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(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 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:—

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 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 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 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 as tend to occur with automotive bat-

teries charged from alternating current sources, e.g. alternators.

According to the present invention the reduction in antimony content of a lead antimony alloy is compensated for by an addition of up to a certain amount of selenium 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%; 0% up to 0.5% arsenic, e.g. 0.05 or 0.2% to 0.5% preferably 0.25% to 0.4%; 0% up to 0.1% copper, e.g. 0.02% to 0.05%; 0% up to 0.5% sulphur e.g. 0.0001% to 0.01% or 0.1% e.g. 0.0002% to 0.001% or 0.01% or 0.05%; 0.01% to 0.5% tin, e.g. 0.01% to 0.4% or 0.02% to 0.04%, and selenium from 0.001% up to less than 0.005%, e.g. 0.002% or 0.003% to 0.004%, the balance being lead, trace elements, known optional alloy ingredients and impurities.

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 I below.

TABLE I

Alloy	Sb%	As%	Cu%	Sn%	Se%	S%
1	2.8	0.05	<0.01	0.01		<0.001
2	2.6	0.05	<0.01	0.01	0.004	<0.001
3	3	0.4	0.05	0.4	0.004	<0.001
4	3	0.4	0.05	0.4	0.001	<0.001
5	1	0.4	0.05	0.4	0.004	<0.001
6	1	0.4	0.05	0.4	0.001	<0.001
7	1	0.25	0.02	0.02	0.004	<0.001
8	1	0.25	0.02	0.02	0.001	<0.001
9	3	0.25	0.02	0.02	0.004	<0.001
10	3	0.25	0.02	0.02	0.001	<0.001

Alloys 1 and 2 are actual compositions, alloys 3 to 10 are % added to the melt based on total weight.

Microscopic examination of alloy 1 cast as a test piece in the form of a bar of cross section 1.6 cms by 0.8 cms revealed a skin region of generally parallel elongated grains about 2.5 cms long extending inwardly from the surface with more compact but irregular shaped and somewhat elongated grains ranging from 0.8 mms to 1.6 mms in maximum dimension in the plane of the cross section. Figure 1 shows alloy 1 at 5 times magnification. Microscopic examination of alloy 2 cast as a test piece in the form of a bar of cross section 2.4 cms by 0.8 cms revealed a much thinner skin region of less elongated grains about 1 mm long extending inwardly from the surface with compact grains ranging from 0.2 mms to 0.6 mms in maximum longitudinal dimension, these grains are very evenly distributed through the material and the majority are 0.4 to 0.5 mms in maximum longitudinal dimension in the plane of the cross section and the majority have maximum transverse dimensions which are well in excess of 50% of their maximum longitudinal dimensions e.g. in the range 60% to 90%. The maximum longitudinal dimension is the longest straight line connecting the grain boundaries on either side of the grain. The maximum transverse dimension is the longest straight line joining boundaries of the grain on either side of the maximum longitudinal dimension and which is perpendicular thereto.

Figure 2 shows alloy 2 at five times magnification.

The alloy 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.

WHAT WE CLAIM IS:—

- 5 1. An electric storage battery grid made from an alloy comprising by weight:—
 - Up to 4.0% antimony,
 - 0% up to 0.5% arsenic,
 - 0% up to 0.1% copper,
 - 10 0% up to 0.5% sulphur,
 - 0.01% to 0.5% tin,
- and selenium 0.001% up to less than 0.005%, the balance being lead, trace elements, known optional alloy ingredients and impurities.
- 15 2. An electric storage battery grid as claimed in Claim 1 in which the alloy contains 1% to 3% antimony.
3. An electric storage battery grid as claimed in Claim 1 or 2 in which the alloy contains 0.25% to 0.4% arsenic.
- 20 4. An electric storage battery grid as claimed in Claim 1, 2 or 3 in each the alloy contains 0.02% to 0.05% copper.
5. An electric storage battery grid as claimed in Claim 1, 2, 3 or 4 in which the alloy contains 0.01% to 0.4% tin.
- 25

6. An electric storage battery grid as claimed in Claim 1, 2, 3, 4 or 5 in which the alloy contains 0.001% to 0.004% selenium.

7. An electric storage battery grid as claimed in Claim 1 in which the alloy contains 30

1.0% to 3.0% antimony,
0.25% to 0.4% arsenic,
0.01% to 0.4% tin,
copper in an amount not exceeding 0.05%, 35
and
0.001 to 0.004% selenium.

8. An electric storage battery grid as claimed in Claim 1 in which the alloy contains

2.6% antimony,
0.05% arsenic, 40
0.01% tin,
0.004% selenium, and
less than 0.01% copper, and
less than 0.001% sulphur. 45

9. A lead acid electric storage battery in which the grids of the electrodes are as claimed in Claim 1.

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which are dusted with cork powder to assist in proper filling of the mould cavity without premature freezing.

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 - 0% up to 0.1% copper,
 - 10 0% up to 0.5% sulphur,
 - 0.01% to 0.5% tin,
- and selenium 0.001% up to less than 0.005%, the balance being lead, trace elements, known optional alloy ingredients and impurities.
- 15 2. An electric storage battery grid as claimed in Claim 1 in which the alloy contains 1% to 3% antimony.
3. An electric storage battery grid as claimed in Claim 1 or 2 in which the alloy
- 20 contains 0.25% to 0.4% arsenic.
4. An electric storage battery grid as claimed in Claim 1, 2 or 3 in each the alloy contains 0.02% to 0.05% copper.
5. An electric storage battery grid as
- 25 claimed in Claim 1, 2, 3 or 4 in which the alloy contains 0.01% to 0.4% tin.

6. An electric storage battery grid as claimed in Claim 1, 2, 3, 4 or 5 in which the alloy contains 0.001% to 0.004% selenium.

7. An electric storage battery grid as claimed in Claim 1 in which the alloy contains

1.0% to 3.0% antimony,
0.25% to 0.4% arsenic,
0.01% to 0.4% tin,
copper in an amount not exceeding 0.05%,
and
0.001 to 0.004% selenium.

8. An electric storage battery grid as claimed in Claim 1 in which the alloy contains

2.6% antimony,
0.05% arsenic,
0.01% tin,
0.004% selenium, and
less than 0.01% copper, and
less than 0.001% sulphur.

9. A lead acid electric storage battery in which the grids of the electrodes are as claimed in Claim 1.

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