NBS CIRCULAR 504

Battery Additives

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

UNITED STATES DEPARTMENT OF COMMERCE • Charles Sawyer, *Secretary*
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National Bureau of Standards Circular 504
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Battery Additives

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Various preparations of liquids and solids have been sold to the public as means of rejuvenating worn out or so-called "dead" batteries. The majority of these materials are composed of varying proportions of magnesium sulfate and sodium sulfate. Extensive laboratory and field tests have been made covering various proportions of magnesium and sodium sulfates. The results show no difference between the batteries treated with these mixtures and similar untreated batteries used as control.

I. General description of lead-acid storage battery

Figure 1 shows a cutaway view of an ordinary automobile battery. Three cells are housed in a hard-rubber or composition container and covered with tops of similar material containing filler wells,

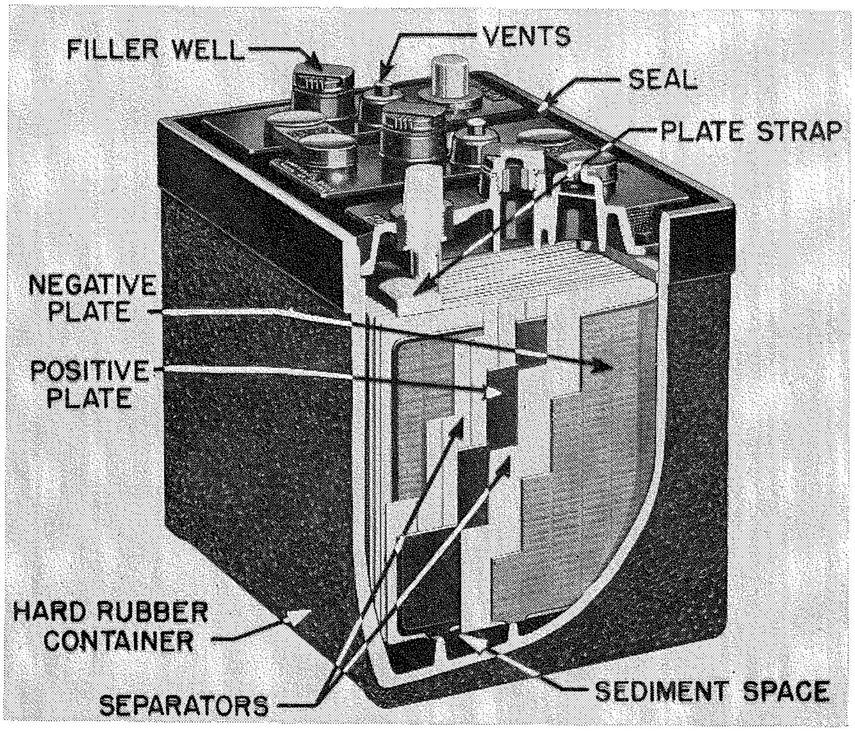

Figure 1. *Cross-sectional view of standard automotive battery.*

with a bituminous material
ı cell is composed of several
by a wood or microporous
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lead-alloy grid into which
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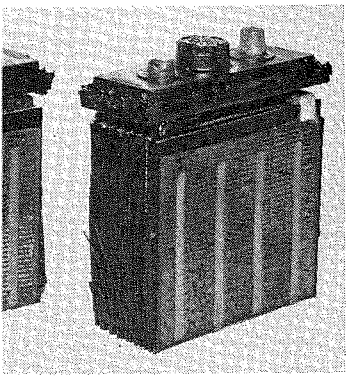

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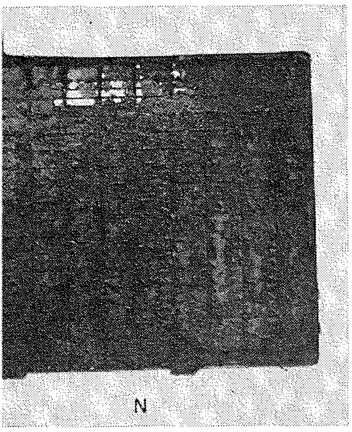

orage battery at end of useful life.
ive.

some of their active material and are badly sulfated. The wood separators are charred by the sulfuric acid, and active material is deposited on their surfaces. Figure 3 shows the condition of the positive plates and negative plates. The positive grid frame is corroded to such an extent that the plate is disintegrated. The negative plate has lost some of its active material in the sulfated area.

II. Fundamental facts about storage batteries

A storage battery may be considered as an electrochemical apparatus in which electric energy is stored as chemical energy.

When a storage battery is discharged the chemical energy is transformed into electric energy as the lead dioxide and sponge lead react with the sulfuric acid to form lead sulfate at both the positive and negative plates. The current flows from the positive to the negative plate externally and from the negative to the positive plate internally to complete the cycle of transformation of chemical energy into electric energy.

The lead sulfate formed during the discharge forms a surface coating over most of the surface of each particle of finely divided sponge lead or lead dioxide. The center of the particle, being nonporous, is not converted to lead sulfate. Each particle is in intimate contact with the next particle so that electrically continuous flow of current is maintained. Thus this normal deposit of lead sulfate forms a relatively thin film over the particles of active material and is easily reconverted to the corresponding lead or lead dioxide during subsequent recharge. The relative size of these particles determines the amount of electrolyte that may be in the pores of the plate at any given time.

If a battery is subjected to a high rate of discharge, the reaction of the lead and lead dioxide with sulfuric acid will be very rapid. This tends to weaken the layer of acid close to the surface of each particle, thus limiting the continuous discharge capacity. However, if the discharge is stopped for a short period and then repeated, the battery will give additional performance. Thus it may appear to the layman as if it has automatically charged itself. This may be repeated a number of times with each succeeding discharge, giving poorer performance until the battery is effectively completely discharged. This phenomenon, which has been known for 70 years, is inherent in all storage batteries and is known as the recuperative power of the lead-acid battery. Each time the battery is rested the acid diffuses into the pores of the plate and replenishes the supply of acid at the surface of the particles of active material.

After the battery has been discharged it is charged by forcing an electric current in the opposite direction so that the lead sulfate is converted back to lead dioxide and sponge lead according to its original condition. This completes the cycle in which chemical energy furnishes electric energy and electric energy is again stored as chemical energy.

The word "charge" as applied to storage batteries is defined as follows in the Standards for Storage Batteries adopted by the American Institute of Electrical Engineers, dated June 22, 1922 (Definition No. 36–250):

"Charge.—The conversion of electric energy into chemical energy within the cell or battery. This consists of the restoration of the

tional current through the cell or
that of the discharge. A cell or
ged" is understood to be *fully*

follow the fundamental electro-
be stated as follows:
t free at an electrode is directly
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d in several senses, and this has
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es of the active material of the
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les of active materials. This
charging current. This type of
eration of a battery and is not a

ı is caused by parasitic currents
ubstances present. The rate at
upon the temperature and con-
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normal discharge process. This
ever, if the battery is not neg-
verted to active material by the
automobile battery the average
fic-gravity change) for different
drop per day at 100° F, 0.002
day at 50° F.
ie battery would need recharging
lowing intervals: At 100° F re-
t 37 days, and at 50° F recharge
the electrolyte will increase the
fation in the plates.
ord sulfation applies to excessive
ı in or on the plates as a result of

in a discharged condition for a

n evidence of trouble within the

n water should have been used.
emperatures.

the electrolyte.
a partially charged condition.

This type of sulfation is more difficult to reduce and may injure the plates. Excessive sulfation can be avoided with reasonable care. It is doubtless true that the liability to troublesome sulfation of lead batteries has been exaggerated by those exploiting so-called cures.

When a battery stands in a discharged condition for some time the lead sulfate crystals tend to grow. In doing this they harden and become larger and may break away from the surface. Also, the growth of the sulfate crystals tends to block the pores of the plate. As these crystals occupy more space than the original active material, their expansion may eventually either fracture the grid frame or loosen the active material.

Lead sulfate is very slightly soluble in sulfuric acid electrolyte at normal temperatures. However, the solubility increases with rise in temperature. One cause of crystal growth depends on a rise in temperature to dissolve the lead sulfate and a drop in temperature to recrystallize it. Thus the larger crystals grow at the expense of the smaller. Another cause is the removal of acid from the electrolyte in the pores as lead sulfate is formed, causing a greater solubility of the lead sulfate in the low gravity acid and a recrystallization as more acid diffuses into the pores or as the amount of electrolyte in the pores is reduced due to growth of the crystals. Both of these causes contribute to troublesome sulfation.

Because of the closing of the pores in the active material by the crystal growth of the lead sulfate it becomes increasingly difficult for the electrolyte to penetrate into the plates. If a battery which has stood for a long time is filled with water and placed on charge with a direct-current source it is found that the initial closed-circuit voltage is much in excess of its normal value. As the electrolyte penetrates into the active material and reconversion begins the voltage will gradually drop to that of a normal cell. If the applied voltage is low and the cell resistance is high, the indications might be that the cell is dead. However, if sufficient time is allowed, there would be a gradual break down of active material and current would begin to flow. This condition is true, regardless of whether or not a battery has been treated with additives, provided it has been in a sulfated condition for a long period.

IV. Types of additives

More than 100 additives have been brought to the Bureau's attention during the past 30 years. A statement entitled "Solutions do not charge storage batteries" was issued in the Bureau's Technical News Bulletin 94, February 10, 1925. Since that time many additional tests on solutions and compounds, the latter in the form of salts to be added to the battery electrolyte, have been made. Bureau Letter Circular 302 was issued in 1931 and has been revised to meet new demands.

Various types of additives have been marketed over the period of years. Analysis of these preparations shows their composition falls into the following categories:

Solids:

(1) Preparations of varying proportions of magnesium sulfate and sodium sulfate in various states of hydration.

V. Experimental Procedure

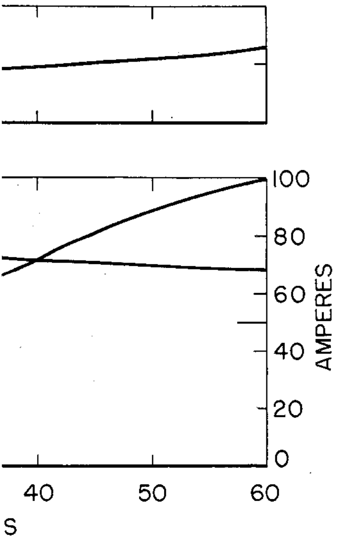
In order to study these combinations it was necessary to devise a test procedure that would cover the main characteristics of the battery and the claims most often used by the manufacturers for their additive. A series of tests was set up to cover the following points:

1. Change in specific gravity of solution produced by the additive.
2. Effect on capacity at normal discharge rates, such as the 5-hour rate, to determine whether there was a decrease in sulfation.
3. Effect on self-discharge or local action as an indication of improvement in retention of charge.
4. Effect on temperature of cells during charge as a means of prolonging life.
5. Effect on water consumption as an indication of whether the battery was taking the charge better with or without the treatment.
6. Simulation of an operational test where the batteries remained just under full charge for a long period but never on a complete discharge cycle to determine whether the treated cells would recharge more completely than untreated cells.
7. High-rate discharges starting at 300 amp then reducing to 200 amp and 100 amp successively to determine whether there is any change in cell performance under these conditions by treating the battery with additives.
8. Determination of the recuperative power of a cell when subjected to 300-amp load for a short interval followed by a rest period and repetition of the cycle. This is to indicate whether any improvement was made by the treatment.
9. Effect of several complete cycles to see if there was an increase in capacity and specific gravity.

In order to make such a series of tests it was first necessary to obtain mechanically sound batteries that were permanently sulfated. Various so-called sulfated batteries were obtained and given a charge for an extended period until there was no further change in gravity. A battery made in 1920 that had been allowed to stand from then until 1949 was dismantled and the negative plates charged in 1.050 specific gravity sulfuric acid against sheet-lead positives. These plates were completely converted to sponge lead. It has been the experience here that most of the so-called sulfated batteries filled with low-gravity sulfuric acid or water will respond to normal charging procedures, provided the charge is slow and over an extended period. However, if the cells are filled with high-gravity acid, the response to charge is very poor.

Six batteries of Army 6-volt type 2H that had stood for 4 years in a charged and damp condition were filled with 1.050 acid and given a 388 amp-hr charge. The results of this charge are shown in table 1. Here the specific gravity did not rise equally in all cells and the capacity was low except in battery 5. This battery recovered all its rated capacity but was high in local action.

Capacity and stand loss were measured on these batteries to establish their characteristics prior to treating. A series of combinations of anhydrous magnesium and sodium sulfates were set up as shown in table 2. Mixtures A and C are commercial products, while mixtures B, D, and E were prepared and included in the group in order to extend the range of compositions studied.



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ıd (4) 50 batteries new but

) were treated with mixture
controls. Monthly checks
the batteries. The results
d 44. Table 42 summarizes
ecific gravity, and table 44
performance. From these
no beneficial effects gained

TABLE 42. *Number of failures out of 50 batteries in each group when treated with mixture C and field tested for 6 months*

Battery condition	Months						Total percentage of failure
	1	2	3	4	5	6	
							%
Mechanically sound, but ready for salvage (treated)	4	12	3	2	2	0	46
Mechanically sound and still in service (treated)	2	4	3	0	0	4	26
New batteries never prepared for service (treated)	0	1	1	1	1	0	8
New batteries never prepared for service (untreated)	0	0	0	0	1	0	2

TABLE 43. *Percentage variation in specific gravity at end of 6-month period on batteries treated with mixture C*

	Group 1, treated	Group 2, treated	Group 3, treated	Group 4, untreated
	%	%	%	%
Increase	34	32	35	40
Same	24	23	21	19
Lower	42	45	44	41

TABLE 44. *Percentage of satisfactory and unsatisfactory batteries after inspection at 6-month period on batteries still in service*

Condition	Group 1, treated	Group 2, treated	Group 3, treated	Group 4, untreated
	%	%	%	%
Satisfactory	47	45	64	75
Unsatisfactory	53	55	36	25

VIII. Conclusions

In the course of this investigation five batteries comprising 15 cells were subjected to an extended series of laboratory tests to determine the effect of adding specified amounts of sodium and magnesium sulfates in varying proportions. These batteries were in sound mechanical condition but were sulfated to the extent that their initial capacity after prolonged charging was about two-thirds of their rated capacity. Ten cells were treated with additives, and the remaining five were not treated.

Tables 4 to 31 show no significant differences in the operating characteristics of the cells that were treated as compared with those not treated. Obviously, the condition of a group of batteries in a sulfated state is not uniform, but the average results of 15 cells covering all tests show a remarkable uniformity in the behavior of treated and untreated cells. The averages are given in table 45.

It appears from table 45 that both sodium and magnesium sulfates are ineffective in improving the condition of the batteries or in prolonging their life.

ests, tables 4 to 31

Untreated cells	Treated cells
amp-hr	120 amp-hr
mp-hr	
mp-hr	
	48 amp-hr.
mp-hr	
	14 amp-hr.
v	1.12 v.
v	2.03 v.
nl/week	59 ml/week.
6	0.007.
0	0.028.
°C	38.4°C.

tests covered in this inves-
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