

May 17, 1955

J. B. EISEN
ELECTRODE AND MATERIAL THEREFOR

2,708,683

365,977

Filed July 3, 1953

FIG. 1

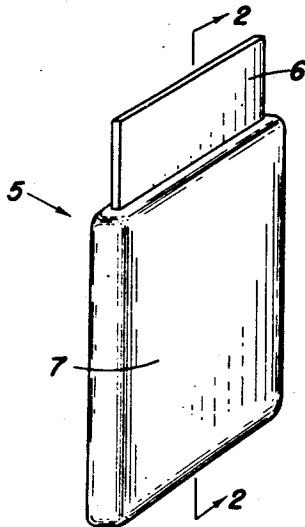


FIG. 2

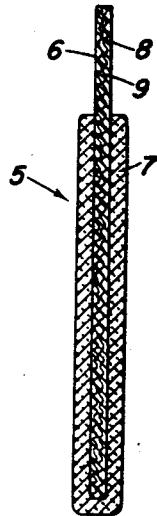
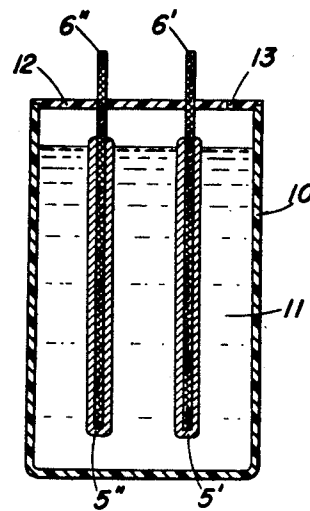


FIG. 3



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2,708,683

ELECTRODE AND MATERIAL THEREFOR

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Application July 3, 1953, Serial No. 365,977

21 Claims. (Cl. 136-19)

This invention relates to electrodes for primary and secondary cells, and to batteries made therefrom and more particularly to a composition comprising active electrode material and a bi-functional adhesive.

This application relates to the general subject matter of my co-pending application Serial No. 268,343, filed January 25, 1952, now Patent No. 2,679,546, which shows the preparation of electrodes by attaching chemically-active particles to one another and to a lightweight conductive backing sheet by means of a novel adhesive.

The adhesive or binder described therein was far better than previously available substances but it has been found possible to provide a far superior binder which is disclosed herein. It is difficult to provide a suitable binder or adhesive for this purpose because most binders or adhesives either tend to fill completely the interstices between the chemically-active particles with resultant excessive internal resistance in the cell, or, on the other hand, do not bind the particles sufficiently firmly to one another and to the backing plate with the result that the particles or the particles and binder tend to flake off and cause shorts when electrodes prepared therewith are assembled in cells.

An object of this invention is an adhesive to firmly bond chemically-active particles to flexible lightweight backing sheets to form an electrode with a minimum of internal resistance in a cell prepared with such an electrode.

Another object is such an adhesive which may be readily handled in solution and which is adapted to form a paste with chemically-active particles which may easily be applied to flexible backing sheets.

Another object is such an adhesive which is adapted to provide both a minimum of internal resistance in the battery and a maximum of adhesion of the chemically-active particles to the lightweight backing sheet.

Another object is an electrode comprising a lightweight backing sheet having chemically-active particles attached thereto by an adhesive providing minimum internal resistance and a maximum adhesion of said particles to said backing sheet.

Further objects will become apparent from the drawings and the following detailed description in which it is my intention to illustrate the applicability of the invention without thereby limiting its scope to less than that of all equivalents and in which like reference numerals refer to like parts and in which:

Figure 1 is a perspective view of an electrode constructed in accordance with the invention;

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Figure 2 is a cross-sectional view of the electrode of Figure 1 taken on lines 2-2;

Figure 3 is a cross-sectional view of a cell assembled with the electrodes of the invention.

Referring now to Figure 1 there is shown an electrode indicated generally as 5 comprising a thin flexible backing sheet 6 having an electrically-active composition 7 adhesively secured thereto. Composition 7 preferably consists of chemically-active particles suspended in the adhesive of the invention.

As shown in Figure 2, the thin conductive backing sheet 6 may consist of fabric 9 immersed in, impregnated with, or coated with metal 8.

In Figure 3 there is shown a cell provided with electrodes according to the invention. Receptacle 10 contains electrolyte 11 in which anode 5' and cathode 5'' are immersed. Thin backing sheets respectively 6' and 6'' extending upward from said electrodes pass through the cover 12 of the cell. The outer edge of cover 12 may be secured to the upper edge of receptacle 10. Cover 12 may suitably be provided with a vent 13 to allow the escape of gas from the cell.

In accordance with my invention I prepare a composition consisting of chemically-active particles suspended in an adhesive. The chemically-active particles are generally most suitably either of a metal which may be an anode in a primary or secondary cell electrolytic system such as for example zinc, cadmium, magnesium, lead or aluminum or of a metal salt, usually a metal oxide, which may be suitable for a depolarizer material for an electrolytic cell system, for example HgO , Ag_2O , Ag_2O_3 , V_2O_5 , MnO_2 and the like. The amount of adhesive is preferably very small in relation to the amount of chemically active particles. The adhesive preferably consists of three components (A) a water-insoluble linear high polymer inactive with respect to either acid or alkali, whichever is to be the electrolyte in the cell, (B) a water-insoluble inorganic salt inactive with respect to the cell electrolytic system in which the adhesive is to be utilized, (C) water.

As component (A) for the adhesive I may employ any linear high polymer adapted to swell in water but at the time time insoluble therein, which at the same time is inert to either acid or alkali. When such a polymer is utilized as a component in an adhesive for attaching chemically-active particles to a conducting backing sheet and when an electrolyte is then added to a cell of which an electrode comprising such an adhesive is a part, the electrolyte, which is generally strongly alkaline or strongly acid, and the water, which is a part of the adhesive combination, diffuse into one another to form a more weakly acid or alkaline solution with the result that water is withdrawn from the solvated polymer and the polymer becomes more rigid. Suitable polymers may include cellulose ethers such as ethyl cellulose and methyl cellulose, cellulose acetate, polyvinyl acetal, borated polyvinyl alcohols, polyacrylamides, and the like.

The second component may be any inorganic salt which is readily soluble in water and which is also readily soluble in the electrolyte, but which is inactive with respect to the cell electrolytic system which it is desired to use.

The examples in Tables I and II are given to illustrate the invention:

Table I

Example	Cathode Powder (100 Gms.)	Cathode Binder Materials (See Table III)												Cathode Binder Water (Gms.)	Cathode Backing Sheet Material (See Table IV)
		Component A (Gms.)								Component B (Gms.)					
		1	2	3	4	5	6	7	8	1	2	3	4		
1	Ag ₂ O		.25									.35		150	1
2	Ag ₂ O					.4							.5	150	7
3	Ag ₂ O	.15								.3				50	3
4	Ag ₂ O			.25							.4			50	4
5	Ag ₂ O				.15							.25		50	7
6	Ag ₂ O						1.0		.5					50	8
7	HgO		.2					.5						40	9
8	HgO			.1						.25				50	7
9	HgO						.8						.7	60	15
10	HgO	.2									1.0			50	10
11	PbO ₂				.4			.1						75	3
12	PbO ₂					.2					.2			75	4
13	PbO ₂						.5		.75					60	7
14	MnO ₂ +C	.1						.1						50	9
15	MnO ₂ +C			.15							.5			50	15

Example	Method of Applying Cathode Powder Adhesive Composition to Backing Sheet	Electrolyte	Anode Material	Anode Collector Conductor	Initial E. M. F., no load (volts)
1	Spraying	20% KOH	Amalgamated Zinc	Amalgamated Zinc Strip	1.18
2	Applicator III	25% KOH	do	do	1.21
3	Handpasting	25% KOH	do	do	1.42
4	do	30% KOH	do	do	1.47
5	Applicator III	31% KOH	do	do	1.58
6	do	31% KOH	do	Silver Strip	1.60
7	do	20% KOH	do	Amalgamated Zinc Strip	1.10
8	do	25% KOH	do	do	1.12
9	do	25% KOH	do	Stainless Steel	0.95
10	Spatula-Pressing	25% KOH	do	Amalgamated Zinc Strip	0.98
11	do	H ₂ SO ₄	Lead Sheet	Lead Strip	2.1
12	do	H ₂ SO ₄	do	Silver Strip	2.0
13	Applicator III	H ₂ SO ₄	do	Lead Strip	1.95
14	do	Sat. NH ₄ Cl	Amalgamated Zinc	Zinc Strip	1.5
15	do	NH ₄ Cl+ZnCl ₂	do	do	1.6

Table II

Example	Anode Powder (100 Gms.)	Anode Binder Materials (See Table III)												Anode Binder Water (Gms.)	Anode Backing Sheet Material (See Table IV)
		Component A (Gms.)								Component B (Gms.)					
		1	2	3	4	5	6	7	8	1	2	3	4		
16	Mg					.2						.3		40	1
17	Mg						.6		.4					45	3
18	Zn			.2				.7						40	4
19	Zn		.25							.4				50	7
20	Zn					.3					.2			50	8
21	Zn						.7					.1		40	10
22	Cd		.5										.4	60	9
23	Cd			.2					.3					70	15

Example	Method of Applying Anode Powder Adhesive Composition to Backing Sheet	Electrolyte	Cathode Depolarizer Material	Cathode Collector Conductor	Initial E. M. F., no load (volts)
16	Spraying	AgCl	MgCl ₂ Formed on H ₂ O Activation.	Mg Foll.	1.72
17	Applicator III	MgCl ₂ aqueous	MgCl ₂	Mg Foll.	1.70
18	do	20% KOH	Ag ₂ O	Zinc Foll.	1.10
19	Spatula-Pressing	25% KOH	Ag ₂ O	do	1.60
20	do	25% KOH	Ag ₂ O	do	1.62
21	Applicator III	31% KOH	HgO	do	1.05
22	do	18% KOH	Ag ₂ O	Cadmium Sheet	1.15
23	do	30% KOH	Ag ₂ O	do	1.48

Table III*

Component A (water-swella- ble water-insoluble linear high polymer):

1. High viscosity sodium carboxymethyl cellulose (Hercules).
2. Sodium salt of polymethacrylic acid (DuPont).
3. Methyl cellulose, 400 cps. (Dow).
4. Polyvinyl alcohol, high viscosity (DuPont "Elvanol" 72-51).
5. Hydroxy-ethyl cellulose (Hercules).
6. Polyvinyl chloride emulsion (Goodrich "Geon" 652).
7. Soluble starch.
8. Sodium alginate.

Component B (electrolyte-soluble water-soluble inorganic salt):

1. Aluminum sulfate.
2. Potassium sulfate.
3. Sodium silicate (low silica ratio).
4. Dried alumina gel (re-dissolved with minimum KOH).

* Use of any component listed is restricted to systems (either acid or alkaline) in which said component is non-reactive with respect to the electrolyte.

Table IV

Backing sheet materials:

1. Silver gauze screen.
2. Platinum gauze screen.
3. Stainless steel gauze screen.
4. Perforated silver foil.
5. Perforated platinum foil.
6. Perforated stainless steel foil.
7. Silver coated glass cloth, by sprayed silver paint.
8. Silver coated glass cloth, by aqueous electrochemical reduction of Ag salts.
9. Silver coated glass cloth, by coating with silver oxides, thermally decomposed.
10. Silver coated glass fiber floc mat, by sprayed silver paint.
11. Silver coated glass fiber floc mat, by aqueous electrochemical reduction of Ag salts.
12. Silver coated glass fiber floc mat, by coating with silver oxides, thermally decomposed.
13. Silver coated nylon fabric, by sprayed silver paint.
14. Silver coated nylon fabric, by aqueous electrochemical reduction of Ag salts.
15. Fabric comprising silver and glass strands as warp and filling (union fabric).
16. Fabric comprising stainless steel and glass strands as warp and filling (union fabric).

To clarify the examples set forth in the above tables, I shall describe one of the examples in greater detail: Referring now to Example 2, a paste of .4 gram of Component A (hydroxyethyl cellulose), .5 gram of Component B (dried alumina gel), 150 grams of water and 100 grams of Ag₂O were mixed as a paste and were then applied to a backing sheet consisting of silver coated glass cloth, which had been coated by spraying silver paint against the glass. The resulting paste was applied to the backing sheet material by use of Applicator III. The term "Applicator III" refers to an applicator of the type described in co-pending application Serial No. 310,778, filed September 22, 1952, by Elmer G. Paquette. The designation "III" indicates that the third experimental model of said applicator was used in the example. A cathode prepared in this manner was assembled as part of the cell containing an electrolyte consisting of 25% KOH and an anode consisting of amalgamated zinc adhered to an amalgamated zinc strip. The resultant cell had an initial E. M. F. under no load of 1.21 volts.

Tables 1 and 2 show the use of as little as .1 part of Component A and .1 part of Component B per 100 parts

of cathode powder or anode powder and show as much as 1.0 part of either Component A or Component B but in some instances as little as .01 part of either Component A or Component B or as much as 2.0 parts of Component A or Component B with respect to 100 parts of cathode or anode electrode powder may suitably be utilized.

It may thus be seen that the invention is broad in scope and is not to be limited excepting by the claims.

Having thus disclosed my invention, I claim:

1. The method of bonding fine particles of electrochemically active material to a flexible conductive base material, which comprises the steps of intermixing the said particles of electrochemically active material with a viscous mixture of water, a water-swella- ble water-insoluble linear high polymer and a water-soluble inorganic salt and then applying said composition to a flexible conductive sheet material.

2. The method of bonding fine particles of electrochemically active material to a flexible conductive base material which comprises the steps of intermixing to form a viscous mixture: about 100 parts of said electrochemically active material, water, .01 to 2.0 parts of a water-swella- ble water-insoluble linear high polymer and .01 to 2.0 parts of an electrochemically inert water-soluble inorganic salt and then applying said mixture to a flexible conductive sheet material.

3. The method of bonding fine particles of electrochemically active material to a flexible conductive base material which comprises the steps of intermixing about 100 parts of said particles of electrochemically active material, water, .1 to 1.0 part of a water-swella- ble water-insoluble linear high polymer and .1 to 1.0 part of an electrochemically inert water-soluble inorganic salt and then applying said composition to a flexible conductive sheet material.

4. As an article of manufacture, a battery electrode comprising a sheet of flexible conductive material having deposited on at least a part thereof and adhered thereto a composition comprising particles of electrochemically active material, a water-swella- ble water-insoluble linear high polymer and a water-soluble inorganic salt.

5. As an article of manufacture, a battery electrode comprising a sheet of flexible conductive material having deposited on at least a part thereof and adhered thereto a composition comprising about 100 parts of particles of electrochemically active material, .01 to 2.0 parts of a water-swella- ble water-insoluble linear high polymer and .01 to 2.0 parts of an electrochemically inert water-soluble inorganic salt.

6. As an article of manufacture, a battery electrode comprising a sheet of flexible conductive material having deposited on at least a part thereof and adhered thereto a composition comprising about 100 parts of particles of electrochemically active material in powdered form, .1 to 1.0 part of a water-swella- ble water-insoluble linear high polymer and .1 to 1.0 part of an electrochemically inert water-soluble inorganic salt.

7. As an article of manufacture, a cell comprising a positive electrode, a negative electrode and an electrolyte, characterized by at least one of said electrodes comprising a thin conductive backing sheet having deposited on at least a portion thereof a composition comprising particles of electrochemically active material, a water-swella- ble water-insoluble linear high polymer and a water-soluble inorganic salt inert to said electrolyte.

8. As an article of manufacture, a cell comprising a positive electrode, a negative electrode and an electrolyte, characterized by at least one of said electrodes comprising a thin conductive backing sheet having deposited on at least a portion thereof a composition comprising about 100 parts of particles of electrochemically active material, .01 to 2.0 parts of a water-swella- ble water-insoluble linear high polymer and .01 to 2.0 parts of water-soluble inorganic salt inert to said electrolyte.

9. As an article of manufacture, a cell comprising a

positive electrode, a negative electrode and an electrolyte, characterized by at least one of said electrodes comprising a thin conductive backing sheet having deposited on at least a portion thereof a composition comprising about 100 parts of particles of electrochemically active material, .1 to 1.0 part of a water-swella-
 5 ble water-insoluble linear high polymer and .1 to 1.0 part of a water-soluble inorganic salt inert to said electrolyte.

10. As an article of manufacture, a cell comprising a housing, an electrolyte contained therein, a positive electrode and a negative electrode, each at least partially immersed in said electrolyte, characterized by at least one of said electrodes comprising a flexible conductive backing sheet having electrochemically active particles adhered thereto and to one another by an adhesive comprising a water-swella-
 10 ble water-insoluble linear high polymer inert to said electrolyte and a water-soluble electrolyte-soluble inorganic salt, also inert to said electrolyte.

11. As an article of manufacture, a cell comprising a housing, an electrolyte contained therein, a positive electrode and a negative electrode, each at least partially immersed in said electrolyte, characterized by at least one of said electrodes comprising a flexible conductive backing sheet having electrochemically active particles adhered thereto and to one another by an adhesive comprising .01 to 2.0 parts of a water-swella-
 20 ble water insoluble linear high polymer inert to said electrolyte and .01 to 2.0 parts of a water-soluble electrolyte-soluble inorganic salt, also inert to said electrolyte.

12. As an article of manufacture, a cell comprising a housing, an electrolyte contained therein, a positive electrode and a negative electrode, each at least partially immersed in said electrolyte, characterized by at least one of said electrodes comprising a flexible conductive backing sheet having electrochemically active particles adhered thereto and to one another by an adhesive comprising .1 to 1.0 part of a water-swella-
 30 ble water-insoluble linear high polymer inert to said electrolyte and .1 to 1.0 part of a water-soluble electrolyte-soluble inorganic salt, also inert to said electrolyte.

13. As an article of manufacture a battery electrode comprising a sheet of electrically conductive flexible material having particles of electrochemically active material adhered thereto and to one another by means of an adhesive comprising a water-swella-
 40 ble water-insoluble linear high polymer and a water-soluble inorganic salt, and water.

14. As an article of manufacture a battery electrode comprising a sheet of electrically conductive flexible material having about 100 parts of particles of electrochemically active material adhered thereto and to one another by means of an adhesive comprising .01 to 2.0 parts of a water-swella-
 50 ble water-insoluble linear high polymer and

.01 to 2.0 parts of a water-soluble inorganic salt, and water.

15. As an article of manufacture a battery electrode comprising a sheet of electrically conductive flexible material having about 100 parts of particles of electrochemically active material adhered thereto and to one another by means of an adhesive comprising .1 to 1.0 part of a water-swella-
 5 ble water-insoluble linear high polymer and .1 to 1.0 part of a water-soluble inorganic salt, and water.

16. An adhesive composition adapted to adhere electrochemically active particles to a flexible conductive backing sheet and to one another comprising a water-swella-
 10 ble water-insoluble linear high polymer, and an electrochemically inert water-soluble inorganic salt, and water.

17. An adhesive composition adapted to adhere electrochemically active particles to a flexible conductive backing sheet and to one another comprising .01 to 2.0 parts of a water-swella-
 15 ble water-insoluble linear high polymer, and .01 to 2.0 parts of an electrochemically inert water-soluble inorganic salt, and water.

18. An adhesive composition adapted to adhere electrochemically active particles to a flexible conductive backing sheet and to one another comprising .1 to 1.0 part of a water-swella-
 20 ble water-insoluble linear high polymer, .1 to 1.0 part of an electrochemically inert water-soluble inorganic salt, and water.

19. A composition of matter adapted to be applied to a thin conductive sheet to provide a cell electrode comprising a viscous mixture of: particles of an electrochemically active material, a water-swella-
 25 ble water-insoluble linear high polymer, a water-soluble inorganic salt, and water.

20. A composition of matter adapted to be applied to a thin conductive sheet to provide a cell electrode comprising a viscous mixture of: about 100 parts of particles of an electrochemically active material, .01 to 2.0 parts of a water-swella-
 30 ble water-insoluble linear high polymer, 0.1 to 2.0 parts of a water-soluble inorganic salt, and water.

21. A composition of matter adapted to be applied to a thin conductive sheet to provide a cell electrode comprising a viscous mixture of: about 100 parts of particles of an electrochemically active material, .1 to 1.0 part of a water-swella-
 35 ble water-insoluble linear high polymer, .1 to 1.0 part of a water-soluble inorganic salt, and water.

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