

Technical Note

Aspects of lead/acid battery technology

I. Pastes and paste mixing

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Abstract

The characteristics of a sulfated leady paste suitable for lead battery production are listed. A detailed description is given for (i) conditions necessary to produce such a paste which will shear and flow well under pressure; (ii) how for any particular attrition mill or Barton-pot oxide the boundaries defining the beginning and end of the plastic flow region can be determined, and (iii) a family of curves established relating paste density with water and sulfuric acid additions making due allowance for losses occurring during the mixing process. Methods of paste application are described together with a code of operating practice to ensure good reproducibility of pasted plates with a minimum of machine 'downtime'. Flash drying is described and the reasons for its adoption.

Background

The preparation of a paste is the start of the production of the active materials that confer to the battery design its life and performance characteristics. The paste has to be capable of flowing under pressure into the lattice framework of the grid and be retained there throughout the subsequent curing and drying process during which the material acquires its rigidity and particle-to-particle cementation.

The main objectives in paste formulation and mixing are to produce a homogeneous paste from grey lead oxide, bulked up by the sulfation of a proportion of it, and water blended in such a manner that the wet paste will:

- (i) shear readily under pressure and exhibit plastic flow properties;
- (ii) readily penetrate and fill the open spaces in the lattice structure of the grid;
- (iii) retain its moisture for sufficient time in a controlled atmosphere to allow the curing reaction to proceed continuously until the free-lead component has decreased to below a permitted maximum which is usually less than 5 wt.%;
- (iv) during the curing and drying processes, maintain a consistent and small reduction in overall volume (shrinkage) without producing local sinkage in individual pellets or noticeable cracking;
- (v) consistently produce, after formation, apparent formed materials densities within the permitted specified range to meet market performance and life expectations.

Initially, most plates were hand pasted using a wooden 'bat' held with the handle forward of the pasting edge so that the mass of the paste was subjected to an inclined

force pushing it into the grid. Various surfaces were used under the grid castings, those were dictated to a degree by personal preferences. The more common surfaces were thick Kraft paper, wet sailcloth or plate glass. Proponents of the former two substrates claimed that the rough surfaces of these materials assisted the escape of gases from the negative plates and produced a more even expansion of the active material. The Kraft paper absorbed some of the moisture in the paste and this reduced the porosity of the set material compared with plates pasted on wet sailcloth or glass. Proponents of pasting on glass claimed that there could not be any water loss during pasting as the glass was completely nonabsorbent and the final pasted plate was more consistent in porosity and dimensions than any other pasted plate. Although the water loss with wet sailcloth should be very small, the maintenance of a thoroughly wet cloth at all times was suspect and could give rise to a greater variation in practice than was admitted.

Hand pasting has now been superseded by machine pasting where the wet paste, held in a paste hopper, is forced downwards into the grids by pasting 'paddles' rotating within the hopper whilst the grids pass under the hopper. The angle of the applied pressure on the paste (shear angle) is determined by the interaction of the paddle rotation speed and the speed with which the grids pass under and away from the hopper. The shear angle applied to the paste dictates the texture and plastic-flow characteristics needed in the paste. For this reason, many pasting machines are supplied with a common motor drive for both the hopper paddles and the grid feed. Where these two functions are separated with individual drives, a change in the grid feed speed relative to the paddle rotation speed may call for a change in the paste texture for optimum pasting conditions.

Water tolerance and plastic flow

The final formed density of an active material is determined by the amount of lead present and the ability of the dried paste to retain a consistently constant proportion of its wet paste volume. Uneven shrinkage leads to poor-formed density control. It is the nature of the formed material — density, pore size and porosity — that determines the ultimate cell performance. The way in which the water is constant within the wet mix, as well as the amount of water held, determines initially the wet paste density, the texture, and the amount of shrinkage that occurs during curing and drying. Unless the total water content lies between limits determined by the particle size and shape, the wet paste will not shear and flow readily under pressure to fill completely the grid structure. The total water contents at the lower and upper limits of plastic flow define the water tolerance or limits of the oxide or its plastic range.

If water is added to grey lead oxide, it initially enters the air spaces between the solid particles. This produces an increase in the apparent density of the water/oxide slurry. The apparent density continues to increase until all the enclosed air has been displaced by water. When this occurs, the slurry registers its maximum density. At this stage the slurry will not shear or flow readily under pressure. Further additions of water are disposed as films surrounding the solid particles. When the thickness of the water film has built up to a particular value that is determined by particle size and shape, the particles become free to move relative to one another. This is the onset of plastic flow and the beginning of the plastic range. Plastic flow is retained with further additions of water but with a reduction in the particle-to-particle adhesion. A point is reached at which the adhesion is so tenuous that a small excess of water

causes the paste to slump into a 'mud' that is incapable of supporting a discrete form. This is the upper limit of the plastic range.

The water tolerance of an oxide is an important characteristic in defining the working limits of any particular oxide. A simple test of water tolerance is described by Bode [1]. It consists of: (i) step-by-step addition of water to 100 g of oxide until the resultant slurry exhibits plastic flow, and (ii) the continuation of the addition until the upper limit of plastic flow has been reached. The amount of water added at each step was 2 cm³. At each addition, the water is mixed with the oxide using a spatula until the resulting slurry assumes a shiny appearance. This coincides with the attainment of maximum density conditions. The water additions are continued until the slurry can be spread under pressure and until it shows signs of slumping. To illustrate how different oxides give different plastic ranges, Bode quotes the excess water required to take oxide samples from maximum apparent density conditions to the onset of plastic flow. The excess water was 8 l and 2 l for 100 g of ball-mill and Barton-pot oxide, respectively. The appreciably greater water required for ball-mill oxide probably reflects the effect of the platelet shape of that oxide. By contrast, the crudely spherical shape of the Barton-pot oxide would be expected to need less 'lubrication' to allow the movement of the particles relative to one another.

Many operators still manually feed their paste mixers and add the total water in three stages, i.e.: (i) as initial or starting water to form a water-oxide slurry; (ii) as the water component of a sulfuric acid addition, and (iii) as an adjustment addition to correct the wet-paste density.

The sum of the amounts in (i) and (ii) should always be sufficient to take the wet-paste density beyond the maximum value, to approach the onset of plastic flow (if not to enter it), and to exclude all air from the slurry. Thereafter, the adjustment of water merely corrects the density by adjusting the thickness of the surface films of water surrounding the solid particles. In reality, the adjustment alters the texture since the sulfuric acid addition controls the solids volume and the final dry volume.

Some operators tend to hold back an appreciable portion of the specified starting water to compensate for high-humidity and/or low-ambient temperatures and if the sum of additions (i) and (ii) fail to reach the maximum density requirements, the risk occurs that the air still present in the mix will not be entirely replaced by water in the final adjustment addition. If this occurs, then the surface film surrounding the solid particles is thicker than intended, the paste is softer than specified, water is expressed from the paste during the pasting process, the formed density is higher than the performance demands, and a greater volume contraction takes place during the curing and drying. If the attainment of the minimum specified performance is difficult when all the paste requirements are met, then the altered paste will fall short of producing the required minimum performance.

In many instances, the choice of paste texture (i.e., the extent to which the slurry is taken into the plastic range) is dictated more by what the available pasting machines will accept than by the benefits to the subsequent curing process. This is understandable as the ability to continue pasting throughout a working shift with little or no down time at a good production level is a major asset to favourable manufacturing economics. Nevertheless, it does introduce some risk as the life of active material depends to a great extent on the production of a strong, crack-free cured material which, in its turn, requires a minimum amount of water in the pasted material in order to allow the curing reaction to continue for sufficient time to produce the maximum recrystallization of lead sulfate and the interlacing of a needle-shaped crystal structure that creates strength, rigidity and internal developed surface area.

The plastic range is greatest with water oxide slurries and decreases with increasing sulfation whilst the water content for maximum density increases. A situation arises where, with a particular high-sulfation level, there is virtually no measurable plastic range. It is necessary to know the deviation from that situation when considering low-density, high-porosity formulations. If the circumstances are such that the plastic range is small then paste control can be difficult, particularly when the water and sulfuric acid feeds are controlled manually. The sight glasses on the feed tanks are capable of significant parallax errors as is the rate of feed of the sulfuric acid solution.

Wherever possible, the oxide characteristics, particle-size distributions, shape, oxidation level and tamp densities should be standardized and held rigidly to that standard. The behaviour of the oxide, when sulfated to varying degrees, to the addition of water should be known, i.e., the amount of water to give plasticity and to lose that plasticity at each sulfation level. With these data and a constant oxide, paste formulations can be planned that will always be workable and that will accept reasonable working tolerances.

Wet-paste density

Whilst the wet-paste density is broadly determined by the amounts of water and sulfuric acid that are mixed with the oxide, there are losses occurring during the mixing operation. The latter are dependent on the type of mixing machine, the amount of cooling provided, the rate of sulfuric acid addition, etc. It is not possible to state precise quantities for water and sulfuric acid that would be independent of those factors. It is possible, however, to derive characteristic curves for paste mixes and to correct these curves from experimental data so that they become basic working data for a particular factory. The following assumptions must be made: (i) no water loss occurs through evaporation during mixing; (ii) no air is included in the resulting paste, i.e., water has replaced it; (iii) no significant chemical change occurs in the grey oxide during the water slurry state, and (iv) the ambient humidity and temperature of the mixing shop is constant.

Justifiably, it can be argued that there is evaporation, the ambient air is not constant and some reaction does occur during the water slurry stage. Nevertheless, if the curves are accepted as providing practical guidelines pointing to what changes in formulation would give certain specified changes in paste densities, the errors are not large and can be accepted, particularly where it is the practice to make a final density adjustment after mixing.

It is common for the sulfuric acid addition to be made using a solution of 1.400 sp. gr., or 50 w/w%. One litre of this solution will react with 1.593 kg of PbO to produce 2.164 kg of PbSO₄ and 0.829 l of water. The following procedure is used to calculate the wet-paste density.

Take a basic oxide containing 70 wt.% PbO, 30 wt.% Pb with a mixing formulation calling for 120 l H₂O and 60 l of 1.400 sp. gr. sulfuric acid.

Weight Pb in 1 tonne of oxide:	300 kg
Volume Pb (note, density of Pb=11.3 g cm ⁻³):	26.55 l

Weight PbO in 1 tonne of oxide:	700 kg
Volume PbO (note, density of PbO=9.5 g cm ⁻³):	73.68 l
Weight PbO reacted by 60 l of H ₂ SO ₄ :	60 × 1.593 kg = 95.58 kg
Volume PbO reacted:	10.06 l
Volume unreacted PbO:	63.62 l
Weight PbO unreacted:	604.42 kg
Weight PbSO ₄ produced by reaction:	60 × 2.164 kg = 129.84 kg
Volume PbSO ₄ (note, density of PbSO ₄ =6.3 g cm ⁻³):	20.61 l
Volume H ₂ O produced by reaction:	60 × 0.829 l = 49.74 l
Weight H ₂ O produced:	49.74 kg
Volume starting water:	120 l
Weight starting water:	120 kg
Total weight of components:	1204.01 kg
Total volume of components:	280.52 l

$$\text{Wet-paste density} = \frac{\text{total weight}}{\text{total volume}} = 4.29 \text{ g cm}^{-3}$$

In American units, this is equivalent to 70.3 g in⁻³.

If the sulfuric acid additions are taken in increments of, say, 10 l per tonne and for each level of acid addition several levels of starting water are taken, the above calculations can be repeated to derive a family of curves that link starting water and density with each value of acid addition. From these data, a more useful set of curves can be obtained that give starting water additions and sulfuric acid additions for increments of wet-paste density (Fig. 1).

The important feature of these curves is the infinite number of water and sulfuric acid combinations that will give each specified wet-paste density. Other criteria narrowing the choice of the water/acid balance are needed to complement these curves. These criteria, in order of importance are, (i) total water required to define the plastic range at each acid level; (ii) the texture of the paste that is required to satisfy the particular pasting machines available; (iii) the additives that are required to give to the paste the desired performance features of cold starting, high low-rate capacity, good charge acceptance, etc., and (iv) the tolerances that are specified for the oxidation level of the lead oxide.

Effect of oxidation level in the starting oxide

Consider two extremes of oxidation: (i) 50 wt.% PbO, 50 wt.% Pb and (ii) 80 wt.% PbO, 20 wt.% Pb. Take the case of a positive mix using, as in the above example, 120 l of water and 60 l of 1.400 sp. gr. sulfuric acid. With an oxide having 70 wt.% PbO, this gave a wet-paste density of 4.29 g cm⁻³.

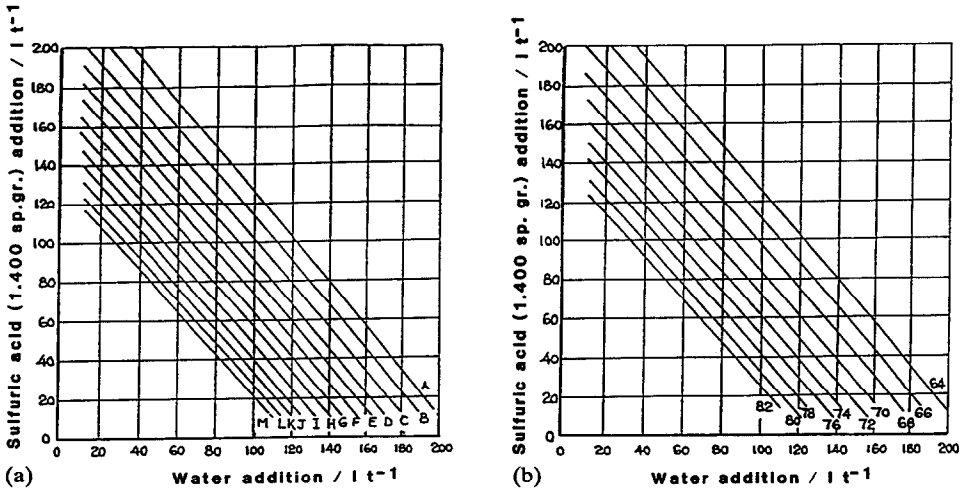


Fig. 1. Initial derived curves of the effect of varying water and sulfuric acid quantities on wet-paste densities (ignoring early stages when maximum densities have not been reached): (a) metric measures; (b) US measures. Resulting density (g cm^{-3}): A = 3.9; B = 4.0; C = 4.1; D = 4.2; E = 4.3; F = 4.4; G = 4.5; H = 4.6; I = 4.7; J = 4.8; K = 4.9; L = 5.0; M = 5.1.

In case (i), the change in materials with mixing would be:

	Weight (kg)	Volume (l)
Lead	500.00	44.25
Lead oxide	404.42	43.49
Lead sulfate	129.84	20.61
Water	169.74	169.74
Total	1204.00	278.08

Resulting wet-paste density = $\frac{1204.00}{278.08} = 4.33 \text{ g cm}^{-3}$; this is an increase of 0.9%.

In case (ii), the change in materials would be:

	Weight (kg)	Volume (l)
Lead	200.00	17.70
Lead oxide	704.42	74.15
Lead sulfate	129.84	20.61
Water	169.74	169.784
Total	1204.00	282.20

Resulting wet-paste density = $\frac{1204.00}{282.00} = 4.27 \text{ g cm}^{-3}$; this is a decrease of 0.55%.

In going from the extremes quoted for the oxidation level and maintaining the same values of starting water and sulfuric acid solution, the paste densities have changed by ~1.5%, or the starting water would need to be increased by about 4 l

when the oxidation level was 50% and decreased by about 2 l when the oxidation level had been raised to 80%. These percentages will vary as the ratio of water-to-acid changes, but the differences will be sufficiently small that the type of oxidation percentage tolerance normally applied can be ignored when using the curves.

Effect of litharge additions in negative pastes

It has been a recognized practice with some firms to add litharge (PbO) to grey oxide, particularly in traction cell negatives. This was originally popular when coarse ball-mill oxides were used. The litharge introduced was generally of low-micron and submicron size and roughly spherical. Much of it was made using the Barton-pot process. It could be made with a higher apparent density than the grey battery oxide and, when blended into that oxide, raised the apparent density. The resultant blend consisted of relatively coarse grey oxide with finer litharge particles in the air spaces. This artifice helped to produce a relatively dense paste with good shear properties which did not impose a high load on the hopper drive motor and which flowed readily into the lattice structure of the grid.

To assess the effect of the litharge additions on the wet-paste weights, assume two levels of litharge/grey oxide blends, 10 and 30 wt.% PbO, in a grey oxide with a 70 wt.% PbO content.

When the proportion of grey oxide is 90%, the amount of PbO (litharge) present will be 63% (i.e., 90% of 70%). This gives a blend composition of 73 wt.% PbO and 27 wt.% Pb. The effect of this change in the PbO content in the previous example of a paste using 120 l of water and 60 l of 1.400 sp. gr. sulfuric acid would be for a positive paste:

	Weight (kg)	Volume (l)
Lead	270.00	23.89
Lead oxide	634.42	66.78
Lead sulfate	129.84	20.61
Total water	169.74	169.74
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Total	1204.00	281.02

$$\text{Resulting wet-paste density} = \frac{1204}{281.02} = 4.28 \text{ g cm}^{-3}.$$

If the percentage of litharge present is 30%, the total amount of PbO present in the dry powder will be 79 wt.% with 21 wt.% Pb. The effect of this on the wet paste will be:

	Weight (kg)	Volume (l)
Lead	210.00	18.58
Lead oxide	694.42	73.10
Lead sulfate	129.84	20.61
Total water	169.74	169.74
	<hr/>	<hr/>
Total	1204.00	282.03

$$\text{Resulting wet-paste density} = \frac{1204}{282.03} = 4.27 \text{ g cm}^{-3}.$$

Thus the effect of a 10% litharge addition has been to change the wet-paste density from 4.29 to 4.28 g cm⁻³ and the 30% PbO addition to decrease it slightly more to 4.27 g cm⁻³. In practical terms, this is equivalent to a change in the water addition of 0.4 and 0.8 l, respectively. Neither of these amounts exceed the normal plant errors.

For litharge additions, characteristic curves derived for simple grey oxide mixes are adequate for estimating water and sulfuric acid changes to achieve particular wet-paste densities.

Effect of red lead additions to positive paste densities

It is still common practice to add red lead (Pb₃O₄) to the grey oxide for positive active materials in flat-plate cells of all types. This artifice reduces the initial free lead in the blend and improves the electrical conductivity in the cured plate, so assisting formation. Compared with lead oxide, less formation ampere-hours per kg are required to convert red lead to lead dioxide. Red lead is virtually a mixture of lead oxide and lead dioxide. With the red lead blend, it is less difficult to control the proportions of α - and β -PbO₂, that are produced on formation. The former is claimed to give strong cementation bonds between the particles of active material, whilst the latter gives a higher capacity per unit weight of material provided there is sufficient electrolyte present to sustain that increased capacity.

There is a danger in adding too much red lead, as the higher the proportion of red lead the weaker are the particle-to-particle cementation bonds and the greater is the risk of premature sloughing of the active material from the surface of the plate. Where the plate is not fully supported over its full surface, it is unwise to exceed 15 wt.% Pb₃O₄, but where the positive material is fully supported this can be increased to 30 wt.%. With this latter level, it is important to ensure that, at all times, the cell element filled with electrolyte is under compression.

The usual factor deciding whether or not to add red lead is the ease, or otherwise, with which competitive capacities can be achieved. Wherever competitive capacities can be achieved without the use of red lead, its use should be avoided as life and cost will be improved.

Assume the level of red lead addition is the maximum, i.e., 30 wt.%. The density of battery grade red lead is 9.1 g cm⁻³. Take the previous examples as the basis, i.e., 120 l water and 60 l sulfuric acid (sp. gr. 1.400) per tonne of oxide blend. The proportion of PbO in the full blend will be 40 wt.% with 30 wt.% red lead Pb₃O₄ and 21 wt.% Pb. The effect of this on the wet paste will be as follows:

	Weight (kg)	Volume (l)
Lead	210.00	18.58
Lead oxide	394.42	41.52
Red lead	300.00	32.97
Lead sulfate	129.84	20.61
Total water	169.74	169.74
Total	1204.00	283.42

$$\text{Resulting wet-paste density} = \frac{1204.00}{283.42} = 4.25 \text{ g cm}^{-3}.$$

Thus, the effect of the 30 wt.% Pb_3O_4 addition has been to reduce the wet-paste density by $\sim 1\%$, and is equivalent to an increase of ~ 4 l water to the original mix without red lead.

Effect of expander additions to negative pastes

Negative active materials require additional elements to maintain the porosity throughout the working life of the battery and, in the case of automotive batteries, to improve and maintain cold start voltage and duration levels. These additional elements, termed 'expanders', are added to the oxide at the paste-mixing stage. The common inorganic expanders are barium sulfate and carbon black and the organic are generally lignosulfonates. Typical proportions are as follows:

(i) barium sulfate (density 4.5 g cm^{-3}) 0.3 to 0.5 wt.%; (ii) carbon black (density 1.8 g cm^{-3}) 0.1 to 0.2 wt.%, and (iii) organic dependent on the nature and activity of the material. One particular brand, density 1.5 g cm^{-3} , is used in the proportions of 0.15 to 0.3 wt.%; the organic materials vary from sparingly soluble to fully soluble in water, the fully soluble types are precipitated in the presence of sulfuric acid.

To illustrate the effect of the expanders on the final wet-paste densities assume the following additions: 0.4 wt.% BaSO_4 , 0.15 wt.% C, 0.25 wt.% organic. The worst result will be when the materials are taken as discrete components. The weight and volumes of the expanders per tonne of oxide will be:

	<u>Weight (kg)</u>	<u>Volume (l)</u>
Barium sulfate	4.0	0.89
Carbon black	1.5	0.83
Organic	2.5	1.67
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Total	8.0	3.39

This gives the following weight and volume proportions:

	<u>Weight (kg)</u>	<u>Volume (l)</u>
Lead	300.00	26.55
Lead oxide	604.43	63.62
Lead sulfate	129.84	20.61
Expanders	8.00	3.39
Water	169.74	169.74
	<hr/>	<hr/>
Total	1212.01	283.91

This gives a wet-paste density of 4.27 g cm^{-3} , i.e., a reduction of 0.5% on the original figure without the expanders. Thus, the latter can generally be neglected in estimating water and sulfuric acid changes.

Effect of water tolerance and plastic flow on derivation of characteristic curves

The characteristic curves in Fig. 1 ignored the effect of water tolerance and plastic flow as well as the fact that, until the air spaces between the particles of the oxide have been filled with water, the apparent densities are lower than that calculated. In the previous section on water tolerance the importance was stressed of knowing, for the oxide used in the factory, the amounts of water needed to reach maximum density conditions and the onset of plastic flow.

If now that simple test to determine water tolerance is extended using sulfuric acid solutions of varying concentrations, a number of water/sulfuric relationships can be established. These plots will define the locus of the onset of plastic flow over the range of possible paste formulations. The locus is a key factor for the technical personnel wishing to understand what can or cannot be done in paste mixing and how much freedom the paste formulation will provide in setting meaningful operating tolerances that will never give pasting problems.

It is not possible to insert into the characteristic curves of Fig. 1 a firm demarcation line that will divide the curves into regions that are representative of pastable material and those that are not pastable. This is dependent on the particular oxide used, its method of manufacture, particle size and shape, etc. Once the data have been obtained of the water additions needed to attain maximum density and the onset of plastic flow for various degrees of sulfation of a given oxide, the curves of Fig. 1 can be modified to show those mixing conditions that are truly valid.

Take, for example, an oxide that has the following water addition data produces plastic flow at various sulfation levels.

Sulfuric acid addition (kg t^{-1})	Water additions to produce	
	maximum density (l t^{-1})	plastic flow (l t^{-1})
0	65	104
15	80	127
30	95	160
40	105	185
50	115	225

These data define: (i) the lower limits of water and sulfuric acid additions at each wet-paste density for which the characteristic curves are valid, and (ii) the lower limits of water and sulfuric acid for the production of spreadable pastes.

In Fig. 2, the characteristic curves have been replotted with the sulfuric acid addition as ordinate in kg sulfuric acid per tonne of dry powder and the total water

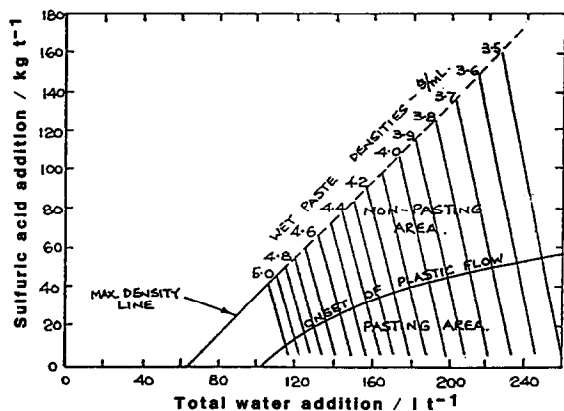


Fig. 2. Conditions determining possible water/sulfuric acid relationships for satisfactory pasting.

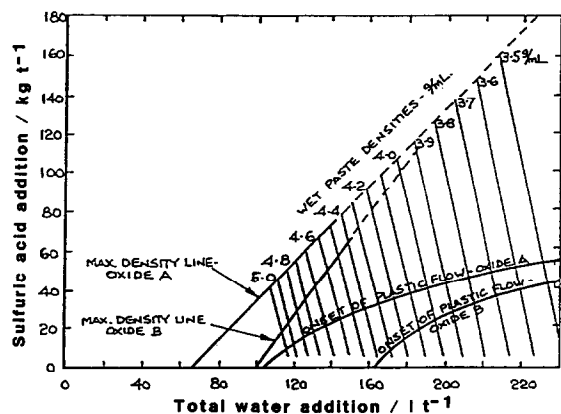


Fig. 3. Effect of plastic-flow characteristics of an oxide on area from which good paste can be produced.

additions as abscissae. The water of reaction from the sulfation reaction has been taken into the wet-density calculations but as this is a reaction product, it does not form part of the total water addition. All portions of the previous curves that would fall outside the maximum density curve, derived from the oxide data, have been omitted as they are no longer valid. They would produce pastes with voids and unsuitable for spreading. The inclusion of the boundary conditions for the onset of plastic flow defines the portion of the characteristic curves that is applicable to the production of pastes that spread under pressure and will fill the grid lattice. Although the area of the characteristic curves applicable to pasting has been defined, it does not define precise water/sulfuric acid relationships for formulating new paste mixes. These are governed by the pasting machine characteristics and the effectiveness of the curing process.

The influence of the plastic-flow characteristics of the oxide adopted cannot be overemphasized. This can be illustrated by comparing the oxide in Fig. 2 with a very reactive oxide that has a greater water tolerance. For the purposes of identification, the initial oxide is called oxide A and the more reactive oxide B in Fig. 3. Whilst oxide B will undoubtedly produce a formed active material with excellent cold-start

characteristics, its activity impose limits on its use. The area of plastic flow is restricted and this limits the maximum wet-paste density that can be adopted. It would be difficult to exceed 4.3 g cm^{-3} wet-paste density without going outside the plastic-flow conditions. Oxide A would give little trouble over the wide range of wet-paste densities from 3.7 to 5.0 g cm^{-3} . Where only automotive pastes are required, oxide B would be fully acceptable and would provide very active, high-porosity formed active materials that are suitable for shallow cycling. It would not be particularly suitable for batteries required for regular medium- to deep-discharging, nor as a compromise oxide for both automotive and traction purposes.

For this reason, companies making both automotive and traction batteries need to examine the restriction that the adoption of a single compromise oxide may have on the performance of their products. Choice of an oxide that will eminently suit traction battery life requirements, may jeopardize the ability of automotive batteries to match the cold-start performance of competitors' products. There is some logic in adopting different oxide characteristics for each main application.

Figure 3 also throws light on the problems that some firms have experienced when an old oxide mill with a relatively coarse-grain product has been replaced by a new and more modern mill producing a finer and more reactive oxide.

Although the area of water/sulfuric acid relationships can be identified, there is still difficulty in deciding which of the many possible relationships available is the best one for the product. The production of a good interlacing needle-shaped crystal structure of lead sulfate is the basis of a strong, self-supporting active material that, in the curing process, will involve only a small decrease in overall volume and will have strong particle-to-particle bonds. The higher the degree of sulfation, the greater will be (i) the excess water over that required for maximum density to produce plasticity and (ii) the greatest potential decrease in volume with the loss of the excess water by evaporation. Alternatively, a low degree of sulfation bequeaths to the paste a minimum of lead sulfate from which to derive the ultimate material strength and porosity although the potential for volume shrinkage will be much reduced.

On balance, it is more helpful to seek the maximum sulfation possible within the working area of water/sulfuric acid relationships and to concentrate on making the curing process highly effective than to restrict the degree of sulfation in the interest of reducing the tendency of the curing paste to shrink. The production of the needle-shaped basic lead sulfate crystals is a phenomenon that is dependent on the maintenance of an adequate humidity/temperature pattern within the paste so that the recrystallization process, which is a slow one, can proceed to completion. When these conditions have been achieved, the growth in the crystal structure often balances the reduction in volume through the loss of the excess water needed to take the wet paste from the condition of maximum density to the onset of plastic flow.

This leads to the first approach in formulating a new paste once the water tolerance and plastic-flow characteristics of the adopted oxide are established. Initially, it is necessary to keep as close to the 'onset of plastic flow' curve as reasonable tolerances will permit in the metering of the water and sulfuric acid. Such an approach sets the water/sulfuric acid relationship for each selected wet-paste density. The arrangement usually produces a dry, crunchy paste that may not suit every pasting machine. If this is the case, the quantity of the sulfuric acid is reduced and that of water is increased in small steps along the same wet-density contour line, until a paste is produced that is acceptable to the pasting machine. This becomes the established paste.

To illustrate the important role that the water tolerance and plastic-flow characteristics play in influencing the water/sulfuric acid relationships, the plots for a

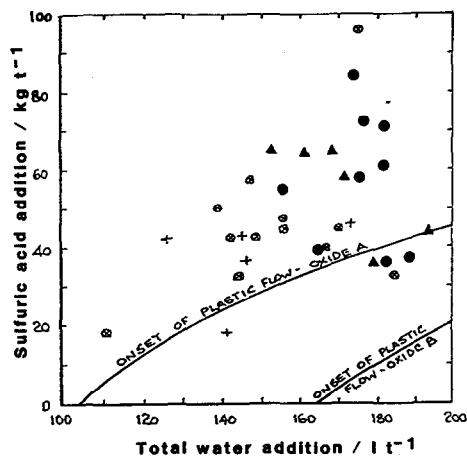


Fig. 4. Comparison of commercially-used automotive and traction battery positive and negative paste formulations with plastic-flow characteristics of selected oxides A and B: (●) automotive battery negative pastes; (▲) automotive battery positive pastes; (⊗) traction battery negative pastes; (+) traction battery positive pastes.

number of commercially-used automotive and traction battery pastes, both positive and negative, have been added to the curves for the 'onset of plastic flow' for the oxides A and B (previously shown in Fig. 3) in Fig. 4. The immediate point of interest is that most of the relationships fall outside of the 'onset of plastic-flow' curves for either oxide. A manufacturer acquiring knowledge of any of the relationships and adopting them on the assumption that the known user was making a commercially-viable product could run into pasting troubles if the oxide being used is as reactive as either oxide A or B. Each of the plotted water/sulfuric acid relationships would have been related to a particular oxide particle shape and size.

Between the two World Wars, it was common for flat-plate traction plates to use relatively dense pastes and this was possible with the coarse oxides produced from Hardinge and similar oxide mills. The competition as regards capacity performance that the introduction of the modern tubular positive traction cell stimulated caused makers to reduce the wet-paste densities and made it possible for the finer oxides to be adopted. Nevertheless, there were difficulties and many makers preferred to use a different oxide type for traction to that for automotive battery purposes.

Relationship between total water content and wet-paste density

The total water content of a paste is made up of the initial water to form the water/oxide slurry, the water of solution in the sulfuric acid addition and the water of reaction from the formation of basic lead sulfates. The data in Fig. 1 can be used to calculate the values of total water for a wide range of wet-paste densities. These are given in Fig. 5 for pastes where the sulfuric acid addition is 7 and 70 kg per tonne, respectively.

The amount of sulfuric acid used has only a small effect on the wet-paste density, the important factor is the total water content.

Estimation of water losses during paste mixing

The reactions taking place during paste mixing produce heat that is dissipated through conduction via the fabric of the paste mixer and its associated cooling system, and via the evaporation of some of the added water. These losses are dependent on the type of mixer and the way the paste is produced, particularly the rate at which the sulfuric acid is added. The characteristic curves relating water and sulfuric acid with wet-paste density are based on the assumption that there is no loss of water during the mixing process. It is essential, therefore, to know how much water is lost during mixing to arrive at how much water should be specified in any particular formulation. Knowing the order of water loss with a particular mixer, the characteristic curves become working curves for that mixer. If, for any reason, a change is made in the mixer or a different mixer is used for the process, then it is expedient to derive the water loss with the changed circumstances and to amend the formulation.

The curves in Fig. 5 identify the total water that will be present in a paste with a given wet density. Using a standardized 'cube' with a known included volume for paste (this can be 1 or 5 in³, or 20 cm³), the weight of the included paste and, hence, its density can be derived. From the curves of Fig. 5 and making allowance for the degree of sulfation, the total water in the paste can be estimated. The difference between this amount of water and the total water added during the mixing process will be a measure of the water loss.

For example, a negative mix using a mixer with mullers required 156 l water (this included the final adjustment water) for an addition of 56 kg sulfuric acid. The cube weight was 78 g in⁻³ giving a wet-paste density of 4.7 g cm⁻³. This order of density required 135 l and indicated that there was a water loss during the mixing process of ~21 l.

The amount of sulfation demanded by the formulation has a bearing on the magnitude of the water loss and, for a particular mixer, it is necessary to determine the water loss for a different level of sulfation to enable the characteristic curve of Figs. 2 and 3 to be valid for any combination of water and sulfuric acid. Using the two determinations of water loss, the ordinate of the operating curves of Figs. 2

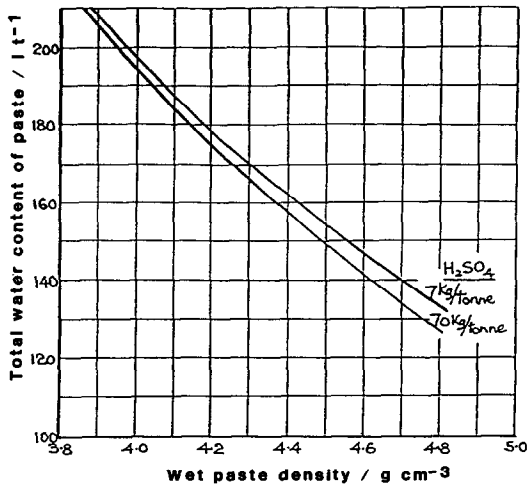


Fig. 5. Relationship between total water content of a paste and its wet-paste density.

and 3 would be redrawn to the left of the origin and would pass through the plots of the two water-loss figures and their relevant sulfation levels. The new abscissa scale starting from the new origin would then represent the actual water and sulfuric acid components required to produce given wet-paste densities with the particular paste mixer in use.

Effect of sulfation level on pasting pressures needed

The degree of sulfation in a wet paste modifies the impression of wetness that the paste exhibits to the touch. With increasing the degrees of sulfation, the paste appears to be drier and there is a reduced tendency for water to be extracted by the pasting machine belt during pasting. Generally, the drier the feel of the paste, the better is the retention of pellets and the freedom of the plate surface from defects.

Highly-sulfated pastes tend to require greater pressures to shear and the load imposed on the drive motor is increased compared with low-sulfated pastes. There is a limit to the size of the hopper drive motors that can justifiably be fitted. With very stiff pastes, there is a recurrent risk of motors being burnt out, or of fuses or circuit-breakers continually breaking the drive circuit.

It is good practice to use the hopper drive motor current as a shop-floor check on the paste consistency. The size of the drive motor sometimes acts as a restraint on the degree of sulfation, particularly in the case of high-performance automotive pastes.

Effect of sulfation level on mixing torque

Much the same effect as that described in the previous section for hopper drive motors is experienced when mixing paste. During the sulfation stage, the mixture becomes very stiff as it passes through the maximum density stage until it approaches the onset of the plastic-flow condition when it turns into a pliable 'dough'. The magnitude of the drive current increases with the degree of sulfation involved and can again introduce a restraint to the maximum level of sulfation. The data given in Fig. 6 refer to one particular type of rapid mixer.

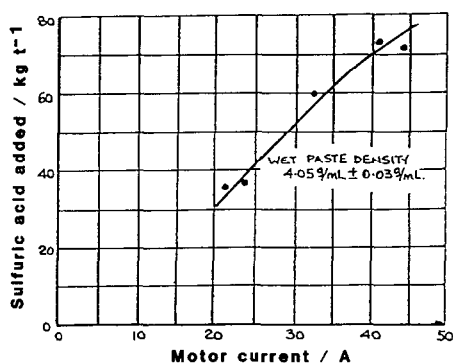


Fig. 6. Effect of sulfation level on mixer motor current.

Operational factors affecting wet-paste density

The characteristics relating water and sulfuric acid additions with the onset of plastic flow and wet-paste density define the operating parameters for paste mixing. In practice, losses occur in the water content of the wet paste and unless compensatory amounts of water are added, the wet-paste densities will be higher than planned. Water losses occur mainly through evaporation both in the preparation of the water/oxide slurry and in the subsequent sulfation reaction.

The water/oxide slurry is usually prepared by introducing the dry oxide first into the mixer chamber and then flooding in the initial, or starting, water. A rise in temperature occurs mainly from the surface oxidation and is dependent on the surface area of the oxide and the speed of wetting. Dry milling the powder before adding the initial water stabilizes the temperature rise and the water loss through evaporation. This enables an allowance to be made that will be constant for each mixing. Significant reductions in both temperature rise and evaporation loss can be achieved by reversing the process, i.e., filling the mixer chamber with water and introducing the dry oxide to the water. The mass of the water acts as a very effective heat sink.

A further factor aggravating the water loss in the slurry mixing stage is the air-extraction system required for environmental health control. This extraction can (and does) remove oxide and solid additives as well as water vapour.

The temperature rises are not usually large and typical figures for a high sulfation mix in a conventional muller type mixer are: (i) dry blending 3 to 5 °C, and (ii) water addition 8 to 12 °C. Most of the heat is generated during the sulfation reaction and is predictable. Some of this heat is absorbed by the fabric of the mixer body, some by installed cooling system, and some by the evaporation of water from the wet mix. The remaining heat is absorbed by the wet mix and thus causes its temperature to rise.

It is common for the sulfuric acid to be introduced as an aqueous solution containing sufficient water of solution to increase the initial or starting water to the full amount required by the specified formulation. The higher the level of sulfation required, the more will be the proportion of the total water included in the sulfuric acid solution and the higher will be the temperature rise in the water/oxide slurry stage. Some manufacturers considered that the losses can be controlled more readily by using a larger quantity of a lower density sulfuric acid solution and, therefore, eliminating the initial water addition. The disadvantage of this is that each mix formulation requires a different solution strength. Whatever the method adopted, the installed cooling system becomes a critical part of a mixer design. A very efficient cooling system can reduce both the water evaporation loss and the rise of temperature in the wet mix. It can also limit the temperature variations at the commencement of consecutive mixings.

A difficulty arises with consecutive mixings when there is insufficient time between mixings for the cooling system to restore the temperature in the chamber to close to ambient. If this occurs, there is a residual temperature carry-over from one mixing to the next. This causes the temperature of the mixer body to rise steadily throughout the working shift and with it the temperature of the water/oxide slurry. To illustrate this, Table 1 shows the temperatures obtained in two mixers of different designs over three consecutive mixings.

TABLE 1
Temperature rise with mixing

Mix number	Temperature of mixer body (°C)	
	Mixer A	Mixer B
1	18	18
2	27	21
3	43	20

The main differences between the two mixers were the mass of metal in the mixer chamber and the amount of forced cooling provided. During the course of the third mixing in mixer A, difficulties were experienced in keeping the wet-mix temperature below 70 °C and the water loss through evaporation below 24 l. As a result, the wet-paste density was higher than specified and the paste was drier than planned with a gritty texture that was very difficult to shear and force into the grids.

In contrast, mixer B stabilized a few degrees above ambient, and the water losses were <15 l per tonne of oxide and were consistent. The texture of the paste was smooth and it could be easily sheared. There was virtually no down-time on the pasting machine.

The objective with any pasting procedure is to know the order of the water losses, to compensate for those losses in the paste specification, and to provide mixing equipment with adequate cooling facilities so that the compensation made on water will give a consistent paste throughout the full working shift.

Operational factors that affect paste texture

Most mixing chambers are not liquidtight and the dry oxide is usually introduced into the chamber first to avoid losses of the liquids. Thereafter, although the proportions of water and sulfuric acid for a particular wet-paste density remain fixed, the way in which these are introduced can vary widely. The sulfuric acid component is more conveniently introduced as an aqueous solution. Many companies have standardized on a 1.400 sp. gr. solutions, but this is an arbitrary decision.

The pattern of mixing, i.e., how/when the water and sulfuric acid are introduced, can be broadly described as follows:

(i) a single addition of sulfuric acid solution for which the concentration has been adjusted to give the specified water and sulfuric acid quantities, or

(ii) a single water addition followed by the appropriate quantity of sulfuric acid solution of a higher concentration than in (i) but sufficient to give the specified water and sulfuric acid quantities, or

(iii) a reduced water addition followed by the appropriate quantity of sulfuric acid solution and then the remainder of the water, or

(iv) an initial sulfuric acid solution addition followed by the full water quantity to meet the specification.

Although all the above can be arranged to provide the same total water and sulfuric acid quantities, the resulting wet-paste textures and quality can vary from very good to lifeless. This can best be illustrated by reference to work carried out by Eagle-Picher [2] in which the effect of varying the pattern of paste mixing was investigated.

The relevant data can be summarized as follows:

● single addition of an aqueous solution of 1.152 sp. gr. sulfuric acid:

Initial water (l)	0
Sulfuric acid (l t ⁻¹)	244
Maximum temperature (°C)	46.5
Paste density (g cm ⁻³)	3.6
Paste quality	Very good

● 1.283 sp. gr. sulfuric acid added:

Initial water (l)	115	60	0
Sulfuric acid (l)	130	130	130
Finishing water (l)	0	55	115
Maximum temperature (°C)	52	50	58
Paste density (g cm ⁻³)	3.54	3.54	3.57
Paste quality	good	good	sandy

● 1.473 sp. gr. sulfuric acid added:

Initial water (l)	173	60	0
Sulfuric acid (l)	73.8	73.8	73.8
Finishing water (l)	0	113	173
Maximum temperature (°C)	47	53	63
Paste density (g cm ⁻³)	3.47	3.6	3.6
Paste quality	good	sandy	lifeless and sandy

One objective in paste mixing is to produce tribasic lead sulfate. If the temperature of the paste rises above 70 °C, then tetrabasic lead sulfate will form. The effect of the presence of the tetrabasic lead sulfate is to change the texture of the paste from a smooth material that readily flows to a gritty or 'sandy' material that is difficult to work and does not produce during the curing reaction the abundance of long, interlacing needle-shaped crystals that gives the material its rigidity and strength. Although none of the temperatures registered above have reached the 70 °C level, the presence of a sandy texture indicates that there has been localized hot spots within the wet mix. It is insufficient to accept that as long as the temperature measured anywhere convenient in the wet mix has not exceeded 70 °C, the paste quality will be satisfactory. Temperature measurements should always be well below the 70 °C limit to ensure good working quality pastes.

Formed active material densities

The formed material density is directly related to the weight of metallic lead in the wet paste and the dimensions retained by the paste after curing. The formed density determines the volume porosity and the total electrolyte volume that can be designed into a specific cell arrangement. The total electrolyte volume limits the reaction at low discharge rates and controls the cell capacity. The material porosity and total internal developed surface area controls, together with other factors, the voltage performance at high rates and low temperatures, whilst the cold-start duration

reacts to the proportion of the total electrolyte that is held absorbed within the active material.

There is a tendency to accept that: (i) there is a fixed relationship between the wet paste and formed densities, and (ii) the formed density remains constant for any particular wet-paste density, irrespective of whether the paste texture is dry, crunchy or soft, creamy. These views are not necessarily correct.

The apparent volume of material in a cured plate is dependent on the ease with which the interlacing needle-shaped basic lead sulfate crystal structure can continue to develop throughout the curing process. If the humidity and temperature conditions are not optimized, then the development of the essential interlacing structure can be prematurely terminated and the material volume reduced. In the extreme case, the material volume may decrease to that pertaining at the maximum wet-paste density condition when the surface films of water surrounding the solid particles and producing plastic flow have evaporated.

The lack of optimum curing conditions can result in a failure to oxidize most of the free lead present in the wet paste. The lead oxide, which is the product of that oxidation, forms at the surface of the solid particles and in the surface water films where it links and reinforces the particle-to-particle contact, so stiffening the crystal structure and spacing apart the solid particles farther than if they had normally touched.

A soft, creamy paste tends to have a greater excess of surface film water than its dry, crunchy counterpart. This reduces the particle-to-particle adhesion and makes it easier to process the material through the pasting machine. Under the applied pressures, some of this water may be expressed from the paste and absorbed by the underlying belt. Even if this does not happen, there is a greater volume of surface-film water to be evaporated and a greater potential for shrinkage. The trend is to a higher formed density than planned.

Most plates after pasting pass through a flash-drying oven to remove the surface moisture and to allow the plates to be stacked in contact with one another without fear of them sticking to each other. The aim of the oven treatment is only to remove the surface moisture and conserve the absorbed moisture so that there will be sufficient humidity within the stack of plates for the curing reaction to continue through to completion. Too high an oven temperature introduces the risk of removing too much of the moisture and of the curing process being terminated before the required time. The amount of free lead present after the curing process is a measure of the degree to which the interlacing needle-shaped crystal structure has developed, and by how much the shrinkage due to the evaporation of the water in the paste has been compensated by the increase in the material external volume that results from the development of the crystal structure. Routine checks on the free-lead values in cured plates provides a quick assessment of the physical well-being of the plate quality.

A visual check of whether or not the process is under control is the freedom from cracking of the pellet away from the grid wires. Not only has the formed material density come down to the designed value but the hazard of loose and lost pellets has also been added to production problems.

It is not uncommon for short plastic fibres to be added to the paste mix to stabilize dimensions and to reduce the incidence of lost pellets from formed plates. These fibres have a value when using very thin plates but they should not be an excuse for relaxed control of flash-drying oven temperatures and/or the curing process. Nevertheless, this is indeed often the case. Too high a quantity of fibres causes a loss of porosity and cold-start performance; it is prudent to err on the low side of fibre content and to concentrate on the proper control of flash-drying ovens and curing.

It is not difficult to avoid the use of fibres and to produce very strong and well-performing plates by paying greater attention to the curing process. (Note, curing will be discussed in a later paper in this series.)

The negative material during the formation process, whether in the battery or in separate tanks, will decrease in true volume since the density of lead is higher than the blend of lead, lead oxide and lead sulfate. This introduces a further shrinkage hazard as the material is converted into sponge lead. The even distribution of the organic and inorganic expanders throughout the mix tends to cause the material to expand and oppose the shrinkage, particularly when the plates are spaced apart and the material is unsupported. The nett effect is for the formed plate to have similar dimensions to that of the pasted and unformed plate.

The positive cured material will be converted into lead dioxide with a true density that is less than the original blend of materials. The solid volume will increase with formation and the reverse of shrinkage occurs. Where the wet-paste density tends to be high, as in the case of some industrial batteries, the material tends to 'puff' or bulge at the centre of the pellets. Where low-density pastes have been used, as in automotive batteries, it is more usual for the material expansion to be absorbed within the actual material by a reduction in the pore volume.

The best method for estimating the possible formed densities of pastes is to assume there is no overall change in the plate dimensions as a result of curing and forming. Given good control of the paste mixing temperatures, the flash-drying oven temperature and the curing process parameters, there will not be a great difference between the original pasted-plate dimensions and the finished formed-plate dimensions. Thus, the assumption is not unreasonable. Given this, if W is the weight (g) of lead in the wet paste and V the overall volume (cm^3), then:

- formed negative apparent density (g cm^{-3}) = $\frac{W}{V}$
- formed positive apparent density (g cm^{-3}) = $\frac{1.155 W}{V}$

Consider the case of a paste made with an oxide containing 70 wt.% PbO and 30 wt.% Pb mixed with 168 l of water and 28 kg of sulfuric acid. In the negative, there is 0.4 wt.% BaSO₄, 0.15 wt.% C and 0.25 wt.% organic expander of density 1.5 g cm^{-3} . The expander weight and volume would be 8 kg and 3.39 l, respectively. The assumption is made that the expanders do not change their weight and volume as a result of the mixing process. Therefore:

	Negative		Positive	
	Weight (kg)	Volume (l)	Weight (kg)	Volume (l)
Added water	168	168	168	168
Reaction water	5.2	5.2	5.2	5.2
Lead	300	26.55	300	26.55
Lead oxide	636.28	66.98	636.28	66.98
Lead sulfate	86.56	13.74	86.56	13.74
Expanders	8.0	3.39		

$$\text{Total weight of lead (kg)} = 300 + \frac{207 \times 636.28}{223} + \frac{207 \times 86.56}{303} = 949.8$$

Total weight of lead dioxide (kg) = $1.155 \times 949.8 = 1097$

Volume of negative (l) = 283.83

Volume of positive (l) = 280.43

All the above refer to a mix containing 1000 kg of dry oxide.

Apparent density of negative formed material (g cm^{-3}) = $\frac{949.8}{283.83} = 3.35$

Apparent density of positive formed material (g cm^{-3}) = $\frac{1097}{280.82} = 3.91$

From the plastic-flow area of the wet-paste density curves of Fig. 2, and taking the various combinations of water and sulfuric acid for each wet-paste density, it is possible to derive characteristic curves of the possible formed densities for any combination of water and sulfuric acid. Whilst these are not as precise as those for wet-paste densities, the curves will give some guidance of the possible order of changes to be made in water and sulfuric acid additions to produce a desired formed density change. With these reservations, they are more helpful than *ad hoc* arbitrary changing of the water and sulfuric acid factors in seeking changes.

One factor has not been examined. There are two main storage systems in common use for battery oxide, viz., bulk silo and drums. The former is preferable since the amount of moisture picked up tends to be quite small. By contrast individual drums are subject to lid damage and, consequently, the amount of moisture absorbed can be appreciable. Most companies try to keep the moisture pick-up level to <0.5 wt.% but this is not always possible, particularly in drums with poorly sealed lids where much higher moisture content are not uncommon.

The presence of 0.5 wt.% water in the oxide, is equivalent to an increase of 5 l per tonne. In humid atmospheres and with drums badly sealed (and this is not as rare as might be expected), the level of moisture can be as high as 1 wt.%. In high sulfation mixes this order of moisture content can become an appreciable proportion of the initial water. Failure to compensate for this situation can result in a density lower than intended. Whenever it is planned to programme a high-sulfation mix where the water and acid are automatically metered and human fallibility is eliminated, the system should be based on the use of silo storage for the oxide rather than individual drums. No matter how good initially are the sealing covers to the drums, both drum bodies and covers soon suffer distortion with handling and the moisture-proof seals are lost. From then onwards, moisture pick-up becomes a significant problem.

Negative paste expanders

The sponge-lead negative active material contracts and becomes more dense with cycling. This is particularly noticeable with repeated high-rate discharges where the capacity loss can be sufficiently large to merit the claim that the material has passivated. This passivation is also present when discharging at low temperatures and at high electrolyte concentrations. It has been attributed to a recrystallization phenomenon in the charged sponge lead.

It was soon recognized that there was a need for additives in the negative material to counteract this material shrinkage and to promote initially the establishment of a

highly-porous, highly-developed internal surface structure to sustain high-voltage levels at high-discharge rates and low temperatures. The precipitation into the pores of the negative material of barium sulfate achieved improvements in capacity. Lead sulfate and barium sulfate are isomorphous and have rhombic crystal lattices with very similar parameters. Highly-dispersed barium sulfate introduced into the mass of the negative material forms numerous centres of crystallization for the lead sulfates formed on discharge and in the initial paste mixing. As a result, the lead sulfate crystallizes out on the barium sulfate in preference to the metallic lead present. The initial porous structure is set and the size reduction from lead sulfate to lead increases the true surface area of the active material in contact with the electrolyte. It is claimed that the particle size of the barium sulfate and the effectiveness of its even distribution throughout the paste mix sets the level of the true internal surface area of the active material, and with it the true current density. Voltage polarization in a cell at high rates of discharge is a function of the true current density and the production of a highly-developed internal structure is essential for high cold-start voltages.

Carbon black has been added to complement the barium sulfate. Its role is not clear. It assists the conversion reaction during the early part of the formation but this was more necessary in the days before the adoption of oxide of today's quality. In those times litharge was commonly used with glycerine as the cementing agent. Some manufacturers have eliminated carbon from their formulations without apparently any ill effects. Nevertheless, there is some evidence to indicate that certain carbon blacks of high surface area assist the distribution of the barium sulfate throughout the wet mix. The proponents take particular care in the selection of the carbon blacks and regularly check the replacement stocks to ensure the characteristics are maintained.

Prior to the introduction of the modern synthetic plastics, natural woods were used for the separators and the addition of barium sulfate and carbon black were sufficient to establish and maintain the needed porous structure to meet the high-rate/low-temperature characteristics of the markets of that age. With the dwindling of the wood stocks, through overlogging, and the need to improve the life potential of batteries at high temperatures, synthetic plastic separators were developed. Their introduction was initially accompanied by a loss of high-rate performance and a failure to maintain the initial performance with cycling. The negative material became more dense and there was a need for an 'anti-shrink' agent to refine and preserve the initial porous structure and to replace the component of wood separators that had resisted material shrinkage.

Sponge lead has a natural tendency to decrease its free energy and this acts as a stimulus to recrystallization with a loss of developed internal surface area. This registers as an increase in the voltage polarisation. An addition agent in the form of an active substance adsorbed on the surface of the metallic lead was needed. This would interpose adsorbed particles between the metal and the lead sulfate crystals and prevent the formation of a dense layer of lead sulfate crystals over the metallic lead. The latter is undesirable as it would deny the access of electrolyte to the active material.

The action of these surface active agents has been explained by Dasoyan and Aguf [3], see Fig. 7. On the basis of this simplified explanation, only those organic substances that are adsorbed on the metallic lead surface can be effective as depassivators. These substances include substances such as humic acid, salt of lignosulfonic acid, and many vegetable dyes.

Initially, wood flour was used on the assumption that within the finely-ground wood there would be that component of natural wood which previously had made

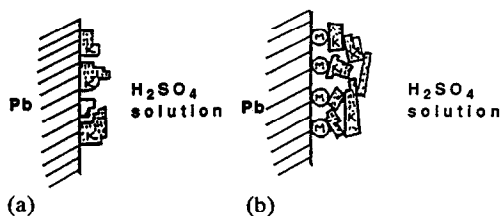


Fig. 7. Mechanism of action of adsorbed surface active agents on the crystallization of lead sulfate: (a) in absence of agent; (b) in presence of agent; K=lead sulfate crystals, M=adsorbed particles.

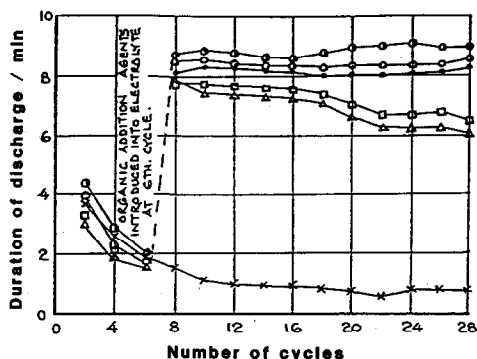


Fig. 8. Effect of adding organic addition agents to electrolyte of automotive batteries of duration of repeated high-rate discharges: (O) 1 wt.% flavantrene; (●) 1 wt.% organic indigo dye; (○) 1 wt.% indantrene brilliant green; (□) 0.4 wt.% sodium lignosulfonate; (Δ) 1 wt.% sodium lignosulfonate; (x) control with no organic addition [4].

the wooden separator so effective. Whilst the addition of wood flour was acceptable in traction batteries not required to deliver high-discharge currents at low temperatures, it was not good enough for automotive use where cold-start performance was the prime requirement.

The search for very active substances centred around lignin derivatives, mainly because of cost; there were, however, many vegetable dyes that were superior in effectiveness. Kurkova [4] gives data on the effect of adding various dyes and sodium lignosulfonate to the electrolyte of cells discharging at high rates. The dyes used were flavantrene, an organic indigo, and indantrene, brilliant green. The results obtained are shown in Fig. 8.

Similar tests were carried out adding the organic materials to the negative active material. The results are shown in Fig. 9. The effect of adding the organic material to the electrolyte after six cycles is impressive and more than justifies the addition. There is a difference in improvement between 0.4 and 1 wt.% additions of sodium lignosulfonate in favour of the lower amount. This underlines the presence of an optimum addition for each expander, and this needs to be established if the maximum improvement in performance is to be achieved.

Vandyke brown dye has been extensively used in the past to capitalize on the activity of dyes without incurring high material costs, but it was difficult to control its quality and activity due to the variable quality of the natural product from which it was derived. There are many proprietary makes of organic expander based mainly

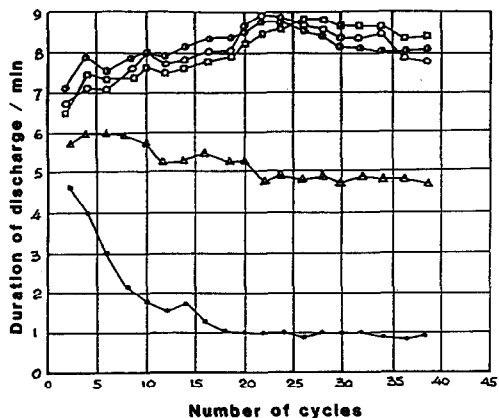


Fig. 9. Effect of adding organic addition agents to negative active material of automotive batteries on duration of repeated high-rate discharges: (●) control with no organic addition; (Δ) 1 wt.% humic acid; (□) 1 wt.% indigo dye; (○) 1 wt.% flavantrene; (⊙) 1 wt.% indantrene brilliant green [4].

on humic acid and lignosulfonates. The optimum amount of each expander varies with the make and it is necessary to determine empirically the best value to suit the grade of oxide used and the formulation.

For one particular make of expander, based on an oxylignin derived from sodium lignosulfonate, the makers recommend using from 0.12 to 0.25 wt.% (based on the weight of the dry oxide). With less-purified expanders, the quantities are greater.

Most organic expanders increase the charge voltage by about 0.2 V/cell when charging at a rate of 0.1 C/20 amperes. This may have the effect with car alternator systems of reducing the charge current to such an extent that the battery does not accept enough input charge to keep it in good condition. In time, the capacity falls drastically and the active materials become sulfated. In such situations, the high-charge voltage can be reduced by the addition of small amounts of a lead-nickel glass in the form of chopped fibres.

Many of the organic expanders are water soluble and are best added as a water solution to the mix, preferably during the initial water-addition stage. In this way, the expander will disperse both rapidly and evenly throughout the mix. (Note, many will precipitate as soon as the mix becomes slightly acidic). One proprietary brand of expander, Vanisperse A, produced by Borregaard in Norway and similar to the US product Marasperse (USA), exhibits this high water solubility, but in the presence of the slightest acidity gives very low solubility levels. The solubility is affected both by the amount of expander per litre of solution and by the acidity. The following data have been quoted by the supplier: (i) 2.28 g l⁻¹ has a solubility of 75 and 55 mg l⁻¹ in 1.100 and 1.280 sp. gr. sulfuric acid, respectively, and (ii) 1.87 g l⁻¹ has a solubility of 45 and 30 mg l⁻¹ in 1.100 and 1.280 sp. gr. sulfuric acid, respectively.

The result of this near insolubility is that during the water-addition stage of paste mixing, the organic expander disperses throughout the water/oxide slurry but, as soon as the sulfuric acid addition commences, it is thrown out of solution to become a fixed addition widely and evenly distributed between the lead oxides and sulfates. Slight acidity in the slurry before the organic expander is added results in the organic

expander being locally concentrated and incapable of carrying out its prime role satisfactorily.

Some manufacturers prefer to add as many as possible of the mix components in the liquid form in order to prevent losses through the environmental extract ducting. The organic expander presents no problems provided it is water soluble. Barium sulfate can be converted into a wet addition in the following manner using barium hydrate crystals as the basic ingredient: (i) dissolve 10 kg of barium hydrate crystals in 16.7 l of nearly boiling water in a nonmetallic container and stir vigorously until all the barium hydrate has dissolved; (ii) slowly add 7.1 l of sulfuric acid solution (sp. gr. 1.250) whilst stirring continuously; (iii) test the 'milk' with litmus which should turn red; if this has not occurred, carefully add further acid until the litmus change occurs; (iv) stand the milk for 20 min, stir again and test for acidity, it should still be acid; (v) use the milk within 12 h of preparation; (vi) stir the milk immediately before adding it to the paste in conjunction with the initial water; (vii) if there is a residue, wash this into the paste with a little of the initial water.

Barium hydrate crystals are usually supplied in the form $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. When deciding how much of the barium milk will be used in each paste mixing, not only must the amount of barium hydrate be adjusted to its barium sulfate equivalent, but an adjustment must be made in the initial water to compensate for the water of crystallization, the water of solution, and the water from the sulfation reaction.

For every 10 kg of barium hydrate crystals used, there will be 7.4 kg of barium sulfate in the barium milk and 28.2 l of water. The weight of barium milk produced will be 18.75 kg. Taking an average barium sulfate addition of 0.35 wt.%, the amount of barium milk addition per tonne of dry powder will be 8.9 kg and the specified initial water will be reduced by 5.4 l.

Where barium sulfate is a dry addition, this is best used in the form known as blanc fixe. A commonly accepted standard of purity is: barium sulfate, 97% minimum; iron, 0.03% maximum; magnesium, 0.25% maximum; chlorides, traces; moisture, 2.5% maximum.

A difficulty arises in accepting barium sulfate on a simple chemical analysis since apparently similar materials from differing sources can give different results when incorporated into a paste mix. To safeguard against this, new sources of supply are tested in a trial mix against the previous standard, and if satisfactory, the supplier added to an approved suppliers list.

The presence of lumps in barium sulfate hinders its even dispersion throughout the paste mix and supplies should be checked for this fault. If lumps are present, the powder should be passed through a 100-mesh sieve before use.

At one time, amorphous carbon (lampblack) alone was considered satisfactory for negative pastes. It was claimed that very fine carbon, such as acetylene soots, leached out of the negative active material during formation. This certainly does happen with very fine carbon blacks and it is prudent to avoid them and keep to carbons with high smear characteristics. They should be free from oily or tarry matters. This can be checked by a colourless extract with benzene. It must be readily wetted by sulfuric acid solutions; the usual test is to pour 15 cm³ of sulfuric acid solution (1.400 sp. gr.) at ~25 °C onto 0.5 g of the carbon black and note the speed with which the liquid is absorbed. At least 75% of the carbon black should be wetted.

The main difficulty for the designer is to decide on the best level of organic expander for the prime performance requirement of the cells under consideration. There is little disagreement over the levels of barium sulfate and carbon black, except in traction cells where some manufacturers adopt a high barium sulfate addition (of

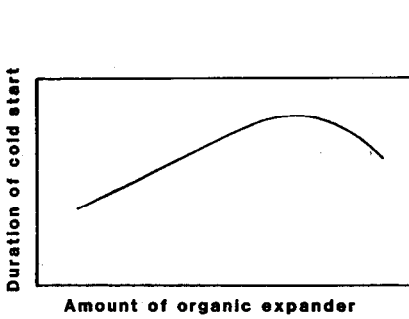


Fig. 10. Pattern of change of cold-start performance with level of organic expander addition.

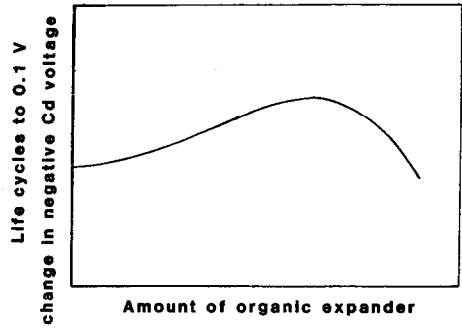


Fig. 11. Change in life cycles with level of organic expander addition.

the order of ten times the usual value) to produce a very stable pore structure and good recharge characteristics, even when regularly deeply discharged. The quantity of organic expander modifies the cold-start performance in automotive cells, whilst in traction units it can affect the cycle life. Both can only be optimized by a manufacturer exploring how varying levels of organic expander addition affect either of these areas. The general effect of organic expander level on the cold-start performance of automotive batteries follows the pattern shown in Fig. 10. If it is found from experiment that the required cold-start performance for a particular type of automotive battery can be met without recourse to the level for maximum performance, there is some advantage in adopting the lower amount. Not only is there some cost advantage, but there are less charge-acceptance problems.

In the case of traction cells the life should be dictated by the performance of the positive plate. To achieve this, the negative should remain substantially constant throughout the life of the cell. This calls for the organic expander to continue to be active throughout life, but not to be so active that the negative active material expands rapidly during the early cycles and exudes from between the separators.

A convenient comparison is to measure the number of cycles before the negative active material changes by 0.1 V with respect to a cadmium reference electrode. If the life cycles are taken to finality, there is the danger that ultimate failure has not occurred through the failure of the positive plate and a comparison of the results does not reflect the effect of the addition of negative organic expander. Figure 11 shows the general pattern of behaviour and if an allowance is made to cover manufacturing tolerances, the choice of expander level should tend to be below the optimum to avoid overexpansion in a proportion of negative plates.

Neutral paste-strengthening agents

Short staple plastic fibres are incorporated into paste mixes to bind together the particles and reduce shrinkage during the curing process. They also assist in reducing the loss of pellets with handling from the curing process onwards in production. The fibres do not affect adversely the battery performance unless they are present in larger amounts than 0.5 wt.%. At this level and beyond, the fibres appear to prevent a change in the active material dimensions during discharge and charge. In particular, the effect on discharge in traction cells is for the increased size of the lead sulfate particles to close the pores and reduce the capacity.

The generally-accepted fibres are made from fine filaments of Dynel chopped to between 3 and 5 mm. The chopping is a high-speed operation and when the cutting blades have been allowed to blunt there is a tendency for the fibres to stick together in bunches due to distortion at the cut ends. The material should always be in the form of discrete fibres. Bunches of Dynel fibres make the task of pasting difficult and, in extreme cases, cause the plate surfaces to become uneven and lumpy. Any batches of Dynel fibres showing bunching should be returned to the supplier. A simple test for bunching is to take a small handful of the fibres and drop them into a vessel containing water. The fibres should visibly separate.

The amount of fibres used should be kept as low as the control of scrap plates will allow. A typical level is 0.1 wt.%, i.e., 1 kg per tonne of oxide.

Paste mixing

The generally-accepted method of paste mixing is to produce a water/oxide slurry and then to react a proportion of the oxide present with sulfuric acid. The amounts of water and sulfuric acid are adjusted to ensure that the resultant wet paste has plastic-flow properties and the wet-paste density is to specification. The only difference between positive and negative pastes is the incorporation into the negative paste of organic and inorganic expanders. Sometimes, in high-performance positive pastes, red lead is added. The main objective in mixing is the even distribution of all the components throughout the mass of the paste. A deviation from this basic method occurs where the manufacturer chooses to combine the water and the sulfuric acid into a single low-density solution. This produces problems where the organic expander is water soluble but precipitates as soon as the added solution is slightly acidic.

The production of the water/oxide slurry can be with oxide added to water or water added to oxide. The former generates less heat. Most mixing machines are not liquidtight and it is more common for the dry oxide to be loaded into the mixing chamber first and milled for a few minutes. Very fine oxides with a large surface area tend to have a low apparent density with a large amount of entrapped air. When water is added, there is an appreciable temperature rise. This temperature rise can be reduced by a short dry milling during which much of the entrapped air is removed. Coarse oxides do not suffer from this problem to any great extent and the dry milling time can be much reduced. The time can be even eliminated if the oxide is added to the total initial water.

Where the dry oxide is introduced first, every effort should be made to flood in the initial water to absorb the heat of reaction.

For expanders added as dry components, there is always a doubt as whether they are evenly distributed in the final wet paste. The success, or otherwise, depends very much on the effectiveness of the previous cleaning of the mixing chamber, as well as the standard of maintenance of the scrapers and ploughs within the chamber that are used to cut and turn over the paste throughout its mass. The following is an example of a fixed routine that should be maintained before starting a new mix:

(i) Examine whether the scrapers that clean the paste from the walls of the mixing chamber are in light contact with the walls and are removing material thrown up against the walls back into the bulk of the paste. If there is visible clearance between the scrapers and the chamber wall, a layer of paste can built up over the walls. When dried, this layer forms an insulating coating that hinders the free extraction of heat via the fabric of the chamber. The scrapers should be trued to be in light contact with the chamber wall over their full length.

(ii) Check that the ploughs (and, in muller-type mixers, the mullers) are in continuous contact with the floor of the mixing chamber. Dried paste insulates the floor and hinders heat extraction in the same way as the walls.

(iii) Check the environmental extract ducting for build-up of materials. Lead oxide, pulled up by the extraction air and not effectively carried away to the lead-dust collectors, falls on to the lower surfaces of the ducts and forms a cake if there is any moisture present. In time, the extraction efficiency falls and the cooling effect of the extracted air is lost. The ducting should be inspected frequently and kept open and free from clogging materials.

The dry expanders are best added with the dry oxide and dry milled. Some difficulty is often met with distributing the carbon. One way to assist this requirement is to purchase the carbon black in pelletized form. After being added to the dry materials, mechanical movement breaks down the pellets and spreads the carbon by smearing as the oxide particles move relative to one another. Plastic fibres, when used to strengthen the active material pellets, acquire a static charge and tend to cling together if added as a single ingredient on their own. It is helpful to premix the fibres into the other dry components before adding to the mixing chamber. Alternatively, add the fibres to dry oxide as part of the organic expander solution where the expander is water soluble. The addition of expander and strengthening fibres requires careful planning when the mixing operation is wholly automated. In such cases, there is an advantage to be gained by preparing a thin slurry of the barium sulfate, carbon and fibres, by keeping the slurry under continuous movement to prevent the solid materials from settling, and by adding the slurry in measured amounts to the oxide/initial-water slurry. Some manufacturers consider that as there is usually an operator available in the paste mixing shop, it is more economic and reliable for that operator to add, by hand, the expander additions. There are dangers of which the most troublesome is, perhaps, the risk of localized high concentrations of the expanders.

After the expanders have been distributed, the sulfuric acid is added as an aqueous solution. Unlike the water addition, the introduction of acid must be at a controlled rate in order to provide sufficient time for the heat of the sulfation reaction to be dissipated via the fabric of the mixing machine, the cooling system provided, and the evaporation of a portion of the initial water.

Typical temperature rises for a high-sulfation mix (i.e., one having 100 l of 1.400 sp. gr. sulfuric acid or more) in a simple muller-type mixer have been recorded as: (i) dry blending 3 to 5 °C; (ii) water addition 8 to 12 °C; (iii) sulfation 27 to 30 °C when added over a short period of time. These refer to a mix containing a tonne of dry oxide.

Since sulfation reaction is rapid, the temperature rise will be greatest at fast rates of sulfuric acid addition. This gives a simple method of controlling the mix temperature by regulating the rate of addition of the acid solution. Figure 12 shows the effect of reducing the rate of acid on the temperature rise in a paste mix prepared in a simple, unidirectional muller-type mixer with only a bottom cooling jacket. The data are particular to the type of mixer and the water/acid balance used but the general pattern of change in temperature rise is typical.

There is a danger in extending the duration of the sulfuric acid addition since, all the time the acid is being fed into the mixing chamber, there is mechanical work being expended on the wet paste. This can be considerable, particularly in the case of muller-type mixers. There is a limit to the amount of work that a wet paste can accept without large changes occurring in the paste. Once this limit has been exceeded, the paste becomes extremely soft and lifeless even though the total water content has

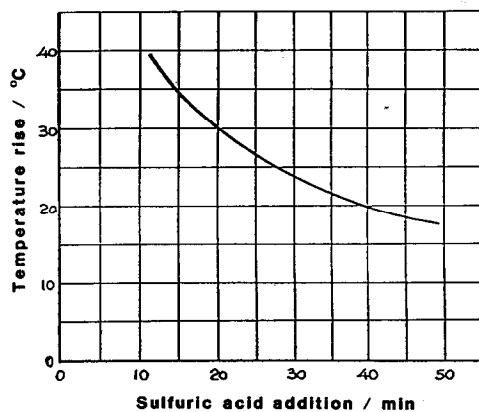


Fig. 12. Effect of sulfuric acid addition time on temperature rise in a wet paste.

TABLE 2

Influence of mix temperature on paste characteristics

Temperature of mix (°C)	Mix temperature 30 min after discharge (°C)	Paste condition
80	72	gritty and hard
70	61	gritty and hard
64	59	sheared well and did not set rapidly
63	57	sheared well and did not set rapidly

not exceeded the upper limit for plastic flow. The flow properties almost disappear and there is difficulty in retaining the overworked paste in the grid lattice. The cured paste is friable and the formed active material is dusty.

Simple unidirectional mixers with limited cooling facilities are prone to produce hot pastes and the total mixing times tend to be protracted. This is especially the case with high activity pastes. The total mixing time is best kept to no more than 45 min in order to avoid overworking the paste. The general rule in paste mixing is to restrict the amount of mechanical work expended on a paste to the minimum commensurate with the even distribution of the basic lead sulfate formed by the reaction and of the expanders and other additives throughout the wet mix and a maximum temperature of 60 °C at any time in the mix. Table 2 gives qualitative data that illustrate the effect of mix temperatures on the subsequent usage value of the paste produced.

The borderline between a difficult, hard and gritty paste that sets hard relatively quickly and a paste that shears well, fills a grid satisfactorily and remains soft for sufficient time to use all the batch, despite stoppages through grid faults, appears to be critical. Below 60 °C in the mixer there is little, if any, trouble. Above 65 °C, the paste can be troublesome and further addition of water does not ease the pasting properties.

Since high cold-start performances in automotive batteries require the use of highly reactive oxides, the incorporation of an efficient cooling system in a paste mixer is of paramount importance. Without it, the process is caught between opposing demands: if the sulfation time is not extended there is the risk of too high a temperature developing in the mix, but if the sulfation time is prolonged there is a risk of denaturing the paste by overworking. There is not the same risk with coarse oxides that are acceptable for traction pastes.

Paste mixing equipment

The type of paste required and the oxide needed to obtain that paste exerts a large influence on the choice of paste mixer. Very fine oxides that are used to produce high sulfation pastes are prone to high mixing temperatures and extended mixing times with the risk of denaturing, unless there is incorporated a very efficient cooling system and the mixing chamber is liquidtight so that the water can be introduced before the oxide. The same problem is less evident with traction oxides. The total mixing time becomes important where labour is required for operating the mixer and the cost of labour per tonne of paste produced is significant in the total costing of the process.

There are three main types of paste mixer common to the industry, namely: (i) 'dough' type, sometimes referred to as Z-blade mixers; (ii) muller-type mixers, uni-directional and counter rotating, and (iii) intensive mixers without mullers.

Dough-type mixers

These mixers generally consist of a near-cylindrical machined body or mixing chamber in which shaped, accurately machined blades move, one within the other, in opposing directions to cut, shear and turn over the paste so that all the load is in continual motion. This cutting and turning or folding action produces a high degree of dispersion throughout the paste of the lead sulfate and the various additives. The mixing chamber is closed by machined covers that are locked in position during the mixing operation.

Since, in this type of mixer, the whole mass of the paste is continually worked, the design of the mixer blades must be rugged and heavy. This is particularly necessary during the acid addition stage when heavy stresses occur during the sulfation reaction. As the total mass of all the components of the paste is being constantly moved, the power requirements are high and this tends to make the use of such mixers more costly than others. They are very effective in distributing the additives evenly throughout the mix.

The partly cylindrical shape of the mixer chamber lends itself to efficient cooling; a water jacket can be fitted to cover over three-quarters of the chamber surface area. A blast of cold air can also be readily incorporated, as well as hollow mixer blades through which is passed cooling water.

The mixer chamber is liquidtight so that the initial water can be introduced first and then the oxide. This eliminates the need for dry milling and reduces the overall rise in temperature. The counter rotation of the mixing blades submits the paste to intensive working and reduces the mixing time providing that the heat of the sulfation reaction can be absorbed by the cooling system. This is a matter for the purchasing specification.

The discharge of the mixed paste is achieved by rotating the mixing chamber about a horizontal axis until the chamber covers are forward of the vertical position when the movement of the mixer blades ejects the paste.

A disadvantage of this type of mixer is the fitting of environmental-control extract ducting. The considerable angular displacement of the mixer chamber from the mixing to the discharge positions demands a very pliable extraction system that is able to withstand continual flexing without developing chafing holes or rapid material deterioration.

At one time, this type of mixer was widely used within the industry and produced very acceptable pastes with little variation from mix to mix. It has tended to be superseded by the muller-type and intensive mixers, mainly because of lower initial costs and lower running costs. Its maintenance tends to be less than that required by muller and other types because of the simplicity and ruggedness of the system.

Muller-type mixers

These mixers depend on the spreading action of heavy mullers or wheels. The latter are positioned slightly above the floor of the mixing chamber and at a location slightly nearer the outside of the chamber walls than to the central drive spindle. In the unidirectional mixers, the chamber remains stationary whilst the mullers rotate around the central spindle. In the counter-rotating mixers, the chamber also rotates but in the opposite direction to the mullers. Ploughs and shears are mounted on the same shafts as the mullers, together with scrapers to remove the paste from the chamber walls and return it into the path of the mullers. In the simpler unidirectional types, the shears are omitted. The action of the mixers depends on the shears cutting through the paste and the ploughs turning the cut paste over into the path of the mullers. These flatten and spread the paste and push it towards the walls of the mixing chamber. The muller wheels are free to rotate about their own spindles and do so by virtue of the friction between them and the paste. Without this rotation, the paste will merely be smeared and not moved bodily away from the centre of the mixing chamber. The combined action of ploughs, scrapers and mullers causes the paste to move constantly outwards from the centre and be turned over and over simultaneously with the outwards movement. In this way, a similar action to that in the dough-type mixers is accomplished but the actual amount of paste in physical contact with the mullers, etc., is only a part of the total. As a result, the power demand of this type of mixer are less than those of a comparable dough-unit. By rotating the mixing chamber as well as the muller system in opposite directions, the mixing time is shortened. Situated above the mullers is a large entry port that allows the water to be flooded into the chamber. The acid addition is via a perforated tube that extends from the central spindle to the chamber walls. This tube moves around with the muller assembly so that the acid addition is distributed over the whole area of the top of the mix. The mixing chamber is not liquidtight and in these mixers the dry oxide is invariably introduced first and is then followed by the initial water. Cooling is achieved by a water jacket on the underside of the simpler mixers and by injecting cold air on to the top of the paste as it is cut, turned over and spread. Often this is insufficient and cooling water jackets are therefore fitted around the outside of the vertical chamber walls. A discharge port is located in the side of the mixing chamber with its own cover. When first used, this discharge port cover can be made liquidtight. After a while, however, dry paste builds up around the edges of the port and destroys the cover joint.

Although the counter rotating muller-type mixers offer the possibility of greatly reducing the total mixing time, the sulfation stage can still present a duration problem unless the amount of cooling provided is fully adequate to absorb rapidly the heat

of reaction. This is not always the case, and must be requested in the original buying specifications.

With muller-type mixers, it has been claimed that it is difficult to avoid an accumulation of paste around the spindles and brackets, and that the removal of this accumulation gives a greater paste loss than with dough-type mixers. Some operators assert that such deposits are difficult to clean, but high-pressure hoses usually provide a rapid and effective solution to the problem.

Intensive mixers

Both the dough- and muller-type mixers are used for purposes other than producing battery pastes and have not been specifically designed for battery manufacturing applications. They are capable of mixing reasonably well a wide range of materials and their design is a compromise to cover this range. In recent years, it has been considered commercially viable to concentrate on the development of a mixing technique suited particularly to battery pastes. It has been recognized that, within reason, the less-mechanical work that can be expended in producing a wet mix, the more reproducible and consistent are successive mixings. This reduction in mixing work can only be achieved if the even distribution of the various components throughout the paste is fast and effective. Continually rising labour costs become a significant proportion of the overall process costs and the time saving that can accrue from an improved mixing system can support an increased initial mixer cost if fully exploited. One type of intensive mixer has been the Beardsley & Piper Speed Compounder (Chicago, USA).

This mixer does not use muller wheels, but relies on a combination of knives, to cut the mix repeatedly, ploughs to turn the cut mix over, and edge scrapers to keep the total mass in the mixing area. Although the principles of mixing are similar to some muller-type machines, excluding the mullers, the particular design of the components and the location both within the mixing chamber and in relation to each other provide a very fast and effective blending of the materials. A sensor incorporated within the chamber registers the paste temperature and will initiate cooling action in adequate time to prevent the mix from becoming too hot. The chamber is fully water-jacketed and there is a supplementary forced-air system.

The mixing chamber is liquidtight to allow the initial water to precede the introduction of the dry oxide. This reduces the initial temperature rise. The water addition is via a wide bore pipe directed against the central spindle and the combination of knives, ploughs and scrapers. In this way, the flooding in of the initial water also acts as a supplementary cleaning wash for the mixer gear. The sulfuric acid addition enters via a perforated bar. Facilities are available for the negative expanders to be introduced as a wet addition through a separate entry port. The magnitude of the mixing motor current gives an indication of the plasticity, or texture, of the paste. A sensor that compares the motor current against a preset value continues the final mixing until the latter is reached. At this state, the discharge doors open and the paste is ejected by the rotating ploughs and scrapers. Typical motor currents in one size of intensive mixer making wet mixes of density 4.02 to 4.06 g cm^{-3} with varying levels of sulfation, are shown in Fig. 13.

The combination of high-efficiency mixing, water addition before loading with dry oxide, and good cooling reduces the mixing time drastically compared with standard muller-type mixers. There is also less of a temperature rise problem with high sulfation mixes. In one particular high sulfation mix, the total paste preparation time was 20 min for an intensive mixer as opposed to 50 min for a standard muller-type mixer, with the added advantage that the wet paste was cooler.

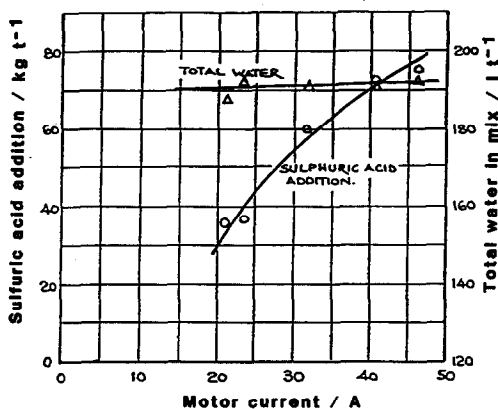


Fig. 13. Variation of motor current in the final mixing of pastes with densities from 4.02 to 4.06 g cm⁻³ with varying levels of sulfation.

A typical cycle for a high sulfation mix using the Beardsley & Piper mixer is:

Water addition (s)	30
Expander additions (min)	1
Dry oxide addition (min)	1-2
Slurry mixing (min)	1
Sulfuric acid addition (min)	5-10
Discharge (min)	1-2
Average time for 1-tonne batch (min)	20

There is an optimum time for the sulfation reaction which takes account of the effect of temperature on the speed of the reaction to ensure that the paste bulks up fully. If this is not allowed the density will vary throughout the paste with areas of overdense paste.

The provision of air extraction to prevent the dry oxide from escaping into the surrounding atmosphere and producing an unacceptably high lead-in-air level is not difficult. Environmental control is simple and straightforward.

Each type of mixer has its advantages and disadvantages. The choice of machine must be dictated by individual circumstances. For example, if a high initial cost is unacceptable, a simple muller-type mixer is preferred. If the cost of labour is more important, then dough-type or intensive mixers must be seriously considered. In the final economic assessment, the cost of environmental control equipment, ducting, filters, etc., must be included since such auxiliaries are essential to the mixing operation.

Specifying a paste mixer

The essential characteristics that need to be specified when inviting quotations for a paste mixer are as follows:

- (i) Maximum weight of wet mix required per mixing.
- (ii) Whether water is to be added before or after the dry oxide.
- (iii) Maximum cycle time from the start of the additions to the discharge of the wet mix.

(iv) Maximum heats of reaction from the water addition and the subsequent sulfation reaction.

(v) Maximum permissible temperature for the wet paste.

(vi) Will the mixing process be totally or partly automatic; what part of any automated control will be required from the mixer supplier.

(vii) Will the expanders be added wet or dry; will the supplier be required to supply any equipment for expander addition.

(viii) All parts coming into contact with the wet mix to be free from corrosion and sufficiently rugged for relatively unskilled handling. There shall not be any significant release of iron into the wet mix. In this respect, some battery makers insist on the mixing chamber being made from corrosion-resistance steels.

(ix) Easy access to the inside of the mixing chamber for cleaning.

The heats of reaction probably give the greatest trouble in formulating specifications. Some indication is necessary as many of the standard designs of paste mixer common in the industry are not suitable for high sulfation mixes; the cooling systems are inadequate to control the temperature without recourse to greatly extending the duration of acid addition by reducing the rate of feed. This limits the use factor of the plant, as well as introduces the risk of overworking the paste. The presence of a truly adequate cooling system not only turns out the paste at a temperature where no grittiness can be produced, but also ensures that the fabric of the mixer remains at a reasonably constant temperature over the full working shift.

Stocking properties of mixed paste

It is important that a mixed paste remains workable for many hours after being turned out from the mixer so that wastage through loss of plasticity and shear properties is negligible. There must be a safety factor to cover down-time on the pasting machine that arises from plant failures, grid jamming, etc. The period of time permitted during which a paste mixing can be used varies between manufacturers. It is often based on what has become traditional from past practice. As paste formulations change to cater for higher market demands, so may the period during which the new paste remains workable. Often the permitted life is limited to short periods, such as four hours. From time-to-time, the vexed question arises whether to scrap paste because the permitted time interval has elapsed before the paste has been fully used, or to take a chance and ignore the requirement. Usually, the latter wins and the practice becomes permanent. A more satisfying approach is to determine periodically the practical life of the paste and to amend this characteristic in accordance with the findings. This can be done by taking a quantity (e.g., 50 kg) of freshly-made paste, positive and negative, putting the paste in a container just larger than the paste and covering it with a wet cloth in a similar manner to normal practice. At roughly one-hour intervals, a sample of the paste is taken from the interior of the mass and the free-lead and moisture content determined. The sampling is continued until the free lead has fallen below 10 wt.% and the results plotted against time.

Figure 14 is a typical set of curves for a high sulfation automotive paste based on an oxide with 70 wt.% PbO, 30 wt.% Pb. The maximum temperature at any time during mixing did not exceed 62 °C. Whilst there is a steady decrease in the free-lead content, the rate of change is slow and a shelf life approaching 24 hours can be expected from such a mixing, provided the moisture content within the paste does not fall below 12%. The interesting feature of these curves is the change in the rate

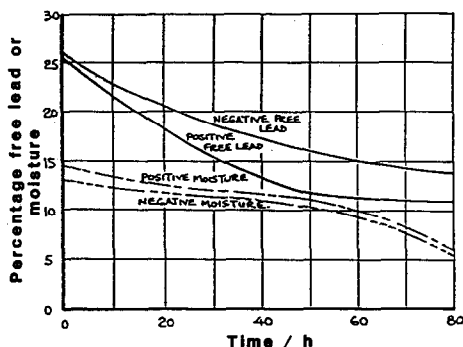


Fig. 14. Change in the levels of free lead and moisture during paste standing.

of fall of free lead once the moisture content has reached $\sim 10\%$. It emphasizes the need to retain moisture within the paste to ensure the curing operation can proceed satisfactorily.

For the practical control of the use life of pastes, it is realistic to limit the shelf life to a duration that will produce 18 to 20 wt.% free lead or 12 wt.% moisture, whichever occurs first. In the case of the paste to which the curves apply, the shelf life of the paste was ~ 20 hours from the time the paste was dumped out from the mixer. It is far more satisfactory to set a limit in this manner and conform to it at all times, rather than to set an arbitrary shorter time based on the experience of other makers or what has been passed down by tradition. It has to be recognized, however, that the set shelf life is still dependent on the temperature of the paste during mixing not exceeding 60 to 62 °C.

With some soundness, it can be argued that paste can be used, and reasonable plates produced, when the free lead and/or moisture are less than the values suggested. There can be difficulties, however, in keeping the temperature of the mixer fabric reasonably constant throughout a full working shift so that the above temperature quoted for the maximum may not be always attainable. The criteria stated to fix a shelf life will cover most situations with a safety factor that is not too difficult to maintain.

The main criticism raised against paste mixes is usually the variable time successive mixings 'set-up', i.e., to become stiff. Such variations point to deviations in the mixing routine and these call for immediate investigation and rectification.

The need to stock paste for extended times should not arise under normal working conditions since, with most pasting machines, the time to paste away a tonne of material can be similar to that required to produce the batch. In the case of traction plates, the usage rate for the paste is often a fraction of the production time. Thus, paste mixing has to start earlier in order to build up sufficient stock to meet the demands of the full shift. The main problem arises when a small amount of paste remains at the end of the shift. It is better to use this up by extending the pasting run but, if this is not acceptable, the excess should be mixed off as an addition to a fresh batch. Rather than remixing, some operators will add a little water (or even sulfuric acid) to give the residue sufficient plasticity to get it through the pasting machine and into the grids. This is a practice that should be stopped because the hopper blades are put under increased strain and the drive motor is overstressed and creates the risk of burning-out. The paste density is lowered in the case of a sulfuric

acid addition and the resultant formed material is liable to suffer from lost pellets and shedding.

Reworking of unused paste

It is uneconomic to scrap unused paste. Further mixing to restore plasticity invariably results in a soft, lifeless material that is hard to force into, and be retained within, the grid. Furthermore, curing is rendered more difficult. The only safe method is to swamp the poor characteristics of the unused paste with a preponderance of good paste. In this way, the unused paste (which is partly cured) does not hinder the full curing reaction of the mass of the paste in which it is incorporated.

In working away unused paste, it is best to make first a full new mix and once the sulfuric acid addition is complete, to add the unused paste in a proportion never exceeding 20 wt.%. The mixer should then be run for a further 5 minutes to distribute the unused paste throughout the new mixing.

Wherever possible, unused positive paste should be added to new positive paste and negative unused paste to new negative paste. This may not be convenient because of the size of the unused amounts of paste. In such situations, positive may be added to new negative paste but never unused negative to new positive paste. The negative paste contains barium sulfate and very small amounts of this compound in a positive paste will reduce the strength of the particle-to-particle bond and thus introduce a high risk of material shedding. Obviously, this leads to a short service life. Where unused positive paste has been added to new negative paste the amount should not exceed 10 wt.%.

The adverse effect of barium sulfate in a positive paste emphasizes the importance of thorough cleaning of the mixing chamber in those cases where the same mixer is used for both positive and negative mixes. Under these circumstances, it is good practice to prepare all positive mixes first, then change over to negative mixing. In this way, the thorough cleaning, required to avoid contaminating positive mixes with barium sulfate, can be scheduled to take place at the end rather than in the middle of a shift.

If unused paste is allowed to dry out, the outer surface tends to become hard and lumpy. This hard material is very difficult to soften and can cause troubles in the paste hopper. It is best to scrap this material. By adopting the discipline of storing the paste under wet cloths, there is virtually a zero risk of obtaining a dried out paste.

It is preferable to retain one paste mixer for positives and another for negatives. It is important when blending unused paste with new paste not to overdo the mixing after the addition has been made. If this is not the case, then the texture of the paste changes relatively rapidly after a certain amount of mechanical working; it transforms from a plastic state to a soft, smooth and characterless, poor condition.

Stocking wet paste for use in factories with no mixing facilities

It is sometimes necessary to supply a small battery making unit with premixed paste. In these circumstances, it is preferable to avoid high sulfation mixes and formulate the paste with medium or low sulfation and adjust the paste density with the water content. The paste mixes should be discharged from the paste mixer into heavy gauge polyethylene (or similar material) bags that will exclude as much air as possible and

prevent the loss of the essential water. The bags are then placed in a steel drum that is sealed for transit. The heaviness of the wet paste makes it difficult to use drums made from alternative, lighter materials.

The sealed drums of paste can be stored for two to three weeks without excessive loss of plasticity or self-curing taking place before use. During the storage period, there may be some surface hardening but this is rarely troublesome and disappears as the material passes through the pasting hopper. The paste behaves as a thixotropic material and changes from an apparently stiff to a flowing material under the pressure of the paddles in the hopper.

Measurement of paste density and texture

The commonly-accepted method of measuring the wet-paste density is by the density 'cube'. This is a cube of metal into which is machined a hemispherical cavity with a volume of either 1 or 5 in³ (16 or 80 cm³). Wet paste is pressed into the cavity and the cube is rapped on a hard surface until the paste takes the shape of the hemisphere. Paste is added until, after rapping, it overflows the top of the cube. A stiff spatule is drawn carefully across the wet paste to true its surface to the plane of the top of the cube. Any paste on the outside of the cube is removed and the combined weight of the cube and paste is measured. The weight of the cube is deducted to give the weight of the paste. The wet-paste density is obtained by dividing the weight of paste by the volume of the hemispherical hollow. It has been common in the industry to express the wet-paste density in g in⁻³ although there is now a trend towards the more acceptable unit of g cm⁻³.

Cube weight determinations are, to some extent, dependent on the skill of the operator, particularly on how thoroughly the cube is rapped to remove any entrapped air. Thorough rapping can be tedious and prone to human impatience so that recorded densities are often lower than the true values. Wherever possible, mechanical rapping should be substituted for manual rapping. The JEL volumeter (Engelman AG, Ludwigshafen, Germany), used for measuring the tamp density of oxides, can be adapted to provide this alternative.

The texture of a paste is a less definable quality and its measurement is more qualitative than quantitative. A crude, but useful, check is to take a small handful of the paste from below the surface of the mix and to squeeze the paste, using both hands, to increase the pressure on the paste. If the paste has been well mixed, there will not be any visible moisture on the hands nor will the paste stick to the hands. Following this, a sample of paste is taken in the palm of one hand and pushed steadily at an angle with the thumb of the other hand. The paste should move smoothly and evenly under the pressure with a sensation of platelets riding over one another. This slight but definite sensation is referred to as the 'crunch' of the paste. This crude check is not positive enough to be accepted as a process control check as it is open to misinterpretation and misapplication in inexperienced hands. There are two generally-accepted tests of texture: (i) the paste slump test, and (ii) the penetrometer test. In the former, the paste is rapped into a cube container that is adapted to allow the sample to be released from a specified height and to fall freely on to a flat metal sheet where it spreads itself in dissipating its potential energy. The maximum diameter of the slumped paste, or the height of the highest point, is taken as a measure of the plasticity or texture of the paste. Concentric circles are drawn on the sheet to speed up the measurement where the maximum diameter is taken as the indicator.

When the highest point of the slumped paste is taken as an indicator of paste texture, the height is referred to as the 'slump height'.

The penetrometer test depends on the measurement of the depth of entry from a free fall into a sample of paste of either a Humboldt or a Globe penetrometer. The Humboldt device is a small cone tipped plunger that is dropped freely into a sample of paste held in a standard density cube. The distance the penetrometer enters the paste is a measure of paste texture. The Globe instrument is a longer two-piece plunger (~40 cm in length) with the lower portion machined to a long, narrow tapered angle. This tapered portion has equally spaced concentric rings turned on its surface, each ring being separately numbered. The penetrometer is dropped vertically into a full mass of paste and the depth of penetration is recorded by reference to the appropriate ring number.

Penetrometers in unskilled hands can give widely varying results and, for this reason, have acquired a poor reputation. Nevertheless, it is worthwhile to apply the technique since, without some check on the paste texture, the variability between consecutive paste mixes can be appreciable. Problems apart, penetrometer readings do alert mixing operators to the importance of adhering tightly to the mixing quantities and timings needed to ensure consistent paste quality and freedom from trouble in the grid-pasting stage.

The other indicator of consistent paste quality that has recently become more common is the magnitude of the load current on the mixer drive motor during the final mixing stage after the addition of sulfuric acid. This can be incorporated in the mixer controls as a sensor of paste texture so that, when the specified drive motor current is matched by the actual motor current, the mixer stops automatically and discharges the wet paste.

Grid pasting

Hand pasting

The standard methods of applying paste to grids are by hand and by machine. The former is rarely used, except for experimental purposes or where special plates are required made to tightly controlled weights and dimensions.

In hand pasting, the paste is applied to the grid with a wooden 'bat' (~15 cm wide) with the handle inclined away from the operator. The pasting action consists of pushing the paste down on to and across the grid away from the operator. When the top face of the grid is covered with paste, the grid is turned over and the underside filled in a similar fashion.

Individual manufacturers have their own preferences for the surface on which the grids are hand pasted. More prefer an absorbent surface such as rough Kraft paper or cotton drill material, although a few insist on a polished glass surface. Those preferring an absorbent surface maintain that the paper or cotton material extracts a small amount of moisture from the paste on the surface against the paper or cotton and this strengthens the surface and enables the pasted grid to retain that surface better during the subsequent processing. The use of paper for the pasting surface has been transferred to one type of pasting machine in which the grids pass between two paper rolls. As an economy measure, one of the paper rolls was removed but there were complaints that paper against one side of the pasted grid led to plate buckling as a result of the varying amounts of moisture removed from either side of the plate.

The roughness of the surface of the Kraft paper and the cotton is reproduced on the surface of the pasted plate. This encourages the free escape of gas bubbles during the early stages of battery service when there is uneven contact between the negative plate surface and that of the neighbouring separator. The effect of this ready escape of gas encourages the active material to expand evenly over the plate surface and remain active throughout the full life of the battery. Once Kraft paper has been used, it has to be discarded. This introduces a health risk as the paper dries quickly and lead dust readily dislodges whenever the paper is moved for disposal.

Where cotton drill material is used, it is necessary to moisten the material to prevent the paste sticking to it and being plucked from the grid when the pasted grid is removed. The material becomes impregnated with paste and loses its absorption so that it becomes necessary to wash the material at frequent intervals.

Hand pasting on to paper or cotton drill material tends to produce a slightly overpasted plate. It is therefore usual to true the surface level with the grid frame by drawing a rigid scraper over the pasted surface using the grid frame as the guide. Some operators have resorted to using a steel scraper as it scrapes cleaner, but in so doing, it often scrapes a fine film of alloy from off the grid surface into the paste. This introduces antimony into the paste as well as removing a more resistant surface to corrosion from the grid. In the case of batteries that are subject to medium- to deep-cycling, these factors lead to an earlier loss of negative potential through antimony deposited on the negative material than would be the case if the original grid surface had not been scarred.

Where plates are pasted on glass, the finished surface is smooth and there tends to be less overpasting. No moisture is extracted from the paste since the glass is nonabsorbent. In practice, the surface of the glass has to be wetted otherwise the suction between the glass and the underside of the plate prevents the plate being slid off without damage to its surface. The need to lubricate the glass surface with water tends to lower the density of the paste below that of the bulk mixing.

Hand-pasted plates will stick to each other if allowed to come and remain in contact. The plates should therefore be hung separate from each other during the curing and drying operation.

The disadvantages of hand pasting are mainly economic since the procedure is labour intensive. The consistency of filling falls off as the shift progresses since the operation is tiring and this leads to larger variations in wet-paste filling weights than desirable, unless regular checks are made. The greatly increased outputs per operator from machine pasting and the greater consistency possible have virtually eliminated hand pasting. There are two types of machines for pasting, namely the belt and beltless types. The former is, by far, the most popular choice in the industry.

Belt-type pasting machines

The pasting surface is supported by a moving, heavy woven cotton belt (~5 mm thick). The belt is driven via a large roller to pass horizontally under a paste-feed hopper where it is supported to withstand the pressure with which the paste is forced into the grid. Paste is directed downwards in the centre of the hopper (by the action of shaped paddles moving within the paste) and into the opening in the base of the hopper under which the grids pass on the belt. The sides of the hopper normal to the line of travel of the grids are shaped so that excess paste not accepted by the grids moves upwards at the front and back of the hopper to join the bulk paste.

The moving belt carries the pasted grids clear of the hopper and past a spreading bar (or trowel) to smooth the paste surface before it travels between cloth-covered rollers that absorb some of the surface moisture and further smooth the surfaces. The plates are then dispensed on to chain conveyors that take them into the flash-drying ovens (where fitted). The latter prepare the pasted plates for the subsequent curing operation.

The endless woven belt serves a number of purposes since, besides conveying grids to the pasting station, it also provides an escape path for any air displaced from the grids as the paste is applied and absorbs a small proportion of the water from the paste to densify the plate surface. This both helps to limit water loss during passage through the flash-drying oven and assists the subsequent curing.

The open nature of the belt needs to be maintained and before any pasting is done it should be thoroughly wetted and then well scrubbed with a stiff bristle brush. The application of water to the belt is to wet any paste remaining from the previous use and, thereby, make it easier to remove that paste with scrubbing. If this cleaning operation is not done conscientiously, the belt loses much of its porosity and its absorption. The former is the more important as there is a risk of incomplete filling if the belt cannot breathe. It is good practice to scrub the belt thoroughly after every working shift, slacken off the tension imposed on the belt by the drive roller, and then leave the belt well wetted and covered with wet cloths to reduce the rate of drying out until the next shift takes over. This procedure increases belt life and should be a normal part of shopfloor discipline as the belt are relatively expensive. A tensioning control is provided and this should be adjusted to take up any slack in the belt before the start of pasting. As the belt returns to the magazine feed for the grids, it passes between nip rollers to remove excess moisture before passing under the paste hopper. The degree of 'nip' should be such that the belt remains damp but not wet.

As there is a considerable pressure on the grids as they pass under the paste hopper, they need to be aged before use to allow age-hardening to develop maximum strength and rigidity. They should be flat otherwise they will not readily enter the clearance slot under the hopper, and will jam and stop production.

Side plates are fitted on the underside of the hopper. These can be adjusted to the width of the grids. The plates close off the sides of the opening through which the paste passes from the hopper into the grids so that the grid side-frames are kept relatively clean and there is little wastage of paste on to the belt. Since it is not possible to prevent paste from passing on to the belt between grids, it is economic to feed the grids so that they are virtually touching each other as they enter the hopper gate.

Several feed methods are adopted to remove grids from the grid magazine and present them singly on to the belt in continuous sequence. The popular ones are 'pecker arms', vacuum cups and 'ferris wheels'. The pecker arms consist of spring steel arms ground to form a hook at their upper ends. A cam causes the peckers to move forwards, down and back in a rotary movement. When moving forward, the pecker clears the magazine of grids and stops immediately over the first grid in the magazine. The downward movement causes the pecker to touch the back edge of the first grid so that, on the backward movement, the hook pulls the first grid on to the moving belt or to a chain drive that leads the grid on to the belt. As soon as the grid touches the belt, it is taken forward into the entry gate of the hopper. The cam or shuttle feed speed is adjustable and is usually set to give a spacing of not more than 1 cm between grids as they pass into the pasting area.

In the vacuum cup system, suction cups are mounted on the cam or shuttle arms and are adjusted so that the suction cups just 'kiss' the face of the forward grid in the magazine. A negative pressure is applied to the suction cups and is sufficient to overcome the mass of the grid and, on the back-stroke of the cam or shuttle, to pull the first grid on to the chain drive or belt take-up.

The ferris wheel principle is usually employed on the slower traction-type pasting machines. Two discs, one on either side of the machine between the grid magazine and the paste hopper, are provided with indentations at regular intervals around their perimeters. The size of the indentations corresponds to the cross section of the lugs on the grids. As the wheel rotates, an indentation passes under the lug of the foremost grid and lifts it clear of the remaining grids in the magazine. A false lug is fitted when single grid castings are being pasted. This ensures that the grid is maintained either in line or transverse to the direction of the motion of the belt, and not at an angle to the belt. The ferris wheel pick-up carries the grid forward until it has moved through 180° from the pick-up position. The grid can then be offered to the chain conveyor that leads to the belt or direct on to the belt, according to the machine design.

The grid magazine is usually spring loaded so that as one grid is removed another automatically takes its place. The effectiveness of the feed mechanism, no matter how carefully and accurately it has been set up, depends entirely on flat grids being presented to the entry gate of the paste hopper. Grids that are transversely bowed in the magazine can be satisfactorily picked up and presented to the belt but invariably will foul the entry gate of the hopper. In order to minimize this difficulty, some grid casting machines have an extra fitting that consists of a flat platen and a heavy, moving block. The latter is synchronized with the trimming die so that as the trimmed grid falls from the die it is subjected to a flattening blow from the moving block. Some companies that do not have the flattening device on their casting machines add a separate flattening operation to a pile of grids before they are moved away for age-hardening. In the absence of a flattening operation, it is helpful to give thin grid castings a slight bow in the vertical, hanging direction so that when the grids are presented to the belt, the leading and trailing edges are in contact with the belt whilst the centre portion of the grid casting is slightly raised. This deliberate bowing stiffens the casting and resists distortion in the other direction. The amount of deliberate bowing given to double automotive grid castings is of the order of 1 to 2 mm.

If the number of grid castings in the magazine is allowed to fall below about 10 pieces, some pasting machines will tend to give trouble in selecting the foremost grid casting cleanly and positively. Keeping the magazine well filled at all times usually avoids these problems.

Most pasting machines of the belt type follow a common working principle and differ, in general, only in small points of design and the position and nature of the adjustments. It is important to study the maker's instructions well before commissioning a machine. Although this may appear too obvious to state, it is surprising how often it is ignored and trouble, with attendant delays, all too frequently experienced.

The starting up and setting procedure for most machines both follow standard routine:

(i) Before filling the hopper with paste, the machine should be lubricated and run dry. The water feed is set to the smoothing rollers so that the cloth covering is only just moist. Too much water on these rollers lowers the density of the surface paste and leads to a higher temperature in the flash-drying oven than is desirable.

The reduced surface density produces dusty plates in due course with an increased environmental hazard:

(ii) Set the flash-drying oven temperature to the specified value.

(iii) Scrub the belt thoroughly to remove dried paste and render the belt supple and absorbent.

(iv) Run the machine with the hopper up disengaged in order to check that the belt is under tension but not stretched. Adjust the belt tension. Check the nip rollers under the bed of the machine to ensure that the belt is squeezed free of surplus moisture, but is not virtually dry.

(v) Check that the side plates fitted on the underside of the hopper are set to the full width of the castings to be pasted excluding the plate lugs where double grid castings are used, or the plate lug and false hanging lug where long traction grids are being pasted transversely. The exact position will show up as soon as a few trial grids have passed under a filled hopper.

(vi) Check the pasting trowel (or roller) to confirm the paste is being spread evenly over the full grid and is of the specified thickness (or weight). Many machines are fitted with a flexible trowel or spreading bar. These tend to wear unevenly and need truing from time-to-time by adjusting the screws spaced across the emergent end of the hopper. Wear is greatest when the spreading bar (or trowel) bears heavily on to the grid to achieve 'scrape pasting' i.e., a pasted plate with the same thickness as the grid casting. Uneven grids, or bowed or deformed grids, presented to the hopper can, in time, score the surface of the spreading bar and these show up on the finished pasted surface. When these occur, the adjustment of the spreading bar should be rechecked and the spreading bar replaced to enable the scored bar to be machined true. Generally, solid spreading bars or rollers present less setting-up problems and require less maintenance than flexible bars and are to be preferred.

(vii) When all the adjustments are deemed reasonable, lower the hopper on to the belt and lock in position; then fill it between half to two-thirds full with paste and run the machine without grids. This leaves a layer of paste on the belt whose thickness is determined by the setting of the spreading bar. Check that the paste covers the width uniformly and is being fed continuously. An approximate idea of the thickness of the paste can be obtained by running a finger across the band of paste. Make sure the thickness is not less than the thickness of the grids, otherwise grids will become jammed under the hopper as soon as they are fed. Position the spreading bar with the adjusting screws to accept grids to the maximum tolerance of the casting thickness.

(viii) Start feeding the grids and check that they are filled with paste and to the specified thickness, taking into account the permissible tolerances. Provided the paste density control is good, the weight of paste in the grids will be a measure of pasted thickness. Where it is design policy to paste the grids tight to the grid thickness there will be the possibility of damage to the spreading bar due to the pressure exerted by the bar on to the grid surface. With flexible bars, there is a great risk of the bar being compressed by the solid grid members but not where the paste is being pressed into the open spaces of the grid. This shows up in extreme cases as depressions in the pellet areas that, when assembled later into cells, can allow gas bubbles to coalesce into larger bubbles and blank off areas of active materials with a loss of performance. Scrape pasting is not recommended where continuity of production and negligible down-time is valuable.

'Level' pasting, where the thickness of the paste is marginally greater than the actual grid thickness (i.e., about 0.05 to 1.0 mm), presents little difficulty as the very

small extra thickness of paste tends to act as a lubricant as the grid passes under the spreading bar. Some difficulties are experienced in situations where it is design policy to produce a finished plate thickness that is appreciably greater than the grid thickness (i.e., 'overpasting'). This is because the underside of the plate is cut from the belt by a fine wire lying on the belt and the pasted surface will be level with the grid surface so that any extra thickness will come from paste standing proud of the upper surface of the grid. All the extra thickness is on one side of the pasted plate and there is a finite limit to how much extra thickness, all on one side, will stand up to the subsequent processing and remain in good contact with the grid. Overpasted plates tend to be more variable in thickness than level pasted counterparts as it is not possible to measure to any accuracy the finished thickness. Automotive batteries, not subject to regular deep cycling, can tolerate a degree of variability but traction batteries are dependent on close control of the plate thickness for life and performance.

Provided there is a close control on wet-paste weights with successive paste mixings, it is sufficient to measure pasted-plate weights to assure an acceptable thickness control. In such cases, it is adequate to weigh ~20 grids and obtain an average weight and, using this weight plus the equivalent weight specified for paste, to load one pan of a balance against which sample pasted plates taken at random are compared. The settings of the trowel or spreading bar should be such that the measured wet-paste weights per grid are as close to the specified average as possible.

It has to be recognized that the assembly process when plates are grouped to form cell elements is based on overall thickness and not on the weight of paste in the plates and, although it is important to maintain wet-paste weight within the specified tolerance, it is even more important to keep the overall element thickness within relatively close limits. This is particularly true in the case of cells with many plates where any variation in pasted plate thickness is multiplied many times. In addition to grid thickness, control of wet-paste weight is essential if control of plate thickness during the pasting process is not to become a continual worry.

It is common practice to specify a tolerance of $\pm 2\%$ on the wet-paste weight of the bulk mixings. It is often difficult, however, to guarantee this as the only practical test of wet-paste weight is the use of the standard cube cup and it is questionable whether the reproducibility of the results is within $\pm 2\%$. In addition, the permissible variations in grid casting thickness and the result of simply accepting a wet-paste weight per grid size can produce finished plate thickness variations of 5%, or higher. The thinner the grid the more troublesome can this become in the assembly stage when the results of cumulative tolerances in grid casting, paste mixing and pasting can produce elements varying from exceedingly slack to oversize for the cell compartment into which they are required to go. Very slack elements are prone to mechanical damage in service through vibration, whilst oversize elements forced into cell compartments can develop short circuits through the separators due to penetration of the separator by the edges of the grids. This effect of cumulative tolerances on the overall element thickness is very noticeable in traction elements where a 5% excess grid thickness on a 4 mm thick grid is 0.2 mm. If this occurs throughout the plates of a 21-plate cell, the element thickness is increased by 4 mm.

The control of pasted-plate thickness starts at the grid-casting stage. It is further assisted by tight control at the paste-mixing stage and, thereafter, little further control other than good setting-up of the spreading bar is required. If these are present, the only real check needed on the wet-pasted plate is that the minimum amount of paste specified is always present.

If the side shoes under the paste hopper are correctly set, there will not be any noticeable paste on the plate lugs. Paste on the lugs gives trouble later in the formation

stage and, subsequently, in assembly. If paste shows up on the lugs there will usually be excess paste outside the grid frame. The side shoes should be moved slightly inwards until the excess paste outside the frame no longer shows and the lugs are clean. Sometimes, no excess paste shows up outside the grid but the lugs remain dirty. This usually means the side shoes are not flat and need trueing.

Having checked the acceptance of the initial pasted plates, the pasting run is started and random plates inspected at intervals to give assurance that the pasting standard is being maintained and the plate thicknesses are within tolerance.

The grid feed mechanism should be adjusted to give about 0.5 to 1 mm between castings. If less spacing is allowed, there is a risk of the ribbon of paste between castings sticking to one or other of the grids and remaining with the grid through the drying stage after. This necessitates a separate cleaning operation or offers the possibility of damage to separators or subsequent short circuits if no treatment is applied. For spacings between castings of > 1 cm, the amount of paste left on the belt is appreciable and there is a decline in the effectiveness of the belt cleaning operation as the belt passes under the machine. The scraped paste is returned via the collecting sump to the hopper. During this process, it can pick up water, and this lowers the density and reduces the density of the hopper paste with which it is remixed. This is particularly noticeable when the sump paste is returned manually to the hopper. If a large amount of scraped paste is allowed to build up in the sump, the addition of this paste to that in the hopper can produce pasted plates wildly out of specification and with a poor life potential, especially in the case of traction plates.

After the pasted plates leave the hopper, they usually pass between spring-loaded smoothing rollers. These rollers are covered with muslin, the purpose of which is to smooth out any imperfections on the plate surface, remove surplus moisture, and present a consistent plate to the flash-drying oven so that the resulting dried plates have relatively constant moisture contents and inner temperatures. In belt-type pasting machines, where the paste is forced down on to and into the grid, the underside of the plate tends to be slightly imperfect since the paste tends to enter the grid structure and curl around the lower rows of the wires to meet on the underside of those wires. This rarely occurs to completion in automotive plates, mainly because the plates pass under the pasting hopper at a relatively high speed and there are usually gaps on the lower plate surface in line with the crests of the lower rows of wires. A cutting wire stretched across the belt and passing under the pasted grid severs the pasted grid from the belt. This cutting wire does not usually smear the underside of the plate so that one action of the rollers is to extend the curl of paste and reduce the magnitude of the gaps on the underside of the plate. If the covering on the rollers is dry, the muslin tends to pluck at the paste and extend the irregularities. If the muslin is too wet, it transfers water to the plate surfaces and, in turn, makes the subsequent flash-drying operation more difficult to perform without raising the oven temperature. With normal temperatures, there is a danger of damp plates emerging from the oven and if curing is performed in a stack, there is a great likelihood of the plates sticking together. For the most consistent plate quality, the muslin should just be sufficiently damp not to damage the plate surface through paste plucking, but able to absorb some of the surface moisture so that the amount of heat required by the flash-drying operation to complete the surface drying is relatively small. Under these conditions, little moisture is taken from below the plate surface during passage through the oven, and the heat and moisture conditions within the mass of the active materials conform to the optimum conditions for satisfactory self-curing, i.e., 10 to 12 wt.% moisture and 30 to 40 °C material temperature.

In the case of traction plates where there has been an excess of moisture on the smoothing rollers, the surface water transferred to the plate tends to run to the lowest point, i.e., the trailing edge. This can soften the paste in the lower rows of pellets so that, as the plate swings from a horizontal to a vertical position ready to engage the carrier chain taking it through the flash-drying oven, the lower rows of pellets of wetted paste physically move leaving pellets with a set of depression on one side and a set of raised portions on the other side. These imperfections increase the effective thickness and cause the plate to appear wedge shaped when assembled into a cell. The depressions also cause polarizing gas pockets in service. Some makers compensate for this and other imperfections by passing the plate through a separate set of sizing rollers interposed between embossed sheets. These form either fine ribs lengthwise or produce a crude woven pattern that eases the escape of gases during the early part of service life until the negative material has expanded sufficiently to marry up with the back profile of the separator in contact with it. This secondary rolling operation also brings the active material into tighter contact with the grid members and eliminates small voids within the wet paste where gases could accumulate during both formation and subsequent charging. Voids present a problem in that the pressure from occluded gases can build up sufficiently to burst through the material and damage the plate surface.

Most pasting machines are fitted with a scraper for removing excess paste from the belt. The excised paste tends to be smoother than the original paste and often picks up moisture from the water feed to the smoothing rollers so that it falls into the excess paste sump with a lower density than the original. Because it differs both in texture and density, the sump paste must be returned to the hopper to be worked away in small quantities to avoid appreciable variations in the quality of the pasted plates. In the extreme case, i.e., large amount of sump paste being fed back into the hopper, complete plates will be produced with much lower density paste than can be tolerated for reasonable life expectancy. Such plates tend to shed material early in life and the cell loses capacity, particularly under repetitive deep-discharge conditions.

Despite spacing the consecutive plates carefully as they pass under the hopper and setting the side plates in the hopper, it is sometimes found that with thick plates some paste adheres to the frame edges. This can often be eliminated by wiping the edges of the unpasted grids in the feed magazine with kerosene or a light lubricating oil. Care must be taken not to use too much oil and this can be achieved by using a sponge, from which most of the oil has been squeezed out, as the wiping medium.

Trouble can also be experienced with paste sticking to the plate lugs, despite careful setting up of the hopper. When this occurs, some easement can often be obtained by fitting fine water jets where the pasted plates pass from the belt via the chain feed to the flash-drying oven. The water pressure in the fine jets is adjusted to provide sufficient force to dislodge the paste. The disadvantages of using such jets are the amount of water used running to waste, the extra contaminated water which has to be treated later in the effluent treatment plant, the tendency for the paste removed from the lugs to collect on the shopfloor, and the further reduction in sump-paste density if the excess paste is channelled back into the sump. When this lug cleaning system is used, it is preferable for the washed-off paste to be channelled into separate collection tanks where it can be checked before being worked into a new paste mixing. The wash waters from the lugs also are better collected near the pasting shop in a separate tank in which the paste contamination can settle and the clearer water weired over into the main channels that lead to the effluent-treatment plant.

Without care and attention the pasting shop can become an accident risk as well as an unpredictable source of high lead in air contamination.

Paste loading to hoppers

The old method of loading hoppers was to shovel paste from paste 'dollies' holding around 500 kg of mixed paste. This is a back-aching operation but can be relatively clean since the physical volume of paste that can be lifted readily is not large and a handling skill can be readily developed whereby the paste is turned cleanly into the hopper. The action is smooth and little lead hazard is created.

Some companies take the dolly from the mixing shop and lift it into a supporting frame above the hopper so that the open mouth of the dolly points down into the area of the hopper top. A rake, or hoe, is then used to drag the paste down into the hopper. At first sight, this seems to be a big improvement over the arduous shovelling operation, but it does impose a greater strain on the shoulder muscles and there is a greater tendency for paste to fall in uncontrollable lumps into the hopper with some falling outside. The operator is in the direct line of fall of the paste and, generally, more paste comes in contact with and adheres to the operator's clothing. It is not uncommon for the lead-in-air levels with this method of working to be higher than with the shovelling method, and the floor around the operator tends to be more contaminated with paste.

Paste that has fallen on to the floor tends to become contaminated and unsuitable for further use. This is lost paste as far as the shopfloor economics are concerned. The method of loading paste into the hopper becomes an important factor in achieving good productivity, sound operator hygiene and economic targets.

There is generally a good economic case for paste-dispensing methods that do not rely on human brawn but mechanically feed the paste direct to the hopper in a safe and controllable manner. Several methods are in now common use: (i) screw conveyor feed from paste mixer to paste hopper; (ii) motorized cone feeders, or dispensers, slung immediately above the paste hoppers, and (iii) motorized belt conveyors from the paste mixers to the paste hoppers.

Methods (i) and (ii) are basically the same, the volume of the screw conveyor or the motorized belt being such that half, or all, the paste can be held in the conveyor, or on the belt, to free the mixer for further use. The screw or belt conveyor can be 'inched' by the paste machine operator to keep the hopper full. In the case of the belt conveyor, it is usually necessary to envelop it in a mist of water vapour to prevent the paste drying out and losing its free working conditions. The mist should be a true mist and should not be allowed to degenerate into droplets as this could alter the paste density during its period of use.

Method (ii), the cone dispenser, has the advantage that it can be filled from the paste mixer and used anywhere in the pasting shop, provided an overhead rail is installed to the various projected usage areas. The dispensers are fitted internally with motor-driven scrapers. These are so shaped that the paste is given a downward thrust that forces it out of the bottom of the cone. Again the operator can be given full control of the motor feed.

The above feed systems ease the lead-in-air control problems in pasting shops and this amply justifies their consideration.

Pasting problems

The reliability of a pasting machine is only as good as the quality of grids presented to it, the thoroughness of setting up, and the cleaning and standard of the routine maintenance. The main troubles encountered include the following.

Paste plucking

This is generally due to poor belt cleaning and preparation but it can also arise if the paste is too wet and soft. If, in the mixing operation, the mixer operators have erred on the low side of the specified water addition when making the water/oxide slurry (either through a parallax error in reading the sight glasses or through an arbitrary reduction because of the prevailing humidity and/or ambient temperature conditions), a large water addition could be required after the paste has had its full sulfuric acid addition in order to correct for density. Water added after the sulfation stage does not blend effectively and the resultant mix tends to be 'rubbery' under compression. Such a paste is incompressible and, unless the air displaced from the grid spaces can freely pass through the belt, the pellets of wet paste do not fully fill the grid spaces and are readily displaced as the pasted grid is parted from the belt.

The belt must be thoroughly free of embedded paste before pasting starts. This is achieved by vigorous scrubbing. It must also be damp, but not wet. If these requirements are met and the paste has been mixed properly in accordance with the relevant process specification, then little trouble from plucking should be experienced. If, however, the belt is allowed to dry, it exerts a suction on the paste and less secure pellets of wet paste are plucked from the grid. If the belt contains embedded paste from previous pasting runs, it loses porosity and again exerts a suction.

Machine jamming

Machine jamming stems, in most cases, from the way in which the grids are presented to the hopper, the degree of flatness of the grids, or the degree of parallelism between the belt support and the pasting trowel or roller has been set. The setting of the grid-feed mechanism must be such that a grid casting taken from the forward end of the magazine will be presented with its leading edge parallel to the hopper entry and with its side frames in line with side shoes that control the width of the paste feed. If a casting enters out of parallel, there is a tendency for it to move across the front of the hopper and jam.

Castings that are not flat or with short runs, i.e., incomplete wires between ribs, can catch the back side of the pasting trowel and be pushed up into the hopper. Uneven setting of the pasting trowel puts greater pressure on one side of a casting and tilts the other side upwards to distort the casting and cause it to come into contact with the paste-feed paddles.

Whenever a machine jam occurs, the equipment should be stopped at once and the hopper lifted. The castings should be removed and the paste dug out — particularly immediately behind the trowel — to make sure that no portions of casting are left in the paste. Whilst this is occurring, some paste will almost certainly fall down on to the belt. This should be removed and the belt cleaned before restarting the process. If this is not done, it is possible that paste plucking will occur. Any paste removed by the remedial action that contains fragments of grids should be discarded. Reuse only creates more problems and increases down-time.

Every care should be taken to avoid jams by paying more than average attention to the preparation of the belt and machine before the start of a working shift. The

cost to plate-pasting productivity and unit costs can be very high if jams become a common occurrence.

Poor paste feed

It sometimes happens that the feeding of paste into grids becomes erratic. When the hopper is lifted, it is seen that paste has consolidated into a hard, compacted mass immediately behind the pasting trowel or roller and has prevented the proper circulation of paste within the hopper. The usual pattern of paste movement is for a main downwards movement in the central part of the hopper. The excess paste is returned upwards immediately behind the pasting trowel. The forward face of the hopper is often shaped as a curve to assist this return movement. Any consolidation of paste at this point blocks the return, upsets the flow pattern, and eventually jams the feed. Belt-pasting machines with independent motor drive to the hopper paddles often suffer more from this fault than machines where the belt and paddle drives are ganged to the same motor. There is a relationship between paddle speed and belt speed that stimulates the circulation of paste. Any alteration in this relationship throws the circulation out of optimum with the result that the movement of the excess paste upwards from the belt slows down and the paste consolidates. The remedial action is to adjust the speed relationship slowly in steps, first in one direction. If this does not clear the fault, the operation is repeated in the opposite direction.

Paste texture can also cause this fault. If paste is mixed for too long a period, the material loses its shear characteristics and becomes lifeless and sluggish under pasting pressures. Overmixing often occurs when a proportion of stale paste is incorporated, or if the final density adjustments are made too timidly and the final water additions demand mixing for periods of time that are far in excess of that specified. This is not unusual when the mixing is controlled manually.

The attempted use of old paste, without diluting it with new paste, is another cause. Whilst this appears obvious, it is sometimes tried by undisciplined operators to avoid the nuisance value of working away in new paste in small controlled amounts.

Most of these faults disappear with good quality control and close operator supervision.

Machine cleaning

Good machine cleaning is the key to minimum down-time and scrap. All machines should be thoroughly cleaned at the end of each working day. The normal procedure is to cease adding paste to the hopper and to continue passing castings through the machine until it is no longer possible to fill the grid spaces completely. At this stage, the magazine of grids is removed and the machine again run until no more paste is forced from the hopper on to the belt. At this point, the paste remaining in the hopper is located mainly around the paddles and on the front and back faces of the hopper. The machine is stopped and the hopper lifted. The residual paste is then removed with a spatula or similar tool. When this is completed, the hopper is washed clean of paste with a water spray and brush, if needed. The paddles, rollers and inner faces of the hopper should be clear of all paste. Wherever possible, all removeable parts should be detached to ease cleaning. After the hopper is clean, all moving parts should be lubricated. The paste removed should be recovered and placed in drums for reuse in negative pastes only. The recovery of this material is part of the overall economics of plate making.

After cleaning the hopper, attention should be directed to the belt. It is first necessary to release the tension on the belt and on the nip rollers that control the

dampness of the belt when pasting. The belt is wetted thoroughly and scrubbed vigorously with a hard bristle brush until the visible paste embedded in the weave has been loosened and washed away. When the water brushed away from the belt is clear, the belt is deemed to be clean. This washing is both tedious and time consuming, but it is necessary since large time losses will occur if it is not carried out correctly. It is better to err on the side of overcleaning than the reverse. After cleaning, the belt is turned until the diagonal splice is uppermost and resting on the machine bed that normally gives support to the moving belt. The belt should then be thoroughly wetted again and all exposed parts covered with wet canvas or similar material.

Again, the feed mechanism and other moving parts should be oiled and greased and the whole machine wiped over with an oily cloth to reduce rusting. The main bearings should then be relubricated.

Densification of paste with pasting

In the days of hand pasting, the density of the wet paste in the pasted plate differed little from that of wet paste dispensed from the mixer. There was some increase in density at the beginning of a shift when the operator was fresh and before wrist and arm fatigue became significant. In the case of soft, smooth pastes with a low level of sulfation this increase in density rarely exceeded 2% and with dry, crunchy pastes less than 1%. With the latter, virtually no water was expressed out of the paste; the free water was held wholly locked between the solid particles.

With machine pasting using formulations made with ball-mill oxides, much depended on the mixing procedures. Where water additions were made at the end of the sulfation stage to bring the wet density to the specified value, the final water did not often fully blend in and could be expressed out of the paste by the action of the hopper paddles. The mechanical action of the paddles also tended to cause the solid platelets of oxide to move relative to one another and to align their major axes roughly parallel to one another. This produced a noticeable change in texture after passing through the hopper. A similar, but not so great, change occurred with Barton-pot oxides.

Even though the paste-mixing process may have been programmed, unless the water content has been controlled to just enter the area of plastic flow (depending on the water tolerance of the particular oxide used), there is still the factor of water expressed from the paste.

The result of the two changes in the paste entering the grid is an increase in the density of the paste in the grid. It is not possible to give a firm figure for this increase in density as the choice of paste texture is a personal one for each individual firm. Very often, it is dependent on the type of pasting machine used, the hopper-paddle design, and the relation of paddle speed to belt speed. To illustrate this, a particular heavy-duty pasting machine using a medium sulfated paste with a creamy texture gave ~8% increase in density. In the case of hand-controlled mixing, where the initial water addition was limited because the operator thought the humidity of the atmosphere could have increased the moisture take-up of the oxide and a greater water addition was needed to bring the paste density to the specified value, an increase in paste density of up to 15% has been noted. Where dry, crunchy pastes have been used, produced in a programmed mixing with no final water adjustment, an increase in density of as low as 3% has been recorded.

Increases in paste density after passing through the hopper make it difficult to calculate the optimum wet-paste density, as dispensed from the mixing process, for

a particular plate performance. It is sufficiently important for regular checks to be made of the paste density, both before and after pasting the grids. These establish the order of density change common to the type of paste specified for each major type of plate manufactured. The data obtained show the extent of densification and the possible range of paste densities in bulk production. The latter is reflected in variation in capacity.

Where no data exist and it is not convenient to derive statistically the order of paste densification, it is suggested that a figure of 5% is taken for design if the standard paste is dry and crunchy one, and 8% if the standard paste is a smooth and creamy. These assumption should be confirmed as soon as possible for each type of paste and pasting machine. When collecting these data, note should be taken whether the machine has the belt and paddle driven from a common motor or whether they are separately driven. If the latter, it must be recognized that operators rarely, if ever, understand that there is an optimum relationship between the belt and paddle speeds, and that variations in this relationship will tend to alter the degree of densification of the paste. As previously stated, manual control of paste mixing will also tend to widen the range of paste densification.

Flash drying

Originally, pasted plates were allowed to dry in air. Consequently, in the subsequent formation, the amount of electrical power required was many times the capacity of the plates and, in addition, there was a risk that during formation the surface of the active material would 'puff' and break away from the remainder of the material. By transferring pasted plates, as soon as they are pasted, to a humid and warm atmosphere they acquire greater strength and are easier to form with less power. The removal of pasted plates from the pasting machine as they emerged from under the pasting hopper is possible with slow-moving traction plates, but is not economic with automotive plates where pasting machines can achieve speeds in excess of 150 double grid castings per minute. To take advantage of these pasting speeds, it is necessary to dry off the surface of individual plates so that pasted plates could be automatically dispensed in a form suitable for transfer to the curing area, or for curing *in situ*.

From the pasting belt, the pasted plates are taken by a chain conveyor into an oven where the temperature is maintained at a level that is just sufficient to remove the surface moisture only. Once this has occurred, the plates will not stick together in contact one with another. Plates treated in this manner can be piled, or racked. This restricts the total evaporating area and the loss of absorbed moisture from all the plates except the top plates. The latter can be protected by covering the batch with a block of wood or a plastic sheet. The heat from the flash-drying oven starts the reaction between the free lead in the paste and the slightly acidic moisture within the paste. This reaction is exothermic and, until the free lead has nearly fully reacted, the essential heat is self-sustaining.

There are handling advantages with flash drying, irrespective of whether the plates are subsequently either racked and spaced apart in a humid setting oven, or piled or racked tightly in contact with each other. Because of this, it is common practice to provide the pasting machine with a flash-drying oven as an integral unit. The wet-pasted plates are usually taken by chain conveyor from the belt into the oven (either vertically or horizontally, according to the oven design) and automatically dispensed at the exit (the take-off end).

The operation of surface drying is a time-temperature system. The larger the surface area of the plates and the greater the mass of material involved, the longer is the time taken at a single controlled temperature to evaporate the surface moisture. This can be achieved by reducing the pasting speed or by increasing the length of the oven. The latter is impracticable, except to have one length for automotive plates and another for traction plates since these are virtually never pasted on a universal pasting machine. Traction plates are normally pasted at a slower speed than automotive plates and a flash-drying oven for a traction plate machine is usually about 30% longer than one for an automotive plates. Within this length restraint, larger and thicker automotive plates require a higher oven temperature to evaporate the surface moisture than smaller, thinner plates. The same holds for traction plates where the greatest variation is in plate length.

Naturally, it is both inconvenient and often not easy to change the oven temperature to suit the size and thickness of the plates, being processed. Therefore, the temperature is set to surface dry the largest and thickest plates. This means the smaller and/or thinner plates will tend to be overdried and subsequent curing will be restricted.

The moisture present in wet pastes generally falls within the following ranges:

automotive:	negative	11 to 14 wt.%
	positive	13 to 16 wt.%
traction:	negative	9 to 13 wt.%
	positive	10 to 14 wt.%

The optimum moisture and temperature conditions for a rapid and effective cure are 7 to 10 wt.% and 25 to 35 °C, respectively.

Automotive plates do not present too much of a problem when a single standardized temperature is used. Except possibly for very thin plates, i.e., of the order of 1.25 to 1.5 mm in thickness. With the latter, the small mass of grid metal and paste conducts the heat rapidly through the full plate thickness and there may be an undesirable evaporation of the inner moisture of the paste. For this reason, the same pasting machine should not be used for short runs that involve a large change in plate thicknesses.

By comparison, traction paste usually has less residual moisture before entering the oven. The setting of the oven thermostat becomes more critical on changing from very long to short plates when the plates are pasted longitudinally. If no change is made, it is possible that the amount of moisture removed will decrease the inner moisture to below the value that is necessary for efficient curing. Under these circumstances, the evaporation losses occurring as the curing reaction proceeds can reduce the inner moisture to such an extent that the curing is drastically reduced or stopped. For traction pastes, it is common experience that the reduction of the free-lead content in negatives proceeds more slowly than in positives and, from time-to-time, difficulty is experienced in achieving a final level better than 8 wt.%. Some easement can be obtained by liberally wetting the smoothing rollers following pasting so that the plates carry an excess of surface moisture before entering the oven. This can be particularly helpful with short plates. As soon as the plates emerge from the oven, they should be racked or piled and immediately covered with damp cloths to minimize evaporation losses.

Provided the amount of moisture in the plates is checked and found to be ~10 wt.%, or slightly higher, and the plates as they emerge from the oven are rapidly covered with wet cloths, there is no reason why the final free-lead content after curing

should not be <3 wt.%. Many companies accept a free-lead level after curing of 5 wt.% but a lower value gives a better negative plate and reduces the open-circuit loss in charged cells that are stored pending assembly into traction batteries.

Flash-drying ovens

Flash-drying ovens are simple tunnel ovens and differ mainly in the way the plates are conveyed through them. The more common system of heating is by gas. The burners are usually located near the bottom of the oven and are baffled from direct contact with the passing plates. Some designs have infrared heaters in which case the heaters are above the passage of plates and are generally unbaffled. The alternative heating system is by radiant heaters fed from the electrical power supply.

The disposition of the heaters along the length of the tunnel is such that the main evaporation of the surface moisture occurs at the entrance end of the oven with a cooling section at the take-off end. The plates are conveyed through the oven either vertically, hanging from a chain conveyor, or horizontally lying on a mesh conveyor belt. The chain conveyor is sited so that there is a smooth transition from the horizontal position of the plates on the pasting belt to the vertical position on the chain conveyor. The speed of the conveyor is adjusted to give a spacing of 1 to 2 cm between the plates so that the heated air can readily pass between the plates. The surface moisture is quickly carried away by convection.

The rate of gas flow to the heaters is controlled by a thermostat. Whilst the setting of the thermostat should be determined by the operators to suit the particular plate thickness, size and wet-paste moisture content, a setting of 180 to 200 °C can be used as a starting point where no experimental data exist. Having set the thermostat to this temperature range, the emerging plates should be examined for adequate surface dryness in order to prevent plates sticking together. If this is acceptable, then the moisture content of the emerging plates should be assessed to ensure that there is adequate moisture within the material for satisfactory reduction of the free-lead content.

The hanging type of flash-drying oven can be troublesome with plates below 1.5 mm in thickness, particularly if there happens to be pasting difficulties calling for machine stoppages. In these situations, the plates remain static in the ovens while the hopper is lifted for remedial action. The danger exists not only of overdrying the plates, but also of melting the grids. A further hazard is that a greater shrinkage than normal can occur and this will promote cracks in the material which will be accentuated during the curing process. The presence of fine barely-visible cracks in the material is not uncommon after flash drying, but these do not increase if the trapped moisture in the material is adequate and the plates are not in a stream of relatively dry air. Some manufacturers pile automotive plates in open-sided boxes in the pasting shop area to create a static atmosphere free from draughts whilst others set apart an area for curing away from doors and traffic to obtain the same effect. In this way, the need for a controlled humid atmosphere and, hence, associated the capital and running costs are avoided.

The presence of visible cracks in the surface dried plates is to be avoided as they can give rise to damaged plates with subsequent handling. If it is observed that the scrap from pasted and cured plates has risen above the normal level, then the first parameter to be checked should be the temperature setting of the flash-drying oven.

For plates conveyed horizontally on a mesh belt or a double-chain conveyor, the best results are obtained when heat is applied on either side of the plates. Acceptable drying has been obtained however, with heaters, usually infrared (above the plates)

or gas (suitably baffled below the plates), similar to the ovens with vertical plates. Gas heating has been offered to accommodate short plates that are hung vertically and long traction plates that are processed horizontally. With horizontal drying, the plate conveyor has to move more rapidly since the rate at which the plates are dispensed will vary with their length. The longer the plates, the faster the speed of the conveyor required to maintain the same output of dried plates per shift. This calls for a more intense heat than in the case of vertical plates and, in turn, this introduces the risk of overdried or melted grids whenever there is a machine stoppage. Some ovens for horizontal drying are provided with automatic heat reduction whenever the conveyor stops.

Most operators agree that the control of surface drying is more difficult with horizontal drying, and that the incidence of excessive loss of internal moisture is greater. This gives rise to a more extensive degree of cracking of active material and poorer curing as demonstrated by a high free-lead value. The problem can be ameliorated by dividing the length of the oven into an initial hot zone followed by cooling zones.

The moving chains or mesh belts, irrespective of the type of oven, are continually passing through the heated area and then out into the shop atmosphere. This causes the chains or belts to be continuously expanding and contracting throughout the working shift. The adverse effect of this on chain or belt life is aggravated by heating the oven at the start of a shift with the chain or belt stationary. For this reason, the conveyor should be set in motion, and kept in motion, before the over heaters are activated. Similarly, when the working shift is complete, the oven should be switched off first and the conveyor kept running until the oven has cooled down.

Environmental control

Environmental hazards from lead-in-air concentrations are exaggerated when paste mixing and pasting are carried out in the same work area, particularly if there is an open door nearby. The use of lead oxide in drums can be troublesome as it entails the trucking of the drums to the work area, the opening of the drums, the upturning of the drums to empty their contents into the paste mixer, and the replacement of the drum lids.

In principle, all the operations can be performed under an extraction hood, except the trucking of the drums to the work area. In practice, the lids of the drums are subjected to mechanical damage and distortion and the good fit is destroyed. This leads to a leakage of powder every time the drums are moved and bumped. During the trucking operation, all the drums should be covered with a flexible plastic cover extending close to the bases of the drums to prevent expelled powder from rising and reaching the truck driver's breathing zone.

Stationary drums awaiting use should be stored under an extraction hood to cater for the expulsion of powder whenever the drums are knocked, and to provide a safe area in which to remove the lids for examination and testing. Drums should be inspected at frequent intervals and rejected if there is any sign of a loss of a sound dusttight seal with the lid.

The removal of the lids, preparatory to emptying the contents into the mixer, should always be carried out with the drum on the hoist to the mixer and under negative pressure relative to the shop atmosphere. Unless the drum hoist is correctly maintained, there is a tendency for the tilt imparted to the drum to be inadequate and the operator has to force the drum over the stop and to knock the drum vigorously

to release the last amount of powder. This leads to drum distortion and powder leakage, particularly when fitting the lids before returning the drums for refilling.

The location of the drum hoist relative to open doorways is important. The drum hoist should face open doorways if these are present so that winds causing air to enter the shop will assist, not hinder, the extraction system.

It is not realistic to ignore the problems of drum distortion and increase the extract velocities at the oxide feed to the mixers to achieve adequate health control. This is because, with any extraction, there is a loss of oxide into the extraction system and any further increase in the extraction velocity merely increases the powder losses and hastens the time when the extract ducting has to be cleaned of hazardous powder accumulations. It is more economic to be strict over the rejection and replacement of drums and certainly safer from the standpoint of operator health.

Most of these problems are removed if the oxide is contained in silos and screw fed or air blown via weighing chambers into the mixing chamber. This markedly reduces the health hazard.

With manual introduction of the initial water, it is common practice for the operator to look into the mixing chamber to check the nature of the water/oxide slurry. An inspection window is usually provided, but all too frequently, it is too dirty for any clear indication of the slurry to be made. As the window is above the mixing ploughs and scrapers, there is no physical danger in looking with the head right inside the chamber. This should not be allowed as there is a high level of lead in the extract air and, therefore, the practice is hazardous to health. If, for any reason, it is necessary to peer inside the mixing chamber, the operator should always wear an approved respirator.

There is a lesser hazard when turning out mixed paste. This comes mainly from small lumps of mixed paste flying and sticking to protective clothing where it dries and, thereafter, every movement of the operator produces a mini-atmosphere of toxic lead dust within the operator's breathing zone. The problem is greatly reduced if the paste mixing is programmed starting from a silo feed through enclosed ducting to give an automatic mixing cycle with covered dispensing of the paste at the end of the cycle into covered dispensers.

Wherever possible, the mixing operation should be divorced from the subsequent pasting and contained in a separate mixing room. Where loads of wet paste are passed directly to pasting machines in close proximity to the mixers with an open door on the opposite side of the mixers to the pasting machines, air currents can readily take toxic lead dust into the pasting area and increase the background lead-in-air level. Whilst the latter may not be large, it does reduce the permissible increase in lead-in-air resulting from the pasting and removal of plates from the far end of the flash-drying oven.

There are two areas that generate lead-in-air concentrations in the pasting of plates. At the hopper, paste tends to stick to the top edges of the hopper walls and dry out. This dry paste is easily dislodged whenever the hopper is raised to clear a plate jam and is dropped back into the pasting position. The dust tends to move towards the operator and to form a cloud slowly falling into the operator's breathing zone. The second hazard is at the paddle drive motor when a separate drive motor is fitted. This motor is usually an enclosed type designed to run relatively hot. Paste falling on to the carcass of the motor dries rapidly and is disturbed by motor vibration to rise as a cloud driven towards the operator by the stream of air drawn through the motor by the cooling fan. Since there is a danger of motor damage if it is hosed down, it is preferable to fit a sheet metal guard over and spaced from the motor to

collect the spilt paste. This guard can be hosed down without fear of damaging the motor.

The hazard from dried paste on the hopper walls can be greatly reduced by fitting a lip extract that draws air at a relatively high velocity across the top of the hopper. The size of the slot forming the lip extract should be aimed at maintaining a capture velocity at the side of the hopper furthest from the slot of not less than 1 m s^{-1} .

The greatest hazard comes from protective clothing. Spilt paste sticking to the clothing dries and is disturbed with every movement of the operator. There is a tendency for operators to wipe their gloves on their clothes, or to remove their gloves to rectify a jam and again to wipe their hands on their clothes before replacing their gloves. Such habits are often involuntary, but should be firmly rectified by the supervisor in charge.

The pasting operators should wear washable caps covering the hair as well as long waterproof aprons that can frequently be hosed down to remove any paste lodged on them.

At the take-off end of the flash dryer, it is customary for operators that are manually removing the plates to take the weight of the plates on their forearms as they load or pile them on to curing racks or stacks. The arms of the protective clothing tend to become heavily contaminated with paste which soon dries and, thereafter, is disturbed with every movement of the operator.

Often, there is a reluctance on the part of the operator to wear waterproof armllets that can be frequently be hosed down to remove paste. This is because the combination of hot plates and the heat generated by the constant lifting causes excessive perspiration below the impervious armllets that, in turn, often produces uncomfortable skin rashes and severe irritation. In these circumstances, considerable operator protection and relief can be obtained if both the operator and the plate-loading racks at the end of the oven are enclosed in an extract booth with the air stream moving downwards, i.e., away from the operator's breathing zone into extract ducting below the level of the oven take-off.

Changes of protective clothing should be conducted frequently (preferably, decided by the amount of material contamination) rather than on a regular basis, unless the latter is more frequent than the former.

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