LEAD INDUSTRIES ASSOCIATION

420 LEXINGTON AVENUE

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SPECIAL REPORT

SUBJECT: SYMPOSIUM ON SECONDARY BATTERIES, ELECTROCHEMICAL SOCIETY MEETING

To Members of the Lead Industries Association:

A symposium on secondary batteries was sponsored at the ninety-eighth meeting of the Electrochemical Society, held in Buffalo, New York, October 11, 12 and 13, 1950.

The following are abstracts and comments on those papers presented which may be of interest to members of the Lead Industries Association:

BATTERY LOADS VS. BATTERY PERFORMANCE
by H. C. Riggs, The Electric Storage Battery Company, Philadelphia, Pennsylvania

Battery design has kept pace with the demand, according to Mr. Riggs. In the past 25 years automobile motors have been getting bigger, the battery load has been getting bigger, the number of miles per year has been getting bigger, and the battery is being expected to start the motor in still colder weather. But the battery, Mr. Riggs pointed out, has remained the same size, and its cost has come down. Expanders are a proven means of improving battery performance.

BEHAVIOR OF THE COMPONENTS OF EXPANDERS FOR LEAD-ACID STORAGE BATTERIES
by A. C. Zachlin, Willard Storage Battery Co., Cleveland, Ohio

Mr. Zachlin pointed out that the effect of various expander components depends on the proportion used and in some cases on the brand chosen. Cold capacity on initial cycles is affected most by lignin, increasing with the proportion of lignin up to 0.5 percent, but not beyond that. Barium sulphate and lamp black affect initial capacity to a lesser degree, but are influential during cycling life on cold capacity and length of service. All three components affect the structure of plate surface during the cycling life test. Charge voltage is affected by the component of expander as well as by its concentration.

PRACTICAL APPRAISAL OF A PATION AGENT IN NEGATIVE PLATES OF LEAD STORAGE BATTERIES
by D. M. Haskell, W. P. Fuller & Co., South San Francisco, California

The opinions of various contemporary investigators regarding expanding agents and cold test performance were discussed. The automobile battery manufacturers' problem of selecting suitable combinations of oxide and expander was considered from the standpoint of three practical categories:

(1) ability to pass the initial cold test; (2) ability to maintain cold test performance at sustained or increasing rate in the later stages of laboratory cycling tests; and (3) ability to give satisfactorily high current discharge rates in a car (as determined by laboratory cold test) after 10,000-25,000 miles and one to two or more years of driving. These tests were correlated by examples and their relative bearing on one another developed.

An in-the-car testing program was described with special reference to cold test performance. Results were described with tables and charts.

Photomicrographs by transmitted and reflected light (Ultrapak) at low, medium and high magnifications in color and monochrome were used in the form of lantern slides to illustrate the behavior of several commercial types of expanders both before and after usage in cars and on laboratory test equipment.

ADDITION AGENTS FOR NEGATIVE PLATES OF LEAD-ACID STORAGE BATTERIES
II. Pure Organic Compounds by E. J. Ritchie, Eagle-Picher Co., Joplin, Missouri

This paper presents some of the results of an experimental study of the effects produced by the addition of pure organic compounds to the negative active material of lead-acid storage batteries. The experimental conditions used in the study were selected to show the greatest differences between compounds of similar structure that were members of a series. These conditions, because they were not standard in the industry, were discussed. The results have been grouped with respect to the organic chemistry and structure of the substances tested. Only those compounds having measurable reducing action appear to have any value as "expanders" in increasing the discharge efficiency of a lead-acid cell at 0° F.

THE EFFECT OF MAGNESIUM SULPHATE AND SODIUM SULPHATE ON LEAD-ACID BATTERIES
By Paul L. Howard and J. A. Vinal, National Bureau of Standards, Washington, D.C.

For many years, preparations using magnesium and sodium sulphates have been exploited as battery rejuvenators. A comprehensive study of these salts was carried out over a wide range of compositions to determine whether there was any beneficial effect on sulphated lead-acid storage batteries. High and normal rate capacities, stand loss, variation in cell temperatures on charge, water consumption, and variation in specific gravity were studied over a six-month period. A simulated field test was set up in the laboratory. Final results compared favorably with actual field tests. The results showed that there was no beneficial effect on a sulphated battery by the use of either magnesium sulphate or sodium sulphate or mixtures of the two in various percentages and/or various degrees of hydration.

STORAGE BATTERY "DOPES"
by Clarence C. Rose, Willard Storage Battery Co., Cleveland, Ohio

The author reviewed the situation regarding battery additives or "dopes." He disclosed the technical and economic absurdity of their claims, and then described more pertinent technical data about automotive storage battery operation which had not been used heretofore in this connection, including data disclosing the cause of failure from scrap battery surveys. He also included most significant battery charge voltage characteristics, together with automotive voltage regulators and their effect upon battery service and life. According to the author, this paper should be a final answer to the annoying and confusing question of storage battery "dopes."

THE EFFECT OF PIG LEAD COMPOSITION ON THE LIFE AND CAPACITY OF LEAD BATTERIES
by D. H. Haskell, W. P. Fuller & Co., South San Francisco, California

Recent changes in composition of available pig leads make it important to know the effect of bismuth on battery manufacture and performance. Automobile batteries have been built and are being evaluated, but as yet no great differences have shown up in the tests. The investigation is being continued.

THE CONSTANT POTENTIAL ANODIZATION OF LEAD IN SULPHURIC ACID SOLUTIONS
by John J. Lander, Naval Research Laboratory, Washington, D. C.

Rates of attack on pure lead, anodized at constant potentials were developed at ONR and are given by the activation equation:

$$w = nke^{a^2FV/RT} \int_0^t a\,dt.$$

The corrosion product is tetragonal PbO at potentials below those for PbO_2 formation.

SOME PRELIMINARY STUDIES OF POSITIVE GRID CORROSION IN THE LEAD-ACID CELL
by John J. Lander, Naval Research Laboratory, Washington, D.C.

Experimental work at ONR revealed that: (1) PbO_2 undergoes solid phase reaction with Pb to form tetragonal PbO; (2) certain tin alloys of lead are more corrosion resistant than pure lead or 6 percent Sb-Pb alloy; (3) electrolyte concentration is an important factor in the corrosion process; (4) an intermediate film of PbO_2 is formed which does not cycle to $PbSO_4$; (5) a relationship exists between growth and film formation. Theoretical explanations for these effects were proposed.

CONSTRUCTION AND PERFORMANCE OF PLASTIC CONTAINER ELECTROLYTE-RETAINING LEAD-ACID BATTERIES

by C. H. Endress and Clarence C. Rose, Willard Storage Battery Co., Cleveland, Ohio

Lead-acid storage batteries, it was pointed out by the authors, have certain inherent advantages with respect to high voltage, high rate and low temperature discharges, rechargeability, etc., which make them desirable for many applications other than automobile starting and lighting and similar heavy duty service. The problem was to redesign the construction to eliminate the excess weight of hard rubber containers and the nuisance of acid leakage, and at the same time, cover a range of sizes down to the truly miniature radiosonde - or weather balloon types. Polystyrene and similar modified plastics make attractive, practical, low-weight acid-proof and leak-proof containers and covers. Fibrite insulation retains 90 percent of the electrolyte, and coupled with cover design, makes the batteries spill-proof. Gravity indicator balls in transparent ball cages give accurate indication of state of charge in batteries with not enough free electrolyte for hydrometer readings. These batteries have been designed and used in many sizes and shapes for special applications. They are now available in a more systematically chosen range of sizes so that in series or multiple, almost every possible combination of voltage and capacity is available within a very minimum volume and weight. Typical discharge characteristics were shown and capacity ratings of the various sizes were given.

THE HYDROSET PROCESS FOR LEAD STORAGE BATTERY PLATES

by A. H. Greenberg, C. .. Finan, and B. Agruss, National Lead Co., Research Laboratories, Brooklyn, New York

In the lead-acid storage battery industry, the trend has been toward the use of litharge containing high percentages of finely divided, unreacted metallic lead. Plates containing this material are cured or "hydroset" at room temperature prior to forming. The setting action involves oxidation of the metallic lead in the presence of water, an exothermic reaction causing the plates to dry. Variations in atmospheric conditions affect the rate of setting. The authors of this paper discussed the effects of temperature and humidity changes on the setting rate. It was shown that there is an optimum plate moisture concentration which corresponds to a maximum oxidation rate.

FLOAT CHARACTERISTICS OF LEAD BATTERIES

by C. D. Knoop, Bell Telephone Laboratories, Murray Hill, New Jersey

The steady-state positive and negative plate potentials of lead-acid storage batteries with lead-calcium and lead-antimony grids were measured at various constant charging currents from 0.008 percent to 40 percent of the eight-hour discharge rate. Above a definite minimum current, the author shows that the polarization voltage follows the equation $E = a \log \frac{I}{I_0}$. "a" is a constant independent of temperature over the range studied (25° - 40° C), while $\log I_0$ increases linearly with

temperature. These constants have characteristic values for the positive and for the negative plates which further depend on the composition of the grid alloy. Lead-calcium plates give slightly higher values for "a" and considerably lower values for I_o than lead-antimony. At currents less than I_o, the plate potentials correspond to the reversible potentials for the positive and negative plates, respectively. It is shown that these data permit the calculation of the negative plate self-discharge rate, the analysis of operating conditions, and the determination of proper float voltage.

NICKEL-CADMIUM BATTERIES FOR MILITARY USE
by C. B. Ellis, U.S. Signal Corps Engineering Laboratories, Fort Monmouth, N. J.

A review is made of the performance of military types of nickel-cadmium batteries. Sintered plate batteries are compared with pocket types. Comparison with the lead-acid battery was religiously avoided by the author who also pointed out this significant fact: the nickel-cadmium battery has certain features, such as good performance at low temperature, which make it useful for special military applications. Beyond this it does not rival the lead-acid battery.

It is expected that all of the above papers will eventually appear in the official "Journal of the Electrochemical Society." This is published monthly by the Electrochemical Society. Editorial office: 235 West 102nd Street, New York 25, New York. Single copies are available at 75¢ to members and $1.00 to non-members.

Very truly yours,

Secretary