

PATENT SPECIFICATION

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(72) Inventor KENNETH PETERS

(54) ELECTRIC STORAGE BATTERY GRIDS

- (71) We, ELECTRIC POWER STORAGE LIMITED, a Company registered under the Laws of England, of 50 Grosvenor Gardens, London, S.W.1, England, do hereby
 5 declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 10 The present invention relates to lead alloy plate grids for lead acid electric accumulators, and to accumulators incorporating such grids.
 Lead antimony alloys are known for such use. Pure lead is too weak and antimony is
 15 added to improve the strength and castability of the alloy. However, at concentrations of above 4% there is a significant tendency for the antimony to be released from the grid into the electrolyte during service and on
 20 charging to be deposited on the spongy lead of the negative plate. This results in a reduction of the hydrogen over voltage and the local cells of lead and antimony set up on the negative plate also cause loss of charge
 25 on open circuit.
 It is desirable to reduce the antimony content to as low as possible to reduce open circuit losses and to render the battery resistant to the bad effects of overcharging such
 30 as tend to occur with automotive batteries charged from alternating current sources, e.g. alternators.
 According to the present invention the reduction in antimony content of a lead antim-

ony alloy is compensated for by an addition of selenium and arsenic in certain amounts, such as to render the alloy castable in the form of thin grids e.g. 1.0 to 3.0 mms thick in a sufficiently strong and durable form for subsequent handling such as automatic pasting with active material.

Thus according to the present invention an electric storage battery grid is made from an alloy which comprises by weight antimony up to 4%, e.g., 0.1 to 4% preferably 1% to 3%; from above 0.2% up to 0.5% arsenic, preferably 0.25 to 0.49% or 0.4%; 0% up to 0.1% copper, e.g., 0.005% or 0.02% to 0.05% or 0.1%; 0% up to 0.5% sulphur, e.g. 0.0001% to 0.1%, e.g. 0.0002% to 0.001% or 0.01 or 0.05%; 0% up to 0.5% tin, e.g., 0.01% or 0.02% to 0.4% or 0.5% or 0.02% to 0.03%; and 0.005% up to 0.5% selenium, e.g. 0.005% to 0.1% or 0.01% to 0.5% or 0.01% to 0.05%, the balance being lead, trace elements, known optional alloy ingredients and impurities.

The invention also extends to a grid in which the alloy comprises 2.3% to 2.6% antimony, 0.25% to 0.5% arsenic, 0.015% to 0.035% tin, 0.01% to 0.035% copper, 0.005% to 0.015% selenium and less than 0.001% sulphur.

The invention may be put into practice in various ways and a number of melt compositions from which grids can be cast will be described by way of example only and are set out in Table 1 below.

TABLE 1

% added to melt based on total weight

Alloy	Sb %	As %	Cu %	Sn %	Se %
1	3%	0.4%	0.05%	0.4%	0.5%
2	3%	0.4%	0.05%	0.4%	0.05%
3	3%	0.4%	0.05%	0.4%	0.01%
4	1%	0.4%	0.05%	0.4%	0.5%
5	1%	0.4%	0.05%	0.4%	0.05%
6	1%	0.4%	0.05%	0.4%	0.01%
7	1%	0.25%	0.02%	0.02%	0.5%
8	1%	0.25%	0.02%	0.02%	0.05%
9	1%	0.25%	0.02%	0.02%	0.01%
10	3%	0.25%	0.02%	0.02%	0.5%
11	3%	0.25%	0.02%	0.02%	0.05%
12	3%	0.25%	0.02%	0.02%	0.01%

The alloys may be made from virgin lead which typically comprises 99.9% lead, traces of copper and traces of sulphur (less than 0.0001) by the addition of antimony, arsenic, tin and selenium in which case very little copper and sulphur is present in the cast grid.

Alternatively the alloys may be made from reclaimed lead acid battery scrap. This is made from scrap lead alloy from plate casting and defunct battery plates. The scrap which contains some lead sulphate and lead oxide is placed in a blast furnace and reduced to produce a molten metal typically containing 3.5% ($\pm 0.5\%$) antimony, 0.05% ($\pm 0.03\%$) arsenic, 0.075% ($\pm 0.025\%$) copper and tin, balance lead. This is placed in a steel pan and heated to 580°C and an approximately two fold excess by weight based on copper i.e. 0.15% ($\pm 0.05\%$) of elemental sulphur added. The mixture is stirred for 30 minutes at 550°C and the copper sulphide which rises to the surface skimmed off and discarded.

This lowers the copper content of the remaining metal to not more than 0.05% e.g. preferably 0.02%. Traces of copper sulphide may remain distributed through the melt. The sulphur content of a sample cast from this

material is typically less than 0.001% e.g. 0.0002% to 0.0005%.

The metal is then mixed with the alloy ingredients to bring it up to the desired composition. The metal is then cast at about 330°C in a cast iron mould the surfaces of which are dusted with cork powder to assist in proper filling of the mould cavity without premature freezing.

Preferred ranges of grid compositions are

Antimony	1.5 to 3.0%
Selenium	0.005 to 0.02%
Arsenic	0.25 to 0.4%
Tin	0.02 to 0.06%
Copper	0.02 to 0.04%

The antimony is added to introduce adequate mechanical characteristics to the battery grid. The selenium is added to modify grain structure and improve ductility and castability. The arsenic is added to increase the rate of hardening.

Six further alloys are described below in Table 2. The contents quoted are percentages by weight of the actual ingredients of the cast alloy.

TABLE 2

Alloy	13	14	15	16	17	18
% Sb	2.56	2.41	2.50	2.55	2.32	2.40
% As	0.05	0.27	0.36	0.45	0.47	0.49
% Sn	0.036	0.03	0.033	0.019	0.015	0.027
% Cu	0.013	0.011	0.028	0.029	0.029	0.032
% Se	0.010	0.008	0.014	0.008	0.007	0.009
% S	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

5 Automotive positive and negative grids were cast with these melt compositions at 14.5 castings per minute for extended casting runs with no significant reductions in casting quality as the run progressed.

The lugs of the grids were then tested for hardness and rate of increase of hardness with age and the results are given in Table 3.

TABLE 3

Alloy	13	14	15	16	17	18
Brinell Hardness initially	11.3	13.2	13.5	13.5	13.1	14.4
1 day	12.5	—	14.5	14.2	13.9	14.9
2 day	—	—	15.1	—	—	—
3 day	—	15.3	—	—	15.1	15.8
4 day	14.1	16.4	16.2	16.8	—	—
5 day	14.7	16.4	—	—	—	—
6 day	14.9	—	—	—	16.3	17.0
7 day	—	—	17.6	18.0	—	—
8 day	—	—	—	—	—	—
9 day	15.2	—	—	—	17.5	18.1
10 day	—	17.6	18.5	—	—	—
11 day	16.0	—	—	18.6	18.5	19.0

The hardness was measured on a Vickers Hardness tester using a load of 4 kg. and 2 mm. diameter ball, i.e.

$$\frac{F}{D^2} = 1.$$

The time of application of the load was ten seconds. As can be seen, the alloys with arsenic contents above 0.2% are harder initially and reach acceptable hardness levels, e.g., 15, more quickly.

Twelve further alloys are described below 20

in Table 4. The contents quoted are percentages by weight of the actual ingredients in

the cast alloy as determined by atomic absorption analysis.

TABLE 4

Alloy	19	20	21	22	23	24
% Sb	2.500	2.500	2.600	2.700	2.600	2.500
% As	0.270	0.070	0.310	0.060	0.310	0.060
% Sn	0.020	0.030	0.030	0.020	0.030	0.030
% Cu	0.020	0.020	0.020	0.010	0.020	0.020
% Se	0.006	0.008	0.008	0.012	0.008	0.008
% S	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	25	26	27	28	29	30
% Sb	2.600	2.500	3.200	3.000	3.200	2.900
% As	0.310	0.070	0.310	0.070	0.310	0.070
% Sn	0.030	0.020	0.050	0.020	0.050	0.030
% Cu	0.020	0.020	0.020	0.020	0.020	0.020
% Se	0.008	0.008	0.009	0.012	0.009	0.008
% S	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

10 Alloys 19 and 20 were cast under identical conditions, namely, casting rate 15 castings per minute, lead pot temperature 380°C., lead pipe temperature 490°C., mould temperature 150°C., mould cooling water inlet temperature 23°C.

15 Alloys 21 and 22 were cast under identical conditions, namely, casting rate 15 castings per minute, pot temperature, mould temperature as alloys 19 and 20, lead pipe temperature 500°C., cooling water inlet temperature 13°C.

Alloys 23 and 24 were also cast under identical conditions as alloys 19 and 20, the casting rate being 12 castings per minute, cool-

ing water inlet temperature 10°C. Alloys 25 and 26 were cast at 13 castings per minute under same conditions as alloys 19 and 20. Alloys 27 and 28 were cast at 14 castings per minute under the same conditions as alloys 19 and 20 with mould cooling water inlet temperature of 12°C. Alloys 29 and 30 were cast under same conditions as alloys 27 and 28 at 15 castings per minute.

The lugs of the grids cast as described above were then tested for hardness and rate of increase of hardness with age as described above and the results are given in Table 5 below.

20

25

30

TABLE 5

Alloy	19	20	21	22	23	24
Initial Brinell Hardness						
1 hour	13.0	11.2	13.6	11.1	13.4	10.3
1 day	13.8	13.0	14.7	13.0	15.7	—
2 days	14.7	13.7	16.1	13.0	16.6	—
3 days	15.9	14.9	16.6	14.7	17.2	13.6
6 days	17.1	—	17.9	15.0	18.5	14.2
7 days	17.4	15.8	18.9	16.6	18.4	15.1
8 days	17.6	16.1	19.2	16.6	18.3	—
12 days	18.4	—	19.7	17.4	19.2	—
	25	26	27	28	29	30
1 hour	13.1	11.1	13.0	10.9	13.1	11.2
1 day	15.4	13.3	14.3	13.0	14.7	13.8
2 days	15.8	—	15.7	14.7	16.0	14.6
3 days	16.6	—	16.5	—	16.5	—
6 days	18.1	16.6	18.2	16.8	18.9	16.7
7 days	18.6	16.9	18.5	17.7	19.0	16.4
8 days	19.1	16.9	19.4	17.5	19.5	17.0
12 days	19.4	—	19.4	17.5	19.1	17.2

As can be seen from Table 5, the alloys with arsenic contents above 0.2% have higher initial hardness values and reach acceptable hardness levels more quickly than those with arsenic contents below 0.2%.

The batteries having grids made from grid alloys in accordance with the present invention have substantially reduced water losses as can be seen from Table 6 below.

Alloy 31 had a composition within the following ranges:—

Sb	5.80—6.40%	
As	0.15—0.20%	
Cu	0.01—0.04%	15
Sn	0.01—0.05%	
balance lead.		

Alloy 32 had the following composition:—

Sb	2.600%	
As	0.300%	20
Sn	0.040%	
Cu	0.020%	
Se	0.009%	
balance lead.		

TABLE 6
Water Losses Per Cell Per 30 Hours Charge (ml.)

No. of Completed Overcharge Units	Alloy 31			Alloy 32		
	0°C.	20°C.	40°C.	0°C.	20°C.	40°C.
0	0.03	0.91	2.41	0.03	0.30	0.88
1	0.11	0.67	2.89	0.02	0.25	1.54
2	0.11	0.94	3.31	0.05	0.67	2.31
3	0.12	1.41	3.81	0.07	0.79	3.00
4	0.16	2.29	4.90	0.10	1.09	3.78

The temperatures quoted in Table 6 are the temperatures at which the overcharge cycles were carried out.

- 5 One overcharge unit comprises the following charge/discharge cycle.

- 10 The battery is charged at 4 amps constant current for five hours and then discharged at 4 amps for one hour and this is repeated 35 times at temperatures of 0°C, 20°C, and 40°C. The battery is then left on open circuit for 96 hours and then discharged at 3C₂₀ rate at 40°C.

- 15 After each unit of overcharge on constant current the batteries were kept at the same temperature, i.e., 0°C, 20°C or 40°C and were re-charged on an alternator and the water losses quoted in Table 6 are measured during the alternator portion of the test.

- 20 The constant current portion of the test was an accelerated ageing sequence.

The alternator cycle was as follows:

- 25 The battery was discharged at a constant current discharge to 50% of its nominal capacity. The battery was then re-charged on a standard uncompensated Lucas type 15 ACR alternator for thirty hours.

This sequence was repeated until the batteries failed to give a four-minute discharge

to an end voltage of 7.98 volts on the 3C₂₀ rate.

The batteries made from alloy 31 had both positive and negative grids made from alloy 31 and these were pasted with conventional positive paste (grid weight 64 grams, total pasted plate weight 565 grams) and conventional negative paste (grid weight 61 grams, pasted plate weight 567 grams).

The batteries made from alloy 32 had both grids made from alloy 32. The grid weights were 57 grams and 55 grams respectively and were pasted with the same pastes as for alloy 31 batteries to give total pasted plate weights of 565 grams and 595 grams.

The plates were then immersed in 500 ml. of 1.260 sp. gr. sulphuric acid and charged at 4 amps for 5 hours followed by 1 hour discharge at 16 amps repeated five times. They were then ready for testing.

Table 6 thus gives a measure of charging characteristics at varying battery ages.

Table 7 below gives the cumulative water losses for the tests shown in Table 6. The overcharge losses are the water losses during the alternator cycle which are quoted in column 1 and the open circuit losses (column 2) are those occurring during the 96 hour open circuit period.

TABLE 7

Alloy	Column 1 Overcharge Losses			Column 2 Open Circuit Losses
	0°C. ml./cell/1,000 hours	20°C. ml./cell/1,000 hours	40°C. ml./cell/1,000 hours	at 20°C. ml./cell/1,000 hours
31	1.7	19.9	75.1	0.8
32	3.5	38.1	113.1	1.4

We do not to use more than 0.5% arsenic
 { nce up to this level very good age hardening
 is achieved but above this level there is a
 tendency for the grids to crack on storage
 and this can interfere with automatic pasting.
 5 This tendency increases markedly at arsenic
 contents much above 0.5%.

When these alloys do not contain selenium,
 the problem of cracking again arises. However,
 10 with arsenic contents below 0.2%, the pres-
 ence of selenium, whilst overcoming cracking,
 leaves the grids too soft for satisfactory mech-
 anical handling as is required in automatic
 pasting.

15 It has been proposed in German Patent
 Specification No. 1193253 to improve the
 castability and corrosion resistance of lead
 antimony arsenic alloys by reducing the antim-
 ony content and increasing the arsenic content
 20 but this proposal teaches that success can only
 be achieved if the content of arsenide form-
 ing components is kept below certain levels.

Thus this proposal teaches that the selenium
 content must be kept to not more than
 25 0.001%.

We have found to the contrary that selen-
 ium in excess of this level combined with
 arsenic contents of above 0.2% produce ex-
 cellent results.

30 German Auslegeschrift 2151733 discloses
 a lead antimony alloy for electric storage
 battery grids comprising 1.5 to 3.5% antim-
 ony, 0.025 to 0.2% arsenic, 0.01 to 0.05%
 tin, 0.005% to 0.1% selenium, balance lead.
 35 This alloy is described as having the required
 hardness, tensile strength and toughness for
 battery grids without the need for heat treat-
 ment, since heat treatment reduces the
 strength. The alloy is also described as
 40 enabling thin battery grids to be cast which
 have adequate corrosion resistance. The
 specification teaches that an arsenic content
 of 0.05% is preferred and that arsenic con-
 tents above this level interfere with the age
 45 hardening process. We have found that the
 alloys with only 0.05% arsenic have relatively
 low initial hardness and that it would be
 desirable for production purposes to be able
 to reduce the time required for the hardness
 50 to rise to an adequate level. Surprisingly,
 we have found that much improved hardness
 and increase of hardness with time is obtained
 when the arsenic content is in the range of
 over 0.2 to 0.5%, especially 0.25 to 0.4%.

55 WHAT WE CLAIM IS:—

1. An electric storage battery grid made
 from an alloy comprising by weight

antimony up to 4%,
 from above 0.2% to 0.5% arsenic,
 0% up to 0.1% copper,
 0% up to 0.5% sulphur,
 0% up to 0.5% tin, and
 0.005% to 0.5% selenium,

the balance being lead, trace elements, known
 optional alloy ingredients and impurities.

2. An electric storage battery grid char-
 acterised in that it is made from an alloy
 comprising by weight antimony up to 4%,
 0.25% up to 0.49% arsenic, 0.005% to 0.1%
 copper, 0% up to 0.5% sulphur, 0.01%
 up to 0.5% tin, and 0.005% to 0.5% selen-
 ium, the balance being lead trace elements,
 known optional alloy ingredients and impur-
 ities.

3. A grid as claimed in Claim 1 or Claim
 2, in which the alloy contains 1% to 3%
 antimony.

4. A grid as claimed in Claim 1, 2 or 3,
 in which the alloy contains 0.25% to 0.4%
 arsenic.

5. A grid as claimed in Claim 1, 2, 3 or 4,
 in which the alloy contains 0.02% to 0.05%
 copper.

6. A grid as claimed in Claim 1, 2, 3, 4
 or 5, in which the alloy contains 0.02%
 to 0.4% tin.

7. A grid as claimed in any one of Claims
 1 to 6, in which the alloy contains 0.01%
 to 0.5% selenium.

8. A grid as claimed in any one of the
 preceding claims in which the alloy contains
 1.5% to 3.0% antimony,
 0.005% to 0.02% selenium,
 0.25% to 0.4% arsenic,
 0.02% to 0.06% tin, and
 0.02% to 0.04% copper.

9. A grid as claimed in Claim 1, in which
 the alloy contains
 2.3% to 2.6% antimony,
 0.25% to 0.5% arsenic,
 0.015% to 0.035% tin,
 0.01% to 0.035% copper,
 0.005% to 0.015% selenium, and
 less than 0.001% sulphur.

10. A grid as claimed in Claim 1 and sub-
 stantially as specifically described herein with
 reference to any one of Examples 14 to 18,
 19, 21, 23, 27 or 29.

11. A lead acid electric accumulator in which
 the grids are as claimed in any one of Claims
 1 to 10.

KILBURN & STRODE,
 Chartered Patent Agents,
 Agents for the Applicants.

We do not to use more than 0.5% arsenic
nce up to this level very good age-hardening
is achieved but above this level there is a
tendency for the grids to crack on storage
and this can interfere with automatic pasting.
This tendency increases markedly at arsenic
contents much above 0.5%.

When these alloys do not contain selenium,
the problem of cracking again arises. However,
with arsenic contents below 0.2%, the pres-
ence of selenium, whilst overcoming cracking,
leaves the grids too soft for satisfactory mech-
anical handling as is required in automatic
pasting.

It has been proposed in German Patent
Specification No. 1193253 to improve the
castability and corrosion resistance of lead
antimony arsenic alloys by reducing the anti-
mony content and increasing the arsenic content
but this proposal teaches that success can only
be achieved if the content of arsenide form-
ing components is kept below certain levels.

Thus this proposal teaches that the selenium
content must be kept to not more than
0.001%.

We have found to the contrary that selen-
ium in excess of this level combined with
arsenic contents of above 0.2% produce ex-
cellent results.

German Auslegeschrift 2151733 discloses
a lead antimony alloy for electric storage
battery grids comprising 1.5 to 3.5% anti-
mony, 0.025 to 0.2% arsenic, 0.01 to 0.05%
tin, 0.005% to 0.1% selenium, balance lead.
This alloy is described as having the required
hardness, tensile strength and toughness for
battery grids without the need for heat treat-
ment, since heat treatment reduces the
strength. The alloy is also described as
enabling thin battery grids to be cast which
have adequate corrosion resistance. The
specification teaches that an arsenic content
of 0.05% is preferred and that arsenic con-
tents above this level interfere with the age
hardening process. We have found that the
alloys with only 0.05% arsenic have relatively
low initial hardness and that it would be
desirable for production purposes to be able
to reduce the time required for the hardness
to rise to an adequate level. Surprisingly,
we have found that much improved hardness
and increase of hardness with time is obtained
when the arsenic content is in the range of
over 0.2 to 0.5%, especially 0.25 to 0.4%.

WHAT WE CLAIM IS:—

1. An electric storage battery grid made
from an alloy comprising by weight

antimony up to 4%,
from above 0.2% to 0.5% arsenic,
0% up to 0.1% copper,
0% up to 0.5% sulphur,
0% up to 0.5% tin, and
0.005% to 0.5% selenium,

the balance being lead, trace elements, known
optional alloy ingredients and impurities.

2. An electric storage battery grid charac-
terised in that it is made from an alloy
comprising by weight antimony up to 4%,
0.25% up to 0.49% arsenic, 0.005% to 0.1%
copper, 0% up to 0.5% sulphur, 0.01%
up to 0.5% tin, and 0.005% to 0.5% selen-
ium, the balance being lead trace elements,
known optional alloy ingredients and impur-
ities.

3. A grid as claimed in Claim 1 or Claim
2, in which the alloy contains 1% to 3%
antimony.

4. A grid as claimed in Claim 1, 2 or 3,
in which the alloy contains 0.25% to 0.4%
arsenic.

5. A grid as claimed in Claim 1, 2, 3 or 4,
in which the alloy contains 0.02% to 0.05%
copper.

6. A grid as claimed in Claim 1, 2, 3, 4
or 5, in which the alloy contains 0.02%
to 0.4% tin.

7. A grid as claimed in any one of Claims
1 to 6, in which the alloy contains 0.01%
to 0.5% selenium.

8. A grid as claimed in any one of the
preceding claims in which the alloy contains
1.5% to 3.0% antimony,
0.005% to 0.02% selenium,
0.25% to 0.4% arsenic,
0.02% to 0.06% tin, and
0.02% to 0.04% copper.

9. A grid as claimed in Claim 1, in which
the alloy contains

2.3% to 2.6% antimony,
0.25% to 0.5% arsenic,
0.015% to 0.035% tin,
0.01% to 0.035% copper,
0.005% to 0.015% selenium, and
less than 0.001% sulphur.

10. A grid as claimed in Claim 1 and sub-
stantially as specifically described herein with
reference to any one of Examples 14 to 18,
19, 21, 23, 27 or 29.

11. A lead acid electric accumulator in which
the grids are as claimed in any one of Claims
1 to 10.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

