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DRAWINGS ATTACHED

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(54) PROCESS FOR COLOURING ANODISED ALUMINIUM
 BY ELECTROLYTIC DEPOSITION

(71) We, ALCAN RESEARCH AND DEVELOPMENT LIMITED, a Company incorporated under the laws of Canada, of 1, Place Ville Marie, Montreal, Quebec, Canada, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing inorganically coloured anodic oxide coatings on aluminium (including aluminium-base alloys). It is already known to colour an anodic aluminium oxide coating by subjecting an anodised article to electrolytic treatment with alternating current in an acidic bath containing certain metal salts which deposit coloured oxides or hydroxides in the anodic oxide coating.

The present invention is specifically related to the step of electrolytic colouring treatment with alternating current passing between the anodised aluminium work load and a counter-electrode, e.g. a metal or graphite electrode. An important aim of the present method is to promote achievement of selected colours or tones, without defects and in a reproducible manner, and to attain a simplified mode of control for applying a desired shade of a given colour.

The known process, described in United States Patent No. 3,382,160, has been used to achieve a variety of colours, for instance bronze, brown, red-brown, gold, grey, black and in most instances a number of shades from pale to dark. The use of nickel salts in the bath and a nickel counter-electrode, has been quite successful, attaining a number of shades of bronze that are in demand for architectural and other purposes, and notable results have been achieved with copper salts to yield pale reds, dark red-brown and darker colours. Other good results have been obtained with silver salts and tellurite and selenite salts of alkali metals.

The popularity of bronze tones has led to

nickel salts being most widely used, but considerable potentiality also exists for other metallic salts such as copper salts. Some difficulty has been encountered in producing darker shades, for instance attainment of dark bronze colours with nickel salts is sometimes accompanied by "spalling", namely the appearance of minute light or white spots where it would appear that the coloured coating has fallen away, leaving small bright patches.

Another difficulty that sometimes arises is in reproducibility, i.e. in matching a colour or shade obtained on an anodised aluminium article with the selected colour or shade of a previously coloured anodised article. This is especially so where the articles are of different sizes, even though care is exercised in selection of voltage or of a program of voltages and in the time or times of treatment. Problems of this sort have occurred in various baths such as nickel and copper, and can be a matter of concern where the user of coloured aluminium requires a large number of pieces or articles to be identical in appearance. Requisite control has sometimes been found very delicate, notably in making voltage adjustment in the case of copper salt baths. For example in utilising a bath containing a copper salt and a copper sheet counter-electrode, it has been difficult even to obtain a medium shade, e.g. maroon, as distinguished from a pale tone or a near-black or black.

According to the present invention there is provided a process for colouring anodically oxidised aluminium in which alternating current is passed between the anodised aluminium and a counter-electrode whilst immersed in a metallic salt bath characterised in that current is passed between an anodised aluminium work load and a counter-electrode structure arranged in a plane parallel to the anodised aluminium work load, regularly spaced areas, within the planar area occupied by current-emitting areas of the counter-elect-

trode, the total current-emitting area of the counter-electrode structure in relation to the adjacent work load comprising 3—50% of said planar area.

- 5 It has now been discovered that advantageous results, especially in the reproducibility of desired shades, are achieved in the colour-depositing step, by employing counter-electrodes that consist in effect of a multiplicity of separate elements. Indeed the counter-electrode may consist of a plurality of widely spaced elements (widely spaced relative to their current-emitting areas), e.g. arranged in an array facing the aluminium article under treatment, so that in the preferred arrangement the current-emitting area of the counter-electrode structure is only minor fraction of the total area of the anodised work load which faces the counter-electrode. Upon operation in this manner, for example with the total current-emitting area of the counter-electrode elements being, say, from 3% to 25% of the area of the plane in which they lie, tendency to spalling, for instance with nickel baths, can be much reduced or obviated in circumstances where it may otherwise exist, as where a dark bronze or like shade is sought. Moreover, the reproducibility of the operation to attain selected tones or shades, is in general improved for various baths, whether containing nickel, copper or other salts, and indeed the present process markedly facilitates attainment of intermediate colours as in the case of copper.

- 35 In practice, the counter-electrode assembly, which is preferably made of the same metal as the salt in the bath, can be fashioned in various ways. A convenient arrangement consists in an array of parallel, vertical strips, rods or tubes of the metal, or like pieces such as the connected elements of a continuous grid or screen and having relatively wide spacing, i.e. a distance between successive elements which may be as much as several times the transverse dimension of each element, conveniently at least four times and most preferably more. With such assembly, the passage of alternating current between the counter-electrode and the facing work load results in the desired colouring deposit in the anodic coating with appropriate uniformity.

- 50 In the preferred arrangement of parallel vertical strips, rods or tubes, the electrode structure has separate current-emitting areas, separated by ineffective areas. In the case of a grid or screen the current-emitting area is continuous, but is interspersed with a regular arrangement of ineffective areas, i.e. areas unoccupied by electrode material.

- 60 The counter-electrode arrangement is especially adapted for use in establishments having conventional anodising equipment, the colouring step being effected in an elongated tank similar to the tanks used for anodising operations, and constructed to receive work loads

at one or more positions parallel to the sides of the tank. Thus for example a work load (an anodised aluminium article) consisting of a sheet or sheets of aluminium, or a collection of rods, bars or various shapes or other articles of aluminium (e.g. as carried on a rack), is submerged along the centre of the tank and a counter electrode structure, consisting of an array of spaced, narrow, metallic elements, faces the work load on one or both sides.

Although the exact reason for achieving the improved results is not known, it is believed that the flow of alternating current spreads radially or fan-like from the spaced current-emitting areas, provided by individual counter electrode elements, toward the work load to promote uniform current density at the surface of the load and to diffuse or counteract localised effects, yet nevertheless unexpectedly providing a large enough flow of current, even though from relatively very small counter electrode areas, to yield the desired intensity of colouring in reasonably short times of treatment. It is now believed that when large pieces of metallic sheet are used as counter-electrode, there is or can be relatively intense flow of current at the severed edges of such sheet elements, but it was not readily apparent or obvious that this situation was or could be a cause of difficulties, such as spalling in the case of nickel salts, or colour mismatch among different work loads, or such problem of adjustment or control of the operation as made it hard to get intermediate colours with copper salts, the last-mentioned problem being found to arise, apparently, from a special voltage criticality in that the voltage range between the production of light and dark tones has seemed very small.

Nevertheless it has been found that the process of the invention, which may involve a considerable multiplicity of sharp edges, in the case of parallel narrow strips of metal sheet or what may be conceived to be an absence of such edges, in the case of parallel round rods or tubes, and which very advantageously allows the actual counter-electrode area to be small relative to the facing area of the work load goes far to ameliorate or avoid the above difficulties, and thus attain desired results.

It has been discovered that an unusually effective control of the colouring step is achieved by maintaining the electrical current at a selected value. Although this may involve a timed program of two or more successive current values, it is preferred to regulate the electrical system so that the current is constant throughout the treatment.

It appears, for example, that non-uniformity previously encountered among different work loads when endeavouring to maintain selected voltage conditions, e.g. a single

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voltage or a program of voltages, is probably occasioned by variation in polarisation at the counter-electrode; tests in the case of a.c. treatment with a nickel bath using a nickel electrode have shown mis-match of colour between work loads with different surface areas, even though the externally applied voltage and time of operation were the same. Maintenance of a selected current density has been found to ameliorate or indeed to obviate the occurrence of mis-match. Effects of polarisation are automatically compensated and the control for a given colour, after setting the total current to suit the size of the work, is the time of treatment.

This feature of constant current control is made possible by the employment of the above-described counter-electrode arrangement; only with the latter has it appeared possible to obtain substantially uniform current density as to make the value of total current a significant measure of the rate of treatment.

By way of example and for illustration of the process, embodiments of apparatus utilising the invention are shown in the accompanying drawings, wherein:

Figure 1 is a perspective view of a tank for the colouring step and with accompanying diagram of electrical supply and control;

Figure 2 is a transverse section on the line 2—2 of Figure 1;

Figure 3 is a schematic plan view of the tank of Figure 1, utilising a different work load;

Figure 4 is a vertical section similar to Figure 2, but of apparatus for handling two work loads in parallel;

Figure 5 is a schematic plan view of the tank and operation of Figure 4;

Figure 6 is a partial view, in perspective, of the tank of preceding figures, showing counter-electrode-supporting means;

Figure 7 is a fragmentary vertical section on line 7—7 of Figure 6; and

Figure 8 is a fragmentary vertical section on line 8—8 of Figure 6.

In the present operations for colouring aluminium, the work is first anodised in a conventional manner to produce an anodic oxide coating, for example by anodising the work with direct current, for periods of 20 minutes to 60 minutes in an aqueous solution of sulphuric acid, e.g. 15% acid by weight. The anodising conditions are selected largely to produce the thickness and other characteristics of anodic coating needed for protective function, the requirements of the subsequent colouring step being satisfied over a considerable range of thicknesses of porous oxide coating on aluminium.

By way of example, an anodised aluminium sheet 20 is submerged in tank 22 (Figures 1 and 2) for the a.c. treatment to effect a coloured oxide deposit in the anodic oxide coating on the sheet. To that end the bath

23 in the tank 22 contains a salt of the selected metal, for instance nickel. Specifically, the bath should be an aqueous acidic solution and may comprise boric acid, nickel sulphate and ammonium sulphate, all in low concentration, and very preferably having a pH value of at least 4.

In accordance with the present invention, and with the work load, i.e. sheet 20, supported by and electrically connected to a bus bar 24 in the middle of the tank 22 (which may have an insulating lining 25), a pair of counter electrode assemblies 26, 27 are disposed inside the tank parallel with the work load. Each of these counter-electrodes consists of an array of narrow metal counter electrode strips or like elements 28 carried by bus bars 30, 31 and extend vertically into the bath.

For electrical energisation the bus bars 30, 31 and the bus bar 24 are respectively connected through conductors 33, 35 and 34, 36 to an a.c. power supply 37. It will be understood that the details of structural support of the bus bars 24, 30, 31, which may be aluminium, copper or other conductive metal, and likewise the details of support of the individual electrode strips 28 are not shown in Figures 1 and 2, and indeed may be of any appropriate nature, one form of support for the counter-electrode elements being illustrated in Figures 6 to 8.

The system includes electrical control to maintain a constant current between the work load and the counterelectrodes, thereby enabling the maintenance of a constant current density at the surface of the work load 20.

Figure 1 shows current-controlling instruments connected between the conductors 33, 34 and the conductors 35, 36 from the a.c. supply 37. Such control means may comprise an ammeter 40 and a current adjusting device 41, the ammeter having appropriate means for adjusting the device 41 to restore the current in the conductors 33, 34 to a selected value when it has departed therefrom in either direction. Although the device 41 may be a variable auto-transformer that actually changes the output voltage in the supplied circuit, the control system is nevertheless related to current and functions to maintain a predetermined current in accordance with the setting of the ammeter 40. Since apparatus of this sort is known the same need not be described in detail. Indeed in some cases a substantially constant current value can be maintained by manual adjustment in accordance with actual reading of an ammeter.

Since the aim is to maintain a selected current density at the surface of the work load 20, the value of current to be maintained in the conductors 33, 34 is determined by multiplying the total area of the work by the desired current density; the ammeter

40 is then set to maintain the selected current. Where the work consists of a plurality of objects, possibly even of irregular shape, carried on a rack which the central bus bar 24 supports, it is usually sufficient to make an approximate calculation of the total area of such work and of submerged parts of the anodised aluminium rack, for computation of the selected current value. Good results, for example with nickel or copper baths, can be achieved by maintaining a single, selected current density throughout the treatment, it being found that the intensity or shade of colour imparted to the work load, up to the darkest colour, is then dependent only on the treatment time. The composition of the bath should, of course, be kept substantially constant, and calibration of the process to determine the relation of time to colour is a simple matter of test. In consequence with only a determination of approximate area of the work (say, within 10%) and setting the control accordingly, colours of successive work loads can be accurately matched by utilisation of the same lengths of time.

A useful value of current density for nickel-containing baths having a pH of about 4 to 4.5, is about 3 amps/sq.ft. (0.32 amps/dm²); more generally preferred results are attained by selecting a current density above 2.5 amp./sq.ft. (0.27 amps/dm²). No advantage has been apparent for operation above about 3.5 amp./sq.ft. (0.38 amps/dm²), while substantially larger values may even be deleterious. The value of 3 amp./sq.ft. (0.32 amps/dm²) appears to have reasonable tolerance, in that values within about 10% still provide a good colour match between successive loads treated for the same length of time. Suitable current densities for baths containing other metal salts can readily be determined by tests. It has been found that a current density of 5 amp./sq.ft. (0.54 amps/dm²) is effective in the case of copper-containing baths, and apparently with a tolerance of at least the same proportion as for nickel.

Reverting to the drawings, Figures 6 to 8 illustrate one way of attaching the counter electrode strips 28. The wall 42 of the tank 22 has an upper flange 43 to which the bus bar 30 may be secured by clamps 44. The surface of the tank exposed to the electrolyte is non-conducting and chemically inert; for example, it may be constructed of mild steel or acid-resistant concrete, with an interior insulating lining (not here shown) of resin or plastic, e.g. synthetic rubber or polyvinyl chloride.

The upper ends of the electrode strips 28 are fastened to the bus bar, as by bolts and nuts as indicated at 46 in Figure 7, while the lower ends of the strips extend through suitable openings in an angle member 48 having one of its webs 49 secured to the tank wall. This member is preferably made of

electrically and chemically resistant material, e.g. a plastic such as polyvinyl chloride, which permits the web 49 to be fastened to the tank lining of like material by welding or fusion. The ends of the strips 28 are held by a pin or key 50 set in an opening in the strip and bearing on the underside of the flange of the angle 48. It will be understood that rod or tubular electrode members can be similarly supported, and may have a nut (not shown) threaded below the flange 48 for similar retaining function. It will also be understood that where an array of counter electrode elements along the middle of the tank is used, as in Figures 4 and 5, a like supporting structure for hanging the strips from the bus bar and carrying their bottom ends by a longitudinal member supported on legs or other means above the tank bottom, may be utilised.

Figure 3 is a diagrammatic plan view of a tank 22 in which a collection of anodised aluminium objects or work pieces 52, 53 are supported by a rack (not shown) and electrically connected to bus bar 24a. In Figure 3 dotted lines 54, 55, fanning out from the counter-electrodes 28 toward the work pieces 52, 53, are an approximate representation of the paths in which it is believed that current flows between the work pieces and the counter-electrodes. It will be appreciated that the electrode structure thus distributes the current with considerable uniformity over the work load, whether such load comprises separate pieces 52, 53 as in Figure 3, or a single sheet 20 as in Figures 1 and 2.

Figures 4 and 5 show a tank 58, including its insulating lining 59, arranged to accommodate two work loads 60, 61, lengthwise thereof, with an array of metal counter-electrode strips 62 down the middle between the localities occupied by the work loads. Spaced metal counter-electrode strips 28 are provided along the side walls, exactly as with the tank 22 of Figure 1. As will be seen in Figure 5, the spacing of the counter-electrode strips 62 is closer together than the side strips 28. Specifically, where all of the strips are of the same size and thus of the same area on each face, the central strips must deliver current from the respective faces in opposite directions to the work loads 60 and 61. On the other hand, the side strips 28 can be considered as delivering current from both faces, including paths that bend around the strip, for travel to a single opposing face of the work load. It is found that the spacing of the central counter-electrode strips 62 should be approximately one-half that of the outer elements and that each work load 60 or 61 can then be situated midway between the central and outer counter-electrode strips. Other adjustments for maintaining a uniform current-emitting area in the electrode systems, such as by employing

wider electrode strips along the middle, can be utilised. However, the arrangement of Figure 5, with twice as many similar-sized strips in the centre as at the side is very satisfactory, tests indicating that with a full work load 60, 61, the current is practically identical in each of the strips 28, 62.

The illustrated electrode structures afford exceptionally good correction of the effects, presumably including edge effect, that now appear to have been responsible for some difficulty in this electrolytic colouring process. Rods or tubes or grids of variously shaped pieces, preferably with large openings, may alternatively constitute the electrode structure. Widely spaced, narrow metal strips 62 form a central counter-electrode of low weight: in consequence, the supporting bus bar 64 can be much smaller in cross section (yet still have ample current capacity) than would be required to support a full sheet or plate electrode; economy of material results and there is better clearance for insertion of full racks of workpieces. The electrode strips are also replaced when necessary, i.e. when consumed as a result of their function of supplying metal ions to the bath.

It is found from consideration of metal consumption that in the case of a large electrode current is emitted mainly from an area adjacent the edge of the electrode and having a width of about $\frac{1}{2}$ inch (1.25 cms).

The consequent loss of uniformity and current density at the workpiece, which arises with large sheet electrodes, is greatly reduced either by eliminating sharp edges or by maximising their composite action, e.g. by having a large number of separate sheet electrodes to provide a plurality of edge zones facing the workpiece, the net result being substantial uniformity of current density at the faces of the work load. Some useful current distribution is attainable with any regular array of sufficiently numerous strip elements, uniform in size and spacing. For instance, 10 inch (25 cms) strips with $\frac{1}{2}$ inch (1.25 cms) space between them can exhibit much the same cms) strips separated by 10 inch (25 cms) spaces, but the widely spaced array of narrow strips has special advantages and appears to afford better results.

The spacing between work and counter-electrode is not especially critical and may conveniently be the spacing used in conventional anodising operations, e.g. from 6 inches (15 cms) to 2 feet (60 cms), a distance of 9—12 inches (22.5 cms—30 cms) affording a convenient balance between shortness of current paths and room to get work loads in and out of the tank. The number of separate elements of the counter-electrode structure should be co-ordinated with the distance between the work and the counter-electrode. Thus there should preferably be a sufficient

number of counter-electrode elements so that their centre-to-centre distances (in the electrode plane) are about equal to or less than the work load-electrode distance. Larger centre-to-centre counter-electrode element spacing, i.e. up to 50% more than the distance to the work is possible in some instances, but for superior results the spacing of counter-electrode element centres should not be more than 1 foot (30 cms) and generally less than 18 inches (45 cms).

The current-emitting area of an array of counter-electrode elements should be at least 3% and preferably at least 5% of the total area over which the counter-electrode elements are distributed. In relation to these percentages, the current-emitting area of a counter-electrode element is intended to mean the total surface area from which current flows to and from one facing work load; under such definition the total current-emitting area of one of the arrays of outside strips 28 is the sum of the areas of both faces of such strips, while the total current-emitting area of the centre array of strips 62 relative to a single facing work load is the sum of the areas of one face of each of the latter strips. The special advantages of an open counter-electrode assembly would appear to be best realised only when the total current-emitting area of the assembly relative to a facing work load is not more than 50% and preferably not more than 25% of the total area, measured as the product of length by height, in which the elements are distributed.

By way of specific example, the a.c. colouring step was performed in a 4 foot (120 cms) wide tank, a size conventional for anodising and similar operations, using an acidic, nickel-containing, aqueous bath of the following composition, maintained at a pH of 4 to 4.5:

NiSO ₄ ·7H ₂ O	25 g.p.l. (grams per litre)
MgSO ₄ ·7H ₂ O	20 g.p.l.
H ₃ BO ₃	25 g.p.l.
(NH ₄) ₂ SO ₄	15 g.p.l.

Operation was first effected using metallic nickel sheets as counter-electrodes at the sides of the tank and along the centre. To attain a dark bronze shade on aluminium sheet which had been anodised to provide a conventional porous oxide coating, alternating current was passed through the bath between work and counter-electrodes, first at 11 volts for 2 minutes, and then at 17 volts for 10 minutes. A dark tone was achieved, but the coating spalled, leaving small or minute bright spots, and other tests indicated that it was practically impossible to obtain more than a medium bronze colour without some spalling.

The sheet counter-electrodes were replaced with metallic nickel strips, $\frac{1}{2}$ inch (1.25 cms) wide, arranged vertically at 9 inch (22.5 cms)

centres along the sides (strips 28) and at $4\frac{1}{2}$ inch (11.25 cms) centres along the centre (strips 62) Operation was controlled to maintain a constant current, a density of 3 amperes/square foot (0.3 amps/dm^2) of surface of the work load. Under such conditions a dark bronze colour was obtained after a treatment time of 12 minutes and slightly darkened colour after 15 minutes, with no spalling or other defect in either case. Tests also indicated that lighter shades were reproducibly obtainable at shorter treatment times.

Advantageous results have also been obtained with copper electrodes using a bath containing copper sulphate (e.g. 35 g.p.l. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sulphuric acid at about pH 1.3. With counter-electrodes consisting of small diameter copper tubing spaced at 9—12 inches (22.5—30 cms) centres, a full range of colours from light to black was reproducibly attainable and when this operation was controlled to maintain current density about 5 amp./sq.ft. (0.53 amps/dm^2) on the anodised work, the colour reached in each operation was essentially determinable by treatment time alone.

While in the foregoing description attention has been given to metal electrode elements, especially nickel elements for nickel baths, copper for copper baths, it may be noted that similar principles of providing uniform current distribution on the work are applicable to counter-electrodes of carbon, i.e. graphite, which can likewise be employed as widely spaced elements.

WHAT WE CLAIM IS:—

1. A process for colouring anodically oxidised aluminium in which alternating current is passed between the anodised aluminium and a counter-electrode whilst immersed in a metallic salt bath characterised in that current is passed between an anodised aluminium work load and a counter-electrode structure arranged in a plane parallel to the anodised aluminium work load, regularly spaced areas, within the planar area occupied by the counter-electrode structure, being unoccupied by current-emitting areas of the counter-electrode, the total current emitting area of the counter-electrode structure in relation to an adjacent work load comprising 3%—50% of said planar area.

2. A process according to claim 1 in which the total current-emitting area of the counter-electrode structure is 5—25% of said planar area.

3. A process according to claim 1 or 2 in which the counter-electrode structure is composed of a grid.

4. A process according to claim 1 or 2 in which the counter-electrode structure is composed of an array of narrow flat strip elements.

5. A process according to claim 1 or 2 in which the counter-electrode structure is composed of an array of narrow elements in the form of rods or tubes.

6. A process according to claim 4 or 5 in which the elements are arranged at centre-to-centre distances not exceeding 18 inches (45 cms) and not exceeding $1\frac{1}{2}$ times the distance between said planar area and the work load.

7. A process according to any preceding claim in which the interval between a pair of adjacent elements is at least four times the width in said planar area occupied by an individual element.

8. A process according to any preceding claim further comprising maintaining the current density at the surface of the work load at one or more preselected values during the a.c. treatment.

9. A process according to claim 8 in which the current density is maintained at a value of about 3 amps/sq.ft. (0.32 amps/dm^2) when using a nickel counter-electrode in a nickel salt bath.

10. A process according to claim 8 in which the current density is maintained at a value of about 5 amps/sq.wt. (0.54 amps/dm^2) when using a copper counter-electrode in a copper salt bath.

11. A process for colouring anodically oxidised aluminium employing a counter-electrode structure and controlled current density conditions substantially as herein described with reference to the accompanying drawings.

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centres along the sides (strips 28) and at $4\frac{1}{2}$ inch (11.25 cms) centres along the centre (strips 62) Operation was controlled to maintain a constant current, a density of 3 amperes/square foot (0.3 amps/dm^2) of surface of the work load. Under such conditions a dark bronze colour was obtained after a treatment time of 12 minutes and slightly darkened colour after 15 minutes, with no spalling or other defect in either case. Tests also indicated that lighter shades were reproducibly obtainable at shorter treatment times.

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7. A process according to any preceding claim in which the interval between a pair of adjacent elements is at least four times the width in said planar area occupied by an individual element.

8. A process according to any preceding claim further comprising maintaining the current density at the surface of the work load at one or more preselected values during the a.c. treatment.

9. A process according to claim 8 in which the current density is maintained at a value of about 3 amps/sq.ft. (0.32 amps/dm^2) when using a nickel counter-electrode in a nickel salt bath.

10. A process according to claim 8 in which the current density is maintained at a value of about 5 amps/sq.ft. (0.54 amps/dm^2) when using a copper counter-electrode in a copper salt bath.

11. A process for colouring anodically oxidised aluminium employing a counter-electrode structure and controlled current density conditions substantially as herein described with reference to the accompanying drawings.

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