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ELECTROLYSIS OF BRINE USING COATED CARBON ANODES

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ABSTRACT OF THE DISCLOSURE

Novel electrodes are described having an electroconductive base and a coating applied to the base. The coating consists of the sulfides, nitrides, borides and carbides of the elements aluminum, tantalum, titanium, bismuth, tungsten, zirconium and hafnium mixed with the metals, oxides, sulfides, nitrides, borides and carbides of the elements gold, silver, platinum, palladium, ruthenium, rhodium, iridium, osmium, nickel, chromium, lead, copper and manganese. The use of the novel electrodes in alkali metal chlorine cells, both diaphragm and mercury type, alkali metal chlorate cells and other similar electrolytic applications is disclosed.

BACKGROUND OF THE INVENTION

In recent years much research activity has centered around the acquisition of improved electrodes for electrolytic cell operation. This activity has been spurred on by the desire to produce electrodes having long life and low voltage characteristics in order to achieve substantial power savings in electrolytic cell operations and reduced electrode and maintenance costs. The evidence of this activity is amply demonstrated by the numerous patents issued in the United States and abroad on new electrodes. Electrodes having platinum group metals on their surfaces and a base of metal such as titanium have been reported (U.S. Pat. 3,242,050). Electrodes of a titanium base with material such as ruthenium oxide as a coating have also been described. While electrodes of these types achieve lower voltage characteristics in operation than a conventional graphite electrode in an alkali chlorine cell for example, they are subject to some drawbacks. Loss of coating in the case of platinum metal coating when a short circuit occurs is sometimes encountered. Contamination by the contents of an electrolytic cell can lead to loss of coating surface. Poor adherence of coatings to the metallic base employed is also encountered during a prolonged electrolytic operation. Since these coatings tend to be composed of costly materials, any loss of coating must be considered undesirable.

In accordance with this invention novel mixtures of materials are employed to provide low voltage electrolytic surfaces for use as electrodes in electrolytic cell operations which are resistant to contamination by cell electrolytes and products and which may be firmly bonded to a base metal with little or no tendency to lose that bond during electrolysis. Furthermore electrodes constructed in accordance with this invention exhibit satisfactory overvoltage characteristics and an inertness to conditions of electrolysis that insure long life.

In accordance with this invention an electrode is prepared for use in an eletctrolytic cell, particularly for use in alkali metal chlorine and chlorate cells by coating a base metal with a mixture of compounds and/or elements. The mixture of materials affixed to the base metal is composed of at least one member of the group of the elements tantalum, titanium, aluminum, hafnium, zirconium, bismuth and tungsten. This member is provided in the mixture on the base metal in the form of a boride, carbide, nitride or sulfide. The novel mixture also contains at least

one member of the group of elements silver, gold, iron, nickel, chromium, palladium, platinum, rhodium, iridium, ruthenium, osmium, lead, copper and manganese. These elements may be in the form of the metallic element itself, or its oxide, nitride, carbide, boride or sulfide.

The coatings of the instant invention may be applied in various ways to provide the desired mixed coating. Thus, for example, titanium sulfide particles may be mixed with a commercial metal resinate, such as platinum resinate or iridium resinate, which are manufactured by Englehard Industries, Inc., and the mixture applied to the titanium anode base and heated to temperatures of 400 to 600° C., with consequent breakdown of the platinum or iridium resinate to the corresponding metal. In such a case the amount of platinum or iridium resinate is enough to provide titanium sulfide in the range of 5 to 95 mole percent, preferably 25 to 75 mole percent of the sum of the platinum metal plus the titanium sulfide on a molecular basis in the coating and the heating is usually conducted under vacuum or in a gas which is inert to titanium sulfide or at least does not substantially decompose the sulfide. Suitable temperatures for this purpose are 300 to 550° C.

In like manner, sulfides of other metals, including bismuth sulfide (Bi_2S_3), tantalum sulfide (Ta_2S_4), aluminum sulfide (Al_2S_3), tungsten disulfides (WS_2), tungsten trisulfide (WS_3), zirconium disulfide (ZrS_2) and hafnium sulfide (HfS_2) may be applied to metal base such as a titanium base with the above platinum type resinates in the same way as titanium sulfide is applied and in the same molecular proportions.

Coatings of metal oxide-metal sulfide and/or metal sulfide mixtures, such as mixtures of ruthenium dioxide, rhodium oxide or palladium dioxide or other corresponding conductive oxides of a platinum group metal, or lead dioxide or manganese dioxide, may be applied to a titanium metal base, for example, by mixing the desired metal sulfide with a solution of a resinate of these platinum group metals and heating a coating of the resulting mixture at 300 to 600° C. The oxide or metal, which forms as the resinate breaks down, forms the oxide and tends to bond the sulfide to the titanium base and/or to provide the base with a conductive coating suitable for the purposes herein contemplated.

Where a resinate of a metal which forms electroconductive oxides or corrosion-resistant metal is employed, the amount of such resinate may be at any convenient level. However, since titanium sulfide, zirconium sulfide and the like are electroconductive, the presence of both a noble metal, or noble metal oxide on the one hand and a conductive sulfide on the other, offers certain advantages. The noble metals or noble metal oxides have high conductivity and chemical resistance but are expensive, and the combination of a less expensive metal such as titanium sulfide permits reduction in chemical cost while retaining the advantageous conductivity and chemical resistance. Films containing 5 to 95 percent, preferably 25' to 75 percent, of the titanium or other metal sulfide on the one hand, and 95 to 5 percent, preferably 75 to 25 percent on a molar basis, of a noble metal or noble metal oxide on the other hand, may be provided.

Additionally, it is to be understood that any other organic solution of noble metal or platinum group metal, which compound or solution decomposes to metal or oxide on heating, can be used in lieu of the corresponding resinate thereof. This includes the application of the aforesaid sulfides with water or organic solutions of palladium di-n-butylamino nitrile, iridium chloride, ruthenium nitrosobromide, chloroplatinic acid, etc. Typical of such solutions is a mixture in the proportion of 20 cubic centimeters of isopropyl alcohol, 1 gram of ruthenium tetrachloride, and 20 cubic centimeters of linalool having dispersed therein any of the aforesaid sulfides.

In the above discussion particular emphasis has been placed upon the use of sulfides of the metals aluminum, zirconium, bismuth, tantalum, titanium, hafnium and tungsten, and in particular titanium sulfide. While any of the sulfides of these metals may be utilized, it is also contemplated that carbides, nitrides and borides of these metals may also be employed in preparing the novel coating mixtures of this invention. Thus, titanium carbide particles can be incorporated in a resinate solution of a platinum group metal and the solution applied to an appropriate electrically conductive base. After the base is coated with the titanium carbide containing resinate, for example, a platinum resinate (7.5 percent platinum), the electrode surface is heated to 300 to 600° C. in air to produce a coating of titanium carbide-platinum on the metal base. A similar procedure can be followed to provide mixtures (in the proportions specified above for sulfide and oxide) of the carbides, nitrides, borides and sulfides of tantalum, tungsten, zirconium, hafnium, aluminum and bismuth with the metals palladium, platinum, rhodium, iridium, ruthenium, osmium, silver, gold, iron, nickel, chromium, lead, copper and manganese.

It is also within the contemplation of this invention to utilize in such proportions the metals of the last enumerated group in the form of sulfides, borides, carbides, and nitrides. Thus, the mixtures produced according to this invention include for example, titanium sulfide-ruthenium sulfide, titanium sulfide-platinum sulfide, titanium carbide-ruthenium carbide, titanium carbide-ruthenium sulfide, tantalum sulfide-platinum sulfide, tungsten carbide-ruthenium sulfide, titanium sulfide-ruthenium oxide, titanium sulfide-palladium oxide, titanium sulfide-rhodium oxide and other similar mixture of compounds of the group platinum, palladium, rhodium, iridium, ruthenium, osmium, silver, gold, iron, nickel, chromium, lead, copper and manganese mixed with one or more of the borides, carbides, nitrides and sulfides of aluminum, titanium, tantalum, tungsten, hafnium, zirconium and bismuth.

In applying mixtures of the metals of the two groups disclosed herein in the form of nitrides, carbides, sulfides and borides, water, toluene or other organic and inorganic liquid medium can be employed to slurry the desired particles and the particles can be painted on the electrode surface to be coated. Subsequent heating to temperatures of 250 to 600° C. to evaporate solution results in firm adherence of the particles to the electroconductive base used. To improve adhesion a small amount of binder such as silicic acid solution, sodium silicate-titanium hydroxide or titanic acid in water may be added to the slurry before its application to the base. Also resinates of titanium, silicon, boron, or platinum group metals may be added. As a further metal a molten mixture of two of the metal members, e.g., titanium and ruthenium may be sprayed on the anode substrate. Then the metal mixture may be heated in sulfur vapor, H_2S, diborane, nitrogen, methane or the like to convert the surface at least partly to sulfide, boride, carbide, nitride, etc. When platinum is so applied, it usually remains in metallic state with the titanium or similar member converting as herein contemplated. With respect to these mixtures, heating is usually in the absence of air, water or oxygen to inhibit breakdown of the compounds into oxides and metals.

Although the above description of anodes had primarily referred to titanium metal as the base substrate, it is to be understood that other corrosion-resistant bases, such as tantalum, zirconium, tungsten or the like, may be substituted for titanium metal and anodes provided according to the above disclosure. Especially advantageous anodes may be obtained using conductive metal oxides, such as lead dioxide, manganese dioxide or magnetite, either as a base or as an undercoating on a metal base such as titanium, chromium, tantalum, lead, stainless steel or other metal base. This oxide base or undercoating may then be coated with ruthenium oxide or other conductive oxide of platinum group metal or with platinum or other platinum

group metal and a sulfide, boride, nitride or carbide of the group titanium, tantalum, zirconium, hafnium, aluminum, bismuth and tungsten to provide a low cost anode for alkali metal chloride electrolysis in mercury or diaphragm cells. Such anodes are light in weight, sturdy, and have a low chlorine overvoltage.

Other anodes which may be used for the electrolysis of aqueous alkali metal chloride solution to produce chlorine and alkali metal hydroxide or alkali metal amalgam are those which provide an anode surface which is exposed to the solution composed of silicides, borides, nitrides, carbonitrides, and carbides of titanium, zirconium, tantalum, hafnium or tungsten. The anode may be composed entirely of one or more of these compounds or the substrate may be metal and the surface carbide, nitride, carbonitride, silicide or boride.

As a typical illustration, freshly cleaned titanium metal or titanium metal alloy containing 0.5 to 5 percent by weight of aluminum, magnesium, molybdenum, tin, chromium or iron, may be heated at 800 to 1000° C. in an atmosphere of methane which may be at a pressure of 0.5 to 10 atmospheres' methane pressure (with or without inert diluent gas) to cause the surface to convert to the carbide TiC or mixed carbide of the base metal. Further titanium metal which has been coated with carbon black may be heated to carbide forming temperature to form carbide on the surface thereof.

Boride surfaces may be obtained by heating the titanium metal anode base in contact with diborane, and nitride surfaces by heating the metal in an atmosphere of nitrogen or ammonia at a nitrogen, ammonia or diborane pressure of 0.1 to 10 atmospheres with or without inert diluent gas.

Tantalum, zirconium, hafnium and tungsten anodes may be coated in the same way using these metals in lieu of the titanium metal substrate.

In a further embodiment, carbon or graphite may be used as the anode substrate, and is coated with an electroconductive coating which is highly resistant or effectively inert to the corrosition and/or erosion which tends to occur when it is exposed as an anode in electrolysis of an alkali chloride such as sodium or potassium chloride such as the mixtures described above. Metallic platinum, palladium, ruthenium, rhodium or other platinum metal, or the corresponding oxide thereof such as ruthenium dioxide or palladium dioxide may be applied above or in admixture with titanium dioxide, silicon dioxide, zirconium dioxide or magnetite to the graphite or carbon base. These coatings may be applied by metal spraying, painting, chemical deposition or by electrodeposition processes.

For example, a metal coated graphite or carbon may be heated to 400 to 600° C. in steam to form the corresponding oxide thereof. Also the carbon or graphite may be thoroughly coated and surface impregnated with a solution of a resinate of a platinum group resinate such as ruthenium resinate and then heated in air at 300 to 500° C. The sulfides, nitrides, carbides and borides of the other metals employed in the novel coatings, that is aluminum, titanium, tantalum, tungsten, hafnium, bismuth and zirconium, may be applied in the spray solutions or as resinates.

As a general rule, graphite or carbon thus coated does not have the desired stability when used as an anode in the electrolysis of alkali metal chloride because the thin coatings (rarely in excess of 0.0001 inch and often in the range of 0.00001 inch or below) flake off the anode during electrolysis.

This may be prevented or suppressed by impregnating the graphite or carbon or treating the surface thereof with a hydrophobic sealant or an agent which renders the carbon or graphite surface hydrophobic or water-repellant.

The graphite or carbon anode base may be of the same carbon which is now conventionally used an anodes in a alkali chlorine cells. In its unimpregnated state, it is por-

ous. As herein contemplated this porous anode is rendered hydrophobic or water repellant before and/or after application of the electroconductive coating. Thus, the anode comprises a hydrophobic or non water wetting or water repellant base with the resistant electroconductive coatings discussed above disposed on the base.

To impart hydrophobic properties to the carbon it may be subjected to the action of methyl trichlorosilane, vinyl trichlorosilane or other chlorosilane containing up to 6 carbon atoms, usually in the vapor state and at temperatures up to 200° C. Also, the graphite or carbon may be impregnated with a liquid silicone resin, such as methylpolysiloxane. In addition, the electrode may be impregnated with solid methyl or other alkyl polysiloxanes or silicones, such as dimethyl silicone, phenylethyl silicone, cyclohexyl silicone resin, diphenyl silicone resin ethyl silicone resin or the like. Also, the electrode may be impregnated with solid polymers of fluoroethylenes, such as polytetrafluoroethylene or polymers of vinylidene fluoride.

The graphite or carbon electrodes may be impregnated with solid hydrophobic or water-repellant resins by dipping the electrode into a solution or slurry of the resin, if desired, under pressure, and then vaporizing off the solvent. Alternatively, the solvent or liquid in which resin is dissolved or suspended may itself be polymerizable. Typical liquids of this type include linseed oil, methyl methacrylate, methyl acrylate acrylamid, styrene, vinylidene fluoride, tetrafluoroethylene or like compound containing a polymerizable —C=C— group. The hydrophobic or water-repellant resin and a polymerization catalyst are dispersed, dissolved or suspended in the liquid to produce a fluid mixture and the carbonaceous electrode is impregnated by dipping it into the suspension, if desired, under a superatmospheric pressure. Thereafter, the impregnated electrode is heated to activate the catalyst and polymerize the solvent.

Following impregnation as described above, the carbonaceous electrode is coated with the novel coating mixtures described above. After the coating operation the anode may be impregnated with or dipped into a solution of the water-repellant material in order to close pores in the coating.

The electrodes described above may be of any convenient construction, such as in the form of screens, grids, expanded metal sheets or rods of any geometric cross-section.

Rod-like electrodes are advantageous in some cases because they have two or more sides and can readily be coated on all sides. Inevitably some loss of the surface noble metal or oxide or sulfide or other coating takes place as for example an alkali metal chlorine cell is operated. This causes a gradual depletion of the coating which will be observed by increase in voltage between anode and cathode. When the voltage rise becomes appreciable to make reduction in power consumption desirable, the rod electrodes may be rotated to present a fresh surface of the coating and this may be continued until the coating on all sides of the rod has been consumed. By this means the life of the electrode is longer and interruption of cell operation for anode change avoided.

As explained above, the anodes hereindescribed have the advantage that they are dimensionally stable and remain unaffected over a long period of time, e.g., one to three or more years, when used in the electrolysis of sodium or potassium chloride in a mercury cathode cell or in a diaphragm cell. Since they are of long life, they may be maintained at a close but essentially constant spacing from the cell cathode, with consequent power savings, decrease in plugging of diaphragms or contamination of mercury amalgam.

The following examples are illustrative of methods suitable for preparing the novel electrodes hereinabove disclosed.

EXAMPLE I

A coating composition is prepared by mixing toluene solution of 3.75 grams of platinum resinate (7.5 percent platinum by weight), 1 gram of titanium sulfide and 4 grams of toluene. The titanium sulfide is thoroughly mixed in the toluene-resinate mixture and the resulting mixture is painted on a titanium strip which is prior to painting, pickled in HCl solution. The painted surface is heated in air to 450° C. for a period of 1 hour. The procedure is repeated five times to provide a tightly bonded coating of titanium sulfide-platinum to the titanium base.

EXAMPLE II

A coating composition is prepared by mixing 0.5 gram of ruthenium oxide and 2 grams of titanium sulfide with 10 cm.^{3} of toluene. The composition is painted on the surface of a titanium metal strip. The strip is heated to a temperature of 350° C. in air. The strip is cooled, recoated and then reheated. This procedure is followed until five coats are applied and subjected to heat in air at 350° C. The finished strip contains titanium sulfide-ruthenium oxide on the surface and is suitable for use as an anode in the electrolysis of alkali metal chloride solutions.

EXAMPLE III

A coating composition is prepared by mixing 1 gram of ruthenium oxide, 1 gram of titanium carbide with 10 cm.^{3} of toluene. A titanium mesh strip is painted with this mixture and heat treated in air at a temperature of 350° C. for 1 hour. The process of painting and heating is repeated five times. The electrode formed contains a coating of titanium carbide and ruthenium oxide and is suitable for use as an anode in the electrolysis of alkali metal chloride solutions to produce alkali metal hydroxide and chlorine.

EXAMPLE IV

A coating composition is prepared by mixing 1 gram of ruthenium oxide and 1 gram of tungsten carbide with 10 cm.^{3} of toluene. A tantalum strip whose surface has been previously cleaned by washing with a concentrated HCl is painted with the above mixture. The painted surface is heat treated to a temperature of 350° C. for one hour in air. The process of painting with the above mixture and heat treating the painted surface is repeated until five coats have been applied and heat treated. The electrode formed contains a titanium base with a coating of tungsten carbide and ruthenium oxide on the surface. The finished electrode is suitable for use as an anode in the electrolysis of an alkali metal chloride solution to produce alkali metal hydroxide and elemental chlorine.

EXAMPLE V

A coating mixture is prepared by mixing 1 gram of platinum sulfide (PtS_2) with 2.5 grams of titanium sulfide in 10 cm.^{3} of hydropropyl alcohol. The mixture is painted on a titanium metal strip and the coated metal strip is then heated at 500° C. for 20 minutes. The strip is then cooled, recoated with said mixture and reheated to the same temperature for the same period of time. This procedure is repeated five times. The finished electrode has a strong, cohesive coating of platinum sulfide and titanium sulfide bonded to the titanium base metal.

EXAMPLE VI

A coating composition is prepared by mixing 1 gram of tungsten boride with 0.5 gram of ruthenium oxide in 10 cm.^{3} of toluene. The mixture so prepared is painted on the surface of a titanium strip which is then subjected to the application of heat at a temperature of 350° C. for a period of one hour. The titanium strip is cooled, coated with another layer of said mixture and reheated under the same conditions. This procedure is repeated five times. The finished electrode contains a strong, cohesive coating

of tungsten boride and ruthenium oxide firmly bonded to the titanium base.

EXAMPLE VII

A graphite slab is impregnated with chlorinated paraffin containing 55 percent by weight of combined chlorine. This slab is subjected to the action of gaseous anhydrous hydrogen fluoride to replace chlorine atoms thereof and to fluorinate the surface of the graphite. The surface of this graphite electrode is painted with a mixture comprising 10 grams of platinum resinate containing 7.5 percent platinum by weight in 30 cm.^{3} of toluene. The electrode is then subjected to the application of heat in an inert atmosphere (nitrogen, argon or the like) at a temperature of 250° C. for one hour. The electrode is then recoated and again heat treated. This procedure is repeated five times, the final heating being at 500° C. The resulting graphite electrode has a thin coating of metallic platinum which has some porosity. Despite its porosity, it is suitable for use in an alkali chlorine cell of the diaphragm or flowing mercury cathode type and has an unusually long life much longer than that of ordinary graphite. It may also be utilized as an anode of an alkali metal chlorate cell.

Various other embodiments are possible. For example, Example VII may be practiced using a graphite anode impregnated with polymeric tetrafluoroethylene in lieu of the chlorinated paraffin in which case the contact with hydrogen fluoride may be dispensed with.

Further, an oxide coating may be provided in lieu of platinum metal by applying ruthenium resinate or rhodium resinate or palladium resinate in place of platinum resinate to either the fluoro paraffin or polytetrafluoroethylene. In such a case the heating may be conducted in steam, air or air diluted with nitrogen since the fluoro ethylene polymer protects the graphite or carbon base from danger of oxidation.

All of the above impregnated carbon bases may be used as such as anodes for electrolysis of alkali metal chloride brine. However, best results (low overvoltage, etc.) may be obtained when the above electroconductive coatings are applied. In either case the graphite surface must be sufficiently exposed to be electroconductive and where the impregnant is present as a film on the surface it should be ground off or otherwise exposed so that electroconductive coating is in electrical contact with the graphite and can conduct current therefrom.

Also it will be understood that a mixture of toluene solution of ruthenium resinate containing 4 percent by weight of ruthenium with enough sodium meta silicate or cobalt ammonium silicate or other soluble colloidal metal soluble in aqueous medium dissolved in water to provide about 5 to 25 percent silicate based on the ruthenium. This mixture may be applied to the graphite base, care being taken to prevent segregation of the aqueous and organic phases following the process of Example I.

As stated above the carbon may be treated with a siloxane silicone, oils or waxy solids or alkyl chloro silane to render it hydrophobic prior to coating. Good results may be obtained using a phenyl silicone. In order to minimize attack of the silane treated surface or the siloxane or silicone thereon it is most advantageous to obtain carbon impregnated with the chloro or fluoro derivatives of such silicones or silanes. This may be done by dipping the silane or silicone impregnated base into liquid chlorine to chlorinate the impregnant and if desired the surface may be fluorinated by then exposing the chlorinated base to anhydrous H_2F_2 in liquid or vapor state to replace the attached chlorine atoms with fluorine.

Also Example VII may be practiced with carbon or graphite which has been impregnated with a toluene solution of a polymerizable polyester of propylene glycol and a hexachloro cyclopentadiene-maleic acid adduct or 1, 4, 5, 7 tetra chloro, 6, 7 difluoro bicyclo-(2,2,1)-5 heptene dicarboxylic acid such as shown in U.S. Pat. 2,783,215. Such solution should contain 0.5 percent by weight of benzoyl peroxide based on the polyester and the impregnated graphite is then heated at a temperature of 60 to 120° C. to polymerize it to its final state of cure. Such product may then be exposed to anhydrous H_2F_2 to replace chlorine atoms thereof.

The electrodes produced in the manner described herein in the description and above examples may be utilized as the cell anodes in both mercury and diaphgram cells used for the electrolysis of alkali metal chlorides. These electrodes are also useful as anodes for the production of sodium chlorate by electrolysis of alkali metal chlorides. Typical cells in which these electrodes may be used are cells such as described in U.S. Pats. 3,337,443; 3,203,882 and 3,308,047. The electrodes are also useful in the electroplating art where they are typically employed as cell anodes. The above are typical of processes where the novel electrodes herein desclosed may be employed but it will be obvious that they may be employed in any electrolytic operation where high chemical resistance of electrodes is desired.

While the invention has been described with reference to certain specific examples and illustrative embodiments, it is not intended that the invention be limited thereby except insofar as appears in the accompanying claims.

I claim:

1. In the method of electrolyzing an aqueous solution of alkali metal chloride, the improvement which comprises imposing an electromotive force between an anode and a cathode, the anode comprising a porous electroconductive carbon base, the pores of said electroconductive carbon base having disposed therein an inert, hydrophobic sealant, an electroconductive exterior surface in direct electrical contact with said porous electroconductive carbon base and in contact with the aqueous alkali metal chloride to be electrolyzed, the said exterior surface comprising at least one member of a first group consisting of aluminum, tantalum, titanium, hafnium, zirconium, bismuth and tungsten, the member of said first group being present as a sulfide, nitride, boride or carbide, and at least one member of a second group consisting of palladium, platinum, rhodium, iridium, ruthenium, osmium, silver, gold, iron, nickel, chlorium, lead, copper and manganese, the member of said second group being present as a metal, oxide, boride, nitride, sulfide or carbide.

2. The process of claim 1 wherein the hydrophobic material is a silicone.

3. The process of claim 1 wherein the hydrophobic material is a polymer of an ethylenic fluoro hydrocarbon.

4. The process of claim 1 wherein the hydrophobic material is a fluoro carbon.

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