# DEVELOPMENTS IN STATIONARY MAINTENANCE-FREE LEAD/ACID BATTERIES

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## Introduction

The development of maintenance-free lead/acid batteries in West Germany started about 1955. At that time, the batteries were mainly required for portable instruments such as radios, tape recorders, medical instruments, photoflash equipment, etc

The first step towards a fully maintenance-free battery was the semi-maintenance-free system shown in Fig. 1. This battery was developed from a motorcycle type and was equipped with an acid-density indicator consisting of three balls with different specific weights. Because of the value of such a device, the battery is still being manufactured today, albeit in small numbers

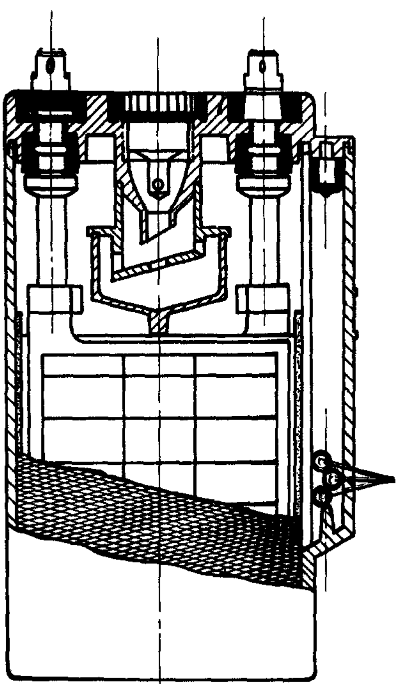

Fig 1 Design of semi-maintenance-free lead/acid cell

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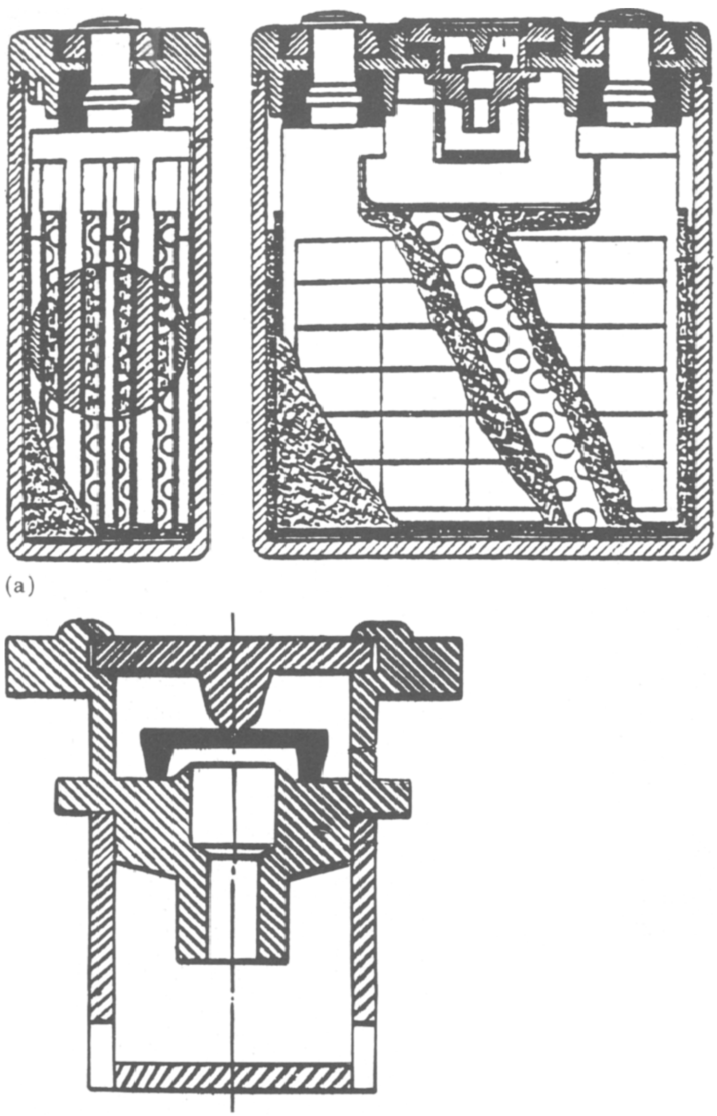


Fig 2 Design of (a) gelled-electrolyte lead/acid cell, (b) vent plug

The electrolyte is not immobilized, a labyrinth system in the top of the container prevents acid leakage through the cell plug when the battery is placed on its side or upside down The batteries are constructed with antimony-free grids when the end-application involves little service from the battery, antimony alloys are used when more frequent operation is anticipated, *e g* , in press-reporters' cameras

## Batteries with gelled electrolytes

*Cell design*

The successful step towards a totally maintenance-free battery has involved the development of a gelled electrolyte type with lead–calcium grids, *i e* , the acid is immobilized in silicic acid to give a thixotropic gel (Fig 2(a)) In this design, each cell is fitted with a vent plug (Fig. 2(b)) to allow the escape of pressure that may build up inside the cell either during operation under high ambient temperatures or during overcharging periods After the pressure has been released, a rubber diaphragm in the vent plug prevents atmospheric air from entering the cell. Apart from being completely maintenance-free, the battery has a very low rate of self-discharge. For example, the self-discharge at 20 °C is about 50% in 17 months (Fig. 3). The battery is also deep-discharge protected, *e g*, after standing with the appliance switched on for about 4 weeks, the battery will recover 100% of its capacity after only a couple of charge/discharge cycles

Normally, the substitution of lead–calcium for lead–antimony in the grid alloy results in a decrease in the cycling ability of lead/acid batteries At the time of the development of maintenance-free batteries for portable instruments, a very high cycle life was required. To obtain this characteristic, phosphoric acid was added to the electrolyte This resulted in a performance of about 200 cycles at 100% depth-of-discharge (DOD) and up to 10 000 cycles at more shallow DODs (Fig 4)

*Charging characteristics*

Maintenance-free lead/acid batteries are charged under constant voltage conditions in order to minimize the loss of water At an ambient temperature of 30 °C, the charging voltage must be maintained at 2.25 V/cell The

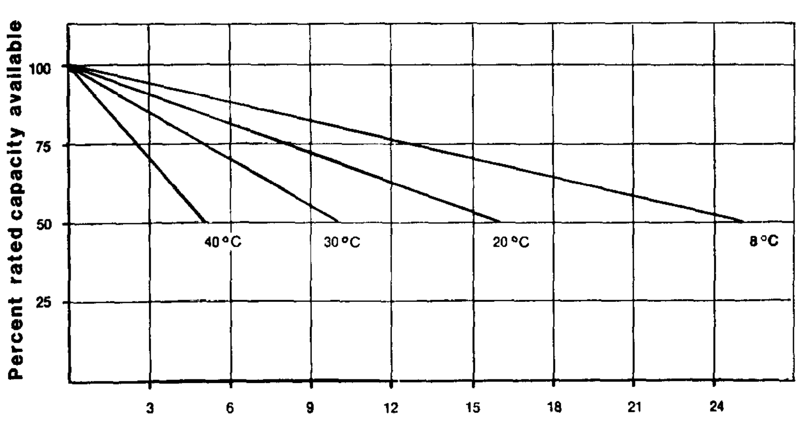


Fig 3 Self-discharge rate of gelled-electrolyte lead/acid battery at various ambient temperatures

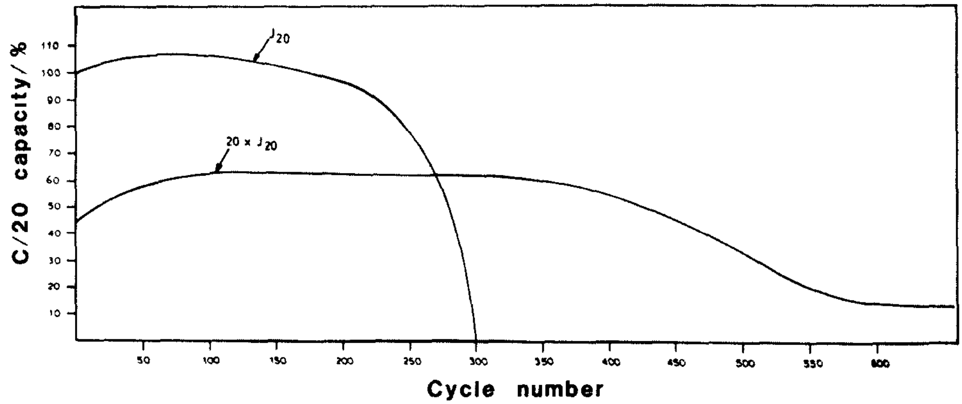


Fig 4 Cycle life of gelled-electrolyte lead/acid battery as a function of depth-of-discharge

charging current of gelled-electrolyte cells is not limited, the battery will accept about 500 mA per 1 A h capacity after complete discharge. During the charging process, the current will drop in relation to the state-of-recharge of the battery. This means that the charging current is regulated automatically by the battery, over-charging is not possible as long as the charging voltage is kept constant The charging voltage of 2 25 V/cell is sufficient to keep the battery fully charged and to recharge the battery, if necessary, in ambient temperatures between +10 °C and +45 °C When the temperature lies outside this range, the charging voltage should be altered accordingly (Fig 5)

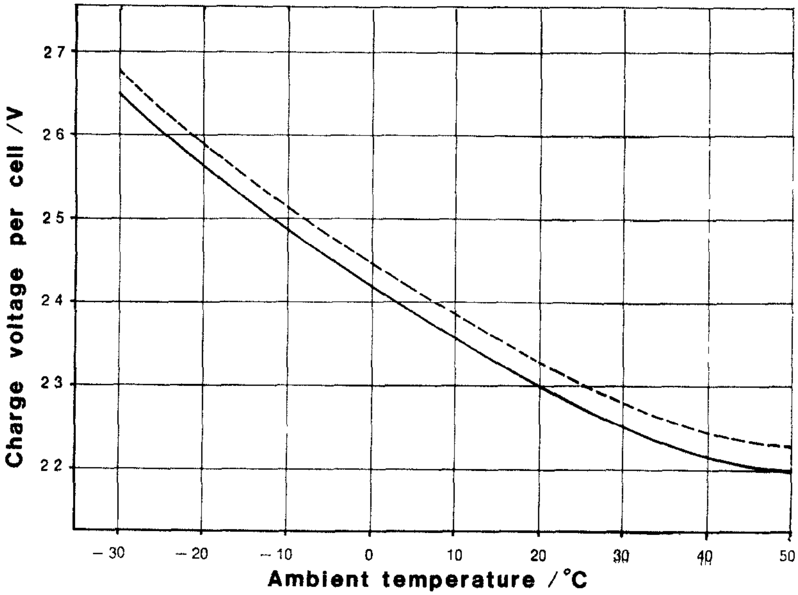


Fig 5 Top-of-charge voltage of gelled-electrolyte lead/acid battery as a function of ambient temperature

Irrespective of the design, all maintenance-free lead/acid batteries exhibit gas evolution after reaching a fully charged state. This gas is recombined to water inside the cell. In the case of gelled-electrolyte systems, the oxygen formed at the positive plates diffuses through the capillary network of the gel to the negatives where it reacts and is returned to the electrolyte as water (Fig. 6), *i e* ,

$$2Pb + H_2SO_4 + O_2 \longrightarrow 2PbSO_4 + 2H_2O$$

The lead sulphate so formed inactivates a small portion of the negative plate material However, because the cell is designed to have a surplus of this material, the battery capacity is unaffected by the water recombination process The overall result is that water loss is kept to a minimum and no additions are required during the entire service life of the battery

*Dryfit batteries*

The demand for maintenance-free lead/acid batteries has now changed from portable and cycling applications to standby power for UPS systems,

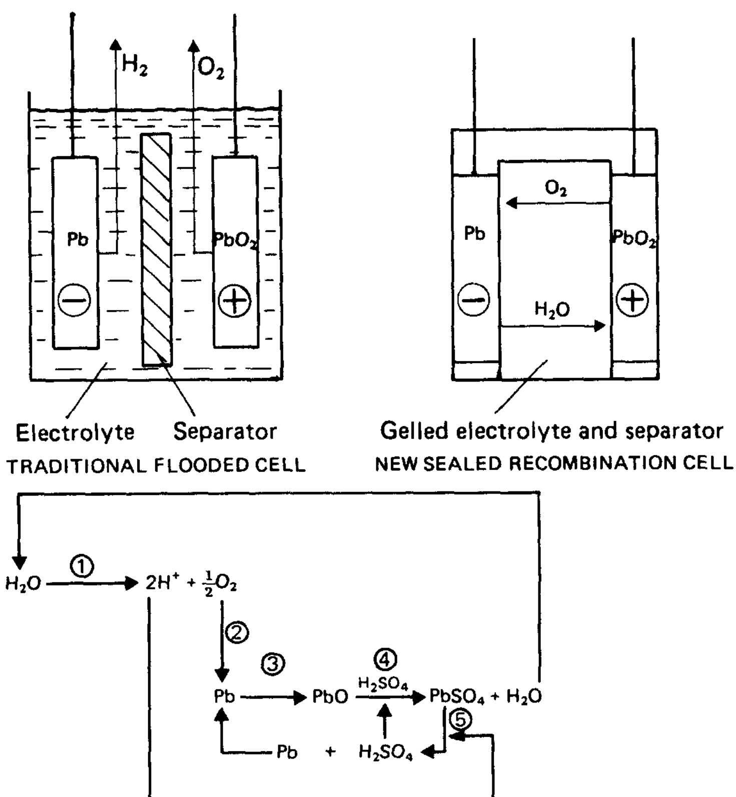


Fig 6 Schematic representation of oxygen recombination mechanism in gelled-electrolyte lead/acid cells

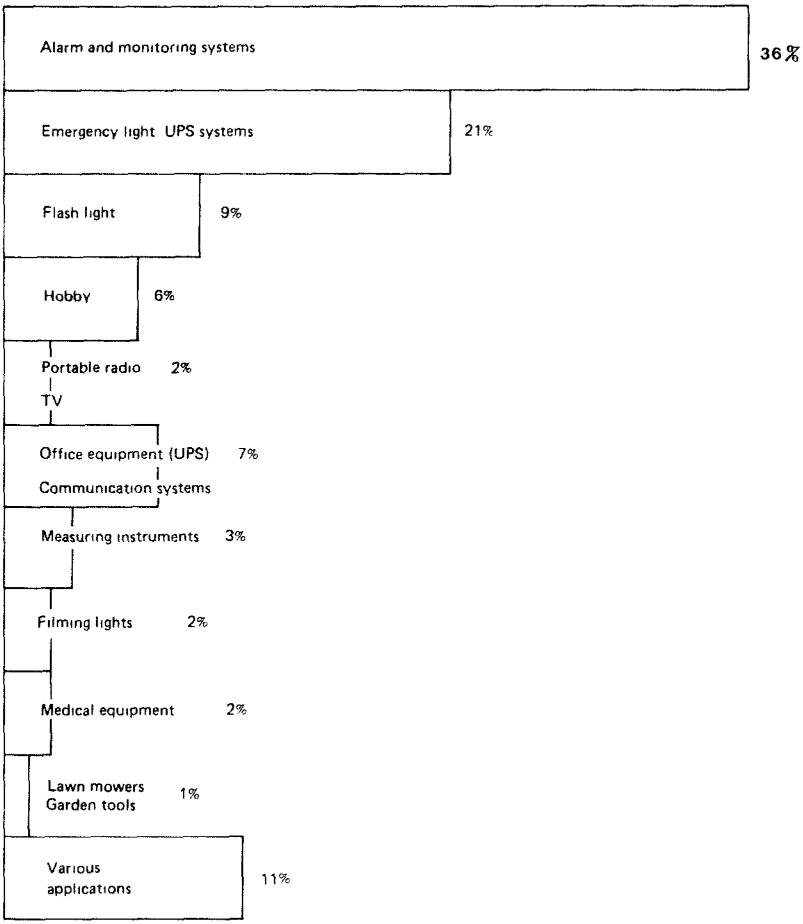


Fig 7 Demand for maintenance-free lead/acid batteries

alarm systems, emergency lighting, etc (Fig 7) Because of increasing labour costs, these batteries are becoming more and more in demand for industrial applications.

Gelled-electrolyte lead/acid batteries produced by the author's company (the "Dryfit" range) are available in 2 V cells from 200 to 1500 A h capacity ($C/10$ rate) and have lead–calcium tubular positive plates and gravity-cast, flat negatives. The cells are fitted with the vent plug described above (Fig 2(b)) The self-discharge rate of these batteries at 20 °C is approximately 50% of the nominal capacity in 25 months (Fig 8) The batteries are charged with a constant voltage, the charging current is regulated by the state-of-charge of the cell Neither equalizing charges nor initial charges are necessary because of the gel-structured electrolyte. The batteries are delivered filled and charged so that acid handling at the installation site is not required A further industrial type of battery (the "Dryfit Block") was introduced to the market about 6 years ago This model uses die-cast grids

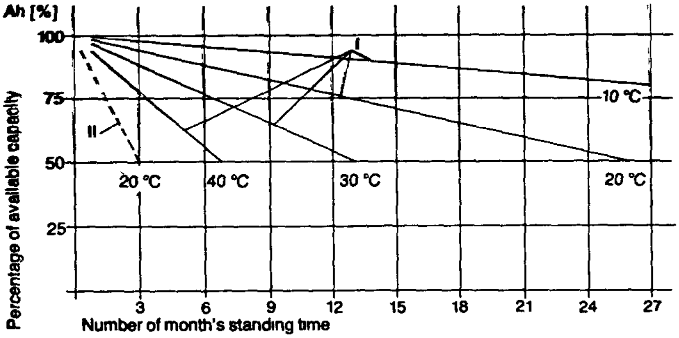


Fig 8 Self-discharge rate of Dryfit A 600 gelled-electrolyte battery (curves I) compared with that for a conventional lead–antimony battery (curves II) at various ambient temperatures

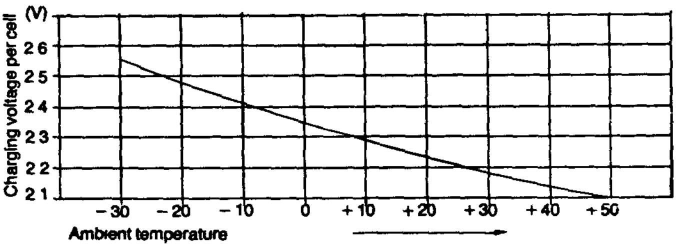


Fig 9 Constant charge voltage setting to achieve full charge condition of gelled-electrolyte battery at various ambient temperatures

for the positive plates and gravity-cast grids in the negatives. The battery has the same performance characteristics as the earlier gelled-electrolyte systems (Fig. 9).

The service lives of the Dryfit batteries vary with the choice of grid construction Those with gravity-cast positive and negative grids have a lifetime of 4 - 5 years, tubular plate industrial types give 15 years' service, whereas about 12 years of operation is obtained from industrial batteries with die-cast positives and gravity-cast negatives

Because of the high water recombination effect of each cell, gas development in industrial batteries is considerably reduced compared with conventional liquid-electrolyte cells (Table 1).

A cost comparison is given in Table 2 showing the clear economic advantages of the gelled-electrolyte, maintenance-free batteries.

Dryfit gelled-electrolyte batteries have now been accepted by some European and overseas institutes and organizations for various applications, *e g* , as an emergency power supply for medium- and low-voltage switching equipment in the Steag power station at Walsum, F R.G. A special version of the battery has been evolved from the tubular-plate industrial type for solar applications. Since this type of service requires the battery to deliver power each night, a very high cycling capability is essential. The current version is able to operate for 1500 cycles at 75% DOD and ~4500 cycles at 30% DOD Because the batteries use an excess of electrolyte with

TABLE 1

Development of hydrogen gas in Dryfit industrial batteries (version A 600) by comparison with flooded type OPzS cells
All values given are per 100 A h nominal capacity (10 h rate)

| Mode of operation | Battery | |
|---|---|---|
| | A 600 | OPzS |
| *Float-operation* (2 23 V/cell) | | |
| $H_2$ development | max 8 ml $H_2$ during 24 h | approx 100 ml $H_2$ during 24 h |
| Residual current | 10 - 15 mA | 25 - 30 mA |
| *C/10 - discharge* (end voltage 1 8 V/cell) | | |
| $H_2$ development | 20 - 70 ml $H_2$ in 10 h | 60 - 70 ml $H_2$ in 10 h |
| *Charge after C/10 discharge* | | |
| $I_{max}$ charging current = 40 A/100 A h | 90 ml $H_2$ during the first 24 h, then dropping to 8 ml $H_2$ in 24 h | 200 ml $H_2$ during the first 24 h then dropping down to 100 ml in 24 h |
| $U_1$ = 2 4 V (boost charge), $t$ = 5 min | | |
| $U_2$ = 2 23 V/cell | Maximum during the 2 h of charge = 19 ml $H_2$ $h^{-1}$ | Maximum during the 2 h of charge = 21 ml $H_2$ $h^{-1}$ |

TABLE 2

Cost comparison of conventional industrial batteries (OPzs and OGi) with Dryfit A 600 and Dryfit block batteries for a 1000 A h, 110 V system (55 cells)

| | Conventional type industrial batteries | Dryfit A 600 and Dryfit Block |
|---|---|---|
| Maintenance (labour) | 400 min/year (one service per year) | No cost |
| Installation cost | Same cost | Same cost |
| First charge | 4 Days | No need |
| Transportation | Same cost | Same cost |
| Transportation of acid | Approx DM 500 for packing plus transportation | No cost |
| Room equipment | Approx DM 200/$m^2$ | No cost |
| Room size | | 67% less than conventional |
| Room ventilation | | 75% less than conventional |
| Maintenance materials and tools | DM 110/year | No cost |

a low specific gravity, the self-discharge rate and corrosion processes are reduced In addition, the batteries may be overcharged during daily peak insolation periods

**Future developments**

There is a trend towards the use of die-cast grids in gelled-electrolyte batteries for industrial applications. This is because the technology of die-cast grids is well developed and is more economical than that of tubular counterparts However, the cycle life of such industrial batteries requires further improvement. This challenge is being taken up by manufacturers and it is anticipated that a solution to the cycle-life problem will be found so that the production of maintenance-free, flat-plate industrial batteries will outstrip that of other types.

Because of high environment pollution, it can be estimated that in the future, especially in countries with warm climates and a lot of sunshine, the use of battery-backed-up solar systems will increase. It is expected that maintenance-free batteries for solar service will be on the market by 1987

Finally, there will be an increasing demand for gelled-electrolyte batteries in emergency power systems (both small and large installations) for safety and protection requirements