## **Technical Note**

# Aspects of lead/acid battery technology 9. Grids

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#### Abstract

The essential characteristics of a battery grid and the methods for its production are described. Design parameters are set out for automotive and traction grids, and include the grids used in tubular positive plates. Worked examples are included. A comparison is made between surface cut and interlock grid moulds for grid casting. The relative merits of large-pellet solid-rib traction grids, lattice-type grids and composite solid-rib/lattice grids are reviewed. Common casting defects are discussed together with the probable causes for their occurrence and what remedial action is required. The formation of dross with lead-antimony alloys is examined, as well as the subsequent financial losses that can occur and the care that is needed in safe handling. The process of mould coating to allow trapped air to escape from the cavity of the mould and to delay freezing until the mould is fully filled is described, together with information on the preparation of the mould-coating slurry.

### Introduction

The grid is a carrier for the active material and a conductor for the current from the active material on discharge and to the active material on charge. In fact, the grid is an unwelcome necessity since it does not contribute to cell capacity from its own material content. It also reduces the energy-weight and energy-volume ratios or densities of a cell. The grid involves the use of relatively expensive lead alloys and adds to the cell material and labour costs.

A grid has to have the following broad characteristics:

- low material cost
- low manufacturing cost
- low weight
- high rigidity
- sufficient elasticity to accommodate the volume changes in the active materials from charge to discharge without permanent deformation
- high resistance to deformation during the pasting operation
- high resistance to direct chemical attack in the presence of sulfuric acid

• high resistance to electrochemical corrosion in the case of positive grids

• a large surface area in contact with the active material to minimize the material/ grid contact resistance

• good electrical conductivity in the main members to minimize voltage losses in the grid, particularly in the case of automotive batteries where the prime function of the battery is to start engines under adverse conditions

These characteristics clash one with the other and the resultant grid design is essentially a compromise. The extent of this compromise depends on the type of battery and its prime function. The containment of the volume changes in the active materials of an automotive battery is less difficult than in a traction battery, and is also less important than keeping the voltage losses at engine-starting rates at low temperatures as low as possible without jeopardizing battery life. In a traction battery, life is all-important and dominates even at the price of material saving.

#### Methods of grid manufacture

Although the developed profiles of grids offer the choice of either mechanically forming or casting in profile moulds, casting has evolved as the most economic method for most applications. Mechanical forming by punching, upsetting and reforming grid members from rolled and sized strip had originally a number of disadvantages. The cost of rolled strip tended to be high and the capital cost of the multi-station punching and profile forming operations was high in comparison with the relatively low cost of profile moulds for casting. Moreover, in the case of lead–antimony alloys, there is a duplex 'lead plus eutectic' structure and a precipitation reaction involved in the agehardening process. The former causes the cast alloy to harden rapidly after casting and the precipitation reaction continues the age-hardening. Mechanical work destroys the duplex structure and fragmented antimony-rich particles in a recrystallized matrix are formed and are accompanied by an appreciable reduction in the mechanical strength of the grid. This phenomenon shows up in a positive grid as an inability to withstand distortion so that the vertical sides of the grid bow severely and the rate of grid corrosion markedly increases. The result is a much reduced battery life.

It is possible to reduce the cost of fabrication by using the expanded-metal technique in which the metal is pierced with slits that are then pulled apart, and twisted alternately in opposite directions to form a series of diamond-shaped pockets on either side of the main frame. This does not make the system acceptable as the same grid distortion and shortened-life problem exist.

Some easement has been obtained by heat treatment of the grids but such treatment calls for the grids to be heated very close to the melting point of the alloy. This leads to many lost grids through lack of precise control of temperature. Furthermore, the treatment is an added cost item.

With the development of 'maintenance-free' batteries, there has been a move away from the use of lead-antimony alloys towards lead-calcium alloys. These behave in a different way to lead-antimony as age-hardening is not dependent on a duplex 'lead plus eutectic' structure. The process involved is that of the precipitation of very fine CaPb<sub>3</sub> crystals from a super-saturated solution. These distort the crystal lattice and promote hardening. Although lead-calcium alloys are not improved by mechanical working, it is possible by careful choice of the fabrication parameters, i.e., the nature of the cold working and alloy composition, to retain the fine crystal structure of the hardened alloy. As a result, the fabrication of grids from a lead-calcium alloy strip does not introduce the same severe grid distortion and rapid corrosion problems as with lead-antimony alloy fabricated grids.

The possibility to produce sized strip direct from the melt leads to cost reductions in producing strip, and the competitive manufacture of fabricated grids becomes possible.

The use of other metals, such as aluminium and brass, heavily lead coated, has been proposed particularly for negative grids. Commercial batterics with lead-coated, brass negative grids were made and sold for buses during the 1930s but did not live up to expectations. The basis of their adoption was that metals electronegative to lead, in theory, can operate free from chemical attack as negative grids as long as the negative active material, in contact with the grid, is never so deeply discharged that it reverses. This state can be controlled in single cells, but in multi-celled batteries it is not feasible for the series of cells to operate in complete unison. The weakest cell will reverse if the battery is deeply discharged and in these circumstances the negative grid of that weak cell will be attacked. Another factor that mitigated against their use was the cost as it was not possible to compete in manufacturing cost with cast lead-alloy grids.

In contrast, casting a grid from the molten alloy did not require complicated or costly equipment, all trimmings could be returned to the lead alloy furnace and the moulds were not expensive to buy or difficult to make. Because of these attributes, casting grids has remained the main grid-making system.

#### Choice of grid alloy for automotive batteries

There is a market for two basic types of automotive battery, free-vented and sealed.

There is no fixed grid alloy for the free-vented battery. Makers have their own preferences and, until recent times, most alloys came within the range of 4.5 to 6.5 wt.% Sb with the main supporting additives of 0.1 wt.% As, 0.04 wt.% Cu, and 0.02 wt.% Bi. In the USA, manufacturers used an alloy with 4.5 wt.% Sb for many years but European manufacturers tended to operate with an alloy nearer to 6 wt.% Sb. The latter is less difficult to cast at high production rates, although production rates of 16 to 18 castings per min were regularly achieved with the 4.5 wt.% Sb alloy down to a thickness of casting of 1.25 mm. This order of output required careful design of the grid to remove sharp intersections and to avoid large changes in section and very thin sections. In the mould design, it was necessary to make special provision for the entrapped air to escape readily and to direct the incoming molten alloy into the side frames and bottom before entering the cross-members, so that the alloy lifted the air to the top of the mould as the molten alloy filled the cavity. The mould coating had to be evenly sprayed and to be of sufficient thickness to delay alloy freezing until the mould had been fully filled, yet not too thick to upset the casting cycle and produce incorrectly dimensioned castings.

Casting with alloys of lower antimony contents requires greater skill and attention to shop-floor details. The choice of which antimony content to adopt is an economic one, and is based on the lowest manufacturing cost after taking into account operator skill factors. The latter are important where there is difficulty in attracting a good standard of labour.

The above alloys are unsuitable for reduced maintenance or maintenance-free batteries. Here, much reduced water losses are required to make tenable the restricted venting and the sales feature of very infrequent or no water additions during the life of the battery. These batteries use lead-antimony alloys with 3 wt.% or less of antimony or antimony-free alloys where the main hardener is calcium.

Alloys for maintenance-free batteries are a different proposition to the standard alloys for casting. Very strict temperature control of the lead furnace, the casting ladle, the mould gate and the surface of the mould blocks is needed. When antimony-free alloys were first used an inert-gas blanket was needed over the exposed molten alloy surfaces in order to prevent oxidation and the formation of dross inclusions in the casting. The design of the automatic casting machines has been greatly improved to give more machine control over the casting conditions throughout a full working shift, and to handle, without distortion, the more delicate castings as they leave the moulds before age-hardening has had time to become effective in giving rigidity. The outcome of the refinements in the casting machines has been that casting rates of the order of 14 to 16 casts per min are regularly possible. A typical calcium-lead alloy is one with 0.07 wt.% Ca and 0.5 wt.% Sn.

Irrespective of which type of battery is considered, the important factor is the works cost of the castings, not the cost of the alloy used but the utilization of every tonne of the alloy, the cost of the labour involved, and the level of the stock inventory. It cannot be assumed that a reduction in the antimony content of the alloy, and with it a reduction in the material cost of the alloy, will automatically mean a reduction in the unit cost of grids. This needs valid checking before it can be accepted.

Often, notional costs are the only ones available. These costs are roughly checked at infrequent intervals on the shop floor. Each month, a reconciliation exercise is required to account for unexplained material losses, high dross costs, etc. It is well worthwhile to institute a daily materials usage production output return that lists the following:

(i) weight of lead alloy issued to the machines at the start of the shift;

(ii) weight of lead alloy unused at the end of the shift;

(iii) weight of finished grids made during the shift;

(iv) estimated weight of lead alloy in the lead furnaces;

(v) weight of alloy dross at the end of the shift, and

(vi) number and type of grids made during the shift.

This return should be examined at the start of the next morning's shift and action should then be taken to correct any deviation from normal practice. In this way, an operating discipline is maintained and operators who need further training are recognized and helped.

Numerical output is only a criterion of the suitability or otherwise, of a particular alloy when it is coupled with a minimum standard of surface finish that must be continually maintained during production.

From time to time, manufacturers find themselves faced with the decision on how to reduce operating costs. The first change that is usually considered is a reduction in the antimony content of the alloy. Before any change is made it is necessary to derive by trials the true cost of casting the thinnest/thickest grids using normal labour, and to ensure that any decision to reduce the antimony content is made from fact and not from emotion.

There is a great temptation to take the considerable work that has been done on improving the corrosion resistance of alloys at face value, and to accept that if the alloy, cast into test pieces, shows a significant improvement over currently used alloys under anodic corrosion tests, with or without mechanical stressing, it will automatically give a better performance life in the batteries. Often, the result is the reverse, or the costs are so inflated by poor productivity or greatly increased scrap levels that it is hard to meet market prices and contribute to company earnings.

The basic aim in design is to ensure that the ultimate cell life is determined by the corrosion life of the positive grid. Negative grids, in most cases, do not present a corrosion problem. Positive grid corrosion can be at preferential sites and at exaggerated rates if, during the casting, there are formed fine hair-line cracks (that are virtually invisible to the naked eye) at the junction of members, or areas of coarse crystal structure from irregular cooling, or minute dross inclusions, or in-built strains. These imperfections of surface quality and strains will often do more to reduce life than the adoption of less corrosion-resistant alloys that will more readily give consistently high quality surfaces to the grids. This aspect of quality control cannot be overstressed and should always be uppermost in the mind of both the designer and the plant manager.

The nearer to the eutectic alloy of lead and antimony, the easier it is, in general, to produce consistently good castings and a higher rate of casting. This is because the transition from liquid to solid will be rapid. One factor should be recognized; moulds designed for one level of antimony are not necessarily suitable for another widely differing level. This point should not be overlooked when experimenting with alternative alloys to prove their suitability, or otherwise. Usually, the trouble is confined to the throat area of the mould and the maintenance of a uniform temperature over the mould faces.

There is an excellent group of corrosion-resistant alloys based on high arsenic additions within the range of 0.45 to 0.55 wt.% As and with tin additions within the range 0.30 to 0.50 wt.%. These alloys are expensive and, in order to exploit their proven good corrosion resistance without making their manufacture too expensive, sections need to be thinner. The disadvantage with them in the past was the difficulty to maintain high productivity using the older designs of casting machines without the present-day improved controls of temperature and grid handling. The high tin contents require more care in the control of the furnace temperature, otherwise the losses through vaporization at the surface of the melt can be high and, at the current prices for tin, the manufacturing cost can be seriously inflated. The maximum temperature should be held at 450 °C and the dross should be assayed before selling in order to recoup as much as possible of the losses.

These variable tin losses reflect variable age-hardening and manufacturers have found that, by sacrifying some of the corrosion resistance and lowering the arsenic and tin levels, a more predictable casting is obtained. This reflects more on the manufacturing control exercised, than on any basic defect in the alloy formulation.

Before deciding to change from one alloy to another, it is as well to ask questions along the following lines:

• Why is the change required? Is it because of poor service life of the product or too high a manufacturing cost?

• If the present alloy is giving a poor service life, is it the fault of the alloy or of the specified minimum standard of quality?

• If poor quality is alleged, how certain can one be that it is a correct diagnosis? Has quality control been set to admit too many grids with imperfections and is this the prime cause and not the alloy? What steps have been taken to examine thoroughly the casting machine settings?

• Has the operator standards been checked recently and have malpractices crept in? What is the state of operator training and retraining? Has any remedial action been taken with operator training to ensure machines and moulds are being set properly? • If the cost of manufacture is too high, what cost is admissible? This gives an opportunity to calculate the minimum productivity that can be accepted. The cost of the new proposed alloy can readily be obtained. If the minimum productivity with the proposed alloy is not easier than for the present alloy, then the chances of meeting an acceptable manufacturing cost are bleak. If the antimony content is reduced for the proposed alloy, casting rates are unlikely to improve and can fall as casting is generally more difficult when the antimony content is reduced to 3 wt.%, and from then slowly improves as the level falls further. Below 3 wt.% Sb, lack of rigidity in the casting as it is ejected from the mould introduces further problems.

If, after asking the above and other relevant questions, it is still deemed realistic to change the alloy, it is advisable to proceed carefully and to keep to a structured test pattern. One approach could be as follows:

(i) Prepare as accurately as possible a factual cost statement for the manufacture of each major grid design based on the statistical average weight of each grid size over the past four weeks' operation, the average production per shift per average operator, the average weight of dross per tonne of alloy used, and the average weight of scrap produced and not returned to the lead alloy furnace for remelting.

(ii) Check the analyses of as many competitors' grids as possible and extract those with the lowest alloy material cost. Increase the tin content by about 0.005% to allow for lost tin in the furnace.

(iii) Consider the lowest cost alloy first and purchase a trial batch. The quantity should be sufficient for several shifts' output.

(iv) Based on the antimony content, assess the probable change in the melting point and adjust the furnace temperature to accept this new value. Adjust the ladle temperature likewise.

(v) Run the first trials with a mould of known good record, and later with a mould with a poor record of productivity. Measure the temperature of the mould surfaces and adjust the bottom heating to give about 150 °C over the bottom half of the mould. Adjust the dwell time during which the melt is held in the mould to bring the upper half in line with the bottom for temperature. This may mean an increase in the speed of casting and may need some persuasion to obtain the operator's willing acceptance. Use a highly skilled operator initially to minimize the operator factor.

(vi) During the trials, measure the temperatures in the lead alloy furnace, the ladle and over the mould surfaces, the speed of casting, and the number/nature of the mould coats. Visually check the grid surface quality and record it against the other measurements. Keep permanent records; they are valuable for the future. Make only small changes at a time and keep full notes of them.

(vii) If and when consistently good castings are obtained, change the operator with an average one. Check and correct his/her actions in the light of the experience gained. Record these actions and use the trials as a training exercise for the operator.

(viii) Once the operator is casting consistently to a minimum specified quality standard, measure the productivity, etc., and calculate the new costs. If an acceptable cost saving is indicated, repeat with another operator, if possible, and, if this repeats the saving, make the alloy change and adjust the target output requirements with the knowledge that the change and targets are based on facts and not pious hopes.

If the cost savings are not large and the economic pressures not sufficiently severe to demand rapid change, it is prudent to test the market with a production quantity that is adequate to cover light, medium and heavy usage areas. Recall samples after 6 and 12 months and carry out a tear-down examination of the positive grids and compare them against standard samples with the original alloy. Examine the amount

#### TABLE 1

Alloy	Alloy metals present other than lead (wt.%)						
	Sb	As	Sn	Cu	Bi	Ag	Te
A	4	0.280	0.030	0.040	0.015	trace	trace
В	5	0.100	0.005	0.045	0.020	0.005	0.005
С	5	0.200	0.100	0.050	0.020	trace	
D	5.5	0.080	0.090	0.010	0.010		
Е	6	0.120	0.004	0.050	0.020	0.008	0.004
F	6	0.150	trace	0.040	0.020	0.004	trace
G	6	0.250	trace	0.010	0.023	0.003	trace
н	6.3	0.130	0.040	0.010	0.015	trace	

Composition of alloys used in free-vented batteries

and nature of any sediment. Although it is not usual to be troubled with sediment in these days of alternator systems, it has been known that a grid alloy has been so resistant to corrosion that there was little or no adhesion of the active material to the grid members and heavy shedding resulted and caused a greatly reduced life in service.

The ability to evaluate what could be a major change carefully and in detail is becoming more rare; quick savings are normally the driving force. In such circumstances, it is prudent to avoid too large a change from those alloys used by other makers. This may appear to be an over-cautious approach but, whilst the effect of the limited change on cost saving is enjoyed, time has been bought to extend the limits more adventurously and with sensible safeguards financially. The danger does exist that having made a limited change no further experimentation is undertaken until the next financial crisis arrives.

Typical analyses of alloys used for standard, free-vented batteries are given in Table 1. These are only a few of the variations in day-to-day use. The final choice must rest with the alloy that most readily is accepted by the equipment available and the standard of operator. The newcomer would be best advised, however, to start with an alloy with the lowest antimony content and seek, through the cooperation of the machine supplier, to develop an expertise. Where a higher antimony content is adopted initially, there is a risk that any reduction contemplated later can produce operator reluctance to accept the change without a reduction in the required output.

## Design parameters for automotive battery grids

Designers are concerned with the most economic use of the materials that comprise a finished plate and associated lead-alloy parts. They also have to optimize the ratio of active material to grid material in relation to the type of performance that is demanded by market conditions for a given price structure.

There are many different terms used in connection with the usage pattern to describe the balance of active material to grid material, electrolyte, etc. One system uses the terms 'specific grid weight', 'specific active material weight' and 'specific electrolyte volume'.

Specific grid weight defines the weight of grid metal (less the material in the lug) per ampere-hour of rated capacity. The weight of the lug is omitted because this portion of the grid does not bear a linear relationship with the capacity rating, and because it tends to be the same for many sizes of grid so that the same fixtures and assembly jigs can be used over a range of cell and battery sizes. This is particularly evident in traction grids where the grid length can vary in stages of up to five or more times the length of the shortest grid for a common grid width.

The higher the specific grid weight the greater is the material cost of the grid. The design aim should be to obtain the lowest specific grid weight commensurate with high productivity of grid casting.

The specific active material weight or more correctly the specific formed material weight, refers to the weight of formed material per ampere-hour of rated capacity, both positive and negative. This parameter gives a measure of the effective material utilization and, indirectly, the volume space within a grid structure that is needed to receive the active material. Automotive batteries are rarely deeply discharged and the amount of lead sulfate formed is a function of the depth-of-discharge and not the capacity rating. Less active material can be allowed in the design per ampere-hour than in a battery that is regularly subjected to deep discharges, such as a traction battery. This is possible as the amount of lead sulfate in the active material determines to a significant extent how easily the discharged battery will accept recharge.

The specific electrolyte volume defines the volume of electrolyte that takes part in the discharge reaction per ampere-hour of capacity. There is a finite volume of electrolyte required in a cell and if the working electrolyte does not reach this level, the cell will not under any circumstances deliver the rated capacity. The higher the specific electrolyte volume that can be designed into a cell, the lower the value of specific formed material, within limits, that needs be provided.

The design of a grid cannot be divorced from the total battery design. In commercial practice, this shows up in the relatively small number of differing profiles and thicknesses of grids for comparable batteries of differing makes. The data in Table 2 come from an examination of a number of European and American manufacturers' products. Although there was a variation between the antimony content of the alloys used in the batteries, there was no correlation between the antimony content and the specific

## TABLE 2

Maker	Specific grid weight (g/Ah, 20-h rate)		
	Positive	Negative	
A	5.0	5.0	
В	6.2	6.5	
С	6.5	6.5	
D	5.9	6.0	
Е	6.1	6.0	
F	7.1	6.0	
G	7.0	6.0	
н	5.4	5.1	
Ι	6.0	5.5	
J	5.5	5.2	

Specific grid weight in different makes of batteries

grid weight. The main impression was that the antimony content was of less importance than either the average quality of the grid castings or the difference permitted between the worst and best grids accepted for further progress in the manufacturing process. The smaller the tolerances that can be accepted in grid quality without unacceptably increasing the grid manufacturing cost, the lower the specific grid weight that can be considered for design within the limits of castability.

Generally speaking, a two-year-life guarantee, based on less than 1% of average manufacturing cost needed to fund the guarantee, can be met by using alloys within the range of 4.5 to 6 wt.% Sb with specific grid weight of 5 g/Ah for negatives and 6 g/Ah for positives (20-h rate). If acceptable productivity figures can be obtained using high arsenic alloys, the above specific grid weights can be reduced to 5 g/Ah for both positives and negatives. Lower levels for negative grids are usually accompanied by difficult casting due to the necessarily restricted cross sections needed to meet the low weight.

There is a great temptation to reduce specific grid weights arbitrarily as the weight of the grid is 'lost weight' as far as output is concerned, i.e., energy per unit weight and energy per unit volume. Whilst these factors may not be of prime importance for engine starting, they are significant whenever the usage of the battery type cannot be confined to starting operations only.

In order to reduce the specific grid weight, either the sections of the ribs and/ or wires have to be decreased, or the number of ribs and wires must be reduced if sections are to be maintained. There is a minimum rib and wire cross-sectional area below which casting is difficult and often impossible. The alternative of reducing the number of ribs and wires lowers the area of contact between the active material and the grid and increases the area of each pellet of active material. These changes tend to increase the resistance losses at engine-starting currents and produce a pellet that will crack and sink during both the curing stage and the subsequent formation process. The nett effect can be a loss of voltage that is sufficient to make cold starting difficult and, in extreme cases, impossible.

The 20-h rated capacity defines the ability of a battery to carry out its true function of engine starting. This capacity rating has been used as a unit by which the engine-starting capability can be expressed, irrespective of battery size. This takes the form of the number of times the numerical capacity has to be multiplied in order to equal the cold-start current in amperes. For example, a cold-start capability of 200 A is equal to  $5C_{20}$  A, where the 20-h rated capacity is 40 Ah and designated as  $C_{20}$  amperehours.

The low-rate capacity cannot be completely ignored since, in an emergency, a minimum reserve of capacity must be available to power essential equipment. The trend in recent years has been to adopt a 'reserve' capacity based on a discharge at 25 A.

The battery cannot be divorced from the associated starting motor since the latter dictates the amount of starting current that will be demanded of the battery. Over the years, in the interests of greater efficiency at lower costs, changes have been made in the design of starter motors. This has resulted in an increase in both the current demand (particularly at low temperatures) for effective starting and the minimum voltage level at which a start can occur. Whereas, at one time, effective starting could be realized at a voltage level of 6 V, this minimum voltage has steadily risen to 7.2 V and latterly to 8.4 V. This trend has been accompanied by higher currents, i.e., a double burden has been placed on the battery. This upward progression has accentuated the importance of a good active-material/grid contact, i.e., as high a contact area as

the design can provide. The lower limits quoted for specific grid weights have become very real values in view of the starter-motor changes.

The current paths in a pasted plate are complex and do not readily lend themselves to a Kirchhoff analysis. In order to design a grid, some approximations have to be accepted that, whilst not precise, are close enough in practice to enable a comparison to be made with other grid designs. The grid members of positive grids will oxidize in use and will become part of the positive active material. They cannot be looked on as permanent current-carrying members that modify the overall resistance, except where the amount of material in the members is sufficient to provide an adequate current-carrying path at the end of service life. Only the ribs come within this category. These are the true current-carrying members. The horizontal wires become almost fully oxidized and their main function is to provide support for the pellets of active material during processing and the early part of battery life. The lead dioxide added to the positive active material as a result of grid oxidation occupies a greater volume than the alloy from which it is formed so that the active-material/grid electrical contact is improved. Although the effective current-carrying members are the ribs, their dimensions are chosen not only for current-carrying capability, but also for imparting rigidity to the active material/grid structure. A compromise has to be sought as the greater the number of ribs, the greater is the cost of the grid and the lower is the volume of active material that can be accommodated within the grid.

In any grid design, there has to be a balance between the solid and open volumes to optimize the space that is available within the cell container. To arrive at what volume can be allotted, the role of the electrolyte has to be examined. By increasing the available volume of electrolyte, reductions become possible in the amounts of both the grid and the active material. This is demonstrated in Fig. 1 which shows the order of changes that have been made in a typical 12 V, 40 Ah automotive battery over the period 1964–1993. These have resulted in a greater use of electrolyte with reduction in the amounts of both grid metal and active material.

Some companies, in the interest of reducing their stock inventory by restricting the variety of grid types and sizes, have adopted a common grid for the positive and negative plates. In such a situation, the grid design must always be that of the positive. As a negative grid is not subject to oxidation corrosion, it follows that the design will



Fig. 1. Change in component weights of automotive batteries (12 V, 40 Ah) over the period 1964-1993.

give a higher grid weight for the negative than needed and less active material or electrolyte volume than could have been provided. Such a rationalization eases production planning but at a price, i.e., the cost of the extra metal. For example, in the case of positive grids made to a specific grid weight of 6 g/Ah with a matching negative grid of 5 g/Ah, the single universal grid would be to a specific grid weight of 6 g/Ah. The excess metal when using the universal grid would give an extra battery weight of  $\sim 2\%$ . This would all be at the lead-alloy price.

Before accepting as policy the universal positive and negative grid design, the financial aspect should be evaluated and sensibly debated to make sure that greater usage of the alloy is truly balanced by economies elsewhere.

#### Components of an automotive battery grid

There have been many designs of grids adopted over the years based on the lattice principle. In this, the horizontal members are approximately half the thickness of the grid and half that of the rib cross section. Furthermore, the lattice is staggered so that alternate members horizontally are on opposite sides of the centre line of the grid section. This arrangement allows the active material to be interlaced between the ribs and the wires.

The prime requirement of the automotive grid is to conduct the high currents for engine starting efficiently and with a minimum of voltage loss from the active material through the grid to the battery terminals. Attempts have been made to design the main ribs to lie normal to the equipotential contours in the plate and this has led some designers to postulate these equipotential contours as being broadly circular at varying radii with a centre in the lug and to make the ribs as radii from the lug. This design has not, however, established itself as being significantly superior to a simple design with vertical ribs and horizontal wires. Other designs have retained the simple format but have made the ribs nearest to the lug closer than those remote from the lug. It is argued that the current increases as it comes nearer the lug and there is good sense in increasing the conductivity where the current is highest.

The electrical resistances of connectors, pillars and plates are considered to contribute about one-sixth of the total voltage loss in a battery that discharges at engine starting rates. There is general agreement that the position of the lug and the conductivity of the main ribs affect significantly the magnitude of the voltage loss; the lowest value occurs when the lug is at the centre of the grid and there is a relatively massive rib immediately below the lug.

Despite the work that has been carried out to provide a theoretical basis for grid design, the simple symmetrical lattice grid has persisted, even with the lug takeoff close to the corner of the grid. Undoubtedly, the main reason for this apparent reluctance to change has been the fact that more can be done to improve the voltage loss by concentrating on the nature and shape of the separation and the spacing of the plates within the cell compartment than by all the elaborate designs of grids with their attendant casting problem.

The structure of an automotive grid is given in Fig. 2. This can be broken down into a number of design areas: (i) surrounding frame; (ii) vertical rib structure, and (iii) horizontal wire structure interconnecting with the ribs.

The choice of frame dimensions is mainly dictated by the rigidity that is required for the grid to pass under the hopper feed of the pasting machine without distortion or tearing, with the proviso in the case of a positive grid that there is sufficient metal



Fig. 2. Typical automotive grid structure.

left at the end of service life to hold the general shape of the plate. In most cases, resilience during pasting is the controlling factor. This usually demands more metal than the oxidation corrosion. Meeting the pasting requirement also meets the corrosion needs. This causes some difficulty when attempting to design individual grids to meet different life requirements: the simple act of reducing the frame dimensions, along with those of the ribs and the wires, may lead to a sufficiently weak frame that scrap levels in the pasting operation can be excessive. Instead of tailoring the grid costs to the reduced life market, the reverse may happen and costs increase rather than decrease. In such situations, it may be necessary to retain the frame dimensions but make the grid thickness less than the design figure and to overpaste the grid to bring the active material up to the specified value, or to ignore any traditional low-rate capacity figure and accept an engine-starting requirement only. Both approaches have been adopted, as determined by the market demands.

In the absence of any data relevant to the particular pasting machine that an operator may be using, a frame width of 2.5 mm is a reasonable minimum in most designs. The cross section should be such that, as the metal freezes, the grid helps

itself out of the moulds. In this way, the casting drops freely from the mould as it opens, and is assisted by only light pressure from ejector pins in the fixed half of the mould. One way to achieve this is to make the inner angles of the frame as shown in Fig. 3. Wherever possible, some increase on the minimum angle of  $15^{\circ}$  is preferable. In the initial design, a figure of  $20^{\circ}$  is suggested as the starting point for working out the frame shape.

It is generally accepted that the horizontal wires should only be sufficient to ensure that the active material is retained effectively and that casting is economic. It is not wise to sacrifice too much metal to the wires to the detriment of the ribs. If this is the case, then there is the risk that the voltage at engine starting may be lower than required and starting may be adversely affected under onerous starting conditions.

The molten metal has to flow both freely and rapidly during the casting operation. It must meet little resistance from friction at the mould surface. Furthermore, the air within the mould must be able to escape easily and not prevent the metal from filling completely the internal mould profile. The path along which the molten metal has to flow is long and tortuous and fluid friction is accentuated by the incorporation of very small sections. To ease this restriction, it is prudent to limit the minimum cross-sectional area to about  $0.005 \text{ cm}^2$  or the inscribed circle to the wire section to  $0.004 \text{ cm}^2$ . The latter has been adopted as it is argued that the molten metal will not flow into the angles of very small sections but will approximate to a circular flow. Both approaches give very much the same final specification for the wire section.

Regions in the mould that accommodate these small sections should have provision for extra mould coating to ease the escape of air. One method has been to extend the wire section into the mating part of the mould and, in effect, provide an increased section for the wire to that shown on the finished grid. Typical arrangements are shown in Fig. 4.

The back relief (or clearance) that is cut in the opposite half of the mould is purposely shallow and rapidly fills with mould coating. It does not, then, accept molten metal but provides an extra porous area through which air can escape. It also delays the onset of freezing in that area and allows more metal to enter the mould profile so that there is less risk of incomplete filling.

The difficult task in any grid design is to decide how to share out the total metal allocated to the grid between the frames, ribs and wires. There is no simple formula nor a theoretical one based on an analytical argument. Most designers rely on past experience and what other makers are using with apparent good results in the field. The latter can be dangerous as it is assumed that the design is, in fact, operating without any serious problem. This is not always so and often the particular maker is already in the process of changing the design in the light of service experience. The



Fig. 3. Side frame section for a negative grid.



Fig. 4. Back relief of thin wire sections in grid moulds.

adoption of that particular design without that knowledge can lead to uncomfortable and expensive production difficulties. Despite this risk, there is a virtue in examining as many competitors' designs as possible as a number of common factors of design can often be seen confirming or otherwise one's own ideas.

Economic pressures drive designers to attempt to work the various materials harder. This, too, has its dangers if based on what other designers are doing, unless there is backing from one's own experimental data. Wherever possible, experimental work should precede a paper design. Although it may not always be able to do this, it is possible to derive experimentally the minimum frame dimensions that can be accepted by the pasting machine without distortion. This is achieved by trimming down the side frames of existing castings in small steps until a degree of damage occurs. This sets a lower limit to which has to be added an acceptable out-of-centre trimming tolerance to set the minimum specified frame dimension.

The action of casting can be compared with the flow of an electric current through a network of conductors. The largest cross-sectional area will take the greatest amount of the molten metal. This area should be preferentially the frames so that the molten metal flows rapidly down the outer members (i.e., the frame) to fill the lower frame sections and to rise up through the mould to scavenge the contained air from bottom to top. The direction which the molten metal takes on entering the mould is a function of the gate design; the ease with which the molten metal flows down the outer frame is dependent on the frame cross section. Mould and grid design cannot be taken in isolation.

This control of metal flow sets some limit on the smallness of frame sections that can be accepted. Some easement can be achieved by further reliefs in the mould directed to assisting the escape of air. These easements, termed air slots, are produced by incorporating inserts in the mould blocks. Clearances are provided between the insert and the surrounding mould metal. Sufficient length of contact between the insert and the mould block is provided to retain the insert positively in position. The width of the clearance slot varies with the type of grid design and the ease, or otherwise, of removing the air as the molten alloy enters the mould. The width can be as low as 0.05 mm, but a more common dimension is 0.2 to 0.3 mm.

Where a very narrow air slot is used, the mould coating can usually be sprayed over the mould surfaces without clogging the slot. With the wider slots, however, it is usual to apply a small back pressure to the mould block whilst spraying on the mould coating. Without this pressure opposing the entry of the coating into the slot, the value of the air slot is quickly lost. One method of incorporating air slots is shown in Fig. 5.



Fig. 5. Incorporation of air slots in a grid mould.

In the absence of adequate experimental data on the minimum frame dimensions that can be handled in any particular factory, a reasonable starting dimension would be a width of 2.5 mm and the thickness as dictated by the grid thickness. In most circumstances, these dimensions meet the design criteria of: (i) flow of metal down the frame is fast; (ii) rigidity of the frame, with some assistance from the ribs, is adequate to withstand the pasting stress, and (iii) rigidity of the oxidized and weakened positive grid during normal service is sufficient to maintain an adequate electrical conductivity through the grid and to retain the grid shape and active-material/grid contact, when a standard 4.5 to 6 wt.% Sb alloy is used. Where a low antimony (3 wt.% Sb or less) alloy or a lead-calcium alloy is employed, the same dimensions can be adopted provided the grids, after casting, are age-hardened sufficiently to develop the necessary rigidity. In the case of lead-calcium alloys, it is helpful to adopt a softer paste to reduce the magnitude of the shear stresses.

Minimum frame dimensions are very much dependent on the type of pasting machine that is used, the skill of the operators in setting-up the machines, and the discipline in conforming rigidly to the paste-mixing routine. Where possible, some small increase on the minimum dimensions quoted is worth considering in the quest for high productivity and low scrap.

A convenient way to commence a grid design is to fix the specific grid weight in line with the lowest values met among competitors. This sets the grid weight, excluding the lug. Take the minimum frame dimensions that have been found acceptable to the pasting process and calculate the frame volume and, from that figure, the frame weight. Subtract this frame weight from the total grid weight to give the amount of metal available to the ribs and wires. As a first approximation, share this between the ribs and wires in equal proportions. Initially, take a pellet size close to the recommended maximum dimensions and calculate the number of ribs and wires. Calculate the total length of ribs and wires. Using these, the cross-sectional areas of ribs and wires can be derived. If the wire's cross-sectional area is less than the minimum value for easy casting, i.e.,  $0.005 \text{ cm}^2$ , increase the metal allocation to the wire's cross-sectional areas is well in excess of the minimum value, decrease the metal allocation to the wires and boost the allocation to the ribs as this will improve the cold-start performance.

#### Maximum pellet dimensions

The aim in paste mixing is to produce the driest paste commensurate with the planned paste density, a texture suited to the type of pasting machine and ultimate formed density. After the paste has been pressed into the grid, it must support itself until the curing operation has been completed and the material has dried.

It is more difficult for low density pastes to support themselves than medium to high density pastes. The pellet size must be adjusted to avoid the centre of the pellet subsiding in the curing and drying process. Pastes with high sulfuric acid additions and low water additions tend to support larger pellets than a similar density paste made with low sulfuric acid and high water additions. The maximum pellet size is dictated by the paste formulation, density and texture.

Wet pastes with apparent densities of the order of 4.0 to  $4.15 \text{ g/cm}^3$  (65 to 68 g/in<sup>3</sup>) made with sulfuric acid (sp. gr. 1.400) additions of about 100 l per tonne of grey lead oxide (65 to 70% PbO) will support a pellet of 1.5 cm×1.0 cm, in grids of thickness 1.5 mm and over. With thinner grids, there is less of a tendency towards sinkage in the centre of the pellet and, if that was the only criterion, a larger pellet could be considered. The surface area of the grid in contact with the active material decreases with reduction in the grid thickness and retaining the paste in the grid becomes a problem. The risk of pellets of active material being knocked out with processing and handling becomes very real. For this reason, it is prudent to decrease the pellet size below that previously given when designing grids below 1.5 mm thick.

Formed positive material expands as it is converted into lead dioxide and locks itself more securely in the grid. Negative paste contracts on formation as it changes to pure lead and tends to become less firm in the grid structure. A reduction in the pellet size to  $1.2 \text{ cm} \times 1.0 \text{ cm}$  is suggested when plates are tank formed as they do not have any support during formation. This is not necessary with container formation.

In general, it makes for easier casting and a better surface quality on the casting when advantage is taken of the maximum pellet size in design to decrease the number of grid members and to increase their cross-sectional area.

## Empirical design of an automotive grid

Consider the case of an automotive grid rated at 12 Ah per positive, with dimensions 11.5 cm  $\times$  11.5 cm and required to accept positive active material with a specific formed material weight of 7 g/Ah with an apparent density of 3.6 g/cm<sup>3</sup>.

A reasonable specific grid weight for a two-year life with less than 1% of manufacturing cost needed to fund the guarantee is 6 g/Ah for a positive grid, excluding the lug.

The thickness of the grid will be dictated by the volume of formed active material it has to accept within the outer framework. It is common, also, for the grid to be overpasted. This means the thickness of active material is greater than that of the grid by as much as 0.025 cm.

#### Grid thickness

Take, for the example, a degree of overpasting of 0.02 cm to give an overall plate thickness of (t+0.02) cm, where t cm is the thickness of the grid. Then:

overall volume of pasted plate = 11.5 cm  $\times$  11.5 cm  $\times$  (t + 0.02) cm = 132.25t + 2.65 cm<sup>3</sup>

volume of grid metal =  $\frac{6 \text{ g/Ah} \times 12 \text{ Ah}}{11 \text{ g/cm}^3} = 6.55 \text{ cm}^3$ 

volume of active material =  $\frac{7 \text{ g/Ah} \times 12 \text{ Ah}}{3.6 \text{ g/cm}^3}$  = 23.3 cm<sup>3</sup>

It is assumed for this example that the grid alloy is one with 4.5 wt.% Sb with a density of 11 g/cm<sup>3</sup>. Therefore:

 $11.5 \times 11.5 \times (t+0.02) = 23.3 + 6.55$ 

t = 0.205 cm

Take 0.21 cm as the design thickness of the grid.

Grid weight

grid weight = 6 g/Ah  $\times$  12 Ah = 72 g

## Frame weight

Take an average frame width of 0.2 cm. Therefore:

average length of frame = 2(11.5 + 11.5) cm = 46 cm

weight of frame =  $46 \times 0.2 \times 0.21 \times 11$  g/cm<sup>3</sup> = 21.25 g

This leaves (72-21.25) g for ribs and wires, i.e., 50.75 g.

## Allocation of grid metal to ribs and wires

The ribs are the main carriers of the charge and discharge currents. They should be made as massive as the economical casting of the thinner wires will permit. In determining the allocation of the available metal, it is preferable to work on the basis of making the pellet size as close to the maximum as possible and make available all the remaining metal for the ribs.

#### Wire numbers and dimensions

If *n* is the number of rows of horizontal wires in the grid, the number of pellets will be (n+1)/2. Initially, ignore the cumulative effect of the average width of the wires (this is unknown at this stage) and take the maximum pellet depth of 1.0 cm as the design factor.

Then,  $(n+1)/2 \times 1.0 = 11.5 - 2 \times 0.2$ , and n = 21

The minimum cross-sectional area of a wire for reasonable casting is  $\sim 0.005$  cm<sup>2</sup>. Take a slightly higher figure to ensure a high casting rate and quality in the first instance, but be prepared to accept the minimum cross-sectional area if the rib sections should subsequently work out to be small in comparison.

approximate length of a row of wires =  $11.5 - 2 \times 0.2 = 11.1$  cm

volume of metal in wires =  $21 \times 11.1 \times 0.006 = 1.3986$  cm<sup>3</sup>

weight of metal in wires =  $1.3986 \times 11 = 15.38$  g

This will provide (50.75 - 15.38) g, for the ribs, i.e., 35.37 g.

The generally accepted shape for wires is a truncated triangle with the truncation heavily radiused or rounded overall. There is a difference of opinion concerning the depth of the wire. Some designers favour a wire of half the grid thickness, whilst others prefer to reduce the thickness so that the tops of the wires are just below the plane of the frame. Both designs give acceptable service performance and life. The former is suited to pasting where the paste is scraped level with the frame of the grid; the multiplicity of wires at the same level as the rest of the grid provide support for the scraper blades, and avoid distortion across the plane of the pasted plate. The latter is better suited to machines where the pasted plate is sized for thickness by trowelling rolls or rigid sizing bars at the outlet of the pasting box.

Take a wire section with the apex of the section 0.01 cm below the plane of the frame. Apex angles between 60 and 90° are suitable angles, although it is not always possible to adhere to these limits, especially in thin grids. Too acute an apex angle results in a cumulative build-up of mould coating in the apex and subsequent loss of the wire section. Too obtuse an apex angle produces a very thin and friable edge to the pellet of active material which readily breaks up with handling.

In thin grids where, to obtain even the minimum cross-sectional area, it is not possible to avoid obtuse-angled wire sections, it is better to introduce a number of solid (full grid thickness) wires to ease casting. Similarly, when the grid thickness is 1 mm or below, it is not uncommon for most of the wires to be of full grid thickness, otherwise casting becomes virtually impossible.

Figure 6 shows two acceptable shapes of wire. The back relief mentioned previously is omitted when calculating the wire dimensions, as this is intended to be filled with mould coating in production.

If  $A_r$  is the cross-sectional area of the wire, then for shape (a) (Fig. 6(a))

$$A_{\rm r} = \frac{b}{2} \left( d - R + \frac{R}{\sin \theta} \right) - \frac{R^2}{\tan \theta} + \frac{180 - \theta}{360} \times \pi R^2$$

where, b is the base dimension, d the depth,  $2\theta$  the apex angle, and R the radius of the top of the wire.



Fig. 6. Two shapes of wire section.

The relationship between the wire cross-sectional area and the wire dimensions is not straightforward as both the base and the apex angle are dependent on each other. Shape (b) (Fig. 6(b)) is simpler to evaluate and the difference in the final dimensions between that arrangement and that of shape (a) is sufficiently small to be ignored. If the wire dimensions are calculated using shape (b), and for ease of machining and subsequent casting a radius is substituted for the radiused flat top, the cross-sectional area will be slightly less than budgetted. As a design area has been chosen in excess of the recommended minimum, no danger exists in adopting the much simpler calculation method.

The relationship between area and the other dimensions in shape (b) will be:

 $A_{\rm r}=0.5(b_1-b_2)\times d$ 

and,

 $2b_1 = A_r/d + d \tan \theta$ 

The boundary condition when there is zero truncation occurs when:

 $\tan \theta = b_1/d$ 

Take shape (b) as an example. The cross-sectional area,  $A_r$ , is 0.006 cm<sup>2</sup> and d=0.095 cm. For the boundary condition with zero truncation:

$$A_r = 0.5b_1 \times d$$

 $b_1 = 2 \times 0.006 / 0.095 = 0.126$  cm

 $\tan \theta = 0.126/0.095$ 

 $2\theta = 67^{\circ}6'$ 

In order to obtain some truncation, the apex angle will need to be less than  $67^{\circ}6'$ . Take an angle of  $60^{\circ}$ .

From the various relationships, the following dimensions are obtained:

base of wire  $b_1 = 0.118$  cm

depth of wire d = 0.095 cm

width of top of wire  $b_2 = 0.016$  cm

The proposed shape is shown, to scale, in Fig. 7.

## Rib numbers and dimensions

Initially, take the recommended maximum pellet size, viz.,  $1.5 \text{ cm} \times 1.0 \text{ cm}$  to determine the number of ribs. The relevant dimension will be 1.5 cm. The inside of the frame will measure between the side frames  $(11.5 - 2 \times 0.2) = 11.1 \text{ cm}$ . This dimension will be divided into (n+1) spaces, where n is the number of ribs. The width of each space will be the pellet width plus the width of each rib. Ignore the unknown rib width initially and divide the inside frame dimension by the maximum pellet length. Thus, the number of ribs=11.1 cm/1.5 cm=7.4.

As there can only be a whole number of ribs, a simple convention is to accept n ribs where the calculated number does not exceed (n+0.25) and (n+1) ribs where the calculated number exceeds (n+0.25). This is a crude approximation, but gives



Fig. 7. Proposed wire shape for grid design example.



reasonable results. On the basis of this convention there will be 8 ribs per grid. The amount of metal available for the ribs has already been fixed at 35.37 g.

An acceptable rib shape is shown in Fig. 8. The ribs are full grid thickness sections binding the top and bottom of the frame. The shape makes allowance for the natural shrinkage on freezing to start the release of the casting from the mould. The length of each rib will be the internal frame dimension, i.e., 11.1 cm. Thus:

volume of rib metal =  $35.37 \text{ g/11} (\text{g/cm}^3) = 3.22 \text{ cm}^3$ 

volume of each rib =  $3.22 \text{ cm}^3/8 = 0.4 \text{ cm}^3$ 

cross-sectional area of rib =  $0.4 \text{ cm}^3/8 = 0.05 \text{ cm}^3$ 

If A is the cross-sectional area of rib, then:

$$A = t(b - 0.5t \tan 20^\circ)$$

or,

 $b = \frac{A}{t} + 0.5t \tan 20^\circ$ 

The dimension b is important for mould cutting since this is the surface dimension of the rib channel. The minimum width dimension will be  $(b-t \tan 20^\circ)$ .

The rib dimensions to give a cross-sectional area of 0.05 cm<sup>3</sup> will be as follows:

depth of rib (grid thickness) = 0.21 cm

maximum width of rib = 0.276 cm

minimum width of rib = 0.20 cm

This rib section is shown, to scale, in Fig. 9.

#### Effect of the choice of specific grid weight on grid thickness

In the 1950s, it was common for automotive grids to have specific grid weights of the order of 8 g/Ah for both positive and negative plates. There was plenty of





#### TABLE 3

Effect of specific grid weight on grid thickness for a given design

Specific grid weight (g/Ah)	Grid thickness (mm)		
5	2.17		
6	2.25		
7	2.33		
8	2.42		
9	2.50		
10	2.58		

scope with such high weights to cover the life penalty of poor surface finishes. This was because small pellets could be used and the greater surface area between active material and grid reduced the oxidizing current density. On the other hand, high grid weights meant thicker grids to support a specified capacity.

Take the grid design example previously examined. Here, the active material weight was 84 g with an apparent density of  $3.6 \text{ g/cm}^3$  in a grid with an overall surface area of 132.5 cm<sup>2</sup>. The alloy adopted was one with 4.5 wt.% Sb with a density of 11 g/cm<sup>3</sup>.

If G g/Ah is the specific grid weight, then:

volume of grid = 
$$\frac{12 \text{ Ah} \times G \text{ g/Ah}}{11 \text{ g/cm}^3}$$

volume of plate (cm<sup>3</sup>) =  $132.5 \times t$ 

where t cm is the grid thickness. It follows that: 132.5t = 12G/11 + volume of active material. Thus, the volume of active material = 132.5t - 1.09G. The volume of active material is also 84 g/3.6 (g/cm<sup>3</sup>), i.e., 23.3 cm<sup>3</sup>. Therefore, 132.5t - 1.09G = 23.3, and t = 0.176 + 0.0082G.

Varying the specific grid weight for the design will produce the grid thickness shown in Table 3 in order to accommodate the specified weight of formed active material.

As well as the extra grid metal arising from a high grid weight, there is a reduction in the electrolyte available for the discharge reaction. This, in turn, leads to a reduction in the capacity and, often, the cold-start performance. There is every incentive to keep the specific grid weight as low as the life requirement will permit. Although the need to maintain a high rated capacity at low rates is subordinated these days to producing a good cold-start performance, there is still a demand for a minimum reserve capacity.

## Grids for motive-power batteries

Motive-power batteries, although modelled to a great extent on automotive batteries, are subjected to regular deep discharges and recharges since this is the nature of the operation of battery-powered vehicles. The effect of regular deep cycling is an increased oxidation corrosion of the positive grid. Consequently, more metal is required per ampere-hour of rated capacity in the positive grid than in the case of automotive batteries.

The amount by which the specific grid weight needs to be increased is dictated by the order of cyclic life expectancy required by the market. Although there are other factors than positive grid corrosion that determine the cycle-life expectancy, the amount of metal in the positive is the most important.

The same basic principle of design applies to motive-power batteries as to automotive batteries, namely, the ultimate failure should be the failure of the positive grid and manufacturing standards should be so set that this, in fact, happens. Under these conditions, the designer can link life expectancy with specific grid weight for the particular alloy chosen.

Whilst it is not possible to give precise relationships between cycle life without involving the operator and process standards, Table 4 provides a broad guide when

Cyclic life expectancy (cycles)	Specific grid weight for positive plate (g/Ah)	
250	6	
500	7	
1000	9	
1500	11 <sup>a</sup>	

TABLE 4Motive-power battery design

<sup>a</sup>Some reduction can be made to this value when short plates are involved.

using a simple lead-antimony alloy with antimony contents from 4.5 to 7 wt.%, and arsenic additions within 0.08 to 0.12 wt.%.

Any increase in the specific grid weight that can be accepted will provide a safety margin against very hard usage and abuse. Whilst it could be argued that any increase in the positive grid metal is an unwelcome cost burden, the general experience with propulsion batteries is that the lightness arising from the use of automotive designs makes them more susceptible to abuse conditions than the heavier traction battery. Indeed, a safety factor on the positive grid metal may be the most economic insurance against undisciplined use.

The minimum guidance specifications are based on an ability to produce grids of a high surface quality economically. Where, for reasons of mould or machine age or uncertain operator skills, high-quality grids cannot be guaranteed and, for productivity reasons, some degree of imperfection on the surface is deemed necessary (particularly on the ribs and frame), some increase on these guidance values is necessary. In these circumstances, as a first approximation, increase the guide figures by 1 g/Ah at least.

The negative grid is not subject to oxidation corrosion unless the battery is so deeply discharged that some cells reverse. This is an abnormal situation and an examination of the active materials would readily confirm that this has happened. The action to be taken is a commercial one with the user. The main requirement for the negative grid is to withstand the pasting stresses without distortion; this is determined by the grid design. There is no technical reason for the specific grid weight of propulsion battery negative grids to be any higher than for automotive batteries, but there is a trend towards values of the order of 6 to 7 g/Ah to ensure that the greater volume changes between charge and discharge are adequately contained.

Motive-power batteries do not have to meet the same high current and low temperature voltage demands as automotive designs. That is, the need to have a large surface area of active material in contact with the electrolyte is not so important. The plate thicknesses can be increased and a lesser number of plates provided per cell of comparable capacity to an automotive element. The grids are thicker; the maximum motor current at the lowest temperature to be encountered will dictate the amount by which the thickness will be increased. Full advantage should be taken of this in design since the manufacturing cost per effective ampere-hour of cell capacity will be less for thick grids than for thin grids.

If the high-production equipment of automotive battery manufacture can be used to produce motive-power batteries equally effectively, then the prime cost (materials and labour) of making motive-power batteries should not be as high as for the automotive product. The danger exists that the design, whilst using many automotive ideas, does not recognize that often the market demand is insufficient to capitalize on the low costs of high-quantity production and the result of using high-production lines does not produce the low level of manufacturing costs envisaged.

The same alloys are used as for conventional automotive batteries. Traditionally, North America has employed 4.5 wt.% Sb and Europe close to 6 wt.% Sb alloys. The minor element additions are of the order of 0.10 wt.% As, 0.04 wt.% Cu and 0.02 wt.% Bi.

Motive-power batteries are used both for industrial and leisure purposes. The need for water additions in industrial applications is a recurring cost burden and any move towards low-maintenance or maintenance-free designs has economic value. Calcium-lead alloys are not fully acceptable for regular deep cycling and this limits the choice of alloy for these improved designs to those with less than 3 wt.% Sb, either as a binary alloy or in combination with such elements as cadmium as a ternary

alloy. Of these, the low antimony alloy is the more proven in cyclic applications. As in the case of the reduced maintenance and maintenance-free automotive batteries, the venting needs to be restricted to limit evaporation losses.

The acceptance of thicker grids in motive-power batteries allows consideration to be given to interlock grid designs in place of the more common surface cut designs. The surface cut moulds are invariably used for automotive grids since the horizontal wires are usually close to the minimum cross-sectional area for economic casting and nothing is gained by attempting to create an interlock mould design. The surface cut moulds are the simplest moulds to machine since the rib and wire profiles are cut into the mould surface and the mould blocks mate face to face in the casting operation. When the mould wears or the blocks warp with successive heating and cooling, it is relatively easy to true the mating faces and to use the existing channels as templates for correcting the frame, ribs and wires. Small changes in grid thickness that arise from minor redesigns can be obtained in the same way as for trueing the mould without incurring total mould cutting costs.

There is a limit to the ratio of active material to grid metal that can be achieved with a surface cut mould. The interlock mould eases this restriction. The interlock design was popular some twenty years ago but fell into disuse with many companies following reductions in the thicknesses of automotive grids. The amount of metal that could be allocated to the wires was inadequate. The difference between surface cut and interlock moulds is shown in Fig. 10.

The criticism levelled at interlock moulds was based on the need to skim off the top surface of the mould and engage in a complete re-cut if the mould blocks warped or a minor change was needed to the grid members. They were more expensive to produce. Both these factors added to their falling popularity although, with thicker grids, they have definite advantages for negatives when allocating the available grid metal to the respective areas of the grid. Savings in weight can be achieved in grids of thickness 3.5 mm or more. Below this lower thickness, however, it is difficult to justify the greater expense.

The same routine as for automotive grids design is applicable to motive-power grids with the following exceptions. The motive-power grid is subject to greater grid corrosion than the equivalent automotive grid as the battery is required to withstand regular deep discharging. As the wires are converted into lead dioxide and merge with the positive active materials, the grid structure becomes a rectangular structure with vertical ribs. The expanding active material on discharge will experience a reducing lateral restraint that, in time, will tend to cause the side frames to bow outwards at the mid-points. The effect of this distortion is to provide more space for the active material and cause a reduction in the formed density and a loss of the essential particle-to-particle conduction and adhesion. The result can be a loss of capacity and early shedding from the material.

It is advantageous to provide a number of full thickness horizontal ribs to tie the two side frames together and to restrain the distortion and bowing. The number of horizontal ribs provided will depend on the height of the plate. An approximate guide would be to limit the distance between restraining horizontal ribs to a maximum of 10 cm.

There are batteries designed for starting large diesel engines for vehicle propulsion or for stationary diesel engines that use many of the components common to motivepower batteries, including containers and lids. These batteries are not subjected to regular deep discharging and are usually maintained in a float condition across a constant voltage supply. This type of application is similar to automotive battery usage



Fig. 10. Part sections of (a) interlock, and (b) surface cut moulds.

and it could realistically be argued that they could be designed with automotive grids or grids conforming to automotive battery specific grid weights. These batteries are often subjected to gross overcharge and this increases the degree of oxidation corrosion of the positive grid metal. It is prudent to adopt higher grid weights than for automotive grids and to treat the positive grid as close to a traction grid as far as the specific grid weight is concerned.

#### Choice of grid alloy

There are two distinct forms of traction battery, the 'pasted-plate' type using flat, lattice grids for both positive and negative plates and the 'tubular' positive type using a flat, lattice grid for the negative plate and a grid for the positive that comprises a top bar and a series of cylindrical spines attached to the top bar. The tubular positive grid is usually pressure die-cast in preference to gravity cast.

Table 5 lists some of the alloys used in the industry defined in terms of the main alloying agents, antimony and arsenic. There are tin, copper and bismuth components and these follow the same pattern as for automotive grid alloys with the exception of one alloy which uses 0.1 wt.% Sn.

## TABLE 5

Grid type	Casting method	Main alloying a	Maker	
51-	momou	Antimony (wt.%)	Arsenic (wt.%)	Tototototo
Positive	Machine	11.5	0.170	1
	Machine	11.3	0.130	2
	Machine	11.2	0.200	3
	Machine	11.1	0.001	4
	Machine	10.0	0.005	5
	Machine	9.0	0.120	6
	Hand	8.5	0.120	7
	Hand	7.0	0.140	8
	Hand	6.5	0.35-0.45	9
	Machine	3.5	0.180	10
Negative	Machine	10.0	0.005	Α
	Machine	9.0	0.120	В
	Machine	7.0	0.160	С
	Machine	6.5	0.180	D
	Hand	6.0	trace	Ε
	Machine	3.5	0.180	F

Grid alloys used for motive-power batteries

The choice of negative grid alloy is an economic one that is determined by the skill of the operators in the casting process and the setting of the pasting machines. Any of the alloys listed will produce grids rigid enough to withstand the pasting machine stresses without distortion if sufficient time is allowed for age-hardening to develop fully. The low-antimony alloy demands greater casting skill and the adoption of machines with automatic temperature control at the furnace, the ladle and in the mould gate. Also, the moulds have to be controlled over the whole surface of the blocks in order to limit the temperature differential from top to bottom of the cavity.

The choice of positive alloy is not so straightforward as the corrosion life of the grid is a dominant factor. This depends not only on the nature of the alloy but on the ability of both the alloy and the casting machine to produce grids of high surface quality at an economic cost. Positive grid life is a function of the corrosion characteristics of the alloy as modified by the presence or otherwise of corrosion stress points in the castings. These stress points arise from the presence of: antimony-rich areas at crystal boundaries; surface blemishes; fine hair-line cracks; porous regions; dross inclusions; short runs; areas of sinkage, and added mechanical stressing from handling or mishandling subsequent to removal from the casting machine. All such factors can initiate premature corrosion life with sometimes an unacceptable level of early failures of cells in service. In addition, there are limitations in pressure die-casting machines to the casting of some alloys and, to take advantage of the lower material cost and greater corrosion resistance of the low-antimony alloys, the type of machine purchased may have to be more complex and expensive than some makers are prepared to accept.

All the above features raise a conflict between the technical and commercial interests within a firm. In general, it is fair to say that a greater emphasis should be placed on the production of a very high standard of surface finish consistently in the

castings with an even crystal structure that is relatively free from antimony-rich areas, rather than on the search for highly corrosion resistant alloys with difficult casting characteristics and poor productivity.

It has been amply demonstrated over more than twenty years that an acceptable traction cell life can be obtained by using grid alloys with an antimony content within the range of 7 to 11.5 wt.% and with appropriate arsenic additions to assist rapid age-hardening. With high quality casting machines, however, this can be reduced to at least 4 wt.% Sb, but there is a greater operator skill involved.

The modes by which positive grid corrosion can promote cell failure have been studied extensively. It appears that the corrosion pattern is one initially of interdendritic corrosion, but this changes to intergranular corrosion later in life. If the intergranular corrosion starts when the battery is relatively new, then there is a high probability that it will fail prematurely as the attack, once started, appears to proceed more rapidly than the interdendritic mechanism. Intergranular attack seems commonest at sites in the grid lattice near to the intersection of grid members or near heavy sections of the grid. This suggests that the condition under which the alloy freezes is the key to its occurrence. Such a conclusion is supported by evidence that in intergranular corrosion of lead–antimony alloys the corrosion product usually contains regions of unoxidized antimony. The presence of fissures or porous areas on the surface of grids cast in a non-eutectic alloy, as well as fine, hair-line cracks not readily visible to the naked eye, provide sites for intergranular corrosion. Non-eutectic alloys are prone to antimony-rich areas at the grain boundaries and these constitute other corrosion sites.

The use of an eutectic alloy minimizes the above problems as the antimony is in true solid solution. With this alloy there is a minimum concentration of antimony at the grain boundaries and there is no significant liquidus/solidus cooling phase. As a result, the casting is generally more perfect, the crystal structure more uniform than in a non-eutectic alloy and, consequently, intergranular corrosion is rare even though the absolute rate of corrosion under ideal conditions may be greater than for a noncutcetic alloy of lower antimony content. The eutectic alloy is, however, more expensive.

The objective in grid casting is to maintain the mould temperature constant both from one cast to the next and throughout the working shift. The temperature of the mould, particularly the moving half, depends on the external heating source plus the heat transferred from the molten metal poured into the mould. The slower the rate of casting the wider will be the fluctuations in the mould temperature and the more variable will be the characteristics of the grids. With the eutectic alloy, a lower melt temperature is required and the heat input from the metal to the mould is less than with a non-eutectic alloy. Freezing is rapid as there is no pasty stage in cooling and the casting rate can be increased. Increased casting rates further lower the heat transference from the metal to the mould, and ease the control of both the temperature and the grid quality.

Some makers have stayed with the eutectic alloy even though the material cost is higher than for alloys with less antimony. The effect of increased casting rates, lower reject levels and lower level of premature cell failure in the field contrive to make the use of the more costly alloy reasonably economic. Nevertheless, the introduction of fully instrumented and temperature-controlled casting machines that are capable of casting heavy grids has made this situation less viable. With such machines, high surfaces quality grids can be cast consistently and economically using low-antimony alloys. In summary, the choice of alloy is primarily one based on the casting conditions. If these cannot be guaranteed, then the evidence indicates the wisest choice is probably an alloy close to the eutectic for flat, lattice grids. The production of 'tubular' types of positive grid is limited by the casting method employed by most makers, i.e., pressure die-casting. Quality casting becomes progressively more difficult as the antimony content is reduced below 8.5 wt.%. Even at this level, the metal is difficult to inject into the mould without producing either rebound ripples due to the pressure needed for injection, or 'piping' in which the metal conforms to the outside of the mould cavity but does not fill the cavity completely. The crystal structure can vary considerably over the length of the casting and this results in variable corrosion. Also, the surface can have blemishes that are active sites for intergranular corrosion.

The use of polished dies, negative mould pressure when injecting the molten metal, and well-controlled temperatures over the full length of the moulds as well as in the melt, all assist the fill. With these aids, it has been possible to reduce the antimony content to around 3 wt.%.

There are a few companies who have first studied the alloy, and then installed an appropriate casting process. In one example, a manufacturer chose a system from the range of high arsenic 'Metallex' alloys (6.5 wt.% Sb, 0.35 to 0.45 wt.% As) and adopted gravity casting. The molten metal was fed into the base of the mould in which was situated the top bar and lug, and the entrapped air was scavenged out of the mould by the rising molten alloy. The spines were cast longer than the plate in order to accommodate the dross within the excess.

When using pressure die-cast machines, one difficulty that arises from the use of high pressures and below-eutectic antimony levels is the production of flashings whenever there is warping in the mould blocks. Whilst it is not difficult in most cases to fettle the castings, the danger exists of surface damage to the metal and the setting up of corrosion sites. The objective in pressure die casting is to produce economically flashfree castings with as good a surface finish as possible. Fettling is an extra operation that adds to the cost and possibly causes an increase in the reject rate.

The lattice-type negative grids to match the tubular positives need not have any higher specific grid weight than automotive negative grids in the short sizes, and only a nominal increase in weight for larger sizes in order to provide rigidity for handling. Specific grid weights of 6 g/Ah are feasible, even though the wire sections are small. This may give some operator problems. The criterion of what should be the specific grid weight for a given design should be that which, after allowing for scrap losses, gives the minimum manufacturing cost.

#### Design of lattice-type grids

The design of lattice-type traction grids is basically the same as for automotive grids, except that in positive grids the active material must be retained within the grid despite the fact that the bulk of the horizontal wires have been converted to lead dioxide and have merged with the actual active material. There are two broad designs in common use that meet this criterion and still retain the rigidity of the grid frame and the active material within the grid structure. North America favours an open lattice where ribs and wires are approximately the same size and a limited number of thin wires of half the grid thickness may be included. The latter wires assist pasting. In the open lattice designs, the pellets are large with a maximum size of  $3.75 \text{ cm} \times 1.75 \text{ cm}$ . The active material is supported by glass filament retainer mats that are held tightly against the material. One very successful design uses a laminated retainer mat. This consists of a thin, closely laid, fine filament mat that is located immediately against the active material and is held in place by a coarse filament mat

with a more open lay. The fine mat immobilizes the active material but has a poor electrolyte to glass volume ratio. By contrast, the outer open mat has poorer materialimmobilization properties, but a much greater electrolyte to glass volume ratio. Space is provided within the open mat for the essential reservoir of electrolyte adjacent to the positive material to secure the maximum usage of that material in the discharge.

The more open coarse filaments give resilience to the retainer mat and to the cell assembly so that it can accept more readily the volume changes that occur within the cell during charge and discharge without relaxing the support to the positive active material. This support is essential for a consistently long cycle life.

The alternative design – common in Europe – follows more closely the conventional lattice grid and uses horizontal wires of half grid thickness, together with solid vertical ribs with solid horizontal bars interposed at intervals so that, when the half-section wires are heavily converted into lead dioxide, the positive active material is still enclosed within a series of large frames formed by the intersection of the ribs and the horizontal bars. These frames are larger than the pellets of the North American designs since, by time the half-section wires have been heavily oxidized, the glass filament retainer mats have embedded into the surface of the active material and immobilized that material. The success of this design depends more on the shop-floor control of plate and retainer mat dimensions to ensure that the positive material is truly supported at all times, than on the North American design.

There are designs that do not provide the series of horizontal bars and reproduce a scaled-up version of automotive grids with, possibly, a few solid wires to act as stiffening and pasting bars to prevent distortion during pasting. These designs rely very much on high surface quality and close dimensional control being maintained at all times to restrain oxidation corrosion and to ensure that the cell assembly is always tight within the cell container. Without this strict shop-floor control, it is difficult to guarantee a good cell life under onerous, but not unfair, working conditions.

The main problem with the large-pellet grid design stems from the relatively massive sections of the grid members where, without maintaining a high casting technique, there are dangers of sinkage, fine cracks and a coarse crystal structure forming at the intersections of the ribs and the horizontal solid wires. The compromise design with the large frame bridged with half-section wires is probably the easier to handle in bulk production with a lower incidence of sinkages, cracks and coarse crystals.

In automotive grids, the thickness is mainly dictated by what minimum surface area will give the rated cold-start current modified, possibly, to give satisfactory pasting without distortion. The pitch of the plates is of less importance. With traction batteries, the pitch of the plates has already been decided by the market leaders as well as the minimum capacities within defined dimensions. The grid design must ensure there is sufficient active material to support the full discharge capacity, as well as adequate electrolyte. The grid thickness is not fixed by common design, but by the volume of active material the grid has to contain and, because of this, there is a large variation in grid thicknesses between makers but the pitch is standardized. This puts a responsibility on the designer to keep the specific grid weight as low as it is consistent with attaining the minimum specified life under the worst accepted conditions in order to provide the maximum volume for electrolyte.

## Choice of specific grid weights

Most motive-power cell designs cover a range of plate heights with a common pitch. This calls for a common thickness for the positives and another common thickness for all negatives. Without this specification, assembly would require a multiplicity of jigs and fixtures and an enlarged stock inventory.

There are opposing requirements to be reconciled if a common thickness is to be adopted for all grids of the same polarity, irrespective of plate length. If the frame sections are to be the same for all grid lengths, the specific grid weight of the shorter grids will be greater than for the longer grids. If the cross section of the frame is based on the minimum to allow the longest to pass under the pasting hopper without distortion, the shortest plates could be unduly expensive and strong.

The selling price of motive-power batteries tends to be based on the rated capacity and reflects a constant price per ampere-hour of rated capacity irrespective of plate length. The labour content in the manufacture of a cell is approximately proportional to the number of plates in the cell. A cell with a few tall plates enjoys a selling advantage over the same capacity cell with a larger number of shorter plates. To reduce this disparity, the specific grid weight of shorter grids should be less than for long grids. This is a classic example where the need to improve margin earnings compromises the elegance of proportional design.

An approximate guide to design is to take a specific grid weight of 10 g/Ah (5-h rate) for flat-plate positive grids not longer than 150 mm to meet a nominal fouryear life with discharging 80% of rated capacity on each discharge. This presupposes the casting quality is consistently good. Longer plates are often pasted transversely to improve productivity and this leads to distortion, particularly at the centre of the grid where the frame is weakest. For this reason, the specific grid weight may need to be increased and a value of 11 g/Ah is suggested for plates up to 400 mm in length. Wherever long grids are pasted longitudinally, the mechanical stresses are less and some small reductions can be considered to the values suggested.

Where there are difficulties in casting regularly to a high surface quality, a safety factor is needed to the above values and, in cases of doubt, an increase of 1 g/Ah is recommended.

Negative grids provide opportunities to economize on metal although consideration must be given to the pasting stresses before settling on the specific grid weight for design. The frame width should be very similar to that for the matching positive grids, but as the grid strength is maintained throughout the full life of the battery, the frame strength needs only to be sufficient to cope with pasting. The number of horizontal tie members must only be just sufficient to withstand the regular expansion and contraction of the active material during cycling. As the active materials are approximately 50% porous, they tend to give in preference to the grid members.

Taking all these points into consideration, adequate grids for a nominal four-year life under onerous, but not unfair, usage can be designed on the basis of a specific grid weight of 6 g/Ah for plates up to 150 mm in length increasing to 6.5 g/Ah for plates of 300 mm length. These figures provide the basis of a proportionality between specific grid weight and grid length which will provide adequate grids for processing and subsequent handling, even when greatly in excess of 400 mm in length. This proportionality is shown in Fig. 11. Any decrease in the values brings in a risk of reduced casting rates and higher scrap levels, both of which increase the labour content of the manufacturing cost and offset any saving in the material cost. The possibility of making some small decrease should not be dismissed since the design objective should be to optimize the cost of manufacture, rather than to produce the most elegant design on paper.

To illustrate the effect on design of differing specific grid weights, consider a grid measuring 22.9 cm $\times$  13.8 cm (excluding the lug) required to accept 525 g of active



Fig. 11. Suggested relationship between specific grid weight and grid length. Recommended minimum design figures.

#### TABLE 6

Effect of specific grid weight on grid design

Specific grid weight (g/Ah)	Grid weight (g)	Grid volume (cm <sup>3</sup> )	Grid thickness (mm)
10	320	29.63	4.35
11	352	32.59	4.44
12	384	35.56	4.54
13	416	38.52	4.63

material in the wet paste form with a paste density of 4.6 g/cm<sup>3</sup> (76 g/in<sup>3</sup>). The standard practice is to overpaste the grid by 0.02 cm. Assume that the capacity required is 32 Ah per plate, then the volume of wet paste = 525 g/4.6 (g/cm<sup>3</sup>) = 114.1 cm<sup>3</sup>. Let t cm be the thickness of the grid giving a finished plate thickness of (t+0.02) cm, then

overall plate volume = 22.9 cm × 13.8 cm × (t + 0.02) cm = 316.02t + 6.32 cm<sup>3</sup>

Depending on the specific grid weight chosen, the grid weights will be as shown in Table 6. The alloy used for the grids is assumed to be one with 7 wt.% Sb with a density of  $10.8 \text{ g/cm}^3$ .

grid volume = plate volume - wet paste volume

= 316.02t + 6.32 - 114.1 cm<sup>3</sup> = 316.02t - 107.8 cm<sup>3</sup>

Substituting, in turn, the grid volume relevant to each specific grid weight, the grid thicknesses listed in Table 6 are obtained.

## Frame dimensions

The main requirements for the frame are:

(i) sufficient material to provide adequate frame strength in a positive grid, after the minimum acceptable service life, to withstand the expansion and contraction of the active materials and to maintain a good electrical contact between the active material and the grid members, and

(ii) sufficient rigidity to withstand the processing and subsequent handling.

Requirement (ii) is usually the more onerous and it demands a greater cross section than requirement (i). This leads to a similarity in frame dimensions for positive and negative grids. The main differences occur in the cross section of the ribs and the horizontal wires.

The rate of oxidation of the positive grid depends very much on the perfection of the casting surface and the conditions of use. The former is as important as the alloy composition.

With cells operating at temperatures between 30 and 40 °C, and regularly discharging 80% of rated capacity on each discharge, a reasonable design guide is to take an oxidation corrosion rate of 0.3 mm per year in the absence of reliable data. This value is representative of most alloys provided the castings are free from surface porosity, hair-line cracks, pinholes and dross inclusions. In order to maintain an adequate strength towards the end of life, sufficient metal must be present to hold the frame together. A reasonable figure for the minimum residual dimension is 2 mm, so that the frame width for a four-year life under the operating conditions stated would be:

## frame width = $(4 \text{ year} \times 0.3 \text{ mm/year}) + 2 \text{ mm} = 3.2 \text{ mm}$

This minimum frame width would have to be increased if, in the pasting operation, it was found there were too high damage figures from pasting or subsequent operations. Thickness has a bearing on the minimum frame width that can be accepted but, within the order of grid thicknesses commonly met in practice, the above provides a reasonable starting point for design.

The greatest stressing in subsequent processing usually occurs in the area of the lug. There are several ways of easing this stress; the following are two:

(i) increase the length of the lug so that the element, when assembled, can take up a relaxed attitude that is unaffected by differences between the dimension of the strap-to-lug fusion and the space allowed for the assembly of plates in the actual container, so that any stresses are confined to the lug itself, and

(ii) increase the cross section of the top bar of the frame in the neighbourhood of the lug, especially at the root of the lug.

Of these two arrangements, the first is preferable as it does not add to the grid weight and gives a much desired resilience to the cell element assembly.

The cast grid is produced with a sprue that is cut off, or trimmed, as part of the casting operation. The usual method is to guillotine along the 'pour' side of the casting at a side frame. With relatively thick grids, there is a risk that the metal may tear along the cut side. This, in turn, may produce visible surface blemishes, as well as internal blemishes such as minute holes at zones of coarse crystals particularly where horizontal wires meet the solid frame and differential cooling occurs. These revealed imperfections are ideal corrosion sites and it is common for the rate of oxidation corrosion at such points to be many times that for the remainder of the casting. This often results in the corrosion product cracking the frame and degrading the active-material/grid conductivity. The ultimate life of the cell is adversely affected if the cutting is not clean and free from these corrosion sites. Some manufacturers substitute a power saw for the guillotine knife. The grid is presented to the saw after it leaves the mould. The 'pour' side is forward and held stationary whilst the saw travels across the grid. This method tends to slow down the casting rate, but through careful choice of the type of saw, less edge damage is produced.

In order to take advantage of the simplicity of a guillotine action and to recognize that, even with the best of control intentions, the guillotine blades will not be removed frequently enough for sharpening to minimize tearing of the cut edge, it is helpful to reduce the cross section of the mould gate so that the sprue section adjacent to the side frame is as thin as consistent filling of the mould will permit. Usually, this results in the mould gate being cut into one half of the mould only.

The effect of this action is to reduce the loading on the guillotine blade and to reduce the area of the cut edge and the amount of internal blemishes uncovered by the cut. The restricted mould gate area also has the effect of increasing the velocity of the molten alloy as it enters the cavity and helps the fill, but it does reduce the escape of the entrapped air in the mould. The castellation of the mould gate and the provision of air slots in the mould ease this problem.

The need to avoid tearing the guillotined side frame is not important in negative grids, provided the imperfections are small and widely spaced. Furthermore, there is no need to complicate casting in the manner described above for positives. This leads to a difference in the cut side frame cross section as shown in Fig. 12.

#### Large pellet positive grid

The experience over the years with large pellet, solid member grids has been that the maximum pellet size can be as much as  $3.75 \text{ cm} \times 1.75 \text{ cm}$ , provided the active material is well supported by a generous glass retainer mat assembled so that it is always under compression. The maximum dimensions of pellets are essentially limiting values. Therefore, it is generally better to adjust the dimensions marginally downwards so that the dimensions are fully divisible into the internal frame dimensions. This gives a symmetrical grid design that does not suffer from differential filling rates across the grid lattice structure during the casting operation. The risk of incomplete filling and air entrapment is also reduced.

The recommended routine of design is, first, to establish the grid thickness using the chosen specific grid weight and the amount of wet paste that has to be contained within the grid. Having established the grid thickness, decide on the frame thickness



Fig. 12. Trimming differences between positive and negative frame sections.

that is necessary to (i) meet the guaranteed life using the empirical formula, if no better data are available, or (ii) to withstand the pasting machine stresses, whichever is the greater.

Next, the cross section of the side, top and bottom frames is calculated. A chamfer of 15 to 20° must be allowed on the inner and outer frame surfaces excluding the 'pour' side where the sprue will be located and where trimming occurs. On this surface, the chamfer is located in one mould block to limit tearing during the trimming operation. The chamfers assist the freezing casting to ease itself from the mould for ejection. From the calculated areas of each frame section and the length and width of the grid, the amount of alloy in the grid frame is determined. This amount is deducted from the total weight of the grid, i.e., the product of specific grid weight and desired capacity, and the remainder is the amount of metal available for the ribs and solid wires.

The total length of the solid wires and the ribs is determined. The volume of metal that remains after deducting the frame volume is divided by the total length of the ribs and the wires. The result is the average cross-sectional area of the solid ribs and wires. This arrangement will give the least problems for casting without appreciable shrinkage at the intersections of the ribs and wires.

The average cross-sectional area has now to be established. It is based on the general shape adopted for automotive grids, see Fig. 8. It is helpful to introduce small radii both at the intersections of the solid ribs and wires, and where the ribs and wires join the frame. This assists the flow of the metal and reduces the risk of hair-line cracks at the intersection.

The sections of the ribs and wires are checked against the empirical formula of 0.3 mm per year corrosion conversion into lead dioxide plus a small residual core of solid metal. The ribs and wires are not required to withstand the same stresses as the frames. Thus, the 2 mm value for residual metal previously stated can be reduced to 1 mm for ribs and wires. It must always be realized that the values are essentially guidelines and cannot be taken as firm data. Wherever possible, more accurate data relevant to the actual alloy and casting conditions should be established.

To illustrate the above procedure, consider a positive grid of dimensions 22.9 cm  $\times$  13.8 cm to be cast in an alloy containing 7 wt.% Sb and with a specific grid weight of 10 g/Ah. The plate is required to deliver within the first five cycles a capacity of 32 Ah and will contain 525 g of wet paste of density 4.6 g/cm<sup>3</sup> (76 g/in<sup>3</sup>). The grid is overpasted by 0.02 cm. If t cm is the thickness of the grid, the thickness of the pasted plate will be (t+0.02) cm. It then follows that:

volume of pasted plate =  $22.9 \times 13.8 \times (t + 0.02)$  cm<sup>3</sup>

volume of grid =  $1.1 \times 10$  (g/Ah)  $\times 32$  Ah  $\times 1/10.81$  (g/cm<sup>3</sup>) = 32.6 cm<sup>3</sup>

A factor of 1.1 has been introduced since, in order to deliver the full rated capacity of 32 Ah within the first five cycles, the cell has to be capable of providing a higher capacity when the capacity has been fully developed. For this reason, the designed capacity is increased from 32 to 35.2 Ah:

volume of wet paste = 525 g/4.6  $(g/cm^3) = 114.1 cm^3$ 

volume of pasted plate = volume of grid + volume of paste

 $= 22.9 \times 13.8 \times (t + 0.02) = 352/10.81 + 114.1$ 

t = 0.444 cm

Thus, it is appropriate to take a grid thickness of 0.45 cm. The average frame width will be  $(4 \times 0.3) + 2 = 3.2$  mm for a four-year life. Take a frame with the shape shown in Fig. 12. Then:

cross-sectional area of 'pour' side

 $=(0.45 \times 0.32) + 5/2[(0.45/2) \times (0.45 \tan 15^{\circ})/2] = 0.178 \text{ cm}^2$ 

cross-sectional area of side, top and bottom frames

 $=(0.45 \times 0.32) + 4/2[(0.45/2) \times (0.45 \tan 15^{\circ})/2] = 0.171 \text{ cm}^2$ 

length of side frame = 22.9 cm

length of top frame =  $13.8 - (2 \times 0.32) = 13.16$  cm

length of bottom frame = 13.16 cm

total volume of frame =  $(22.9 \times 0.178) + (49.22 \times 0.171) = 12.49 \text{ cm}^3$ 

In these calculations a chamfer angle of 15° has been used:

volume of grid = 32.56 cm<sup>3</sup>

volume of frame =  $12.49 \text{ cm}^3$ 

volume available for ribs and wires = 32.56 - 12.49 = 20.07 cm<sup>3</sup>

This volume has now to be shared between the ribs and the wires. Initially, take the maximum pellet size of  $3.75 \text{ cm} \times 1.75 \text{ cm}$ , and ignore the width of the ribs and wires. The number of horizontal wires will be one less than the number of horizontal pellets.

Approximate number of horizontal pellets =  $\frac{\text{internal frame width}}{\text{pellet width}}$ 

 $=\frac{13.8-(2\times0.32)}{1.75}=7.52$ 

Thus, take 8 pellets horizontally, then:

approximate number of vertical pellets =  $\frac{\text{internal frame height}}{\text{pellet height}}$ 

$$=\frac{22.9-(2\times0.32)}{3.75}=5.94$$

Thus, take 6 pellets vertically. This arrangement will give 5 ribs and 7 wires of equal cross-sectional area.

The next step is to determine the total length of the ribs and the wires. If the full distance between the top and the bottom frames is taken for the rib length, then the effective wire length across the grid will be the distance between the side frames less 7 times the average rib width.

Let t cm be the average rib and wire width. Then:

length of a solid rib =  $22.9 - (2 \times 0.32) = 22.26$  cm

length of a row of solid wires =  $13.8 - (2 \times 0.32) - 7t$  cm

cross-sectional area of a rib or wire =  $0.45 \times t$  cm

total length of ribs and wires = 7(22.26) + 5(13.16 - 7t) cm = 221.62 - 35t cm

total volume of ribs and wires = 0.45t(221.62 - 35t) cm<sup>3</sup>

This volume must equal the volume available for ribs and wires, 20.07 cm<sup>3</sup>, i.e., 0.45t(221.62-35t)=20.07, which gives: t=6.12 or 0.21 cm. The larger value is inadmissible. Thus, the average rib and wire width is 0.21 cm.

Allowing a release angle of 15° to the rib or wire section, the width dimension at the surface of the rib or wire will be:

 $0.21 - (0.45/2) \tan 15^\circ = 0.15 \text{ cm}$ 

The average rib width is checked against the guide value of 0.03 cm per year plus 0.1 cm residual. This would give a guide value of 0.22 cm for the average width. Although the calculated value is less than the guide value it is very close and, in this instance, can be accepted. If, however, the calculated value is less than the guide value by 5% or more, then the guide value should be taken and the volume of metal needed to give the higher width figure determined. This should be added to the frame metal and a new grid weight obtained.

Figure 13 shows a part view of a grid that conforms to the above dimensions. The pellet size will be  $3.5 \text{ cm} \times 1.5 \text{ cm}$ .

Some manufacturers find that the addition of half-wires within a large pellet helps in the pasting and subsequent pellet retention prior to cell assembly. The addition of the half-wires will reduce the amount of metal in the solid ribs and wires if the same grid weight is maintained and, therefore, will decrease the cross section. The size of the half-wire section need not be larger than would be required to ensure full wires in the casting, even though they may relatively soon be converted to lead dioxide in service. Typical arrangements of these modified large-pellet grids are shown in Fig. 14.

#### Composite positive grids

This type of grid is a compromise between the large pellet grid with equal solid ribs and wires and the common lattice grid with solid ribs and half-section wires typical of automotive grids. In the composite design, the grid metal previously shared between



Fig. 13. View of solid rib and wire grid with large pellets.



Fig. 14. Views of modified large pellet grids: (a) modified large pellet grid with horizontal wires; (b) modified large pellet grid with vertical wires.

solid ribs and wires is now shared between solid ribs and a few solid wires with a larger number of half-wires. The solid wires form the boundaries of very large pellets when the half-wires have been converted into lead dioxide during battery service. Experience has shown that if a generous glass filament retainer mat is always kept in compression against the positive active material, the increase in the volume of the active material as the half-wires are converted into lead dioxide will maintain the essential contact between the grid members and the active material, even though the ultimate large pellet reaches dimensions as large as 10 cm  $\times 1.75$  cm. This presupposes that there is: (i) sufficient metal left in the solid members at the end of the guaranteed life to resist fracture from the expanding and contracting active material, and (ii) sufficient strength in the grid structure to resist deformation. These are dependent on the dimensions of the solid ribs and wires. By time the half-wires have been converted into lead dioxide, the glass filaments are firmly embedded into the active material. The only noticeable effect of the loss of the half wires is usually a slight reduction in the discharge voltage at the 0.5-h rate.

The minimum cross-sectional area of automotive grid wires was stated to be  $0.005 \text{ cm}^2$ . This is acceptable since automotive grids are not often required to withstand regular cycles of discharge and charge over several years. In traction grids, the criterion of minimum cross-sectional area is better set at  $0.01 \text{ cm}^2$  to maintain metal in the half-wires for at least three-quarters of the guaranteed life. The initial pellet size will be smaller than for large pellet grids as the conducting members will have a higher resistance than the solid wires and more are needed to produce the same overall conduction. A maximum pellet size of  $1.75 \text{ cm} \times 1.75 \text{ cm}$  is suggested.

Consider the same grid as in the previous example, i.e., a grid with dimensions 22.9 cm  $\times$  13.8 cm  $\times$  0.45 cm to develop 32 Ah within the first five cycles, to contain 525 g of wet paste, and to meet a four-year guaranteed life. The frame size will also be the same and, therefore, will leave 20.07 cm<sup>3</sup> for the ribs and the wires.

The number of ribs and wires is determined using the procedure outlined above. As the pellet width is the same as before, the number or ribs will be the same, i.e., 7 ribs. The number of solid and half-wires will be one less than the distance between the top and bottom frames divided by half the length of a pellet. Thus:

approximate number of solid and half-wires =  $\frac{22.9 - (2 \times 0.32)}{0.5 \times 1.75}$  -1=24.4 i.e., 25 wires

If the maximum distance between solid wires is to be 10 cm, then:

number of solid wires = 
$$\frac{22.9 - (2 \times 0.32)}{10} - 1 = 1.26$$
 i.e., 2 solid wires

In order to obtain a symmetrical arrangement of solid wires to assist casting and the flow of metal into the mould cavity, the number of sections containing half-wires is 3 and the number of half-wires should be divisible by 3. This would require either 21 or 24 half-wires instead of the 23 half-wires from the calculation. Take the higher number of 24 half-wires, 8 in each section bounded by solid wires.

Initially, take the same cross section for the ribs and solid wires as for the previous example, i.e., an average width of 0.21 cm with a minimum width of 0.15 cm, a depth of 0.45 cm, and release angles of 15°. It follows that:

length of rib = 22.26 cm

length of a row of wires =  $(13.8 - 0.64) - (7 \times 0.21) = 11.69$  cm

total length of 7 ribs and 2 solid wires =  $(7 \times 22.26) + (2 \times 11.69) = 179.2$  cm

volume of ribs and solid wires =  $179.2 \times 0.45 \times 0.21 = 16.93$  cm<sup>3</sup>

volume of half-wires = 20.07 - 16.93 = 3.14 cm<sup>3</sup>

total length of 24 half-wires =  $24 \times 11.69$  cm

cross-sectional area of half-wire =  $3.14/24 \times 11.69 = 0.011$  cm<sup>2</sup>

There is general agreement that a reduction in the rate of oxidation corrosion of the half-wires is achieved if the half-wires are completely covered by active material. Consequently, it is common for the tops of the half-wires to be set below the surface of the finished pasted plate. With the half-wire set 0.025 cm below the plane of the plate, the height of the half-wire would become 0.2 cm. Thus:

average width of wire = 0.011/0.2 = 0.055 cm

Taking a triangular section with a radius at the apex, the base dimension would be 0.1 cm with an apex dimension of 0.01 cm. Therefore:

apex angle =  $2 \tan^{-1}(0.05/0.2) = 28^{\circ}$ 

This apex angle is too acute for reasonable casting and arises through the grid being 0.45 cm thick. The move from the simple large pellet grid to the compromise design has made it more expensive in metal to meet minimum oxidation and casting guidelines.

For thick grids, a minimum apex angle of  $40^{\circ}$  is more realistic. Taking the same half-wire depth of 0.2 cm and an apex angle of  $40^{\circ}$ , a half-wire section triangular in shape and with a base dimension of 0.145 cm can be obtained allowing for the apex to be radiused. This section will have an area of 0.145 cm<sup>2</sup>. This is well above the

minimum for easy casting. Nevertheless, the grid weight will be increased by 10.8 g and will raise the specific grid weight from 10 to 10.3 g/Ah.

The arrangement of solid and half-wires in a composite grid is shown in Fig. 15. In the foregoing, the corrosion guideline of 0.3 mm per year has been adopted irrespective of the grid thickness. It could justifiably be argued that this should only apply to one grid thickness. The rough figure generally applies to grids of about 3.5 to 4 mm thick. A reduction could be considered for thicker grids if the maximum saving in grid metal is vital. In such cases, the cross-sectional area proportionality should be adopted to arrive at the new corrosion value for design.

The adoption of lower antimony content alloys will reduce the corrosion rate. It should be recognized, however, that the lower antimony alloy grid is softer. This could present a pasting problem with reduced sections.

#### Simple lattice-type grids

In these grids the half-wires, constituting all the horizontal members, need to be able to outlast the full service life and should be of greater section than for the other grid designs. As a guide, the average wire width should approach the dimension 0.3 n mm, where n is the guaranteed life. The method of calculating the dimensions of the various grid members follows the same pattern as for the automotive grid worked out above.

It is often helpful in long grids to insert a solid wire at intervals, particularly where the grids are pasted transversely. These solid wires are often referred to as pasting bars and generally have a cross-sectional area that is twice that of the halfwires.



Fig. 15. View of composite grid.

## Negative grids

The only characteristic that needs to be met in designing negative grids is sufficient cross section to permit a high and economical casting rate compatible with sufficient rigidity to withstand the pasting stresses. The frame dimensions usually dictate the grid rigidity and reduced section ribs and wires can be adopted compared with positive grids. The oxidation corrosion observed with positive grids is absent in negative grids. The higher density of the formed negative active material leads to a reduced volume compared with the positive and also to a thinner grid.

Take, for example, a matching negative grid to the positive previously examined, i.e., a negative grid measuring  $22.9 \text{ cm} \times 13.8 \text{ cm}$  with a thickness determined as follows.

A typical amount of wet paste, density 4.5 g/cm<sup>3</sup> (74 g/in<sup>3</sup>), for this grid is 460 g, and it is common for the finished plate thickness to be 0.02 cm greater than the grid thickness. As in the positive example, a safety factor should be allowed to ensure that the full rated capacity is realized within the first five cycles, if this requirement is specified. This would give a maximum capacity with continued cycling of  $(1.1 \times 32)$  Ah, i.e., 35.2 Ah, for a rated capacity of 32 Ah.

It is assumed for the example that an alloy with 4.5 wt.% Sb will be used with a density of 11 g/cm<sup>3</sup>. The specific grid weight chosen will affect the metal used and the volume of the grid as shown in Table 7.

If t cm is the grid thickness, then:

plate volume =  $(t + 0.02)(22.9 \times 13.8)$  cm<sup>3</sup> = 316.02t + 6.32 cm<sup>3</sup>

wet paste volume = 460/4.5 = 102.2 cm<sup>3</sup>

grid volume = plate volume - wet paste volume

= 316.02t + 6.32 - 102.2 cm<sup>3</sup> = 316.02t - 95.9 cm<sup>3</sup>

Taking each specific grid weight in turn, the values of grid thickness shown in Table 7 are obtained.

For the example, take a specific grid weight of 6.5 g/Ah as this is acceptable to modern casting machines. Some reduction can be considered for the frame as there is no corrosion to take into account. The only requirement is adequate strength and a realistic frame value could be 2.5 mm average width. This gives a frame volume for a grid 0.37 cm thick of 8 cm<sup>3</sup>. The grid volume for a specific grid weight of 6.5 g/Ah is 20.8 cm<sup>3</sup> and this would leave 12.8 cm<sup>3</sup> for ribs and wires. This is shared equally, initially, between ribs and wires and then modified if the wire section should be too acute for easy casting. Thus:

volume of metal allocated to wires = 6.4 cm<sup>3</sup>

## TABLE 7

Negative grid parameters

Specific grid weight (g/Ah)	Grid weight (g)	Grid volume (cm <sup>3</sup> )	Grid thickness (cm)
6	211.2	19.2	0.364
6.5	228.8	20.8	0.370
7	246.4	22.4	0.374
7.5	264	24.0	0.379
8	281.6	25.6	0.384

Take the same pellet size as for the composite positive grid, i.e.,  $1.75 \text{ cm} \times 1.75 \text{ cm}$ . As in the positive grid this will give 25 wires. If the grid is to be pasted transversely, there is a danger of distortion occurring. It is therefore good practice to insert stiffening bars at intervals. These bars would be twice the wire cross section, at least, and a reasonable spacing would be every 12 cm. This would give one stiffening bar per grid and the total volume of wires and stiffening bar would be equivalent to 26 wires.

As in the positive grid example, there would be 7 ribs per grid. Therefore: internal distance between top and bottom frames =  $22.9 - (2 \times 0.25) = 22.4$  cm

total length of 7 ribs =  $7 \times 22.4$  cm

volume of rib metal =  $6.4 \text{ cm}^3$ 

cross-sectional area of rib =  $6.4/(7 \times 22.4) = 0.04$  cm<sup>2</sup>

average width of rib section = 0.04/0.37 = 0.108 cm

The calculation of the rib section dimensions follows the same procedure as for the positive section, i.e.:

length of a row of wires =  $13.8 - (2 \times 0.25) - (7 \times 0.108) = 12.54$  cm

total effective length of 26 wires =  $26 \times 12.54$  cm = 326.04 cm

cross-sectional area of wire =  $\frac{6.4}{26 \times 12.54}$  = 0.02 cm<sup>2</sup>

cross-sectional area of stiffening  $bar = 0.04 \text{ cm}^2$ 

Taking a minimum apex angle of  $40^{\circ}$ , this would give a base dimension of 0.168 cm and a truncated apex dimension of 0.05 cm.

Alternatively, the truncation can be reduced to 0.02 cm and the apex angle increased to  $53^{\circ}$  to give a base dimension for the wire of 0.198 cm. The latter is preferable; the relative rib and wire shapes are shown in Fig. 16.

It so happens that the cross section of the rib and the stiffening bar are both  $0.04 \text{ cm}^2$  in area and the latter can either be of the same shape as the rib or double the wire shape. The latter is easier to accommodate in the mould cutting.

If the wire section cannot be obtained within the grid thickness with an apex angle of  $40^{\circ}$  or more using the initial metal allocations to ribs and wires, either the allocation of metal to the ribs is reduced or the rib allocation is maintained and the metal for the wires is increased with a concomitant increase in the grid weight. The possibility of reducing the rib allocation should first be examined in order to raise the apex angle of the wire to the minimum of  $40^{\circ}$ . If this should so weaken the rib section that there are doubts whether the grids will pass through the pasting machine without distortion, there is no alternative to increasing the overall grid weight.

#### Interlock grid design

Surface cut moulds are criticized as being too wasteful of grid metal, particularly for negatives where no oxidation corrosion problem demands a minimum of metal to ensure adequate strength at the end of life. In the interlock mould, the wires are spaced away from the split line of the mould; they can be close to a parallelogram in shape with less acute angles than where the wires are approximately triangular in



Fig. 16. Relative shapes of rib and wire in the negative grid design.



Fig. 17. Section through an interlock grid.

shape. This makes it possible to design the wire section closer to the minimum area for satisfactory casting in thick grids. The section of an interlock grid in Fig. 17 illustrates this feature.

When deriving the allocation of metal to each section of the grid, it is easier to fix the metal for the wires first using a minimum cross-sectional area of  $0.01 \text{ cm}^2$  for the wires. The pellet size remains the same as previously stated for surface-cut moulds.

Consider the same grid as for the previous example, viz., a grid measuring 22.9 cm  $\times$  13.8 cm and with a capacity rating of 32 Ah to be attained within five cycles. The thickness is determined as follows.

The number of ribs and wires will be the same as in the previous example, i.e.:

number of ribs = 7

number of solid and half-wires = 25 (1 solid wire)

Taking the cross section of the solid wire as equal to that of a rib, this cross section will be affected by the grid thickness. The latter will be less than that of the surface-cut grid, but the volume of the wires will remain unaffected by the grid thickness since this is determined by the choice of a minimum cross section for easy casting.

volume of 24 half-wires =  $24 \times 0.01 \times 12.54 = 3.01$  cm<sup>3</sup>

Let the thickness of the interlock grid be t cm compared with 0.37 cm for the previous grid. Based on the frame and rib volumes for the previous grid example:

volume of frame metal =  $8 \times t/0.37 = 21.62t$  cm<sup>3</sup>

volume of rib metal =  $6.4 \times t/0.37 = 17.3t$  cm<sup>3</sup>

volume of solid wire metal =  $0.04 \times 12.54 \times t/0.37 = 1.36t$  cm<sup>3</sup>

From the previous example:

volume of pasted plate = 316.02t + 6.32 cm<sup>3</sup>

volume of wet paste =  $102.2 \text{ cm}^3$ 

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The grid volume will be the difference between the plate volume and the wet paste volume, i.e.:

volume of grid = 21.62t + 17.3t + 1.36t + 3.01 cm<sup>3</sup> = 316.02t + 6.32 - 102.2 cm<sup>3</sup>

Solving this equation, gives:

t = 0.359 cm, i.e., 0.36 cm

From the previous example, this grid thickness corresponds to a specific grid weight of 6 g/Ah, an improvement of  $\sim 8\%$  in the use of grid metal over an equivalent grid cast in a surface-cut mould. Generally, an interlock mould can be designed on the basis of a reduced grid weight compared with a surface-cut mould of  $\sim 0.5$  g/Ah.

To illustrate a complete design exercise, take the case of a negative grid rated at 70 Ah to fit the dimensions  $30.5 \text{ cm} \times 18 \text{ cm}$  and required to accept 940 g of wet paste, with a density of  $4.5 \text{ g/cm}^3$ . Previously, a specific grid weight of 6.5 g/Ah was acceptable for a surface-cut grid and, for this example, it is decided that the maximum saving in grid metal would be made and an interlock grid would be used. From the earlier example, the specific grid weight can be reduced to 6 g/Ah. Some margin over the rated capacity is required if the full rated capacity is to be achieved regularly within the first five cycles; a factor of 1.1 is assumed. If the full rated capacity is not to be achieved so early, a lower factor can be adopted, dependent on the paste mix.

Assuming an alloy containing 4.5 wt.% Sb with a density of 11 g/cm<sup>3</sup>, then:

grid weight = 70 Ah × 6 g/Ah × 1.1 = 462 g grid volume = 462 g/11 (g/cm<sup>3</sup>) = 142 cm<sup>3</sup> wet paste volume = 940 g/4.5 (g/cm<sup>3</sup>) = 208.9 cm<sup>3</sup> plate volume = 208.9 + 42 = 250.9 cm<sup>3</sup>

If t cm is the grid thickness and the plate is overpasted by 0.02 cm, then: plate volume =  $30.5 \times 18 \times (t+0.02)$  cm<sup>3</sup> = 549t + 10.98 cm<sup>3</sup> 549t + 10.98 = 250.9t = 0.437 cm

Take t = 0.44 cm.

If a frame width of 0.25 cm average was acceptable for the surface-cut grid, it will also be acceptable for the interlock grid. A frame width of 0.25 cm will give internal frame dimensions of  $30.5 \text{ cm} \times 17.5 \text{ cm}$  and a total length of frame of 2(30+17.5) cm, i.e., 95 cm.

volume of frame = 
$$95 \times 0.25 \times 0.44 = 10.45$$
 cm<sup>3</sup>  
volume available for ribs and wires =  $42 - 10.45 = 31.55$  cm<sup>3</sup>

Before attempting to allocate this amount of metal to each of the ribs and wires, it is necessary to find the number of wires and stiffening bars over the internal length of the grid. Initially, take the suggested maximum pellet size of  $1.75 \text{ cm} \times 1.75 \text{ cm}$ :

approximate number of wires and bars =  $\frac{30 \text{ cm}}{0.5 \times 1.75 \text{ cm}} - 1 = 33.28$ , i.e., 33

Allow a maximum of 12 cm between stiffening bars, then:

number<sub>s</sub> of stiffening bars = 30 cm/12 cm - 1 = 1.5, i.e., 2

The horizontal members will then consist of 31 wires and 2 stiffening bars.

Until the rib width is known, the actual length of a row of wires cannot be calculated. Also, neither can the rib width be determined until the wire dimensions are calculated. An approximation has to be made to one or the other before progress can be made. Initially, ignore the rib width and assume the effective length of a row of wires is the internal frame width, i.e., 17.5 cm. With this assumption, take the minimum wire cross-sectional area for easy casting also, i.e.,  $0.01 \text{ cm}^2$ :

approximate volume of 31 wires =  $31 \times 17.5 \times 0.01 = 5.425$  cm<sup>3</sup>

volume available for ribs and stiffening bars = 31.55 - 5.425 = 26.125 cm<sup>3</sup>

Next find the total length of ribs and stiffening bars assuming the cross section of the stiffening bars are the same as the ribs:

number of ribs = 17.5/1.75 - 1 = 9

total length of ribs and stiffening bars =  $(9 \times 30) + (2 \times 17.5) = 305$  cm

cross-sectional area of ribs = 26.125/305 = 0.086 cm<sup>2</sup>

average rib width = 0.086/0.44 = 0.195 cm

Using the same basic shape as for the previous examples with release angles of  $20^{\circ}$ , the maximum and minimum dimensions of a rib section would be 0.275 cm and 0.115 cm, respectively. Rounding these dimensions to 0.28 cm and 0.11 cm would alter the release angle to  $21^{\circ}8'$ .

It is a personal choice whether to make the stiffening bars the same shape as the ribs, but having them the same assists in the casting process as the risk of shrinkage cracks at the intersection of the ribs and stiffening bars is less than if there was a large disparity between them. If it was felt there was an advantage in making the wires larger to assist productivity, then the cross-sectional area of the stiffening bars could be reduced somewhat to give closer to a diamond shape with a cross-sectional area nearer to, say,  $0.04 \text{ cm}^2$  which has been shown in previous examples to give a strong member.

For the example, it is assumed that there is an advantage in keeping the rib and stiffening bar sections the same. Having fixed the rib average width, it is now possible to fix the effective length of a row of wires more accurately:

effective length of a row of wires =  $17.5 - (9 \times 0.195) = 15.745$  cm volume of 2 stiffening bars =  $2 \times 0.086 \times 15.745 = 2.71$  cm<sup>3</sup> volume of 9 ribs =  $9 \times 0.086 \times 30 = 23.22$  cm<sup>3</sup> volume available for 31 wires = 31.55 - (23.22 + 2.71) = 5.62 cm<sup>3</sup> cross-sectional area of wires (A) =  $5.62/(31 \times 15.745) = 0.012$  cm<sup>2</sup> As there are 2 stiffening bars within an internal length of 30 cm, the distance between the bars will be 10 cm. This distance has to be shared between one-third of the wires. This is not possible with 31 wires if an equal distance is to be maintained between the stiffening bars. Thus, the wires are shared symmetrically so that the upper and lower sections of the grid have 10 wires and the middle section has 11 wires.

As there are 33 wires and stiffening bars, there will be 17 pellets over the internal length of the grid. The effective internal length will be  $30-(2\times0.195)$  cm, i.e., 29.61 cm. Thus:

wire pitch = 29.61/17 = 1.74 cm

The spacing of the stiffening bars will be 9.93 cm and 20.58 cm, respectively, from the top edge of the grid frame.

Having set the wire pitch and the position of the stiffening bars, the next stage is to develop the cutting angles for the projection of one half of the mould into the other. Figure 18 is an enlarged view of a section of the grid and shows one wire in relation to the inner frame. This sets the angle of the sides of the parallelogram forming the offset wire and the line of the mould containing the wire profile.

The cutting angle  $\theta$  is defined by the relationship:

 $\tan \theta = 0.44/0.87$ 

from which:  $\theta = 26^{\circ}50'$ 

The wire dimensions can now be determined. Figure 19 is a section of an offset wire.

cross-sectional area of wire  $A = 2(h \times b)$ tan  $\theta = h/b$  $b = H \times 1/tan \ \theta = A/2h$  $h^2 = 0.5A$  tan  $\theta$ Substituting A = 0.012 cm<sup>2</sup>:  $h^2 = 0.5 \times 0.012$  tan 26°50' h = 0.055 cm b = 0.11 cm



Fig. 18. Relationship of offset wire to frame in an interlock design of grid.



Fig. 19. Section of wire of an interlock grid.



Fig. 20. Comparison of wire sections for interlock and surface-cut grids for a 70 Ah negative grid.

The major and minor axes of the parallelogram forming the wire will be 0.22 cm and 0.11 cm, respectively.

The difference between the wires for an interlock and a surface-cut mould are shown in Fig. 20, where the surface-cut wire has an apex angle of 40°.

The effective internal width between the side frames will be  $(17.5-9\times0.195)$  cm. As there are 9 ribs, there will be 10 pellets across the plate and the pellet width will be  $(17.5-9\times0.195)/10$  cm, i.e., 1.575 cm.

Summarizing, the design provides a grid with:

(i) 9 vertical ribs, each with a cross-sectional area of  $0.086 \text{ cm}^2$  and maximum and minimum widths of 0.275 cm and 0.115 cm, respectively, with 20° release angles;

(ii) 31 horizontal wires of diamond shape, each with a cross section of 0.012  $\text{cm}^2$  and major and minor axes of 0.22 and 0.11 cm, respectively;

(iii) 2 horizontal stiffening bars with the same dimensions as the ribs;

(iv) pellet dimensions of 1.74 cm×1.575 cm, and

(v) a design weight of 462 g accepting 940 g of wet paste and supporting an excess capacity of 10% above the rated 70 Ah when the active material is fully developed.

#### Tubular positive grids

In 1890, S. Curie patented a positive plate in which the active material was introduced into a series of woven asbestos tubes in the centre of which were brass rods. The rods were withdrawn leaving cylindrical holes into which was poured molten lead to form a series of lead alloy spines. These were later joined to a top bar to form a grid. The system was both inefficient and costly, but the construction showed that it was sufficient to have only a top bar and spines if the active material could be adequately retained within a porous enclosure such as a woven plastic filament tube.

The simplified grid structure offered:

(i) a reduced specific grid weight compared with lattice-type grids;

(ii) a higher productivity casting system using pressure die-casting techniques, and

(iii) greater dimensional stability than with gravity casting as no mould coating other than a mild lubricant was required on the mating surfaces of the mould blocks.

Not all makers were convinced that pressure die-casting was necessary or desirable since the simplified design of a tubular positive grid made the task of gravity casting easier than with the more complex lattice grid. Gravity-cast, tubular positive grids have been produced using high arsenic corrosion-resistant alloys with good results, even to the extent, it is claimed, of better life characteristics.

Most makers do prefer pressure die-casting. Usually, very high injection pressures are avoided because of the considerable turbulence and air entrapment that can occur in castings where the entry velocity of the molten alloy is very high. Where die evacuation can be used, these disadvantages disappear but productivity usually suffers. The evacuation of the dies prior to the injection of the molten alloy complicates the machinery and increases the amount of maintenance. It is doubtful whether these complications are compensated by such an improvement in the castings and service life that savings in the material content can be made that are sufficiently large to offset the increased manufacturing costs.

By far the most important factors in choosing a pressure die-casting machine for tubular positive grids are ruggedness, high and positive clamping pressures holding the mould blocks in close contact during alloy injection, and the ability within the machine to collect the charge of molten alloy from well below the surface in the lead furnace and to ram that charge, free of dross inclusions, into the mould at a constant and reproducible rate. The mould blocks should open in such a manner that the operator can both easily and quickly apply lubricant over the mould surfaces without slowing down the optimum casting cycle.

The molten alloy is either injected into an extension of the grid lug or via a slit gate directly on the top bar. The virtue of the latter is claimed to be a more even flow of metal to each of the spine channels. Both systems are capable of producing satisfactory castings that meet the full-life requirements of the cell. As the molten alloy passes down the spine channels, it drives the air initially in the mould before it enters into a false bottom bar that is later cropped. The lower portions of the spines tend to be porous as the false bottom may not be sufficient to absorb all the air that fails to leak away through the mould blocks. Some makers provide an overflow channel that surrounds the complete grid profile and the false bottom so that air can be scavenged completely from the grid section of the mould. It is reckoned that incomplete filling here, with possible coarse crystal structures and dimensional variations, will produce more perfect dimensions and a more uniform crystal structure in the working section of the total casting. Other makers prefer to crop a substantial length of the spines to remove the imperfections. This simplifies the mould design and eases the ejection of the casting.

Normally, hardened-steel mould blocks are used instead of the Meehanite type of cast iron common to gravity-cast grid moulds. After machining, the moulds are often diamond polished to reduce surface friction between the mould surfaces and the molten alloy, as well as to impart a high surface finish to the casting and, thereby, to improve its corrosion resistance.

The moulds are more expensive than gravity-cast grid moulds and it is not uncommon for grids of differing lengths to be cut from castings from a single mould. This arrangement usually incurs only a small cost penalty.

The tubular positive grid comprises a top collector bar with take-off lug and a number of cylindrical spines cast integrally with the top bar. The number of spines is dictated by the dimensions of the finished plates and the diameter of the enclosing porous and inert tube that retains the active material as an annular pencil of lead dioxide surrounding the central conductor.

#### The top bar

The dimensions of the top bar depend on the following factors:

(i) The rate of oxidation corrosion. Sufficient metal must be provided to maintain the strength of the top bar for the full guaranteed life of the battery, despite the conversion of some of the bar into lead dioxide with successive discharging and charging.

(ii) The nature of the tube filling operation. During filling, the casting with retainer tubes over the spines is usually inverted in a filling jig and vibrated or tamped whilst a dry powder or an oxide slurry is fed into the base of the plate. During the filling operation, the top bar must not distort, bend or crack.

The top bar usually requires more material than the top frame section of a lattice type grid, more because of the stresses imposed on it by the filling operation than by the reduction in section through oxidation corrosion. Where data are not available of the rate of oxidation corrosion of the particular alloy under the type of usage more frequently met in service and a design decision has to be made, a realistic guide based on an alloy with 8 to 9 wt.% Sb is to accept an average depth of 10 mm for a nominal four-year life and a tamp filling that involves amplitudes of up to 2 cm. This order of bar depth is a safe one that may be decreased with the acquisition of supporting data.

The current density increases from the side of the plate farthest from the plate lug to the plate lug. It is customary, therefore, to taper the top bar so that the thicker section is nearer the lug. A typical taper is 1.5 mm per 100 mm of bar length (Fig. 21).

Beneath the top bar are located bosses that enter the tops of the porous tube enclosures that surround the active material. The shape of these bosses, whilst not critical, can aggravate or minimize the effect of the oxidation corrosion problems at the top of the plate. Large and rapid changes in the sections immediately below the top bar should be avoided since the coarse structure and surface imperfections frequently present at large sectional changes often become preferential corrosion sites. This leads to premature failure in service through corrosion. The bosses consist of cylindrical sections that change smoothly down to the dimension of the spines. Figure 22 shows a number of designs that have been adopted.



Fig. 21. Top bar of tubular positive grid.



Fig. 22. Typical transition shapes from boss to spine.

Where it is known that the alloy is sufficiently corrosion resistant that, throughout the full service life of the cells, little or no elongation of the spines will occur then design (a) in Fig. 2 is acceptable. This situation is usually confined to service patterns where there is very little onerous working but, in most applications, there will be instances where the cells are regularly discharged to the full extent allowed by the guarantee. In such circumstances, even the best of the commercially viable allovs will show some elongation of the spines towards the end of life. The increased volume of the lead dioxide formed on the surface of the spine being oxidized exerts a stretching force on the skin of the underlying alloy and causes it to distort in the longitudinal direction. This shows up as a growth in the length of the spines over the life of the cells which may, in certain circumstances, be as much as 6 mm in plates of length 300 mm. Whilst the spine stretches, the woven plastics retainer tube remains virtually unstretched so that either: (i) the bosses are partially uncovered; (ii) the lower end of the pencil of lead dioxide is exposed, or (iii) some of the bosses and some of the pencils of lead dioxide are exposed. If all the growth should take place at the top of the plate then the length of the thicker portions of the boss and the start of the reduced diameter should not be less than the expected growth. The corrosion rate of exposed spines is many times that of a spine surrounded by lead dioxide. Some makers anxious to guard against these high growth conditions adopt design (c) shown

in Fig. 22. This design is wasteful of material and reduces the amount of active material at the top of the plate. This reduces capacity and should be avoided if at all possible. Design (a) tends to allow preferential corrosion to occur just below the radius, particularly when the operator is careless about maintaining the electrolyte level correctly and allows the level to fall below the top bar before adding water. Design (b) is a realistic compromise.

The amount of metal in the spines depends on the life expectancy of the cell design. An alloy with  $\sim 9$  wt.% Sb would experience about 1.0 mm of metal conversion for every 1000 cycles of discharge removing 80% of rated capacity at each discharge. High-quality castings with a uniform crystal structure throughout the length of the casting would perform better, but it could be imprudent to base a design dimension on the attainment always of near-perfect castings. It is necessary to retain a core of unoxidized metal to the end of the guaranteed life. Thus, a realistic core would be 1.5 mm in diameter. This would give a spine diameter of 3 mm for a cell with a nominal four-year life under extreme permitted conditions. The combination of a highly corrosion-resistant alloy and casting techniques that produce high-surface quality and uniform and fine crystal structures in the castings would allow the spine diameter to be reduced, but it is doubtful whether this could be reduced much below 2.5 mm without incurring serious risks.

It is known that the rate of corrosion of the spines is less when they are covered by lead dioxide. Simple anodic corrosion tests of spines with and without the presence of the active material covering quickly demonstrate this. For this reason, the spine should be evenly covered by the active material, i.e., it is concentric in the pencil of lead dioxide. Centralizing fins are cast on to the spines and these retain the outer plastics tube concentric to the spine. This eases the filling and reduces the risk of voids occurring in the active material. These, if present, form premature corrosion points where grid oxidation can proceed at an increased rate. Early designs had the centralizing fins disposed along the length of the spines alternating from lying in the plane of the mould blocks to lying at right angles to the blocks. The latter is difficult to machine without making the fin large and out of proportion with the other fin. The difficulty lies in having to use a small circular saw or milling cutter; even with the smallest diameter cutter compatible with clearing the surface of the mould block, the resultant cavity is elongated and the cast fin larger than is necessary or desirable. During the service life of the cells, the fins are oxidized and increase in size in proportion to the area exposed. The fins at right angles to the mould blocks increase more than those in the plane of the blocks and the outer tubes are distorted out of the round. This sometimes leads to the tubes splitting and the active material silting out. Many makers use only fins in the plane of the mould blocks and find they can maintain approximately the circular shape of the filled tubes. The removal of the fins at right angles to the mould blocks eases the stress on the tubes and reduces the incidences of tube splitting under onerous working conditions.

There is less variation between makers in the specific grid weight of tubular positive grids adopted than with lattice-type grids. Most makers adopt the same spine diameters and conform closely to the guideline values quoted earlier and differ only in the dimensions and shape of the top bar.

Typical specific grid weights for plates of about 50 cm in length lie between 9.0 and 9.2 g/Ah. The top bar dimensions are chosen as much to give rigidity and strength to withstand the filling stresses as to withstand oxidation corrosion throughout the guaranteed life. Generally, there is little difference in the dimensions whether the plate is short or long. The effect of this is to make the specific grid weight of short



Fig. 23. Effect of a common top bar on the specific grid weight of a tubular positive grid.

plates much greater than that of long plates. This is particularly so where, for the sake of economizing on tool costs, a common grid casting is used for all lengths of grid of a given width and the individual grid lengths are obtained by cropping the full casting to the required length.

To illustrate the effect of the common top bar to grids of differing lengths, take the case of a plate approximately 42 cm in length, for which a reasonable casting weight would be 586 g, using a spine 3 mm in diameter. If this casting is cropped to produce grids of shorter lengths, the effect of the common top bar would be to change the specific grid weights as shown in Fig. 23. Plates of approximately 15 cm length would have nearly 37% more material per ampere-hour than the full length (42 cm) plate.

The labour cost to produce plates of differing lengths remains substantially constant so that the cost of producing cells with short plates will be greater than cells of the same capacity with less but longer plates. The possibility of trimming the top bar for short plates should be explored before accepting a common casting for all sizes of grid.

## Practical criteria of grid-casting quality

It has frequently been stressed that the quality of a grid casting has, perhaps, more bearing on the commercial life of the battery than the choice of alloy. This does not mean that the alloy is unimportant, but rather that the corrosion resistance of an alloy can be cancelled out by poor casting quality and poor surface finish. Too often, the very resistant alloy is difficult to cast at an economic rate and, to achieve an acceptable rate of casting, the quality of the casting leaves much to be desired. The final choice of a grid alloy is essentially a compromise between good corrosion resistance and good productivity. The great difficulty lies in deciding how far the alloy corrosion resistance can be sacrified to commercial expediency, and how good is good quality since the definition of good quality can be adjusted to whatever standard is deemed acceptable to the market.

The basic requirements for a lattice-type grid casting may be summarised as follows:

(i) The negative lattice structure should be sufficiently complete to retain the pellets of active material until the battery is assembled. Thereafter, the action of the expanders cause the material to lock itself more firmly into the grid lattice and the normal softening of the surface material further assists this.

(ii) The structure of the positive casting should not have obvious hair-line cracks, severe frame weaknesses or visible dross inclusions. All these tend to stimulate preferential corrosion spots and, thereby, to produce local weaknesses and, possibly, frame breakages.

(iii) The lugs should be clean and free from porosity or sinkages since these lead to fractures and, in bad cases, to loss of grid-to-strap contact.

The common defects are: sinkage; short runs in ribs and wires; hair-line cracks; obvious cracks; porosity due to air inclusions, and dross inclusions. These are reviewed in the following sections.

#### Lattice-type grids

#### Sinkage

Sinkages are areas of reduced thickness. In a negative casting for traction, these are relatively innocuous provided the structure is not weakened to the extent that the grid distorts or breaks up under the pressures of pasting. Generally, a sinkage of up to half a frame width to a depth not exceeding half the frame thickness with lengths not exceeding twice the frame width can be accepted on the frame of traction grids. The number of such sinkages in a long side of a negative grid is very much dependent on the closeness of the sinkage. A rough guide is to divide the length of the grid by 15 and the nearest whole number is the maximum number of sinkages that can be accepted. In the case of sinkages longer than that quoted, the maximum length of all the sinkages taken together should not exceed the empirical number times twice the frame thickness or width, whichever is the higher.

Some degree of sinkage can be tolerated in a positive casting. Nevertheless, the amount is much less than for a negative since not only is the frame weakened but subsequent oxidation corrosion weakens it further. A rough guide is to limit the sinkage to no more than one sinkage per frame side, with a length not exceeding twice the frame width and a depth such that the estimated effective cross section at the sinkage is not less than twice the cross section of a rib. This ensures adequate corrosion life at the sinkage point.

A similar easement can be accepted for automotive grids. The sinkage areas, however, will be smaller as the frame sections are smaller than in traction grids. Usually, sinkage is less of a problem than with traction grids.

A common sinkage area is in the lugs. No sinkage should be accepted at the root of the lug because of the risk of breakage on subsequent handling, particularly during assembly. A sinkage area not more than a quarter of the root area can be accepted where the sinkage is clear of the root area, provided the depth of the sinkage is not greater than one-quarter of the grid thickness. Sinkage in the lug area is usually symptomatic of an uneven mould coating and should be remedied as soon as possible. It may not be possible to remove sinkages from the lug area completely, but they can

usually be moved by careful mould coating away from the root area into the upper part of the lug which is later fused into the strap during assembly.

Whenever sinkages appear, the quality control staff should call for a machine check to limit the number of castings affected.

#### Short runs in ribs and wires

Short runs or incomplete wires occur from time to time, often when working-in a mould, or as the mould coating starts to wear thin and allows the metal in the mould at particular wire areas to freeze before all the mould cavities are filled with molten metal. A greater degree of imperfection can be allowed in negatives than in positives. The main criteria for negative castings are that sufficient wires are complete, and the short runs are not so reduced in length, that the pellets of active material cannot be retained and the conduction of the discharge current is not sufficiently affected that the minimum cold-start voltage performance in automotive batteries is not achieved.

A crude guide for traction battery negative grids is to allow not more than one incomplete wire per 50  $\text{cm}^2$  of grid area, with the proviso that there are no more than two short runs per row of wires and there should be not less than five pellets between them. These are safe guidelines and, with experience, may be exceeded.

Short runs weaken the lattice of automotive grids and the main criterion is that the grids can pass under the pasting hopper without deforming or breaking. Up to four short runs per grid can usually be accepted, provided they are well spaced apart. This crude guideline may need to be tightened when grids of less than 1.25 mm in thickness are concerned. There should not be any short runs immediately below the lug area.

If economics permit, it is safer not to accept any short runs in traction positive grids. In an emergency, the same standard as for negative traction grids may be adopted temporarily, provided not more than half the grids in any one cell element are so affected. Remedial action to eliminate the cause of the short runs should be instituted as soon as possible.

Not more than two short runs per automotive positive grid is acceptable for top quality batteries, with an easement to four per casting for second quality batteries.

Whenever short runs appear, it is an indication of air entrapment in the mould. This can be due to a poor or a wearing mould coating, or to poor preparation of the mould gate. Remedial action should be taken to remove the cause of the fault before too many castings are affected and casting quality reaches rejection levels.

## Cracks

Obvious cracks should be rejected without question. In a negative grid, cracks lead to poor electrical contact between grid and active material and encourage grid distortion. In a positive, cracks actively encourage increased corrosion and the early break-up of the grid structure. Cracks in automotive grids invariably cause hitches in the pasting machine and increased down-time.

Hair-line cracks are not so dangerous in negative castings as in positives. They form premature corrosion sites in positive castings and are troublesome. In negative castings, they can be rectified by flaming the metal around the cracks. In an emergency, the same flaming procedure may be adopted with positives on a temporary basis if the cracks are surface cracks and not deep. The number in any one element, however, should be limited to less than one-half and remedial action to eliminate the fault instituted immediately.

### Tubular positive grid castings

Porosity in the top bar is probably the most common fault; followed by sinkages in the top bar and spines, 'piping' in the spines, and rough, uneven spine surfaces.

## Porosity in top bar

Porosity in the top bar weakens the bar and can lead to the development of distortion and fine cracks during the filling operation. The only simple test of porosity in the top bar is a destructive one. This is no excuse for avoiding it and a statistical sampling plan is recommended to check for its presence since its appearance is not sporadic. An alternative to a breaking test is to flame quality control samples gently along both surfaces of the top bar. If there is porosity some sinkage will occur. The extent and depth of the sinkage is an indication of the amount of porosity. These samples can then be accepted back into production if the amount of sinkage does not exceed the guidelines previously stated.

If the flaming test indicates there is porosity, selective samples, taken at various stages of production, should be examined to determine if the fault is increasing in severity. If this is not the case and the amount of sinkage is slight and within the guidelines, the castings can be accepted with the precaution that the machine settings and operation are examined as soon as is practicable. If the sinkage from flaming is considerable and/or increasing as production proceeds, the batch should be impounded and machine checking immediately put into operation. The impounded batch should then be re-inspected to determine how many can safely be recovered.

## Sinkage in top bar and spines

If sinkage is present in the top bar there is a danger of porosity there also. Samples should be checked by flaming to determine whether the sinkage is an indication of incomplete filling of the mould or porosity. If further sinkage occurs with flaming, suspect porosity and reject if the further sinkage with flaming is appreciable. Institute immediate machine checks. If there is little or no further sinkage with flaming, accept castings with single sinkages not exceeding twice the maximum depth of the bar in length and not more than half the depth of the bar in width. The same criteria apply to the lug area for sinkage limits as for lattice-type grids. Sinkages in the spines and spine bosses should not be accepted. These lead to premature failures on onerous service.

#### Piping

Piping is best described as lengths of hollow spine caused by mould and metal conditions that favour the extrusion of the injected metal with the metal in contact with the mould surface moving faster than that in the centre of the spine channel. The danger with piping lies in the loss of the centre core of metal in the spine (which gives the spine its strength) when the outer surface has been oxidized. Piping can only be detected by destructive testing. By combining checks for porosity with checks for piping, the number of control samples that are destroyed in testing can be reduced. Where a common casting is used for several lengths of grid, an examination of the cropped ends of the spines can often show up the piping defect. The quality control samples should be cut at a number of specified points along the length of a spine to ensure that the presence of piping is not missed. If piping is close to the bottom of a plate, it will have a less deleterious effect on cell life than if it was close to the top bar. A rough guide would be to accept no piping close to the bostses and up to 2 cm in length at the bottom of a grid with a proportionate length in between.

## Rough uneven surfaces on spines

Rough uneven surfaces are to be avoided. The rate of surface oxidation is greater with rough surfaces than with smooth surfaces, and poor surface conditions tend to reduce grid life. It is difficult to set empirical standards of permissible roughness other than to say that if the as-cast surfaces of the spines are dull, or they show slight ripples, or a mixed shiny and dull mosaic, then a machine check should be requested and the mould cleaned and, if deemed necessary, repolished. The ideal surface is a highly polished one free of blemishes.

## Dross formation with lead-antimony alloys

The economics of grid manufacture have led to the casting of grids rather than mechanical formation, particularly where lead-antimony alloys have been adopted. Relatively large amounts of the lead-antimony alloy are held above the melting point for extended periods of time in order to achieve continuous casting. Under such conditions, there is considerable oxidation of the metal at the metal/air interface and this leads to the formation of dross. Dross formation can be reduced by the use of a flux cover or by maintaining an inert atmosphere above the melt. Such controls, however, tend to complicate the casting operation so that the use of dross controls is not common, except in the case of antimony-free alloys. A lack of controls will mean that the rate of dross formation and the amount of dross produced will be significant economical factors in the running of a grid and components casting department. Melts producing heavy drossing require frequent skimming and involve a heavy waste of metal. It is not uncommon for the dross to be of the order of 5% of the total metal usage. This factor has to be allowed for in determining departmental costs.

Apart from the cost factor, the entrapment of dross in the molten metal poured into a mould is a forerunner of high oxidation corrosion at the dross points.

It is generally agreed that the purest types of commercial lead are more susceptible to drossing than less refined lead. Ultra-pure lead, however, shows little, if any, tendency to dross. In the examination of the factors that promote drossing, all reported experiments have shown very significant trends in drossing rates connected with the presence of various elements.

In test melts of lead containing the impurities bismuth, nickel and cadmium at levels of 0.01 wt.% each, the addition of 0.01 wt.% Sb over a period of 100 s at a temperature of 400 °C produced a fourfold increase in the thickness of the dross film. The addition of 0.01 wt.% As produced an increase of 3.5 times, whilst similar amounts of silver or copper produced an increase of 3 times. If the arsenic content was increased to 0.05 wt.%, the oxide dross increased approximately 10 times, but the rate of increase of the dross decreased with further increases in the arsenic content.

In the case of tin, the rate of increase of dross formation reaches a maximum at about 0.035 wt.% Sn and the amount of dross formed is about 2.5 times that without tin. The interesting feature about tin is that when the tin content reaches 0.06 wt.%, the dross formed is slightly less than with unalloyed lead. At 0.1 wt.% Sn the rate of dross formation is about one-quarter that of unalloyed lead. Some manufacturers specify up to 0.1 wt.% Sn in their alloy formulation for grid casting on the basis that this amount of tin is an excellent dross inhibitor. In practice, however, much of the tin can be lost readily from the melt in the bulk lead furnace by allowing the temperature to exceed 450 °C and, instead of reducing drossing, it can fall to a level at which it can greatly increase drossing. Furthermore, tin is an expensive material and should be preserved to ensure that the extra cost involved in the alloy is recouped by savings in the dross losses.

The free energy of metal oxide formation for each of the common impurities in lead alloys is as follows:

lead oxide	-45 kcal/mol
cadmium oxide	-54 kcal/mol
bismuth oxide	-119 kcal/mol
stannic oxide	-124 kcal/mol
arsenious oxide	-185 kcal/mol
antimony oxide	-188 kcal/mol

These figures relate to the relative stability of the oxide and the tendency of one oxide to form in preference to another, as determined by the metal/metal oxide ratio, the composition of the oxide layer, and the rate of diffusion of the impurity metals in the melt.

Antimony oxide forms most readily in preference to other metal oxides associated with lead. Antimony diffuses readily through the melt and its oxide, when formed, greatly distorts the lead oxide film. Only a small percentage of the total antimony is removed as antimony oxide and, therefore, the drossing rate is high and the quantity of dross produced is persistent. Arsenic does not differ greatly from antimony and these two elements stand out as the more serious promoters of drossing; they are also the more common hardeners for grid alloys.

Most of the work on dross formation has been carried out at a temperature of 400 °C. With the more usual lead-antimony grid alloys, this temperature is close to the melting point of the alloys. This temperature has to be exceeded in order to obtain fluidity in the melt for rapid filling of the mould cavity. The effect of this is to exaggerate the dross formation and the indiscriminate raising of the lead furnace temperature can raise the dross losses to well above 5%. At 500 °C, some alloys have registered dross losses as high as 10%.

The composition of the dross invariably differs from that of the original melt. Table 8 illustrates how the original antimony content of an alloy can modify the composition of the dross formed at 400  $^{\circ}$ C.

With tin contents of  $\sim 0.1$  wt.% in lead-antimony alloys it is found that the dross can contain up to 10 times that value when the lead-furnace temperature has been allowed to rise close to 500 °C. The maintenance of the lowest temperature in the lead alloy furnace compatible with continuous casting cannot be overstressed. In all circumstances, there should be an assay made of bulk dross before selling since any concentrating up of expensive metals (such as tin) should attract full recognition in

TABLE 8

Antimony in original alloy (wt.%)	Antimony in dross (wt.%)	
0.00002	0.0065	
0.00005	0.011	
0.0005	0.033	
0.005	0.32	
0.055	1.0	
0.5	1.6	

Effect of antimony content on dross composition

establishing a fair selling price. Records of the variation in the levels of dross formation should be kept if good production economics are to be maintained.

Super-pure leads of not less than 99.999% purity show little tendency to dross. These leads are expensive and the substitution of lower standards of purity in the mother lead for alloy production can introduce higher dross formation levels and this should be recognized. Impurities (such as bismuth, copper and silver) are not so active in producing dross and some operators claim that their presence can reduce the effect of antimony, arsenic or tin and are to be welcomed as a cost-saving addition. Irrespective of the data and the claims, the real test is the amount of dross measured day-by-day in the actual grid-casting shop and its effective control.

The presence of dross formation on the surface of molten lead or lead alloy shows first as an iridescent blue sheen over the surface. There are opposing views within the battery industry whether or not to dross (i.e., skim the dross off the surface) whilst the blue sheen can be readily seen, or to allow the dross to build-up to such an extent that the blue sheen is broken up and obscured. The general view is to allow the dross to accumulate on the assumption that if the important impurity element stimulating dross formation is substantially removed in the first dross films, the rate of dross formation will fall and the retention of a dross skin will restrict the availability of atmospheric oxygen to the underlying layer of the molten lead alloy.

The skimming off of the dross layer from the surface of the molten alloy constitutes a high environmental risk since the dross can emit toxic lead dust and arsenious fumes. The operation, therefore, needs to be carried out in a careful and disciplined manner, preferably when the work area is relatively free of personnel. The hot dross should be deposited carefully into heavy gauge iron or steel pots, and as soon as the dross is deposited, the pots should be covered with well-fitting heavy lids and should remain covered until after removal from the work area.

#### Grid mould preparation

The mass of the mould blocks is greater than that of the molten metal poured into them. The heat in the poured metal would be extracted rapidly if the metal was in direct contact with the metal of the mould as the temperature of the mould blocks must be at a lower temperature than the metal to ensure that the metal freezes. Some delay must be introduced to prevent the molten metal freezing before the cavity of the mould has been filled. This is obtained by interposing between the metal of the mould blocks and the molten alloy metal an insulating coating that adheres to the surface of the mould cavities. This insulation is termed the 'mould coating' and is made from finely ground cork that is held together by an adherent binder. The coating is made in the form of a thin suspension of the cork in the binder which is sprayed on to the mould surfaces and, with the loss of the liquid component on drying, leaves discrete particles of cork attached to the mould with minute air spaces between the particles. These air spaces provide a multitude of minute escape routes for the air within the mould so that, as the molten alloy enters the mould, the air within the mould is forced out of the mould via these escape routes. Without them it would be difficult to fill the mould cavities fully.

In the past, acetylene soot or French chalk was used as the insulating medium with restricted air escape, and it was common practice to scratch the outer mould surface that surrounded the grid frame to provide rough escape routes for the entrapped air. This process was very much 'hit and miss' and, after a period of time, the mould surfaces became sufficiently damaged to upset casting. It is considered a better practice, nowadays, to pay greater attention to the quality and texture of the mould coating and the way the molten metal is directed into the mould and to eliminate any scoring of the mould surface. A good mould coating, properly applied, is sufficient to reduce the rate of heat removal from the molten alloy, and to delay freezing sufficiently for all the air within the mould originally to be removed and the mould cavity to be filled completely. The role of the mould coating is vital to the operation of an economic and effective grid-casting operation.

The established mould coatings are all based on the use of natural cork ground to a fine powder, but not necessarily superfine. The cork powder is made into a thin slurry with adhesives (such as gum arabic, sodium silicate, casein glue or similar materials) and then sprayed in a thin, but uniform, coating over the internal surfaces of the mould blocks. During the spraying, the mould blocks are held at approximately the same temperature as for grid casting. As the cork siurry impinges on to the mould surfaces, the water content rapidly evaporates to leave a dry powder that covers the mould surface.

There is no universal formulation for mould coating that will satisfy all gridcasting conditions and operators. It is still very much an art, and no two casters necessarily get the same results from any one formulation. The Independent Battery Manufacturers Association (IBMA) lists different formulations and leaves the choice to the individual operator [1].

Part of the difficulty lies in cork being a natural product and, therefore, exhibiting great variations in properties. For example, the rate of growth of the tree determines the primary physical characteristics of the cork and the position within the thickness of the bark from which the cork is taken dictates its overall quality and density. The nearer the centre of the tree, the better is the quality and texture of the cork. One simple test often applied to cork powder is to take a pinch of the powder and rub it between thumb and finger. If it feels very smooth, like talc, it is likely to be too fine; if it feels gritty, indicating the presence of large particles, it is likely to give trouble by blocking the jet of the spray gun. The best description for the desired condition of the powder is 'mildly gritty'. Nevertheless, this is a very crude test and open to much misjudgement as sensitivity of touch varies tremendously between operators. A more controlled approach is necessary for good day-to-day maintenance of coating consistency and quality. This is easy to state, but not so easy to achieve since bought-in cork powders are very variable and each supplier has difficulty in matching consecutive consignments. The histograms in Fig. 24 show the variation registered over a relatively short period of time between ten consignments of cork powder from six different sources. Some of these were so different one from another that it was impossible to reproduce any degree of consistency in mould coatings prepared from them. If these are used without some selectivity of particle-size distribution before use, the difficulties introduced into the casting shop are enormous and make a mockery of mould preparation.

There are two alternative approaches to achieve greater consistency:

(i) specify a relatively tight particle-size distribution and attempt to buy in to that standard, and

(ii) buy recognized cork powder from a reputable source, stay with that source but sieve all incoming material before use to reduce the spread of particle size and reject the extremes of coarse and fine.

Whilst option (i) is the more scientific, it stands or falls on the feasibility that the supplier is aware of the great variability in the base product. Option (ii) is workable and more economic.





The definition of what constitutes acceptable limits for particle size is fraught with difficulty as quality of mould coatings is subjective and personal; it reflects the individual casting operator's acquired casting techniques and expertise. There is, however, some agreement that cork particles that will not pass through a 300  $\mu$ m sieve and those that will pass through a 25  $\mu$ m sieve should be rejected. The drawback with sieving production quantities of cork powder is the length of time that it takes. Two alternative procedures are common in the industry:

(i) use commercial brush sieves, one for the elimination of coarse and one for fines particles, and

(ii) carry out simple sedimentation volume tests coupled with Scott volumeter, apparent density, tests, and use the results to accept those within limits and to work out blends to enable the others to be used without jeopardizing the quality of the subsequent mould coating.

Initially, the sedimentation test consists of screening the powder to eliminate the coarse particles over 300  $\mu$ m. Then, 1 g of the screened powder is placed in 40 cm<sup>3</sup> of methanol and shaken vigorously for 1 min. The cork and methanol are then set aside for 10 h or until all the cork has settled at the bottom of the cylinder. The sedimentation volume should be between 14 and 18 cm<sup>3</sup>. A measured weight of the powder is then allowed to fall freely through a Scott volumeter and the volume of the powder recorded. The resulting density of the powder should lie between 0.04 and 0.06 g/cm<sup>3</sup>.

Dark powders tend to have a higher density than pale-coloured powders, but char less readily in use. Both types of powder can be used in the preparation of mould coatings. Nevertheless, coatings made from dark powders generally have to be built up into thicker coats to give the same heat insulating properties compared with those made using pale powders.

If standard analytical sieves are available, the following order of particle-size distribution, determined by automatic shaking for 3 h, has been found to produce an acceptable base cork powder from which to process a mould coating:

residue on 300 $\mu$ m sieve	nil
residue on 180 $\mu$ m sieve	not greater than 10%
residue on 150 $\mu$ m sieve	not greater than 10%
amount passing through a 45 $\mu$ m sieve	not greater than 10%
amount passing through a 31.5 $\mu$ m sieve	nil

The important characteristic to be sought is consistency.

If there is a residue on either the 300 or 31.5  $\mu$ m sieves, the powder may give trouble. If the residues are very small, it may be economic to accept the powder and warn the shop-floor personnel. If the residues are appreciable, it could be uneconomic to attempt to sieve all the consignment; this can only be decided with a knowledge of the costs involved in the sieving operation.

A shrinkage is usually allowed when cutting the grid impression in the mould blocks to allow for the reduction in the casting dimensions as the alloy freezes. Variations in the thickness of the mould coating (applied to the mould surfaces directly) affects the dimensions of the finished castings. Thick coats produce thin castings, and vice versa.

#### Mould coating preparation

There is a great divergence of opinion regarding the preparation of mould coatings. Most battery makers prefer to have a single solution sprayed directly on to the hot mould surfaces. There are some who claim that the cork slurry will adhere better to the mould surface and will not oxidize so rapidly if the mould surfaces are first sprayed with a protective coating of the following:

0.6 kg sodium silicate, density 1.35 g/cm<sup>3</sup>
0.4 kg superfine silica (aerosil)
10 l demineralized water or distilled water

This mixture is sprayed over the surface of cleaned or unused moulds. It is not intended to be sprayed over cork surfaces.

The procedure is to mix the sodium silicate with 6 l of the demineralized water. When this is thoroughly mixed, the aerosil is slowly added with the mixer agitator working so that the aerosil is completely assimilated. The remainder of the water is then added and well mixed. Finally, the mixture is given a further mixing for 1 h at a medium mixer speed. It is then ready for use. The mixture tends to form into granules or lumps if not used soon after preparation. Where this occurs the mixture should be given a short remix or, failing that, passed through a 300  $\mu$ m sieve before spraying.

The protective spray coating is then applied evenly over both mould blocks to produce a uniform white covering. The generally recommended spray procedure is to hold the gun about 25 to 30 cm from the mould surface and to move the spray gun parallel to the mould surface starting from the top of the mould and working downwards. Care should be taken not to overlap more than fractionally the mould coating immediately above. The mould blocks should be at a temperature of about 180 °C during the spraying. A crude guide to a good mould temperature in the absence of measuring devices is to watch the coating hit the mould surface and dry. If, momentarily, it should appear wet and be seen to dry rapidly, the temperature is roughly correct.

This first coating has functions other than that of a basis for a good adherent cork layer. It fills in minute imperfections on the mould surfaces, so that the cork coating is presented with a more imperious and smoother surface, and assists in the casting of truer replicas of the machined profile.

Following the spraying of the protective coat, the portion of the mould surface that surrounds the grid frame profile with the main frame and lug surfaces is scraped clean of the protective coat to leave the protective coating in the cavity of the grid profiles.

The cork slurry usually adopted with the protective coating is as follows:

0.95 kg sodium silicate, density 1.35 g/cm<sup>3</sup>

0.5 kg superfine silica (aerosil)

0.35 kg sieved cork powder

10 I demineralized or distilled water

The mixing procedure is similar to that for the protective coating up to the assimilation of the aerosil. At this stage, the cork powder is added and again totally assimilated into the slurry. The slurry is then left for a minimum of 8 h after which it is worked through a 300  $\mu$ m sieve to remove coarse particles and lumps swollen in the presence of the liquid. After this, the slurry can be bottled or, if necessary, used. When the slurry is bottled, it must always be shaken vigorously before filling the spray gun. Most operators prefer to leave the slurry for 24 h before use.

The same spraying technique is used for the cork slurry as for the protective coating. When a thin even coating has been produced, the mating surfaces of the mould blocks should then be scraped clean of cork using a blunt scraper to avoid damaging the mould surfaces. This allows the true machined surfaces to come into intimate contact and set the profile dimensions to the designed value. The lug section is usually more massive than the frame sections and will require a greater transfer of heat before freezing. It is common practice to remove, or reduce, the amount of cork coating on the lug area to speed up the freezing in that area. The amount of coating removed is a decision for the operator to make based on the way the mould is behaving. Cork coating in the mould throat or gate will delay the freezing of the solid sprue; here again, reduction or removal of the cork covering will be required.

With the two-coat system, it is claimed that touching up only is needed during the working shift. If it is considered necessary to remove the coatings and respray completely, it is important that the moulds are first cleaned thoroughly. Most of the coatings can be removed with a brass wire brush, but the coatings deep in the rib and wire recesses often defy brushing out. In such cases, the moulds need either to be chemically washed with hot 10% KOH, or cleaned electrolytically. In the latter process, the mould blocks are made the cathode in an electrolytic cell in which the anode is either a grid of the type normally cast in the mould or a sheet of pure lead placed between the mould blocks and separated from the blocks by sheets of absorbent paper that have good wet strength. Soft crepe toilet tissues are usually satisfactory.

For electrolytic cleaning, the mould blocks are placed in a container that contains an aqueous solution of caustic soda (between 10 and 20% KOH), along with the grid or lead sheet anode and surrounding tissues. A current between 0.5 and 1  $A/in^2$  is passed for about 10 min between the mould blocks and the grid (or sheet) anode. The blocks are then removed and well washed with water to remove all traces of caustic soda. In the washing, most of the ingrained coating comes away with the tissues. Any that fails to do this can be removed with a pointed brass rod or a brass wire brush.

Hard steel probes or steel wire brushes tend to score the mould surfaces and the irregularities are thereafter reproduced on every grid cast. Deep scores can also hinder the free flow of the molten alloy though the mould cavities and make it difficult to obtain consistent full filling.

Where single mould coatings are used, the formulation has to aim at producing a strongly adherent cork slurry that is compatible with the metal surface of the mould. The difference with the two-coat system is that the latter concentrates on preparing the mould surface with a very adherent coating that needs not to be highly resistant to charring but will readily accept the cork slurry. The single coat must combine adhesion and resistance to charring.

The simplest of cork coatings relies entirely on the sticky nature of sodium silicate; it consists of water, sodium silicate and cork. This mixture has a very limited life in storage since there is a reaction between the bacteria in the cork and the sodium silicate. The latter is converted to silicic acid. This is not sticky and the coating will have poor adhesion and soon peel off in use. This simple coating follows the general formulation:

water	21
sodium silicate, density 1.35 g/cm <sup>3</sup>	0.125 1
cork powder	0.15 kg

The main objective in mixing is to produce a thin slurry in which the cork powder is evenly distributed and which is acceptable in a standard spray gun. The actual consistency of the slurry is very much the operator's choice, although it is better to build up the required thickness by many thin passes of the spray gun rather than to reduce the number of passes by thickening the slurry to the consistency of thin paint. Invariably, this latter practice leads to frequent clogging of the gun and irregular coating thicknesses. This makes the task of controlling the thickness of the cast grids very difficult.

A number of factors affect the choice of slurry consistency and the amount of sodium silicate used, such as the time between making the mould coating and using it, the temperature of the mould blocks, the distance away from the mould blocks when spraying, and the pressure of the spray gun. For these reasons, some companies confine the use of the cork coating to certain skilled operators to stabilize the coating technique and, in order to maintain a tight control on the age of the coating, they make it in small batches continuously throughout production. Where it is not expedient or convenient to confine mould coating to specialists, the supervisors should be thoroughly trained, and should insist on their technique being followed by the operators with maximum and minimum time limits placed on the use of the cork slurry after it has been made. Effective mould coating is a skilled operation and should be recognized on the shop floor. Well-trained operators become a valuable asset.

With the simple formulation of cork and sodium silicate, a crude guide is that: (i) less sodium silicate is needed if the coating is to be used fresh from making, (ii) the longer the interval between making and using, the more sodium silicate will be needed to maintain a mould coating life of several hours.

Although some companies use domestic food mixers in preparing the coating, the method standardized over many years relies on using a double jar pebble mill. The IBMA [1] recommends a double jar pebble mill of about 10 l capacity to make 5 l of mould coating. The procedure described comprises adding water, sodium silicate and cork to the jars, making sure all the sodium silicate is removed from its measuring cylinder using some of the water, and then sealing the jars with their proper closures. The jars are then placed on their mill frame and rotated at ~50 rpm for ~8 h. The recommended size of the grinding pebbles is about 2.5 cm×4 cm. At the end of the grinding period, the cork slurry is drained from the jars into airtight cans or bottles and stored for 6 to 10 days before use. The long milling or grinding period specified is irksome, but it is important in this simple formulation for the sodium silicate to be thoroughly incorporated into the cork particles to cause the slurry to mature and to form a tightly adherent cork layer on the mould surfaces.

The simple formulation has been greatly modified to dispense with the long milling, and even longer maturing time, before use. The main change has been a reduction in the amount of the sodium silicate by replacing it with additions of such materials as bentonite clay and various glue solutions. Such modifications make it possible to produce consistent slurries with stirrup-type mixers. Nevertheless, many battery makers still retain the pebble mills but reduce the milling to 1 to 1.5 h with a maturing time of 24 h.

Wherever sodium silicate is used, there is the risk of chemical changes occurring that convert it to silicic acid and destroy its adhesion properties. Care should be taken not to store prepared coatings in hot places since they are liable to ferment, lose their adhesion and attract considerable mould growth. These modified coatings should be used within 96 h.

When buying cork powder, care should be taken to check whether the powder is the natural product or treated with a glue additive. In the latter case, some reduction in the sodium silicate is recommended. In all formulations it is recommended that the powder, as received, is passed through a 300  $\mu$ m sieve before incorporation into a mould coating.

Some idea of the large variations common to the industry in the formulations for mould coatings can be seen from the comparison given in Table 9 of a number

#### TABLE 9

Formulation no.	Cork (kg)	Total water (1)	Sodium silicate (1.38 sp. gr.) (cm <sup>3</sup> )	Other ingredients
1	1	9.1	170	None
2	1	10.3	150	None
3	1	15.0	880	None
4	1	13.2	215	Bentonite 250 g
5	1	16.7	372	Bentonite 375 g
6	1	21.0	331	Bentonite 400 g Casein glue 225 g
7	1	53.2	510	Bentonite 1670 g Tannin 67 g
8	1	6.2	515	Gum tragacanth 30 g plus fermentation inhibitor
9	1	20.0	0	Glue solution Gypsum

Formulations for mould coating

of formulations based on a kilogram of sieved cork powder. Such wide differences in what would appear to be essential components, i.e., cork, water and sodium silicate, must make it difficult to accept any one of the above as a general purpose mould coating. There are a few empirical rules that help namely:

(i) the slurry should be thin as it is usually more effective to use many coatings to build up the desired thickness of the mould coating;

(ii) high sodium silicate quantities per litre of finished slurry tend to produce a mould coat that does not keep well and will tend to peel more readily in the presence of the molten alloy;

(iii) if in doubt, hold the amount of sodium silicate (1.38 sp. gr.) at between 1.5 and 2% of the total water;

(iv) the addition of bentonite clay should not exceed 30 g/l in the final solution;

(v) the addition of bentonite clay in small amounts helps to bind the cork and sodium silicate and increases the resistance of the coating to charring, and

(vi) the total solids determine the final consistency; these should not exceed 100 g/l in the final solution.

These provide guidelines within which to work, but the final quantities of each component must depend on the individual manufacturer's preference, based on trials.

Because of the variable density of cork, the argument has been advanced that a more consistent product is produced if, in the formulations, the cork powder is specified by free volume instead of weight. There is a real justification for this but, in practice, difficulty is encountered in controlling the free volume as the way the operator scoops up the powder and levels it in the measuring cup can significantly alter the physical amount taken up. Some easement in this difficulty can be obtained by testing the cork powder on receipt for tamp density. A jolting volumeter is employed and a new weight is calculated for the formulation based on the tamp density so that the tamp volume of the cork powder remains a constant, regardless of the mixing. Once an acceptable formulation has been developed it should be standardized and properly documented. The life of the mould coating after being sprayed on to the mould is dependent on the temperature of the molten lead that enters the mould. The higher the lead temperature, the greater is the oxidation of the cork and the quicker is the heat insulation characteristic of the coating destroyed. This is a further reason to keep the temperature of the lead alloy as low as is consistent with the regular achievement of full filling of the mould.

## Reference

1 N.E. Hehner, *Storage Battery Manufacturing Manual*, Vol. 3, Independent Battery Manufacturers Association, Largo, FL, USA, 1986, pp. 10–12.