



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Dry Cell Cathode Compositions

We, AMERICAN CYANAMID COMPANY, a corporation organised and existing under the Laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, 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:—

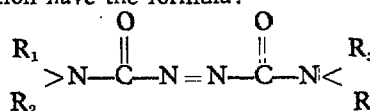
This invention generally relates to improved electric cell compositions and to the cells which contain them and, more particularly, it relates to improved cathodic compositions for both primary and secondary battery cells.

The most common and least expensive primary battery known as the Leclanche cell, conventionally employs manganese dioxide as the depolarizer in combination with a zinc anode and a zinc chloride-ammonium chloride electrolyte solution. This battery is inefficient as a secondary cell and has the deficiency of rapid polarization. An improvement in these characteristics is obtained with a zinc-mercuric oxide cell, but such a cell is much more expensive and too heavy for certain uses. Mercury is often in short supply.

A large number of substitutes for manganese dioxide as depolarizer in the Leclanche cell have been employed or proposed for use. Among the suggested substitutes are many organic compounds which are reducible and have high oxidizing potentials. Such compounds include nitro and nitroso compounds and nitrois among others. In general, all of these show some improvements over manganese dioxide in cell characteristics, but these compounds possess other deficiencies as primary or secondary cell components. These deficiencies include poor shelf-life, self-discharge, inadequate voltage, inefficient rechargability and inability to be recharged efficiently after dis-

charge beyond relatively high cut-off points. Thus, there has been a continuing need for improved depolarizers for both primary and secondary cells that result in improved battery characteristics while at the same time avoiding the aforementioned deficiencies.

It has been found that compounds of the substituted azodicarbonamide type, when used as depolarizers in cells, produce batteries of excellent discharge characteristics, while overcoming many of the deficiencies of conventional cell depolarizers. The substituted azodicarbonamides used in accordance with this invention have the formula:



where R₁, R₂, R₃ and R₄ may each be hydrogen, or an alkyl of 1 to 8 carbon atoms, aryl or substituted aryl, cycloalkyl, aralkyl, alkoxy-alkyl, cyanoalkyl, haloalkyl, nitroalkyl, or alkenyl group; and where R₁ and R₂ and/or R₃ and R₄, when alkyl, may be joined together directly or through a nitrogen, sulfur, or oxygen atom to form a heterocyclic ring; and not more than three of R₁, R₂, R₃, and R₄ are hydrogen.

Therefore, in accordance with this invention, there is provided a cathode composition for an electric current-generating cell, which comprises a mixture of carbon, an electrolyte, and, as a depolarizer compound, a substituted azodicarbonamide in accordance with the definition above. Furthermore, the present invention also provides an electric current-generating cell comprising an anode of an electropositive metal and a cathode composition in accordance with this invention.

Thus, it is possible, for the purposes of this invention, to use the substituted azodicarbonamides [azobis(formamides)] as depolarizers

in batteries, whether the organic compounds are substituted symmetrically, unsymmetrically, or contain a heterocyclic ring. The structures which are preferred are those wherein each of the two nitrogen atoms carries as the only substituent an alkyl radical of 3 or 4 carbon atoms. Symmetrical compounds are often more economically available, but symmetry is not essential.

The compounds of the present invention, when employed as depolarizers in cells, in addition to providing such cells with increased shelf-life also offer additional advantages. These additional advantages include flatter discharge curves at various drain rates, rechargeability, extended useful life over multiple discharge-charge cycles, recoverability from relatively deep discharges, limited adverse effects due to over-charging, little or no loss of chemicals through side reactions, negligible gassing, use of inexpensive materials, and favorable size and weight ratio to power available. Thus, the compounds of the present invention as depolarizers in both primary and secondary cells provide batteries that have improved efficiency and extended life.

Mixtures of azodicarbonamides may be used in cells, as well as the compounds individually.

By adding an oxide such as zinc oxide, barium oxide or magnesium oxide, to react with acid which may be formed, the substituted azodicarbonamides of this invention may be formed in situ in the cell by adding the corresponding substituted biurea, and oxidizing by charging the cell. The reaction is comparable to that shown for the second equation of Example 2 or 3, with variations based on the substituents chosen within the classes here outlined. A secondary battery, charged at time of first use is storage stable for a long time; and also primary cells containing the substituted azodicarbonamide have excellent shelf-life characteristics. Ready to use items usually meet with better commercial acceptance than do items requiring preparation for use by the consumer. Some users will choose to use cells of this invention as discardable primary cells—others will choose to recharge when voltage drops, or on a fixed schedule.

A higher drain rate is obtainable if the substituted azodicarbonamide is finely divided. Good cells result if the substituted azodicarbonamide is in the particle size range 20 to 40 microns. Subdividing to about 1 micron permits a higher drain rate. The larger surface area is preferred also for the more insoluble azodicarbonamides. The smaller size is obtainable by grinding, or by crystallizing under conditions which yield smaller crystals.

The compounds may be used in the cathodic mix in the range of from 10 to 50% of the total weight of the cathodic mix. The cathodic mix additionally contains electrolyte solution and carbon in any of its various forms, such as graphite, acetylene black, or high surface

area carbon or other known forms of carbon black.

The electrolyte solution itself may be an aqueous solution containing a soluble salt, such as sea water, or water to which one or more soluble salts have been added. Halide salts or mixtures of halide salts containing cations such as ammonium and metals such as zinc and manganese ions are preferred soluble salts in the electrolyte. The electrolyte may be prepared by dissolving the salt in water at a concentration of between 30 grams per liter and that producing a saturated solution at ordinary temperatures. The concentration does not appear to be especially critical, although for best results certain concentrations are preferred depending upon the particular salt or combination of salts that are used.

For primary cells of this invention a combination of 170 grams of zinc chloride and 270 grams of ammonium chloride per 1000 grams of solution has been found satisfactory. For secondary cells, a combination of 170 grams of zinc chloride and 270 grams of ammonium bromide per 1000 grams of solution has been found especially useful. It will be noted that the nature of the cell, i.e., primary or secondary, will influence to some extent the choice of salts employed in the electrolyte, with bromide-containing mixtures being preferred in secondary cells. The bromide containing mixtures provide a particularly useful combination with the substituted azodicarbonamides, in secondary cells, in that their use tends to overcome undesirable effects resulting from overcharging.

The anode of the batteries of the present invention is an electropositive metal, usually zinc, magnesium, aluminium, or other metal standing high in the electromotive series, or certain mixtures or alloys thereof, including such additional metals as manganese, zirconium, cerium and calcium. Zinc in pure or alloyed form is the preferred metal, especially with secondary cells.

The cells are frequently cylindrical, and of standard sizes, to fit electrical equipment. Flat, rectangular, button, or other shape of cells may be made using the present cell compositions. The size and shape are determined by capacity requirements and space available. Preferably, but not necessarily, the cells will have a conventional size to fit e.g. standard size flashlights, radios, recorders, emergency exit lights.

Satisfactory results are obtained using conventional type separators such as kraft paper; kraft paper coated or impregnated with starch or other gel-like material such as carboxymethyl cellulose and/or cereal paste; and vegetable parchment. Superior results are achieved if a laminated regenerated cellulose, e.g., "Cellophane" (registered Trade Mark) separator is used. This separator may be described in somewhat more detail as a laminate

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of a film of small pore size (such as "Cellophane" with an average pore diameter of $16\text{\AA}$) with a cellulosic paper of high water retention properties which may have as an adhesive a material such as gum arabic. Other films such as porous nylon, polyester films, polyolefin films, polyacrylate films, polyvinylacetate films, or polyvinylchloride films, and other low porosity films, having pore sizes in the range of 5 to 40 Angstrom units are useful. The pores must permit ions to pass readily, and inhibit diffusion of other materials.

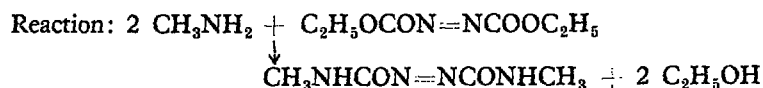
Although it is not necessary for producing a useful rechargeable cell, the use of this laminated "Cellophane" type separator results in considerable improvement in the cycling characteristics of the cell. Thus, using a regular

porous kraft paper separator (or one which is impregnated with starch or carboxymethyl cellulose or composed of porous nylon, vegetable parchment, etc.), the cells normally give satisfactory performance through at least 10 charge-discharge cycles. Using the "Cellophane" laminate separator, the cell is normally satisfactory through up to 40 or more cycles. Thus, although not actually necessary, the "Cellophane" laminate type separator is definitely preferred for superior performance in these cells.

The invention is illustrated by the Examples which follow; Examples 1—3 illustrate the preparation of the substituted azodicarbonamide compounds used in accordance with this invention.

EXAMPLE 1

Preparation of 1,1'-Azobis(N-methylformamide)



Into a suitably equipped reaction vessel was placed 50 grams (0.275 mol) of diethyl azodicarboxylate and 400 ml. of ethyl ether. 85 ml. of 20% methylamine (0.55 mol) in methanol was added to the reaction vessel slowly with stirring over a period of 30 minutes. The resulting dark orange slurry was stirred for an

additional 15 minutes, filtered, and the filter cake washed with ether. The resulting orange solid had a melting point of $176.5\text{--}177^\circ\text{C}$.

By similar procedures, using the indicated starting materials and solvents, the additional compounds listed in Table I were also prepared.

TABLE I
Preparations from Dichthyl Azodicarboxylate and Amine

Compound	Amine	Solvent	Melting Point, °C.	Decomposition Point, °C.
1,1'-Azobis(N-allylformamide)	allyl	methanol + ether	—	150—151
1,1'-Azobis[N-(2-methoxyethyl)formamide]	2-methoxyethyl	methanol + ether	105—108	—
1,1'-Azobis[N-(2-cyanoethyl)formamide]	2-cyanoethyl	methanol + ether	—	188—189
1,1'-Azobis(N-methylformamide)	methyl	ether	176.5—177	—
1,1'-Azobis(N,N-dimethylformamide)	dimethyl	methanol + ether	—	108—109
1,1'-Azobis(N-ethylformamide)	ethyl	ether	—	132—133
1,1'-Azobis(N,N-diethylformamide)	diethyl	ether	—	—
1,1'-Azobis(N-n-propylformamide)	n-propyl	ether	—	156—157
1,1'-Azobis(N-isopropylformamide)	isopropyl	ether	—	169—170
1,1'-Azobis(N-n-butylformamide)	n-butyl	methanol + ether	—	165
1,1'-Azobis(N-isobutylformamide)	isobutyl	methanol + ether	—	161
1,1'-Azobis(N-sec-butylformamide)	sec. butyl	methanol + ether	—	179—180
1,1'-Azobis(N-ter-butylformamide)	ter. butyl	none	—	187—190
1,1'-Azobis(N-n-hexylformamide)	n-hexyl	ether	—	—

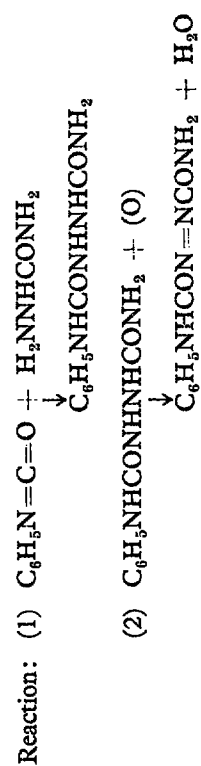
TABLE I (Continued)
Preparations from Diethyl Azodicarboxylate and Amine

Compound	Amine	Solvent	Melting Point, °C.	Decomposition Point, °C.
1,1'-Azobis(N-n-octylformamide)	n-octyl	ether	—	—
1,1'-Azobis(N,N-pentamethylethylformamide)	piperidine	ligroin	135—137	—
1,1'-Azobis(N,N-oxydiethylethylformamide)	morpholine	ligroin	—	—
1,1'-Azobis(N,N-tetramethylethylformamide)	pyrrolidine	ether	—	—
N-n-butyl-N'-methyl-1,1'-azobisformamide	methyl* n-butyl	ether	—	150—152
1,1'-Azobis(N-benzylformamide)	benzyl	methanol and ether	—	197—202

* Equimolar amounts.

EXAMPLE 2

Preparation of N-Phenyl-1,1'-Azobisformamide



Into a suitably equipped reaction vessel was placed 2.25 grams (0.03 mol) of semicarbazide and 25 ml. of methanol. While this solution was stirred and cooled, 2.2 ml (0.02 ml.) of phenyl isocyanate was added slowly in dropwise fashion, forming a white precipitate. The reaction mixture was stirred for 30 minutes after addition was complete. The solid product was recovered by filtration, washed with boiling methanol, and allowed to dry in air. The N-phenylbiurea obtained was recrystallized from acetic acid and had a melting point of 234°C. (also named 1-phenylbiurea).

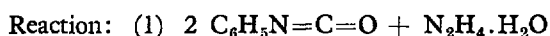
The compound (0.5 gram) obtained from the above reaction was mixed in a reaction vessel with 2 grams of ammonium nitrate, 0.05 gram of cupric acetate monohydrate, and 25 grams of acetic acid. This mixture was heated in a

water bath at 70°C. for 5 minutes during which time the color changed from yellow-green to dark green. The mixture was then poured onto ice to give an orange solid which was filtered and dried in air. The N-phenyl-1,1'-azobisformamide was recrystallized from ethanol and yielded a red-orange solid which decomposed at 184°C.

By a similar procedure starting with 22.6 grams of 4-phenyl-semicarbazide in benzene with a trace of pyridine and adding 8.54 grams of methyl isocyanate, N-methyl-N'-phenylbiurea(1-methyl-6-phenylbiurea) was obtained as a white solid of decomposition point 239—240°C. This product upon subsequent oxidation as described above yielded N-methyl-N'-phenyl-1,1'-azobisformamide, an orange solid of decomposition point 162—163°C.

EXAMPLE 3

Preparation of 1,1'-Azobis(N-phenylformamide)



Into a suitably equipped reaction vessel was placed 15 grams (0.3 mol) of 100% hydrazine hydrate and 200 ml. of benzene. The solution was stirred and cooled in an ice bath while 85 grams (0.7 mol) of phenyl isocyanate dissolved in 200 ml. of benzene was slowly added in dropwise fashion. A white precipitate formed. The mixture was stirred for 2 hours, filtered while cold and the solids were recrystallized from dimethylformamide. The white solid N,N'-diphenylbiurea obtained had a melting point of 250°C. (also named 1,6-diphenylbiurea).

The above product (0.5 gram) was oxidized according to the procedure described in Example 2. The color change observed was from blue first to green and then to yellow

and orange. The orange needles of 1,1'-azobis(N-phenylformamide) obtained after recrystallization from acetone decomposed at 177°C.

1,1' - azobis[N - (3 - chlorophenyl)formamide] was obtained by a similar procedure starting with 32.2 grams (0.21 mol) of m-chlorophenyl isocyanate and 5.0 grams (0.1 mol) of hydrazine hydrate in a total reaction medium of 150 ml. of benzene. The N,N'-bis(3-chlorophenyl)biurea was characterized as a white product decomposing at 244—245°C. The 1,1' - azobis[N - (3 - chlorophenyl)formamide] obtained after oxidation as described above was found to decompose at about 180—200°C.

EXAMPLE 4

Primary Cells

Primary cells of construction similar to Leclanche cells except for the cathodic mix were prepared using the following as cathodic mixes:

- A. 2.40 g. 1,1'-azobis(N-n-butylformamide)
0.64 g. carbon black (HR 1670—P6303) (Columbian Carbon Co.)
2.0 ml. 17% ZnCl_2 , 27% NH_4Cl , 56% H_2O
- B. 1.80 g. 1,1'-azobis(N-isobutylformamide)
0.48 g. carbon black (SA 40—220) (Columbian Carbon Co.)
3.0 ml. 17% ZnCl_2 , 27% NH_4Cl , 56% H_2O
- C. 2.38 g. 1,1'-azobis(N-n-butylformamide)
0.64 g. acetylene black
2.1 ml. 17% ZnCl_2 , 27% NH_4Cl , 56% H_2O
- D. 2.32 g. 1,1'-azobis(N-n-butylformamide)
0.62 g. carbon black (HR 1670—P56303) (Columbian Carbon Co.)
1.8 ml. 10% ZnCl_2 , 50% $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 40% H_2O
- E. 2.32 g. 1,1'-azobis(N-n-propylformamide)
0.61 g. carbon black (SA—40—220) (Columbian Carbon Co.)
2.2 ml. 17% ZnCl_2 , 27% NH_4Cl , 56% H_2O

Curves showing the battery discharge characteristics, represented as cell voltages as functions of nominal capacity thereof, were plotted for primary cells containing the above-described cathodic mixes.

Flat discharge rates are obtained throughout most of the cell life at varying rates of discharge. This behaviour illustrates the highly desirable depolarizer characteristics which the substituted azodicarbonamides possess when used in primary cells.

EXAMPLE 5
Secondary Cells

- 15 Cathodic Mix
0.50 g. 1,1'-azobis(N-n-propylformamide)
0.50 g. carbon black (SA 40—220) (Columbian Carbon Co.)
2.0 ml. 17% ZnCl_2 , 27% NH_4Br , 56% H_2O

20 Cell Construction

- A glass cylinder was enclosed at one end with carboxymethyl cellulose coated kraft paper to which a strip of α -cellulose was attached. On the outside of the α -cellulose was placed a strip of pure zinc metal. The cathode mix was placed in the enclosed glass cylinder and a weighted carbon rod was inserted as a contact to the cathode mix. The cylinder was then stoppered at the top. The completed cell was dipped in the electrolyte for 15—30 seconds and then placed in an atmosphere saturated with electrolyte vapour. The cell was continuously discharged through a 24-ohm resistor to 0.985V and then charged to 1.535V. This cycle was repeated. After

its 17th discharge cycle, the secondary cell is shown to have good characteristics comparable to its initial characteristics.

EXAMPLE 6

The solubility of various substituted azodicarbonamides in electrolyte solutions was determined by preparing a saturated solution, removing excess compound by filtration, and assaying by iodometric titration the amount dissolved. The solubilities determined are given in Table II.

The stability of the various substituted azodicarbonamides was determined by placing a given amount of the compound in the electrolyte, stirring for one hour at 100°C., and then determining the amount of compound remaining by iodometric titration. These results are also given in Table II.

The shelf-life of cells containing cathodic mixes having azodicarbonamides as the depolarizers therein was determined by preparing normal dry cell cathodic mixtures and storing for 30 days at 45°C. Analyses to determine the amount of depolarizer remaining were then made. Results are also given in Table II.

The results of one hour stability tests at 100°C. indicate that the various substituted azodicarbonamides are virtually unaffected by such storage conditions (95—100% of compound remains) while the parent compound, azodicarbonamide, is essentially completely hydrolized. The stability of the substituted azodicarbonamides is independent of their solu-

bility in the electrolyte relative to that of azo-dicarbonamide itself, i.e., compounds both more and less soluble than the parent compound are more stable.

Shelf-life data, as determined by the experiments of this example, indicate the improvements obtained by use of the compounds of this invention for cell depolarizers. 5

TABLE II
Solubility and Stability of Various Azodicarbonamides in Contact with Electrolyte

Compound	Solubility (1)	Stability (2)	Shelf-Life (3)
Azodicarbonamide	85	2.0	35—40
1,1'-Azobis(N,N-dimethylformamide)	191,000	97.0	—
1,1'-Azobis(N-ethylformamide)	9,100	95.0	—
1,1'-Azobis(N-n-propylformamide)	330	99.5	88
1,1'-Azobis(N-isopropylformamide)	1,360	98.5	—
1,1'-Azobis(N-n-butylformamide)	10	99.5	90
1,1'-Azobis(N-isobutylformamide)	13	99.0	—
1,1'-Azobis(N-sec. butylformamide)	136	99.1	—
1,1'-Azobis(N-ter.-butylformamide)	155	99.5	90
1,1'-Azobis(N-phenylformamide)	10	100.0	—
1,1'-Azobis(N,N-pentamethylenefornamide)	730	99.5	—
N-Phenyl-1,1'-azobisformamide	—	53.0	—
N-butyl-N'-methyl-1,1'-azobisformamide	460	—	—
1,1'-Azobis(N-allylformamide)	1,700	—	—
1,1'-Azobis[N-(2-methoxyethyl)formamide]	40,500	—	—

(1) Milligrams per liter of electrolyte solution, 17% ZnCl₂, 27% NH₄Cl, 56% H₂O, at 25° C.

(2) Percent compound remaining after 1 hour at 100° C. in presence of electrolyte.

(3) Percent compound remaining after 30 days at 45° C. in a dry cell construction.

EXAMPLE 7

An "AA" size cell was prepared using a zinc can, a "Cellophane" laminate as separator, and a cathodic mix containing:

- 5 2.0 grams 1,1'-azobis(N-n-proylformamide)
0.67 gram carbon black (1300 sq. meters per gram)
2.3 ml. 17% ZnCl_2 , 27% NH_4Br , 0.3% HgCl_2 , 55.7% H_2O

- 10 This cell was cycled more than sixty times before shorting out. A cycle consisted of a 4.0 hour discharge through a 25 ohm load followed by a 4.5 to 5.0 hour charge at 40 milliamperes.

- 15 Dry cells prepared from each of the other 1,1'-azodicarbonamides listed in Table I and Table II gave comparably good results. The capacity is, of course, proportional to that expected from the molecular weight of the compounds, the larger molecular weight compounds having less capacity per gram of depolarizer.

EXAMPLE 8

- 25 An "AA" cell was prepared as Example 7 except for the cathodic mix which had the following composition:

- 2.25 grams 1,1'-azobis(N-n-butylformamide)
0.67 gram carbon black (1300 sq. meters per gram)
30 2.0 ml. 17% ZnCl_2 , 27% NH_4Br , 56% H_2O

- This cell was cycled more than thirty times before shorting out. A cycle consisted of discharge through a 24 ohm-resistor to 1.00V followed by a tapered charge to 1.50V.

EXAMPLE 9

- An "AA" size cell was prepared using a zinc can, a "Cellophane" laminate having a pore size of around 16 Angstroms, and a cathodic mix containing:

- 40 1.5 grams N-n-butyl-N'-methylbiurea
1 gram of carbon black, surface area 1300 sq. meters per gram
0.66 grams of zinc oxide
45 3.5 ml. electrolyte containing:
35% ZnCl_2
20% NH_4Cl
0.3% HgCl_2
44.7% H_2O

- 50 The zinc can was lined with the laminate as a separator with the laminate extending about $\frac{1}{4}$ inch above the can. The above cathodic mix was taped into the cell. A carbon rod having a brass cap was inserted into the mix. The laminate was folded over the top of the cathodic mix and the cell sealed with epoxy resin.

- The cell was charged for 16 hours at 20 milliamperes; then discharged through a 20 ohm-resistor until the voltage drops to 0.96 volts. The cell was then charged at 20 milliamperes until the voltage reached 1.65. The cell performed satisfactorily for 4 cycles, at which time the test was discontinued.

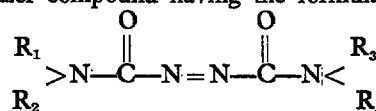
- 65 The substituted biurea was used as a starting

material with N-n-butyl-N'-methyl-1,1'-azobisformamide being synthesized in the cell, by the use of the charging current. Corresponding biureas may be used as a source for other substituent azobisformamides, with the cells being charged to produce the azobisformamides either at the time of manufacture, or other convenient time prior to use.

As the substituted azobisformamide is stable over a long period of time, in these cells it is usually more convenient to preform the substituted azobisformamide and add as a component of the cathodic mix, rather than synthesize in situ.

WHAT WE CLAIM IS:—

1. A cathode composition for an electric current-generating cell, which comprises a mixture of carbon, an electrolyte, and a depolarizer compound having the formula:



in which R_1 , R_2 , R_3 and R_4 are each hydrogen, or an alkyl of 1 to 8 carbon atoms, aryl, substituted aryl, cycloalkyl, aralkyl, alkoxyalkyl, cyanoalkyl, haloalkyl, nitro-alkyl, or alkenyl group; and R_1 and R_2 and R_3 and/or R_4 when alkyl, may be joined directly or through a nitrogen, sulfur or oxygen atom to form a heterocyclic ring; and not more than three of R_1 , R_2 , R_3 and R_4 are hydrogen.

2. A cathode composition according to Claim 1, wherein each of the terminal nitrogen atoms of the depolarizer compound carries as the only substituent an alkyl group of 3 or 4 carbon atoms.

3. A cathode composition according to Claim 2, wherein, in the depolarizer compound, R_1 and R_3 are hydrogen and R_2 and R_4 are *iso*-propyl groups, or *iso*-butyl groups.

4. A cathode composition according to any preceding Claim wherein the depolarizer compound is present in an amount of from 10 to 50% by weight, of the total weight of the composition.

5. A cathode composition according to any preceding claim, wherein the depolarizer compound has a particle size range of about 1 micron.

6. A cathode composition according to any preceding claim, wherein the depolarizer compound is any one of the substituted azodicarbonamide compounds hereinbefore mentioned.

7. A cathode composition according to any preceding claim, containing an halide salt in the electrolyte.

8. A cathode composition according to Claim 7, containing a bromide salt in the electrolyte.

9. A cathode composition according to Claim 1 and substantially as hereinbefore described.

10. An electric current-generating cell comprising an anode of an electro positive metal



EXAMPLE 7

An "AA" size cell was prepared using a zinc can, a "Cellophane" laminate as separator, and a cathodic mix containing:

- 5 2.0 grams 1,1'-azobis(N-n-propylformamide)
0.67 gram carbon black (1300 sq. meters per gram)
2.3 ml. 17% ZnCl₂, 27% NH₄Br, 0.3% HgCl₂, 55.7% H₂O

- 10 This cell was cycled more than sixty times before shorting out. A cycle consisted of a 4.0 hour discharge through a 25 ohm load followed by a 4.5 to 5.0 hour charge at 40 milliamperes.

- 15 Dry cells prepared from each of the other 1,1'-azodicarbonamides listed in Table I and Table II gave comparably good results. The capacity is, of course, proportional to that expected from the molecular weight of the compounds, the larger molecular weight compounds having less capacity per gram of depolarizer.

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- 2.25 grams 1,1'-azobis(N-n-butylformamide)
0.67 gram carbon black (1300 sq. meters per gram)
30 2.0 ml. 17% ZnCl₂, 27% NH₄Br, 56% H₂O

- This cell was cycled more than thirty times before shorting out. A cycle consisted of discharge through a 24 ohm-resistor to 1.00V followed by a tapered charge to 1.50V.

EXAMPLE 9

- An "AA" size cell was prepared using a zinc can, a "Cellophane" laminate having a pore size of around 16 Angstroms, and a cathodic mix containing:

- 40 1.5 grams N-n-butyl-N'-methylbiurea
1 gram of carbon black, surface area 1300 sq. meters per gram
0.66 grams of zinc oxide
45 3.5 ml. electrolyte containing:
35% ZnCl₂
20% NH₄Cl
0.3% HgCl₂
44.7% H₂O

- 50 The zinc can was lined with the laminate as a separator with the laminate extending about ¼ inch above the can. The above cathodic mix was taped into the cell. A carbon rod having a brass cap was inserted into the mix. The laminate was folded over the top of the cathodic mix and the cell sealed with epoxy resin.

- The cell was charged for 16 hours at 20 milliamperes; then discharged through a 20 ohm-resistor until the voltage drops to 0.96 volts. The cell was then charged at 20 milliamperes until the voltage reached 1.65. The cell performed satisfactorily for 4 cycles, at which time the test was discontinued.

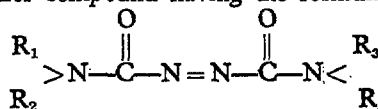
- 65 The substituted biurea was used as a starting

material with N-n-butyl-N'-methyl-1,1'-azobisformamide being synthesized in the cell, by the use of the charging current. Corresponding biureas may be used as a source for other substituent azobisformamides, with the cells being charged to produce the azobisformamides either at the time of manufacture, or other convenient time prior to use.

As the substituted azobisformamide is stable over a long period of time, in these cells it is usually more convenient to preform the substituted azobisformamide and add as a component of the cathodic mix, rather than synthesize in situ.

WHAT WE CLAIM IS:—

1. A cathode composition for an electric current-generating cell, which comprises a mixture of carbon, an electrolyte, and a depolarizer compound having the formula:



in which R₁, R₂, R₃ and R₄ are each hydrogen, or an alkyl of 1 to 8 carbon atoms, aryl, substituted aryl, cycloalkyl, aralkyl, alkoxyalkyl, cyanoalkyl, haloalkyl, nitro-alkyl, or alkenyl group; and R₁ and R₂ and R₃ and/or R₄ when alkyl, may be joined directly or through a nitrogen, sulfur or oxygen atom to form a heterocyclic ring; and not more than three of R₁, R₂, R₃ and R₄ are hydrogen.

2. A cathode composition according to Claim 1, wherein each of the terminal nitrogen atoms of the depolarizer compound carries as the only substituent an alkyl group of 3 or 4 carbon atoms.

3. A cathode composition according to Claim 2, wherein, in the depolarizer compound, R₁ and R₃ are hydrogen and R₂ and R₄ are *iso*-propyl groups, or *iso*-butyl groups.

4. A cathode composition according to any preceding Claim wherein the depolarizer compound is present in an amount of from 10 to 50% by weight, of the total weight of the composition.

5. A cathode composition according to any preceding claim, wherein the depolarizer compound has a particle size range of about 1 micron.

6. A cathode composition according to any preceding claim, wherein the depolarizer compound is any one of the substituted azodicarbonamide compounds hereinbefore mentioned.

7. A cathode composition according to any preceding claim, containing an halide salt in the electrolyte.

8. A cathode composition according to Claim 7, containing a bromide salt in the electrolyte.

9. A cathode composition according to Claim 1 and substantially as hereinbefore described.

10. An electric current-generating cell comprising an anode of an electro positive metal

and a cathode composition as defined in any preceding claim.

11. A cell according to Claim 10, wherein the anode is zinc.

5 12. A cell according to Claim 10 and substantially as hereinbefore described.

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