United States Patent

Lohr

[15] **3,671,412**

[45] **June 20, 1972**

[54] PROCESS FOR THE REMOVAL OF IONIC CONTAMINANTS FROM AN ELECTROCOATING BATH

[72] Inventor: **James E. Lohr,** Wallingford, Pa.

[73] Assignee: **E. I. du Pont de Nemours and Company,** Wilmington, Del.

[22] Filed: **April 28, 1970**

[21] Appl. No.: **32,663**

[52] **U.S. Cl.** **204/181,** 204/301

[51] **Int. Cl.** **B01k 5/02,** C23b 13/00, B01b 13/02

[58] **Field of Search** 204/181, 301

[56] **References Cited**

UNITED STATES PATENTS

3,419,488	12/1968	Cooke	204/181
3,444,064	5/1969	Johnson	204/181
3,444,063	5/1969	Brewer et al	204/181

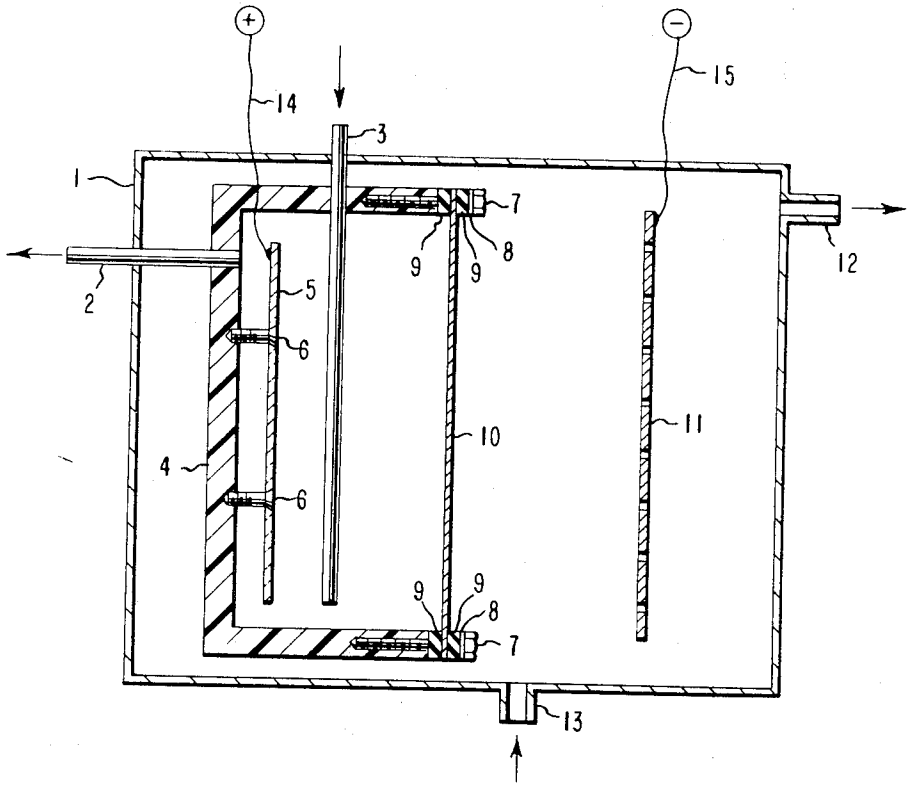
Primary Examiner—Howard S. Williams

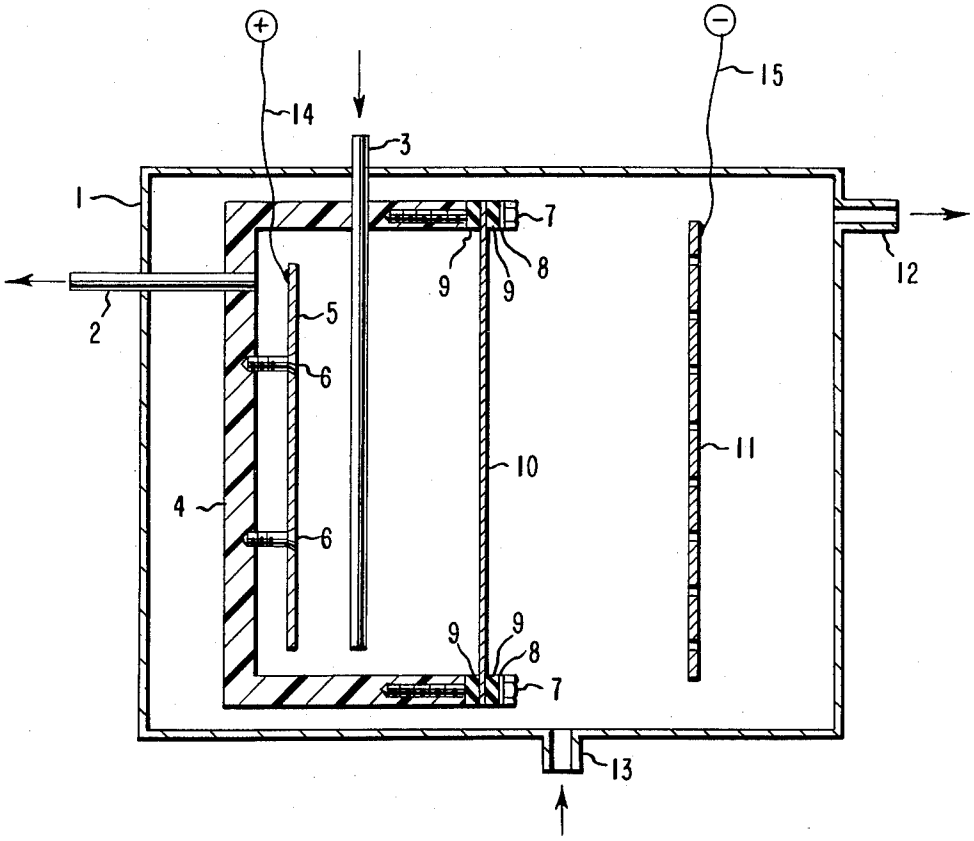
Attorney—Hilmar L. Fricke

[57] **ABSTRACT**

An electrolysis cell for the removal of ionic contaminants from an electrocoating bath and the utilization of this electrolysis cell in an electrocoating process are the subjects of this invention; the electrolysis cell comprises an anode assembly of a frame having attached thereto a metal anode and an anion permeable membrane that is held by the frame in close relationship with the anode and forms a compartment between the membrane and the anode; a cathode is positioned in a close relationship to the anode assembly; the electrocoating bath is brought into contact with the membrane and anionic impurities that are present in the bath migrate toward the anode and are removed from the compartment in the anode assembly; the membrane is impermeable to the film-forming polymeric materials and pigments utilized in the electrocoating bath and is selectively permeable to the water-soluble anionic impurities in the bath; the electrolysis cell can be positioned directly in the electrocoating bath utilized in the electrocoating process or may be positioned outside of the bath and have the bath passed through the electrolysis cell and recycles into the bath. It is also possible to remove cationic contaminants from the bath by using a cation permeable membrane positioned in a cathode assembly similar to the above anode assembly in the electrolysis cell.

5 Claims, 1 Drawing Figure





INVENTOR
JAMES E. LOHR

BY Hilmar L. Fricke
ATTORNEY

PROCESS FOR THE REMOVAL OF IONIC CONTAMINANTS FROM AN ELECTROCOATING BATH

BACKGROUND OF THE INVENTION

This invention is related to an electrocoating process in which articles are immersed in a bath containing a film-forming polymeric material and the film-forming material is electrodeposited as a coating on an article. In particular, this invention relates to a electrolysis cell which is utilized for the removal of ionic contaminants from an electrocoating bath.

Electrodeposition of carboxylic film-forming polymeric material is well known and is taught in Gilchrist U.S. Pat. No. 3,230,162, issued Jan. 18, 1966, Gilchrist U.S. Pat. NO. 3,382,165, issued May 7, 1968. Various methods have been used to remove the contaminants and unwanted by-products from the bath as shown in Gilchrist U.S. Pat. No. 3,304,250, issued Feb. 14, 1967; Cooke U.S. Pat. No. 3,419,488, issued Dec. 31, 1968 and Brewer et al. U.S. Pat. No. 3,444,063, issued May 13, 1969. However, none of these processes are directed specifically to the removal of the anionic contaminants that are particularly undesirable in a coating bath since these contaminants are electrodeposited with the anionic film-forming polymeric material on the anode forming an inferior coating. Contaminants are introduced into the electrocoating bath through the addition of water to the bath, leeching of pigments, entrainment of salts with incoming work pieces, absorption of carbon dioxide from and air and the like. Unwanted phosphate ions, sulphate ions, chloride ions and the like are thereby introduced into the bath and must be removed.

The novel process of this invention is utilized in combination with a conventional electrocoating process rapidly and efficiently removes the anionic contaminants from the bath, thereby, rendering the bath useful over long periods of time, which eliminates the need of frequent cleaning and replenishment of the electrocoating bath.

SUMMARY OF THE INVENTION

The novel electrolysis cell of this invention is utilized in a conventional electrocoating process for the removal of anionic contaminants from the electrocoating bath that contains film-forming polymeric materials and pigments; the electrolysis cell comprises

a frame,

a metal anode that is attached to the frame and is electrically insulated from the frame and electrically coupled to a positive electrical source;

an anion permeable membrane is attached to the frame and positioned in adjacent relationship to the anode to form a compartment between the anode and the membrane, the membrane is impermeable to the film-forming polymeric materials and pigments of the electrocoating bath and is selectively permeable to the water-soluble anionic impurities in the bath;

wherein the membrane comprises an anion exchange resin which selectively permits the passage of water-soluble anions into the aforementioned compartment;

means are attached to the cell for the removal of anionic impurities from the aforementioned compartment;

a metal cathode is coupled to a negative electrical source and is positioned in adjacent relationship to said anion permeable membrane with sufficient area between the cathode and the membrane to allow for the passage of electrocoating bath; and

means for causing electrocoating bath to flow into the area between the cathode and the anion permeable membrane.

The novel electrolysis cell is utilized in a conventional electrocoating process and the cell can either be positioned in the electrocoating bath and operated when the electrocoating process is not being utilized, or can be separate from the electrocoating bath with the bath composition being pumped into the cell and recycled to the electrocoating cell after the anionic contaminants have been removed.

DESCRIPTION OF THE INVENTION

The drawing illustrates one preferred embodiment of this invention. The novel electrocoating cell comprises a tank **1** of a reinforced polymeric material, preferably a polymeric material reinforced with glass fibers is used. Other materials may be used equally well for the tank. The tank is provided with inlet **13** in which the electrocoating composition from a conventional electrocoating tank is pumped into the cell and the composition is passed between the cathode **11** and the anion permeable membrane **10**. The composition is then recycled into the electrocoating tank through outlet **12**.

An anode assembly is positioned in tank **1**. The anode assembly has a frame **4** of a non-conducting material, preferably a plastic material and the frame is provided with an inlet **3** and outlet **2**. Water is passed into the assembly through inlet **3** and circulates through the assembly and is removed from the outlet **2** along with the anionic contaminants which have been removed from the electrocoating bath. The water used to flush the cell preferably has a conductance of about 500 micromhos per centimeter. One water solution which can be used contains about 0.04 percent by weight of sodium bicarbonate.

The anion permeable membrane **10** is bolted to the frame **4**. The anion permeable membrane **10** is then positioned over the gasket **9**. A second gasket **9** is positioned over the anion permeable membrane and then an assembly of a washer **8** and a bolt **7** is utilized to fasten the gaskets and anion permeable membrane to the frame. A metal anode **5** is electrically coupled to a positive electrical source by wire **14** and is attached to the frame **4** by screws **6**. The anode is positioned so that it does not touch the walls of the frame. Care is taken that the screws **6** do not pass through the frame **4**. Preferably, the anode is constructed of an inert metal to prevent corrosion from the acid which forms at the anode.

A cathode **11** is positioned in the tank and coupled by wire **15** to a negative electrical source. The cathode can be a metallic grid screen or plate with holes punched therein and can be positioned in the tank by utilizing clamps or braces or any other conventional means. However, care must be taken that it does not touch the anion permeable membrane and must be positioned essentially opposite the anion permeable membrane and the anode assembly.

The drawing illustrates an electrolysis cell which is separate from the electrocoating bath in which the electrocoating bath is pumped into the cell and then recycled back to the cell after the anionic contaminants have been removed. It is possible to position the anode assembly and the cathode in an electrocoating bath in the above relationship and operate the cell when the electrocoating bath is not being utilized. Preferably, the above assembly is not positioned in an electrocoating bath but is separate from the tub.

It is also possible to remove cationic contaminants from the electrocoating bath by using a cation permeable membrane in conjunction with the cathode. A cathode assembly which is the same as the above anode assembly is utilized, except the metal anode **5** is a metal cathode and is coupled to a negative electrical source. The unwanted cationic impurities are then flushed from the cathode assembly as above. The cation permeable membranes that can be used are described in Cooke U.S. Pat. No. 3,419,488, the disclosure of which is hereby incorporated by reference.

The electrocoating cell is operated at an amperage at which paint will not be deposited on the anion permeable membrane. Operable conditions are, for example, about 1–10 volts and a current density of about 0.005–0.3 milliamps per square centimeter of membrane. Preferably, about 0.05–0.10 milliamps per square centimeter of membrane are utilized in the process. High voltages and high current densities are not necessary for the removal of the small amounts of anionic or cationic contaminants from the electrocoating bath. Generally, the cell is in operation when the electrocoating bath is not being utilized, however, with the above cell, the cell can be utilized when the bath is in operation. Also, it is possible to revitalize a bath which is no longer useful for electrocoating because of the

contaminants in the bath. By cycling the electrocoating bath through the novel cell of this invention, these contaminants can readily be removed making the bath useful again for electrocoating.

The anion permeable membrane utilized in the novel electrolysis cell of this invention selectively permits the passage of water-soluble anions into the compartment of the anode assembly, but does not permit the passage of the pigments and film-forming polymeric material utilized in the electrocoating bath. Preferably, the membrane has a support of a synthetic fibrous material and is coated with an anion exchange resin.

One preferred membrane has a support of a woven synthetic fabric coated with a synthetic polymeric material and the membrane has an anion permselectivity of 70–95 percent, and an anion exchange capacity of 0.1–10, and preferably, 0.70 to 1.30 of milliequivalents of ions per gram of membrane.

The anion permselectivity is the percentage of anions based on the total number of ions that pass through a membrane. This is determined by exposing one side of the membrane to a 0.1 molar sodium chloride solution and the opposite side of the membrane to distilled water. The concentration of sodium ions and chloride ions are then measured after a given time and the permselectivity of the membrane is then calculated.

The anion exchange capacity is the milliequivalents of ions that can be absorbed per gram of membrane.

One particularly preferred anion permeable membrane has a support of a woven fabric of a polyester fiber which is coated with an anion exchange resin and the membrane has an anion permselectivity of 85–90 percent, an anion exchange capacity of 0.70 to 1.30, a gel/water content of 15–30 percent and a thickness of 3–6 **mils**.

One preferred cation permeable membrane that can be used in this invention to remove cationic contaminants has a cation exchange capacity of about 1.05 milliequivalents per gram of membrane and a cation permselectivity of about 96.2 percent.

The novel electrolysis cell of this invention is utilized in conjunction with conventional electrocoating cells. A wide variety of aqueous polymeric dispersions are utilized in conventional electrocoating processes. These aqueous polymeric dispersions have a solids content of about 3–30 percent and a pH of 6–11 and generally comprise a uniformly dispersed film-forming polymer which consists of a polymer which has an acid number of about 6–300, a thermosetting resin and the film-forming polymer is neutralized with a water-soluble basic compound, such as ammonia, primary amines, and secondary amines.

The preferred film-forming polymers utilized in conventional electrocoating compositions contain about 95–50 percent by weight, based on the total weight of the film-forming polymer, of a carboxylic acid resin which has an acid number of 6–300, and correspondingly, about 5–50 percent by weight of a water dispersible thermosetting nitrogen containing resin.

These electrocoating compositions contain any of the conventional pigments in a pigment volume concentration up to 30 percent, preferably, pigment volume concentrations of 1–15 percent are used.

The pigment volume concentration is the ratio expressed on a percent basis of the volume of pigment to the total volume of pigment plus film-forming materials of the composition; the "-volume of pigment" is the volume of vehicle displaced by the pigment wet with vehicle.

A wide variety of carboxylic acid polymers can be utilized in these electrocoating compositions, for example, alkyd resins, epoxy resins, acrylic resins, epoxidized drying oils, and reaction products of a dicarboxylic acid anhydride and a drying oil.

Preferably, a thermosetting nitrogen resin is used with the aforementioned carboxylic acid polymers. Typical resins are condensates of formaldehyde with phenol, melamine, urea, benzoguanamine, for example, phenol formaldehyde resin, alkylated melamine formaldehyde resins, such as partially methylolated or butylated melamine formaldehyde resins, wholly alkylated melamine formaldehyde resins, such as hexamethoxy methylol melamine and the like can be used.

The carboxylic acid polymers utilized in conventional coating compositions are neutralized with a water-soluble basic compound. Typical compounds which can be used are, for example, ammonia, primary amines, secondary amines, tertiary amines, polyamines, hydroxy amines and alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide and the like. The typical amines are, for example, monoethanol amine, methylethanol amine and methyldiethanol amine, diisopropanol amine, hydroxyl amine, butanol amine and the like. The conventional electrocoating compositions have a pH of about 6–11, and preferably, a pH of about 7.5–9, which can be adjusted utilizing one of the aforementioned water-soluble basic compounds.

The following examples illustrate the invention.

EXAMPLE 1

An electrolysis cell as described in the drawing is utilized. The membrane used in the cell is an IM–12 anion permeable membrane, sold by the Ionac Chemical Corporation. This membrane has a support of a woven fabric of polyester fibers which is coated with an anion exchange resin. The membrane has an anion permselectivity of 85–90 percent, an anion exchange capacity of 0.7 to 1.30, a gel/water content of about 23 percent, a thickness of 4.5–5.5 and an areal resistance of 2–4 ohms/centimeter^2.

	Parts by Weight
Epoxy ester resin (soya oil fatty acid/ "Epon" 1004/trimellitic anhydride weight ratio 38/59/3)	6.37
Benzoguanamine resin	1.91
Potassium hydroxide	0.11
Antioxidant (1-methyl-3-hydroxy-4-isopropyl benzene)	0.06
Titanium dioxide pigment	1.41
Yellow iron oxide pigment	0.20
Carbon black pigment	0.02
Red iron oxide pigment	0.02
Butyl cellosolve	3.95
Water	85.95
Total:	100.00

The above composition is adjusted to a pH of about 8.0 with potassium hydroxide. This composition is placed in a conventional electrocoating cell and is used intermittently for several months. After several months' use, the composition electrocoated as a rough film onto steel panels.

The composition is passed through the above electrolysis cell and recycled into the electrocoating bath. The electrolysis cell is operated for 4 hours at 3 volts and at a current density of 0.015 ma/cm^2 and for 5 hours at 0.03 ma/cm^2 at 3 volts. Periodically, the anode assembly is flushed with water containing 0.04 percent by weight of sodium carbonate to remove anionic contaminants. After this treatment, the electrocoating bath was used to coat steel substrates. In each case, films are deposited that are smooth and even and give a hard glossy finish after baking at 175° C. for 30 minutes.

EXAMPLE 2

An electrocoating paint is formulated using the identical constituents as in example 1. This paint is neutralized with 45 percent aqueous potassium hydroxide solution. The resulting paint has a pH of about 7.48.

To simulate anionic contaminants in an electrocoating bath 0.05 percent by weight of potassium chloride and 0.05 percent by weight of $NaH_2PO_4 \cdot H_2O$ are dissolved in the above neutralized paint.

This composition is placed in a conventional electrocoating cell which consists of a galvanized tank having about a 100 millimeter capacity. The steel panels, about 2 × 6 × 1/32 in., are positioned in the center of the tank and form the anode of

the electrocoating cell while the tank itself forms the cathode of the cell. A direct voltage of about 250 volts is applied for 1 minute and a 0.5 mil of coating is deposited on each side of the steel plate. The coating is extremely rough and spotty.

The composition is then pumped through the electrolysis cell described in example 1 for about 3.25 hours using 3 volts and a current density of 0.10 milliamps per square centimeter. The anode assembly is flushed periodically with water containing 0.04 percent by weight of sodium carbonate to remove anionic contaminants.

Steel panels are again electrocoated as above. The coating deposited is smooth and even and bakes to a hard finish which indicates that the anionic contaminants were removed from the paint by the above treatment.

EXAMPLE 3

An electrocoating paint is formulated that has the following coating composition:

	Parts by Weight
Alkyd resin (tall oil fatty acid/trimellitic anhydride/hydrogenated bisphenol A/diethylene glycol, weight ratio 23.8/24.7/35.7/15.8 ACID NUMBER 19–23 and a Gardner Holdt viscosity at 25° C. of Z)	2.27
Alkyd resin (tall oil fatty acid/trimellitic anhydride/hydrogenated bisphenol A/diethylene glycol, weight ratio 23.0/25.7/36.0/15.3 ACID NUMBER 20–24, Gardner Holdt viscosity at 25° C. of Z_2–Z_4)	6.80
Carbon black pigment	0.40
Diacetone alcohol	5.93
Methylisobutyl ketone	0.37
XM-1116 melamine fomaldehyde cross-linking resin (tetrakisethoxymethyl-bis-methoxymethylmelamine)	0.36
Antioxidant (1-methyl-3-hydroxy-4-isopropyl benzene)	0.02
Diethylethanol amine	0.05
Water	83.80
Total:	100.00

The above composition is neutralized with potassium hydroxide. This composition is placed in a conventional electrocoating cell and is used intermittently for several months. After several months' use, the composition electrocoated as a rough film onto steel panels.

The composition is passed through the above electrolysis cell and recycled into the electrocoating bath. The electrolysis cell is operated for 4 hours at 3 volts and at a current density of 0.01 ma/cm² followed by 4 hours at 0.015 ma/cm² at 3 volts which is followed by 5 hours at 3 volts at 0.03 ma/cm². Periodically, the anode assembly is flushed with water containing 0.04 percent by weight of sodium carbonate to remove anionic contaminants. After this treatment, the electrocoating bath was used to coat steel substrates. In each case, films are deposited that are smooth and even and give a hard, glossy finish after baking at 175° C. for 30 minutes.

EXAMPLE 4

An electrolysis cell identical to the cell used in example 1 is modified by incorporating a cathode assembly into the cell. The cathode assembly is identical to the anode assembly, except the cathode is attached to a negative power supply and a cationic exchange membrane is used. The cationic exchange membrane is an Ionac MC-3470 membrane, sold by Ionac Chemical Corporation, and has a cation exchange capacity of about 1.05 milliequivalents per gram of membrane and a cation permselectivity of 96.2 percent.

The electrocoating composition prepared in example 3 is utilized in a conventional electrocoating cell. The composition is passed through the above electrolysis cell to remove cationic and anionic contaminants. The electrolysis cell is operated at 3 volts and a current density of 0.1 milliamps per square centimeter of membrane. Periodically, the anode and cathode assemblies are flushed with water containing 0.04 percent by weight of sodium carbonate to remove contaminants. Films deposited from the bath are glossy, smooth, even and uniform even after the bath is used for several months and replenished a number of times with additional electrocoating composition.

I claim:

1. In the process for electrocoating a film-forming polymeric material and pigments on the anode of an electrocoating cell having a cathode, said anode being a work piece and consisting of a metal article, by immersing said anode in an aqueous bath containing a dispersed film-forming polymeric material and pigments and passing direct current through said cell to deposit a coating of the polymeric material and pigments on the anode, removing the coated anode from the bath and baking the coated anode to form a continuous film, the improvement in use therewith comprising

an electroysis cell for the removal of anionic contaminants from the electrocoating bath wherein the cell comprises a metal cathode, a frame, a metal anode which is attached to the frame and electrically insulated from the frame and electrically coupled to a positive electrical source separate from the source utilized in the electrocoating cell, an anion permeable membrane attached to the frame and positioned in adjacent relationship to the anode forming a compartment between the anode and the membrane, said membrane being impermeable to the film-forming polymeric material and pigments of the electrocoating bath and being selectively permeable to the water-soluble anionic impurities in the bath,

wherein the membrane selectively permits the passage of anions into the compartment and consists of a woven fabric coated with a synthetic polymeric anion exchange resin and has an anion perm-selectivity of 70–95 percent and an anion exchange capacity of 0.1 to 10 milliequivalents per gram of membrane,

a means for removing the anions from the compartment,

said electrolysis cell being operated at an amperage sufficiently low to prevent deposition of film-forming material on said membrane.

2. The process of claim **1** in which the membrane comprises a woven fabric of a polyester fiber coated with an anion exchange resin and the membrane has an anion perm-selectivity of 80–95 percent, an anion exchange capacity of about 0.7 to 1.3 milliequivalents per gram of membrane, a gel/water content of about 15–30 percent and a thickness of 3–6 mils.

3. The process of claim **1** in which the electrolysis cell is positioned in the electrocoating cell and operated when the electrocoating cell is not in use.

4. The process of claim **1** in which the electrolysis cell is separate from the electrocoating cell and the electrocoating bath is continuously pumped into the electrolysis cell and recycled into the electrocoating cell after the ionic impurities have been removed.

5. The process of claim **1** in which the electrolysis cell comprises a second frame wherein the cathode is positioned and said cathode is coupled to a separate negative electrical source and a cation permeable membrane is attached to the frame and forms a compartment between the cathode and the membrane,

said membrane being impermeable to the film-forming polymeric material and pigments of the bath and being selectively permeable to the water-soluble cationic impurities in the bath and comprises a cation exchange resin, and

means for removing cations from the compartment.

* * * * *