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Phillips et al.

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[54] **ELECTRODEPOSITION OF BONE WITHIN A PLASTIC MATRIX**

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[51] **Int. Cl.** **B01k 5/02;** C23b 13/00

[58] **Field of Search** ..... 204/181; 128/92 C; 3/1

[56] **References Cited**

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[57] **ABSTRACT**

A method of improving orthopedic implant material by the simultaneous electrodeposition of bone particles and an inert plastic binder onto a prosthesis is provided. A polyamic acid is dissolved in a solvent such as dimethylsulfoxide and an amine is added to the solution to produce the organic salt of a free carboxyl group. A colloidal suspension of the organic salt and fine bone particles in a mixed solvent comprised of acetone and dimethylsulfoxide is placed in a receptacle and a voltage is applied to a pair of electrodes immersed in the solution causing the deposition on the anode of bone in a polyamic acid plastic matrix. After subsequent cure, the result is a coating of bone within a polyimide matrix on the electrode.

20 Claims, No Drawings

ELECTRODEPOSITION OF BONE WITHIN A PLASTIC MATRIX

The present invention concerns the improvement of orthopedic implant materials and, more particularly, the anodic formation of bone coatings on prosthesis by electrodeposition of a composite of bone particles within a polyamic acid matrix which on subsequent heat cure results in bone particles within a polyimide plastic matrix.

Advances in the field of total prosthetic replacement of bones include electrodepositing bone particles on prostheses and, also, coating such prosthesis by the rf sputtering process. The objective in such orthopedic implants is to determine a reliable and effective method and means for enhancing bone growth around the implant and into the pores of the implant wall. Enhancing bone growth is particularly important in bone-bridge operations where necrosis is inevitable if the bones are not united in a reasonable time. Often, the bone gap in such cases is filled with autogenous bone but this usually requires a second operation. In certain instances, the bone gap has been successfully bridged with ivory which also is itself replaced in time with living bone. The present invention provides stronger and more easily formed implants or prostheses which have bone replacement characteristics similar to ivory.

In general, the present invention provides a method of electrochemically depositing bone particles and organic binder onto the external surface of a bone prosthesis to form a coating which stimulates bone attachment. The organic binder is preferably of the polyamic acid family such as Dupont Pyre-M.L. which when cured provides a polyimide of high thermal stability and is inert to attack from most chemicals.

Accordingly, it is an object of the present invention to provide a method of enhancing bone growth on prostheses by binding bone particles to a prosthesis.

Another object of this invention is to provide a method of blending bone particles and a binder to promote the formation of a coating of controlled thickness on a prosthesis.

A further object of this invention is to provide an improved method of depositing bone and a plastic material simultaneously on an orthopedic implant to enhance bone repair rates and promote success in bone bridge operations.

Other objects, advantages, and novel features of the present invention will become apparent from the following description thereof.

The electrodeposition of some of the polyamic acids and their subsequent conversion to corresponding polyimides has been accomplished in the prior art. The teachings and techniques of such processes have not, however, been applied to the electrodeposition of particles of human or animal matter on prosthetic or other substrates. This application is the subject of the present invention.

The formation of a colloidal suspension suitable for electrodeposition is a necessary precedent to at least one process for forming a coating on a prosthesis. According to the present invention, such a colloidal suspension is obtained by dissolving a commercially available polyamic acid such as Dupont Pyre-M.L. in a solvent such as dimethylsulfoxide. An amine when added to this solution produces an organic salt of free carboxyl groups which are present in the polyamic acid. The solution is heated to approximately 40°C and maintained at this temperature for 15 minutes. The former solution is added to a rapidly stirred non-solvent such as acetone and ground bone is then added to the vigorously stirred solution, resulting in a colloidal suspension of the organic salt and bone contained in a mixed solvent system which is comprised of acetone and dimethylsulfoxide.

Using the foregoing colloidal suspension as the electrolyte and an electrolytic apparatus comprising a Pyrex glass reaction kettle with cover and two metal electrodes $2 \times 1 \times 0.02$ inches, a coating is obtained on the anodic electrode when a voltage is applied to the metal electrodes. In a preferred embodiment process, 300 ml of solution is used and the anode-to-cathode separation is maintained at 1 inch. The potential applied between the electrodes is derived from a variable voltage dc power supply and coatings of various thickness and hardness are obtained and tested for mechanical, physical and thermal properties.

Tests conducted on the coatings obtained according to the foregoing procedure show the following mechanical, physical and thermal properties of electrodeposited Pyre-M.L. Pyre-M.L. is a 16.5% by weight solution of an aromatic polymellitamic acid in N-methyl-2-pyrrolidone solvent.

TABLE I

Property	Typical Value at 25°C	Test Method
Folding endurance*	>30,000 cycles	ASTM D-2176-63T
Ultimate elongation*	60–70%	ASTM D-882-64T
Impact test+	80 in-lb (direct and reverse)	Falling Ball impact
Abrasion resistance+	>400g	Hoffman scratch test
Adhesion & flexibility+	No cracking or loss of adhesion (1/16 in. bend)	Conical mandrel
Thermal aging+	Expected life >10,000 hr at 250°C	AIEE Method 57
Tensile strength*	24,000 psi	ASTM D-882
Coefficient of friction*	0.42	ASTM D-1505

*Test evaluated on stripped film.
+Test evaluated on substrate (Cu and Al).

The effect of applied voltage on bone/Pyre-M.L. colloidal dispersions is shown in the following table. The test specimen consisted of 5 grams of bone contained in 50 ml Pyre-M.L., 10 ml triethylamine, 200 ml dimethylsulfoxide and 1,000 ml acetone. The coatings were cured to 300°C in an oven for one hour.

TABLE II

Applied Voltage (volts)	Deposition Time (secs)	Anode	Coating Thickness mils	Adhesion
50	60	steel	~0.5	good
50	60	steel	~1	good
50	60	Cr	~1	good
100	60	Al	~2	good
100	60	Cu	~2	good

The effect of electrodeposition time on various coating thickness of bone/Pyre-M.L. is indicated in the following table. The colloidal suspension contained 10 grams of bone contained in 50 ml Pyre-M.L., 10 ml triethylamine, 200 ml dimethylsulfoxide and 1,000 ml acetone. The coatings were cured to 300°C in an oven for one hour.

TABLE III

Applied Voltage (volts)	Deposition Time (secs)	Anode	Coating Thickness mils	Adhesion
100	60	steel	~1	good
100	100	steel	~2	good
100	120	steel	>5	good
100	300	steel	>10	very poor

Table IV below shows the results of applying various voltages to varying weights of bone over varying deposition times. In these tests, an organic matrix composition of 50 ml Pyre-M.L., 10 ml triethylamine, 200 ml dimethylsulfoxide and 1,000 ml acetone was used and the coatings were cured at 300°C in an oven for one hour.

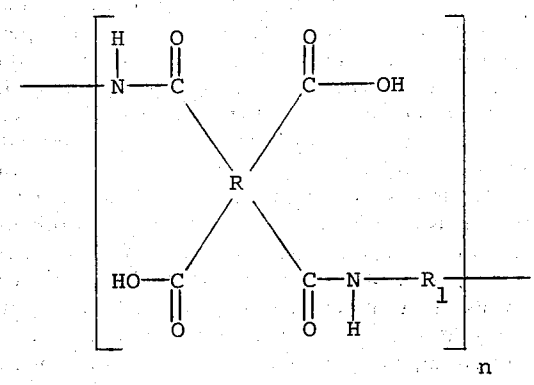
TABLE IV

Weight of Bone g	Applied Voltage V	Deposition Time secs	Anode	Approximate Coating Thickness mils	Adhesion
5	30	60	steel	0.5	good
5	50	60	steel	1	good
5	50	60	Cr	1	good
5	100	60	Al	2	good
5	100	60	Cu	2	poor
10	50	120	steel	2	good
10	100	120	steel	5	poor
10	100	300	steel	>10	very poor
25	50	30	steel	1	poor
25	100	60	steel	4	very poor
25	100	120	steel	6	very poor
25	100	300	steel	>10	very poor

Four different bone concentrations were investigated. Under the influence of the electric field, bone particles were transported within the organic matrix to the anode and deposited at this electrode. Concentrations of lower weights of bone produced cathode coatings which have good adhesion to the stainless steel substrate. When the concentration is increased twofold or more, thicker coatings are obtained in all but one instance but these coatings have poor or very poor adhesion properties.

The best coatings for adhesion and thickness are achieved utilizing a solution comprised of an organic matrix of 50 ml Pyre-M.L., 10 triethylamine, 200 ml dimethylsulfoxide and 1,000 ml acetone. It appears that the mobility of Pyre-M.L., under the influence of the electric field, far exceeds that of the bone particles. It is believed for this reason that the final coatings have a bone composition of approximately 10% in each category. Using greater initial bone concentrations has very little effect on increasing the percentage of bone in the coating, the bone level appearing to be arbitrarily limited to substantially 10%. Adhesion is excellent for coatings of <2 mils but deteriorates rapidly as coating thicknesses of 10 mils are approached.

Other suitable aromatic polyamic acid polymers can be represented by the recurring unit:



in which n is at least 15.

Suitable solvents for the polyamic acids are dimethyl acetamide, dimethyl formamide, N-methyl-2-pyrrolidone and dimethylsulfoxide. Preferred non-solvents, in addition to acetone, for the polyamic acid include methyl isobutyl ketone, methyl ethyl ketone, methyl n-propyl ketone, diethyl ketone, mesityl oxide and cyclohexanone. Suitable bases, for salt solution, include triethylamine, trimethylamine, N,N-dimethylbenzylamine, N-ethylpiperidine, pyridine and 1-methylimidazole.

The present invention thus teaches a process by which bone and organic matrix may be simultaneously adhered by electro-chemical deposition onto orthopedic implants. In the electro-deposition process, both bone particles and organic matrix are formed on the orthopedic implant. The organic matrix, which is evenly dispersed within the bone particles, is believed to promote healing at least partly because of the spacing of the bone particles which makes them accessible to attachment of living bone within the matrix. In the preferred embodiment, electrodeposition of finely divided bone particles from polyamic acid dispersions onto metal substrates provides a basis for the preparation of

prostheses for both joint and/or socket replacement, bone bridge, etc. These prostheses enhance bone repair rates by providing a coating to which living bone may adhere and which ultimately is completely replaced by living bone.

The electrodeposition process provides several advantages in the forming of superior prosthetic devices, one being a controlled thickness of electrodeposition and another being a uniform coverage of irregularly shaped substrates. The controlled thickness feature reduces the finishing required to produce a frictionless freely movable joint. A further advantage is obtained through the dissolution of the metallic electrode during electrodeposition.

The process of the invention is also rapid in relation to normal body processes or other forms of bone repair such as pins, clamps, etc. The process also is exceedingly economical since all of the compounds used therein are readily available and no complex equipment is required.

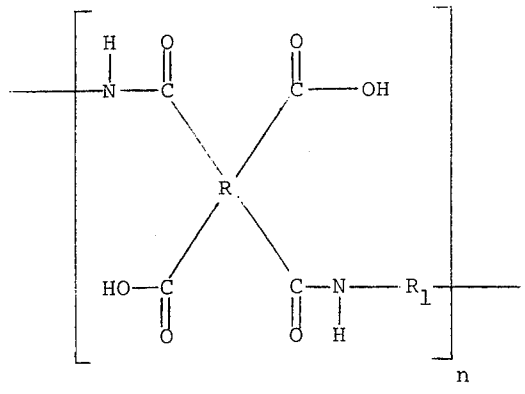
Obviously many modifications and variations of the present invention are possible in the light of the above teachings.

What is claimed is:

1. A method of forming a prosthesis for bone repair or replacement comprising:

electrodepositing finely divided powdered bone particles from colloidal suspensions of said bone particles in a solution comprising acetone, dimethylsulfoxide, an organic amine and a polyamic acid onto a metallic substrate in the form of said prosthesis.

2. The method of claim **1** wherein the polyamic acid is taken from a group of aromatic polyamic acid polymers having the recurring unit:



in which *n* is at least 15.

3. The method of claim **2** wherein the polyamic acid is a 16.5% by weight solution of an aromatic polymellitamic acid in N-methyl-2-pyrrolidone solvent.

4. The method of claim **3** wherein said amine is taken from the group including triethylamine, trimethylamine, N,N-dimethylbenzylamine, N-ethylpiperidine, pyridine and 1-methylimidazole.

5. The method of claim **4** wherein said solution is characterized by the presence of an organic salt of free carboxyl groups,

said solution heated to substantially 40°C and maintained at said temperature for substantially 15 minutes prior to initiating said electrodeposition.

6. A method of producing in orthopedic implant for enhancing bone repair rates in bone bridge and other bone operations comprising:

dispensing ground bone particles in a solution containing a polyamic acid and an organic salt in a solvent taken from a group including dimethyl acetamide, dimethyl formamide, N-methyl-2-pyrrolidone and dimethylsulfoxide, and a non-solvent taken from the group including methyl isobutyl ketone, methyl ethyl ketone, methyl n-propyl ketone, diethyl ketone, mesityl oxide, cyclohexanone and acetone so as to obtain a colloidal suspension of an organic salt and bone.

7. The method of claim **6** wherein said solvent is dimethylsulfoxide, said non-solvent is acetone and said solution is heated to substantially 40°C and maintained at said temperature for substantially 15 minutes before initiating said electrodeposition.

8. The method of claim **7** wherein said implant is the anodic electrode of an electrolytic deposition system wherein a dc voltage of from 50 to 100 volts is applied across the electrode thereof.

9. The method of claim **8** wherein said organic salt is taken from the group triethylamine, trimethylamine, N,N-dimethylbenzylamine, N-ethylpiperidine, pyridine and 1-methylimidazole.

10. A method of forming a prosthesis for bone repair or replacement comprising:

electrodepositing finely divided powdered bone particles from a colloidal suspension of said bone particles in an inert plastic binder onto a metallic substrate in the form of said prosthesis.

11. The method of claim **10** wherein the inert plastic binder is an organic matrix formed by a polyamic acid dissolved in a solvent:

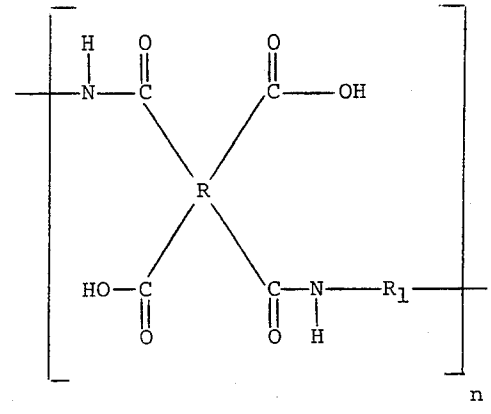
an amine added to the solution to produce the organic salt of a free carboxyl group; and

said solution and said bone particles stirred into a non-solvent electrolyte so as to form a colloidal suspension of said organic salt and said bone particles in said solvent and non-solvent.

12. The method of claim **11** wherein said solution is heated to substantially 40°C and maintained at said temperature for substantially 15 minutes prior to initiating said electrodeposition.

13. The method of claim **12** wherein said substrate is the anodic electrode of an electrolytic deposition system in which a dc voltage of from 50 to 100 volts is applied across the electrodes thereof.

14. The method of claim **13** wherein the polyamic acid is taken from a group of aromatic polyamic acid polymers having the recurring unit:



in which *n* is at least 15;

the solvent is taken from a group including dimethyl acetamide, dimethyl formamide, N-methyl-2-pyrrolidone and dimethylsulfoxide;

the amine is taken from a group including triethylamine, trimethylamine, N,N-dimethylbenzylamine, N-ethylpiperidine, pyridine and 1-methylimidazole; and

the non-solvent is taken from a group including methyl isobutyl ketone, methyl ethyl ketone, methyl n-propyl ketone, diethyl ketone, mesityl oxide, cyclohexanone and acetone.

15. The method of claim **14** wherein the polyamic acid is a 16.5% by weight solution of an aromatic polymellitamic acid in N-methyl-2-pyrrolidone solvent.

16. The method of claim **15** wherein the solvent is dimethylsulfoxide.

17. The method of claim **16** wherein the non-solvent is acetone.

18. The method of claim **17** wherein the amine is 1-methylimidazole.

19. The method of claim **17** wherein the amine is triethylamine.

20. The method of claim **19** wherein the portions of the components are 5 grams bone, 50 ml polyamic acid, 10 ml triethylamine, 200 ml dimethylsulfoxide and 1,000 ml acetone.

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