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Johnson

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[54] **REDUCTION OF ALUMINUM WITH IMPROVED REDUCTION CELL AND ANODES**

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Related U.S. Application Data

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[52] **U.S. Cl.** ..... **204/243 R**, 204/290 R, 204/294

[51] **Int. Cl.** **C22d 3/02**, B01k 3/06, B01k 3/08

[58] **Field of Search** ..... 204/243 R, 244–247, 204/67, 290 R, 294

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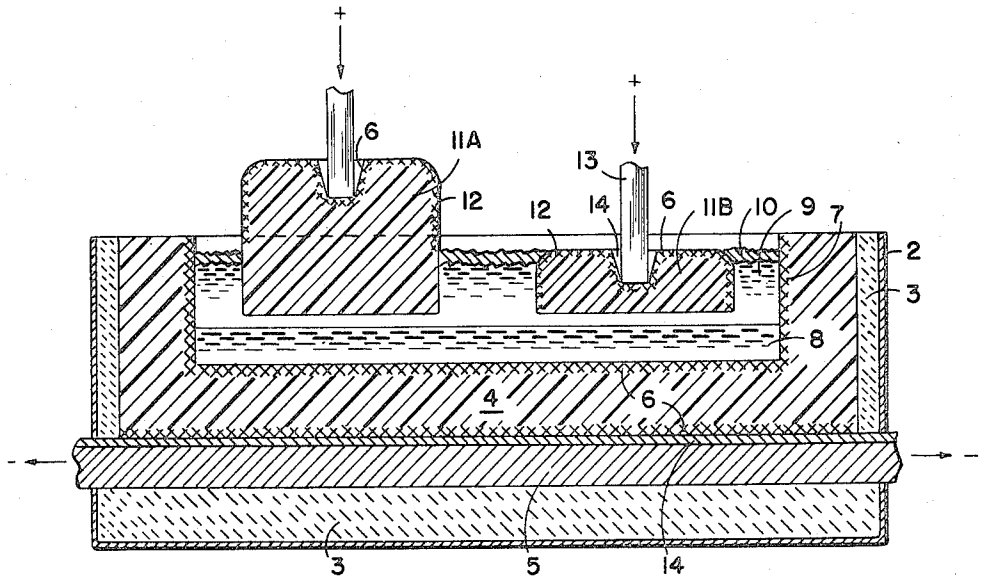
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Assistant Examiner—Donald R. Valentine
Attorney, Agent, or Firm—James J. Burke

[57] **ABSTRACT**

A system for the fused floride electrolysis of aluminum in a potcell wherein a carbonaceous anode and potlining are preserved against deterioration by impregnating their respective surfaces with a pitch-fluoride mixture and a pitch-graphite mixture. Atmospheric oxidation of anode surfaces is prevented so maximum anode cross sectional area is preserved and, hence, has minimum resistance for current travel through the anode and through the underlying electrolyte. The more dense carbon surface also reduces corner erosion of anodes. Impregnation is preferably carried out with one or more applications of aluminum fluoride suspended in a high melting, low volatile coal tar pitch. An improved potlining protects against electrolyte penetration and circulating metal erosion of the potlining surface, and improves conductivity; the lining bottom is sealed and smoothed with graphite suspended in molten pitch, which is absorbed by capillary attraction, and which increases conductivity. The lining walls are sealed and smoothed with a similar mixture of fluorspar and pitch, which decreases conductivity.

6 Claims, 3 Drawing Figures



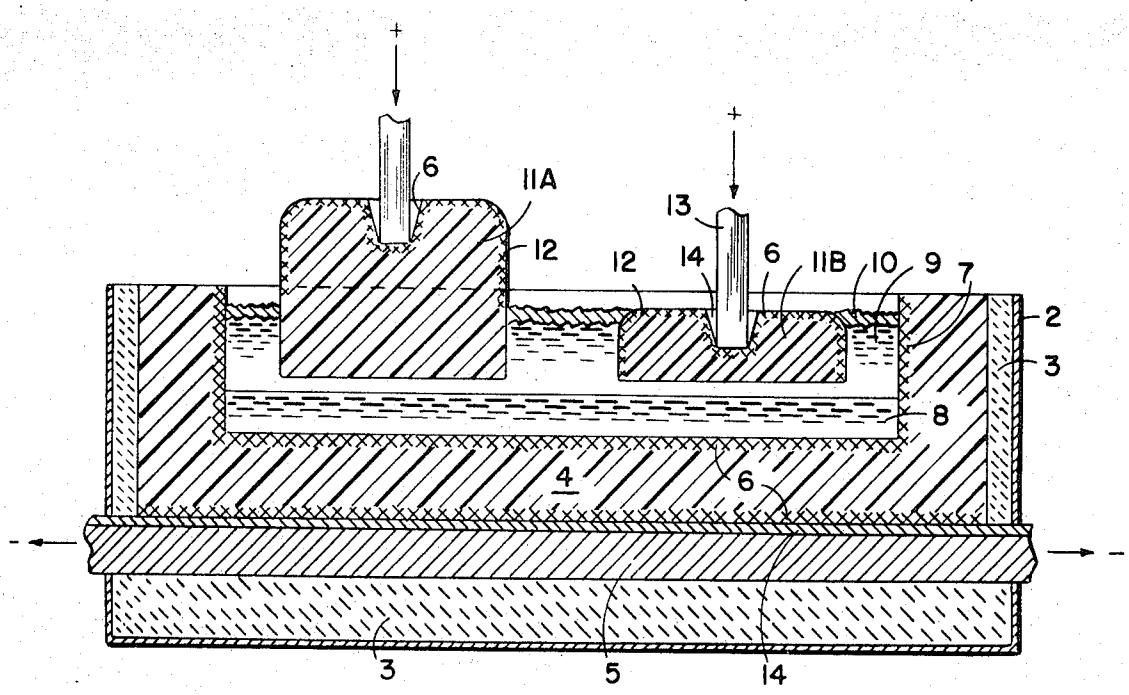


FIG. 1

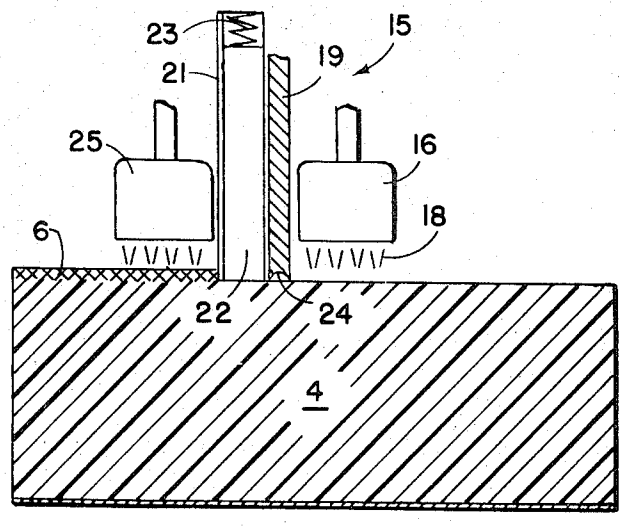


FIG. 2

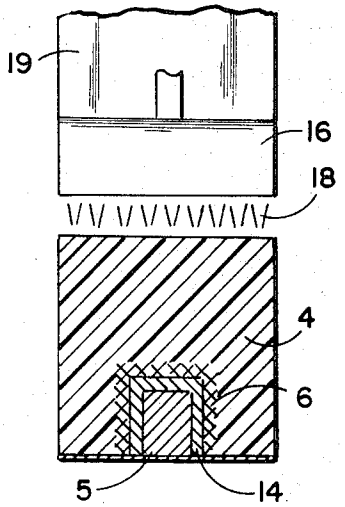


FIG. 3

REDUCTION OF ALUMINUM WITH IMPROVED REDUCTION CELL AND ANODES

This is a division of application Ser. No. 172,047 filed Aug. 16, 1971.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to aluminum electrolysis in a molten cryolite bath, commonly referred to as the Hall process. More particularly, the present invention relates to avoiding atmospheric oxidation of anodes, a problem which has long plagued the industry. Additionally, the present invention relates to means for increasing cell life.

In the production of aluminum by the Hall process, large numbers of individual electrolytic cells are employed. Each cell has a carbonaceous lining forming the cathode, with cathode collector bars buried therein. Suspended above each cell on iron rods are a plurality of carbon anodes. As electrolysis proceeds carbon on the anodes is gradually consumed and they are lowered further into the bath. Because of the high temperatures involved, carbon on the sides and top of the anodes exposed to the atmosphere tends to oxidize (i.e., to burn in air), considerably reducing the anode size. Anodes are further eroded in contact with the bath, particularly at the corners, which are current concentration points. The molten bath tends to erode the lining and to penetrate into cracks and pores therein, eventually causing the latter to become dimensionally unstable. At that point, a shut-down for re-lining is required.

2. Prior Art

In the past, many attempts have been made to improve the resistance to decomposition of both anodes and cathodes. As noted above, atmospheric oxidation above the forzen crust of the electrolytic bath is the main problem with anodes. In the case of the carbon potlining, penetration by bath elements causes cracking and heaving.

Historically, the greatest savings in power consumption in aluminum reduction potcells has come about by using lower and lower anode current densities with larger and larger anode areas, providing thereby greater areas in the underlying electrolyte and cathode for the current to flow at lower electrical resistance. Atmospheric oxidation of anode periphery not submerged in the electrolyte reduces anode area, increases carbon consumption, and so is doubly undesireable.

One of the oldest methods of preventing surface oxidation of the anodes, since the commercialization of the Hall process about 80 years ago, has been to splatter molten bath on the upper parts of the anodes or dip them in the molten electrolyte bath. Stirring tools or tools especially made for the purpose have long been conventionally used to splatter and coat the anodes with a fraction of inch of bath after they become red hot during operation. Also for 50 years or more, cryolite powder has been dusted on red hot anodes to which it adheres and wets. However, as labor becomes more expensive this type of hot hand work around a potcell becomes prohibitively expensive.

If the anodes are dipped in a molten bath in a rodding room production line operation prior to being introduced into the aluminum reduction furnace, they must be heated to red heat to make the bath adhere, and it never adheres well enough so that some is not broken off in handling and transportation, and it can be contaminated with unwanted silica and other impurities on the plant floors swept to recover the bath particles.

For 20 years or more it has been common practice to use as much as a 6 inch layer of alumina on the bath crust of a potcell to prevent the atmosphere from contacting the anodes where their temperature is highest near the bath. Since about 1.9 pounds of alumina are used per pound of aluminum produced, it has been advantageous to preheat alumina in this way while at the same time preventing atmospheric air from contacting and oxidizing the anode surfaces which are at the highest temperature. In more recent years more accurate control of the alumina content of molten electrolyte and better operating efficiencies resulting therefrom have made it expedient to add most of the alumina almost continuously, directly to the molten electrolyte. This makes it increasingly important to prevent surface oxidation of anodes by means other than thick layers of alumina on the crust of the electrolyte.

Anode oxidation by the atmosphere can be greatly reduced on a commercial scale by coating prebaked anodes with a layer of aluminum between 1/32 and 1 inch thick, depending on whether the aluminum is sprayed or cast on the surface. The disadvantage of this method is the inevitable oxidation of some of the aluminum when it is being applied and, again, when subjected to a week or more of heat from the red hot anode which it covers. The cost of the aluminum so oxidized is a substantial part or greater than the cost of anode carbon which would be lost without such protection.

U.S. Pat. No. 3,303,119 of Dell discloses coating anodes with a thin metal sheet attached with a bitumin mastic. The patent of Clukey et al, U.S. Pat. No. 3,442,786, discribes coating anodes with a stream of aluminum directed against them. The patent of Skantze et al, U.S. Pat. No. 3,236,753 discloses coating anodes with a cryolite mixture by dipping them in a molten bath.

My own patents, U.S. Pat. No. 3,372,105 and U.S. Pat. No. 3,428,545 disclose the use of a graded refractory material bonded to a flexible strip which is wrapped around the outer surface of an anode to render it immune to oxidation.

While these measures will indeed prevent unwanted oxidation, they are disadvantageous to some extent by being either expensive in materials or labor of application, imperfect in protection or in introducing unwanted elements such as phosphorus, sulphur, titanium, silicon or other elements harmful to ampere efficiency, life of the cathode potlining, or the purity of aluminum reduced.

In my prior U.S. Pat. No. 3,457,149, cathode potlining decomposition is prevented by impregnating the potlining with molten halide material of relatively low melting point, while applying a vacuum to the potlining. Also, in U.S. Pat. No. 2,270,199, of I. Thrune, there is disclosed means of applying to a once-baked graphite article a further coating of graphite paste made from graphite powder, a binder of liquid coal tar, an excipient and hardening agent, the excipient preferably being a volatile liquid boiling below about 150° C., and an antioxidant. This coating is baked on. The finished article will have a smoother surface and be freer

from minute cracks or pores than was the article after a single baking.

OBJECTS OF THE INVENTION

A general object of the present invention is to provide an improved method of producing aluminum.

A further object of the present invention is to increase aluminum reduction cell operating efficiency by maintaining anode dimensions during operation.

Another object of the present invention is to provide means for automatic addition of bath make-up materials.

A still further object of the present invention is to increase the life of an aluminum reduction cell by preventing bath penetration into the cathodic cell lining.

Yet another object of the present invention is to provide means of decreasing electrical resistance between anode and anode rod collector bar and cathode in aluminum reduction cells.

Still another object of the present invention is to provide a method of impregnating aluminum reduction cell anodes and cathodes.

Various other objects and advantages of the invention will become clear from the following description of embodiments thereof, and the novel features will be particularly pointed out in connection with the appended claims.

THE DRAWINGS

Reference will hereinafter be made to the accompanying drawings, wherein:

FIG. 1 is a vertical cross section through an aluminum reduction cell employing the protective coatings of the present invention;

FIG. 2 is a side elevation of a prebaked carbon cell lining block or segment being coated in accordance with the invention; and

FIG. 3 is an end elevation of FIG. 2.

SUMMARY OF THE INVENTION

In one aspect, the present invention comprises impregnating the top and sides of aluminum reduction cell anodes with aluminum fluoride or other compounds normally required in aluminum reduction baths and which are depleted by volatilization and gradual adsorption into the cell lining. This increases cell operating efficiency by preventing atmospheric anode oxidation and, at the same time, maintains bath composition at a constant level with respect to the compounds added. The carbonized pitch presents a more dense carbon surface to the bath, even after melting of the fluoride or other ingredient, lessening corner erosion and other undesireable effects. The protected anode provides maximum anode area and lower electrical resistance, not only through the anodes but also within the bath between anode and cathode. This allows higher currents to be used with resultant production increase.

A further aspect of the present invention comprises impregnating the cathode bottom with a penetrating graphite coating which seals up minute cracks and pores therein and, by preventing penetration by the molten bath or molten aluminum, significantly increases cell life. The graphite also increases conductivity. Similarly, the cathode side walls are impregnated with a fluorspar-pitch mixture which decreases conductivity while at the same time sealing cracks, etc.

Another aspect of the invention is in applying the above-described materials so they penetrate into and become integral with the underlying carbon.

DESCRIPTION OF EMBODIMENTS

Generally, these coatings consist of a solid bitumastic adhesive such as coal tar pitch and an electrolytic bath ingredient like aluminum fluoride, cryolite, sodium fluoride, sodium carbonate, calcium fluoride or alumina, mixed with the bitumin. Such adhesive coating mixtures are applied to the hot baked anode surface or hot surface of the anode sides and top, to densify and protect the surface.

When the baked cathode potlining is treated, graphite is mixed with the coal tar pitch and applied to a heated surface of the potlining, which absorbs the bitumin and graphite into the surface pores and cracks by capillary attraction, and thereby densifies and lessens penetration of the fused bath into the potlining during potcell operation.

The method of applying and sealing the coatings comprises preheating and evacuating relatively small surface areas of the carbonaceous anode or cathode immediately before applying the adhesive coating mixture. Only a limited amount of the mixture, that which can be absorbed in the surface, is applied at one time. After application the surface is further heated, gradually, to burn off most of the volatiles in the pitch and cause the mixture to penetrate further into the surface being treated. As that surface area cools, the pore spaces from which air has been at least partly expelled by heating or other evacuating means draw inward the coating mixture to fill the vacuum. When the heating flame or radiant mass moves over the surface to be sealed, followed closely by an applicator of the coating mixture, a continuous and economical sealing process results. The coal tar pitch may be kept molten and continuously stirred with powdered fluoride or other ingredient of the bath or graphite, or the premixed and proportioned coating may be cast in block form which is pressed against the preheated carbon surface to be sealed and thereby melted where and as needed.

Many other binders may be used as adhesives, such as other hydrocarbons, or carbohydrates like molasses, but coal tar pitch of high melting point and low volatile content makes more dense carbon and a more adherent coating.

The invention may be carried out by heating and evacuating a part of the anode surface quickly, with radiant or conducted heat or a clean gas flame, to a temperature of about 300° C., and applying proximate thereto a melted coal tar pitch, also at 300° C., in which there is suspended 5 to 80 percent of an electrolyte ingredient such as aluminum fluoride or mixture of these. As the anode heater is moved along the anode surface, the pitch-AlF_3 mixture is applied in only sufficient quantity to be absorbed into the surface. A second heating step gradually heats the impregnated surface to a temperature sufficient to drive off most of the volatile content of the pitch, which is preferably very low. A preferred mixture for this operation is three parts of a high-melting, low-volatile coal tar pitch with one part of dry aluminum fluoride (−300 mesh) suspended therein. The abovedescribed fired coating essentially fire-proofs the anode under conditions and for the du-

ration of potcell use. However, a second treatment may be desireable, with the mixture in this instance containing either aluminum fluoride or other molten bath ingredients. For example, the second coating may comprise sodium fluoride or a mixture of aluminum fluoride, sodium fluoride, sodium carbonate, cryolite and alumina. If the second coating is applied directly after firing of the first coating, preheating the surface is not required. When this procedure is followed, the pitch-additive mixture is forced into the interstices of the anode carbon surface, tightly sealing these. When all the anode sides and top which would be exposed to atmospheric oxidation are sealed, the anode is ready to be used in a potcell for reduction of aluminum. As the anode heats during operation, its upper portions gradually heat and carbonize the absorbed pitch, which should have a high melting point and coking value. If the heating of the anode is gradual in the potcell, any remaining pitch volatiles will tend to escape inwardly from the anode areas away from the sealed surface. An important feature of this practice of the invention is the fact that the anode surface when sealed with pitch is more dense and difficult to oxidize even when the amount of aluminum fluoride or cryolite admixed with the pitch is relatively low. It appears at least possible that a reactive mechanism is present (aluminum fluoride is known as a Friedel-Crafts reagent).

As an alternate to using a molten mixture of fluoride and coal tar pitch, a precast slab or block of the mixture may be rubbed on the anode surface which may then be somewhat hotter than 300° C. to melt but not volatilize the pitch ingredients.

When the above temperatures are used for preheating and application of the mixture, a coal tar pitch of the following specifications gives satisfactory results. The temperature of application is chosen so that no volatiles are given off by the pitch during initial application.

EXAMPLES OF COAL TAR PITCH SPECIFICATIONS

Softening pt. C-A	115°C.	Distillation: 0°–270°C.	0.0%
Benzene insoluble	30.42%	0°–300°C.	0.0%
Quinoline insoluble	11.51%	0°–360°C.	2.2%
Conradson coking value	59.39%	0°–400°C.	13.0%
Specific gravity 25°C./25°C.	1.320		
Ash	0.16%	Analyses:	
		carbon	92.34%
		hydrogen	4.33%
		sulphur	0.61%

Instead of the above described adhesive, coal tar binders may be used with or without hardening agents like carbon tetrachloride which convert the tar to pitch upon heating. In fact, almost any adhesive may be used which will bind pulverized bath ingredient particles to a carbonaceous anode without introducing elements harmful to either the electrolytic bath or the aluminum reduced therefrom. Hydrocarbons or carbohydrates which carbonize with the least possible loss of volatile matter are best to make a dense, nonporous surface which will not oxidize. Specifically, molasses may be used mixed with pulverized bath ingredients like cryolite, alumina or aluminum fluoride, and heated above boiling temerature before application to the anode face, which should be preheated at least equally hot so the mixture may be applied as thin as possible. Immediately after the molasses-solid mixture is applied, additional powdered material may be pressed into the wetted surface of the anode and the surface allowed to cool. When the anode is used, it heats slowly from its bottom end, which is immersed into the molten bath at about 960° C. Since only the upper sides and top of the anode are not immersed in the bath, it is only these upper portions which need be coated with the nonoxidizing coating. Actually, all binders containing carbon which carbonizes will have some carbon surface exposed to oxidation, and at red heat (about 500° C) such carbon will oxidize leaving the bath ingredient particles exposed to protect the anode surface from air until it is submerged in the molten bath fusion.

Bath ingredients which are suitable for practice of the invention in preventing oxidation of anodes by the atmosphere are: aluminum fluoride, sodium fluoride, sodium carbonate, cryolite, calcium fluoride, lithium fluoride, magnesium fluoride and alumina or mixtures thereof. Alumina is not preferred, in that it leaves a more porous coating through which the atmosphere more easily penetrates. Where alumina is added to an adhesive binder such as molasses, cryolite should be pressed into the surface of the anode after it has been wetted by the molasses-alumina mixture. Alumina does have the advantage of having a coefficient of expansion closer to that of carbon than cryolite.

Aluminum fluoride is the material of choice, at least for the first application, because of its exhibited ability to penetrate with the pitch into the surface. Aluminum fluoride mixtures with pitch penetrate a carbon surface as much as three times the depth penetrated by cyolite pitch mixtures under similar conditions of application. As burning off of the volatiles from the first application will leave at least some porosity, mixtures of sodium fluoride, sodium carbonate, cryolite, calcium fluoride and alumina, which don't penetrate as readily may be employed in the second impregnation. Sodium fluoride or sodium carbonate may be mixed with aluminum fluoride on either the first or succeeding applications since mixtures of 40% AlF_3 and 60% NaF begin to sinter together to form cryolite at temperatures as low as 500° C. and provide more perfect oxidation resistance.

The adhesive binder or mixture with non-oxidizing ingredients should not contain any substantial amounts of the following, which are either insoluble in or deleterious to the bath fusion or aluminum reduced therefrom: fused alumina, nitrides, silicon, titanium, sulphur, phosphorous or other metal impurities.

About 0.02 to 0.06 lbs. of bath ingredients are consumed per pound of aluminum reduced, or about 0.04 to 0.12 lbs. of bath per pound of anode carbon used. Bath ingredients are partly recovered by dissolving them out of potlinings where they have been absorbed, or from the filters for fume evolved from the reduction furnaces, but in all cases some new bath ingredients must be added as make-up for these losses, whether they are ultimately recovered or not.

It is to be noted that anode makers sometimes provide anodes with sloped shoulders at the top and cut-off or rounded corners, for the simple reason that these are the areas subject to the most severe oxidation and erosion. With the impregnating coatings of the present invention such current-limiting shapes may be and preferably are avoided. Even when the aluminum fluoride or other bath ingredient melts and flows into the bath, the carbonized pitch surface is more dense than an ordinary anode surface and erosion due to electrical and other effects is reduced.

As an alternative to the second step noted hereinabove, wherein cryolite, alumina or other bath-ingredient particles are mixed with pitch and impregnated over the aluminum fluoride-pitch, these particles may be blasted directly onto the hot surface of the anodes immediately following the first aluminum fluoride-pitch application, before volatiles are burned off. These particles will become embedded in the hot, still soft surface and fill what pores there may be.

For the highly penetrating aluminum fluoride-pitch treatments, the particle size of the fluoride or bath ingredient mixed therewith should of course be small; 80 percent minus 300 mesh (tyler screen) is preferred. With other, less penetrating mixtures, size-graded particulates will produce a more dense surface. A mixture of 50 percent −28 mesh +48 mesh and 50 percent −100 mesh +300 mesh is typical.

When the invention is applied to the protection of potlining against the erosion of molten bath due to electromagnetic circulation and due to sodium penetration which decomposes and heaves the potlining, the procedures outlined above for anode protection are generally followed. In operation, it is desired that the cell bottom be conductive but that the sides, while still part of the cathode, be relatively nonconductive. Thus, for bottom coating, graphite powder is substituted for powdered bath materials. To make the side potlining electrically non-conducting, a calcium fluoride (Fluorspar) -pitch mixture may be used either in a continually molten or pasty condition or premixed and cast in a solid block. In any case the preferably prebaked side potlining surface is heated over a little area at a time and the mixture applied to the extent that it absorbs into the potlining surface, coats it and makes it more dense and hard.

When a carbonaceous bottom (cathode) potlining is treated, it has preferably been already baked. Surface parts are then reheated in relatively small areas at a time, evacuated, and the pitch-graphite mixture containing 5 to 70 percent graphite is applied in a continually mixed liquid or pasty from, or in a premixed proportion and then cast in block form which may be rubbed against the hot, evacuated cathode surface to seal it. Where a rammed potlining is used (rather than a potlining built of prebaked blocks), the potlining is baked out by passing current through the potlining from the anodes which rest on it (or are spaced from the potlining with perhaps an inch of crushed coke to act as a resistance heater), the hot cathode potlining bottom is conveniently sealed by cleaning it and rubbing thereon a precast block made of a mixture of graphite powder and pitch. Since the potlining area is very hot and the fumes from the pitch irritating, a handle with pipe attached to hold the block is necessary. Where large and deep cracks have formed in the bottom potlining, molten pitch continuously mixed with graphite powder is squirted under pressure into the cracks. After the mixture has time to bake enough so no more fumes are evolved from the pitch, an additional layer is applied. Where prebaked carbon blocks are used to build the cathode potlining, only the top surface need ordinarily be treated with the graphite-pitch mixture before or after the blocks are set in place, but an application of the mixture on the upper surface of the lining between blocks is preferable after it has baked, as it helps to seal these narrow spaces or cracks that develop in baking them.

An application of the pitch-graphite mixture to the inside of the slot in potlining blocks adapted to receive the collector bar, and the hole for the stub of prebaked anodes, improves electrical contact, provided the mixture is baked sufficiently to drive off all or most of the pitch fumes before the cast iron is poured in the potlining block to secure the steel cathode collector bar thereto or before the cast iron is poured in the anode hole to attach the steel anode stub thereto. With less RI^2 heat from the contact, the anode top is cooler and suffers less atmospheric oxidation.

The invention may be better understood by reference to the drawings, where FIG. **1** illustrates a potcell cross section which is conventional excepting that novel kinds of coatings of the invention have been applied to the anodes to protect them from oxidation and to the side and bottom potlining to inhibit erosion and sodium penetration. FIG. **2** illustrates a side view and FIG. **3** and end view of a prebaked potlining segment for use in the bottom potlining of the potcell of FIG. **1**, during coating with a graphite-pitch mixture.

The apparatus illustrated in FIG. **1** comprises the usual rectangular steel shell with a flat bottom **1** and upright sides **2**, supported and reenforced by structure not shown. The refractory alumina lining **3** lines the shell around the steel bottom and sides, and the carbonaceous cathode potlining and side potlining segments **4** which are prebaked and made in the usual manner from anthracite coal, tar and pitch binder. Bottom lining **4** has a graphite-pitch coating **6** in accordance with the invention, with reference to FIG. **2** and **3**. As common in potcells made with prebaked segments, rectangular steel collector bars **5** are positioned in each segment and held there by pouring cast iron **14** between the carbonaceous segment **4** and steel bar **5**. However, before the cast iron is poured, the area of carbon surface which the cast iron contacts is sealed with a graphite-pitch mixture in a manner similarly described with reference to FIGS. **2** and **3**. In a similar manner, the calcium fluoride (fluorspar)-pitch coating **7** is applied to the side potlining segments. The process may be performed on individual segments before the segments are assembled to form the potlining and repeated after the lining is complete.

After the cell has been operating as a reduction cell for a few days, it accumulates a layer of molten aluminum **8** reduced from the fusion of electrolytic bath **9** which overlays it and on which the crust **10** is normally present and in which a variety of lengths of anode carbons **11** are suspended depending on the number of days in which they have been in service. The extremes of length illustrated are shown by the new anode **11A**, which is about 18 inches high and the old anode **11B**, only 7 inches high, which is called an anode butt because it is about ready to be taken out and replaced by a new anode. These anodes have been protected

against atmospheric oxidation by one or more impregnating treatments 12 applied before introduction into the potcell as new anodes, but only on the anode top and sides down as far as the molten electrolyte. The bottom of the anode and the sides about 6 inches up from the bottom need no protective coating (the coating may be applied to these areas if needed for make-up purposes).

Current for electrolytic reduction enters the reduction cell through the steel anode studs 13 suspended by overhead structure not shown, and secured to the anodes 11 by cast iron poured after the prebaked anodes have been baked and after the anode stub hole has been coated with a graphite-pitch mixture 6 to make the surface in contact with the cast iron more electrically conductive.

A preferred method of applying the novel coatings and one which may be used in coating either anodes or potlining is illustrated in FIG. 2 and FIG. 3, where the potlining segment top surface is coated with the graphite-pitch coating 6 by the coating apparatus 15 which is moved from one end of the top surface to the other in the course of the coating operation.

The burner manifold 16 provides flames 18 of gradually increasing lengths to superficially preheat the potlining surface as it moves along it. The asbestos sheet 19 heat insulates the burner from the metal framework 21, which houses a freely moving block of graphite-pitch mixture 22, which has been proportioned, premixed and precast in a shape of slightly less horizontal cross section dimension than the framework 21. Mixture 22 is pushed downward against the hot potlining surface by a spring 23, so that the block of graphite-pitch mixture melts and spreads the coating 6 uniformly over the top of the potlining, sealing its surface against penetration. It will be appreciated that when a liquid suspension is applied, as with aluminum fluoride-pitch, framework 21 will be an open-bottomed container and spring 23 would be replaced with stirring means. After the coating 6 is applied, a second burner 25 burns out the volatiles therein.

Optionally, the asbestos board 19 may have a cup-shaped surface 24 which rubs on the anode surface as it moves with the apparatus 15. The cupped surface is evacuated through pipes and pumps (now shown) so that the graphite-pitch mixture which melts is forced into the surface interstices by atmospheric pressure. The creation of a more perfect vacuum beneath the plastic mixture is aided by the subsequent cooling of the potlining surface in which the remaining gases in the potlining surface contract and the volatiles condense. The elements of the assembly 15 are held together and moved by a suitable framework (not shown). Either manual or automatic operation may be employed. The method illustrated is intended to provide the final coating on carbonaceous pieces whether these be pieces of anode or cathode. As previously described, it is preferable to use bath ingredient-pitch mixtures when coating the anodes. Cryolite, sodium fluoride and especially aluminum fluoride are the major bath ingredients, although the lesser constituents of the bath may also be used.

Various changes in the details, steps, materials and arrangements of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as defined in the appended claims.

For example, unbaked anodes or cathodes (as well as baked anodes and cathodes) may be impregnated or coated with the materials and in a manner similar to that described above.

What is claimed is:

1. An electrolytic cell for use in the reduction of alumina dissolved in a molten salt bath comprising:
   a steel shell having a refractory alumina lining;
   a carbonaceous cathode having a bottom and side walls defining the interior of said cell and including cathode collector bars embedded therein;
   a plurality of carbonaceous anode means suspended in said cell spaced from said bottom and side walls;
   the bottom of said cathode having a conductivity-increasing and densifying coating of graphite and pitch baked therein; and
   the side walls of said cathode having a conductivity-decreasing and densifying coating of fluorspar and pitch baked therein.

2. The cell as claimed in claim 1, and additionally comprising an oxidation-resistant impregnation on at least the portion of said anodes exposed to the atmosphere during operation of said cell, said impregnation comprising particles of an ingredient of said molten salt bath.

3. The cell as claimed in claim 2, wherein said oxidation-resistant coating comprises particules of a material selected from the group consisting of cryolite, aluminum fluoride, sodium fluoride, sodium carbonate, calcium fluoride, lithium fluoride, magnesium fluoride and alumina adhered to said anodes with a bitumastic adhesive.

4. The cell as claimed in claim 1, wherein said pitch is a high-melting, low volatile coal tar pitch.

5. The cell as claimed in claim 3, wherein said bitumastic adhesive is a high-melting, low-volatile coal tar pitch.

6. The cell as claimed in claim 1, and additionally comprising a baked coating of graphite and pitch adjacent said cathode collector bars.

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