

PATENT SPECIFICATION

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(54) DEPOLARISER MASS FOR PRIMARY CELLS

(71) We, VARTA BATTERIE AKTIENGESELLSCHAFT, a German Company, of 3000 Hannover, Stöckener Str. 351, Germany, 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 invention relates to a depolariser mass for galvanic primary cells which comprises, as the main solid constituents, manganese dioxide, graphite and/or carbon black and, in some cases, zinc oxide and an aqueous solution of ammonium chloride and/or zinc chloride as electrolyte, and to methods of making.

Manganese dioxide, graphite and/or carbon black and, in some cases zinc oxide and ammonium chloride and/or zinc chloride in aqueous solution, as electrolyte, are the main constituents of depolariser masses used in primary cells based on the Leclanche and zinc chloride systems. In these cells, a carbon rod serves as an electronic conductor, and zinc or magnesium serves as the anode, a separator being provided between the anode and the depolariser which is in the form of an electrode or bobbin. The amount of electrolyte present in depolariser bobbins used in cells of this kind generally exceeds 25% by weight. However, cells of this kind have an unsatisfactory storage life compared to cells provided with a drier or less moist depolariser mass. The depolariser masses widely used at the present time and which contain a large proportion of water (24 to 30 wt.%) and in which the electrolyte usually contains a major amount of zinc chloride, result in cells which are particularly susceptible to trouble and which have a short storage life. Drying out can be prevented or substantially prevented, so improving the storage life or shelf characteristics of such cells, by providing the cells with a hermetically sealed closure (for example, by using paraffined carbon rods and bitumen or an elastomer as sealing compound); however, changes by which the efficiency of the cells is severely impaired, nevertheless still occur during storage. For example, an evolution of gas, particularly hydrogen at the anode, may rapidly appear and

the pressure in the cell may thereby be increased to such an extent as to cause, for example, buckling of the zinc can with the result that part of the previously existing contact between the surface of the anode and the electrolyte is lost. However, even if this disadvantage is disregarded, a loss of active surface area occurs as a result of the presence of gas bubbles on the surface of the anode. Once a gaseous phase has formed at the surface of the anode, the process is at once accelerated owing to increased corrosion at the three-phase boundary anode/gas/electrolyte. This disadvantageous behaviour is particularly evident in cells which are stored at elevated temperature (storage under tropical conditions, for example at a temperature of 45° C). Attempts to reduce the evolution of hydrogen at the anode by means of suitable inhibitors have failed to provide any substantial improvement.

It has been found that the storage life of the cells deteriorates as the time taken for mixing the depolariser mass increases. This applies particularly to masses which contain a high proportion of electrolyte and which are thus particularly wet to the touch. It has been found that after storage the moisture content at the bottom of depolariser bobbins produced from such a mass is greater than the moisture content at the top thereof. The electrolyte must have shifted under the influence of the force of gravity during storage, since the evaporation losses, determined by weighing, were found to be minimal. Drier depolariser masses inspected after storage exhibited, however, a more homogeneous distribution of the electrolyte, no substantial evolution of gas and thus a good electrode contact and an improved storage life.

It is an object of the invention to provide a depolariser mass which does not undergo any appreciable physical change during storage, without substantially changing the chief constituents and particularly the proportion of electrolyte used.

In accordance with the invention there is provided a depolariser mass for a galvanic primary cell, the mass comprising manganese dioxide, graphite and/or carbon black, as solid constituents and an aqueous solution of

ammonium chloride and/or zinc chloride as electrolyte, the portion of electrolyte in the mass amounting to at least 25% by weight and at least a part of the surface of the solid constituents being rendered water-repellent by means of a hydrophobic agent.

It is known *per se* to render cathode mixtures hydrophobic in gas diffusion electrodes, for example, in air-oxygen cells or in fuel cells. These mixtures are rendered hydrophobic in order to prevent the electrolyte from entering into the porous electrode and to keep the pores open for the gaseous depolariser (gas diffusion electrode). A hydrophobic binding agent, such as polystyrene or polyisobutylene, is frequently used in pressed cathodes for alkaline cells. This binding agent is used for the purpose of preventing a softening of the pressed cathodes by the alkaline electrolyte entering from without. However, it is a particular object of the present invention to ensure that the largest possible quantity of liquid be embedded between solid particles without the mixture assuming the characteristics of a paste. A similar effect is known to be obtained in the case of "dry water" which is a fine dispersion of water droplets between particles of hydrophobic silica of large surface area (Aerosil). Aerosil is a registered Trade Mark.

The depolariser mass according to the invention, when used in a cell comprises the entire neutral or weakly acidic electrolyte of the cell, which is present in an above average quantity together with a very small amount of a liquid or fatty or greasy hydrophobic agent. The electrolyte constituent of the depolariser mass comprises between 25% and 45% by weight corresponding to a water content of the mass of about 18 to 36% by weight. The electrolyte constituent preferably forms from 28 to 40% by weight of the mass, and the quantity of the hydrophobic agent is between 0.02 and 0.5% by weight based on the solid constituents. Any hydrophobic liquid, oil, grease or fat which is resistant to manganese dioxide is a suitable hydrophobic agent. Silicone oils and greases produced by the hydrolysis of alkylchlorosilane mixtures (polyorganosiloxanes) have given particularly good results. The solid starting substance, for example manganese dioxide and/or carbon black, may be rendered water-repellent by impregnation with the hydrophobic agent which may be dissolved in a solvent (for example, benzene (petroleum ether or naphtha or acetone) to improve the uniformity of its distribution. The depolariser mass is produced from the impregnated materials after evaporation of the solvent.

An oil-in-water emulsion of the hydrophobic agent may be used instead of a solution, and at least part of the water may be evaporated subsequently. The mass may be rendered water-repellent more simply and

cheaply by adding and homogeneously intermixing the aqueous emulsion of the hydrophobic agent with the solid constituents of the depolariser mass or with the electrolyte. The previous impregnating process and, in some cases, additional costs incurred for the solvent and the drying process may thereby be avoided. However, the presence of small quantities of emulsifiers used for stabilising oil-in-water emulsions of hydrophobic liquids or greases has been found to have detrimental results. According to the particular properties of such emulsifiers, the hydrophobic agent may be prevented from passing from the electrolyte on to the surface of the solid constituents in the depolarising mass, so that, where a drying process is not employed, the quantities of hydrophobic agent used have to be substantially increased in order to obtain adequate results. The wetting properties of the emulsifiers may even be so effective as to produce the opposite effect to that which is desired. Thus care has to be taken in the preparation of the emulsion to use only the smallest possible quantity of emulsifier.

Suitable oil-in-water emulsions based on silicone oils are commercially available under the Trade Marks "Baysilon-Oelemulsion T" (an emulsion of medium viscosity of a higher molecular weight silicone oil) and "Persoftal 4242" (a metal salt-free, 35% aqueous emulsion of polydimethylsiloxane) of Farbenfabriken Bayer AG, Leverkusen. Tests have shown that the best results are obtained by using an emulsifier which is sensitive to hardness and the effect of which is neutralised by multivalent ions of the electrolyte, for example Zn^{2+} ions; the electrolyte then acts as an emulsion-splitting agent or demulsifier. An emulsion of such kind breaks when it is mixed with the electrolyte. The demulsification proceeds, however, so slowly that there is generally sufficient time for the preparation of the depolariser mass. Thus, the hydrophobic agent can still be mixed homogeneously with the depolariser mass, but it is then gradually deposited on the surface of the solid constituents. The hydrophobic action is then particularly effective and may be obtained with the use of minimum quantities. However, if the emulsion breaks down at a rate which prevents homogeneous distribution of the hydrophobic agent in the electrolyte, then the depolariser mass may initially be mixed with a very dilute aqueous emulsion of the hydrophobic agent and the electrolyte in the form of a concentrated solution may be added last. Demulsification does not then occur until after the homogeneous distribution of the hydrophobic agent in the depolariser mass is complete. According to the type of emulsifier used, it may be necessary to add a demulsifier in order to ensure demulsification. Numerous demulsifiers are known, among which, for example, organic compounds which contain

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sulphonate groups are suitable.

5 Suitable emulsifiers for the preparation of emulsions which are unstable in electrolytes containing zinc chloride include particularly organic compounds which contain carboxylate groups, for example polyacrylates or various soaps. The commercially obtainable "Collacral P" (a Registered Trade Mark), a polyacrylic acid salt containing amide groups which is a product of BASF, Ludwigshafen has produced very good results.

10 Instead of rendering the whole depolariser mass water-repellent prior to its use in a cell, only individual constituents thereof, for example manganese dioxide or carbon black, or a portion of the mass may be rendered water-repellent, and that constituent or portion may then be admixed subsequently with the remainder of the depolariser mass. Manufacturing costs may thereby be reduced.

20 The invention is illustrated in the following examples.

Example 1.

25 5250 grams electrolytic manganese dioxide were impregnated with a solution of 2.4 grams silicone oil in 180 grams benzine, the benzine being subsequently evaporated. Seven hundred and fifty grams acetylene black, 150 grams zinc oxide, and an electrolyte comprising 1050 grams zinc chloride and 2800 grams water

were then added to the impregnated manganese dioxide and the whole mass was then mixed to produce a homogeneous mixture.

The mixture was then compressed into bobbins and incorporated in primary cells. 35

Example 2.

270 grams of a 35% silicone oil-in-water emulsion commercially available under the Trade Mark "Baysilon-Oelemulsion T" were stirred into 39.6 kg of an electrolyte solution comprising 13.5 kg zinc chloride, 1.1 kg ammonium chloride and 25.0 kg of water. The mixture was immediately worked into a homogeneous depolarising mass by mixing with 46.9 kg manganese dioxide, 2.8 kg graphite, 9.6 kg acetylene black and 1.1 kg zinc oxide. Paper-lined R 20 cells IBC were then produced in known manner from the depolariser mass thus obtained. Table 1 shows the open circuit voltage, the short circuit current and the discharge time for a standard discharge in dependence upon the period for which the cells according to the invention were stored compared to completely similar, commercially available reference cells produced without an admixture of silicone oil emulsion. The discharge was for 4 minutes per hour, 8 hours per day, over 4 ohms. The values given are the average values with their average errors. 40 45 50 55 60

TABLE 1

Period of storage at 45°C (months)	Cells according to the invention			Reference cells		
	Open circuit voltage (V)	Short circuit current (A)	Time of discharge 4 min/hr, 8 hrs/day -4 ohms (min.)	Open circuit voltage (V)	Short circuit current (A)	Time of discharge 4 min/hr, 8 hrs/day -4 ohms (min.)
0	1.658±0.001	10.38±0.03	989 ± 6	1.662±0.001	10.08±0.02	909 ± 36
1	1.636±0.001	8.92±0.03	933 ± 12	1.639±0.001	8.41±0.03	874 ± 99
2	1.627±0.001	8.27±0.03	963 ± 4	1.629±0.001	7.23±0.04	691 ± 66
3	1.619±0.002	7.50±0.08	901 ± 6	1.624±0.001	6.30±0.07	418 ± 15

Example 3.

0.18 grams "Collacral P" (a Registered Trade Mark) (an aqueous solution containing about 16% of a polyacrylic acid salt containing amide groups) was dissolved in 175 grams of water, 95 grams silicone oil (a polydimethylsiloxane having a viscosity of 1000 centipoises at 20° C.) were added to the solution and the mixture was emulsified by means of a high-speed stirrer. The emulsion was diluted with 15 kg of water and the emulsion was then mixed with 46.9 kg of manganese dioxide, 2.8 kg graphite, 9.6 kg acetylene black, 1.1 kg zinc oxide and 1.1 kg ammonium chloride until a homogeneous mixed was obtained. An electrolyte solution comprising 13.5 kg zinc chloride and 10 kg water was then added and mixing was continued for a short time. This depolariser mass was then pressed into bobbins or dollies and incorporated in primary cells.

The depolariser masses obtained according to the invention in each of Examples 1, 2 and 3 were perceptibly drier to the touch than depolariser masses of a similar kind which had not been rendered water-repellent.

The tests have shown that depolariser masses produced directly with emulsions of hydrophobic agents and having a neutral or weakly acid electrolyte, when used in primary cells, do not undergo any appreciable loss in electrochemical activity even when a hydrophobic agent in the form of a surface active liquid, such as a silicone oil is used. It is even more surprising to find that the surface of the zinc anode does not suffer any loss in activity as a result of the presence of a depolariser mass made water-repellent with an emulsion, and that neither the short circuit current nor the capacity is reduced despite the apparently drier consistency of the depolariser mass which is obviously due to

partial isolation of droplets of electrolyte. The depolariser mass according to the invention behaves as if the total amount of electrolyte present therein is usable. It is known that the volume and chemical composition of the solid and liquid phases originally present in the mass according to the invention change during discharge and it may be assumed that these changes ensure that a sufficiently large surface area or amount of electrolyte is always activated.

WHAT WE CLAIM IS:—

1. A depolariser mass for a galvanic primary cell, the mass comprising manganese dioxide, graphite and/or carbon black, as solid constituents and an aqueous solution of ammonium chloride and/or zinc chloride as electrolyte, the portion of electrolyte in the mass amounting to at least 25% by weight and at least a part of the surface of the solid constituents being rendered water-repellent by means of a hydrophobic agent.

2. A mass according to Claim 1, in which the mass contains between 0.02% and 0.5% by weight of hydrophobic agent relative to the solid constituents.

3. A mass according to Claim 1 or Claim 2, in which the hydrophobic agent is a silicone oil or a silicone grease.

4. A mass according to any one of the preceding claims, in which the mass contains zinc oxide.

5. A depolariser mass comprising a hydrophobic agent, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

6. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of impregnating the solid constituents with a solution of the hydrophobic agent dissolved in a solvent, evaporating the solvent, and mixing the impregnated solid constituents with the electrolyte.

7. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of impregnating one of the solid constituents with a solution of the hydrophobic agent dissolved in a solvent, evaporating the solvent, and mixing the impregnated solid constituent with the remaining

solid constituents or constituent and with the electrolyte.

8. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of impregnating a proportion of the solid constituents with a solution of the hydrophobic agent dissolved in a solvent, evaporating the solvent, and mixing the impregnated proportion of the solid constituents with the remaining proportion and with the electrolyte.

9. A method according to any one of Claims 6 to 8, in which the solvent is benzene or acetone.

10. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of making an oil-in-water emulsion of the hydrophobic agent, stirring the emulsion into the electrolyte, and working the resultant mixture into the solid constituents of the depolariser mass.

11. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of making an oil-in-water emulsion of the hydrophobic agent, mixing the emulsion with the solid constituents of the depolariser mass, and adding the electrolyte to the mixture.

12. A method according to Claim 11, comprising the step of evaporating part of the water of the emulsion subsequent to the step of mixing the emulsion with the solid constituents.

13. A method according to any one of Claims 10 to 12, comprising the step of mixing a demulsifier with the electrolyte or with the solid constituents prior to the final step.

14. A depolariser mass substantially as hereinbefore described with reference to Example 1, Example 2, or Example 3.

15. A method of making a depolariser mass substantially as hereinbefore described with reference to Example 1, Example 2, or Example 3.

16. A primary cell including a depolariser mass according to any one of Claims 1 to 5 and 14.

EDWARD EVANS & CO.,
54—63 Chancery Lane,
London WC2A 1SD,
Agents for the Applicants.

partial isolation of droplets of electrolyte. The depolariser mass according to the invention behaves as if the total amount of electrolyte present therein is usable. It is known that the volume and chemical composition of the solid and liquid phases originally present in the mass according to the invention change during discharge and it may be assumed that these changes ensure that a sufficiently large surface area or amount of electrolyte is always activated.

WHAT WE CLAIM IS:—

1. A depolariser mass for a galvanic primary cell, the mass comprising manganese dioxide, graphite and/or carbon black, as solid constituents and an aqueous solution of ammonium chloride and/or zinc chloride as electrolyte, the portion of electrolyte in the mass amounting to at least 25% by weight and at least a part of the surface of the solid constituents being rendered water-repellent by means of a hydrophobic agent.
2. A mass according to Claim 1, in which the mass contains between 0.02% and 0.5% by weight of hydrophobic agent relative to the solid constituents.
3. A mass according to Claim 1 or Claim 2, in which the hydrophobic agent is a silicone oil or a silicone grease.
4. A mass according to any one of the preceding claims, in which the mass contains zinc oxide.
5. A depolariser mass comprising a hydrophobic agent, substantially as hereinbefore described with reference to any one of Examples 1 to 3.
6. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of impregnating the solid constituents with a solution of the hydrophobic agent dissolved in a solvent, evaporating the solvent, and mixing the impregnated solid constituents with the electrolyte.
7. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of impregnating one of the solid constituents with a solution of the hydrophobic agent dissolved in a solvent, evaporating the solvent, and mixing the impregnated solid constituent with the remaining

solid constituents or constituent and with the electrolyte.

8. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of impregnating a proportion of the solid constituents with a solution of the hydrophobic agent dissolved in a solvent, evaporating the solvent, and mixing the impregnated proportion of the solid constituents with the remaining proportion and with the electrolyte.

9. A method according to any one of Claims 6 to 8, in which the solvent is benzene or acetone.

10. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of making an oil-in-water emulsion of the hydrophobic agent, stirring the emulsion into the electrolyte, and working the resultant mixture into the solid constituents of the depolariser mass.

11. A method of making the depolariser mass claimed in any one of Claims 1 to 4, comprising the steps of making an oil-in-water emulsion of the hydrophobic agent, mixing the emulsion with the solid constituents of the depolariser mass, and adding the electrolyte to the mixture.

12. A method according to Claim 11, comprising the step of evaporating part of the water of the emulsion subsequent to the step of mixing the emulsion with the solid constituents.

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