

QUALITY-CONTROL TECHNIQUES FOR DRY CHARGING LEAD/ACID BATTERIES

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Introduction

Dry-charged lead/acid batteries were introduced because of the problems inherent in the storage of wet-charged types. At the time, the materials used to construct batteries were such that wet-charged batteries suffered high rates of self-discharge and sulphation on standing, and generally deteriorated on the shelf. Many slow-movers were, in fact, scrapped prior to sale. The dry-charged battery provided the customer with a fresh battery, and gave distributors and retailers a means of safely carrying both a wider range of products and larger stocks. In many cases, transportation was simplified and made cheaper by using dry-charged types.

Technical developments, resulting in low maintenance and maintenance-free batteries, have removed the original problems with wet-charged systems. In some markets today, dry-charged batteries are rarely seen at the point of retail. However, other markets still demand these batteries, and dry charging is carried out to facilitate shipment to export markets.

Methods of dry charging

The choice of the best drying or preservation process for plates is determined by the requirements of the finished product, as well as by economic considerations such as investment, available space, labour costs and energy demands.

The requirements of the finished products may be separated into two broadly different areas:

(1) *Conventional dry-charged.* Here the market requires dry-charged batteries and the product must satisfy the expectations of the consumer. Specifications often need to be met and quality control is imperative. The batteries are manufactured with plates processed by one or other of several well-known methods [1] which preclude the action of atmospheric oxygen during drying. These methods include: (a) vacuum drying; (b) drying in an inert gas atmosphere; (c) drying using superheated steam; (d) drying by solvent displacement, (e) hot platten drying.

(11) *Convenience dry-charging* Here the finished product is not likely to reach the end point of sale and is basically used within the confines of the company and its own distributors. The process is used mainly for the purpose of avoiding transport of electrolyte either for weight savings or for regulatory reasons. Before final distribution, the batteries are usually filled and given a refreshing charge. Outside specifications are irrelevant and a degree of relaxation in quality control is permissible.

Additionally, it may be necessary to dry-charge batteries in an emergency, for example, when conventional dry-charged manufacturing equipment is in need of maintenance or replacement. Two distinct methods have been employed for such situations: (a) drying the plates in a hot-air oven after impregnation of the plates with an oxidation inhibitor or anti-oxidant, (b) using a conserve-charge method which involves draining the battery of fluid electrolyte and sealing against the ingress of oxygen, the plates, separators, etc., remain moistened with electrolyte.

Product specification

In practical terms, the traditional dry-charged battery should be capable of starting a vehicle, without the necessity for a boost charge, within 15 - 20 min of filling with electrolyte at ambient temperatures. Quality-control procedures should be in place within the manufacturing plant to ensure that batteries meet this performance requirement. Process-proving procedures and final product-testing should be carried out on a regular basis (at least weekly) in the quality-control laboratory. Quality-control monitoring of components should be conducted continuously in the factory using inexpensive equipment and a minimum of skill.

Laboratory testing

The following tests should be performed: (a) battery activation, (b) measurement of the water content of both positive and negative plates, (c) measurement of the moisture content of the separators, (d) measurement of the oxide content in the negative plate, (e) determination of the efficiency of the oxidation inhibitor.

Quality-control monitoring

Quality-control monitoring should be performed continuously and should include simple yet indicative tests on all components relevant to the dry-charge nature. Tests should include: (a) cadmium electrode testing of both positive and negative plates, (b) measurement of the moisture content of positive plates, (c) water absorption testing of negative plates, (d) determination of the ohmic resistance of cell packs. As well as these procedures, factory personnel should routinely check the temperature of the ovens used for drying positive plates, the control of plate washing (via pH measurements) and, where installed, the reading of oxygen-analysis meters.

Battery activation testing

This test determines the ability of the battery to start a vehicle without a prior boost charge. The test should be carried out regularly on freshly produced batteries, as well as on batteries taken from stock or returned by the distribution network. Measurements taken during the test also give some indication of any component or area of processing that may be at fault. The steps involved in the test are listed in Table 1.

Figures 1 to 4 show the deterioration in the dry-charge activation characteristics during battery storage. If the battery fails to pass the activation test, the measurements recorded can indicate those areas of the process requiring investigation. A typical analysis is outlined in Fig. 5.

Quality control monitoring

Cadmium electrode test

One of the most valuable tools available for continuous monitoring of both positive and negative plates is the simple cadmium electrode test.

TABLE 1

Activation test for dry-charged (12 V) lead/acid batteries

Stage	Experimental procedure	Test requirements*
1	Stabilise the battery to a temperature of 25 °C	
2	Fill the battery with electrolyte whose temperature is 25 °C and S G is 1.260	
3	Immediately after filling the positive-end-cell, measure the potential against cadmium	See Tables 2 - 4
4	Immediately after filling the negative-end-cell, measure the potential against cadmium	See Tables 2 - 4
5	Immediately after filling the complete battery, measure the open-circuit voltage across the terminals	12.00 V
6	20 min after filling measure <ul style="list-style-type: none"> ● temperature ● S G of each cell, or at least centre cell ● open-circuit voltage across terminals 	Rise of 8 °C (maximum) — see Fig 1 Drop of 0.025 S G. (maximum) — see Fig 2 12.30 V
7	Discharge the battery to 6 V using a discharge current equal, in amperes, to $3C_{20}$ <ul style="list-style-type: none"> ● measure voltage at 5 s ● measure time to 6 V ● monitor potential of positive and negative plates against cadmium 	9.5 V (minimum) — see Fig 3 3.0 V min (minimum) — see Fig 4

*Specifications for a fresh battery, i.e., less than 60 days storage

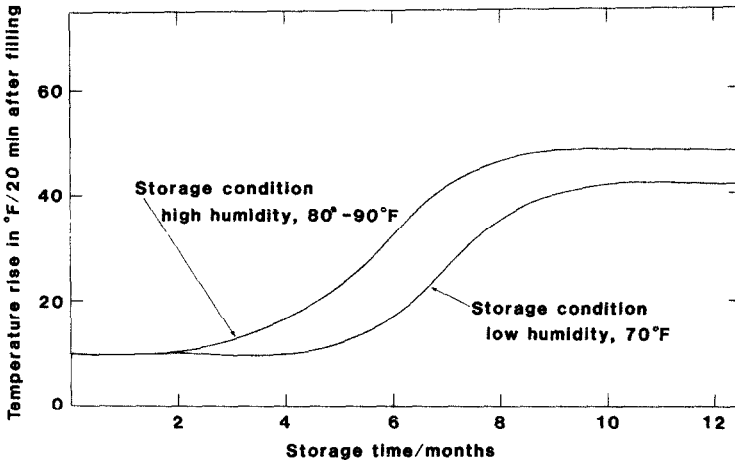


Fig 1 Activation test characteristics for dry-charged batteries temperature rise (20 min after filling) vs storage time

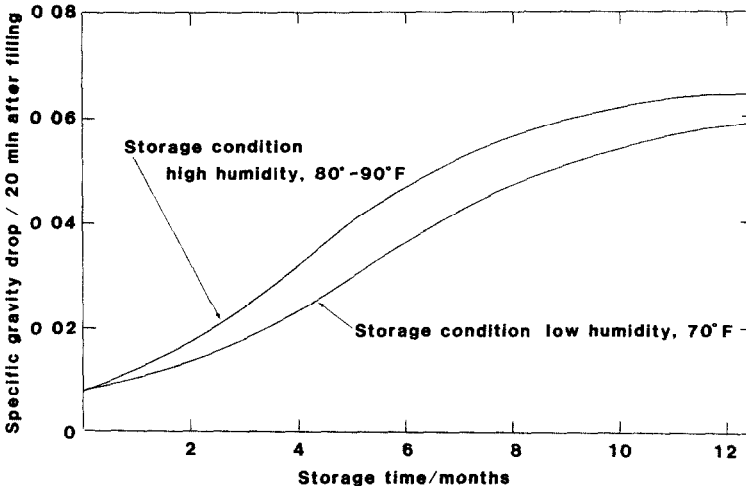


Fig 2 Activation test characteristics for dry-charged batteries acid S G drop (20 min after filling) vs storage time

Plates can be tested immediately on emerging from the drying machine, during storage in the factory, and immediately prior to assembly

The testing equipment is inexpensive, and the tests can be carried out on a table in the plant by an operator with minimal training. All that is required is (i) a voltmeter with two probes, one of which carries a cadmium stick, (ii) an empty battery box with one cell containing sulphuric acid electrolyte of 1.260 - 1.270 S G (Fig 6(a)), (iii) a stop clock. A single positive, or negative, plate is dropped into the cell containing the electrolyte and the potential against the cadmium reference electrode is measured (Fig 6(b)).

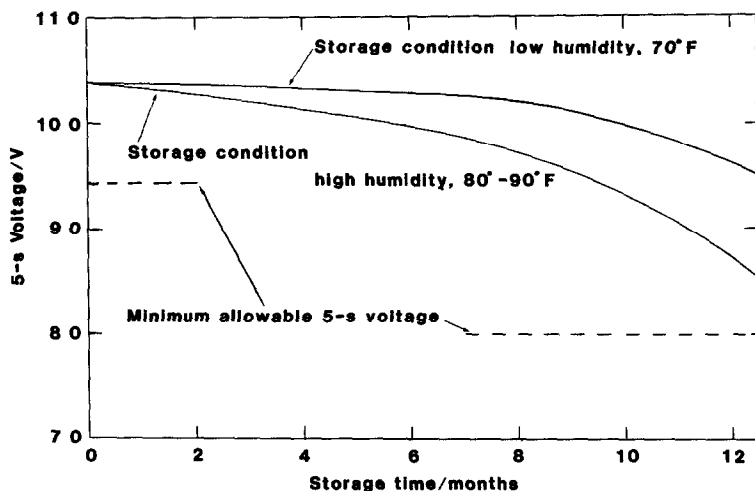


Fig 3 Activation test characteristics for dry-charged batteries 5 s voltage vs storage time. Filling acid 1 260 S G at 80 °F Discharge at 144 A (3 C_{20}) 20 min after filling

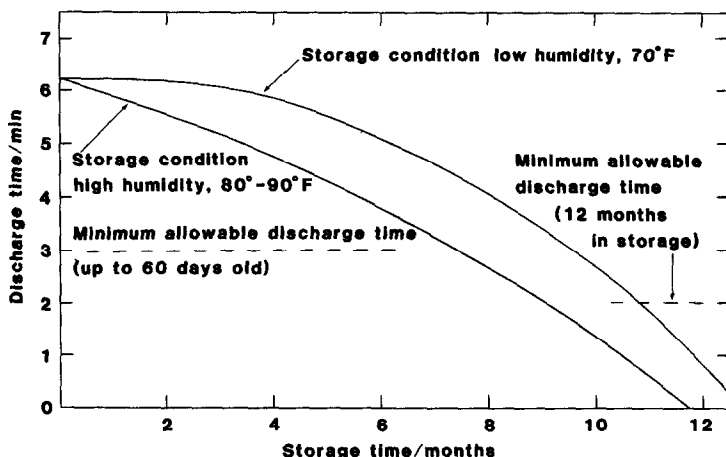


Fig 4 Activation test characteristics for dry-charged batteries discharge time vs storage time Filling acid 1 260 S G at 80 °F Discharge at 144 A (3 C_{20}) 20 min after filling Cut-off voltage 6 V

The time taken for each plate potential to reach the appropriate value indicates the ability of each plate to perform satisfactorily in an activation test if those plates had been assembled into a battery. Table 2 shows the relationship between the elapsed time to a given potential and the respective condition of the plate. The degree of oxidation of the negative plate and the grading of the positive plate are given in Table 3. Finally, Table 4 presents experimental results obtained from a negative plate that was seriously oxidized, together with those for a positive plate that was suffering from extensive thermopassivation.

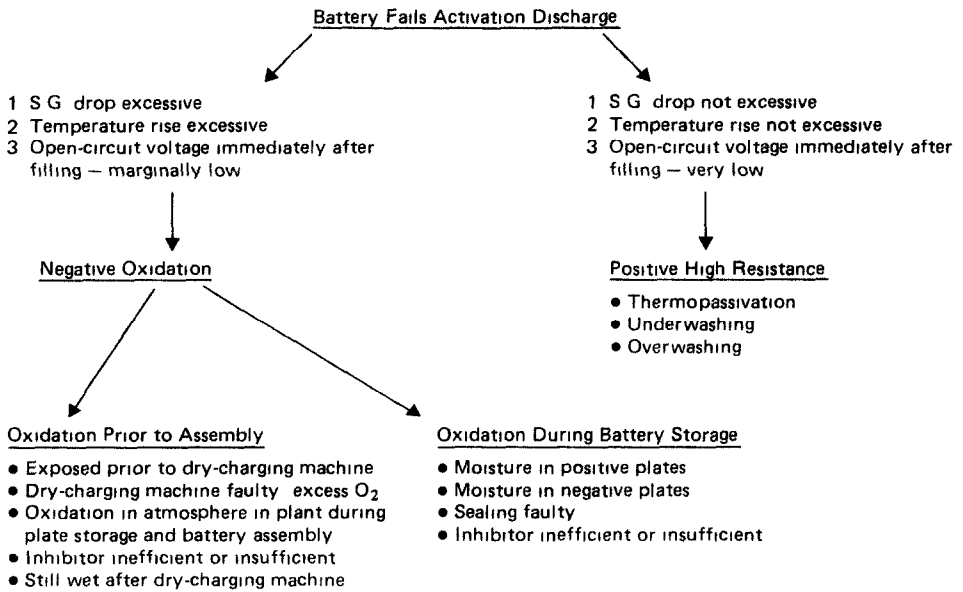


Fig 5 Interpretation of results from activation test

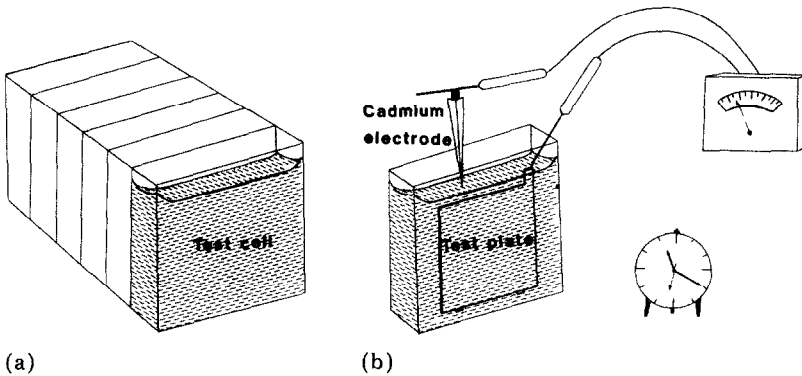


Fig 6 Equipment for cadmium electrode test

TABLE 2

Cadmium electrode test for dry-charged batteries

Time (s)	Negative plate voltage (V)	Positive plate voltage (V)	Plate condition
0	0 15	2 15	Excellent
15	0 15	2 15	Excellent
60	0 15	2 15	Good
120	0 15	2 15	Satisfactory
> 120	0 15	2 15	Unsatisfactory

TABLE 3

Guidelines for cadmium electrode testing of dry-charged batteries

Time (s)	Negative plate wt % oxide*	Positive plate process**
0	< 4	Excellent control of washing and drying
15	2 → 6	Excellent control of washing and drying
60	5 → 8	Good control of washing and drying
120	8 → 12	Washing suspect
> 120	> 12	Thermopassivation

*Time to 0 15 V

**Time to 2 15 V

TABLE 4

Data from a cadmium electrode test on a defective dry-charged battery

Time	Negative plate potential (V)	Time	Positive plate potential (V)
0	0 35	0	1 68
30 s	0 30	1 min	1 85
5 min	0 30	5 h	2 15
<i>Conclusion</i>	oxide > 20 wt %	<i>Conclusion</i>	heavy passivation and overheating

Moisture content of plates

Measurements of the moisture content of plates should be conducted regularly, together with similar moisture testing of the separators. Such action is essential in establishing that the drying process is adequate and that the storage facilities offer sufficient protection against the environmental conditions in the plant. The maximum water content should be zero and 0.3 wt.% for negative and positive plates, respectively.

Continuous monitoring by the quality control technique (Table 5) should be carried out to ensure that the process is taking place as required and that operators are not deviating from the prescribed procedures.

Inhibitor test

Oxidation inhibitors are used to limit the oxidation of the negative plate during the dry-charge process and/or to retard the oxidation during storage prior to battery assembly and during battery storage. Some inhibitors are added directly to the paste mixture, whereas others are applied by soaking the charged and washed plates in solutions of the inhibitor for periods of up to 1 h prior to the dry-charging process.

As well as providing protection for the negative plate, the inhibitor should have the following properties

TABLE 5

Quality control of moisture content in dry-charged plates

Stage	Procedure
1	Place a sample positive or negative plate on an electrically heated hot plate whose surface temperature is 100 - 120 °C
2	Place a cold, dry watch glass on the battery plate Within 15 s a fog will appear beneath the glass
3	<ul style="list-style-type: none"> ● If this fog forms condensation on the glass, then plates are too wet for use ● If this fog does not form condensation and disappears quickly on lifting the watch glass, then plates are satisfactory

TABLE 6

Oxidation inhibitors for dry-charged plates

Materials added directly to paste	Materials added through soaking charged plates
Long chain carboxylic acids, <i>e g</i> , stearic acid (0.8 wt %)	Boric acid (saturated solution)
Oxynaphthoic acids, <i>e g</i> , alpha oxynaphthoic (1.0 wt %)	Dihydroxy and trihydroxy benzenes, <i>e g</i> , resorcinol and pyrogallol
Polymerized resins containing 10 - 80 wt % abietic acid (0.2 wt %)	Phenols, <i>e g</i> , cresol
Non-additive motor oils, <i>e g</i> , 30 W grade (1 litre per tonne)	Polyhydroxy alcohols, <i>e g</i> , sorbitol Combination of boric acid and phenol

- Quantity used should not inhibit formation.
- If added to the mix, should not be lost in processing.
- Should be permeable to the electrolyte on activation
- Should not convert to an organic acid, *e g* , acetic acid
- Should not cause deficits in battery performance

Some typical inhibitors are listed above in Table 6

Laboratory tests are needed, firstly, to determine whether the inhibitor is the correct choice for the particular production unit or factory, and, secondly, whenever a new inhibitor is being tested. Quality-control testing should be carried out continuously to ensure that deviations from prescribed procedures are not occurring. The two methods that are most commonly used are given in Table 7

Separator moisture

Most separators absorb moisture readily under high humidity conditions. Care should be taken with storage, and conditions should be such that humidity is below 30%

TABLE 7

Methods for testing oxidation inhibitors in dry-charged plates

Laboratory method	Water drop absorption method
1 Measure oxide content of plate	1 Place a drop of water on the negative plate and monitor the time taken for absorption
2 Expose plates to 80 °F/80% humidity in oven	● instant absorption — no protection
3 Measure oxide content over 8 weeks	● 5 - 10 min — low protection
4 Increase in oxide content 3% maximum	● 4 - 8 h — good protection

Some companies apply an ohmic resistance test on each group or element just prior to assembly of the battery cover. If a resistance of 50 000 Ω or more is obtained, the battery is considered satisfactory from the separator moisture point of view.

Oxygen content of drying medium

The oxygen content of an inert gas used in the negative drying process should be maintained below 0.2%. This usually requires the composition of the gas to be burnt to contain less than 1% oxygen.

Experience shows that platten dry-charging produces a negative plate with an oxide content in a very low range (*i.e.*, 2 - 4 wt %). On the other hand, gas-drying techniques usually yield plates whose oxide contents are somewhat higher and generally in the 5 - 10 wt % range.

Internal resistance of positive plate

Physico-chemical and electrochemical investigations have shown that the positive electrode is thermally damaged during the drying process. The effect of drying temperature on the internal resistance of the positive plate has been recognised for some time. Badger [2] has discussed the effect of internal resistance on battery performance, and the change in internal resistance with increase in the process temperature has been reported by Tiegel [1]. The latter's findings are reproduced in Fig. 7. Here, curve (A) represents the change in resistance with temperature of drying for well-washed plates, and curve (B) represents the change for plates after only rinsing off the acid instead of a good washing. The data show that the temperature of drying ovens must be limited so that a maximum plate surface temperature of 180 °F (82 °C) is obtained.

Anastasijević *et al.* [3] have discussed changes in the structure of the active mass and in the composition of the passivating layers during drying. Except for very short drying periods (exposure to heating < 4 min), thermo-passivation resulting from the changes occurs at temperatures lower than 180 °F (82 °C) and is dependent on exposure time.

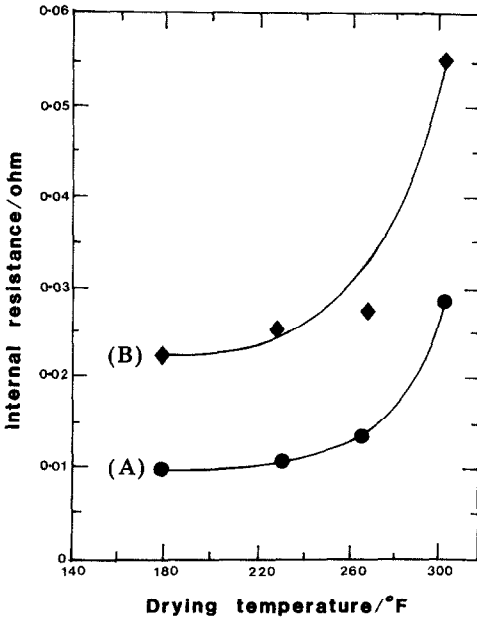


Fig 7 Internal resistance of dry-charged batteries as a function of plate drying temperature [1]

When drying temperatures are not extreme, the resultant thermopassivation has little effect on cell potential when the battery is discharged at moderate temperatures (15 - 25 °C). The effects increase, however, with decrease in the discharge temperature, and when combined with errors in washing procedures. It has been shown that there is at least 600 mV difference in electrode potential between cells discharged at 20 °C and -18 °C.

It should be noted that the thermopassivation decreases with increasing soak time in the electrolyte prior to discharge, and although the initial battery performance is poor, the thermopassivation and the structural changes mentioned above disappear on recharging.

Care must be taken in washing positive plates. The final washing water should have a pH between 4 and 5. Underwashing (*i.e.*, pH < 4) causes an increase in electrical resistance, a short-circuit element is formed between the grid and the active mass with the formation of lead sulphate in the region. Note, this can also occur if plates are left to stand in formation electrolyte on open circuit prior to washing. Overwashing (*i.e.*, pH > 5) leads to a situation where the positive plates take up CO₂ from the air to form basic lead carbonates. This occurs more quickly at elevated temperatures such as those found in positive storage ovens (> 40 °C).

Conclusions

With the availability of maintenance-free and very low maintenance batteries, it is no longer necessary from a product storage point of view to

produce dry-charged batteries. The process is also expensive and labour intensive. Where markets demand dry-charged batteries, however, the manufacturer has very little choice but to produce such units

For good product reliability, stringent quality control is required: not only during the process itself, but also during component storage, battery assembly, and battery distribution and storage. The techniques discussed in this paper assist manufacturers to limit the effect of deviations caused by machine problems, operator failings, and environmental conditions.

References

- 1 E G Tiegel, *LEAD 68, Edited Proc 3rd Int Conf on Lead, Venice*, Pergamon Press, Oxford, 1969, p 191
- 2 J P Badger, *Proc SAE Meeting, Detroit, MI, June 6, 1966*
- 3 N Anastasijević, J Garche and K Wiesener, *J Power Sources*, 7 (1982) 201