

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
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Battery Compounds and Solutions

The Bureau of Standards receives many inquiries about materials which are said to charge storage batteries or otherwise improve their performance. More than one hundred of such materials have been brought to the Bureau's attention during the past few years. A statement entitled "Solutions do not charge storage batteries" was issued in the Bureau's Technical News Bulletin No. 94, dated February 10, 1925. This statement was based on tests of typical materials available at that time. Since then additional tests on solutions and compounds, the latter in the form of salts to be added to the battery electrolyte, have been made. The later tests confirm the Bureau's previous conclusions that these materials do not charge storage batteries nor do they materially improve the performance of the batteries.

Careful tests have shown that batteries containing these solutions behave essentially the same as similar batteries not containing the materials in question; that is, no essential improvements in the capacity of the batteries, the time required for charging them, the operating temperatures, or the amount of water which must be added to maintain them, have been observed.

It has been shown that batteries are not charged by changing the solutions and that the time required for charging is not decreased. The word "charge" as applied to the storage batteries has a distinct technical meaning. The American Institute of Electrical Engineers has defined the word "charge" as follows: "Charge. The conversion of electrical energy into chemical energy within the cell or battery. This consists of the restoration of the active materials by passing a unidirectional current through the cell or battery in the opposite direction to that of the discharge. A cell or battery which is said to be 'charged' is understood to be fully charged." This definition indicates clearly that the charging process is the restoration of the active materials of the battery by an electric current.

Careful comparison of batteries containing such solutions or compounds with similar batteries not so treated have shown that in either case a half-hour charge, the battery being discharged initially, will permit the operator to withdraw ampere-hours equal to about what has been

put in during the one-half hour charge, and similarly, if the charge is continued for one hour the equivalent of the one-hour charge can be withdrawn. This is in accordance with fundamental laws of physics and chemistry.

The claim is often made that batteries containing these solutions will operate at lower temperatures when being charged by an electric current. The temperature to which the battery will rise depends upon the amount of heat energy which is liberated within the battery and the radiation of heat from the battery. Assuming two batteries to radiate heat equally, the one which has the higher internal resistance will operate at the higher temperature. The electrolyte is only one of several factors in determining this resistance. Careful comparison between batteries containing these solutions or compounds and similar batteries not so treated have shown that there is very little, if any, difference in the operating temperatures under comparable conditions.

Likewise the claim is often made that the use of such solutions or compounds will prevent freezing. The freezing point of a battery electrolyte varies with the specific gravity. If extra acid has been added so that the battery, in a state of discharge, has a high specific gravity the freezing point is correspondingly lower, but this introduces other difficulties.

The claim is sometimes made that these solutions and compounds make an old battery work like new. Such a statement is rather vague, but one interpretation which might be placed upon it is the following: If a battery which has been giving less than its rated capacity is treated with such a solution or compound it might be expected that the full rated capacity of the battery would be restored. Experiments have indicated that this is not the case.

The storage battery has a descriptive name because the energy of an electric current applied to the battery at one time may be held and used at a later time. The chemical reactions which occur in such a battery are reversible. During the charging process the chemical reactions proceed in one direction, while the delivery of electrical energy results from the chemical reactions proceeding in the opposite direction. The fundamental reactions in the battery during discharge result in the formation of lead sulphate at both the positive and negative plates. When the battery is being charged, on the other hand, the lead sulphate is broken down into constituents of the plates and electrolyte. No case has been found in which this fundamental reaction is ma-

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terially altered by the use of these battery compounds and solutions.

Since the storage battery stores chemical energy rather than electricity as such, the question may be asked how far the chemical reactions may proceed in the battery. Experience shows that, on the average, only 25 to 40 per cent of the active materials in the cell are actually used during discharge. A battery which has been discharged, therefore, to a voltage which is below the useful limit can recuperate to a limited extent if allowed to stand on open circuit for a short time so that the electrolyte has an opportunity to penetrate farther into the pores of the plates and thereby come into contact with active materials which have not been previously converted to lead sulphate. Successive discharges of a battery may be made, therefore, before the battery becomes completely exhausted. Even then much of the original active material still remains. Changing the solution in the battery may permit some further discharge to be made as a result of the fresh solution making contact with active materials already present. This can not, however, be regarded as evidence that the battery has been charged, because the active materials of the plates have not been restored in any sense of the word.

A battery which is almost completely discharged may have nearly the same voltage as one which is fully charged. In this condition the battery may be able to turn the starter of an automobile or light the lamps, but its exact state of charge can be determined only by making a measured discharge upon it, using suitable measuring instruments.

The lead sulphate which is formed on the plates during the discharge is finely crystallized and quite invisible. If, however, the battery is allowed to stand in an exhausted condition for a considerable period of time the crystals of lead sulphate tend to grow larger and there is also some increase in the amount as a result of local action. In time the plates may become encrusted with a coarsely crystallized lead sulphate which is difficult to break down. The condition of the battery at such a time is not due primarily to the alleged pernicious effects of the sulphuric acid but rather to failure to charge the battery properly. Lead sulphate is sparingly soluble. Introducing a new solution may dissolve a small amount of it, but when the solution becomes saturated with the lead sulphate no more will dissolve.

Analyses of some of the solutions have shown them to contain about 40 per cent sulphuric acid and some coloring matter. Other solutions contain about the same amount of

sulphuric acid and in addition significant amounts of some or all of the following: sodium, magnesium, potassium, aluminum and other less common materials. The sodium, for example, may have been added as soda, lye, or Glauber's salts, but it seems probable that the metallic ions mentioned above were introduced into the solution in the form of the common sulphate salts, such as Glauber's salts, Epsom salts, and alum.

Battery compounds which are not in liquid form have been found to contain more or less of the materials mentioned above, with the exception of the sulphuric acid. Since the directions for using such compounds ordinarily state that they are to be added to battery electrolytes or to fresh solutions of sulphuric acid, the result in the battery is essentially the same.

The use of sodium sulphate, Glauber's salts, in batteries is an old story. It was suggested more than forty years ago, but various authorities have stated since that time that such a material is without beneficial effect in a battery. The Bureau's recent experiments on the determination of the rate of sulphation of battery plates indicates that even 4 to 5 per cent of Epsom salts or Glauber's salts do not materially reduce the rate of sulphation.

The indiscriminate addition of these solutions and compounds to a battery is not advisable, although in some cases no particular harm may be done. If the solution is used to replace the electrolyte of a completely discharged battery, as is frequently the case, the battery may be spurred on to give a little more current because of the surplus of active material in the plates, but when the battery is recharged by an electric current and the lead sulphate in the plates is reconverted into the active materials of the plates and has replenished the electrolyte, the specific gravity will probably rise much above the limitations for good operation. In some of the Bureau's experiments it rose to a specific gravity of 1.365. This is not desirable because the local action or self-discharge within the battery is materially increased. A battery containing one of these solutions lost 47 per cent of its charge in four weeks as compared with 8 per cent which was lost by a similar battery with the ordinary electrolyte. Batteries containing solutions of higher than normal specific gravity may have considerably less capacity at high rates of discharge, as when cranking the engine of an automobile, depending on the behavior of the negative plates. The high specific gravity of the electrolyte is also injurious to the wood separators. It is a well-recognized principle in battery operation that acid should be added only to replace that which has been spilled, or in rare instances to adjust the specific gravity to the required standard after the completion of a full charge.

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