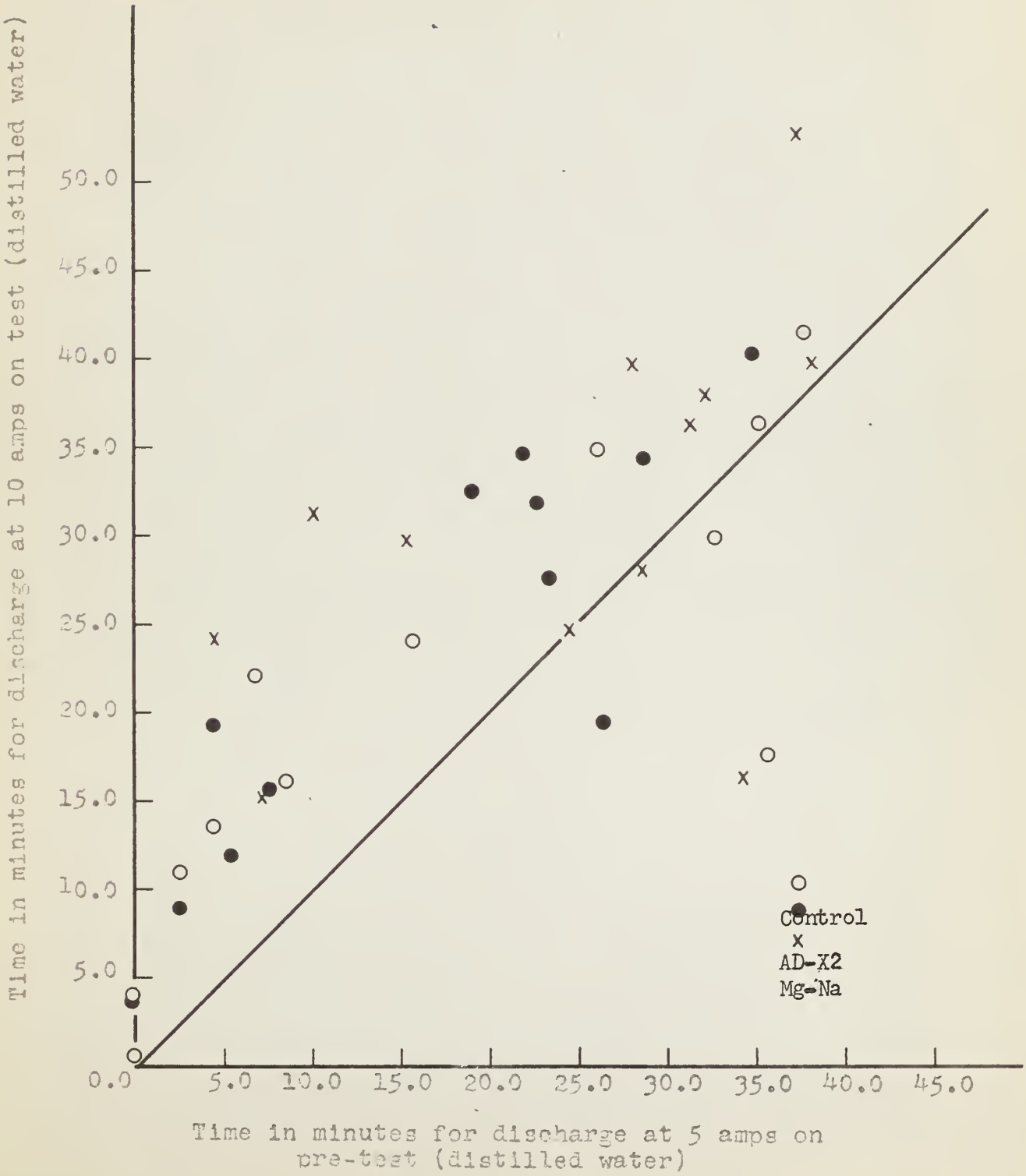

Time in minutes for discharge at 10 amps on test (distilled water)
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
Time in minutes for discharge at 5 amps on pre-test (distilled water)
Control
AD-X2
Mg-Na

Figure c

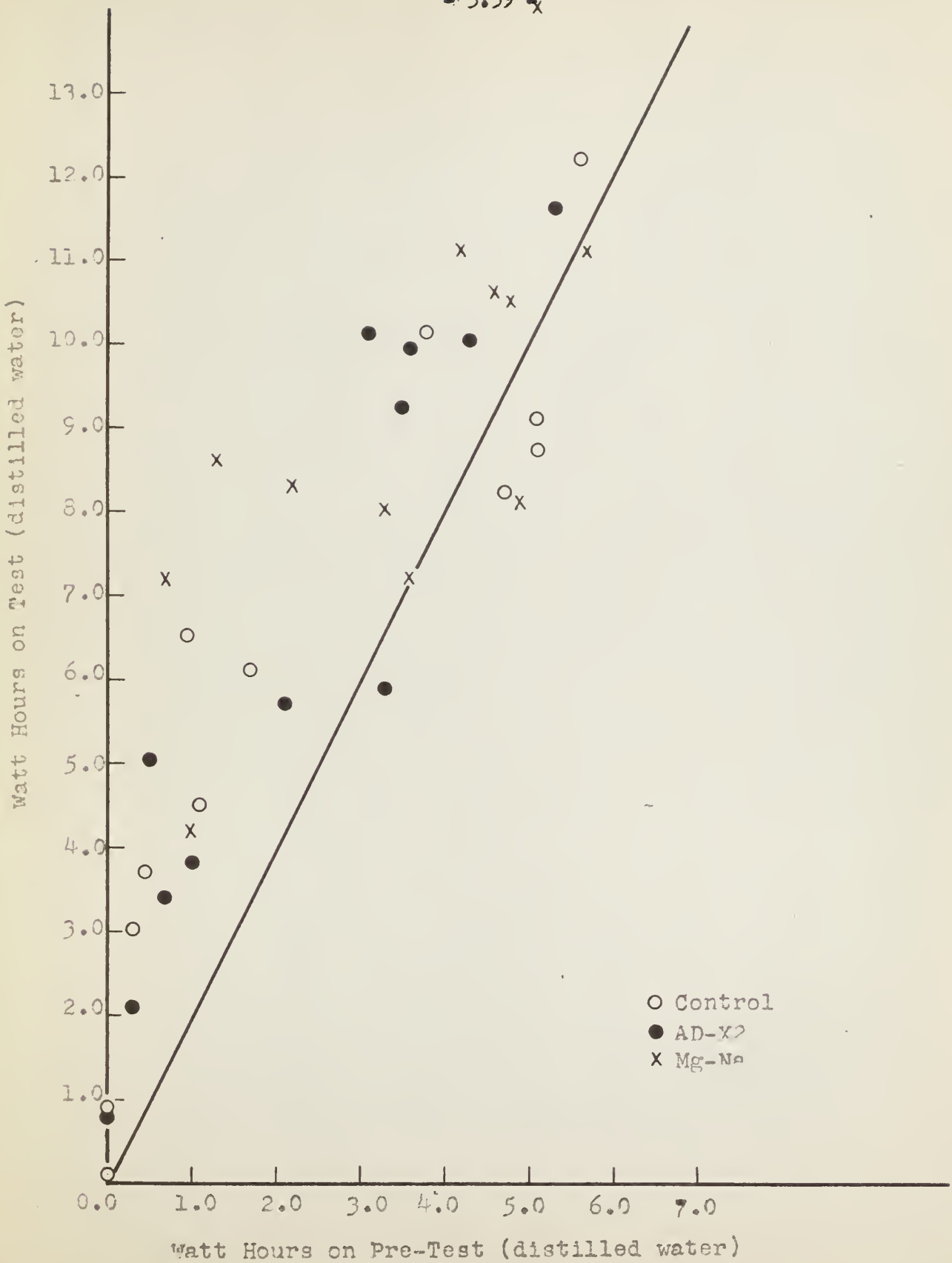

13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Watt Hours on Test (distilled water)
Watt Hours on Pre-Test (distilled water)
Control
AD-X2
Mg-Ne

Figure d

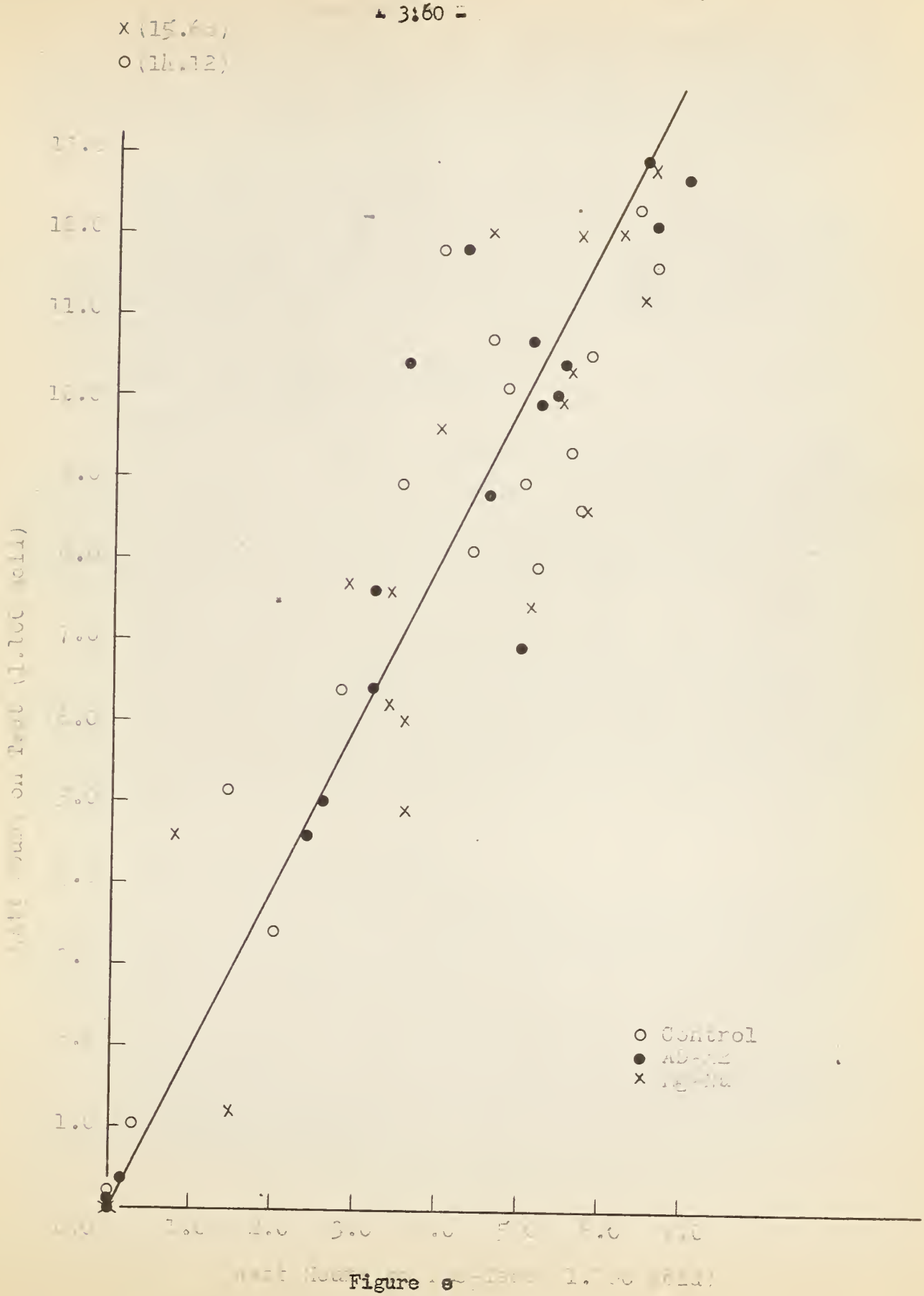


Figure - 6

Linear covariance analyses were made on the data which partly corrected for the inherent variation between the cells. The results of both analyses show that there are no significant differences between those cells treated with AD-X2, the Mg-Na mixture or the control cells. The calculations for these analyses are shown in Section 4.3.

Comparisons of cells within the same battery

Tables 31, 32, and 33, 34 give breakdowns of the number of cells treated with AD-X2 which performed better or poorer than the other cells within the same battery for the 1.100 acid and distilled water batteries respectively. None of these tables is different from what one would expect if theingredients added to the cells had no effect whatsoever.

(c) Temperature change during charging

Comparison of averages

The temperature change of each cell during charging is recorded for both the pre-test and the test in tables 35 and 36 for the 1.100 acid and distilled water battery cells respectively. The analyses of variance show that the differences among the three averages are not significant for either the 1.100 acid or the distilled water battery cells. The computations for the analyses of variance are shown in Section 4.3.

Comparison of cells within the same battery

Tables 37, 38 and 39,40 give the breakdown of the number of batteries for which the AD-X2 cells gave smaller or larger temperature changes than the corresponding Mg-Na cells or control cells within the same battery for the 1.100 acid and distilled water cells respectively. None of thest tables is significantly different from what one would expect if the ingredients added to the cells have no effect on the temperature change during charge.

(d) Output on recovery discharge

The recovery output data is summarized in Tables 42, 43 and 44,45. The analyses of variance show that the differences among the three treatment averages for both the 1.100 acid and the distilled water experiments are not statistically significant. The computations for the analyses of variance are shown in Tables 41a-41d.

4.3 Details for Analysis of Variance and Covariance

This section contains the tables for the analyses of variance and covariance which were used in Section 4.2 to search for differences between the treatment averages.

TABLE 17

Analysis of Covariance for Time on Discharge to Cut-Off Voltage (1.100 acid) 1/

Source	Degrees of Freedom	Sums of Squares			Sums of Squares Corrected For Regression	Mean Square	F
		Pre-Test (x^2)	(xy)	Test (y^2)			
Treatments	2	1.7423	9.9845	65.2039	57.0134	28.51	2.17 3/
Batteries	11	2112.6656	1720.3845	1975.6756			
Error	22	1069.7977	451.1088	466.5694	276.3473	13.16 2/	
Total	35	3184.2056	2181.4778	2507.4489			

Adjusted treatment averages	
Control	30.5
AD-X2	33.1
Mg-Na	30.4

1/ Omitting Batteries 4, 12, 13, 14, 16, 17

2/ Based on 21 degrees of freedom

3/ Critical value of F at .05 level is $F_{.05} = 3.47$

TABLE 18

Analysis of Covariance for Time on Discharge to Cut-Off Voltage (distilled water) 1/

Source	Degrees of Freedom	Sums of Squares			Adjusted Sum of Squares	Mean Square
		(x^2)	(xy)	(y^2)		
Treatments	2	51.0742	45.2135	75.6819	35.8121	17.9060
Batteries	9	3967.5792	2037.9955	2044.1580		
Error	18	339.0378	280.0645	619.0280	387.6788	22.8046 2/
Total	29	4357.6912	2363.2735	2738.8679		

Adjusted Treatment Averages	
Control	24.52
AD-X2	27.28
Mg-Na	27.13

1/ Omitting batteries 22,27

2/ Based on 17 degrees of freedom

TABLE 19

Analysis of Covariance for Watt-Hours (1.100 acid) 1/

Source	Degrees of Freedom	Sums of Squares Pre-Test (x^2)	Sums of Squares (xy)	Sums of Squares Test (y^2)	Sums of Squares Corrected for Regression	Mean Square	F
Treatments	2	1.4359	3.5330	8.8770	4.4587	2.2294	1.70 3/
Positions	2	10.0476	13.0271	17.4138	3.1370	1.5685	1.19 3/
Batteries	11	51.5905	84.7813	195.6474			
Error	20	21.4836	14.5737	34.8488	24.9625	1.3138 2/	
Total	35	84.5576	115.8937	256.7840			

Adjusted treatment averages	
Control	8.95
AD-X2	9.07
Mg-Na	8.25

1/ Omitting batteries 4, 12, 13, 14, 17, 18

2/ Error based on 19 degrees of freedom

3/ Critical F ratio at .05 level is $F_{.05} = 3.52$

TABLE 20

Analysis of Covariance for Watt-Hours (distilled water) 1/

Source	Degrees of Freedom	Sums of Squares			Sums of Squares Corrected For Regression	Mean Square
		Pre-Test (x^2)	(xy)	Test (y^2)		
Treatments	2	1.1601	3.0127	11.0305	3.7425	1.8712
Batteries	9	87.9681	107.3654	151.5376		
Errors	18	8.7302	16.3574	68.9622	38.3140	2.2533 2/
Total	29	97.8584	126.7356	231.5303		

Adjusted Treatment Averages

Control	7.2
AD-X2	7.7
Mg-Na	8.1

1/ Omitting batteries 22 and 27

2/ Error based on 17 degrees of freedom

Table 21

Analysis of Variance for Temperature Changes During Charging (1.100)[1/]

Source	Degrees of Freedom	Sums of Squares	Mean Square	F
Treatments	2	1.185077	.592539	2.58[2/]
Positions	2	5.425633	2.712816	
Batteries	17	35.680866		
Latin squares	5	25.912133		
Batteries within Latin squares	12	9.768733		
Error	32	14.237157	.444911	
Position x Latin squares	10	9.189034	(a).918903	
Treatment x Latin squares	10	2.478390	(b).229460	
Remainder	12	2.569733		
Total		56.528733		

1/ Value for Mg-Na test cell, battery 10 estimated to be 2.58.

2/ F ratio using error (b). Critical F ratio at .05 level, $F_{.05} = 3.44$.

TABLE 22

Analysis of Variance for Temperature Changes During Charging (Distilled Water)

Source	Degrees of Freedom	Sums of Squares	Mean Square	F
Treatment	2	.9895	.4948	1.94[1/]
Batteries	11	15.7799		
Error	22	5.6228	.2556	
Total	35	23.3922		

1/ Critical value of F at .05 level is $F_{.05} = 3.44$

TABLE 23

Time on Discharge to Cut-Off Voltage

(Batteries drained and filled with 1.100 acid)

Battery No.	Pre-Test Minutes discharged at 5 amps.			Test Minutes discharged at 10 amps.		
	C*	T*	M*	C	T	M
1	24.8	24.0	26.1**	31.4	28.3	24.2
2	27.3	29.2	31.4	39.7	40.2	40.6
3	42.4	37.1	41.4	41.1	40.4	40.4
(4)	0.0	51.2	0.0	53.1	46.4	47.3
5	27.2	35.7	37.9	27.6	33.4	29.6
6	37.3	33.9	26.8	31.6	27.7	32.4
7	45.2	31.0	18.6	30.4	30.2	25.8
8	42.6	42.8	42.4	38.1	39.8	37.2
9	34.3	37.6	37.1	31.7	36.6	34.6
(10)	14.8	23.9	11.0	13.2	24.9	4.9
11	30.9	23.2	22.2	33.3	33.7	25.1
(12)	31.3	1.7	38.3	38.7	2.0	37.5
(13)	19.6	0.0	22.5	22.2	0.0	20.9
(14)	2.7	15.6	25.2	4.1	16.9	21.8
15	9.3	17.0	36.8	18.1	20.4	28.5
(16)	38.2	34.7	5.0	35.5	32.8	16.1
(17)	0.0	0.0	0.0	1.0	0.5	0.0
18	33.9	41.6	41.7	27.9	42.8	41.6
Grand Total	462.8	480.2	464.4	518.7	497.0	508.5
Average	25.7	26.7	25.8	28.8	27.6	28.3
Total omitting ( )	355.2	353.1	362.4	350.9	373.5	360.0
Average	32.3	32.1	32.9	31.9	34.0	32.7
Standard deviation of average				1.9	2.1	2.1

* Designates "treatment" subsequently applied. C = control; T = treated with AD-X2; M = treated with Mg-Na mixture.

** Gave nothing first day; next morning gave listed value.

TABLE 24

Time on Discharge to Cut-Off Voltage

(Batteries drained and filled with distilled water)

Battery Number	Pre-Test Minutes discharged at 5 amps			Test Minutes discharged at 10 amps		
	C*	T*	M*	C	T	M
19	15.7	19.2	24.7	24.0	32.4	24.6
20	35.4	34.9	38.2	36.3	40.0	39.7
21	37.8	23.4	28.2	41.8	27.5	39.5
(22)	0.0	0.0	37.4	4.0	3.9	52.8
23	26.1	24.7	31.4	34.9	31.7	36.3
24	32.6	28.7	28.7	29.7	34.4	28.0
25	35.8	26.1	34.7	17.5	19.4	16.3
26	8.2	22.0	15.4	16.1	34.6	29.7
(27)	0.0	7.7	32.4	0.5	15.6	37.8
28	2.6	5.5	7.3	11.0	12.0	15.4
29	6.9	4.5	4.7	22.0	19.4	24.4
30	4.0	2.6	10.1	13.5	8.9	31.2
Grand Total	205.1	199.3	293.2	251.3	279.8	375.7
Average	17.1	16.6	24.4	20.9	23.3	31.3
Total omitting ( )	205.1	191.6	223.4	246.8	260.3	285.1
Average	20.5	19.2	22.3	24.7	26.0	28.5
Standard deviation of average				3.32	3.32	2.73

* Designates "treatment" subsequently applied. C = control; T = treated with AD-X2; M = treated with Mg-Na sulfates mixture.

TABLE 25

Summary of Number of Times the Cut-Off Voltage Times for Control Cells Exceed Those for AD-X2 Cells Within the Same Battery (1.100 acid)*

	Pre-Test	Test	Total
No. of control cells greater than AD-X2 cells	7	6	13
No. of AD-X2 cells greater than control cells	8	9	17
Total	15	15	30

* Excluding batteries 4, 13, 17

TABLE 26

Summary of Number of Times the Cut-Off Voltage Time for Mg-Na Cells Exceed Those for AD-X2 Cells Within the Same Battery (1.100 Acid)*

	Pre-Test	Test	Total
No. of Mg-Na cells greater than AD-X2 cells	8	5	13
No. of AD-X2 cells greater than control cells	7	10	17
Total	15	15	30

* Excluding batteries 4, 13, 17

TABLE 27

Summary of the Number of Times the Cut-Off Voltage Times for Control Cells Exceeds Those for AD-X2 Cells Within the Same Battery (distilled water)

	Pre-Test	Test	Total
No. of Control cells greater than AD-X2 cells	7	5	12
No. of AD-X2 cells greater than control cells	4	7	11
Total	11*	12	23

* one set of values were tied

TABLE 28

Summary of the Number of Times the Cut-Off Voltage Times for Mg-Na Cells Exceeds Those for AD-X2 Cells Within the Same Battery (Distilled Water)

	Pre-Test	Test	Total
No. of Mg-Na Cells greater than AD-X2 cells	10	7	17
No. of AD-X2 cells greater than Mg-Na cells	1	5	6
Total	11*	12	23

* One set of values was tied

Table 29

Watt Hours Output
(Batteries drained and filled with 1.100 acid)

Battery Number	Pre-Test Watt-Hours			Test Watt - Hours		
	C*	T*	M*	C	T	M
1	3.52	3.16	3.59	8.94	7.56	4.86
2	4.01	4.31	4.63	11.80	11.84	12.02
3	6.41	5.67	6.22	12.30	10.74	11.95
(4)	0.00	7.02	0.00	14.12	12.72	15.68
5	4.36	5.43	5.75	8.06	10.00	8.56
6	5.62	5.00	4.05	9.33	6.94	9.62
7	5.73	4.59	2.87	8.65	8.78	7.69
8	6.60	6.60	6.48	11.61	12.07	11.19
9	4.96	5.50	5.50	8.86	10.38	9.91
(10)	1.99	3.18	1.52	3.44	6.37	1.18
11	4.75	3.55	3.40	10.08	10.37	7.64
(12)	4.65	0.17	5.65	10.74	0.38	10.27
(13)	2.79	0.00	3.43	6.43	0.00	6.19
(14)	0.31	2.35	3.65	1.01	4.63	6.01
15	1.40	2.58	5.19	5.13	4.95	7.44
(16)	5.82	5.25	0.71	10.47	9.91	4.65
(17)	0.00	0.00	0.00	0.21	0.11	0.00
18	5.16	6.53	6.55	7.93	12.93	12.79
Grand total	68.08	70.89	69.19	149.11	140.68	147.65
Average	3.78	3.94	3.84	8.28	7.82	8.20
Totals Eliminating( )	52.52	52.92	54.23	102.69	106.56	103.67
Average	4.77	4.81	4.93	9.33	9.69	9.42
Standard deviation of average				0.95	0.99	0.97

*Designates treatment subsequently applied; C = control, T= treated with AD-X2, M treated with Mg-Na sulfate mixture.

TABLE 30

Watt Hours Output

(Batteries Drained and Filled with Distilled Water)

Battery No.	Pre-Test Watt-Hours			Test Watt-Hours		
	C*	T*	M*	C	T	M
19	1.71	2.07	3.29	6.12	5.71	8.03
20	5.14	5.27	5.69	9.13	11.64	11.56
21	5.64	3.29	4.22	12.16	5.88	11.57
(22)	0.00	0.01	5.14	0.92	0.78	13.99
23	3.83	3.48	4.64	10.07	9.25	10.58
24	4.73	4.31	3.65	8.18	10.04	7.19
25	5.08	3.58	4.87	8.69	9.87	8.10
26	1.11	3.14	2.17	4.54	10.07	8.28
(27)	0.00	0.97	4.81	0.10	3.82	10.49
28	0.33	0.69	0.98	3.02	3.30	4.21
29	0.96	0.53	0.70	6.48	5.03	7.19
30	0.49	0.29	1.26	3.67	2.13	8.63
Total	29.02	27.68	41.42	73.08	77.52	109.82
Average	2.42	2.30	3.45	6.09	6.46	9.15
Total omitting ( )	29.02	26.65	31.47	72.06	72.92	85.33
Average	2.90	2.66	3.15	7.21	7.29	8.53
Standard Deviation of Average				0.93	1.04	0.71

* Designates treatment subsequently applied; C = control, T = treated with AD-X2, M = treated with Mg-Na sulfate mixture.

TABLE 31

Summary of Number of Times Watt Hour Readings for Control Cells Exceeded Those for AD-X2 Cells Within the Same Battery (1.100 Acid)*

	Pre-Test	Test	Total
No. of control cells greater than AD-X2 cells	7	6	13
No. of AD-X2 cells greater than control cells	8	9	17
Total	15	15	30

* Excluding batteries 4, 13, and 17.

TABLE 32

Summary of Number of Times the Watt-Hour Readings for Mg-Na Cells Exceed Those for the AD-X2 Cells Within the Same Battery (1.100 Acid)*

	Pre-Test	Test	Total
No. of AD-X2 Cells greater than Mg-Na cells	6	9	15
No. of Mg-Na cells greater than AD-X2 cells	9	6	15
Total	15	15	30

*Batteries 4, 13, 17 were omitted in this summary

TABLE 33

Summary of Number of Times Watt Hour Readings for Control Cells Exceed Those for AD-X2 Cells Within the Same Battery (Distilled Water)*

	Pre-Test	Test	Total
No. of control cells greater than AD-X2 cells	6	5	11
No. of AD-X2 cells greater than control cells	4	5	9
Total	10	10	20

* Excluding results from battery numbers 22 and 27

TABLE 34

Comparison of Number of Times Watt Hour Readings for Mg-Na Cells Exceeded Those for AD-X2 Cells Within Same Battery (Distilled Water)*

	Pre-Test	Test	Total
No. of Mg-Na cells greater than AD-X2 cells	8	6	14
No. of AD-X2 cells greater than Mg-Na cells	2	4	6
Total	10	10	20

* Excluding battery numbers 22 and 27

TABLE 35

Temperature Change During Charging
(Batteries drained and filled with 1.100 acid)

Battery No.	Pre-test Temperature Change (°C)			Test Temperature Change (°C)		
	C*	T*	M*	C	T	M
1	0.00	0.00	2.20	0.85	0.30	1.90
2	0.55	1.70	0.00	1.10	0.75	0.45
3	0.20	1.10	0.30	0.50	0.40	0.75
(4)	0.60	0.90	0.90	0.80	0.90	0.60
5	0.88	0.80	0.48	1.50	1.05	1.10
6	0.75	1.00	1.00	0.40	0.90	0.50
7	0.70	0.80	1.60	0.90	0.90	0.80
8	-0.05	-0.14	-0.13	0.68	0.21	0.39
9	0.20	0.40	0.20	1.10	1.10	1.00
(10)	2.10	1.00	4.70	4.30	1.10	10.30
11	-0.23	0.61	0.15	0.05	1.08	0.62
(12)	0.60	0.90	0.40	1.60	1.80	0.70
(13)	1.00	0.90	1.10	1.30	1.10	1.30
(14)	1.70	2.60	1.60	1.80	2.50	2.00
15	1.80	1.30	1.20	1.50	1.60	1.10
(16)	0.50	0.50	1.80	2.10	1.90	3.80
(17)	2.30	1.65	0.60	3.20	3.80	2.00
18	0.80	0.30	0.50	4.90	1.80	1.10
Grand Total	14.40	16.32	18.60	28.58	23.19	30.41
Average	0.80	0.91	1.03	1.59	1.29	1.69
Total omitting ( )	5.60	7.87	7.50	13.48	10.09	9.71
Average	0.51	0.72	0.68	1.23	0.92	0.89
Standard deviation of average				.37	.15	.13

* Designates "treatment" subsequently applied
C = control; T = treated with AD-X2; M = treated with Mg-Na sulfates mixture.

TABLE 36

Temperature Change During Charging
(Batteries drained and filled with distilled water)

Battery No.	Pre-Test Temperature Change (°C)			Test Temperature Change (°C)		
	C*	T*	M*	C	T	M
19	2.3	2.1	2.5	2.0	1.8	2.4
20	0.8	0.6	0.5	1.7	1.0	0.8
21	0.9	1.5	1.0	1.5	1.8	1.0
(22)	2.6	2.2	1.0	1.4	2.7	1.1
23	1.3	0.4	0.3	1.6	0.8	0.6
24	1.1	1.2	1.1	1.6	2.5	1.2
25	0.4	0.7	0.5	1.0	1.1	1.8
26	0.3	0.4	0.0	0.9	0.7	0.3
(27)	2.1	2.3	2.7	3.3	3.2	2.1
28	1.8	2.0	1.9	3.0	3.2	2.6
29	1.5	1.6	1.8	1.6	1.4	2.5
30	0.8	1.5	1.6	1.9	2.5	1.6
Grand Total	15.9	16.5	14.9	21.5	22.7	18.0
Average	1.6	1.6	1.5	1.8	1.9	1.5
Total Omitting ( )	11.2	11.5	11.2	16.8	16.8	14.8
Average	1.1	1.2	1.1	1.7	1.7	1.5
Standard Deviation of Average				.18	.26	.26

* Designates "treatment" subsequently applied; C = control

T = treated with AD-X2; M = treated with Mg-Na mixture.

TABLE 37

Summary of the Number of Times AD-X2 Cells had Lower Temperature Changes During Charging Then Control Cells Within the Same Battery (1.100 acid)*

	Pre-Test	Test	Total
No. of control cells having lower temperature changes than AD-X2 cells	9	7	16
No. of AD-X2 cells having lower temperature changes than control cells	7	9	16
Total	16*	16*	32

*Two temperature changes were exactly the same

TABLE 38

Summary of the Number of Times AD-X2 Cells had Lower Temperature Changes During Charging than the Mg-Na Cells Within the Same Battery (1.100 acid)

	Pre-Test	Test	Total
No. of Mg-Na cells having lower temperature changes then AD-X2 cells	9	11	20
No. of AD-X2 cells having lower temperature changes than Mg-Na cells	7	7	14
Total	16*	18	34

*Two temperature changes were exactly the same

TABLE 39

Summary of the Number of Times AD-X2 Cells Had Lower Temperature Changes During Charging Than the Control Cells Within the Same Battery (Distilled Water)

	Pre-Test	Test	Total
No. of control cells having lower temperature changes than AD-X2 cells	8	6	14
No. of AD-X2 cells having lower temperature changes than control cells	4	6	10
Total	12	12	24

TABLE 40

Summary of the Number of Times AD-X2 Cells Had Lower Temperature Changes During Charging Than the Mg-Na Cells Within the Same Battery (Distilled Water)

	Pre-Test	Test	Total
No. of Mg-Na cells having lower temperature changes than AD-X2 cells	8	9	17
No. of AD-X2 cells having lower temperature changes than Mg-Na cells	4	3	7
Total	12	12	24

TABLE 41a

Analysis of Variance for Time on Recovery Discharge to Cut-Off Voltage (1.100 acid)*

Source	Degrees of Freedom	Sums of Squares	Mean Square
Treatments			19.7931
Batteries	10	407.7897	
Error	20	592.9939	29.6497
Total	32	1040.3697	

*Omitting batteries 4, 10, 12, 13, 14, 16, 17.

TABLE 41b

Analysis of Variance for Time on Recovery Discharge to Cut-Off Voltage (Distilled Water)*

Source	Degrees of Freedom	Sums of Squares	Mean Square
Treatments	2	31.0207	15.5104
Batteries	9	806.3947	
Error	18	830.4793	46.1377
Total	29	1667.8947	

*Omitting batteries 22, 27.

TABLE 41c

Analysis of Variance for Watt-Hours Recovery Output (1.100 acid)*

Source	Degrees of Freedom	Sums of Squares	Mean Square
Treatments	2	0.7378	0.3689
Batteries	10	7.8184	
Error	20	9.1968	0.4598
Total	32	17.7530	

*Omitting batteries 4, 10, 12, 13, 14, 16,17

TABLE 41d

Analysis of Variance for Watt-Hours Recovery Output (Distilled Water)*

Source	Degrees of Freedom	Sums of Squares	Mean Square
Treatments	2	0.3354	0.1677
Batteries	9	12.1427	
Error	18	11.8348	0.6575
Total	29	24.3129	

*Omitting batteries 22, 27.

TABLE 42

Time on Recovery Discharge to Cut-Off Voltage

(Batteries drained and filled with 1.100 Acid)

Battery	Minutes discharged at 5 amps.		
	C	T	M
1	4.9	22.3	0.0
2	3.7	4.9	4.2
3	11.1	12.1	13.2
(4)	14.2	0.0	13.7
5	6.6	12.1	8.7
6	14.0	8.1	3.0
7	20.9	17.2	9.7
8	10.8	9.8	8.4
9	17.4	12.6	12.3
(10)	0.0	14.6	0.0
11	9.8	9.1	5.7
(12)	1.9	0.0	6.2
(13)	17.6	0.0	4.7
(14)	0.2	1.4	1.5
15	8.3	10.3	23.8
(16)	18.2	15.4	2.3
(17)	0.0	0.0	0.0
18	0.0	7.8	8.2
Grand Total	159.6	157.7	125.6
Average	8.9	8.8	7.0
Total omitting()	107.5	126.3	97.2
Average	9.8	11.5	8.8
Standard deviation of average	1.84	1.45	1.91

TABLE 43

Time on Recovery Discharge to Cut-Off Voltage
(Batteries drained and filled with distilled water)

Battery No.	Minutes discharged at 5 amps.		
	C	T	M
19	30.8	15.2	25.5
20	10.2	8.2	9.5
21	9.4	26.0	11.5
(22)	0.0	0.0	10.1
23	14.5	20.3	17.0
24	0.2	3.7	20.0
25	17.5	19.4	16.3
26	13.0	14.1	21.3
(27)	0.0	0.0	12.5
28	8.3	9.1	6.7
29	13.1	19.5	3.0
30	5.5	0.0	16.6
Grand Total	122.5	135.5	170.0
Average	10.2	11.3	14.2
Total omitting ()	122.5	135.5	147.4
Average	12.2	13.6	14.7
Standard deviation of average	2.57	2.59	2.21

TABLE 44

Watt-Hours Recovery Output
(Batteries drained and filled with 1.100 acid)

Battery No.	Watt Hours		
	C	T	M
1	0.62	2.71	0.00
2	0.44	0.60	0.48
3	1.58	1.60	1.85
(4)	2.05	3.37	1.95
5	0.98	1.78	1.28
6	2.03	1.11	0.40
7	2.81	2.50	1.41
8	1.55	1.40	1.20
9	2.43	1.71	1.78
(10)	0.00	1.68	0.00
11	1.43	1.34	0.83
(12)	0.24	0.00	0.83
(13)	2.40	0.00	0.66
(14)	0.00	0.15	0.18
15	1.15	1.38	2.80
(16)	2.64	2.24	0.27
(17)	0.00	0.00	0.00
18	0.00	1.13	1.21
Grand Total	22.35	24.70	17.13
Average	1.24	1.37	0.95
Total omitting ()	15.02	17.26	13.24
Average	1.37	1.57	1.20
Standard deviation of average	0.26	0.18	0.24

TABLE 45

Watt-Hours Recovery Output

(Batteries drained and filled with distilled water)

Battery No.	Watt Hours		
	C	T	M
19	3.49	1.76	2.89
20	1.40	1.10	1.30
21	1.30	3.03	1.59
(22)	0.00	0.00	1.14
23	2.06	2.86	2.36
24	0.02	0.50	2.44
25	2.36	2.64	1.85
26	1.76	1.96	2.90
(27)	0.00	0.00	1.74
28	1.08	1.15	0.84
29	1.88	2.33	0.41
30	0.66	0.00	2.02
Grand total	16.01	17.33	21.48
Average	1.33	1.44	1.79
Total omitting ()	16.01	17.33	18.60
Average	1.60	1.73	1.86
Standard deviation of average	0.30	0.32	0.26

Part IV

Important Properties of the Components of Lead-acid Storage Batteries

1. Determination of solubility of lead sulfate.

2. The Charging Process and the rate of conversion of lead sulfate to lead and sulfuric acid.

3. Tests of prevention of "Sulfation".

4. Sediment.

5. The Discharge Process at various rates and for electrolytes of various specific gravities.

6. Viscosity.

7. Resistivity.

8. Cell Voltages and Plate Potentials during discharge of Automotive Cells Containing treated or untreated Electrolyte at various specific gravities.

9. Summary of Part IV.

IV. Important Properties of Components of Lead-Acid Storage Batteries

In the foregoing part data on charge and discharge were given for 162 cells and 32 batteries at different current drains and for different specific gravities. The data have not indicated significant differences between treated and untreated cells in regard to several characteristics covered in the studies but showed that "AD-X2" produces a small but detectable detrimental effect at high-rate discharges and that batteries of low specific gravity and treated with "AD-X2" take a charge more slowly than untreated batteries.

1. Determination of solubility of lead sulfate.

In this section several physical properties of the constituents of the lead-acid batteries are considered. It is frequently stated that mixtures of magnesium sulfate and sodium sulfate, or the proprietary material AD-X2 increase the solubility of lead sulfate ($PbSO_4$) in sulfuric acid (H_2SO_4) solutions. It was felt, therefore, that these solubilities should be determined. The method chosen for these determinations was the dithizone method. Dithizone is the commonly-known name for diphenylthiocarbazone, a reagent that provides a very sensitive method for the determination of small quantities of lead. Dithizone imparts a noticeable green tint to a carbon tetrachloride solution but the lead-dithizone complex, however, has a bright cherry-red color. The intensity of this color offers a means of determining lead content of solutions and using a spectrophotometer, values accurate to 0.2 microgram can readily be obtained. The absorbency of the red lead-dithizonate is is measured at 515 millimicrons. The amount of lead in the sample is read from a calibrated curve which is prepared daily. The lead value is then converted to micrograms of lead sulfate per ml of solution. Saturation is reached when determinations of lead agree on successive days to less than 0.1 microgram of lead per ml.

In table 1*, values determined by this method for a temperature of 25°C are listed. In table 2 , the solubility of lead sulfate in battery electrolyte at various specific gravities is given as determined by the same dithizone method. These data were obtained for solutions removed from batteries at various states of charge or discharge. In this case, the temperature of the battery electrolyte was different depending on the state of charge, the battery characteristics, and the room temperature. In the columns marked ratio, the ratio of the solubility of $PbSO_4$ at the experimental temperature to the known solubility at 25°C is given. Within the experimental error, the solubility of lead sulfate in sulfuric acid solutions of various specific gravities or percentages is not significantly different between pure solutions and those containing AD-X2: what little difference there is indicates that lead sulfate is less soluble in sulfuric acid containing AD-X2 than in pure acid.

* All tables of this part (Part IV) are given in Part VII, Appendix 6.

2. <u>The Charging Process and the rate of conversion of lead sulfate to lead and sulfuric acid.</u>

As "AD-X2" does not increase the solubility of lead sulfate in sulfuric acid, the question then arises whether the rate of solubility of lead sulfate in sulfuric acid solutions might not be enhanced by the presence of "AD-X2" or a mixture of magnesium and sodium sulfates. To this end, old sulfated negative plates were removed from discarded batteries, inspected for mechanical soundness, and the rate with which the lead sulfate on their surface and in the plate pores was converted to lead during the charge was determined. In this work, the plates were paired; plates of any one cell of any one battery were paired for comparison of the effect of the "additive." On charge, lead sulfate is reduced by the electric current to lead (the "active material") on the surface and in the pores of the old negative plate. When lead sulfate is electrochemically reduced to lead, sulfate ion is also formed in an amount stoichiometrically equal to the amount of lead formed. This reaction may be expressed as follows:

$$\underset{\text{lead sulfate}}{PbSO_4} + 2\underline{e} \longrightarrow \underset{\text{lead}}{Pb} + \underset{\text{sulfate ion}}{SO_4^{=}} \qquad (1)$$

where $\underline{e}$ is the electron coming from the external electrical charging current. For the outside plates a hard Planté type lead plate was used. The Planté plate will be covered immediately with a surface layer of lead dioxide and thereafter oxygen will be produced on its surface according to the reaction:

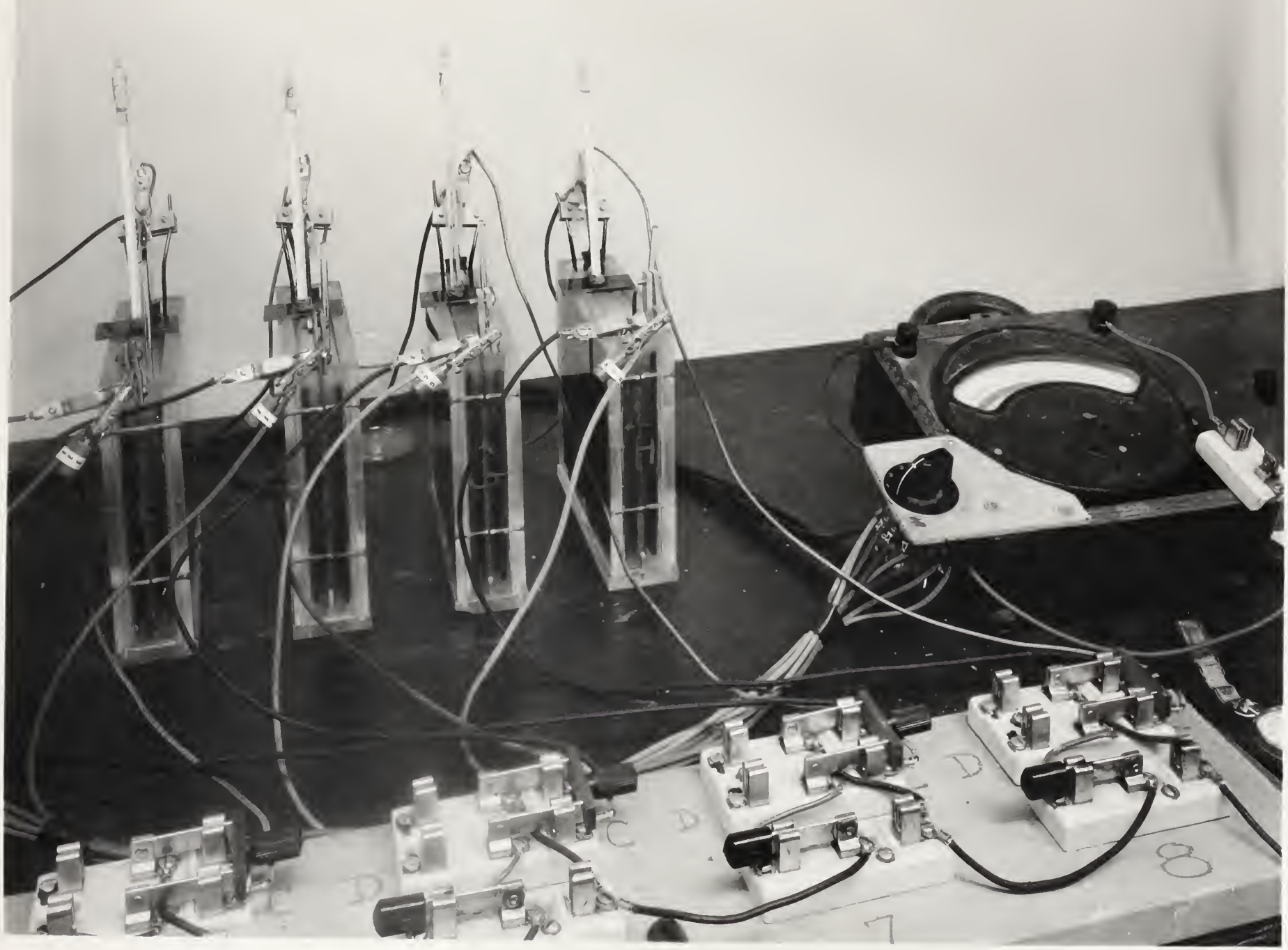
$$H_2O \longrightarrow \tfrac{1}{2} O_2 + 2H^+ + 2\underline{e} \qquad (2)$$

Thus the overall cell reaction will be:

$$PbSO_4 + H_2O \longrightarrow H_2SO_4 + Pb + \tfrac{1}{2} O_2 . \qquad (3)$$

Therefore, determinations of sulfuric acid formed (right side of equation) during charge will indicate the effectiveness and rate at which lead sulfate is reduced to lead during charge. The cells and equipment used in these measurements are shown in accompanying photographs.

Results of these experiments are given in tables 3 to 9, inclusive. Data for low specific gravities and low charge rates are given in tables 3 to 6 inclusive for various ampere-minutes of charge. Before start of the initial charge and at end of the final charge, the acid content was determined with standard alkali with phenolphthalein indicator. Results show that less acid is produced when "AD-X2" or a mixture of sodium and magnesium sulfates is added to the electrolyte. This means that the rate or efficiency for the conversion of lead sulfate to lead and sulfuric acid is not enhanced by the addition of "AD-X2" but instead is curtailed during the charging process. It should be noted in table 4 that this is true for acid specific gravities of 1.020, 1.100 and 1.150.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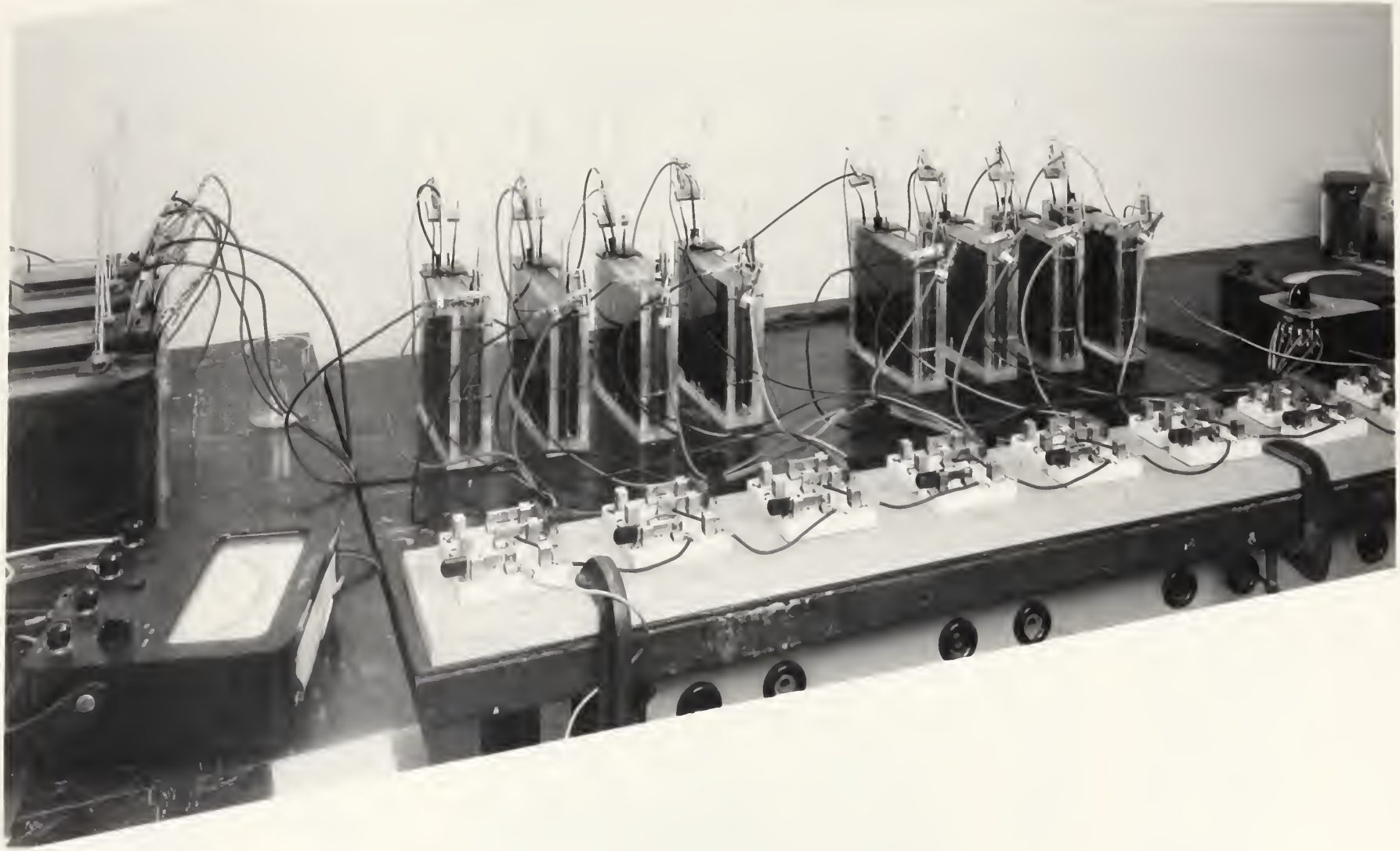


In table 7 similar results are given for various amounts of "AD-X2" per unit volume of solution and for successive charges at different rates. This experiment was conducted to ascertain if the amount of "AD-X2" had an appreciable effect on the results. Within the limits of difference in plate characteristics, the curtailment of the conversion of lead sulfate to lead and sulfuric acid becomes more marked for larger additions of "AD-X2."

In tables 8 to 9, similar data are given for much higher charging rates. Here the detrimental effect of "AD-X2" on the charging efficiency is very marked; the efficiency is only about 50% of that obtained with pure sulfuric acid solutions.

As a confirmation of these results some of the charged negative plates of the above experiments were removed from their respective charging solutions, washed in distilled water, and discharged in 1.200 sp.gr. sulfuric acid. A reference cadmium electrode was immersed in the solutions and the potentials of the negative plates were measured in reference to the cadmium electrode throughout the discharge. All these discharges were calculated to a cutoff of 1 volt, i.e., when the difference between the negative plate and the cadmium electrode became one volt. At one volt, the change in potential is rapid. Results are given in table 10, and the discharge curves in figures 1 to 11 inclusive. Without exception and at different discharge rates more ampere-minute output was obtained for plates that had been charged in pure sulfuric acid solutions as opposed to those charged in solutions containing "AD-X2." This shows that more lead had been produced on charge as exemplified in equation (1). In short, titrations show that more H_2SO_4 and discharges show that more lead is produced during charge in solutions free of "AD-X2." The difference between 100% efficiency and that observed is used to discharge H^+ ions; therefore "AD-X2" induces more gassing and water losses during the charging process.

3. <u>Tests of prevention of "Sulfation"</u>

Another claim frequently made by proponents of battery additives is that they prevent "sulfation." The term "sulfation" as applied to lead-acid storage batteries usually refers to pernicious sulfation. It is so used here. The term refers to the formation of lead sulfate on the surface and in pores of the active material of the plates as a result of local corrosion and other factors. When a battery discharges lead sulfate forms in a finely crystalline state at both plates. This formation is an essential feature of the operation of a battery; prevention of its formation would render a battery useless. However, on open circuit when the battery is delivering no useful energy, the formation of lead

sulfate unfortunately continues at low rates. It forms because of local action or self-discharge of the plates brought about by parasitic currents or by action of the acid solution with the material of the plates; plates made with antimony-lead alloy grids corrode at a faster rate than do plates made of pure lead, since local action is enhanced by the presence of antimony.

When a battery has stood for long times on open-circuit, especially in an environment of fluctuating temperatures, the crystals of lead sulfate become large, dense and coarse. Such crystals are more difficult to convert to the active materials of the plates by the charging current but can be achieved by successive charges and discharges at low current densities. Pernicious sulfation also occurs as a result of (1) allowing the battery to stand in a discharged condition for a considerable time, (2) neglecting to make repairs when evidence of trouble within cells becomes apparent, (3) filling the cells with electrolyte when water should have been used, and (4) persistent undercharging.

"AD-X2" is stated to prevent pernicious sulfation. To ascertain if "AD-X2" does work in this sense, 18 new batteries were obtained, 4 in glass containers, and all these were given different treatments and stored under conditions of fluctuating temperatures which should enhance "sulfation". The batteries were stored at 50°C for 9 hours and allowed to cool the remaining 15 hours each day for five days; they were allowed to cool the entire two days over weekends. Photographs of the glass batteries* prior to and after storage are given as figures bearing the battery numbers. The 18 batteries were divided into 9 groups of 2 batteries each; each group was treated differently as follows:

(1) Group 1: Batteries 1A(U) and 1B(T). These 2 batteries were given a charge at 10 amperes and a finishing charge at 5 amperes, "AD-X2" being added to all three cells of one battery during the charge; the other battery was left untreated. The batteries were then discharged and given 2 additional cycles of charge and discharge and then stored at fluctuating temperatures in the discharged state. Each discharge was terminated when the battery voltage reached 4.50 volts.

*Photographs of a pair of batteries show them prior to storage; photographs of single batteries show them after 186 days storage.

(2) Group 2: Batteries 2A(U) and 2B(T). These 2 batteries were treated in the same way as the two batteries of group 1 except at the end of the third discharge, they were first given an additional discharge at 10 amperes to a terminal voltage of 4.00 volts followed by a 5 ampere discharge to a terminal voltage of 3.00 volts. These 2 batteries were then stored in an "over-discharged" state under conditions of fluctuating temperatures.

(3) Group 3: Batteries 3A(U) and 3B(T). These 2 batteries were treated the same as those of group 1 except that they were given an additional charge after the third discharge and were therefore stored in the charged condition. These were stored under conditions of fluctuating temperatures.

(4) Group 4: Batteries 4A(U) and 4B(T). These 2 batteries were stored in the condition as received. "AD-X2" was added to cells 1 and 3 of battery 4B; cell 2 (middle cell) was left untreated. "AD-X2" was added to cell 2 (middle cell) of battery 4A ; cells 1 and 3 were left untreated. These were stored under conditions of fluctuating temperatures.

(5) Group 5: Batteries 5A(U) and 5B(T). These were given a 10 ampere charge and a finishing charge of 5 amperes to full charge. During charge, "AD-X2" was added to cell 2 (middle) of battery 5A and to cells 1 and 3 of battery 5B. The other cells were left untreated. These batteries were likewise stored under the condition of fluctuating temperature.

(6) Group 6: Batteries 6A(U) and 6B(T). These 2 batteries were given 4 cycles of charge and discharge and "AD-X2" was added to battery 6B during the fourth charge. The two batteries were then discharged and stored in the discharged state under conditions of fluctuating temperatures.

(7) Group 7: Batteries 7A(U) and 7B(U). These were in glass containers. Both batteries were left untreated and given 3 cycles of charge and discharge and were stored in the discharged state under conditions of fluctuating temperatures.

(8) Group 8: Batteries 8A(T) and 8B(T). These were also in glass containers. Both batteries were treated with "AD-X2" on first charge. Three cycles of charge and discharge were completed and the batteries were stored under conditions of fluctuating temperatures.

(9) Group 9: Batteries 9A(U) and 9B(T). These were control batteries stored at room temperature. Battery 9B was treated with "AD-X2" on first charge; battery 9A was left untreated. Both batteries were given 3 cycles of charge and discharge and stored in the discharged state at ambient room temperature.

As "sulfation" forms on storage, the internal resistance of storage batteries increases. This is due to the fact that lead sulfate is a non-conductor whereas lead (active material of negative plate) and lead dioxide (active material of positive plate) are good conductors. Therefore, as "sulfation" ensues and lead sulfate builds up on the plates during storage in an idle condition, the internal resistance of the battery increases. The internal resistance of these batteries was measured by the direct current method. Although measurements made by this method are affected by polarization, the method does simulate battery operation more closely than the alternating current method and undoubtedly gives values which are relatively significant. After intervals of storage, each battery (or cell) was given a momentary flash charge at a constant current of 25 amperes. The charge was continued for 15 seconds with readings taken at second intervals. The internal resistances, R, of the batteries (or cells) were then determined by the relationship

$$\left| E_{closed} - E_{open} \right| / I = R$$

App. 6

where E_{closed} is the voltage obtained at 2 seconds, E_{open} the electromotive force when there is no flow of current and I is the current flowing. Values obtained in this manner are given in table 11 for the various batteries (or cells) after various periods of storage. Values for the batteries in glass jars were determined first after 49 days of storage and the others for the first times after 86 days of storage. Readings of internal resistances for the batteries containing 2 treated and 1 untreated or 1 treated and 2 untreated cells were taken only after 148 and 207 days; earlier readings were for the whole battery.

In table 11 values of the internal resistances for the batteries (or cells) after 49, 89, 189, and 207 days of storage are listed; table 12 lists average values obtained for treated and untreated batteries and cells. Within the experimental error no significant differences in the relative internal resistance between treated and untreated batteries (or cells) are noted. As compared with batteries stored at room temperature, the periodic changes in temperature between 50°C and room temperature have enhanced "sulfation" and "AD-X2" has neither prevented nor retarded sulfation.

4. Sediment.

In the foregoing it was shown that "AD-X2" neither increases the solubility of lead sulfate in sulfuric acid solutions of various specific gravities nor does it increase the rate of solubility of lead sulfate during the flow of electric current during charge; in fact "AD-X2" decreases the rate of conversion of lead sulfate to lead and sulfuric acid during the charging process. It is, therefore, difficult to explain why it has been stated that "AD-X2" dissolves the sediment or the "mud" on the bottom of batteries and redoposits it in an insoluble state back on the plates. If "AD-X2" makes lead sulfate soluble on the bottom of the battery it should likewise do so on the plates, and thereby lead to enhanced corrosion of the grids.

In part III, two photographs of the relative amounts of sediment taken from the 3 cells of 4 batteries after a series of charges and discharges and an overcharge show that the amounts of sediment found in treated and untreated cells is not substantially different and what little difference there is favors the untreated cells (see figures bearing the battery numbers). Also, in the cells mentioned above under "prevention of sulfation", sediments can be seen in all four of the batteries in glass containers (none was present at the start of test) and no significant differences in the amounts of sediment in the treated and untreated batteries can be observed (see figures bearing battery numbers).

The formation of sediment results from the periodic expansion and contraction of the plates on discharge and charge. At the negative lead plate lead sulfate is formed on discharge; on charge the reverse process occurs. At the positive plate lead dioxide is converted to lead sulfate on discharge and the reverse process occurs on charge. Lead, lead sulfate, and lead dioxide have different molecular weights, densities, and therefore occupy different volumes. These are listed below:

Name	Chemical formula	Molecular weight	Density	Molecular volume
Lead	Pb	207.21	11.337	18.28
Lead sulfate	$PbSO_4$	303.27	6.2	48.91
Lead dioxide	PbO_2	239.21	9.375	25.52

Therefore, on discharge both the negative and positive plates expand in volume with the expansion being more for the negative (lead) plates. On charge a contraction of both plates ensues. This process of expansion and contraction of the plates during cycles of charge and discharge inevitably leads to "shedding" of the active material of the plate and the formation of sediment or "mud" at the bottom of the battery. "AD-X2" cannot alter the molecular weights or densities of lead, lead sulfate, or lead dioxide and it is, therefore, inconceivable how it could prevent or decrease sediment or battery mud.

5. The Discharge process at various rates and for electrolytes of various specific gravities.

In a foregoing section it was shown that "AD-X2" or a comparable mixture of magnesium and sodium sulfates was detrimental to the charging of lead-acid storage batteries. We have next, therefore, to consider the effect of "AD-X2" on the discharge and the relationship between charge and discharge.

To this end, negative plates obtained from discarded batteries as above were chosen and after charge were studied on discharge in sulfuric acid solutions of 1.200 (normal range for practical operations) and of 1.100 or 1.050 (specific gravity obtained at end of discharge in some cases) and of 1.020 which is extremely low and rarely found in actual operation. Also various rates of discharge were chosen for this study in order to give an overall picture of the phenomena that might occur.

First, we shall consider the problem of extremely low specific gravities and the effect that "AD-X2" or a mixture of magnesium and sodium sulfates has on the discharge in such extremely dilute solutions. In table 13, data are given for 2 pairs of negative plates. "AD-X2" was added as shown. These were first given a one ampere charge for 120 minutes and discharged at the low rate of 2 amperes; recharged at 1 ampere for 180 minutes and again discharged. For this condition, we find that "AD-X2" has a slightly beneficial effect. This is not surprising, however, since the sulfate content of sulfuric acid of 1.021 specific gravity is 3.2% whereas it is 6.96% when "AD-X2" is added.

However, one must bear in mind that since "AD-X2" is detrimental to the charging process, the "apparent" beneficial effect discussed above can be of only momentary existence, and will vanish on the next of succeeding cycles. This is shown by the data of the second part of table 13 . After 180 minutes of charge at the very low rate of 0.5 ampere, treated cells gave a few more minutes of discharge on a constant current drain of 2 amperes. However, on the next cycle of charge and discharge the differences between treated and untreated cells became insignificant (two treated cells gave fewer minutes, one gave more, and one was practically equivalent to the untreated cell). In other words, on normal cycling "AD-X2" has no lasting benefits. It should again be stressed that the effect here depicted is observed for a specific gravity much lower than ordinarily obtained in practical operations.

Next, we shall consider high-rate charges for this extremely dilute solution. In table 14, data are given for charges and discharges at 6 amperes. For this higher charging and discharge rate , "AD-X2" is detrimental to the discharge (some detriment is introduced by the charge as less acid and lead are formed when "AD-X2" is present). The difference observed, even for this extremely dilute solution, between low and high rates of charge may be explained on the basis of diffusion of sulfate ions to the electrode (lead) surface on discharge and the diffusion of acid away from the plate on charge. Solutions containing "AD-X2" are more viscous than those without the additive (see section on viscosity), and "AD-X2" by its presence adversly affects the diffusion of sulfate and hydrogen ions toward or away from the plates.

In tables 15 and 16 additional results are given for low charging rates and extremely dilute solutions. Here, data are also given for a mixture of magnesium and sodium sulfates comparable in composition to "AD-X2". Discharge data are given in table 15 and ratios of outputs of treated to untreated in table 16. Here again we see that "AD-X2" produces a momentary "apparent" beneficial effect which vanishes as the cells are cycled. Also, the specific gravity (1.020) is lower than that encountered in practice.

Next, we shall consider whether or not the above effects are observed for the normal range of specific gravity encountered in practical operations. First, we shall consider a specific gravity of 1.100, the gravity most frequently observed at the termination of discharge when the voltage shows a very rapid drop and the battery has reached the end of its useful capacity or is "down". In table 17 data are given for low charge rates; in table 18 for high-charge rates. For low charge rates no significant difference is noted between treated and untreated cells. For high charge rates it will be seen that "AD-X2" has a detrimental effect; discharge times for the treated cells ~~is~~ are only 60 to 80%

of those obtained for untreated cells. In short, therefore, at the lower range of specific gravity for normal operation, "AD-X2" is of little or no benefit and for fast charges is detrimental.

Next, we shall consider results obtained for specific gravities of 1.200, the specific gravity corresponding to about 50% of full charge. Since it has already been shown that "AD-X2" is detrimental to the charging process, the plate pairs were all charged in 1.200 acid for 2 cycles. The acid was then dumped from all cells and either (1) pure acid (sp.gr. = 1.200) or (2) pure acid plus "AD-X2" (sp.gr. = 1.235), or (3) acid plus a mixture of magnesium and sodium sulfates in composition comparable to that of "AD-X2" (sp.gr. = 1.232), or (4) acid of specific gravity (1.233) equal to that for pure acid plus "AD-X2" was added to individual cells. Data given in table 19 show that neither "AD-X2" nor $MgSO_4$-Na_2SO_4 mixture improve the discharge characteristics for a normal specific gravity found for batteries in practical operation.

In summary therefore, "AD-X2" is detrimental to charge in all specific gravities and at low and high rates of charge. It likewise adversely affects discharges at high rates from 1.020 to 1.200 sp.gr. and only leads to an "apparent beneficial effect" for low rates and extremely dilute solutions and this effect is only of momentary existence and vanishes on cycling.

6. Viscosity

Rate of diffusion of ions to the plate surfaces has an important bearing on the discharge process. Also the rate of diffusion of sulfuric acid away from the plates has an important bearing on the charging process. The higher these two rates are the less is the concentration polarization and the higher is the watt efficiency of the electrode processes. Thus, lead-acid storage batteries behave differently when subjected to low- or high-rate charges or discharges; the efficiencies becoming higher as the rates of charge or discharge are lowered.

The rate of diffusion of ions is inversely proportional to the viscosity of the medium in which they exist. Thus, any material which would increase the viscosity of the electrolyte in a lead-acid storage battery would decrease the rate of ionic movement and thereby accentuate electrode polarization and lower electrical watt efficiency. Accordingly the viscosities of sulfuric acid solutions with or without "AD-X2" were determined at temperatures of 0°C, 25°C and 45°C. Description of the solutions used in these measurements is given in table 20. Values of kinematic viscosities are

given in table 21; absolute values in table 22. "AD-X2" increases the viscosity of sulfuric acid solutions at 25°C by about 6.6% for specific gravities from 1.050 to 1.300 and by 8% for the more dilute solutions. This increase in viscosity caused by the addition of "AD-X2" presumably accounts in part for the adverse effects mentioned above for "AD-X2" in the charging and discharging processes.

7. Resistivity

Although the internal resistance of lead-acid storage batteries is low (order of 0.001 to 0.01 ohm), any material that would increase the resistivity of the electrolyte would affect the performance of the battery especially for high-rate discharges such as are encountered in the cranking of an automobile engine. Accordingly the specific resistance of sulfuric acid solutions with or without "AD-X2" were measured at temperatures of 0°C, 25°C and 45°C. Description of solutions used in obtaining the resistivities is given in table 23; values of resistivities in table 24. It will be noted that "AD-X2" increases the resistivity of sulfuric acid solutions by about 5% for solutions exceeding about 1.2 percent by weight in sulfuric acid. Only for extremely dilute solutions (less than 1%, specific gravity below 1.01) is sulfuric acid containing "AD-X2" less resistant than pure aqueous sulfuric acid and this range is not encountered in normal operation of a battery. This increase in resistance of the electrolyte by addition of "AD-X2" is without detectable influence on the performance of lead-acid batteries under normal rated discharges, but has a small but detectable detrimental influence on discharges at high rates of discharge (300 amperes) as are encountered in the starting of automobile engines. This detrimental effect would be more marked for low temperatures where higher rates of discharge are required to start an automobile engine.

8. Cell voltages and plate potentials during discharge of automotive cells containing treated or untreated electrolyte of various specific gravities.

In sections IV.2 and IV.5 given above we have discussed the effect during charge and discharge of AD-X2 on hard sulfated negative plates which on initial charges took the charge inefficiently. Those results showed, contrary to the claims of the manufacturer, that the addition of AD-X2 to the electrolyte deterred the redevelopment of hard sulfated negative plates during the charging process.

We have next to consider the effect of AD-X2 on the discharge of good non-sulfated plates, or on ones that can readily be charged. In this then we are concerned primarily with the "efficacy" of the electrolyte to support the discharge. As additions of AD-X2 increase the total sulfate-ion concentration and introduce extraneous sodium and magnesium ions in battery electrolyte, it is to be expected that such additions will affect favorably or adversely the electrode kinetics and the thermodynamics of the electrochemical system.

To this end, a series of tests were made in which the cell voltages and the potentials of the positive and negative plates (relative to a reference cadmium electrode) were measured during the discharge of cells containing treated and untreated electrolytes of various specific gravities. An automotive cell was used in this study and each cell of this battery was provided with a drain cock. By repeatedly filling and draining the cells the composition of the electrolyte in each cell could be accurately adjusted. In preparing the cells for each discharge they were first fully charged and then the electrolyte was drained from each cell. Each cell was then filled with a portion of a sulfuric acid solution of the desired specific gravity, allowed to stand for approximately one half hour, and then drained of electrolyte. This process was repeated with fresh portions of electrolyte until the specific gravity of the solution drained from each cell was the same as that of the initial solution used in filling the cells. It was thereby assured that the sulfuric acid concentration of the solution in each cell was identical for a given experiment. Finally cell 3 was filled with the required volume of the sulfuric acid solution, cell 1 with the required volume of the same sulfuric acid solution in which the contents of one envelope of AD-X2 had been dissolved and cell 2 with the required volume of the same sulfuric acid solution in which the contents of two envelopes of AD-X2 had been dissolved. The cells were then ready for discharge.

The specific gravities of the sulfuric acid solutions used in these experiments covered the range from 1.010 to 1.160. Although specific gravities below 1.070 to 1.100 are not within the range that give either practical or normal outputs; they were included in this study in order to give a complete picture of the phenomena that occur. The output of the cells was accordingly curtailed and limited primarily by the electrolyte rather than by the plates as distinct from the experiments described in sections IV.2 and IV.5. Thus, the experimental results are a measure of the efficacy of the various electrolytes to support the discharges.

Note: This and the three succeeding pages were added May 4, 1953 and have to do with work in progress on the date of this report.

In the first three experiments all the cells contained dilute sulfuric acid solution, 1.010 sp. gr. Cell 3 contained no AD-X2, cell 1 contained the contents of one envelope of AD-X2 and cell 2 contained the contents of two envelopes. In the first experiment each cell was discharged at 5 amperes, in the second experiment at 15 amperes and in the third experiment at 50 amperes. The cell voltages and the plate potentials (measured relative to a reference cadmium electrode) for each cell at each rate of discharge are shown graphically in figures 12, 13 and 14 respectively, for 5, 15 and 50 amperes. At each rate of discharge it is seen that the additive prolongs the discharge of the negative plates at a useful plate potential. The prolongation is greater for cell 2 which contained the greater quantity of sulfate as a result of adding the larger quantity of AD-X2. This is in accordance with the discharge reaction of the negative plate, viz.,

$$Pb + SO_4^{--} \longrightarrow PbSO_4 + 2\,\underline{e}.$$

Although the additive prolongs the discharge of the positive plate at low plate potentials it does not, however, cause any significant prolongation at useful potentials. This is not surprising since the additive, although it does supply sulfate ions, does not supply hydrogen ions which are indispensable for the normal discharge of the positive plates. This reaction is

$$PbO_2 + 4\,H^+ + SO_4^{--} + 2\,\underline{e} \longrightarrow PbSO_4 + 2H_2O$$

Consequently since the additive causes no significant improvement in the potential of the positive plates there is accordingly no significant improvement at useful cell voltages. This is shown by the data in table 25. Although the results in this table show that the additive prolongs the discharge at low cell voltages this prolongation is to be attributed not to any particular merit of the AD-X2 but solely to the excess of sulfate ions. Furthermore any prolongation of the discharge of the negative plates, caused by the additive, can be realized not only at the negative but at the positive electrode, both at useful voltages by the addition of an equivalent quantity of sulfuric acid, and therefore at useful cell voltages by the addition of an equivalent quantity of sulfuric acid.

Table 26 gives the results of a series of discharges of the above cells at 50 amperes. The specific gravities of the untreated electrolyte used in this series of discharges ranged from 1.010 to 1.160. In each experiment the concentration of the sulfuric acid of the electrolyte in each cell was the same. The specific gravities of these solutions and also their specific gravities after the addition of the additive are given in table 26. The cell voltages during discharge are shown in figures 14 - 17, inclusive, in addition figures 14 and 17 also show the plate potentials. The duration of each discharge to each of a series of closed-circuit voltages is given for each cell in table 26. To facilitate the comparison of the performance of cell 3, untreated, with the performance of cells 1 and 2, both treated, the maximum time of discharge to each closed-circuit voltage for each experiment is marked with an asterisk *. It can be observed for each experiment that cell 3 which contained untreated electrolyte sustained the discharge for longer periods at the higher voltages, 1.75, 1.50 and 1.25 volts whereas cell 2 which contained the most additive sustained the discharge for longer periods at the lower voltages, 0.50, 0.25 and 0.00 volts. The prolongation of the discharges at these lower voltages is of no practical value and furthermore since the untreated cell had a higher average voltage until the voltage falls to one volt it follows that the untreated cell must have had higher watt-hour outputs than the treated cells at all voltages above 1.0 volt. These lower discharge voltages for the treated cells are in conformity with the data given under sections IV.6 and IV.7. Therefore it must be concluded that the additive has a detrimental rather than a beneficial effect on the electrical characteristics of lead acid batteries.

Further comparisons of the outputs of treated cells with the outputs of untreated cells can be made. For example; cell 3 in experiment 5 contained untreated electrolyte, specific gravity 1.040 and cell 1 in experiment 4 contained a treated electrolyte of the same specific gravity. Cell 3, untreated, gave an output of 8.2 minutes to 1.50 volts and 9.5 minutes to 0.00 volts whereas cell 1, treated, gave outputs of only 1.3 and 4.7 minutes to the respective voltages. Another example; cell 2 in experiment 5 contained treated electrolyte, specific gravity 1.074, and cell 3 in experiment 6 contained untreated electrolyte of lower specific gravity 1.070. Nevertheless cell 3, untreated, gave an output of 18.5 minutes to 1.50 volts and an output of 20.6 minutes to 0.00 volt whereas cell 2 gave outputs of 7.0 and 12.2 minutes to the respective voltages. These examples show, for a given specific gravity, that the output of the untreated cells exceeds the output of the treated cells to corresponding voltages.

9. Summary of Part IV.

This part of the report has dealt with some of the physical chemistry of lead-acid storage batteries pertinent to the problem at hand. All data show that the observed behavior of aqueous solutions of sulfuric acid containing AD-X2 follows known laws of physical chemistry. Effects observed for AD-X2 are also observed for a comparable mixture of magnesium and sodium sulfates.

If we are willing to accept the basic laws of physical chemistry, experiments under a variety of conditions and over a period of time will reflect and only reflect the operation of these laws. The alleged success obtained with AD-X2 must be due to (1) conclusions drawn from experiments without adequate controls (concurrent observations on treated and untreated batteries), (2) to "psychological effects" including misunderstandings regarding the recuperative power and the ability of a battery to take a charge, (3) to the use of batteries believed to be defective but actually useable, and (4) confusion relating to the rebuilding and repair of batteries and the need for AD-X2 in such operations. The last three of these are discussed in Part VI of this report.

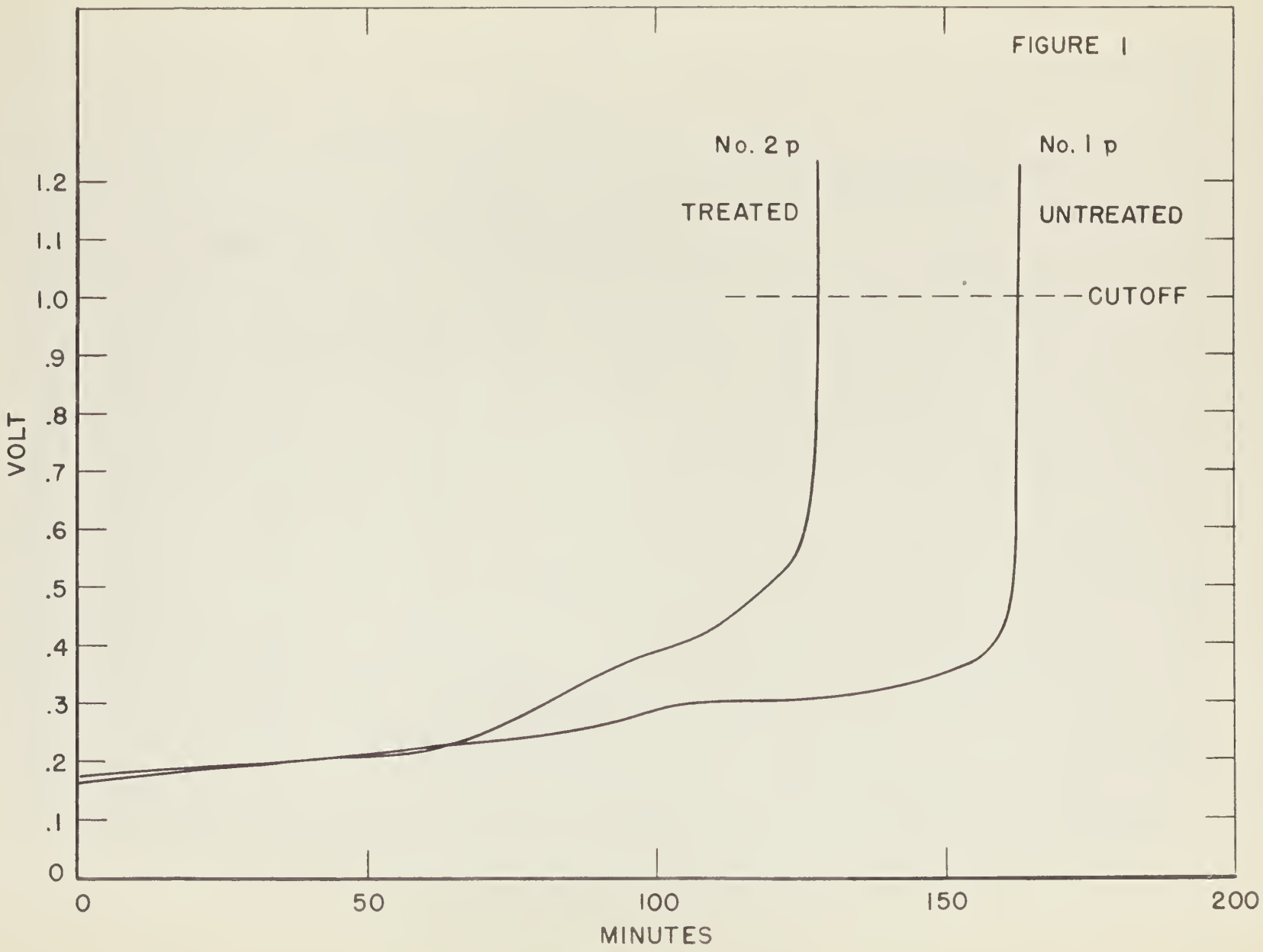


FIGURE 1
No. 2 p
TREATED
No. 1 p
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
50
100
150
200
MINUTES

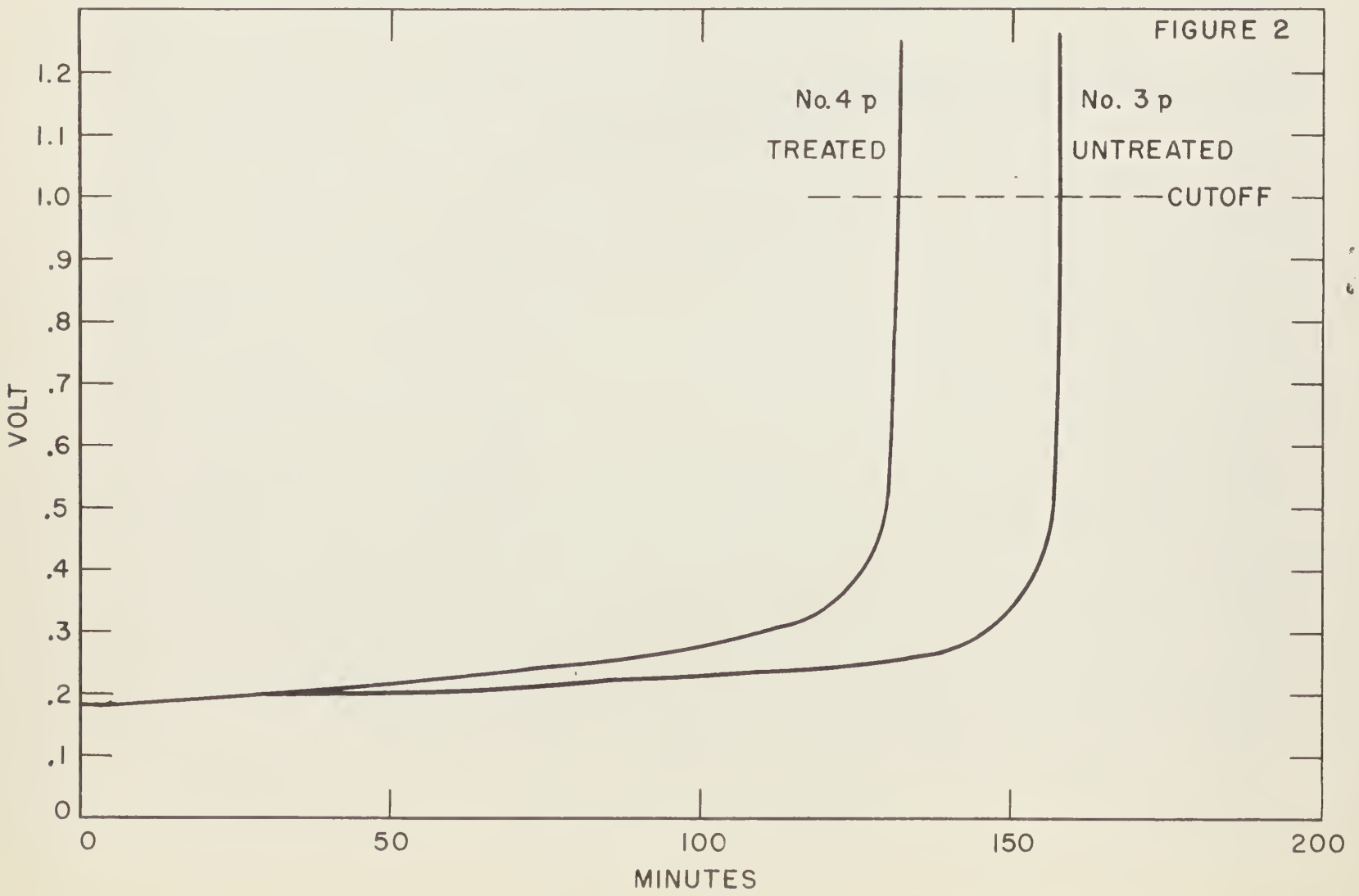


FIGURE 2
No. 4 p
TREATED
No. 3 p
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
50
100
150
200
MINUTES

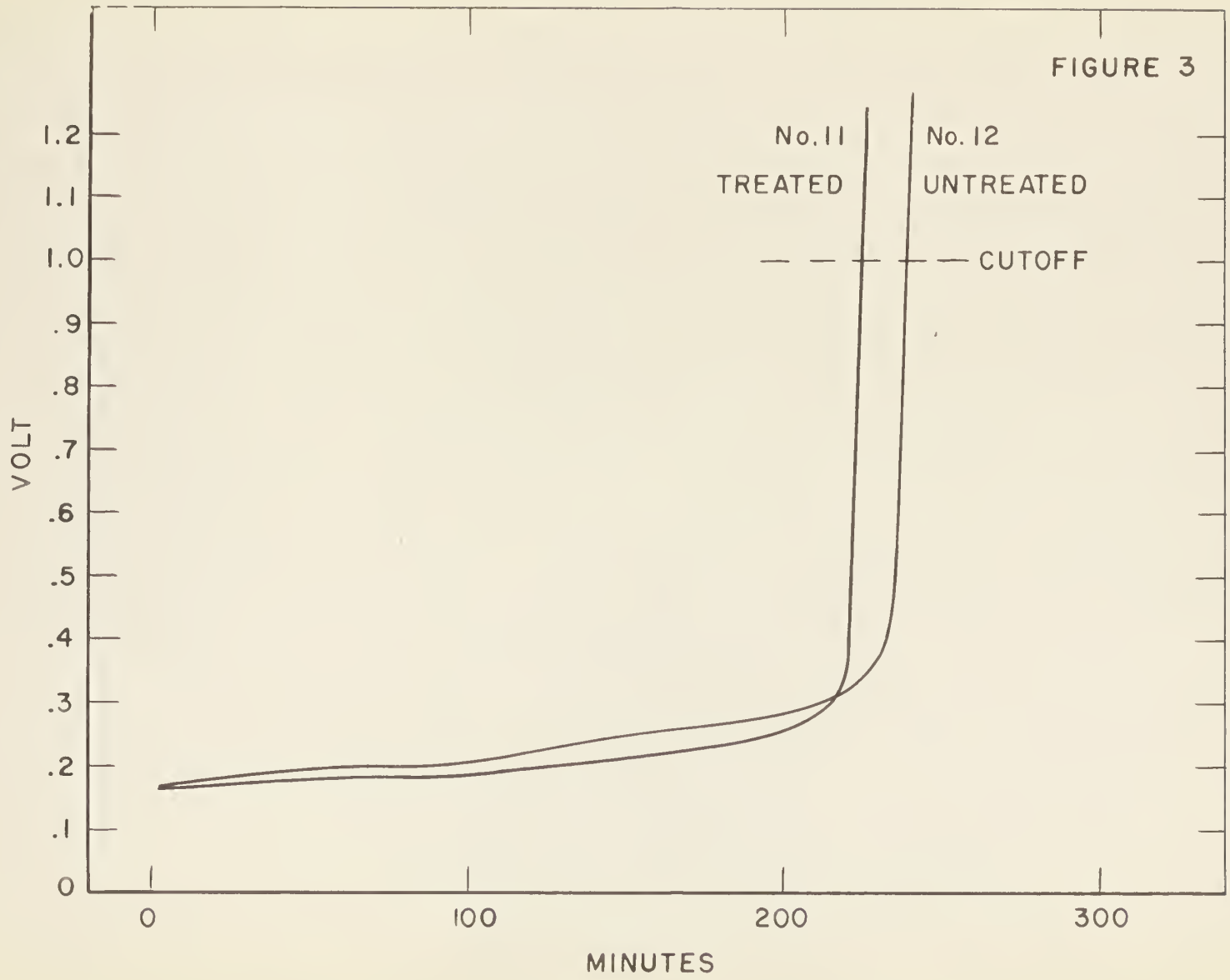


FIGURE 3
No. 11
TREATED
No. 12
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
100
200
300
MINUTES

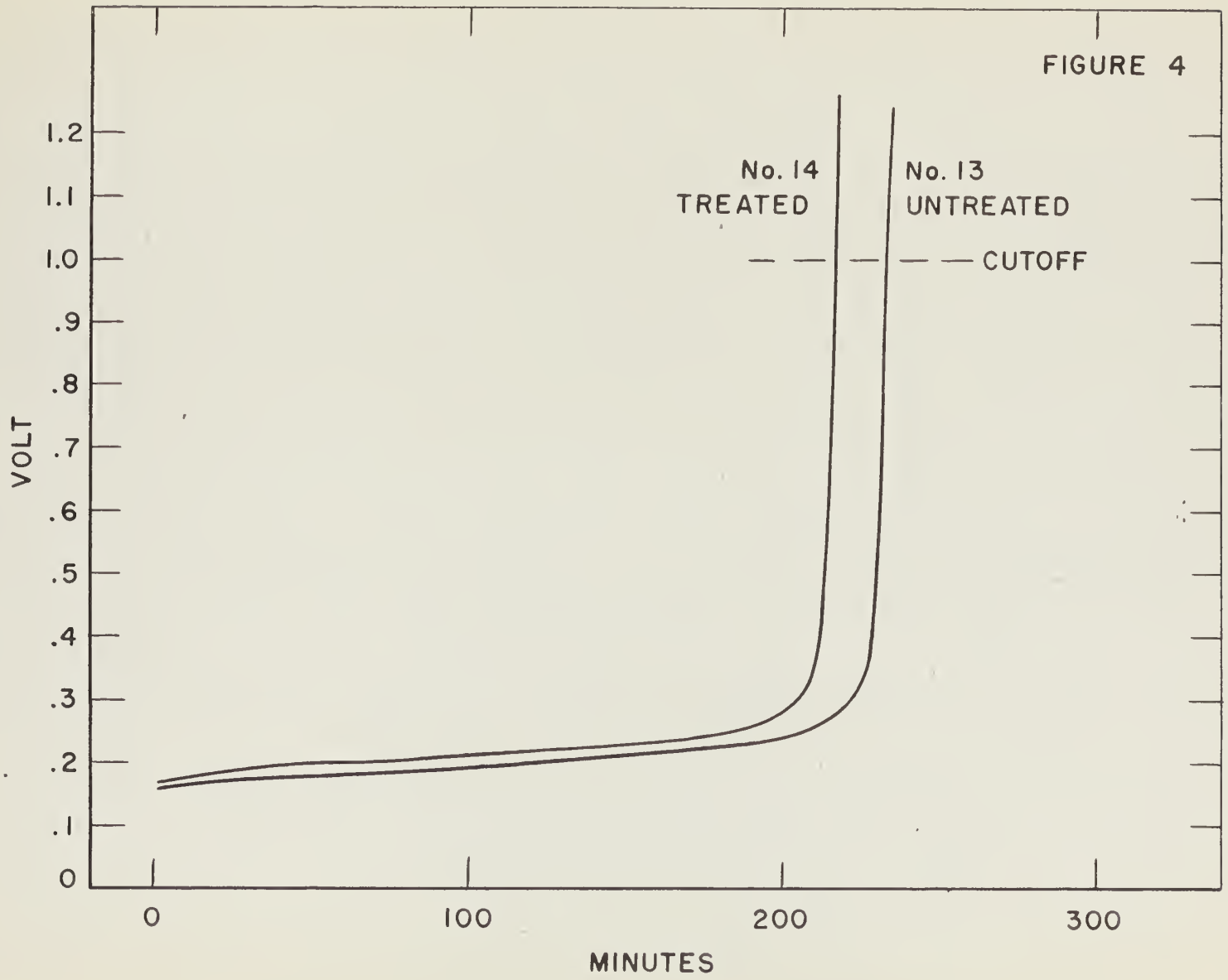


FIGURE 4
No. 14
TREATED
No. 13
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
100
200
300
MINUTES

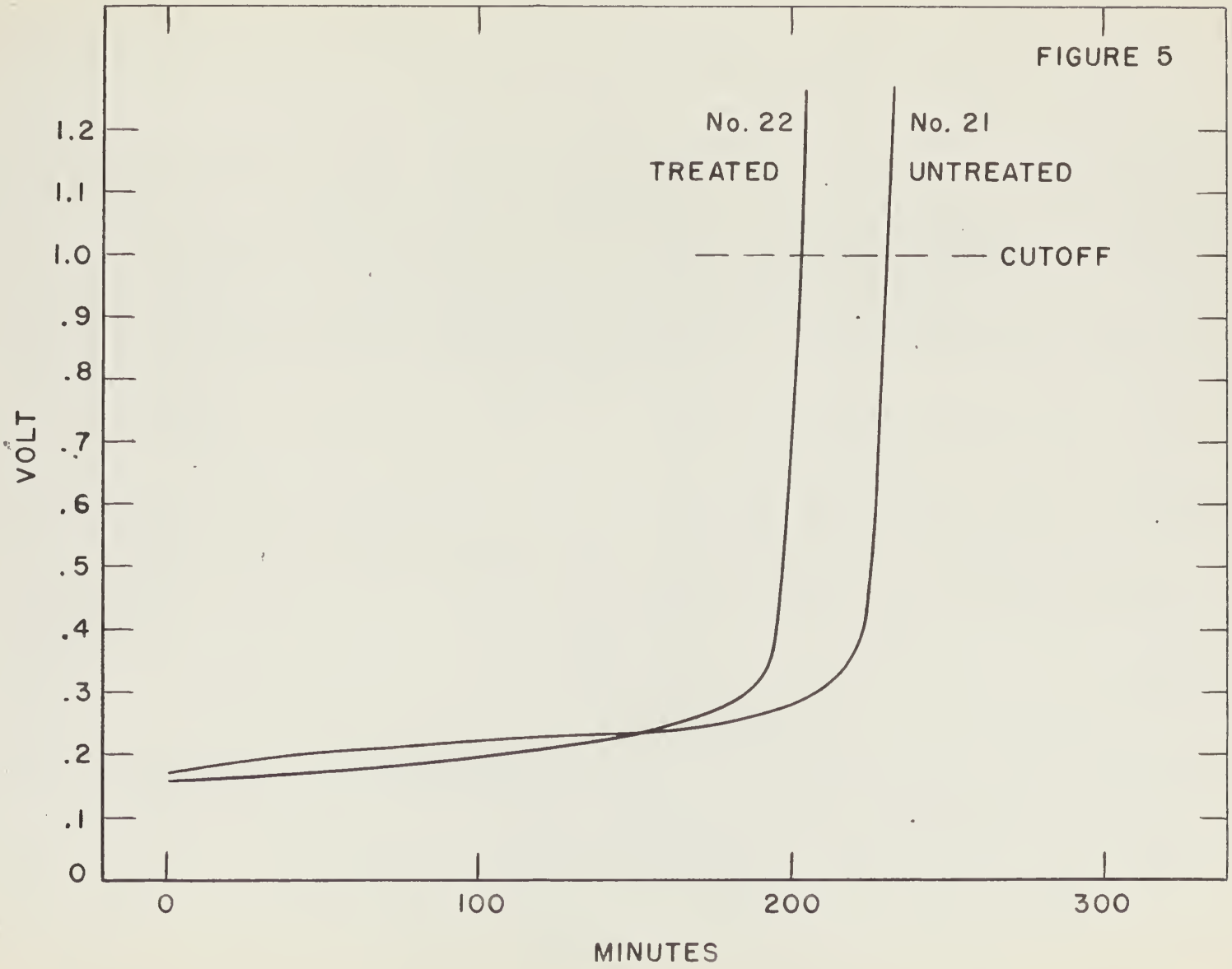


FIGURE 5
No. 22
TREATED
No. 21
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
100
200
300
MINUTES

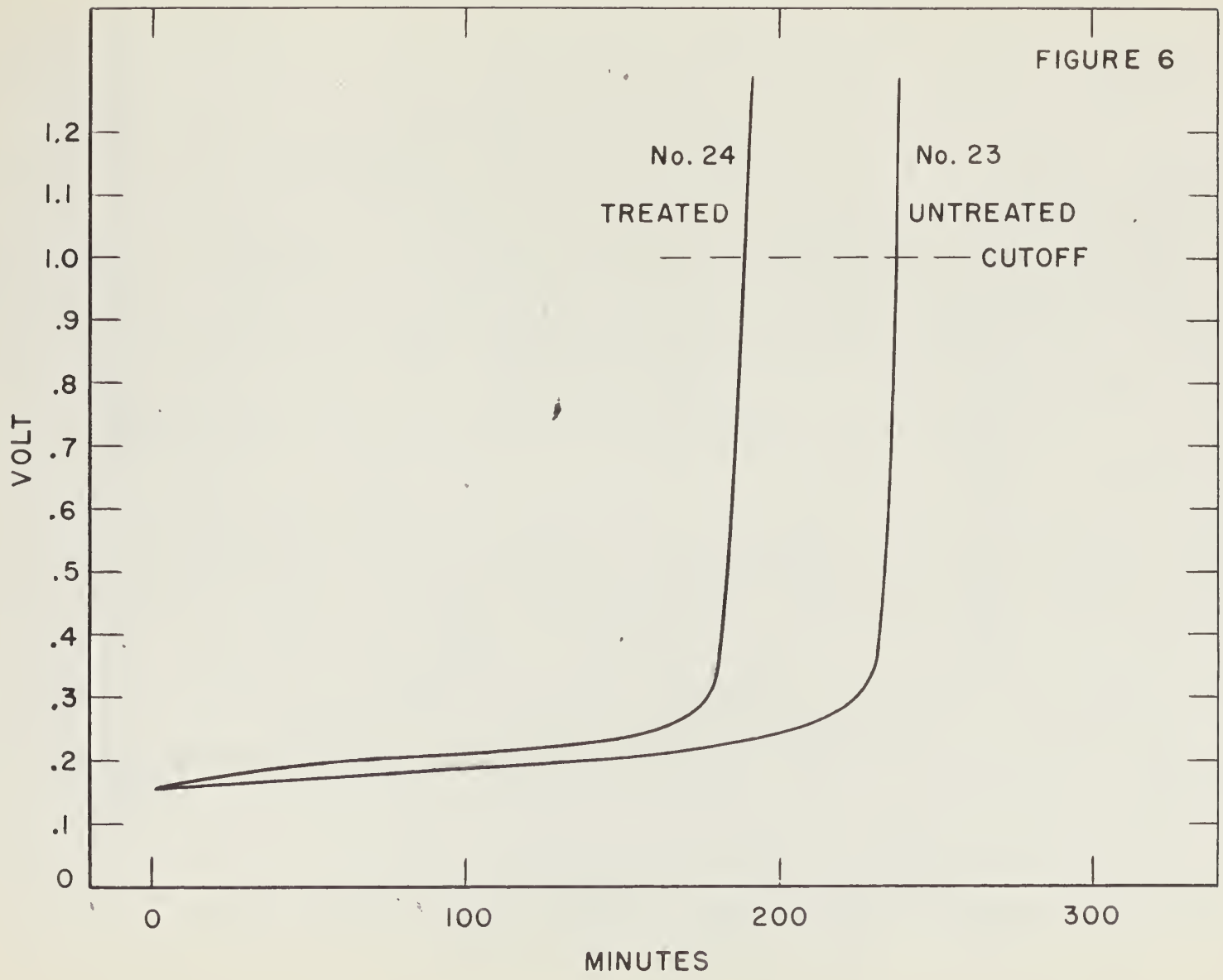


FIGURE 6
No. 24
TREATED
No. 23
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
100
200
300
MINUTES

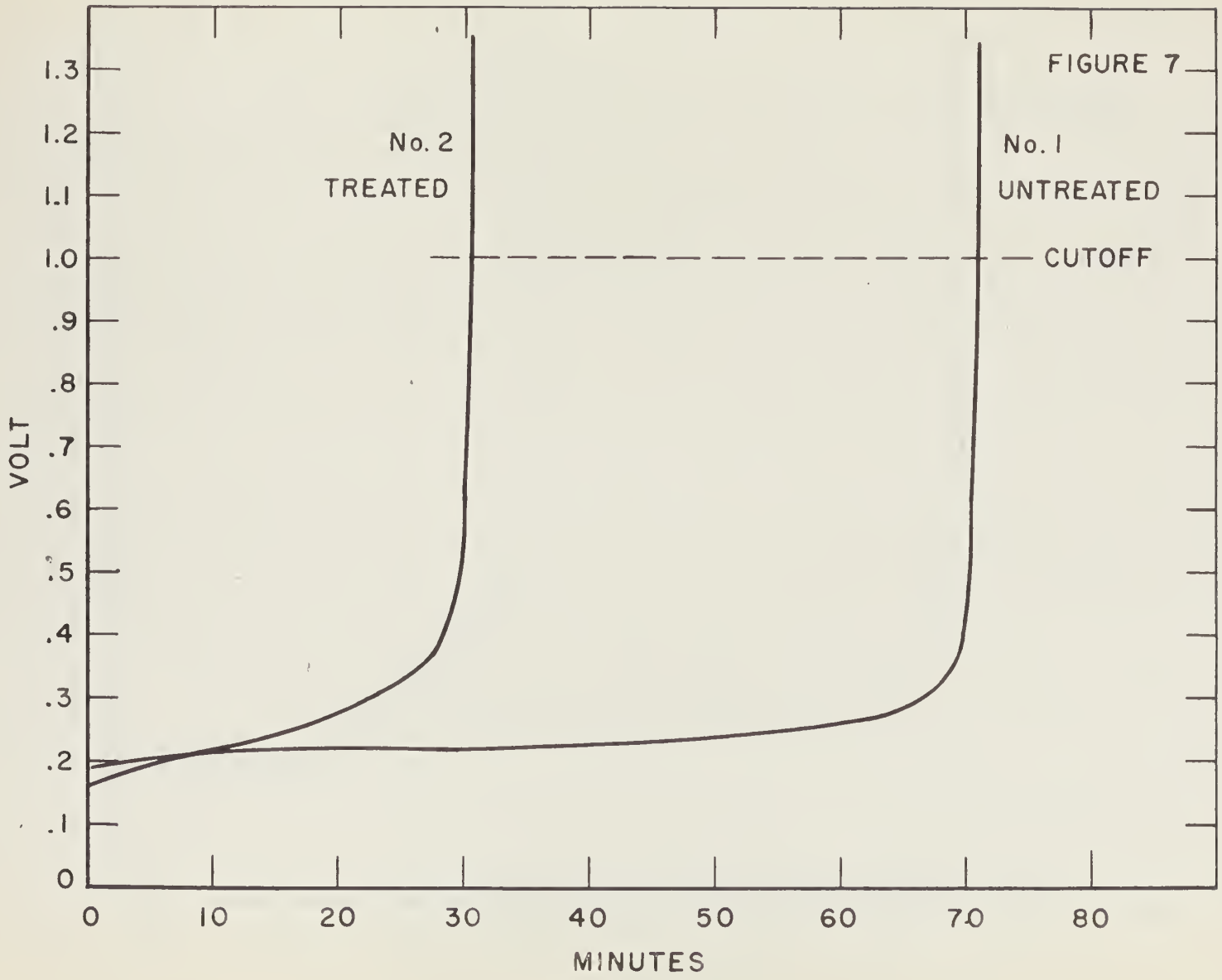


FIGURE 7
No. 2
TREATED
No. 1
UNTREATED
CUTOFF
VOLT
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
10
20
30
40
50
60
70
80
MINUTES

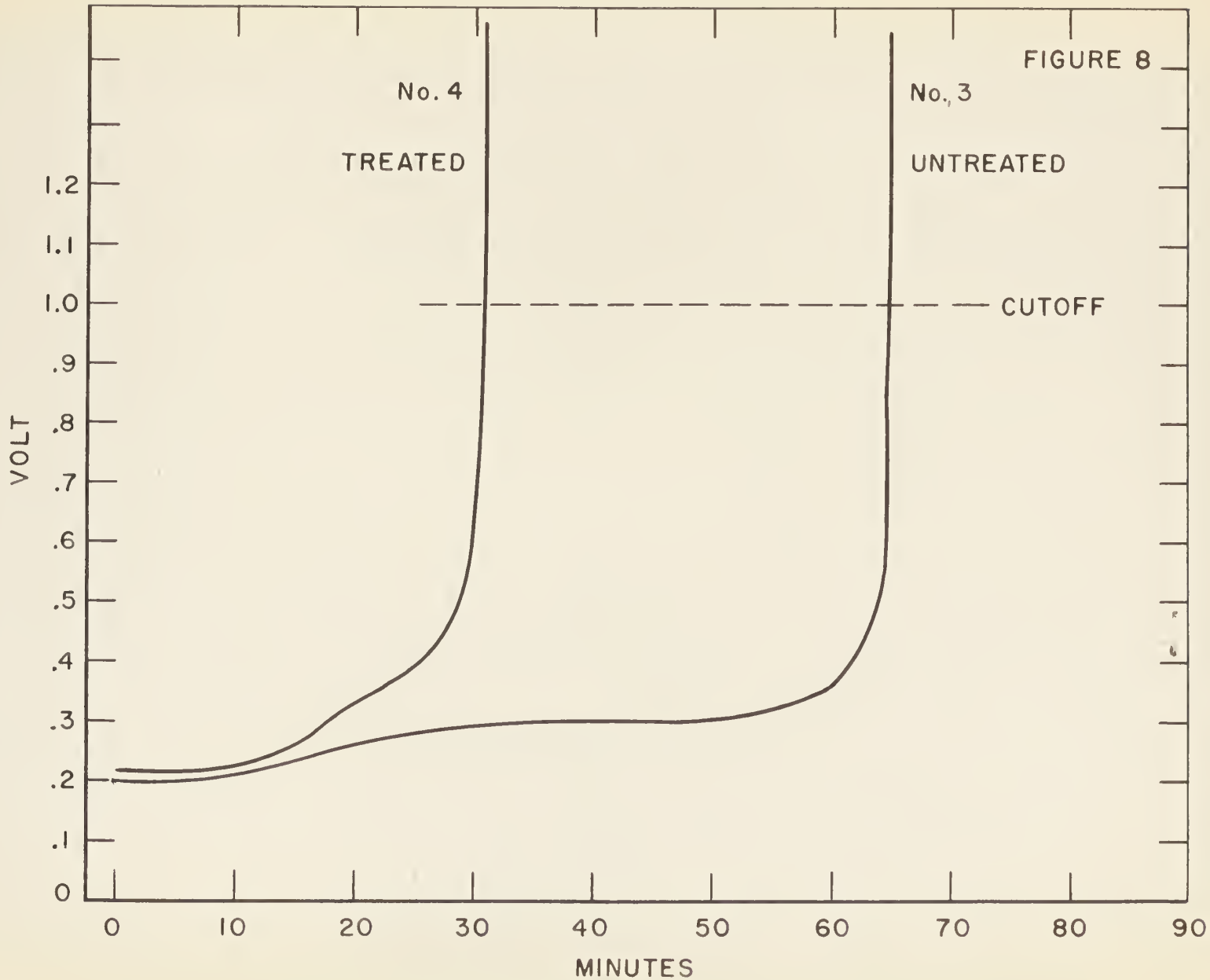


FIGURE 8
No. 4
TREATED
No. 3
UNTREATED
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
10
20
30
40
50
60
70
80
90
MINUTES

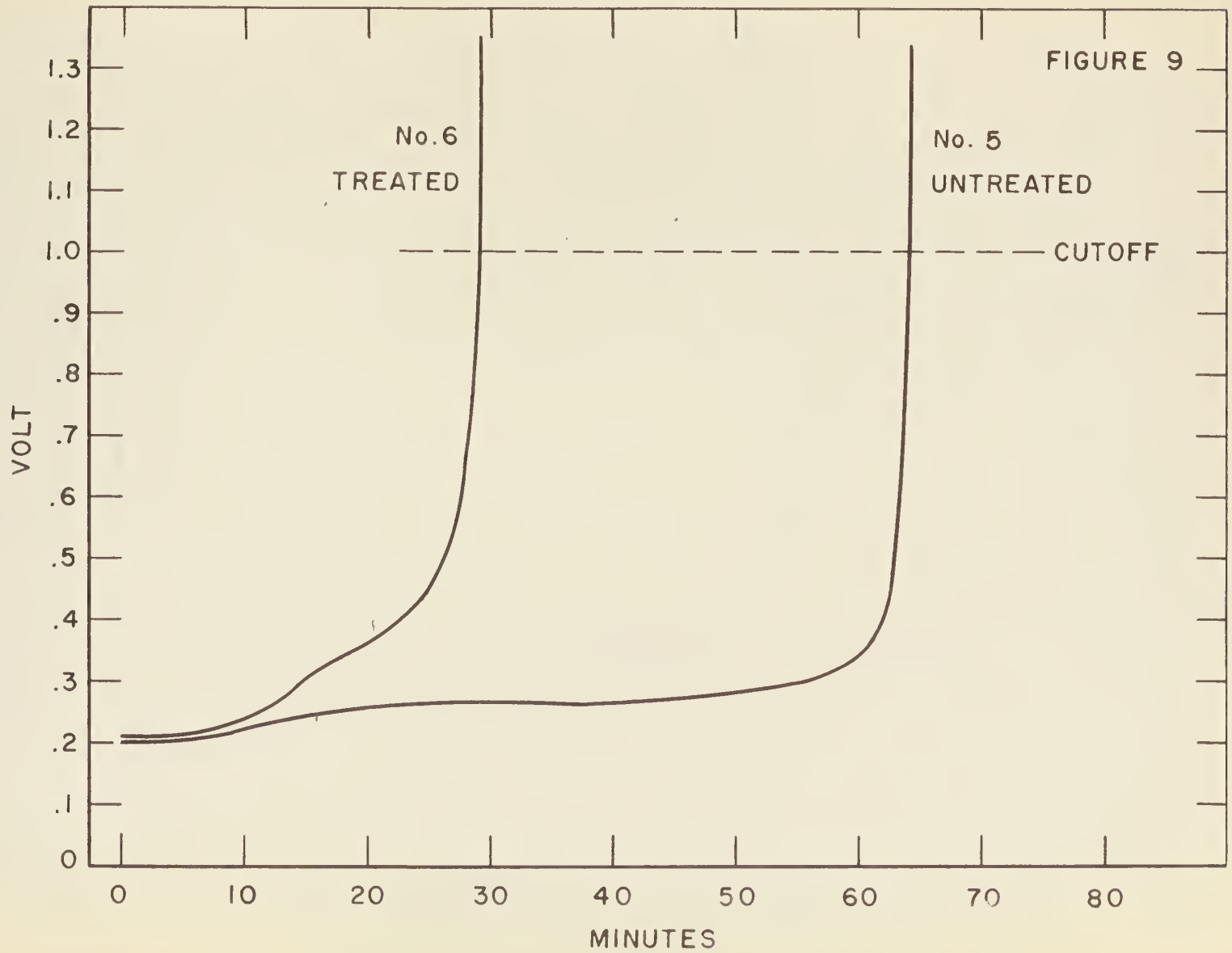


FIGURE 9
No. 6
TREATED
No. 5
UNTREATED
CUTOFF
VOLT
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
10
20
30
40
50
60
70
80
MINUTES

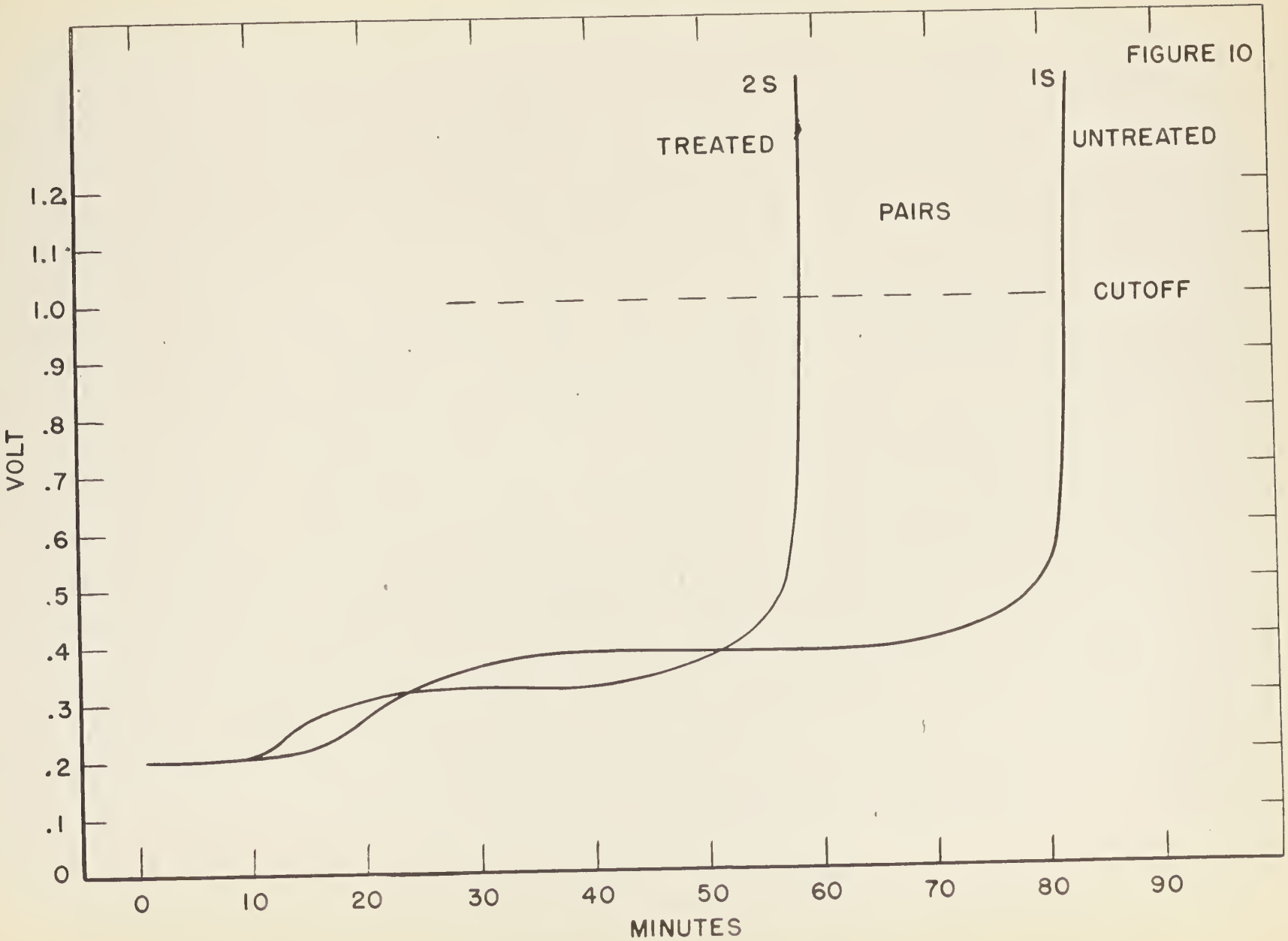


FIGURE 10
2S
TREATED
1S
UNTREATED
PAIRS
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
10
20
30
40
50
60
70
80
90
MINUTES

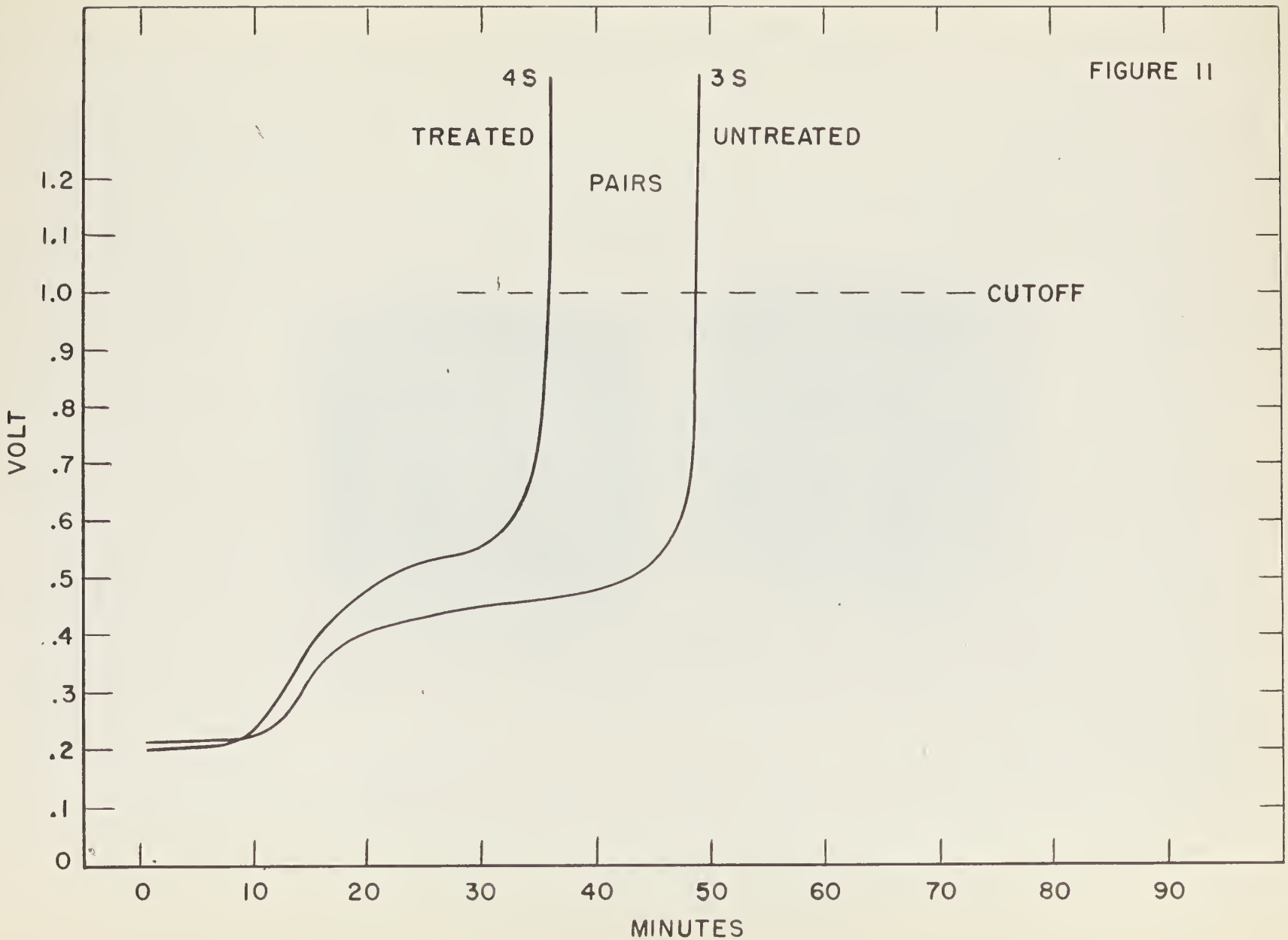
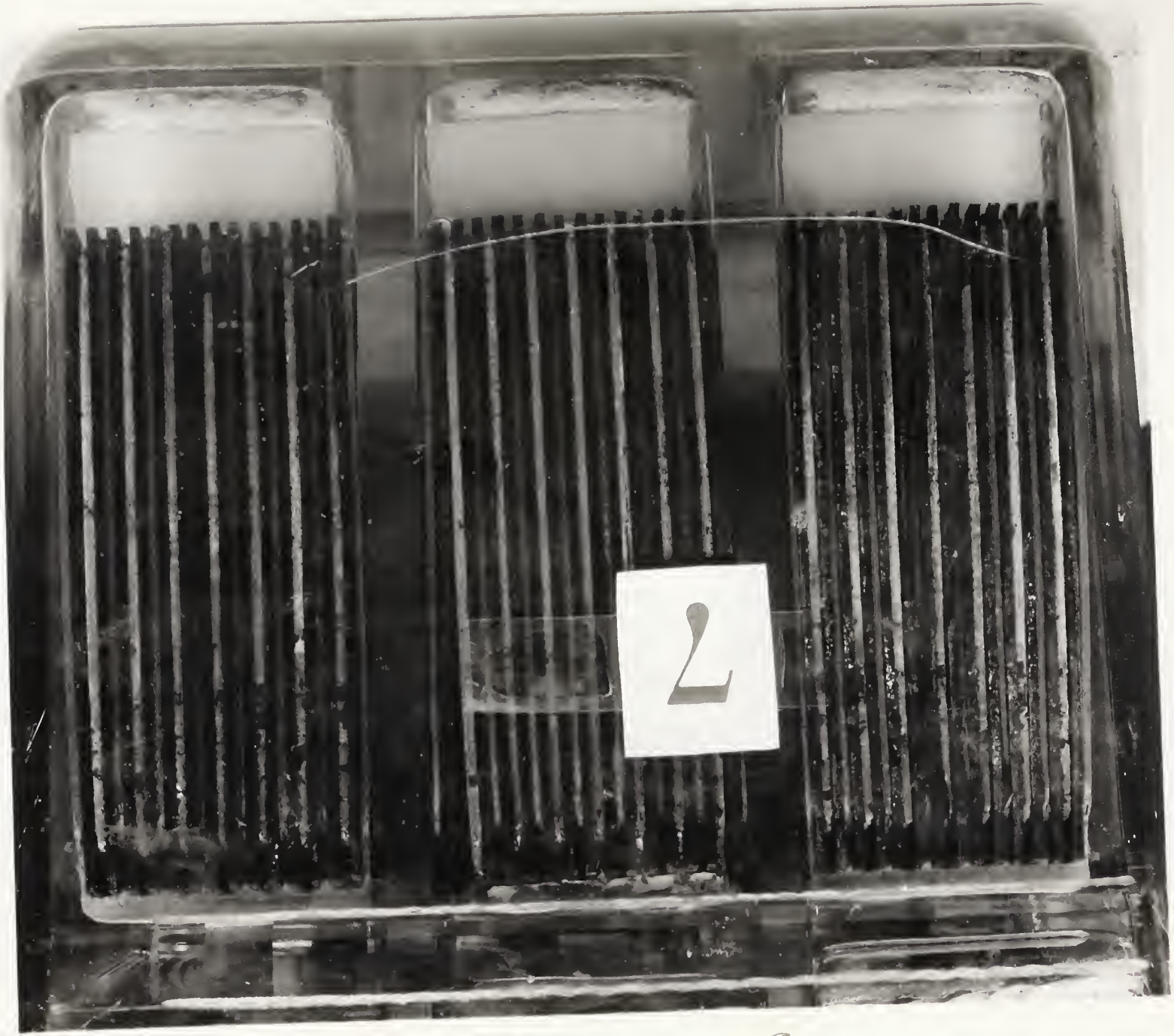


FIGURE 11
4 S
TREATED
3 S
UNTREATED
PAIRS
CUTOFF
VOLT
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
10
20
30
40
50
60
70
80
90
MINUTES


8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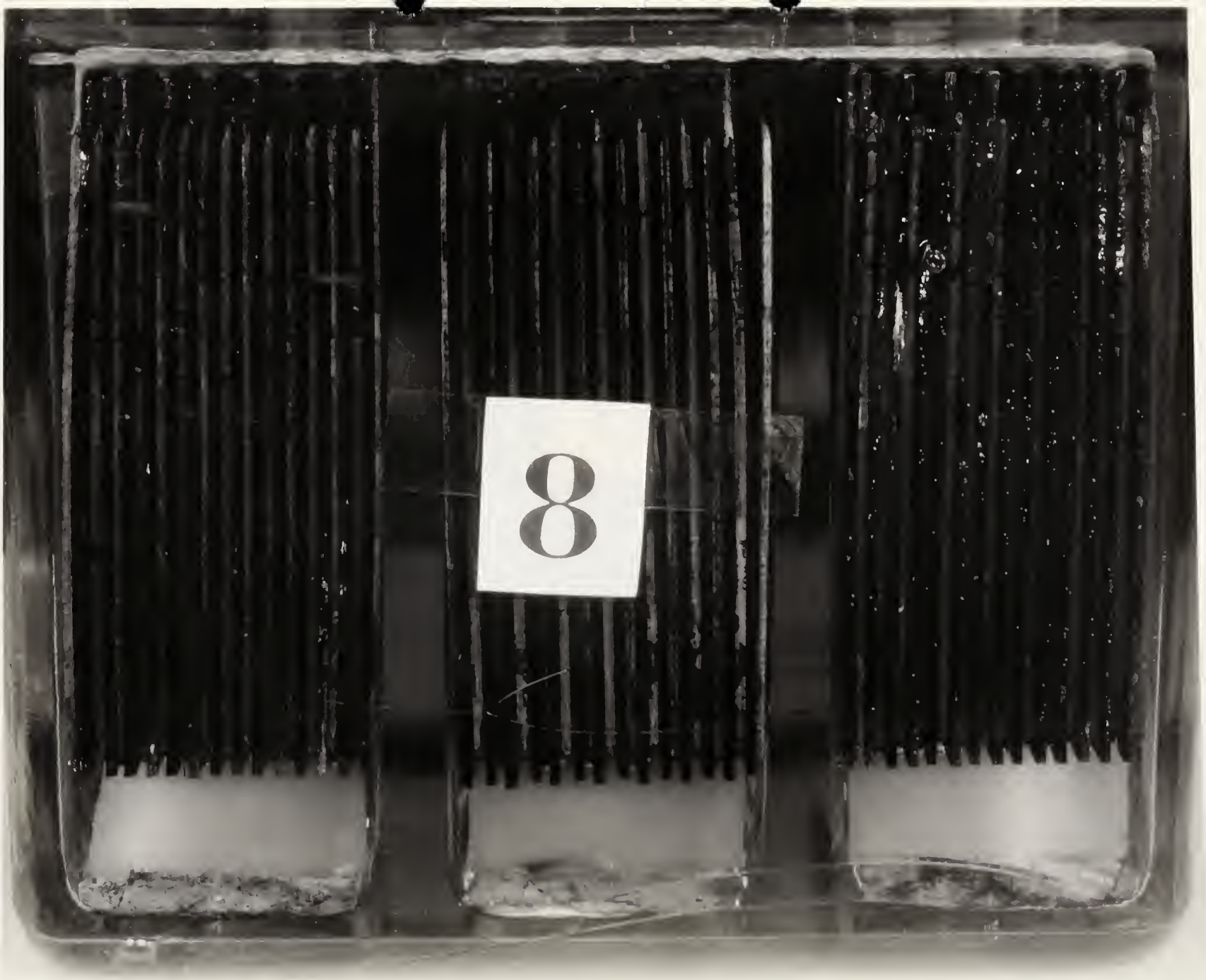
7 A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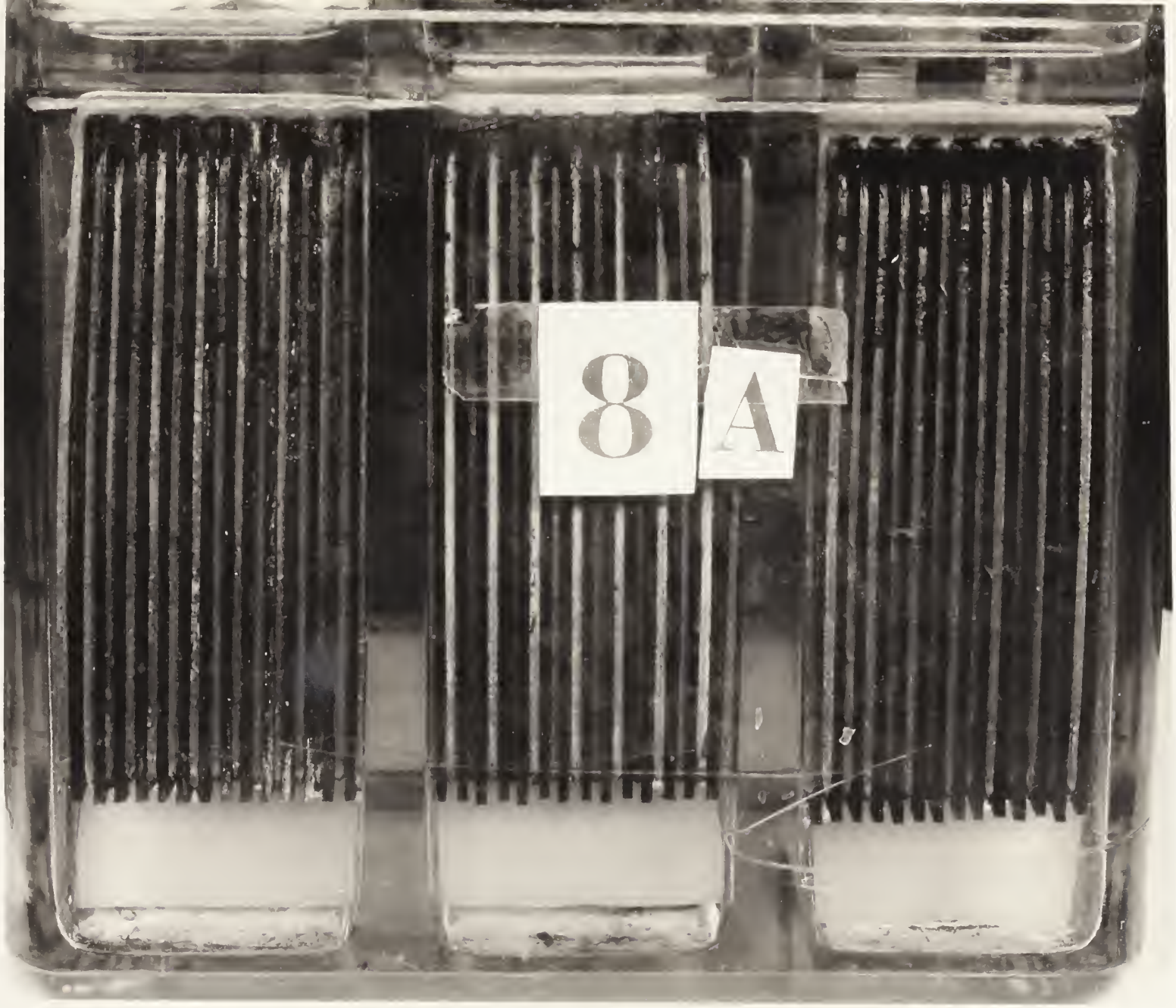
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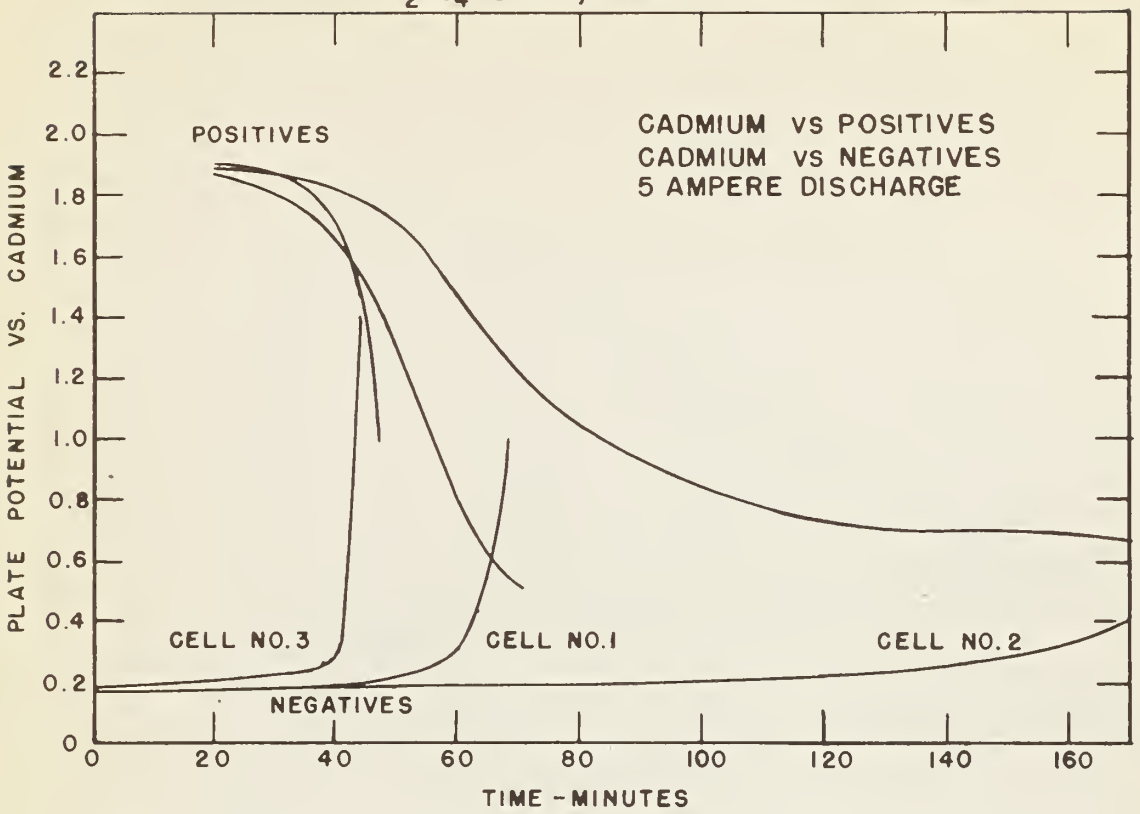
FIGURE 12

EXPERIMENT NO. 1

H_2SO_4 SOLN., SP. GR. 1.010



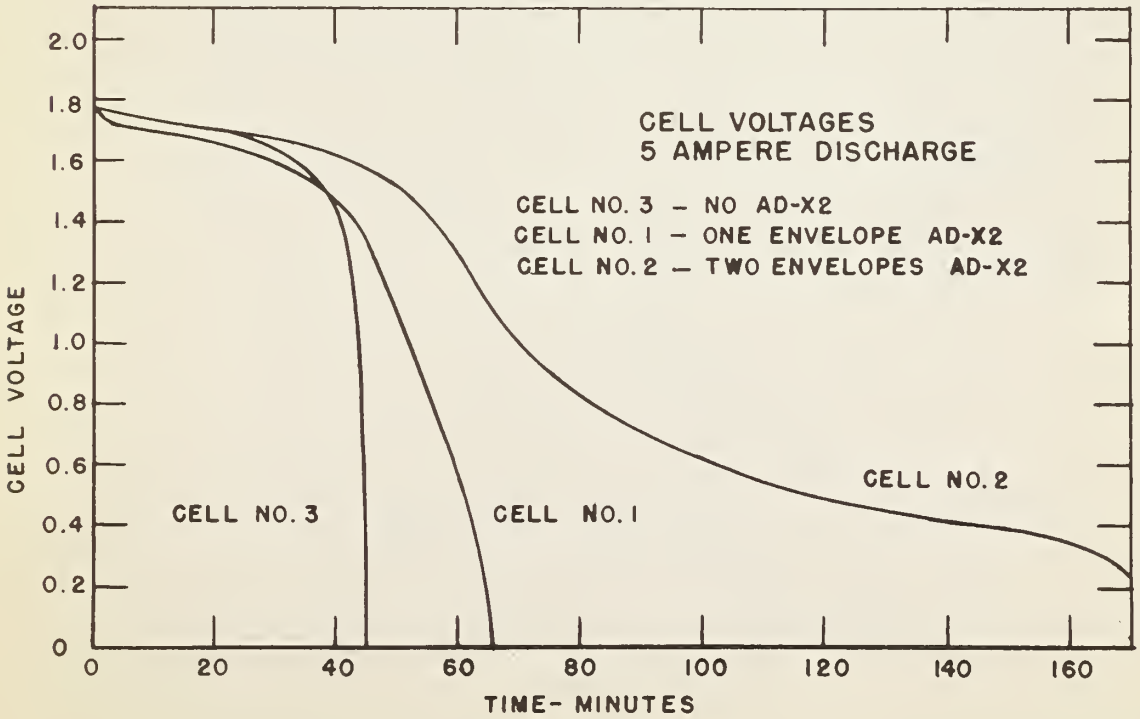
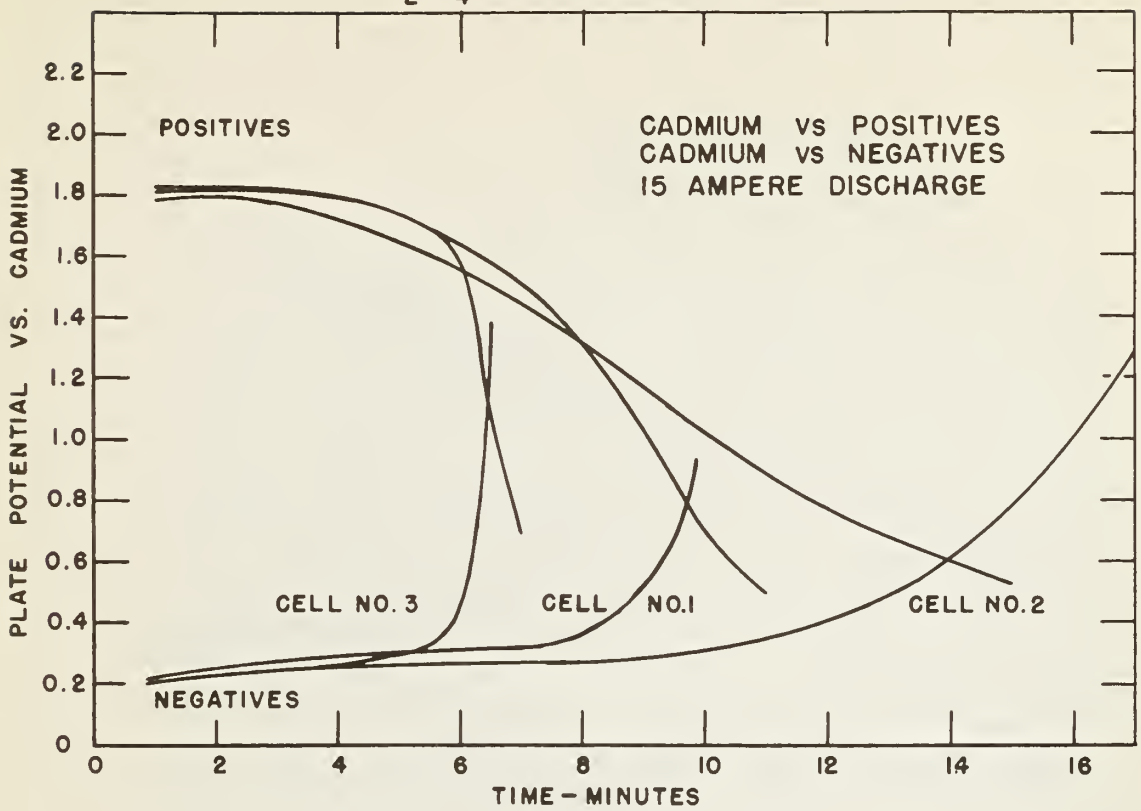


FIGURE 13

EXPERIMENT NO. 2

H_2SO_4 SOLN., SP. GR. 1.010



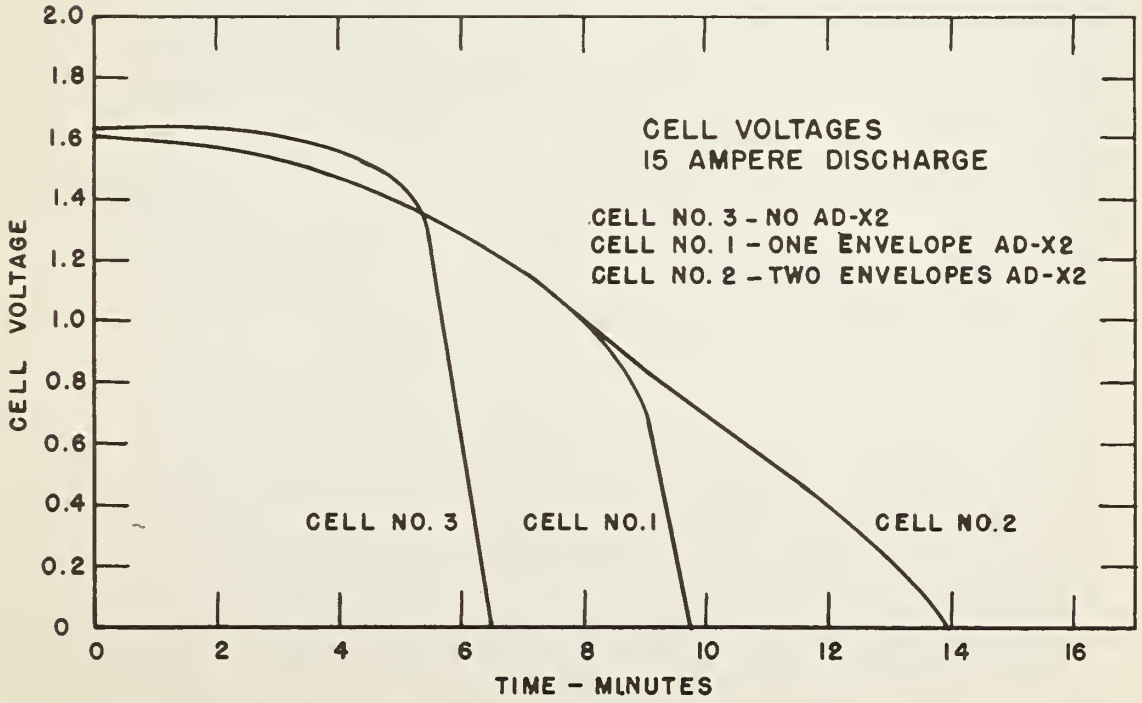
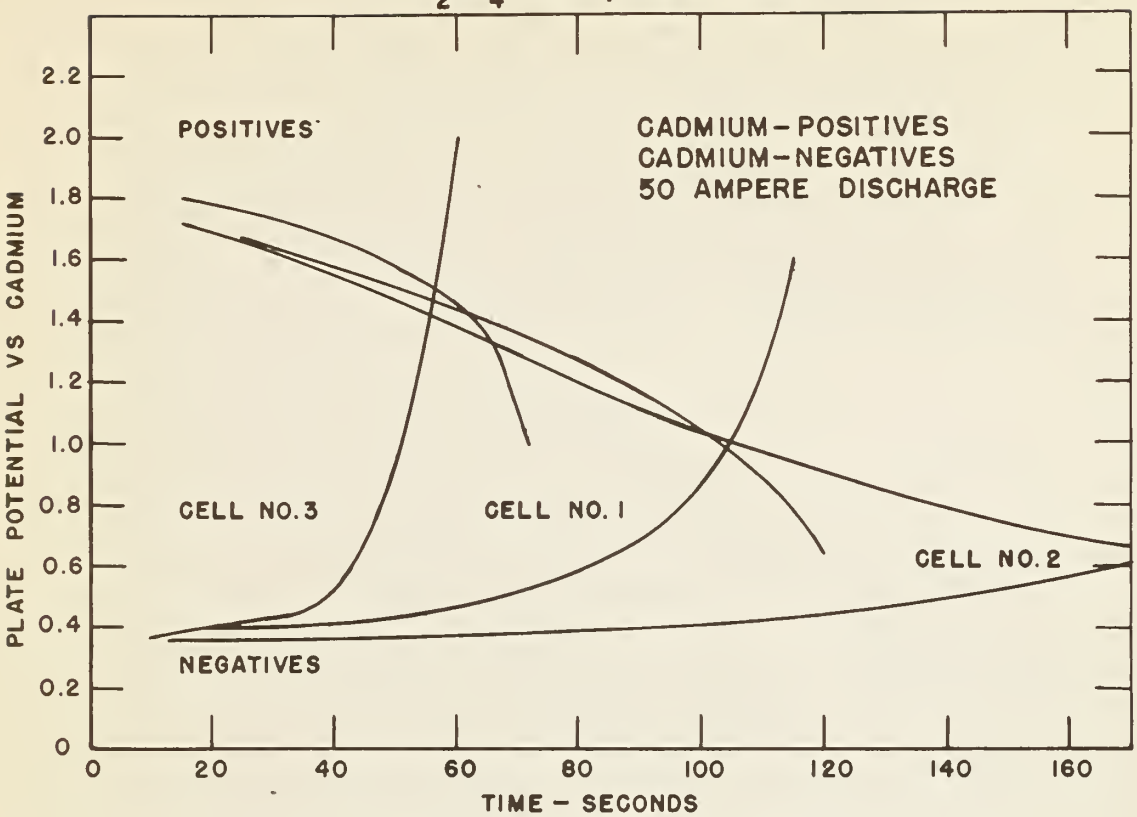


FIGURE 14

EXPERIMENT NO. 3

H_2SO_4 SOLN., SP. GR. 1.010



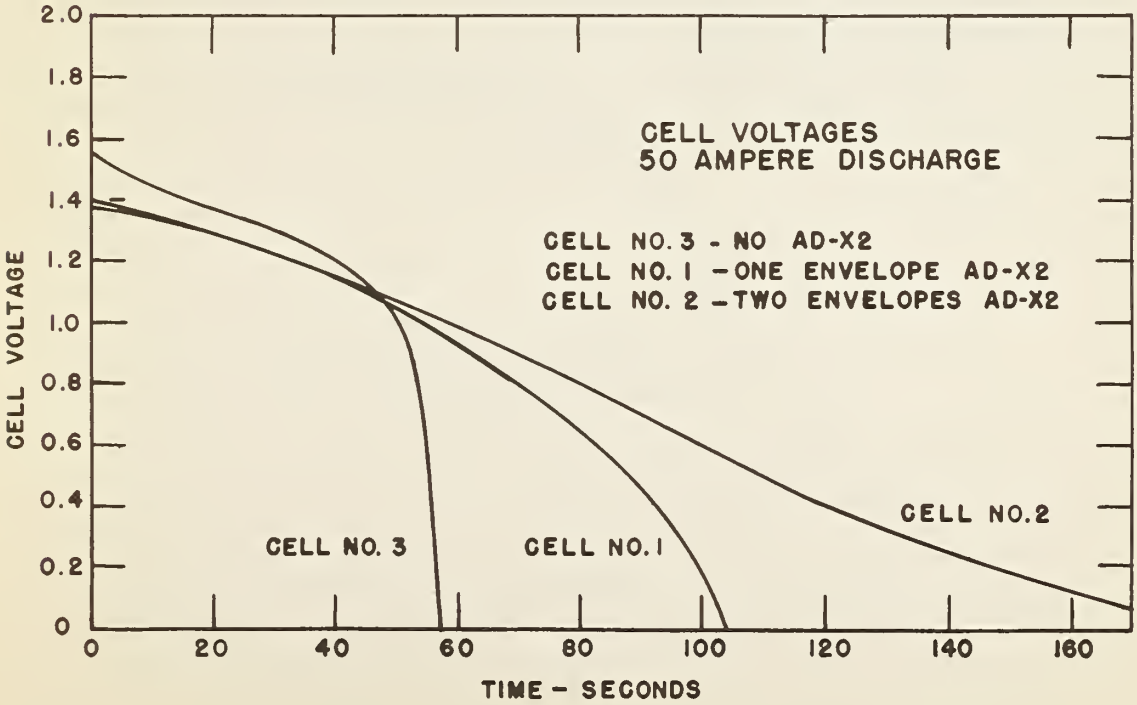


FIGURE 15

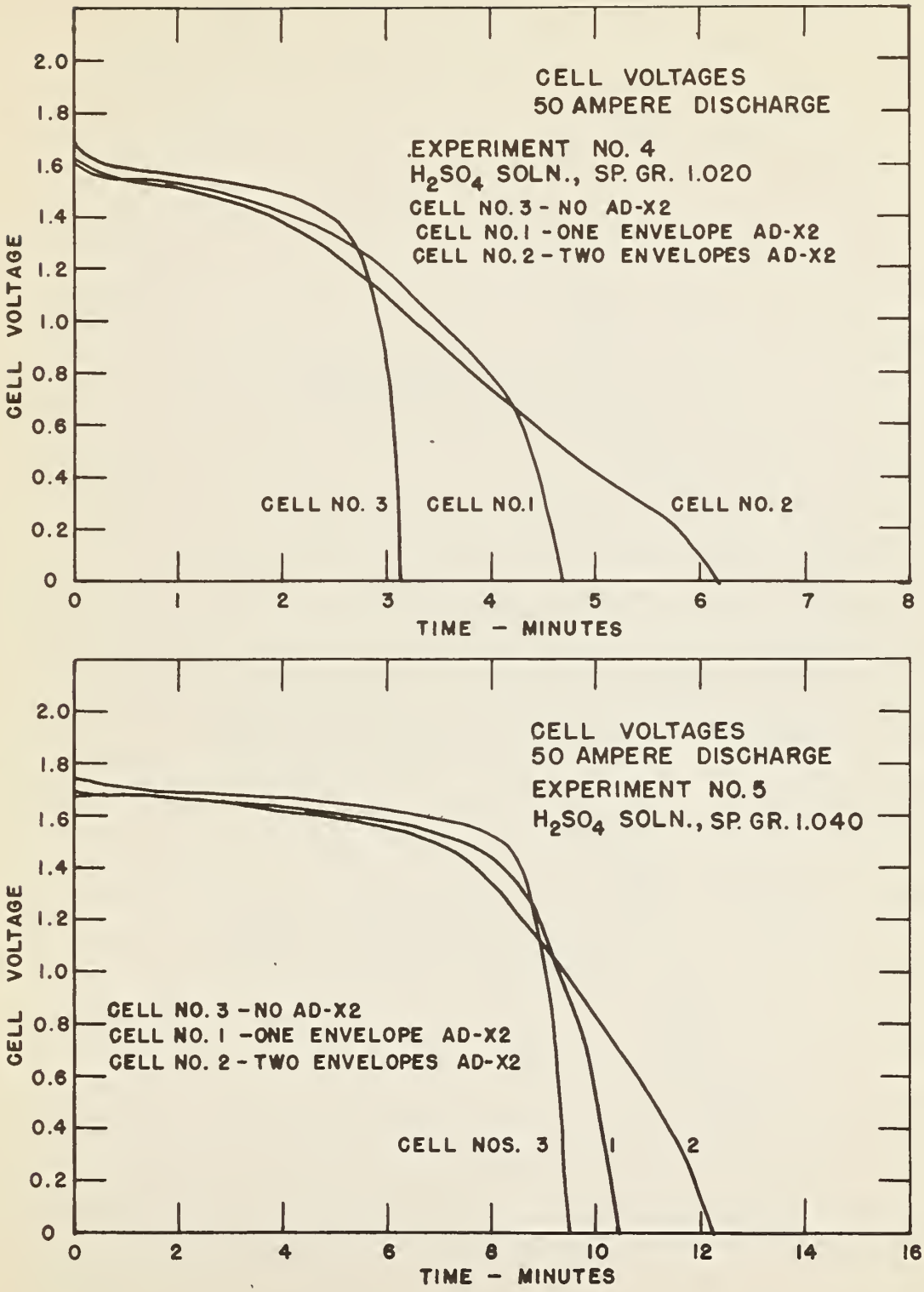
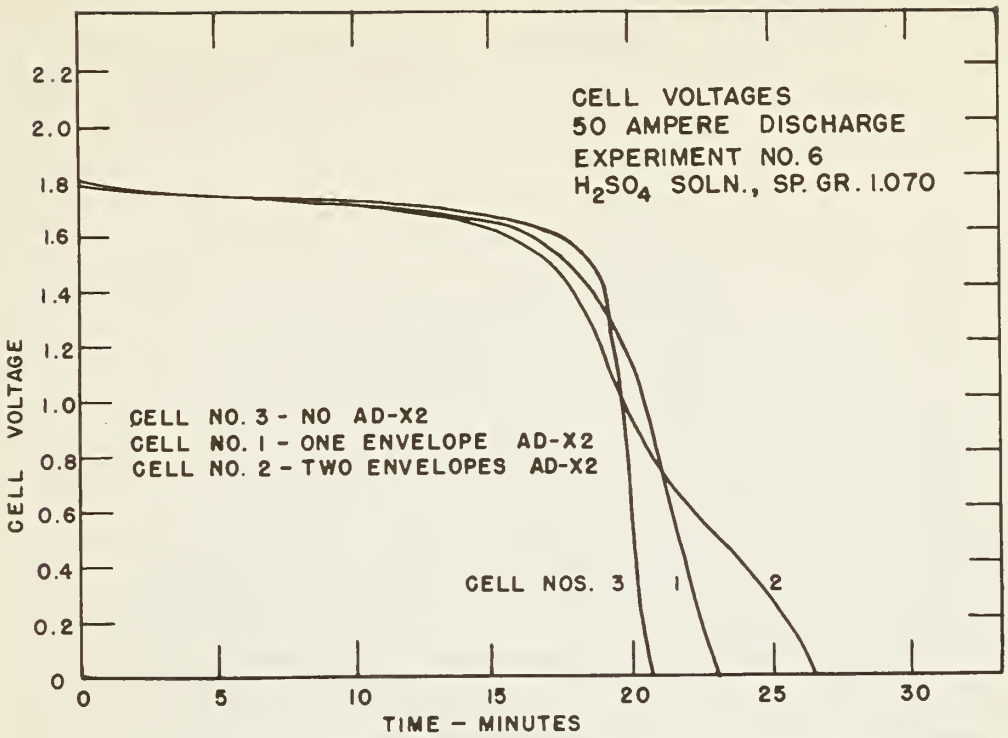
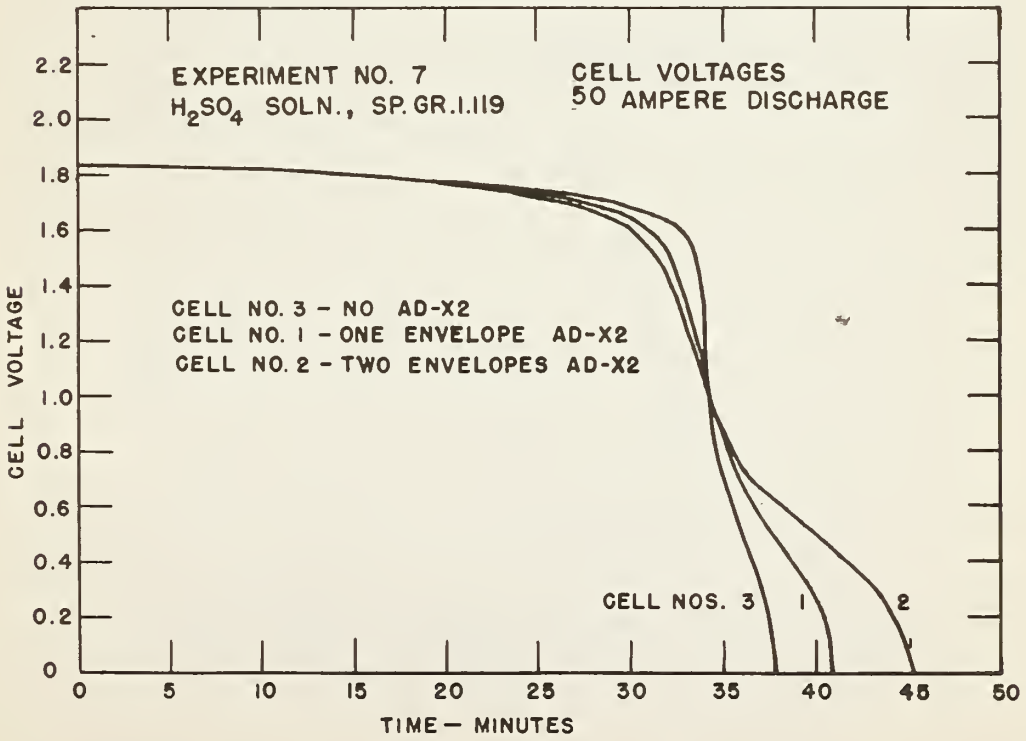

CELL VOLTAGES
50 AMPERE DISCHARGE
EXPERIMENT NO. 4
H_2SO_4 SOLN., SP. GR. 1.020
CELL NO. 3 - NO AD-X2
CELL NO. 1 - ONE ENVELOPE AD-X2
CELL NO. 2 - TWO ENVELOPES AD-X2
CELL NO. 3
CELL NO. 1
CELL NO. 2
CELL VOLTAGE
TIME - MINUTES
CELL VOLTAGES
50 AMPERE DISCHARGE
EXPERIMENT NO. 5
H_2SO_4 SOLN., SP. GR. 1.040
CELL NO. 3 - NO AD-X2
CELL NO. 1 - ONE ENVELOPE AD-X2
CELL NO. 2 - TWO ENVELOPES AD-X2
CELL NOS. 3
1
2
CELL VOLTAGE
TIME - MINUTES

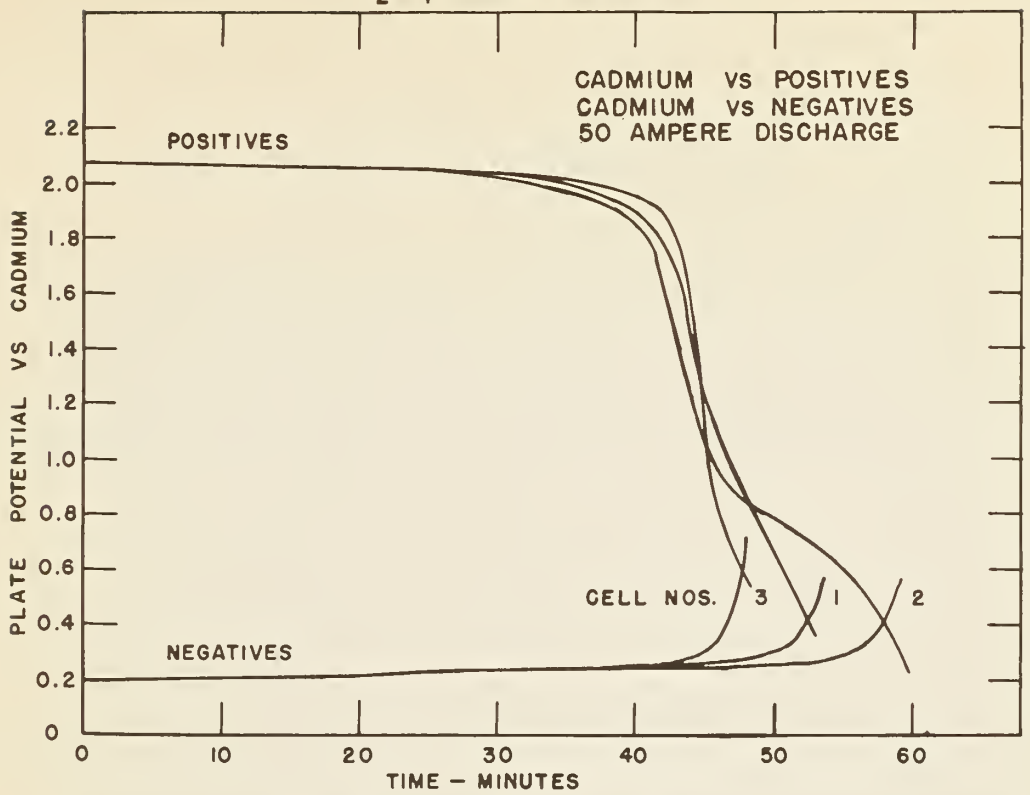
FIGURE 16

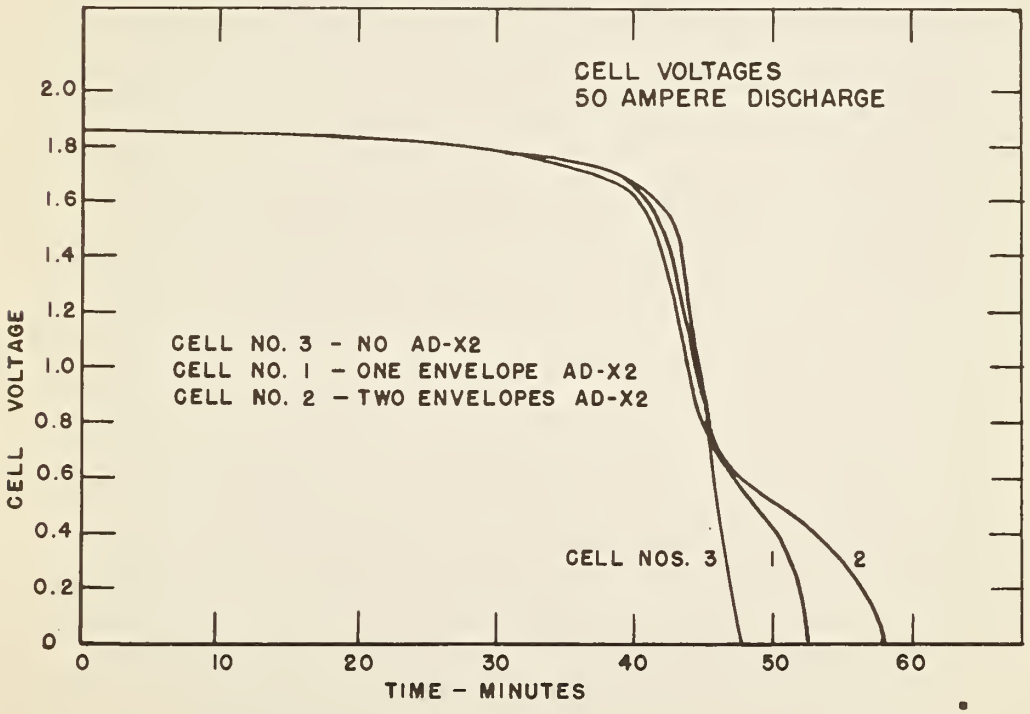

CELL VOLTAGES
50 AMPERE DISCHARGE
EXPERIMENT NO. 6
H_2SO_4 SOLN., SP. GR. 1.070
CELL NO. 3 - NO AD-X2
CELL NO. 1 - ONE ENVELOPE AD-X2
CELL NO. 2 - TWO ENVELOPES AD-X2
CELL NOS. 3
1
2
CELL VOLTAGE
TIME - MINUTES
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
0
5
10
15
20
25
30


EXPERIMENT NO. 7
H_2SO_4 SOLN., SP. GR. 1.119
CELL VOLTAGES
50 AMPERE DISCHARGE
CELL NO. 3 - NO AD-X2
CELL NO. 1 - ONE ENVELOPE AD-X2
CELL NO. 2 - TWO ENVELOPES AD-X2
CELL NOS. 3
1
2
CELL VOLTAGE
TIME - MINUTES
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
0
5
10
15
20
25
30
35
40
45
50

EXPERIMENT NO. 8 FIGURE 17

H_2SO_4 SOLN., SP. GR. 1.160





Part V

Chemical and Physical Properties of AD-X2

1. Summary and conclusions.

2. Chemical analyses of Battery AD-X2.

3. Spectrochemical analysis of battery electrolytes and technical sulfuric acid.

V - CHEMICAL AND PHYSICAL PROPERTIES OF AD-X2

1. Summary and Conclusions

Over a period of years the Chemistry Division has conducted numerous analyses of various preparations sold as battery additives, that is, materials to rejuvenate or otherwise beneficially affect lead-acid storage batteries. The principal constituents of most of these materials were sodium sulfate, magnesium sulfate, and water of hydration of these salts.

The samples of Battery Additive AD-X2 submitted by Div. 1.8 likewise consisted of magnesium sulfate, sodium sulfate, and water of hydration. The proportions of these compounds varied, however. For example, the percentage of sodium sulfate varied from 38.9 to 42.9 and that of magnesium sulfate from 40.6 to 47.3. This variation in composition was probably the result of loss of water of hydration of the hydrated salts on exposure.

The analyses show that a mixture of commercially available sodium sulfate and magnesium sulfate has practically the same composition as Battery Additive AD-X2, even including the trace elements, with the possible exception of barium, calcium and lithium which, however, are present in technical sulfuric acid or the electrolytes of ordinary batteries.

In the MIT report, it is stated that*

> "When AD-X2 was added to cells containing sediment, the amount of sediment decreased both while the battery was on charge and while it was not on charge."

The sediment and electrolyte from 8 typical battery cells were tested with AD-X2 to determine whether any sediment would disappear while the battery was not on charge. Thirty-eight attempts failed to show any disappearance of sediment. Tests on the effect of AD-X2 on the sediment in batteries under various conditions of charge and discharge are described elsewhere in this report. (See p. 3.46 and 4.7)

*Harold C. Weber, "Some Facts Concerning the Effect of Battery Additive AD-X2 on Lead Acid Batteries", Cambridge, Mass., December 1, 1952; transmitted to the Senate Select Committee on Small Business by cover letter dated December 16, 1952, signed by J. A. Stratton, Vice President and Provost, Massachusetts Institute of Technology. The reference is to pages 3 and 11.

2. Chemical Analyses of Battery AD-X2

Typical analyses are given in the following two reports dated April 13, 1950 and September 10, 1951.

REPORT OF EXAMINATION

of

BATTERY ADDITIVES
Submitted by
Federal Trade Commission
thru Division 1, Section 8

Marked: AD-X2
Pioneers Inc., Oakland, Calif.
and as below

Refer to
Lab. Nos. 522z/3085
3086

Received: March 28, 1950
Test Request of March 28, 1950

Laboratory No. 3085 consisted of a white powder contained in one paper envelope bearing the identifying mark "No. 1948". The powder weighed 23.7 grams.

Laboratory No. 3086 consisted of a white powder contained in three paper envelopes packed in a pasteboard carton. Each of the envelopes contained about 26.0 grams of material. It was assumed that the contents of all three envelopes were identical and the contents of one of the envelopes was used for analysis.

Analysis:

	% by weight	
	Lab. No. 3085	Lab. No. 3086
Loss at 450°C (water of hydration)	21.2	10.1
Magnesium (Mg)	8.4	9.4
Sulfate (SO_4)	58.3	66.2
Sodium (Na), calc.	12.0	13.9

Calculated as the anhydrous molecular species, Lab. No. 3085 contained 37.2% of sodium sulfate (Na_2SO_4) and 41.5% of magnesium sulfate ($MgSO_4$). Lab. No. 3086 contained 42.9% of sodium sulfate (Na_2SO_4) and 46.6% of magnesium sulfate. The remainder of both samples consisted of water of hydration. While the materials were not examined microscopically, on the basis of our knowledge of these substances it is likely that the sodium sulfates were anhydrous while the magnesium sulfates were degraded Epsom salts. In Lab. No. 3085 the average composition of the degraded Epsom salt was $MgSO_4 \cdot 3.4\ H_2O$, while in Lab. No. 3086 it was $MgSO_4 \cdot 1.2\ H_2O$.

April 13, 1950.

REPORT OF EXAMINATION

of

BATTERY ADDITIVE AD-X2
Submitted by
Post Office Department
thru Division 1, Section 8
Project No. 0199

Received: September 10, 1951 Lab. No. 522z/3190
Marked: Pioneers Hant Ced Aug. 28, 1951
Div. Request No. 1-65, dated 9/10/51

The material submitted consisted of a white powder, weighing about 28 grams. The sample was well mixed before analysis.

Analysis:

Loss at 450°C (water of hydration)	20.8%
Magnesium (Mg)	8.2
Sulfate (SO_4)	58.8
Sodium (Na), calculated	12.6

This is equivalent to 40.6 percent magnesium sulfate and 38.9 percent sodium sulfate calculated as anhydrous salts, the balance being water of hydration. Examination of the less dense and the more dense fractions obtained after an ethylene dibromide separation, indicated that the magnesium sulfate was the partially dehydrated heptahydrate and the sodium sulfate was the partially hydrated salt.

December 10, 1951.

Another sample of AD-X2 received from the Post Office Department on April 5, 1952, and designated as Lab. No. 522/3211, had the following analysis:

99.77% of the sample as received was soluble in water;
0.23% was insoluble

Analysis of water soluble material:

	%
Magnesium sulfate, anhydrous ($MgSO_4$, calculated from total MgO)	46.1
Sodium sulfate, anhydrous (Na_2SO_4, calculated from excess SO_4)	43.0
Water of hydration (by difference)	10.9
Total	100.00

Analysis of insoluble material:

Silica (SiO_2)	11.7
Magnesium oxide (MgO, calculated from total Mg)	1.5
Barium sulfate ($BaSO_4$, by difference)	86.8

The composition of the sample as received is therefore as follows:

	%
$MgSO_4$	46.0
Na_2SO_4	42.9
Water (by difference)	10.9
$BaSO_4$	0.2
MgO	0.003
SiO_2	0.03

The sample as received contained minute amounts of a number of elements. The following were detected in amounts less than 0.01% - Iron (Fe), Aluminum (Al), Boron (B), Calcium (Ca), Copper (Cu), Manganese (Mn), Phosphorus (P), Strontium (Sr).

By centrifuging the sample in a non-solvent liquid of suitable specific gravity, (intermediate between that of sodium sulfate and magnesium sulfate) a physical separation of sodium sulfate and magnesium sulfate was achieved. These separations showed clearly that this preparation is a <u>mixture</u> of sodium sulfate and magnesium sulfate. There is no intermolecular or alumlike compound present.

In addition to the above, a sample received directly from Div. 1.8 on June 5, 1952 was analyzed. This sample was given by Dr. Jess M. Ritchie to a member of Div. 1.8

	%
Sodium Sulfate (Na_2SO_4)	37.84
Magnesium Sulfate ($MgSO_4$)	46.97
Barium Sulfate ($BaSO_4$)	.08
Calcium Sulfate	.12
Magnesium Oxide (MgO)	.003
Silica (SiO_2)	.07
Carbon	.01
Water of hydration	14.86

This sample was examined spectroscopically and found to contain the following also:

	%
Aluminum	<.001
Boron	.0005-0.001
Copper	0.001
Iron	0.005
Potassium	<0.0005
Lithium	0.005
Manganese	0.002
Strontium	0.0005-0.001

The following were not detected spectroscopically:

Ag, As, Au, Be, Bi, Cb, Cd, Ce, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, La, Mo, Ni, Os, P, Pb, Pd, Pt, Rb, Rh, Ru, Sb, Sc, Sn, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr.

A mixture of equal parts of technical grade sodium sulfate and magnesium sulfate contained the same minor elements as were found in AD-X2, with the exception of barium and calcium (and possibly lithium). A less pure grade of chemicals may have been used in making up the AD-X2, or the small amounts of barium and calcium may have been added intentionally.

3. Spectrochemical Analysis of Battery Electrolytes and Technical Sulfuric Acid

Elements found in battery electrolytes are, in the order of descending concentrations:

Na, Mg, Ca, Al, Fe, Si, Pb, K, Li, Mn, Cu, Cr, Ni, Sn, Zn, and Ag.

In technical sulfuric acid the following elements were shown to be present, in the order of descending concentrations:

Fe, Ca, Mg, Na, Ba, Al, Mn, K, Pb, Si, Cu, B, Sr, Cr, Ti, Ag, Ni, Sn.

The above analyses show that the electrolyte in a commercial battery bought in the open market contains nearly all the trace elements in AD-X2, and that technical sulfuric acid contains all the trace elements in AD-X2 with the possible exception of lithium.

Part VI

Supplementary Information

1. Changes in the specific gravity of the electrolyte of untreated and treated cells during charge.

2. Inspection of discarded batteries turned in for purchase of new batteries.

3. Rebuilding and repair of batteries.

Part VI

1. Changes in the Specific Gravity of the Electrolyte of Untreated and Treated Cells During Charge

One frequently sees the statement that batteries "fail to take a charge". One reason for this belief is that when an exhausted battery is first put on charge the heavy sulfuric acid formed by the charging process tends to settle to the bottom of the battery. Hence, the usual test of the top liquid with a hydrometer will show at first only a small change in specific gravity and may be thought to indicate the battery "is not taking a charge". After further charging, diffusion and the stirring by the bubbles evolved when gassing is reached, bring the dense acid to the top where it mixes with the less dense acid and the hydrometer reading then becomes significant. If an "additive" is added between the two readings, one may falsely conclude that the "additive" had made possible the charging of a battery that "would not take a charge". Also on standing the dense acid at bottom of battery formed on initial charge will diffuse into the less dense acid until uniformity in acid composition throughout the battery is attained. Likewise if an "additive" were added and sufficient time allowed for diffusion of the dense acid into the less dense acid, one may also falsely conclude that the "additive" had brought the specific gravity up more than could be accounted for by its mere addition.

A detailed discussion of these effects follows. We shall consider first the changes that occur during charge in the specific gravity of the electrolyte when measured in the usual manner, that is at the top, and what occurs when the rate of gassing becomes appreciable. Data obtained on two automotive cells at charging rates of 6 and 10 amperes are given in table 1 . The table shows the specific gravity of the electrolyte in the top of the two cells containing untreated electrolyte (H_2SO_4). These specific gravities and the rate of gassing are tabulated for successive increments of charge. As the charge progressed it was observed that the rise in specific gravities increased with successive increments of charge and that the most rapid rise occurred when the increase in the rate of gassing was greatest whereby the stirring of the electrolyte was enhanced.

Next, we shall present a more detailed study of changes in the specific gravity of the electrolyte during charge. In order to measure the specific gravity of the electrolyte at the bottom and top of the cells during charge, some cells of the automotive type were provided with valves at the bottom of the cells whereby electrolyte could be periodically removed during charge for hydrometer readings. The hydrometer readings of the electrolyte in the top of the cells were taken in the usual manner. To eliminate any initial concentration gradients, the electrolyte was drained from each cell and thoroughly mixed. It was then returned to its respective cell and this process was repeated until the specific gravity of the electrolyte at the top and bottom of the cell was the same.

In table 2 the specific gravity of the bottom and top of an untreated cell and a treated cell (AD-X2 added to top in usual manner) are shown during the charge. The differences in specific gravities for top and bottom are also listed. It is seen that these differences are quite uniform for any given increment of charge and that the two specific gravities (top and bottom) again approach a common value at the end of charge when gassing, which then becomes pronounced, mixes the lower and top portions of the battery electrolyte. It will be noted that the differences in top and bottom specific gravities between treated and untreated cells do not reveal any significant difference between the behavior of treated and untreated cells.

In order to ascertain the magnitude of the above phenomena on the estimation of state of charge as determined by hydrometer readings, two untreated cells were run concurrently in which the electrolyte was continuously circulated from bottom to top in one and the other was left uncirculated. Data are given in table 3 . The results for the first part of the charge show that the increase in the specific gravity of the electrolyte for a given increment of charge is less for the electrolyte at the top of the cell in which the electrolyte is not circulated than for the increase observed for the cell in which the electrolyte is circulated. During the first part of the charge the charging efficiency is high and the linear relationship observed for the circulated electrolyte is in accord with theory. During the latter part of the charging period when gassing ensues the charging efficiency is lowered and the rate of the rise in the specific gravity of the electrolyte in the top of the cell containing the uncirculated electrolyte rises sharply because the gassing causes effective mixing of the more dense electrolyte in the low part of the cell with that above the plates.

If we consider that a linear relationship exists between state of charge and the specific gravity we can calculate the percent of charge at each state of the charging process. These percentages are listed in the table. It will be noted that after 3 hours of charge (30 ampere-hour input) that the specific gravity of the uncirculated cell indicates that the cell had received only 17.5% of charge, whereas in fact it had received about 35% (see last column) of full charge. If now, "AD-X2" were added to the uncirculated cell, and sufficient time allowed, the specific gravity in cell 1 (uncirculated) would rise to about 1.158 + 0.014 (approximately the rise due to addition of AD-X2) and one would falsely conclude that the "additive" had charged the cell by about 17%. Similar calculations may be made for the other ampere-hour inputs.

TABLE 1

Specific Gravities of the Electrolyte and 'Rate of Gassing' During Charge

	Cell #1 Charge at 6 Amps.			Cell #2 Charge at 10 Amps.		
Chge. A. hrs.	Sp. Gr. of Electrolyte	Δ Sp. Gr.	gas ml/min	Sp. Gr. of Electrolyte	Δ Sp Gr.	gas ml/min
0	1.152	———	0.0	1.125	———	0.0
15	1.159	0.007	0.0	1.128	0.003	0.1
30	1.173	0.014	0.2	1.137	0.009	0.4
45	1.191	0.018	0.5	1.154	0.017	0.6
60	1.212	0.021	2.0	1.180	0.026	2.8
75	1.265	0.053	32.0	1.260	0.080	50.0
90	1.275	0.010	54.0	1.276	0.016	98.0

TABLE 2

Specific Gravities of the Electrolyte in the Bottom and Top of an Untreated Cell and a Treated Cell during charge at the 10-ampere Rate.

Charge Amp. Hr.	UNTREATED CELL Specific Gravity Bottom	UNTREATED CELL Specific Gravity Top	UNTREATED CELL Specific Gravity Difference	TREATED CELL Specific Gravity Bottom	TREATED CELL Specific Gravity Top	TREATED CELL Specific Gravity Difference
0	1.103	1.103	0.000	1.115	1.115	0.000
2	———	———	———	treated		———
15	1.137	1.115	.022	1.152	1.130	0.022
30	1.169	1.131	.038	1.185	1.147	.038
45	1.200	1.150	.050	1.217	1.167	.050
60	1.227	1.172	.055	1.242	1.189	.053
75	1.250	1.201	.049	1.264	1.216	.048
90	1.267	1.244	.023	1.279	1.265	.014
100	1.275	1.268	.007	1.285	1.280	.005

Table 3

Comparison of the Specific Gravities of the electrolyte in the top of a cell with the Specific Gravities observed for a Circulated Electrolyte. Both Cells Untreated. Charged at 10 amperes.

Chge.	Cell 1 Uncirculated Electrolyte			Cell 2 Circulated Electrolyte		
A hrs.	Sp.Gr.	Δ Sp.Gr.	Calc. % Chge.	Sp.Gr	Δ Sp.Gr.	% Chge.
0	1.102	---	---	1.103	---	0
15	1.115	0.013	7.8	1.130	0.027	17.2
30	1.131	0.016	17.5	1.158	0.028	35.0
45	1.150	0.019	28.9	1.185	0.027	52.2
60	1.172	0.022	42.2	1.210	0.025	66.2
75	1.201	0.029	59.6	1.232	0.022	82.2
90	1.244	0.043	85.5	1.254	0.022	98.1
100	1.268	0.024	100.0	1.260	0.006	100.0

2. Inspection of Discarded Batteries Turned in for Purchase of New Batteries.

Frequently, batteries are turned in for new batteries when considerable residual capacity is left in them. With proper chargingthese batteries would undoubtedly give further service. Batteries operate less efficiently during the winter months and with the approach of cold weather, the number of batteries turned in generally increases. Also many batteries are turned in due to neglect and with proper repairs may be made useable.

During the early part of 1952, 184 discarded batteries that were turned in for new ones were inspected in order to determine the percentage of these batteries that were useable. This inspection consisted of measurements of individual cell voltages on open circuit, specific gravities, and individual cell voltages under a load of approximately 300 amperes or more.

A commercial cell tester was used for the measurements of load voltages. This cell tester or stabber consists of a voltmeter and a fixed resistor of 0.033 ohms. Automotive battery cells in good operating condition should register at least one volt or higher under this load.

Batteries were classified in three groups: (a) suitable for use, (b) unsuitable for use, and (c) doubtful.

(a) Batteries suitable for use:

This group consisted of batteries which contained cells of uniform voltage and gravity, and whose cells registered more than one volt under load.

(b) Batteries unsuitable for use:

This group was subdivided into two classes: (1) batteries whose cell voltages or specific gravities were not uniform and which contained cells that would not register at least one volt under load; (2) batteries which were obviously mechanically unsound, i.e., batteries which had broken terminal posts or cracked covers or containers.

(c) Doubtful batteries:

Batteries classified as doubtful were those that contained cells of uniform voltage and gravity but had cells which would not register at least one volt under load, or contained cells which registered one volt or more under load but whose cells were not of uniform voltage and gravity.

This inspection was made at various times between the tenth of February and the nineteenth of May 1952. The results of this inspection showed that of 184 batteries tested 40% were found to be in suitable condition, 38% unsuitable and 22% were classified as doubtful. (Table 4). Inspection data are given in Appendix 7.

The average specific gravity of the cells in batteries found suitable for use was 1.187 as compared to 1.171 for those unsuitable for use and 1.181 for those doubtful. Because the specific gravities readings of the batteries classified as unsuitable and doubtful were so close to the specific gravities of those classified as useful it is probably true that some of those classified as unsuitable or doubtful failed because of mechanical difficulties. It is highly probable that among these doubtful and unsuitable batteries there were a number which if rebuilt would have given further service. It may be noted further that the batteries classified as suitable for use constitute a group of batteries which can cause misunderstandings to arise regarding the effects derived in the use of additives.

Table 4 . Summary data on "turned-in" batteries inspected during 1952

Date of inspection	Number of batteries inspected	Number of batteries suitable for use	Number of batteries unsuitable for use	Number of batteries doubtful
Feb. 18, '52	30	14	11	5
Feb. 26, '52	38	14	11	13
Mar. 3, '52	43	19	20	4
Mar. 10, '52	48	14	22	12
May 19, '52	25	13	5	7
Total	184	74	69	41
Percentage	100	40	38	22

Date of inspection	Average temp. °C	Average specific gravity		
		Suitable	Unsuitable	Doubtful
Feb. 18, '52	16	1.179	1.202	1.149
Feb. 26, '52	17	1.191	1.150	1.207
Mar. 3, '52	16	1.190	1.173	1.160
Mar. 10, '52	14	1.186	1.156	1.175
May 19, '52	23	1.188	1.200	1.184
Average (weighted)		1.187	1.172	1.182

3. Rebuilding and Repair of Batteries

Lead-acid storage batteries fail before their guarantee period for a number of reasons. The main causes of failure are: (1) broken separators, (2) shedding of the plates, (3) grid disintegration, (4) internal shorts, (5) sulfated negative plates, (6) buckled positive plates, (7) leaky containers, (8) cracked partitions, and (9) broken straps or terminals. Many of these causes of failure result from neglect and/or abuse. Even if batteries are properly serviced they will not last indefinitely.

Some batteries are guaranteed for 12 months, others for 18 months, and others for 24 months or longer; a 12-month battery cannot be made a 24-month battery by addition of an "additive." Also, lead-acid batteries are constructed differently for different services. Batteries for torpedo testing are made with acid of specific gravity of 1.360 and aircraft batteries with 1.275 to 1.300 acid, whereas stationary or stand-by batteries are filled with 1.220 - 1.225 acid. Low-discharge batteries intended for long life (15 to 20 years) are made with pure lead plates (no antimony or other element is used).

Many batteries may be rebuilt to give additional service. In this rebuilding process, "additives" serve no useful purpose but the consumer may be readily misled. The "rebuilding" or repair obliterates any effect that might be attributed to the additive in the sense that the consumer has no way of telling whether the rebuilding or the "additive" is responsible for the additional life he may have obtained. The situation is even more confused if the battery "rebuilt" were of the "doubtful" or "useable" class discussed in the preceding section (Part VI.2)

Broken separators, internal shorts and broken straps or terminals may easily be repaired in most cases. If a cell partition or the case is cracked the elements may readily be removed and transferred to another container thereby extending the useful life. If the plates have lost or shed all or most of their active material the battery is dead or "shot" in the true sense. If the grids have disintegrated the battery has seen its useful life. Additives cannot cause the redeposition of active material on a plate that is totally disintegrated or nearly so. Additives cannot repair disintegrated grids.

Normally buckled positive plates and broken separators can readily be replaced by new ones. Sediment or "battery mud" may be removed to eliminate shorting of the plates at their lower sections. Hard sulfated negative plates may be "desulfated" by successive charges and discharges at low current densities.

Therefore batteries can be rebuilt or repaired to increase their useful life and no additive with "catalysts" or "trace elements" is necessary to this rebuilding or repair. Unfortunately, proponents of additives have frequently and inadvertently confused the two operations: (1) rebuilding and repair and (2) the mere addition of an "additive" to a new or useable battery.

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the front cover.

Reports and Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers and reports. Reports are issued to the sponsoring agency of a particular project or program. Published papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three monthly periodicals, available from the Government Printing Office: The Journal of Research, which presents complete papers reporting technical investigations; the Technical News Bulletin, which presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions, which provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: The Applied Mathematics Series, Circulars, Handbooks, Building Materials and Structures Reports, and Miscellaneous Publications.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.00). Information on calibration services and fees can be found in NBS Circular 483, Testing by the National Bureau of Standards (25 cents). Both are available from the Government Printing Office. Inquiries regarding the Bureau's reports and publications should be addressed to the Office of Scientific Publications, National Bureau of Standards, Washington 25, D. C.

NBS