

Technical Note

Aspects of lead/acid battery technology

4. Plate formation

L. Prout

Aydon Road, Corbridge, Northumberland NE45 5EN (UK)

(Received April 4, 1990)

Abstract

By design there is usually an excess of positive over negative material in plates. This compensates to an extent the lesser formation charge input required by positive and renders the mismatch when forming positive plate against negative plate of minor importance. Open tank and container formations are described and the dangers of incomplete formation when 'no-burn' connections are used. The mechanism of material conversation is illustrated from microsections taken from a traction negative. Variations of container formation to suit factory conditions are detailed and economies in electrolyte usage in open-tank formation. The benefit of rest periods during charge are examined particularly for traction. The drying of the positive plates after formation requires careful control; when used in dry-charged automotive batteries poor initial starting can occur if the drying temperature exceeds 70 °C and the moisture content is below 0.25 wt.%.

Background

Cured and dried active materials consist broadly of the following:

(i) positive: lead oxide, basic lead sulfates, lead and lead dioxide (as a component of red lead, when used);

(ii) negative: lead oxide, lead sulfates, lead, inorganic expanders, organic expanders and moisture inhibitors.

These active materials have to be converted mainly into lead dioxide in the positives and pure lead in the negatives. The process of formation is the electrochemical conversion of the constituents of the cured plates into the working materials of the positive and negative plates. The positive cured material is oxidized to lead dioxide by the transfer of sulfate ions to the electrolyte and the acceptance of oxygen from the negative material. Concurrently, sulfate ions are transferred from the negative cured material to the electrolyte and oxygen is transferred to the positive material.

The differing materials comprising the cured materials vary in the amount of electricity required to produce the system conversions. The following conversion factors are given in Table 1. Using these conversion factors, it is possible to calculate the theoretical minimum power input to form positive or negative cured materials. Whilst the theoretical power inputs are obviously not practical values on which to base a

TABLE 1

Conversion of cured-plate materials

Initial material	A h kg ⁻¹ needed to convert to	
	Positive PbO ₂	Negative Pb
Lead (Pb)	514	0
Lead oxide (PbO)	240	240
Lead sulfate (PbSO ₄)	176	176
Red lead (Pb ₃ O ₄)	156	313

formation input schedule, they do indicate what cannot be done. (Note, short cuts have often been considered when needs have been pressing and it has been difficult to convince executives that these are a guaranteed path to trouble.)

Take the case of a high-capacity positive paste formed from the mixing of a blended powder of 70 wt.% mill oxide (30 wt.% Pb) and 30 wt.% red lead with 110 l per tonne (110 l t⁻¹) of water and 52 l t⁻¹ of a 50 wt.% aqueous solution of sulfuric acid after subtracting the water loss in the paste-mixing process. The initial dry ingredients will consist of:

PbO	490 kg
Pb	210 kg
Pb ₃ O ₄	300 kg

Assume that in the paste mixing, the PbO is converted to PbSO₄. Now, 1 l of 50 wt.% H₂SO₄ will react with 1.593 kg of PbO to produce 2.164 kg of PbSO₄ and 0.829 l of H₂O. The effect of this will be to produce a wet paste broadly consisting of the following:

PbO	407.16 kg	
PbSO ₄	112.53 kg	
Pb ₃ O ₄	300.00 kg	
Pb	210.00 kg	
H ₂ O	153.11 kg	Total weight = 1182.80 kg

During the curing process, assume that the humidity and temperature control will allow the free lead to be reduced to 3% of total dry powder weight. This will involve the oxidation of (0.97 × 210) kg of Pb to PbO, i.e., 203.7 kg of Pb. This leaves 6.3 kg of Pb unreacted. The amount of PbO produced will be 223/207 × 203.7 kg i.e., 219.44 kg of PbO.

In the curing process, the water content of the wet paste will be evaporated, or used up, in the free-lead oxidation or will combine with the lead sulfate to form the tribasic lead sulfate, 3PbO · PbSO₄ · H₂O.

The cured plate will contain the following:

PbO	626.60 kg	
PbSO ₄	112.53 kg	
Pb ₃ O ₄	300.00 kg	
Pb	6.30 kg	Total weight = 1045.43 kg

TABLE 2
Design parameters for plate formation

Battery type	Specific formed weight ($\text{g A}^{-1} \text{h}^{-1}$)	
	Positive	Negative
Automotive	7.5 to 9	4.5 to 6
Traction		
flat plates	14.5 to 16	11.5 to 12.5
tubular plates	13.5 to 14.5	

On the basis of this solids distribution, the theoretical minimum ampere-hour input needed to convert the material into lead dioxide will be:

$$\text{PbO to PbO}_2 = 626.60 \times 240 \text{ A h} = 150384 \text{ A h}$$

$$\text{PbSO}_4 \text{ to PbO}_2 = 112.53 \times 176 \text{ A h} = 19805 \text{ A h}$$

$$\text{Pb}_3\text{O}_4 \text{ to PbO}_2 = 300.00 \times 156 \text{ A h} = 46800 \text{ A h}$$

$$\text{Pb to PbO}_2 = 6.30 \times 514 \text{ A h} = 3232 \text{ A h}$$

$$\text{Total} = 220221 \text{ A h}$$

Based on 1182.8 kg of wet paste, this gives a theoretical minimum formation input of $186.2 \text{ A h kg}^{-1}$ of wet paste.

For comparison, take a simple matching negative paste comprising 1 t of similar mill oxide (30 wt.% Pb) and 7 kg of expanders with 100 l of H_2O and 60 l of 50 wt.% H_2SO_4 after subtracting the water loss during mixing. With the same assumptions, this will require a theoretical input of 243150 A h for 1191 kg of wet paste, i.e., $204.2 \text{ A h kg}^{-1}$ of wet negative paste. These values will vary with the paste formulation.

The pattern of a greater formation input for negative material conversion than for positive can give rise to an imbalance when forming positive plates against negatives if the criterion of completion of formation is based on the positive conversion. In most designs, however, there is an appreciable excess of positive material over negative material. Typical design parameters common to the industry are summarized in Table 2.

In most automotive designs, there is ~30% more positive than negative material; in traction cells, this is nearer 25% for flat-plate designs and 20% for tubular designs. This tends to compensate for the differences in formation inputs required by the cured materials per unit wet paste weight, although it is still not uncommon for one type of plate to reach the fully formed condition before the other, and for an appreciable degree of electrolysis and loss of water to occur.

Formation systems

Two main formation systems are in general use: (i) open tank, (ii) container formation. In tank formation, positive and negative plates are mounted in vats in convenient numbers; positives are interleaved with negatives. All the plates of the same polarity are connected in parallel in each vat and the vats are connected in series up to the maximum number that can be accepted across the mains supply voltage. It is common to allow a nominal 3 V per vat so that if the supply was 120 V d.c., there would be 40 vats connected in series. By allowing 3 V per vat, the

formed plate voltages can rise to 2.7 to 2.8 V and there will still be sufficient excess voltage to make current control easy.

No firm rule governs the maximum number of plates that can effectively be connected in parallel in a single vat. Nevertheless, the greater the number of plates, the more difficult it becomes to ensure that the current entering the vat is equally shared between the pairs of plates. Wherever the numbers of plates in parallel exceeds about 20, the unequal sharing of the current becomes sufficient of a problem to demand attention. The usual remedy is to make several connections from the mains supply spaced along the paralleling system that connects plates of the same polarity.

The original practice in mounting plates in a vat was to tack burn, or fuse, a lead strip to the lugs of each plate of the same polarity. This is both time consuming and a health hazard. In addition, when the plates were formed, the tack-burn had to be broken and, often, a trimming operation was needed to remove the scar left behind. In formation, no oxidation or poorly conducting material film is produced at the negative; in fact the formation reaction product is pure lead. This makes it possible for the tack-burn to be dispensed with at the negative and physical contact between the plates and a negative feed bar exploited. Most manufacturers drop the negative plates, lug downwards, between slots in loose boards at the side of the vats (or moulded integrally into the side of the vats) on to a relatively massive lead bar near the bottom of the vat. The combination of the weight of the grid and a settling tap is generally sufficient to make an acceptable electrical contact with the bottom bar. The latter is connected permanently to the negative supply.

Attempts have been made to repeat this 'no-burn' procedure with positive plates, results have been variable. Whilst the positive bottom bar connection is clean, the formation current flows readily across the physical contact between plate and the bar. During formation, not only the positive cured material is converted to lead dioxide but also the grid and the bottom bar surfaces and contact. This lowers the conductivity of the physical contact and has the effect of varying the current through individual plates in the parallel groups. In between formation cycles, there is a tendency for some of the lead dioxide on the bottom bar to sulfate and to reduce sharply the surface conductivity (note, lead sulfate is a nonconductor). The overall conversion efficiency falls and the proportion of poorly formed plates in a vat increases. Reversal of the positions of the positive and negative plates in the formation vats and the direction of the current every formation cycle reduces the oxide on the positive bottom bar to lead and improves the situation, but not always to such an extent that no further action is needed. To ensure a high level of effective formation, the bottom bars should be shaped so that as the plates are tapped into position they meet a shallow taper and bite into the connector bar, this slight sideways movement breaks through the lead dioxide film and brings the side of the plate lug into direct contact with the lead metal of the bottom bar.

The shape of the bottom bar is much dependent on the size and thickness of the plate lugs. With very thin plates, too shallow an angle on the bar tends to cause the lugs to turn and distort and the plates to buckle. Too great a taper bends the lugs at the plate root. The most effective angle is obtained by experimentation with the type of plate mix for which the formation vats will be regularly used.

The discipline required when operating a 'no-burn' or 'tackless connection' formation system needs to be strict and vats must be cleared frequently of silted material. With these safeguards, the system can and is operated very effectively in many firms. Where the essential strict shop-floor discipline cannot be guaranteed, it is prudent to revert to fused or 'burnt' connections on all positive plates.

The spacing of plates in a vat is usually between 0.75 and 1 cm. This wide spacing allows evolved gases to escape readily, so minimizing gas polarization losses, and the relatively large mass of electrolyte per kg of cured material provides a sink to absorb heat developed during the electrochemical conversion process. The latter permits formation to be performed at relatively high-current densities and the full conversion to be completed within 24 h or less. Even so, the efficiency of conversion is only of the order of 55 to 60%, based on positive wet-paste weights.

With spacings between plates of 0.75 to 1 cm, satisfactory formation can be obtained using a conversion factor of 325 A h kg^{-1} of wet paste (positive). As the spacing between plates is reduced, so the ease with which evolved gases can be cleared is reduced and the amount of electrolyte that is available to absorb the heat generated is decreased. The temperature rise increases for the same current density or duration of formation and, in practice, the current density has to be reduced to keep the maximum temperature within sensible limits; this increases the duration of the formation cycle. The efficiency of conversion decreases with plate spacing so that in the case of container formation, where there is little freedom for evolved gases to escape and the volume of electrolyte is as low as 10 cm^3 per A h of capacity, the efficiency falls to between 33 and 45%.

In container formation, the cured plates are assembled into cells and batteries and then formed within the confines of the cell containers. The main reasons for container formation are: (i) reduced process cost, and (ii) less lead-in-air problems. Generally, tank-formed plates are used in the production of dry-charged batteries where, in addition to the cost of formation, there is the added cost of dry-charging the negative plates. These batteries are stored dry and are activated when required by the simple action of filling with electrolyte. Where the market will accept filled and charged batteries, there is no need to incur the extra costs arising from dry-charging. The handling of cured plates is less of a lead dust hazard than formed plates, particularly positives where the particle-to-particle cementation in the formed material is appreciably weaker than in the cured, but unformed, material. In the latter, the bonds are at their strongest due to the presence of the interlacing needle-shaped crystals of basic lead sulfate.

Automotive batteries destined for initial equipment are invariably container formed, whilst those for the replacement market tended, before the advent of maintenance-free batteries, to be dry charged.

Two systems of container formation are currently used; (i) two-step formation, and (ii) one-shot formation. The two-step method is based on the greater efficiency that arises from the use of very weak electrolyte. The process requires the discarding of the electrolyte when the formation is complete and its replacement by stronger electrolyte that, after a further period of charging, attains the working concentration of the fully charged battery.

The one-shot method is designed to avoid the messy discarding of the initial electrolyte and its replacement by stronger electrolyte. Initially, the battery is filled with a stronger electrolyte of such a concentration that when the formation is complete, the final concentration is that of the fully charged battery. The concentration of the filling electrolyte is dictated by the amount of lead sulfate in the cured plates. The one-shot method tends to be less efficient than the two-step method. It requires a tighter control of the processing of the pastes and the subsequent curing to ensure a minimum variation in the sulfate contents of the plates and a balanced amount of lead sulfate between positive and negative cured materials.

Electrolyte concentration changes during formation

During formation, the concentration of the electrolyte increases due to the release of sulfate ions from both positive and negative cured materials.

Consider the case of a formation vat where the assembly of plates is such that there is about 2 l of 3 wt.% H₂SO₄ electrolyte per kg of wet-positive paste. Assume the cured materials conform to the proportions calculated earlier when determining the theoretical formation inputs, i.e.:

<u>Positive</u>		<u>Negative</u>	
PbO	626.6 kg	PbO	917.16 kg
PbSO ₄	112.53 kg	PbSO ₄	129.84 kg
Pb ₃ O ₄	300.00 kg	Pb	9.00 kg
Pb	6.30 kg	Expanders	7.00 kg
Wet-paste weight =	1182.8 kg	Wet-paste weight =	1191.00 kg

These are essentially traction paste-mixes. Further assume that they are used in flat-positive and -negative plates and that there is ~25% more positive material, by weight, than negative material. This would mean 1.25 kg of positive wet paste to 1 kg of negative paste.

The amount of SO₄, by weight, in the pastes would be given by:

$$\frac{96}{303} \times \frac{\text{weight PbSO}_4}{\text{weight wet paste}} \times 100\%$$

This gives 3 wt.% SO₄ from the positive and 3.45 wt.% from the negative paste, or 72.0 g. This is equivalent to 73.5 g H₂SO₄.

The concentration of H₂SO₄ in a 3 wt.% solution is 31 g l⁻¹. As a result of the formation, this will be increased by 73.5 g l⁻¹ to 104.5 g l⁻¹, and the volume of the electrolyte by 73.5/1.8305 cm³, i.e., 40 cm³. The resultant electrolyte concentration will be 104.5/1.04 g l⁻¹ and is equivalent to a change in the specific gravity from 1.020 to 1.062.

In order to maintain constant conditions for the formation process, this rise in the concentration of the electrolyte needs to be corrected by discarding a portion of the electrolyte and diluting the remainder to the original concentration. This produces a revenue loss and an environmental problem in disposing the discarded acid safely within required effluent contamination limits. Some manufacturers take advantage of the ability to form in electrolyte concentrations varying from 3 up to 20 wt.%. Taking full advantage of this range, a change in the amount of H₂SO₄ generated of 195 g l⁻¹ can be accepted before any electrolyte needs to be discarded. In the case of the example, it would mean that the electrolyte could be used for four formation cycles before being reduced by dilution to the original 3 wt.% level. There can be a build-up of antimony with successive formations, and some manufacturers have set an arbitrary limit of 30 ppm above which the electrolyte is completely discarded and replaced by a fresh amount.

It has to be recognized that the efficiency of the formation process decreases with each cycle when using the same electrolyte. An economic balance has to be made before adopting either the system in which the electrolyte is partially discarded and the remainder diluted before each cycle and that in which the same electrolyte is used several times over before discarding.

The adoption of repeated formations with the same electrolyte is more relevant to tank-formed automotive plates than traction plates. The latter are usually sulfated

or 'pickled' prior to formation to increase the amount of lead sulfate in the cured plate. With this process, it is not unusual for the amount of lead sulfate in traction plates to be increased to as much as double that in the cured and dried plate. There is more danger from antimony deposition with traction plates (and the consequences of that deposition on the cycle life more troublesome financially) than in the case of automotive plates. As a consequence, few of the manufacturers using tank formation for traction plates are willing to risk using the same electrolyte more than once. A compromise is often made where both automotive and traction plates are made in the same factory. The formation electrolyte after one cycle of traction formation is passed to automotive formation where it is used for two or three cycles depending on the rise in the acid or the antimony content, whichever reaches the specified limit first.

The choice of the initial concentration of the electrolyte is also a compromise. Generally, the lower the initial concentration, the shorter is the time to complete the formation, provided the period of immersion of the plates in the electrolyte is kept short. One factor favouring the lower concentration is the degree of sulfation due to the standing period in the electrolyte prior to current flowing. The difference in the amount of lead sulfate on the surface of the plates can be as much as five times between electrolytes of 1.020 and 1.250 sp. gr. With extended standing periods, the concentration of the electrolyte within the mass of the material can fall to that of water and the formation conversion of the inner material delayed until such time as acidic electrolyte diffuses inwards to the material. Whilst many firms would prefer to use an electrolyte as weak as 1.020 sp.gr., they have difficulty in mounting all the plates in the vats, filling with electrolyte and switching on the current in a sufficiently short time to avoid the delay in inner material conversion that arises from the complete loss of sulfate ions in that material. In these circumstances, a sp.gr. of 1.050, or slightly higher, is adopted.

Figure 1 illustrates the effect of the standing period before switching on the formation current when using an electrolyte concentration 1.020 sp.gr.

The effect of standing in electrolyte before the formation current is switched on becomes more significant in the case of container formation. This is because the volume of electrolyte per unit of active material is much less than that in tank formation, and low concentrations of electrolyte within the mass of the material occur earlier.

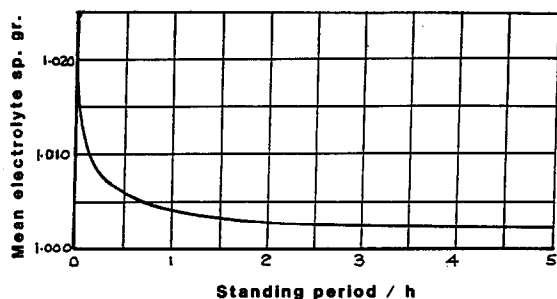


Fig. 1. Variation in mean electrolyte sp. gr. within the material of automotive plates standing in a formation vat containing 1.020 sp. gr. electrolyte.

Tank-formation procedure

Plates allocated to formation should have had their full curing period and should show a very low free-lead content, 4 wt.% or less. Free lead in incompletely cured negative plates will be untouched by the formation process and will remain as metallic lead particles. As the percentage of free lead in a plate leaving the flash-dryer oven can be as high as 20% or more, the presence of lead of that magnitude can appreciably reduce the true active material developed surface area. This will show up as a reduced engine-starting capability in automotive batteries, and as reduced capacity in traction batteries.

A full circuit of series-connected vats should not contain plates of differing sizes since either the smaller-area/thickness plates are overformed to ensure that the larger-area/thickness plates are fully formed, or if the smaller plates receive their scheduled formation input the larger plates will be underformed. In an emergency, risks of this nature may have to be taken but, in such circumstances, the variation in the cured material weight over the whole range of plates in a circuit should not exceed 20% of the mean plate weight. The formation current is then set to fully form the largest plate in the circuit. The risk attached to this variable plate-formation arrangement lies in the 'puffing' of the negative material and the softening and loosening of the cementation bonds in the positive material.

Plates allocated to tank formation should be reasonably flat. Distorted plates should be flattened before mounting into the vats. This is necessary to prevent plates of opposite polarity from touching each other and, consequently, not being adequately formed.

The soaking time after the plates have been placed in the vats and the electrolyte has been introduced should not be prolonged. Rather, it should be just sufficient for the internal structure of the material to be thoroughly wetted. With too long a soaking time, the conductivity of the internal electrolyte and the sulfated material is reduced appreciably and considerable difficulty is experienced in obtaining the initial current setting. The time limitation for the soaking period depends to a great extent on the concentration of the electrolyte. Less time would be allowed for a 3% than for a 10% H₂SO₄ electrolyte. In the former, a typical maximum soak period would be 3 h, whilst with the stronger electrolyte up to 6 h can be tolerated. It is always helpful to control the soak period closely since variable periods show up as differences in the time required to ensure that all plates are fully formed. A variable proportion of incompletely formed plates in any formation cycle upsets the process schedule and the smooth running of the plant.

The routine starts with the insertion of positive and matching negative into adjacent slots in the formation vats. This procedure starts with a negative and finishes with a negative. Although the process is simple, it can introduce a health hazard where operators are dragging cured plates from a rack or pile and allowing the plates to rub against each other. Following such action, the insertion of the plates into the appropriate slots in the vats will create lead dust and this will rise to the operator's breathing zone. The hazard is amplified if the operator bends over the vat whilst loading in the plates. Several procedures can be adopted to minimize this lead-dust risk. Some firms arrange for the cured plates to be loaded externally into open-bottom, slotted crates under extract. When full, the crates are passed into the formation shop and then placed into filled vats. Other firms provide a moveable slot extractor that can be moved from vat to vat and create a high-velocity air extraction across the top of the vat away from the operator's breathing zone.

When the plates are all loaded into a vat, they should be tapped individually to ensure they are making good electrical contact with any bottom strip connections provided in lieu of burned connections.

Where no bottom paralleling connections are provided in each vat, both the positive and the negative groups of plates in each vat require to be individually connected in parallel by tack burning each plate lug to a pure lead bar. Lead alloy bars are not acceptable as often the bars are either below the level of the electrolyte or awash with electrolyte. As pure lead strip is extremely ductile it can be readily bent to fit more exactly the lugs. Further lead bars are burned to the paralleling bars to form the series connecting of consecutive vats; the negative connecting bar of the first vat and the positive connecting bar of the last vat are connected to the input terminals of the formation power supply. These latter connections should not contain joints, despite the fact that the distance may be troublesome to bridge with a single bar. Joints tend to be weak. In addition, sagging can occur and result in breakage. If this should happen, there is an explosion risk from the ignition of the hydrogen/oxygen mixture evolved during formation.

With a single connection to/from the supply, it is likely that the formation current will be shared unequally between parallel strings of vats. This can be checked with a 'tong-tester' type of ammeter by clipping the tongs of the ammeter around various connecting bars throughout the full arrangement of the vats. Unequal sharing of the current can be eased by using more than one bar per vat to connect plates of the same polarity to the next vat, and by spreading these bars apart so that they are burned to a different part of the group paralleling bar in the vat.

The tack burning of the paralleling bars to the plate lugs, in particular, introduces a lead-dust hazard. This can be minimized by adopting a stance, when burning, to one side of the paralleling bar with the blow torch directed away from the operator. When the operator happens to be short or cannot tack burn in any other way than right over the connections, it is advisable for the operator to wear an approved respirator.

After completion of the connections to the supply, the electrolyte levels in the vats should be checked and corrected, where necessary. The formation current can then be switched on.

Formation starts first at the contact surfaces between the grid and the active material since these are the points of maximum conductivity. Little passes beyond this interface initially because of the poor conductivity of lead sulfate but, as the material at the interface forms into lead and lead dioxide, respectively, so the conductivity of the material increases and the current feed spreads into the pellet of material. As the conductivity of the cured material and the electrolyte is initially low, it is not unusual for the voltage-current relationship to register a high value. Whereas 3 V per vat had been allowed when determining the supply voltage, this may not be sufficient to accept the high voltage-current ratio and the scheduled current may not be attained until some of the surface material has been converted. In the case of manual control of the current, this could mean that a lower current than scheduled has to be applied and, later, an increase made to compensate for this.

Care has to be taken with manual control to check the initial rise in the current. For example, if the current control has had to be set at its maximum value, the eventual stabilized current could exceed the specified value by an appreciable margin and cause an excessive gas evolution. The latter, in breaking through the surface of the material, can disturb the material sufficiently for it to puff and become dislodged from the plate. The gassing is usually greatest at the grid-material interface where it

erodes the material and produces a series of cracks around the periphery of the pellet that reduce the physical locking of the material to the grid members.

With very high-current densities, the high rate of gas evolution creates a foaming action that can be particularly harmful with thin automotive plates.

As the formation proceeds, the voltage falls. This indicates a progressive improvement in the material conductivity as well as the electrolyte conductivity. The behaviour continues until the material immediately in contact with the grid structure has been converted and the electrolyte concentration in that area has risen. Diffusion inwards into the mass of the material commences and the electrode potential rises. This continues steadily as the conversion of the material proceeds inwards to the centre of the material pellets. There comes a time when the movement of the gas bubbles outwards restricts the diffusion of electrolyte inwards; this is aggravated by the tendency for electrolysis to occur in the immediate vicinity of the material that has already been converted. It is helpful at this stage to switch off the formation current to allow the higher concentration electrolyte to diffuse inwards. The rest period also allows both the plates and electrolyte to cool. The negative plates are less affected by the gassing due to the denser nature of the converted material; the density of the positives does not change significantly. Lack of a rest period shows up as a softening of the material around the edges of the pellets and often is more noticeable in thick plates. Some operators recommend two rest periods with thick traction plates in tank formation; the first approximately midway in time in the main voltage rise portion of the voltage-time characteristic; the second when the voltage is exhibiting signs of stabilizing. The second rest period coincides with the occurrence of a marked decrease in the conversion efficiency.

Where two rest periods are adopted, it is common practice to lower the formation current density to reduce the amount of gas evolved in the final stage when the efficiency of power usage is low. This practice causes a minimum of material damage, particularly around the periphery of individual pellets.

The choice of current density is dictated by the surface area of the plates that is exposed to the electrolyte. The duration of the formation depends on the weight and thickness of the material in a plate. Automotive plates of 1.5 to 2.5 mm thickness can satisfactorily be formed in 18 to 20 h, including a rest period. Thicker traction plates may require more than 50 h.

Where two rest periods are used, a good arrangement is for the three formation stages to be with the currents in the ratio of 1:0.75:0.5. Where a constant formation current is used throughout, typical current densities, based on the geometric plate area, are from 2 to 5 mA cm⁻² of total area exposed to the electrolyte, i.e., both sides of a plate. Take, for example, an automotive plate measuring 11.4 cm × 11.4 cm, the surface area exposed to the electrolyte will be 260 cm². The range of acceptable formation currents will be from 520 to 1300 mA per plate. If double-plate castings are to be formed, the individual current per casting will be twice the above. The precise value will be related to the time available for the process.

A typical wet-paste weight for the above plate is 80 g for a thickness of 1.75 mm. In this case, experience shows that an adequate formation input is 320 A h per kg of wet paste. On this basis, if there are no complications such as a proportion of other size plates, the input per plate will be 80 g/1000 g × 320 A h, i.e., 25.6 A h.

If a constant formation current is adopted over a period of 18 h, excluding rest periods, the formation current will be 1.42 A per plate. If two rest periods are adopted with the current progressively decreasing in the ratio 1:0.75:0.5, using a time pattern of charge: 10 h charge/2 h rest/4 h charge at 0.75 rate/2 h rest/4 h charge at 0.5 rate,

the average charge rate would be equivalent to a constant-current charge for 15 h. For the example quoted earlier that requires 25.6 A h/plate, the new formation rates would be 1.7 A for 10 h, 1.3 A for 4 h, and 0.85 A for 4 h.

The above empirical approach gives good practical values for most automotive plates, but some care should be exercised when forming high-performance plates of high porosity. Typical instances are when the wet-paste density has been deliberately reduced to the region of 4 g cm^{-3} (66 g in^{-3}), and below. Unless these plates are reinforced with binders such as plastic or glass filaments or materials such as carboxymethylcellulose, they may suffer from an excessive shedding due to the inherent weaker cementation of the material. In such circumstances, it is prudent to err on the side of even lower formation currents than previously quoted. When tank formed, these pastes tend to suffer from surface erosion, blistering and loosening pellets. They lend themselves better to container-formation systems.

The completion of formation is indicated by:

(i) the disappearance of white patches on the surface of the plates and the development of a uniform colour overall;

(ii) all plates are gassing to the same degree, and

(iii) the voltages across each vat in a series-connected circuit are roughly the same, as are the voltages of the negatives measured against an independent electrode, such as a cadmium electrode.

It is inadequate to check on only one of these three features since this can lead to misjudgements of the completion of formation and a proportion of the plates being underformed. The result of incorporating these underformed plates into a battery is a poor initial performance, particularly for engine starting. The reliance on voltage measurements only can be misleading as the voltages change very slowly near the completion of formation and, moreover, are temperature sensitive.

In practice, it is usually safer to measure the power input and then check the plates after the full input has been confirmed. At this point, the surfaces of both positive and negative plates should be an even colour overall and be devoid of significant white discolouration that would indicate the presence of unconverted lead sulfate. Whilst it would be preferable to reject any plates with white discolouration this is liable to necessitate the reforming of quantities of plates with consequent upsetting of the smooth running of the total manufacturing process for dubious excellence. As a guide, if the amount of white discolouration is less than 10% of the plate surface, and is not continuous but is present as a fine surface film only, the degree of underforming can be accepted. The depth of the discolouration can be assessed by running a fingernail across the surface; if the discolouration is only on the surface it will be removed where the fingernail has passed. If it resists simple dislodging or is clearly more than just a surface film, the plates should either be put back for further formation or collected until there are sufficient numbers for a complete circuit and then reformed. The latter usually leads to a more disciplined routine for formation and there is less disturbance in productivity.

During formation, the temperature will rise in both the material and the electrolyte; the extent of the rise will depend on the formation current density (based on geometric area) and the volume of electrolyte. Generally, temperatures in excess of $60 \text{ }^\circ\text{C}$ should be avoided. If the temperature should exceed this value, it is prudent to reduce the current to allow the temperature to fall well below the limit. Negative plates are claimed to give increased cold-start performances when formed below $40 \text{ }^\circ\text{C}$, whilst positives are improved when formed at $50 \text{ }^\circ\text{C}$. Lower temperatures call for lower formation current densities, but extend the duration of formation and reduce the

weekly throughput of batteries. Some compromise has to be made to maintain a good economy without too great a sacrifice in performance. Generally, this compromise lies in adjusting the current densities to achieve an operating temperature between 40 and 50 °C. Some heating is essential in the formation shop during the winter months to ensure a consistently good plate quality and performance. The above applies mainly to automotive plates that are tank formed. Traction plates do not have the same problem of having to maintain a consistently high cold-start performance, the criterion is mainly a good open texture with good capacity outputs. The traction positive benefits from formation at the higher end of the temperature range and formation rates should be calculated to give an operating temperature nearer 50 °C.

When formed negatives are removed from the vats, they are extremely active and hungry for atmospheric oxygen. Left out in the air, they will rapidly react with atmospheric oxygen and become very hot. In the early days of battery making, negatives were allowed to dry in air that was cooled to limit the rise in plate temperature. These plates, oxidized mainly to lead monoxide PbO , were known as 'long first charge' negatives since the first charge given to a complete battery incorporating them had to provide the same order of ampere-hour input as would be required to convert lead oxide to pure lead. It was not uncommon for the first charge of such batteries to exceed 100 h because of the poor heat dissipation of the battery. There is virtually no demand for air-dried negatives except, perhaps, in some traction cells where it is not convenient to container form before despatch from the works or to assemble with dry-charged negatives.

Where cells or batteries are required to be stocked for extended periods without any attention, or to be shipped overseas in a dry condition, dry-charged negatives are essential. In these circumstances, the negative plates when removed from the formation vats must be immersed immediately in water and kept there until required for the dry-charge process. This procedure retains the material in a fully formed condition. The water restricts access of atmospheric oxygen to the material and dilutes any formation electrolyte that is absorbed in the material.

Positive plates when removed from the formation vats are virtually fully oxidized and will not be affected adversely by exposure to the atmosphere other than to suffer a degree of drying. Preferably, the positive material should be washed to reduce the concentration of electrolyte absorbed in the material, but it is unnecessary to carry the washing to the extent that the sulfuric acid content is close to zero. The trouble arising from leaving electrolyte in the positive is that, after drying, the presence of sulfuric acid makes the material slightly hygroscopic. Such plates, when used with dry-charged negative plates, have a tendency to take up moisture from the surrounding atmosphere, to pass that moisture to the separators and, eventually, to the negative material. The oxygen present in the moisture causes the negative material to be partially discharged.

Some makers do not wash the positive plates at all after formation. Where the same electrolyte is used several times (as in some automotive-plate processing), the risk of subsequent discharge of the dry-charged negative material increases with each time the electrolyte is used. The danger to the storage quality of the dry-charged batteries in such cases can be high. A degree of positive-plate washing is recommended.

Although an excess of formation power input is adopted, there is a limit to the conversion of the cured material into the lead and lead dioxide of the fully converted materials. Typical conversion levels are given in Table 3.

The final conversion of the remaining $PbSO_4$ is a very slow process and would make the full conversion uneconomic. The presence of some $PbSO_4$ in the materials

TABLE 3
Levels (%) of formed plate materials

Theoretical input	Positive			Negative		
	α -PbO ₂	β -PbO ₂	PbSO ₄	Pb	PbO	PbSO ₄
P	30	45	14	82	8	10
1.5×P	31	54	4	90	6	4
2.0×P	31	55	1	91	6	3

TABLE 4
Influence of plate thickness on formation input per kg wet positive paste

Plate thickness (mm)	Formation input (A h kg ⁻¹)
1.15	300 to 310
2.0	325 to 330
3.0	350 to 360
4.5	380 to 400

after formation is accepted as normal and this is one factor causing the capacity of a cell to increase progressively during the initial stages of charge/discharge service.

Typical formation inputs and patterns

The thickness of automotive plates varies according to usage, from ~1.25 to 2.5 mm. The level of formation input is very much a matter of individual maker's choice and is based on experience. Nevertheless, there seems some agreement that different inputs should be used for different plate thicknesses. Typical inputs per kg of wet positive paste are given in Table 4. These will vary a little with change in the concentration of the filling electrolyte. The difference between using a 3 and 20 wt.% solution of H₂SO₄ can be as much as 10% more for the latter. It has been stated by some makers that the cyclic life of the plates will be improved by using a higher concentration electrolyte, but no data are readily available.

The duration of formation depends very much on whether a constant or decreasing formation current is adopted. Common durations for formation, ignoring rest periods, are given in Table 5.

The point at which a single rest period is introduced will be where the rate of change of voltage starts to decrease appreciably and therefore indicates that a significant degree of electrolysis is occurring. In practice, this occurs close to the point at which the theoretical formation input has been applied. For example, in the case of thin automotive plates where the positive material calls for, say, 210 A h kg⁻¹ and the scheduled input is 300 A h kg⁻¹, the rest period would be inserted after 13 h in a planned 20 h formation cycle. This is often taken as three-quarters of the way through the cycle. Where two rest periods are deemed to be of assistance, suitable positions are at 55% and 75% of the total duration. The duration of the rest periods should

TABLE 5

Influence of plate thickness on formation time

Plate thickness (mm)	Formation time (h)
1.5 to 2.0	18 to 24
2.5 to 3.0	24 to 32
3.5 to 4.5	35 to 50
5.0 to 6.0	50 to 70

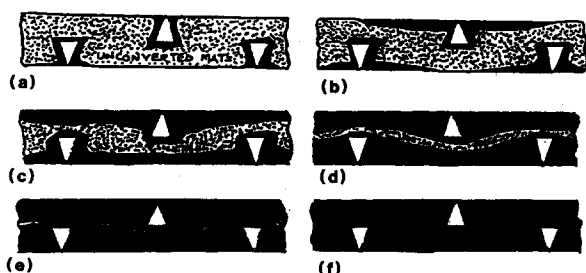


Fig. 2. Conversion stages in the tank formation of traction negative plates after: (a) 50, (b) 110, (c) 180, (d) 220, (e) 290, (f) 320 A h per kg of wet paste.

be sufficient to reduce noticeably the plate voltages and are typically about 10% of the charge duration.

Mechanism of active material conversion in tank formation

An examination of the cross section of plates at various stages during formation illustrates vividly the part played by the grid members and the surface of the active material. The manner in which a negative plate is converted from the cured state to pure lead is shown in Fig. 2 as a series of microsections of traction plates withdrawn at intervals during a tank formation.

It is generally accepted that the conversion of a pasted negative plate into a sponge of pure lead is essentially an electroplating process. The grid is the electrode and the lead component in the cured paste slowly dissolves in the electrolyte to provide divalent lead ions. The passage of the formation current causes these to deposit on the electrode and form crystals. As the overvoltage for the deposition of lead is low and as the concentration of lead ions in the cathode film is also low, the lead deposits as a porous sponge. The concentration of lead ions in the cathode film can be varied by changing the concentration of the electrolyte and/or the current density. This results in a corresponding change in the crystal structure of the deposited sponge. A higher concentration electrolyte and current density produces a finer grain deposit, and vice versa.

The sequence shown in Fig. 2 illustrates the deposition effect as the lead sponge grows in the two directions from the grid members across the material surface until adjacent centres of crystallization meet. At this stage, the growth of sponge lead

changes direction and proceeds toward the centre of the material mass. It is thought that organic expanders reduce the solubility of the lead ions in the electrolyte with the result that a finer grain lead sponge is formed with a greatly extended surface area. The effect of this is to reduce concentration polarization on discharge and increase the effective terminal voltage, particularly at engine-starting currents.

By changing the concentration of the electrolyte and the current density, the structure of a negative material can be modified from coarse dendritic to fine fibrous to fine granular. The former occurs with processing in very dilute electrolyte, particularly where the amounts of inorganic and organic expanders have been reduced. A fine fibrous structure arises when formation is conducted in 1.030 sp.gr. acid, whilst formation in 1.100 sp.gr. acid or higher produces a fine granular structure.

When viewed under a microscope practically all plates will show some metallic lead of a nonporous nature. This was present initially in the cured plate. The shape of the metallic lead is variable but the more common shape is long and sinuous.

A reduction in the size of the pellets reduces the time that is required for conversion of the surface material. In all other respects, the pattern of conversion remains substantially as described.

Formation of surface blisters

Negatives in tank formation are prone to develop surface blisters. These can now show up immediately after formation, or develop during early cycle life. They tend to be large as there is little support in the formation vats and there are deliberate additions of 'expanders' to the mix. Plates that have been sulfated or pickled before formation tend to blister more readily. The pickling process produces a layer of lead sulfate on the surface of the negative material which, with relatively high pickling solutions, can be as thick as 1 mm. The centre of the active material mass tends to be unaffected, particularly in thick traction plates. The sulfated layer has an increased volume compared with the original material, and this expansion tends to be accommodated by a decrease in the pore diameters rather than by an increase in the plate geometric volume. As a consequence, free access of the electrolyte to the material is denied and results in an increase in the true current density and early gassing, since the efficiency of conversion falls off as the true current density increases. The hydrogen produced occupies some 1200 times the volume of the water from which it has been produced. Thus, unless the texture of the material allows ready diffusion of the gas outwards, there will be an internal pressure build-up behind the sulfated/unsulfated material interface. This will force the sulfated layer outwards and cause a separation of the sulfated and unsulfated portions. In general, negatives should not be too highly sulfated or pickled, despite the temptation to do so because cracks in the material after drying are closed and pellet retention up to formation is greatly improved. It has been used as a palliative to compensate for poor curing or poor initial paste mixing, but is not a satisfactory answer to such processing weaknesses. The effect of extended standing in the formation acid before switching on the current is similar and, for this reason, the soaking time should be only as long as is necessary to wet the material thoroughly.

The above should not be confused with blistering produced by the action of the expanders in situations where the duration of the formation has had to be extended because of poor conductivity at the plate-to-vat connection. In such situations, which

should be rare in a properly controlled shop, it is better to reduce the formation rate and extend the time.

Blistering tends to be more prevalent where plates are pasted from each side, as on some 'beltless' pasting machines or double-hopper machines with automatic plate reversal in which the original underside of the plate is presented to a second pasting operation.

The appearance of blisters early in life usually results from a combination of material presulfation and a slack assembly of the tank-formed plates in a cell. It can also result from uneven dispersion of the expanders throughout the initial paste mix, coupled with a slack assembly.

Two-step container formation

In this system, the initial filling electrolyte has a low concentration and the amount of power input is sufficient to form the materials fully. The magnitude of the formation currents are calculated on the basis of the total positive surface area (both sides), and the duration of the process on the weight of wet-positive paste used in preparing the plates. In this respect, it is similar to tank formation routine.

When the formation is complete, the concentration of the final electrolyte is measured and the electrolyte then discarded. The battery is then refilled using a higher concentration electrolyte such that when the previously absorbed and the new electrolyte have thoroughly mixed together through the application of a short finishing charge, the final concentration of the electrolyte is that required for service use.

In order to arrive at an approximate value for the concentration of the refilling electrolyte, it is reasonable to assume that approximately half the total electrolyte in the battery has been discarded and that the remaining electrolyte is held absorbed within the active materials and the separators.

Take, for example, a battery initially filled with 3 wt.% sulfuric acid and finishing at 11 wt.% acid. Each litre of electrolyte will have 118 g of H_2SO_4 . In the discarded portion (when about half the electrolyte is lost) there will be left 0.5 l that contains 59 g H_2SO_4 . If it is required to finish with an electrolyte containing 37 wt.% H_2SO_4 (1.278 sp.gr. at 20 °C), the added 0.5 l of new electrolyte must have sufficient acid to bring the mixed electrolyte up to a concentration of $472 \text{ g l}^{-1} \text{H}_2\text{SO}_4$. The replacement electrolyte of 0.5 l must have 413 g H_2SO_4 . This calls for an electrolyte containing 826 g H_2SO_4 , i.e., 1.461 sp.gr. at 20 °C.

It is common for an electrolyte of 1.400 sp.gr. to be used as a standard and it is realistic to use this as the refilling electrolyte. The quantity added is adjusted to produce a convenient finishing concentration at the end of the first stage that is compatible with the use of the standard electrolyte for refilling.

Whilst it is convenient to assume that about half the total electrolyte is absorbed within the components, this assumption needs to be verified. Its values lies in the ease with which approximate values for the concentrations of the initial and refilling electrolytes can be derived and from which corrections can be readily made.

The disadvantage of the two-step system is the nuisance value of discarding the initial electrolyte and then refilling. The discarded electrolyte has to be disposed safely and cleanly, and the refilling operation is an added cost item. These limitations and the need to wash and dry the battery containers and covers before despatch has led to the use of the 'one-shot' system in some companies, although the latter system is by no means universal.

One-shot container formation

The objective in one-shot formation is to eliminate the discarding and refilling process, as well as the cleaning and drying of the containers and covers.

The concentration of the filling electrolyte is determined by the amount of basic sulfate species in the cured plates. Take, for example, a tubular positive traction cell in which the following processing parameters apply: specific formed positive weight $13.5 \text{ g A}^{-1} \text{ h}^{-1}$, specific formed negative weight $11.0 \text{ g A}^{-1} \text{ h}^{-1}$, and specific electrolyte volume $12.0 \text{ cm}^3 \text{ A}^{-1} \text{ h}^{-1}$.

Assume for the example that the plates have been subjected to a separate sulfation or pickling process that has converted all the PbO into PbSO_4 . If the original constitution of the positive filling powder is: PbO 64 wt.%, Pb 21 wt.%, and Pb_3O_4 15 wt.%, then the amount of SO_4 present in the sulfated plate is 22 wt.% and the PbSO_4 component will be 870 kg in an original 1000 kg of dry powder. This increases the powder weight to 1230 kg.

In the subsequent formation of the positive material, the reactions can be summarized as follows:



From these reactions and taking 1000 kg of original powder, the following apply:

(i) 210 kg Pb uses 36.5 l H_2O and produces 165.6 kg PbO_2 ;

(ii) 870 kg PbSO_4 uses 103.4 l H_2O and produces 686.2 kg PbO_2 and 281.4 kg H_2SO_4 ;

(iii) 150 kg Pb_3O_4 uses 8 l H_2O and produces 157 kg PbO_2 .

Overall, 1230 kg of sulfated powder (or 1000 kg of original powder) has produced 1009 kg PbO_2 and 281.4 kg H_2SO_4 , and breaks down 147.9 l H_2O in the process. This gives a conversion factor from formed positive weight to the original filling powder weight of 1000/1009 or 0.991.

Based on the design parameters of $13.5 \text{ g A}^{-1} \text{ h}^{-1}$ of formed material, 1 kg of the initial powder will produce: $\frac{0.991 \times 1000}{13.5} = 73.4 \text{ A h kg}^{-1}$. The weight of matching

negative material (formed) will then be given by $11.0/13.5 \times 1 = 0.815 \text{ kg}$.

Assume the negative material is the same as in an earlier example, i.e.:

PbO	917.91 kg
PbSO_4	129.84 kg
Pb	9.00 kg
Expanders	7.00 kg

These react in the following manner:

(i) 917.9 kg PbO reacts with the H_2 released from the positive reaction to produce 852.05 kg Pb and 73.4 l H_2O ;

(ii) 129.84 kg PbSO_4 produces 88.7 kg Pb and 41.7 kg H_2SO_4 to give a total of 956.75 kg of formed material produced from 1191 kg of wet paste with the release of 73.4 l H_2O and 41.7 kg H_2SO_4 . This gives a conversion factor from formed material to wet-paste weights of 1.244.

The weight of wet-negative paste matching 1 kg of positive filling powder is then 1.244×0.815 , i.e., 1.014 kg.

In the total formation reaction, the amount of working electrolyte will be 12×73.4 , i.e., 881 cm^3 per kg of filling powder. In this volume of electrolyte, if it is assumed that the concentration at the completion of formation is 37 wt.% H_2SO_4 at 20°C (1.277 sp.gr.), then the weight of H_2SO_4 will be $0.881 \times 473 = 417 \text{ g l}^{-1}$.

The weight of H_2SO_4 produced from 1 kg of positive filling powder is 281.4 g, and the weight of H_2SO_4 produced from 1.014 kg of matching wet-negative paste is 35.5 g. This gives a total weight of H_2SO_4 produced during the formation of 316.9 g, say 317 g. This leaves a deficit of $(417 - 317)\text{g}$, or 100 g, in 881 ml of electrolyte. This deficit has to be supplied from the initial or filling electrolyte.

The concentration of the filling electrolyte will be $100/0.881 \text{ g l}^{-1}$, i.e., 113.5 g l^{-1} , or 10.6 wt.% which is equivalent to a sp.gr. of 1.070 at 20°C .

In summary, for this hypothetical cell, the initial filling electrolyte will be 1.070 sp.gr. at 20°C , and this should give a finishing electrolyte of 1.277 sp.gr. at 20°C . In practice, there will be permissible manufacturing variations and this will result in a similar variation in the electrolyte density at the end of formation. Corrections will be needed to bring all cells within permissible limits of electrolyte concentration. Most operators find that it is both easier and quicker to have to correct upwards than to reduce the electrolyte concentration. The usual practice is to use a filling electrolyte concentration that is $\sim 2\%$ lower than the calculated value. It is also the aim to achieve the lower value of the permitted electrolyte concentration range so that in service any shortfall in formation, plus the effect of that portion of the lead sulfate content allowed to be unconverted by virtue of the economics of operation, will not produce a rise in the working concentration during service that will be sufficiently large to take the concentration above the maximum of the permitted range.

Voltage changes during container formation

Both automotive and traction cells behave similarly on one-shot container formation, except for the duration of the process—traction cells require a considerably longer time. The main reason for this is the lower ratio of total plate surface area to active material volume in traction cells. Nevertheless, the longer formation time of traction cells makes it easier to follow the voltage changes.

Initially, the cells behave as an impedance network with an equivalent circuit containing resistive, inductive and capacitive elements. There is very little effective cell EMF (electromotive force) particularly in the case of tubular positive cells with highly sulfated material. At a nominal formation current of $\sim C/12.5 \text{ A}$, where C is the rated capacity of the cell in A h, the voltage rises rapidly to well above 3 V and can approach 4 V. This rapidly decreases as electrochemical conversion occurs and the electrolyte concentration starts to rise and produces measurable electrode potentials at both positive and negative plates. As the formation proceeds and the lead sulfate present starts to be converted to lead and lead dioxide, the cell electrical impedance decreases and the electrode potentials (which determine the cell voltage) begin to assert themselves. The initial rate of fall of cell impedance is faster than the development of cell voltage and this shows up as a continued fall in the measured charging voltage. Thereafter, as appreciable proportions of the active materials are converted into increasing amounts of lead and lead dioxide, the electrode potentials predominate and the charging-cell voltage rises steadily and relatively slowly until the onset of significant gas evolution. At this stage, the cell voltage rises rapidly until about 60% of the formation has been completed. There now occurs a slowing down of the voltage

that leads to voltage stability. Examination of the plates at this stage shows that the materials of the plates are substantially lead and lead dioxide, respectively, but that the surfaces of the plates are still covered with lead sulfate. The formation efficiency falls due to gas polarization and because the lead/lead sulfate and lead dioxide/lead sulfate interfaces have moved away from the grid members towards the central area of the pellets of material, and thus increase the impedance presented to the passage of formation current.

In the case of traction cells, it has been customary to interpose a slow discharge (20 h rate, or thereabouts) to produce the maximum volume expansion of the active materials. This opens up the pores and assists the clearance of occluded gases from the interior of the materials and, thereby, makes space for the inward diffusion of electrolyte.

In the earlier days of traction cell manufacture, it was the policy to produce relatively dense pastes and to use the deep formation discharge to open up the materials after they had been supported by the separators in the element assembly. The effect of this was to cause the active material of the negative, in particular, to expand and conform closely to the separator profile. At the same time, the density of the material was lowered. The advantage of this expedient was to change the gassing pattern, from that of gas escaping between the negative plate and the adjacent separator face to the outside, to that where the gases pass through the porous structure of the separator in exceedingly fine bubbles to emerge adjacent to the positive material. This serves to stir up the electrolyte at the positive and to assist the irrigation of the positive material with fresh electrolyte. Modern pastes do not need this treatment, particularly with the availability of purer and more active organic expanders and, often, it is sufficient to insert only a rest period to allow the occluded gases to escape of their own volition.

There are limitations with using only a rest period, as permissible variations in paste mixing (manufacturing tolerances) produce variations in the pore structure of the cured materials and, subsequently, the rate of release of gases from the materials during formation. As a result, the cells in a single circuit tend to be uneven in completeness of formation. A limited discharge in place of the rest period, considerably less than the older deep discharge, produces a more even formation throughout a circuit of cells. This limited discharge need not be greater than 30 to 50% of the rated capacity. Nevertheless, the decision whether or not to use a rest period or a limited discharge is an economic one; more elaborate equipment is required for the latter with greater risk of faults in operation. In deciding this, a major factor is the number of adjustments requested by the customers during the early months of the battery life that can be attributed to the presence of individual cell differences in a series-connected assembly.

The order of changes taking place in a cell, as indicated by the variations in the voltages of the positive and negative materials (measured against a cadmium electrode) are shown in Fig. 3. Shop-floor checks are usually limited to the negative plates since these tend to lag behind the positives, particularly where, by design, an ample excess of negative material has been provided to safeguard against gross abuse in service. The negative-to-cadmium voltage should change from positive to negative at about the same time as the overall charging voltage starts to rise at a more rapid rate. Failure for the negative-to-cadmium voltage to change polarity, or 'to turn' at the normal time, calls for an examination of pasting and curing procedures. This is necessary since deviations from specifications in these latter areas not only upset the formation routine but promise possible further trouble later in service.

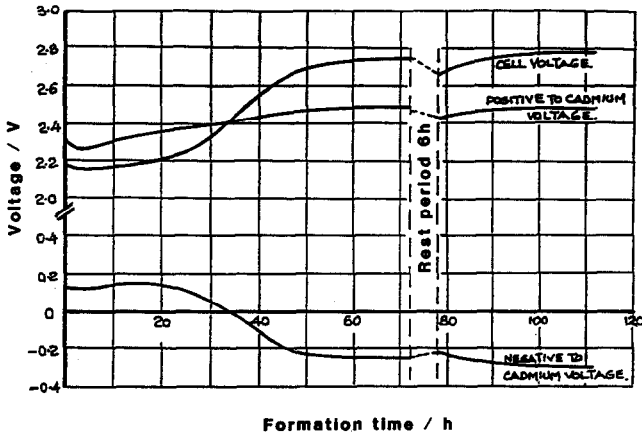


Fig. 3. Voltage changes during a nominal 96 h container formation of a typical traction cell.

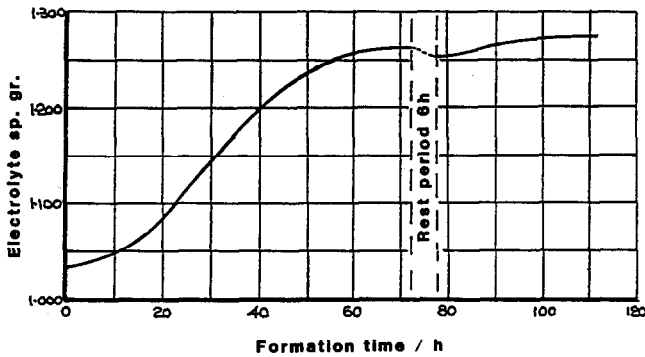


Fig. 4. Change of electrolyte concentration during container formation of a typical traction cell.

The other indicator of normality in formation is the pattern of change in the concentration of the electrolyte. Figure 4 is typical for a traction formation cycle where there has been a rest period at about three-quarters through the cycle. The completion of formation is accompanied by a constancy of electrolyte concentration similar to that indicating the condition of full charge following a discharge.

During the rest period, the magnitude of the fall in the specific gravity (or concentration) of the electrolyte is a measure of the completeness of free-lead oxidation in the positive during curing. Where decrease in the free-lead content has been halted, usually by premature drying, the remaining lead tends to react with the lead dioxide and discharge the positive by an amount commensurate with the magnitude of the free-lead component. This discharge results in a reduction in the sulfate content of the electrolyte and is accompanied by a temperature rise from the heat of reaction.

Temperature rises during formation

There are several periods during the formation cycle when heat is generated and causes the temperature to rise, i.e.:

- (i) after filling with electrolyte and during the soaking period;
- (ii) during the first few hours following the application of the formation current;
- (iii) towards the end-of-formation when the efficiency of material conversion is low and considerable electrolysis occurs.

The initial temperature rise derives from the direct reaction between the sulfuric acid and the cured materials, particularly lead dioxide. In general, the temperature attained during this stage will determine the temperature level that will be reached during the actual formation. The lower the cell temperature at the end of the soaking period, the lower will be the maximum temperature experienced.

A reduction in the cell temperature at the end of the soaking period can be achieved in the following ways:

- (i) reduce the sulfation reaction during the soaking period by separately sulfating the plates beforehand, and/or
- (ii) prolonging the soaking period until there is a loss of heat through radiation and convection.

Greatly extended soaking periods tend to produce sluggish cells on formation due to the presence of very low concentration acid within the mass of the material with poor electrical conductivity. This adds to the cost of the process and reduces the throughput of cells. On balance, the prior sulfation of plates leads to better process control and consistency among cells, as well as reduces the level of the maximum temperature. Figure 5 illustrates this by comparing the temperature rise in cells of the same size and construction after the following process variations:

- (i) control cells with standard cured positive and negative plates;
- (ii) standard positives with sulfated negatives;
- (iii) standard negatives with sulfated positives;
- (iv) sulfated positives with sulfated negatives.

The sulfation process involved in the comparison consisted of an immersion in a 21 wt.% sulfuric acid solution for 16 h followed by washing and drying.

The lowest temperatures occurred when both positive and negative plates were sulfated after curing. The second temperature rise took place as soon as the current was switched on and reflected the lack of capacity in the cells and the behaviour of the cells as electrical impedances across the charging system. Once material conversion commences the cell impedance decreases and the temperature starts to fall. This decline in the temperature continues until the cell voltage starts to rise more quickly

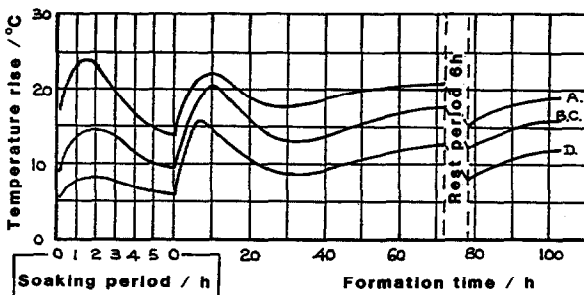


Fig. 5. Variation in temperature rise in equivalent traction cells during filling and soaking followed by container formation. Tubular positive design: (A) standard cured positive and negative plates; (B) standard positives with sulfated negatives; (C) standard negatives with sulfated positives; (D) sulfated positives with sulfated negatives.

with the onset of copious gassing. When this occurs the heat developed in the cell begins to exceed the heat loss through radiation and convection and the temperature starts to rise again. The interposing of a rest period at this point provides an opportunity for natural cooling to dominate.

The overall temperature pattern is independent of the plate type that is sulfated where only one can be so treated. Usually, in such circumstances, the positive is chosen as the act of sulfating tends to make the material more coherent and more amenable to handling without incurring damage.

When sulfating plates, it is important that a clear space exists between the plates in the sulfating solution. This ensures that both sides of the plates are sulfated equally and there is no risk that the opposite faces of a plate can be differentially stressed due to differing depths of sulfate film on either side of the plate. There is a temptation to layer plates in the sulfating solution. This leads to gross inequalities in the degree of sulfation both between plates and between sides of the same plate. Such a situation causes the formed cells to be variable unless the duration of the formation cycle is extended to cater for the poorest plates.

Completeness of container formation

There are large differences between companies as regards the amount of formation input necessary to form completely traction cells. For comparative tubular positive cells, specified inputs can vary from 400 A h kg⁻¹ of dry filling powder to as much as 540 A h kg⁻¹. The variation does not follow a consistent pattern dictated by the composition of the filling powder and the theoretical minima of formation inputs. As a result, some designs of traction cell tend to show a greater rise in the electrolyte concentration during the first few cycles of service life. Most companies seem to agree that a good criterion of completeness of formation is the amount of lead sulfate remaining in the formed materials. A target level of ~0.5 wt.% PbSO₄ indicates a very high level of capacity stability, but it is recognized that the attainment of this level would probably demand a greatly extended formation time.

In order to accommodate a reasonable component variation and a duration of formation that is not economically prohibitive and does not result in an unacceptable rise in the electrolyte concentration during the early cycles of life, a maximum level of 2.5 wt.% PbSO₄ is often accepted and the duration/magnitude of formation input is adjusted to suit. To illustrate the effect this has on the change of specific gravity of the electrolyte in service, take the case of a traction cell made to the following design parameters:

- specific formed positive material weight 13.5 g A⁻¹ h⁻¹
- specific formed negative material weight 11.0 g A⁻¹ h⁻¹
- specific electrolyte volume 12.0 cm³ A⁻¹ h⁻¹

Assume both plates, after formation, have 2 wt.% of unconverted SO₄ based on total material weight, then: the amount of SO₄ in positive is 0.02 × 13.5 = 0.27 g, and the amount of SO₄ in negative is 0.02 × 11.0 = 0.22 g. The equivalent H₂SO₄ released into the electrolyte during the early part of the cell life will be 98/96 × (0.27 + 0.22) = 0.50 g.

Electrolyte of 1.280 sp.gr. contains 478 g l⁻¹ of H₂SO₄ at 20 °C. At 12 cm³ A⁻¹ h⁻¹, 12 cm³ of electrolyte contains 5.736 g H₂SO₄ and will weigh 15.36 g, thus giving a H₂O content of 9.624 g.

When the unconverted SO_4 is finally converted and released into the cell electrolyte, the resulting electrolyte will contain $(5.736 + 0.50)$ g H_2SO_4 in $(15.36 + 0.50)$ g of electrolyte. This gives a concentration of $6.236/15.86 \times 100 = 39.3$ g H_2SO_4 per 100 g of electrolyte. This is equal to a sp.gr. of 1.297 at 20 °C.

As a result of working the cell and converting the previously unconverted sulfate, there is an increase in the operating sp.gr. from 1.280 to 1.297. Wherever the maximum level of unconverted sulfate is adopted, it is prudent to adjust the sp.gr. of finished cells to the lower end of the working tolerance stated in the operating instructions given to the customer. This usually means ~ 1.260 sp.gr., where the nominal working value is 1.280. This arrangement serves the dual purpose of reducing the inconvenience to the customer of high sp.gr. levels with the possible demand on a service engineer's time to make an adjustment, as well as the extra costs of ensuring that in all plates the sulfate content has been reduced to a low enough value to avoid the inconvenience.

Usually, it is more satisfying to both manufacturer and customer to adopt a relatively high formation input per kg of wet paste or dry filling powder, and to ensure that the residual sulfate after the formation cycle is well below the maximum of 2.5 wt.%.

Positive plate drying after formation

Where positive plates are required for automotive batteries that are stored dry with dry-charged negatives and receive only electrolyte before commissioning, they must remain active after drying and during the subsequent storage. The manner and degree to which they are dried is critical. The effect of 'overdrying' is to reduce the high-rate discharge voltage after the cells have been filled with electrolyte and stood for a period of the order of 20 min. The practical significance of this is a sluggishness on the part of the battery to start the engine after being fitted; the benefits that should derive from dry-charging the negatives no longer apply.

It is found that, with certain drying conditions, the instantaneous voltage on engine starting falls to less than half the open-circuit voltage and, generally, the engine does not turn over. This phenomenon, sometimes called 'positive blanking off' can often be overcome by allowing the battery to stand for several hours by which time areas of the plates that have not fully wetted initially will have become wet. It can also be eased by giving a short charge, but this presupposes that the sales outlet has the ability to do this. This is frequently not the case and the necessity to stand the filled batteries for extended times is unacceptable.

Whilst there is no clear explanation for this blanking off effect, it is thought that prolonged drying of the positive plates produces extremely dry areas within the active material that do not readily accept the electrolyte due to surface tension forces. The effect of the bulk drying of formed positive automotive plates over a period of 8 h at varying temperatures is plotted in Fig. 6. The data cover a manufacturing period of several years with random sampling of plates from each batch of positives taken from the drying ovens. The plates were analysed for moisture content after which they were made into cells and discharged at a nominal 4C/20 A. Based on the total results, the percentage probability of effective engine starting was estimated.

The results in Fig. 6 indicate that if the drying time is of the order of 8 h, there is a possibility of poor starting performances with dry-charged batteries if the drying temperature exceeds 70 °C. Moreover, the level of the failure to start increases as the temperature increases until with temperatures approaching 90 °C there is little

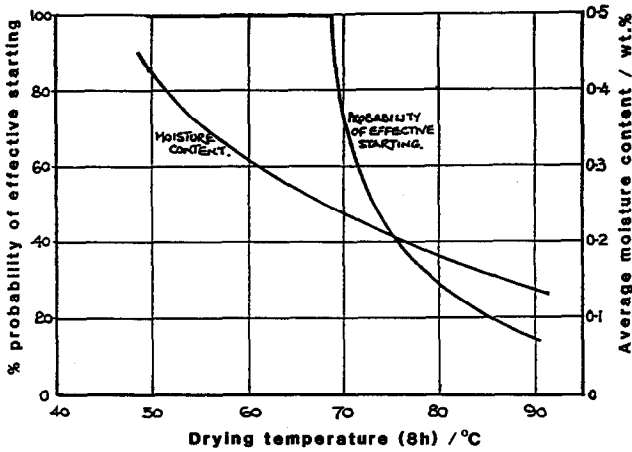


Fig. 6. Effect of drying temperature on the engine-starting capability of dry-charged automotive batteries after filling with electrolyte and standing for 20 min before discharge.

chance of effective starting. Generally, the drying temperature should be controlled within the range 55 to 65 °C and the moisture content held between 0.25 and 0.4 wt.%. The lower limit is the more important one. The upper limit is given to ensure that there is not sufficient moisture within the material to migrate to the separator and from the separator to the negative material and cause a partial discharge and loss of dry charge.

A similar effect shows up with traction plates that are dried before formation. Positive traction plates dried, (after curing) at low temperatures tend to form more readily in tank formation and develop higher capacities initially than those dried at higher temperatures. This statement depends for its validity on the duration of the drying process since short periods at relatively high temperatures tend to produce the same result as a long treatment at lower temperatures. The regime to be avoided is one that extends for a long duration at temperatures that ordinarily would evaporate the moisture in the plates rapidly. This appears to be more critical in tubular positive traction plates than in flat plates. When drying traction plates overnight before formation, a safe practice is to limit the temperature to 60 °C.

Static ovens can be used satisfactorily for the drying of formed automotive positives and unformed traction positives. Nevertheless, there is always the problem of a varying temperature distribution horizontally and vertically with the result that the degree of drying will vary according to where the plates are located within the oven. If the system of oven heating is based on hot air blown into the oven and circulated by fans before extraction, the air inlets should be well covered by baffle plates to prevent the hot air coming into direct contact with plates in the line of entry of the air. This produces overdrying in those plates on to which the hot air has directly impinged. The position of the racks carrying the plates is also important since, if the tracks are sited with the plate surfaces facing the incoming air, the outer plates will blank off the rows of plates behind and hinder the evaporation of the absorbed moisture. The plates should be placed edge on to the direction of the air and should be spaced apart by 0.5 to 1 cm.

Tunnel-drying ovens are the most appropriate. The cross section of the tunnel can be made small and the plates can be taken across the convective flow of heated air. The tunnel can be split into a number of temperature zones so that the plates can be dispensed at the take-off end of the oven and cooled near to room temperature for easier handling.