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MAGNETITE-STABILIZED LEAD ANODE

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2 Sheets-Sheet 1

FIG. 1

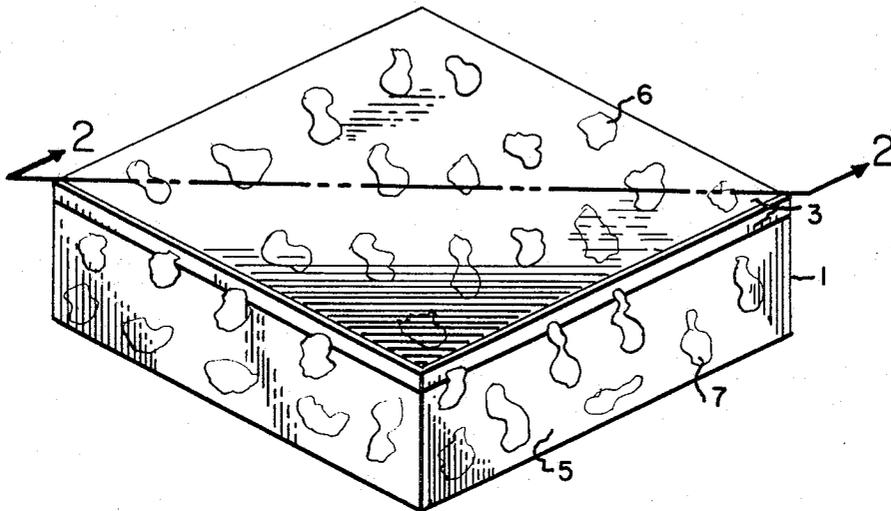
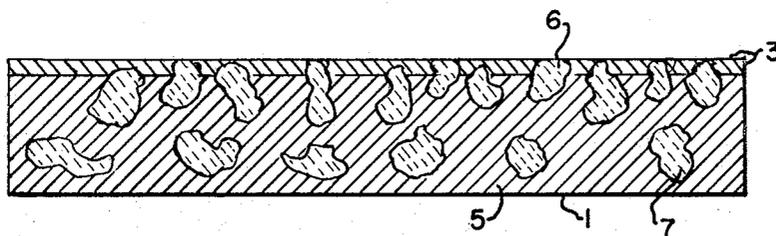


FIG. 2



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FIG. 3

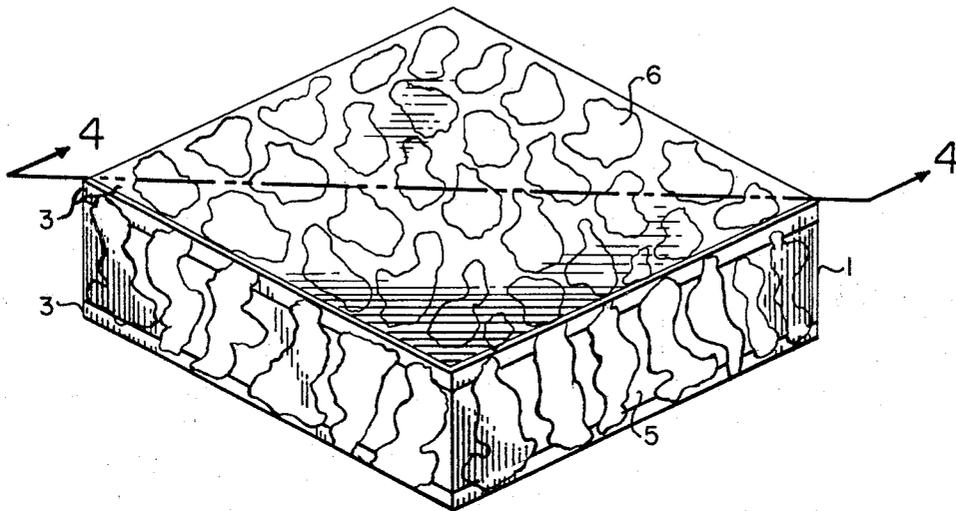
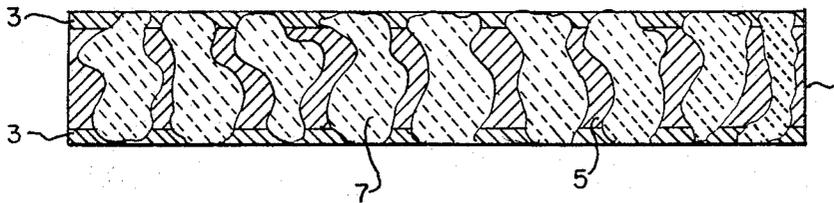


FIG. 4



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MAGNETITE-STABILIZED LEAD ANODE

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5 Claims. (Cl. 204-290)

This invention relates to anodes as articles of manufacture, the method of making the same, and their use in electrolytic systems. More particularly, it is concerned with a method for fabricating anodes comprising at least one metal component, and magnetite (ferroso-ferric oxide). Specifically, it relates to bielectrodes to be used as non-corroding anodes in the electrolysis of electrolytic solutions containing chloride ions as, for example, in caustic-chlorine cells. More specifically, it relates to the use of said anodes in impressed current cathodic protection systems. The word "bielectrode" is used in this disclosure to define an electrode comprising more than one electrically-conductive material.

In electrochemical processes such as electrolysis, electrodialysis, and in the field of cathodic protection, it is a matter of prime importance—especially where the anode comes in contact with a solution containing chloride ions—to properly select the materials from which to manufacture such anodes. In these processes there are only a few-known materials which may effectively constitute the anode because most materials, while acting as an anode, are susceptible to intense corrosion by oxygen and chlorine gases which are evolved at said anode. If only chemical characteristics of the metal were to be considered in the selection of a suitable anodic material, the metals of the platinum group would be the universal choice because of their high resistance to corrosion. However, the high cost of these precious metals prohibits their extended commercial use in most processes.

A continuous search has been made for anode material which has the desirable anti-corrosive characteristics of the platinum metals, but which lacks their prohibitive cost. It has long been known that lead can be used as an inexpensive and satisfactory anode especially when employed in a sulfuric acid medium. During the anodic process the lead surface of the anode is oxidized to lead peroxide (PbO₂) which possesses chemical stability with high electronic conductivity. Thus a PbO₂/Pb system makes an ideal anode—provided the covering of lead peroxide remains in contact with the underlying lead and provided it is reformed if a discontinuity occurs in the peroxide coating. However, where such an anode is used in the presence of chloride ions, the lead peroxide film cannot be maintained on the entire lead surface; hence, the chloride ions penetrate the peroxide film and form a non-conducting layer of lead chloride on the underlying lead base. This causes the lead peroxide to become insulated from said lead base. Under these conditions, it has been found that at a constant current density, the voltage drop increases rapidly, and eventually the anode completely disintegrates.

It is known that the anodic corrosion of lead in a chloride electrolyte can be prevented by introducing a platinum wire into the surface of one cm.² lead anode ("Anodic Behavior of a Lead-Platinum Bielectrode in Chloride electrolytes," E. J. Littauer and L. L. Shreir, *Platinum Metals Review*, 1961). Also co-pending U.S. application, Serial No. 196,758, filed on May 22, 1962 discloses a novel method of fabricating large bielectrodes in which numerous discrete particles of platinum or other noble metals are embedded onto the lead base material. When such bielectrodes become anodic in a medium containing chloride ions, a film of lead chloride is first produced.

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However, it is rapidly replaced with stable lead peroxide which initially forms at the interface of the lead and platinum. The platinum metal on the surface of the lead anode acts as a nucleus for the formation of lead peroxide in the vicinity of said platinum. When the peroxide completely covers the lead surface, the only anodic reaction taking place is the oxidation of chloride ions to chlorine gas with the peroxide-coated base metal remaining stable.

The cost disadvantage of platinum has been effectively overcome by the present invention. In all of the prior art, only noble metals are employed as the protective microelectrode materials. As is well known, the noble metals are expensive and their substitution by an inexpensive material affording the same protective characteristics would be an important and useful advance in the art. It is well known that magnetite alone is a satisfactory anode material because of its high electrical conductivity and its impermeability to attack by chlorine and other oxidizing agents liberated at the anodes during electrolysis. Such anodes can be formed by fusing the native mineral particles with the addition of flux and casting into plates of a dense impermeable mass. This fusion process requires temperatures too high to be economical. Another method of forming the anode is to oxidize the surface of an iron plate by heating to high temperature with the simultaneous passage of superheated steam over the iron surface for several hours. This method is also uneconomical with the added drawback that minor pin holes of iron remain in the oxide coating to be later exposed to the effects of corrosion.

The cost disadvantage of platinum and the difficulties in magnetite anode fabrications have been effectively overcome by the present invention in that magnetite is employed in preference to platinum in fabricating stable lead-magnetite bielectrodes. Additionally, magnetite will afford greater protection to the anode because its low cost will allow incorporating more of the same into the lead to act as a nuclei for more rapid and complete coverage of the lead metal with the peroxide coating.

The term magnetite as used herein refers to solid magnetic iron oxide having the formula Fe₃O₄, whether it be the purified or non-purified natural mineral or the synthetic material.

In general the bielectrodes are fabricated so that the magnetite material is embedded and held firmly into the lead metal. The embedding may be accomplished by pounding or rolling the magnetite into the lead. The magnetite material can be in the form of a powder, granular, lumps, chips, or the like since shape and size will not adversely affect their protective qualities. The maximum size of the magnetite particles is generally determined by the desired thickness of the finished article. For example, a bielectrode in sheet form which has a thickness of one-half inch should not have magnetite particles very much greater than one-half inch in size. It is only necessary that the magnetite be of a sufficiently small size to be firmly embedded into the lead base material used. Other methods of embedding the magnetite into the lead are, for example, to employ sand or vapor blasting methods which are especially effective where only small surface particles are desired. The magnetite material can also be added to molten lead, compressed in a pressure mold, and cooled until solid. It is obvious that there are many ways to accomplish the embedding process, and it is understood that the invention is not limited to only those enumerated. Since the cost of magnetite is not an important consideration, the bielectrode can be fabricated with the major component comprising magnetite. Satisfactory bielectrodes have been prepared containing as little as 0.1% by weight

of magnetite and in excess of 60%. Preferably, the magnetite should be the major component by weight of the finished bielectrode. It is also preferred that the working surface of the bielectrode be covered by a predominant amount of the magnetite. The greater the amount of magnetite exposed to the electrodes' working surface, the better its stability against corrosion. An electrode having its surface covered with 75% magnetite has been found to be very satisfactory.

It is therefore an object of this invention to provide an improved method for manufacturing anodes of any size and shape which are stable in electrolytic processes—especially those involving chloride-containing solutions.

Another object is to make an improved bielectrode comprising magnetite material dispersed throughout a lead anode and/or on its surface.

A further object is to achieve these results in a simple, rapid, and most economical manner.

Further objects and various advantages of this invention will be apparent from a study of this disclosure, the drawings, and appended claims.

FIGURE 1 is one embodiment of the invention and represents a perspective view of a fully-formed bielectrode anode constructed in accordance with the present invention;

FIGURE 2 is a side elevational view of the bielectrode in cross section taken in a plane represented by the line 2—2 of FIGURE 1;

FIGURE 3 is a modified embodiment of the invention in which the magnetite particles are relatively large and constitute the major component of the finished bielectrode; and

FIGURE 4 is a side elevational view of the bielectrode taken in cross section in a plane represented by line 4—4 of FIGURE 3.

The drawings illustrate an anode in sheet form 1 which is comprised of a lead base metal 5 having embedded therein magnetite particles 6 and 7. The upper portion of the drawings represents the active working area of the anode which comprises a solid adherent layer or coating of lead peroxide 3 and surface magnetite particles 6. Below the coated area are sub-surface particles 7 also of magnetite embedded within the lead base metal 5. It can be appreciated that a bielectrode could be constructed which would contain only surface particles 6 since it is only necessary for the required protection to have the magnetite particles on the anode surface.

The drawing of FIGURES 3 and 4 illustrates a bielectrode containing relatively large magnetite particle sizes 6. The dimensions of the particles are approximately the same as the thickness of the electrode sheet 1 so that the magnetite extends from one surface of the electrode to the other. An electrode constructed in the manner illustrated has a working surface which predominates in magnetite 6 with the smaller remaining surface area comprising the lead peroxide coating 3. Since both surfaces of the bielectrode contain a sufficient amount of exposed magnetite particles and the peroxide coating, it is obvious that the bielectrode can be employed as a common electrode; that is, both sides can be employed as the working area simultaneously. The manner of producing the above-illustrated bielectrode types is hereinafter more fully described.

It is intended that the term "lead" as used herein include the commercial form containing a wide range of minor impurities. The present invention is also applicable to electrodes having base metals comprising alloys of lead and antimony as well as lead and silver.

The process of this invention involves embedding numerous particles of magnetite on the surface and/or throughout the lead anode. However, where the bielectrode contains only small surface particles, it is possible for these to flake off or to become dislodged during operation. This would result in a lead anode having

no further protection; thus, eventual disintegration would occur. However, this does not occur in a bielectrode constructed with magnetite particles throughout since the deeper embedded particles would eventually become exposed to the surface, preventing further corrosion of the base metal.

As can be appreciated, bielectrodes of any desired shape or size can be made, for example, by molding, rolling, hammering, etc. It should also be noted that the present article of manufacture is not limited to any specific shape or form so long as portions of the magnetite material are exposed to the electrode surface. It is, therefore, recommended that, prior to any coating operation, the surface of the bielectrode be sanded to obtain a smooth surface and to expose more of the magnetite particles to the electrode's surface.

The electrolytic coating operation is preferably carried out by employing the bielectrode as an anode in the electrolysis of a chloride or sulfate solution. The concentration of the chloride ions can range from 0.1 normal to 1.3 normal—the preferred concentration being from 0.4 to 0.6 normal. In concentrations much below 0.1 or above 1.3 normal, it is difficult to obtain a satisfactory coating of lead peroxide. Where the coating operation is carried out in a sulfate solution, it is preferred that the concentration of sulfate ions be in a range above 0.05 normal. When a direct current is impressed across the electrolytic coating cell, a thin peroxide film forms on the anodic lead surface. The more numerous the exposed magnetite material, the more rapid the formation of the coating. How the magnetite causes the formation of a protective oxide coating on the lead is not definitely known, but it appears that the magnetite particles act as catalysts in the formation of the lead peroxide coating. The thickness of the coating depends primarily on the current density and coating time. Anode current densities of 30–90 milliamperes per square centimeter will produce the most satisfactory protective coatings—the greater the current density, the more rapid the peroxide formation.

The following examples are illustrative of preferred modes of carrying out the invention and are not intended to be limiting.

Example I

One side of a sheet of commercial leads having the dimensions 1 ft. x 1 ft. x 1/4 inch was sprinkled with magnetite particles to form a surface layer of magnetite thereon. The magnetite was the impure natural mineral product. The particle sizes ranged from 30 to 60 U.S. standard mesh. A flat press was used to apply an even pressure on the magnetite layer sufficient to force the hard particles into the lead surface. This resulted in an article in which the working surface area comprised about 60% magnetite and 40% lead, and the magnetite comprised 8% by weight of the article. The surface was sanded lightly to remove any loosely-held particles. The bielectrode surface was then made anodic in an electrolytic bath containing a 0.5 normal aqueous solution of NaCl. The cathode material was stainless steel. A direct potential was impressed across the electrodes equal to a current density of 50 milliamperes per square centimeter of anode area. Since chlorine gas was evolved at the anode and hydroxide at the cathode, it was necessary to add HCl to the electrolytic solution at various intervals to neutralize the hydroxide formed and to keep the concentration of the chloride ions at ~0.5 normal. After one hour of anodizing, the anodic lead surface had developed a deep adherent coating of lead peroxide. The bielectrode surface prepared and coated as above was employed as an anode in an electro dialysis unit demineralizing 3,500 p.p.m. brackish water down to 350 p.p.m. Although the brackish water contained 2,400 p.p.m. of dissolved NaCl, the anode revealed no appreciable corrosion or increase in voltage drop after three days of continuous operation.

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Example 2

A bielectrode was prepared as in Example 1 except that the magnetite particles employed were approximately one-quarter inch in size. The particles were forced into and through the lead sheet so that magnetite particles became exposed on both sides of the electrode. The magnetite covered approximately 70% of both surface areas of the bielectrode. Each surface of the electrode was anodized until a deep layer of peroxide had formed on the exposed lead areas. The finished bielectrode contained 54% by weight of magnetite. This bielectrode was employed as a common anode in a caustic-chlorine cell operating in saturated brine solution. A current density of 90 amperes per square foot of working anode area was used, and after 52 hours of continuous operation, no noticeable corrosion was evident.

Example 3

Powdered antimonial lead and magnetite (both of which had passed through a U.S. standard 100-mesh sieve) were thoroughly mixed together, put into a flat square mold and subjected to heat and pressure sufficient to cause sintering of the lead particles to form a solid mass. This article contained 30% by weight of magnetite particles, the particles substantially dispersed on the surface and throughout the lead base material. The article was lightly sanded (to surface expose more of the small magnetite particles), and anodically oxidized in a 1 normal sodium sulfate solution at a current density of 90 milliamps per square foot of active anode area. When a sufficient coating of peroxide had formed on the lead surface, the finished article was employed as an anode in a cathodic protection system operating in flowing sea water under an impressed current of 100

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amps per square foot of anode area. After 12 days of operation, only slight anodic attack was visible.

What I claim is:

1. A composite article of manufacture for use as an anode electrode comprising a lead metal base having particles of a magnetite at least partially embedded therein, the working surface of said anode comprising an adherent layer of lead peroxide and exposed particles of magnetite.
2. The article of claim 1 where the magnetite particles are dispersed throughout the lead base metal.
3. The article of claim 1 wherein the magnetite particles are embedded only on the surface of the lead base metal.
4. The articles of claim 1 wherein the base metal is an alloy of lead and antimony.
5. The article of claim 1 wherein the base metal is an alloy of lead and silver.

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