CONTINUOUS ELECTROLYTIC TREATMENT FOR CLEANING AND CONDITIONING ALUMINUM SURFACES

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15 Claims

ABSTRACT OF THE DISCLOSURE

High speed continuous treatment of aluminum, e.g., aluminum strip, is obtained for cleaning the surface and conditioning it for subsequent application of lacquer or other organic coating, by electrolytic treatment in hot acidic electrolyte maintained in turbulence at the surface of the travelling sheet, employing current at levels that preferably involve a very low total coulombic charge, for example in a range up to 3 coulombs per square inch. Special advantage is taken of pretreatment and the like realized with electrode sequence such that the strip is cathodic both before and after anodic action, and additionally improved efficiency is achieved with a substantially larger anodic area than the total area of cathodic polarity. Efficient cleaning at high speeds is obtainable in the lower portion of the above range of coulombic charge, advantageously with electrode areas reduced to afford relatively high current densities.

BACKGROUND OF THE INVENTION

This invention relates to continuous treatment of aluminum surfaces for cleaning and conditioning, and in a particularly important sense is concerned with high speed, electrolytic treatment of aluminum strip, for example, to prepare it for subsequent application of lacquer or similar coatings. The growing demand for aluminum sheet which has been lacquered or otherwise coated has impelled the use of high speed lacquering processes, for example at operating rates of 300 feet per minute and above, preferably 500 feet per minute and upwards, with corresponding economy of production. Conventional cleaning and other pretreatments of the aluminum surfaces, if effective and otherwise moderate in cost, have generally been slow or required much turbulence or submersion in cleaning and similar tanks that an impossible length of such equipment would be required in order to be compatible with the lacquering process itself. As will be understood, the usual treatments, necessary because of materials deposited on or left on aluminum strip after rolling or other forming, i.e., materials conveniently classified as dirt and grease and usually including a residue of the oil composition used as rolling lubricant, have involved degreasing operations followed by other chemical conversion steps or in some cases a direct current anodizing stage, as well as necessary rinsing and drying. Certain proprietary chemical treatment is available for assiduously expeditious operation, but still fails to achieve maximum security of lacquer adhesion, especially when sought to be applied continuously at high speeds.

If the aluminum surface is not essentially clean, and indeed preferably conditioned by a suitable film or coating, the lacquer will not adhere properly in one area or another of the sheet, and whereas anodic coatings of thicknesses suitable for general purposes are capable, if properly prepared, of accepting lacquer, their production is deemed a relatively expensive way of serving this function. Indeed as noted below, procedure and equipment for continuous cleaning and anodizing of aluminum strip has been developed and is available, to the extent of itself providing a rapid operation for continuously delivering an anodized strip, upon which lacquer or other coating materials can be usefully applied, as compared with more conventional non-electrolytic degreasing and conditioning operations. A continuous electrolytic cleaning operation has also been used, employing alternating current in open tanks. As heretofore exemplified in practice, however, these prior procedures are now found to be susceptible of improvement for superior results in one or another of the areas of economy, high speed operation or effectiveness for present purposes.

An important aim of the present invention is therefore to provide, especially as an improvement upon and at least in considerable part with the utilization of the indicated continuous anodizing-type treatments, a notably superior and highly economical operation whereby aluminum sheet is efficiently cleaned, and more particularly, is conditioned in a special manner for optimum adhesion of lacquer or the like.

Thus the objective of the invention include the provision of improved methods and apparatus for reliable, high speed, continuous treatment of aluminum surfaces to remove foreign matter and also, more advantageously to yield a cleaned sheet which is especially conditioned for lacquering or similar operations. A special object is the accomplishment of these aims in a more economical manner than has heretofore appeared possible.

SUMMARY OF THE INVENTION

To the foregoing and other ends it has been discovered that unusually effective results in the conditioning of aluminum sheet are attainable by continuous electrolytic treatment upon the sheet while it travels through an enclosed, elongated vessel filled with acid electrolyte and while direct current is passed through the electrolyte to and from the travelling sheet surfaces, as supplied by electrodes facing the strip and spaced along the length of the vessel. The electrolyte is maintained at a suitably high temperature and is circulated along the passing strip in a manner to maintain a significant and preferably high degree of turbulence adjacent to the surface. In these respects, the operation, which results in the formation of an extremely thin but nevertheless functional anodic film, may advantageously embody procedures and may advantageously utilize apparatus embraced by one or more of the following U.S. patents, namely, No. 3,359,189, granted Dec. 19, 1967; No. 3,359,190, granted Dec. 19, 1967; and No. 3,471,375, granted Oct. 7, 1969.

It has more particularly been found that especially satisfactory results are achieved, in operations of the described sort, where the electrical conditions are such that only an extremely low total coulombic charge is employed, e.g., of the order of one or a few coulombs per square inch, while to like advantage the process may be performed in an essentially simple apparatus, wherein the successive electrodes are arranged along a single tank of more or less continuously uniform internal cross section, provided with suitable inlet and exit seals for the rapidly travelling strip at its ends. A new feature of unusual merit is an electrolytic treatment sequence for conditioning in which the ratio of current between the electrodes and the strip is most advantageously effected at more than two localities along the strip path, a highly effective arrangement being such that the strip is successively cathodic, then anodic, and finally cathodic again. With such operation the strip is found to be conditioned for excellent adhesion of a lacquer coating while at the same time an unexpected
3 economy of electrical energy is attained. That is to say, by operating in this manner, it is found that the voltage required by a selected total current, and thus of a selected charge density, is markedly less, as compared with electrode arrangements which simply provide for flow of current to and from the strip at two corresponding localities, e.g. successively cathodic and anodic. Since power requirements are measured by the product of the voltage and current, the savings can be very considerable, especially for production in large quantities at high rates of strip travel, e.g. upwards of 500 feet per minute.

While lacquer adhesion in theory improves with increase of charge density in the treatment, i.e. the total coulomical charge per unit area, it has particularly been found that satisfactory characteristics, at least from the standpoint of obtaining a very clean sheet, are attainable in a number of instances with operations represented by a charge density of one coulomb per square inch or even less. On the other hand, for more difficult situations of lacquer or paint adhesion and particularly with the economy afforded in operation using the novel electrode configuration, somewhat higher charge densities, but still in a relatively low range, have been found desirable in many cases, and indeed very useful, e.g. up to a total coulomical charge, measured as explained hereinafter, of the order of 3 coulombs per square inch.

Another unusual effect has been discovered in relation to cleaning or conditioning of aluminum surfaces for application of lacquer coatings. For many purposes the aluminum utilized is a magnesium-containing alloy, yet it has been found that the presence of magnesium tends to be detrimental to lacquer adhesion. More particularly, it has been discovered that on naturally oxidized surfaces or even under usual conditions of moderately thin oxide coatings, there tends to be a preponderance of magnesium in the oxide film, presumably as magnesium oxide. While the effect is overcome by using substantially thicker coatings, it has now been discovered that in the case of extremely thin films, produced in conditions where the hot electrolyte is sufficiently circulated along the surface under effective turbulence, there appears to be a reduction in relative content of magnesium in aluminum in the outermost oxide surface, the assumption being that this is an effect of some selective dissolution of the film under the described conditions. Hence with operation at a charge density of 3 coulombs per square inch and below, and indeed even at charge densities as low as one coulomb per square inch, there is a significant decrease in magnesium content at the oxide surface, for example as compared with analysis of a naturally-occurring, air-produced oxide film on the surface of the described aluminum alloy. In any event, whether or not this explanation is correct, a special advantage has in fact been noted for performance of the continuous cleaning and anodizing operation at high speed and low coulomical charge, on magnesium-containing alloys, with respect to the attainment of excellent lacquer-accepting surfaces while affording unusual economy as compared to operations producing significantly thicker oxide coatings, even coatings as thin as 0.01 mil.

The overall results utilizing one or more features of the present invention as described, are the attainment of superior, cleaned and conditioned aluminum surfaces at very high production rates, preferably 500 to 1000 feet per minute, and with unusual economy in respect to electrical energy and voltage and in respect to size and requirements of equipment.

Further the various advantages of the invention and likewise additional features, characteristics and fields of use are described or will be apparent in the following detailed disclosure, in reference to certain desirable embodiments.

4 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a longitudinal, vertical section of one embodiment of apparatus, shown in structurally simplified form, relating to the invention and procedure thereof. FIG. 2 is an essentially diagrammatic view of further equipment and operations, as in a complete process including lacquering, shown as a continuation of FIG. 1. FIG. 3 is a vertical cross-section of the apparatus of FIG. 1, as on line 3—3', showing certain electrode details. FIG. 4 is a vertical section of FIG. 3, showing certain electrode details. FIG. 5 is a diagrammatic view of apparatus as in FIG. 1 showing another mode of operation and connection.

DETAILED DESCRIPTION

Although the procedures of the invention or certain of them may be performed in suitable adaptations of apparatus shown in one or another of the above mentioned patents, notably effective results have been achieved with the continuous treatment of aluminum strip in the specific manner indicated in FIGS. 1–4 inclusive, especially for conditioning the strip to receive lacquer. For such purpose the strip 10 is continuously advanced lengthwise through an elongated electrolytic cell generally designated 12 (FIG. 1) and may thereafter proceed immediately, i.e. without interruption through a rinse section 13 and then, if required, a drying section 14. As illustrative of a complete process of conditioning, FIG. 2 also indicates at 15, apparatus for continuously applying a lacquer coating to one side, or more usually to both sides, of the strip, and thereafter, if desired, subjecting the applied lacquer to a conventional heating treatment. As indicated by the broken line at 16a, the strip may conceivably move forward from the first rinse section 14 into and through the lacquering stage, or may alternatively be coiled and then uncoiled if such procedure is better suited to production practice. Other optional steps may include application of a primer or electro-coating prior to lacquering, and passing the lacquered strip through apparatus which applies a lubricant such as diocetyl sebacate, desired by some users for convenience and avoidance of scratches, in handling separate sheets.

Specifically, the cell 12 comprises a body structure 16 of insulating material, e.g. suitable, reinforced plastic having appropriate resistance to hot acid and the like, designed to provide a long, completely enclosed passage or chamber 18 having a rectangular contour in cross-section and of sufficient width to accommodate the desired range of strip widths to be treated. In an entering chamber 20 at one end, there is an appropriate seal constituted by a pair of rolls 21, 22, mounted to turn on horizontal axes and having a suitable covering of resilient acid-resistant material such as neoprene, so that the sheet 10 may be drawn between the rolls with the latter in compressive, sealing contact. At the exit end of the cell 12, there may advantageously be a terminal chamber portion 24, providing an extension of the cell passage 18, and an exit tank section 25 which is provided with a pair of resiliently covered rolls 27, 28 functioning, like the rolls 21, 22, to afford an exit seal for the strip 10.

Further rolls 29, 30 similarly covered with resilient surfaces, may serve as wringer rolls to squeeze most of the remaining entrained electrolyte off the strip. It will be understood that suitable means, not here shown, are provided for advancing the strip at the desired rate of speed, such means usually comprising an ultimate rewind or take-up reel, for re-coiling the strip at the end of its path, and for cooperating with the payoff means, likewise not shown, whereby strip is delivered from a coil to the left hand end of the cell in preparation for entering the cell.

Electrolyte, advantageously an aqueous sulphuric acid solution, is circulated lengthwise of the chamber 18 so as to keep the latter completely full at all times and in-
deed so as to insure rapid passage along the faces of the strip to carry away foreign matter and to cooperate in maintaining a high order of turbulence adjacent to all regions of strip surface. Thus the electrolyte advantageously is directed through suitable ports at 31, 33 in the terminal structure 24, these ports being arranged to extend crosswise of the strip either continuously or as a series of openings, in such fashion that the liquid is caused to travel along both strip surfaces, countercurrent to the movement of the latter. Thus as the strip advances from the left to the right in FIG. 1, liquid travels from the ports 31, 33 along the entire length of the chamber 18, filling the same, to the left-hand end chamber 20 where it is prevented from escaping from the strip by the rolls 21, 22, and may discharge through an outlet 34. The chamber 20 may also have venting means (not shown) to allow partial removal of evolved gases, e.g. hydrogen. While conceivably the advance of strip and liquid may be concurrent, special advantage is achieved in the illustrated relation, both for maintaining maximum turbulence by reason of maximum relative velocity of liquid and strip, and also for best removal of foreign matter suspended in the liquid in that the fresh electrolyte first contacts only the cleaned strip that has progressed the entire length of the cell.

For connection and functioning as will be described further below, and indeed for affording a selectivity of connection to suit desired variations of treatment, the apparatus includes a multiplicity of pairs of electrodes situated in successively spaced relation along the cell 12 as indicated by the designations E-1, E-2, E-3 and so forth to and including E-8. Each such pair is composed by upper and lower electrodes 36, 37 respectively facing the strip on opposite sides and extending entirely across the chamber so as to be appropriate for any of the entire range of positions described above. While conceivably for special purposes the upper and lower electrodes 36, 37 of each pair may be differently connected, the preferred operations of the invention contemplate their connection together, to have the same electrical polarity. This arrangement is more particularly shown in FIGS. 3 and 4 but for clarity of illustration is also indicated by the connectors 38 in FIG. 1, i.e. at each electrode pair.

As will be appreciated, the electrodes may be embodied in any desired structural form and may be composed of any desirable material, such as lead or graphite, or of other metal or material (e.g. steel, where used at negative polarity) appropriately inert to the electrolyte. From the standpoint of inertness with reasonable economy and conductivity, lead electrodes have been found especially advantageous.

Thus as shown in FIGS. 3 and 4, the upper and lower electrodes 36, 37 can be considered as constituting elements of lead having surfaces at 36a, 37a, in facing relation to opposite sides of the strip 10, the electrodes being essentially embedded in upper and lower structures of the cell chamber, so that an essentially continuous passage 18 is afforded for the strip, past the faces of the entire series of eight pairs of electrodes. For best electrical efficiency and structural support, each electrode may have a channel-shaped core 40 of copper or other highly conductive metal. The arrangement or assembly also includes lead-clad connecting elements or plates 42, 43, of copper, extending upward from the respective electrode structures 36, 37 at each side, i.e. at the crosswise ends of the assemblies, whereby appropriate bus elements 45, 45 can be held between the unclad ends 42, 43 to afford actual electrical connections. In this fashion optimum electrical attachment is achieved to the upper and lower electrodes of each pair, as for any of the various circuit connections shown, it being understood that the bus elements 45, 45 of each set as in FIG. 3, are suitably connected together in the ultimate electrical circuit.

The electrolyte circulation system also includes suitable means for positively advancing the electrolyte in the described manner, as well as means for removing suspended or otherwise collected foreign matter, both liquid and solid, and likewise gases if necessary, and for maintaining the electrolyte at a desired, advantageously high temperature. Thus in FIG. 1 the discharge pipe or drain 34 may extend to a settling tank 48, which may have a valve clean-out passage 49 or other suitable arrangements for removing settled, floating or otherwise unwanted materials and may also be taken to represent any further arrangements needed for renewing or replenishing the electrolyte, including filtration means, if required, and means for supplying additional water or acid. From the settling tank, clean, essentially fresh electrolyte is continuously withdrawn through temperature control means 50, which may embrace heating or cooling means, as may be necessary depending on such factors as sheet speed, sheet gauge and electrical power input. Such withdrawal is effected by a pump 52 which directs the electrolyte at an appropriate rate into branch pipes 53 and 55 that lead respectively to the cell inlet ports 31, 33 described above. Thus continuous circulation of renewed or renovated electrolyte is achieved, with the provision for separation of foreign matter that has been removed from the surface of the strip.

After the electrical treatment in the cell 12 the aluminum strip can be suitably rinsed and dried. The rinse section 13 (FIG. 2) may include a series of alternating water spray devices 57 and pairs of wringer rolls 58, wherein by rinse water is repeatedly delivered to and squeezed from both faces of the sheet and a thoroughly rinsed and partially dried strip is thus delivered to the drying section 14. In the latter the strip may traverse a vertical circuit past suitable heating elements, if desired, and can finally be delivered for coiling, or even for direct travel to a locality of further treatment such as the lacquer application indicated at 15.

The cleaned, electrolytically treated strip is suitable for many purposes, but is unusually effective for lacquering, which is an extremely important mode of treating aluminum surfaces, especially for use of aluminum sheet in making cans and other containers, for example notably containers or parts for them, to be employed in the food and beverage canning industries. Indeed more generally, lacquered sheet is useful for any of a variety of container and lining applications wherein special resistance of the surface to various solid or liquid materials is necessary. As will be understood, lacquers for these purposes are well known and of considerable variation, e.g. as to their bases, which are commonly dissolved or dispersed in solvents such as alcohols, ketones or the like. Examples include lacquers with cellulosic bases and vinyl-type resin bases; epoxy-type lacquers are presently of particular importance. Many of the same requirements as to adhesion are found in other coating materials, especially organic coatings, that are frequently desired to be applied to aluminum sheet. These include materials generally classed as paints, and also electro-coatings, e.g. electrophoretically applied materials, whether serving as primers or otherwise. All of the above, for which the treatment of the present invention is suitable, can be generally identified as organic coatings, being usually liquid-applied substances that dry or solidify on the sheet surface upon or after application. In an alternative sense, they comprise film-forming agents, which may be carried in liquid solvents, and they may or may not include supplemental materials such as pigments, plasticizers and the like.

As will be understood, further mechanical features of the cleaning or conditioning line may be employed as desired, including payoff, takeup and tensioning means as mentioned above, and likewise appropriate devices such as any smooth protuberances or guides (not shown) as may be needed to maintain desired centering of the strip in its
passage or to avoid damage to the electrodes should there be an inadvertent breakage of the strip. Another feature of special significance both in the sense of procedure and apparatus is that the successive electrode pairs E-1, E-2, E-3 and so forth are mutually spaced along the path, by insulating structure of the cell wall, so as to obviate significant shortcircuit of electrical current through the electrolyte between any two adjacent pairs that are connected to opposite terminals of the electrical source, this being in accordance with improvements embraced in the aforesaid Pat. No. 3,471,575.

The practice of the invention, in one presently preferred manner may be conveniently described in connection with the pretreatment of a strip of aluminum strip, continuously advanced as at 10. Hot sulphuric acid electrolyte, consisting of 15% sulphuric acid in water (all percentages here and elsewhere being given by weight, unless otherwise noted) is delivered through the ports 31, 33 so as to travel lengthwise through the cell 12 to the exit chamber 20 at a suitable velocity, say 2 feet per second, the cell being kept entirely filled with the electrolyte, for submergence of the strip. The strip is advanced at a selected rate, such as 750 feet per minute or 1000 feet per minute, in the indicated direction countercurrent to the electrolyte. In accordance with the invention, cathodic cleaning is accomplished so that the strip is successively cathodic, then anodic, and finally cathodic again, special further advantage being realized with a substantially greater number of the electrode pairs being such as to render the strip anodic than the pairs near the entrance and exit providing much shorter path length when the strip is advanced.

Specifically, the electrode pairs E-1 and E-2 are connected to the positive terminal of the source 60 of direct current, while all of the six remaining electrode pairs E-2 through E-7 inclusive are connected together to the negative terminal. Thus current can be considered to flow from the electrodes E-1 and E-8, through the electrolyte, to the faces of the strip, and then from the strip, through the electrolyte to all of the other electrodes between the first and last pair as designated. The current supplied by the source 60 is appropriately controlled or adjusted by a conventional meter for governing voltage and current flow (not shown) so that the total charge density, conveniently here designated as total coulombic charge, is kept at an appropriately low figure. An unusual balance of effectiveness and economy is found attainable, at least for many lacquer-applying and similar purposes, with such a current at the value of about 1 to 3 coulombs per square inch, a general range of usefulness and efficiency being from 0.1 to 5 coulombs per square inch, depending on requirements of cleaning and requirements of oxide coating or the like, i.e. needed to characterize the finished sheet.

The total charge or total coulombic charge, as used herein, is taken as the total current at the strip surface divided by the surface area velocity of the strip, e.g. in square inches per second past a given point. Inasmuch as the flow of direct current through the electrolyte in an arrangement as indicated, with positive and negative electrodes exposed to the electrolyte, extends both into and out of the strip, such total current through the strip surface is taken as twice the actual value of electrical current in the circuit from the source 60. Since a flow of one amper at one second represents one coulomb of charge, the total charge or charge density is conveniently determined as the total strip surface current divided by the area of strip passing a given point in one second, such area being the velocity of the strip in inches per second, multiplied by the width, and further multiplied by two where both sides of the strip are treated and the current flow is in fact the sum of the portions of current respectively affecting the two sides. Hence the charge density, or total coulombic charge, measured in coulombs per square inch, is calculated as twice the actual current flow (from the source) divided by the product of the multiplication of the sheet width, in inches, by the sheet velocity, in inches per second.

In the above process example with the sheet travelling as stated and the current supplied in the described manner to achieve a total charge of 2 to 3 coulombs per square inch, and with the electrolyte maintained at a suitable temperature, say 90° C., the delivered strip is found to be extremely well cleaned and furthermore is found to be appropriately conditioned for excellent adhesion of lacquer or the like. It is characterized by an extremely thin oxide film of anodically formed character, and it also has been discovered that even though the strip may be a magnesium-containing alloy, there is no interference with lacquer treatment or adhesion for such reason. Although the invention is not limited to any particular theory, it is believed that the operation of passing the strip through the entire length of the apparatus, including the cathodic-type electrolytic cleaning action adjacent the entering and leaving regions of the cell, coasts with the formation of the anodic film so as to leave the treated metal surfaces in excellent condition, and particularly coats with the effects of some significant solution of the formed oxide by the acid electrolyte, to provide a condition which is unusually suitable for subsequent lacquer treatment.

As will now be understood, the actual current needed (as from a source 60) is to achieve a given total coulombic charge density readily determinable from the selected strip speed and strip width. Thus at a strip speed of 750 feet per minute a current flow from the source of 150 amperes per inch of strip width is required to provide a total charge density of one coulomb per square inch. At 1000 feet per minute, the value is 200 amperes per inch of strip width. Correspondingly for a 12 inch wide strip at 750 feet per minute, a current of 1800 amperes must be supplied to achieve one coulomb per square inch, and 2400 amperes at 1000 feet per minute.

By way of example, one useful embodiment of the apparatus of FIGS. 1-4 employs electrolytes such as 36, 37, each having dimension, in the direction of strip travel, of 8 inches, and a width across the width of the strip path, of 48 inches, with a spacing of about 10 inches along the path between each electrode pair and the next one. The internal passage may correspondingly have a width of slightly over 48 inches and a height of 2½ inches, for advantageously close spacing of the electrodes along the strip, and for accommodating strip widths of up to 4 feet. The total length of the cell is thus of the order of 10 feet, being specifically about 12 feet through the enclosed portion of the path where full liquid turbulence is effective, i.e. between the chamber 20 and the electrolyte inlets 31, 33.

Although some effective cleaning and pretreatment action can be obtained in relatively short cells, it has been found that for higher speed operation, as at 750 feet per minute and more, a cell of the total length indicated above affords superior results. For best adhesion of lacquer or paint, it appears that some modification of the as-formed oxide film by electrolyte dissolution is very desirable. Whereas the rate of film formation can be raised by using a higher current density, to suit higher strip speed, the desired chemical dissolution, which appears to alter the surface topography and perhaps the chemical activity of the film, is not so much a function of current density and inner-surface current density as the time in the hot, preferably or advantageously at least a total contact time in the cell of about 0.5 second to 1.5 seconds, or more, up to 3 seconds. In a 10-foot cell, which is suitable, the contact times at 750 and 1000 feet per minute are respectively 0.8 and 0.6 seconds.

Lacquer adhesion has been demonstrated by a test as follows: a conventional, commercial lacquer (Roxalin, Tuna AS100X3004) is applied to the surface of a piece
of the aluminum strip and the coated strip is then held at a temperature of 400°F. for 10 minutes, to produce a coating weight of 4 mg. per square inch. In most cases, the strip piece is formed into a cup shape after lacquer application, but the test piece has been formed severely without such shaping. In either case the lacquer-coated piece is immersed in an aqueous test solution of 2% tartaric acid and 5% acetic acid for 75 minutes at 212°F. After this boiling chemical treatment, the dried coating is scored, by suitable implement, and covered with pressure-sensitive adhesive film tape. Upon pulling off the tape, the surface is examined for removal of the lacquer coating, the following rating classes being utilized: A, no removal; B, removal up to 5%; C, 5% to 25%; D, 25% to 50%; E, more than 50%, considered equivalent to total removal.

When subjected to the foregoing test, aluminum strip in its as-rolled condition, without cleaning or pretreatment, generally showed a lacquer adhesion rating of E, and essentially no ratings better than D. While chemical treatments have been evolved for cleaning and preparing aluminum surfaces to be employed in lacquering, experience indicates that it is sometimes difficult, with such treatments, to obtain optimum adhesion. This is particularly true in the case of magnesium-containing aluminum alloys, which are quite commonly employed to make cold-rolled thin aluminum strip for the manufacture of containers and the like. As indicated above, the magnesium content appears to interfere with proper lacquering, and it is found that the difficulty of securing good lacquer adhesion increases with higher magnesium content. For example two commonly used alloys are AA-5052, which has a composition of 2.2 to 2.8% magnesium, and AA-6061, with a composition of 4 to 5% magnesium and 0.2 to 0.5% manganese, the balance in each case being aluminum and minor or incidental elements. Experience has shown that AA-5082 and AA-5182 (each 4.5% Mg) are more difficult to pretreat and to obtain satisfactory adhesion upon, than AA-5052 (2.5% Mg).

A known chemical treatment of proprietary nature was selected for purposes of comparison, such being believed to be as good a chemical pretreatment for lacquer as has been commercially used for even moderate speeds of treatment. It conventionally involves cleaning and treatment stages, in succession, each ordinarily requiring a duration upwards of at least several seconds. When a strip of AA-5052 was treated with this chemical operation (involving no electrolytic process), ratings as high as B were only obtainable in a reliable way in special tests with 30 seconds cleaning time and 20 seconds treatment time. In contrast, using electrolytic treatment according to the present invention, and advancing the AA-5052 strip at 1000 ft./min., B ratings were consistently achieved at a total charge density of no more than about 2 coul./sq. in., and in a number of cases at considerably less charge. Unprocessed AA-5052 yielded E ratings.

In the case of alloy AA-5182, ratings of B were only inconsistently attained with the special, prolonged adaptation of the above chemical operation. When the latter was employed in a manner more appropriate for commercial practice, ratings in the range of C to D resulted from 8 seconds cleaning time and 6.8 seconds treatment time. Utilizing the present invention, notably with the preferred electrode sequence such as in FIG. 1, the following results, for example, were achieved on AA-5182 strip: B to C ratings at 750 ft./min. and 2.7 coul./sq. in.; C ratings at 1000 ft./min. and 2 coul./sq. in.; A to B ratings at 300 ft./min. and 1 to 3 coul./sq. in. Unprocessed AA-5182 yielded E ratings.

While the improvement is particularly remarkable for the alloys having higher content of magnesium, e.g. upwards of 4% or at least upwards of 3%, it is nevertheless conceived to be significant for alloys of down to about 2% magnesium. Indeed this aspect of improve-

ment is believed to be basically realized with any alloy containing magnesium about 0.5%, e.g. notably for the recognized AA-5xxx series of alloys, having various magnesium contents from about 0.5 to about 5.6%. Of course, on less difficult test pieces, e.g. substantially free of magnesium, the treatment also provides a good base for lacquer.

The unexpected special advantages of the preferred electrolytic treatment sequence, wherein the strip is successively cathodic, anodic and then again cathodic have been abundantly demonstrated by tests. One such set of investigations was conducted in a cell generally similar to that shown in FIGS. 1–4, having a total length of about 12 feet and including six successive pairs of electrodes, adequately spaced along the strip path, in the general fashion of electrodes E-1 and so forth in FIG. 1. These tests were made with 2 inch wide aluminum strip, being sheet of 0.010 inch gauge, of the high magnesium alloy AA-5052, with 15% phosphoric acid solution advanced through the cell, at 90 °C. and a flow rate of about one foot per second, countercurrent to the strip travel.

In the following Table A the results of treatment are given for three selected electrode sequence configurations, for strip speeds of 300 feet per minute. As will be understood, the electrodes were stationed from 1-6 in order in the direction of strip travel, and in the table the connection of the electrodes is indicated by letters c, a, or by blanks, respectively representing connection to the positive, negative or neither terminal of the direct current source, so that the sheet at such localities is cathodic, anodic, or not electrically affected. Hence in test series I, the sheet was cathodic as it passed electrodes 1 and 2 and anodic at the region of electrodes 5 and 6, there being no electrical connection at electrodes 3 and 4. In test series II the split electrode arrangement was utilized, as noted, with no energization of electrodes 2 and 5. In test series III the first and last electrodes were connected to make the strip cathodic, while a much larger electrode area, at numbers 2–5 inclusive, was utilized for the intermediate anodic condition. In each run, the voltage applied to the complete cell was adjusted to provide the stated flow of current from the source, e.g. at 100 amperes and 200 amperes respectively. With the 2 inch wide strip at 300 feet per minute these yielded total coulombic charge values of 0.85 and 1.7 coulombs per square inch. The results were as follows:

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As will be seen, the adhesion ratings, especially for the preferred electrolytic sequence, were uniformly good, reaching the optimum value of A with the higher current. Of unusual significance is the lower voltage requirement for the split electrode sequence as in test series II and III. This represents voltage savings of at least about 5%, being significantly very high for the split electrode sequence such as indicated in series III and utilized in FIG. 1 of the drawings. It is now correspondingly recognized that the further special advantage in this latter arrangement may be attributed to the substantially lower anodic current density at the strip in arrangement III (as distinguished from arrangement II) which results in a decrease in cell voltage, inasmuch as most of the voltage drop across the cell is due to the anodic treatment. In all cases, of course, the decrease of voltage requirement
affords a corresponding decrease and saving of power requirement, and thus of the cost of treatment. The relative saving, moreover, is greater at higher current values. The power lost in the strip is proportional to the current squared while the power consumed in anodizing increases at a lower rate; as is true generally of anodizing, the effective electrical resistance of the anodic film tends to decrease at high current levels. This results in an increase in the power lost in the strip as a fraction of the total power, as current increases. Thus, the proportionate savings due to the cathodic-anodic-cathodic configuration increase with increasing current levels.

As will no doubt be seen, the optimum arrangement affords, in effect, a double action of economical and efficient character in the first cathodically cleaning and activating the aluminum surface, then forming a thin oxide film by anodic action, and finally modifying and cathodically re-cleaning the surface, while utilizing a minimum of electrical power.

A further set of tests, confirming the basic and unusual voltage saving achieved with a split electrode sequence, was effected with suitable 2 inch strip, of alloy AA-5052, and the same cell arrangement and electrolyte conditions as for Table A, but with the strip travelling at 1000 feet per minute. The results of these tests, for the electrolytic sequences as noted and for successively increasing current values are as follows:

![Table B](image)

The total coulombic charge for the operations at 200, 400 and 600 coulombs per square inch. The very significant voltage reductions and corresponding percent savings attained with the split electrode sequence were as specified in the table. Basically the voltage reduction arises because for the same total current, the split electrode sequence provides a reduction of average current flowing through the sheet cross-section and there is therefore less voltage drop (and lower power loss) in these portions of current path. It was further noted that the voltage reduction and saving increase with thinner strip; whereas the above tests were made with strip of 0.010 inch gauge, calculation indicated twice the reduction and saving to be attainable with strip of 0.005 inch gauge.

In order to obtain the particularly desirable electrode arrangements for successive cathodic, anodic and cathodic situations of the travelling strip, direct current, meaning unidirectional current as distinguished from alternating current where the polarity is reversed, is required. Moreover, direct current is preferred, in distinction to alternating current, in that single phase alternating current may well be more costly in view of its lower effectiveness, and direct current has been found to be more efficient, particularly in producing anodic oxide coatings. Large single phase A.C. power loads, moreover, create unbalance in 3-phase distribution networks, and the utility supplier may charge a premium.

The hot acid solution used as electrolyte in the procedures here described may conceivably be any such as is generally useful for continuous anodizing operations, for example including mineral and other acid solutions as disclosed in the above mentioned patents, but special advantages of convenience, economy and effectiveness have been found for sulphuric acid solutions in water, suitably selected in the range of 5-50% sulphuric acid, preferably not over 40% (all composition percentages herein being given by weight). Best concentrations appear to be from 10% to 35%; indeed highly superior results have been attained with the moderately dilute 15% solution conventional in anodizing.

With lead electrodes, it has been found desirable to keep a small concentration of aluminium ions in the solution, for example by adding an aluminium salt such as aluminium sulphate and appropriately checking and controlling the aluminium ion content to avoid either too little or too much, i.e., so as to prevent appreciable attack on the electrodes and to avoid impairment of the surface of the treated strip. An aluminium ion concentration of about 2 to 5 grams per liter is found appropriate, and convenient practice is to control the concentration at about 3 grams per liter.

As explained, the electrolyte should circulate at a velocity in the cell of suitably effective value, preferably in the range of about 1/2 to 5 feet per second. The electrolyte should ordinarily be hot, e.g. above 40° C, very preferably in the range of about 70° to 100° C and most advantageously at 80° C or above. A presently preferred practice is to advance the electrolyte counter current to the strip, at 90° C, and at a velocity (in the above range) of 2 feet per second, i.e., relative to the cell. This affords effective removal of the foreign matter such as dirt and grease and cooperates with the selected speed of strip travel so that a very high relative velocity between strip and electrolyte is afforded, for correspondingly very high turbulence. As has been stated, strip speeds up to 1000 feet per minute have been satisfactorily treated, it being conceived that higher speeds, e.g. 1500 feet per minute, are obtainable. While advantages of the invention are realized at speeds of 300 feet per minute and upwards, unusual efficiency is reached at the higher rates of travel, mentioned hereinabove.

As also stated, a preferred arrangement is with a substantially greater area of the passing strip constituted to be anodic, relative to the total of the cathodic areas at opposite ends of the cell, special advantage being realized where there is at least twice as much anodic area, or even three times as much (as in FIG. 1) as the cathodic area. This provides a correspondingly reduced current density at the anodic regions of the aluminum, it being understood that the current density at each type of region can be computed by dividing the current flow (from the source) by the total area of strip which directly faces the electrodes of a given polarity, below and above the strip. It is presently understood that in effecting pretreatment for lacquer or other coatings, the anodic treatment time in the cell is the more important phase of the process. Therefore in a cell of given length, it is unusually advantageous to have considerably more anodic area than cathodic area, in order to make most efficient use of the available cell length.

Although actual or absolute values of current density may be selected to suit practical operation, and relative values are significant in the sense just explained, attainment of desired results in the present process has been more particularly related to total coulombic charge density. Some cleaning and even conditioning effects are attainable with total charge as small as 0.1 coulomb per square inch, notably where the aluminum surface happens to be fairly clean as received. Most often a coulombic charge of at least 0.5 coulomb per square inch is desirable, ranges of such value up to 1.5 for cleaning (and sometimes for conditioning), and up to about 3 for pretreatment for lacquer or the like, being presently representative of a convenient balance between greatest economy and generally satisfactory results. In most cases substantially more than 3 coulombs per square inch appears unnecessary, although the actual amount depends on the condition of the received surface in that higher charge densities may be needed for removal of unusually heavy deposits of grease and dirt.
the electrolyte, for example, a sulphuric acid solution, the temperature of the electrolyte, and its rate of advance may be the same as has been described above, for treatment of aluminum strip at rates up to 1000 feet per minute and indeed substantially higher. When operating in this relatively simple manner and primarily for cleaning, there is a maximum of economy in utilizing a coulombic charge density of not more than 1.5, indeed preferably less, for example at 0.5 to 1 coulomb per square inch.

Comparative tests have shown that when a clean strip is required without a high level of lacquer adhesion there is an increase of cleaning effectiveness with restricted electrode area, e.g. as shown in FIG. 5, this result being particularly notable at the lower coulombic charges mentioned above as appropriate for such cleaning. In these tests the cleanliness of the sheet after treatment was determined by a dye-drop test, which involved utilization of liquid mixtures of water and methanol in various proportions, the mixtures containing a blue dye for ready observation and the test being such as to afford a cleanliness rating in accordance with the proportion of water which could be tolerated while still achieving a prescribed spread of the drop on the surface. Specifically, a liquid consisting of 100% water is denominated as 10, while 100% methanol is 0, intermediate values being related to the percentage of water (volume) of water. Thus a value of 8 represents 80% water, and 20% methanol, a value of 5 is 50% water and 50% methanol, a value of 2.5 is 25% water and 75% methanol, and so on. The test is conveniently effected by depositing small drops, e.g. from a standard size dispenser such as a small syringe, on the surface of the sheet, using liquids of successively lower proportions of water, until a spread of the drop to a standard diameter, e.g. 8% inch, is achieved. As will be understood, a drop of pure water on an unclean surface will not spread at all, whereas with increasing methanol content and correspondingly decreasing surface tension of the liquid, the tendency to spread is increased. Values of 0 to 1 represent uncleaned or poorly cleaned surfaces, whereas values upwards of 2 correspond to a fair degree of cleanliness (and absence of grease or oil), while truly superior results are reached with values upwards of 4, e.g. 5.

The comparative treatments were run with 2 inch wide strip of alloy AA-5182 at 1000 ft./min., utilizing the cell described above as having 6 successive pairs of electrodes. In one set of operations the electrodes were all employed to provide a cathodic-anodic-cathodic arrangement for the strip as indicated in the table below; while in another set, only the first two pairs of electrodes were used, being connected for a simple cathodic-anodic sequence. In each set of runs, the voltage and current were adjusted to provide total coulombic charges respectively of 0.5 and 1.0 coul./sq. in. The cleanliness of the treated strip was examined by the dye-drop test above, the results being as follows:

<table>
<thead>
<tr>
<th>Electrode sequence given as strip polarity</th>
<th>0.5 coul./sq. in</th>
<th>1.0 coul./sq. in</th>
</tr>
</thead>
<tbody>
<tr>
<td>c a n a e</td>
<td>2.5</td>
<td>2.75</td>
</tr>
<tr>
<td>c a n a e</td>
<td>2.75</td>
<td>4.00</td>
</tr>
<tr>
<td>c a n a e</td>
<td>11.6</td>
<td>19.8</td>
</tr>
</tbody>
</table>

As will be seen, the dye test ratings were significantly higher, for the same coulombic charges in this low range of such values, where the simple electrode configuration was employed with a markedly smaller electrode area. Indeed the unusually high rating of 5, meaning an extremely clean surface, was obtained with the last-mentioned configuration and electrode area at the total charge of 1 coul./sq. in. While there was a substantial increase in voltage, the latter was more than compensated for by the increased cleaning efficiency. In other words, when the primary requirement is for cleaning, there is special advantage in operating at relatively high current density at the sheet surface, while still maintaining a relatively very low coulombic charge. Specifically, current densities (opposite each electrode) of at least 100 amperes per sq. ft., and preferably as much as 600 amperes per sq. ft. or more, were found unusually suitable under these circumstances.

It is particularly noted that degreasing is usefully achieved in these instances as well as all other embodiments of the invention, yielding a treated aluminum product which, when rinsed and dried, requires essentially no further cleaning for most uses.

Examples of other acid solutions found very useful as electrolytes, most particularly where the process is performed as a pretreatment for electro-coating, e.g. electrophoretic deposition of paint coatings (including primers) or the like, are: a solution containing 15% phosphoric acid, used at 90° C; a like solution also containing 1% sulphuric acid, similarly used; a solution containing 10% nitric acid, employed at 50° C; and a chromic acid-sulphuric acid solution, prepared to contain 50 grams per liter CrO₃ and 5 grams per liter H₂SO₄, used at 90° C. As pretreatments for electrophoretically applied paints, these are effective only with a bloom of 0.5% acid.

It is to be understood that the invention is not limited to the specific embodiments herein shown and described, but may be carried out in other ways without departure from its spirit.

What is claimed is:

1. A method of continuous high speed treatment of an elongated aluminum article to provide a clean surface thereon, comprising advancing the article lengthwise at a speed of at least about 300 feet per minute along a path through a treatment zone filled with acidic electrolyte, while passing direct current between said article and adjacent electrodes at least 20 amperes, and using an electrolyte successively disposed in the direction of travel of the article, said current being passed from the electrolyte to the article surface at a first region whereby said surface is there cathodic, then from the article surface to the electrolyte at a second region whereby the said surface is there anodic and also from the electrolyte to the article surface at a third region whereby said surface is there again cathodic, and while advancing said electrolyte along the article surface and maintaining turbulence of said electrolyte relative to and throughout said surface of the article in the zone, said current providing a total coulombic charge density affecting said surface of the article in said zone, selected in the range of 0.1 to 5 coulombs per square inch, which is sufficient to impart said clean surface to the article and insufficient to effect formation on said surface of more than 50 milligrams of anodic oxide film per 100 square inches of surface.

2. A method as defined in claim 1, in which the passage of current between the article and the electrodes is effected so that the article surface region which is anodic has an area which is substantially greater than the total area of the article surface regions which are cathodic.

3. A method as defined in claim 2, in which said current passage is effected so that said anodic area is equal to at least twice said total cathodic area.

4. A method as defined in claim 1, in which said electrolyte is an aqueous solution of sulphuric acid and is maintained at a temperature of at least 70° C, and said article is advanced through the zone at a speed of at least about 500 feet per minute.

5. A method of continuous high speed treatment of aluminum strip to provide a clean surface thereon, com-
While lacquer adhesion tends to improve with higher current or higher charge densities, possibly to 5 coulombs, the operating examples given herein have been found satisfactory for various strip conditions. Thus for instance a charge density of one coul./sq. in. is useful when the primary purpose is to clean the strip and provide lacquer adhesion for light duty, examples of such use being: (a) for a lacquer with outstanding adhesion characteristics; (b) for a lacquer exposed only to a mildly corrosive environment; and (c) in most cases for application of lacquer to an alloy such as AA-5052. Further examples involving more severe duty have been noted above, as to treatment of alloy AA-5182: good lacquer adhesion results at 2.7 coul./sq. in., and a treatment adequate for many purposes at 2 coul./sq. in., these being obtained with current of 400 amperes per inch of strip width at speeds of 750 and 100 feet/min., respectively.

Under favorable circumstances, a relatively light treatment may suffice. Thus in one set of tests with strip of alloy AA-5182, treatments at 750 feet/min. with 15% sulphuric acid and 90° C. yielded a C lacquer rating for 0.15 coul./sq. in. and an A rating for 0.3 coul./sq. in., where a preceding heat treatment had left the strip unusually clean, and also had improved its ductility in a manner that reduced the severity of the lacquer adhesion test.

It should be noted that although a definite anodic oxide film is contemplated to exist as a result of the electrolytic treatments herein described, it is preferably to be measurable by weight rather than any actual dimension of thickness. Present indication is that coating weights of 5 to 50 milligrams per 100 square inches are appropriate, and very advantageously such weight in the range of 20 mg. and less. It is understood that in the one coulomb per square inch circumstances of treatment, attained coating weights are generally well below 20 mg. per 100 square inches. As indicated, best efficiency and excellent results are obtainable with coatings that have weights substantially less than 50 mg. per 100 sq. in., and that are substantially thinner than 0.01 mil.

Although the unusual superiority of the present procedures for high speed cleaning and conditioning of magnesium-containing aluminum alloys has been demonstrated by direct test, special experiments have shed some light on the Johnson and Anodic conditions for three or more successive localities, of which a simple but effective example is the specific sequence illustrated in FIG. 1, it has been noted that the basic electrolytic operation, at very high speed and with relatively low coulombic charge, is of itself significant value for treatment of aluminum strip or like continuous articles. Thus operations with a single sequence of polarity, such as illustrated in FIG. 5, where the strip is simply cathodic at one locality and anodic at another can perform an effective cleaning action, such being achieved by re-connection of the apparatus of Figs. 1-4. For example, the electrode pair E-1 is connected to the positive terminal of the D.C. source 60 and the next electrode pair E-2 to the negative terminal for making the strip successively cathodic and anodic, the remaining electrode pairs being electrically inoperative. Where cleaning is the primary purpose, it appears that a reverse electrode arrangement is also effective, i.e., where the moving sheet or other elongated article under treatment is first anodic and then cathodic; indeed it is presently understood that in either case the major part of the cleaning action takes place when the sheet is cathodic.

Cleaning action with a simple arrangement as in FIG. 5, using total coulombic charge densities of 0.1 coulomb per square inch and upwards, is significantly useful, and indeed in a number of cases has been found to provide a fairly good base for lacquer or paint application. The special advantages in the treatment of magnesium-containing alloys are significantly realized. The nature of

<table>
<thead>
<tr>
<th>Treatment type</th>
<th>Total charge (coul.)</th>
<th>Speed (ft/min.)</th>
<th>Al-Mg ratio in removed oxide</th>
<th>Time (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.2</td>
<td>50</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>0.1 a s</td>
<td>0.9</td>
<td>50</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>0.1 a s s c</td>
<td>0.9</td>
<td>50</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>0.1 a s s c</td>
<td>0.9</td>
<td>50</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

The results are most significant in the first column of the ratio values, which show the effect of the electrolytic treatments in selectively removing magnesium from the outermost layer of oxide. The aluminum-magnesium ratio is seen to be greatly increased in these outer portions of the oxide films formed and remaining upon the metal after the electrolytic treatments. It is believed that this reduction in magnesium concentrations can be directly or indirectly correlated with improved lacquer adhesion, because the samples treated electrolytically showed progressively improving lacquer adhesion, while other evidence, including past knowledge, has made it clear that it is more difficult to obtain adhesion on alloys having high magnesium content.

The above-described electrolytic treatments of aluminum surfaces afford an unusually superior action in cleaning or conditioning continuous surfaces of strip or other articles at extremely high rates of travel. Although special emphasis has been placed on the magnesium-containing aluminum strip or the like for subsequent application of lacquer or paint, and although in a specific sense the invention can be considered to be directed to procedure for such operations, the described treatment is conceived to be of general use in the cleaning of thin aluminum sheet, whether gauges used for various structural and fabricating function or whether of extremely thin nature, e.g. foil. An unusually well cleaned surface s very rapidly obtained, while the extremely thin oxide coating formed thereon represents no obstacles to most uses and indeed is conceived to contribute to the cleanliness of the surface, at least by virtue of the electrochemical action involved in its formation.

While a particularly important virtue of the invention resides in the specific electrolytic sequence described above, including alternating situations of the aluminum surfaces between cathodic and anodic conditions for three or more successive localities, of which a simple but effective example is the specific sequence illustrated in FIG. 1, it has been noted that the basic electrolytic operation, at very high speed and with relatively low coulombic charge, is of itself significant value for treatment of aluminum strip or like continuous articles. Thus operations with a single sequence of polarity, such as illustrated in FIG. 5, where the strip is simply cathodic at one locality and anodic at another can perform an effective cleaning action, such being achieved by re-connection of the apparatus of Figs. 1-4. For example, the electrode pair E-1 is connected to the positive terminal of the D.C. source 60 and the next electrode pair E-2 to the negative terminal for making the strip successively cathodic and anodic, the remaining electrode pairs being electrically inoperative. Where cleaning is the primary purpose, it appears that a reverse electrode arrangement is also effective, i.e., where the moving sheet or other elongated article under treatment is first anodic and then cathodic; indeed it is presently understood that in either case the major part of the cleaning action takes place when the sheet is cathodic.
prising advancing the strip lengthwise continuously along a path through a treatment zone enclosed closely around the strip and filled with hot, acidic electrolyte, while passing direct current between said strip and adjacent electrodes in the zone, at least through three regions of said electrolyte successively disposed in the direction of travel of the strip, said current being passed from the electrolyte to the strip surface at a first region whereby said surface is there cathodic, then from the strip surface to the electrolyte at a second region whereby the said surface is there anodic, and also from the electrolyte to the strip surface at a third region whereby said surface is there again cathodic, and while advancing said hot electrolyte along the strip surface and maintaining turbulence of said electrolyte relative to and throughout said surface of the strip in the zone, said current providing a total coulombic charge density affecting said surface of the strip in said zone, selected in the range of 0.1 to 5 coulombs per square inch, to impart said clean surface to the strip.

6. A method as defined in claim 5, in which the passage of current between the strip and the electrodes is effected so that the strip surface region which is anodic has an area which is equal to at least twice the total area of the strip surface regions which are cathodic.

7. A method as defined in claim 5, in which the strip is advanced through the zone at a speed of at least about 300 feet per minute, and the strip is composed of a magnesium-containing aluminum alloy and in which said current provides said selected charge density sufficient to provide a strip surface conditioned for capability of adherent coating by materials having sensitivity against adherence to such alloy.

8. A method as defined in claim 7, in which said current provides said charge density of at least about 2 coulombs per square inch.

9. A method as defined in claim 8, in which said electrolyte is an aqueous solution containing 10% to 35% sulphuric acid.

10. A method as defined in claim 5, in which said electrolyte is maintained at a temperature of about 90° C., and in which said current provides said charge density selected in the range of 0.5 to 3 coulombs per square inch.

11. A method as defined in claim 10, in which said strip is advanced through the zone at a speed of at least about 750 feet per minute, and in which said electrolyte is advanced through the zone countercurrent to the strip at a velocity of at least about 1 foot per second.

12. A method of continuous high speed treatment of an elongated aluminum article to provide a clean surface thereon, comprising advancing the article lengthwise at a speed of at least about 500 feet per minute along a path through a treatment zone enclosed closely around the article and filled with electrolyte which is an aqueous, acidic solution having an acid content not greater than 35%, while passing electric current between the electrolyte and the article surface at least at two localities in the zone spaced lengthwise of the article path, said current following a circuit which includes, in series, the electrolyte adjacent to the article at one such locality, the body of the article between the two localities, and the electrolyte adjacent to the article at the other such locality, and while advancing said electrolyte along the article surface and maintaining turbulence of said electrolyte relative to and throughout said surface of the article in the zone, said current providing a total coulombic charge density affecting said surface of the article in said zone, selected in the range of 0.3 to 1.5 coulombs per square inch, sufficient to impart said clean surface to the article and insufficient to effect formation on said surface of more than 20 milligrams of anodic oxide film per 100 square inches of surface.

13. A method as defined in claim 12, in which said passage of current is effected to provide a current density at the article surface at each of said localities of at least about 600 amperes per square foot.

14. A method of continuous high speed treatment of aluminum strip to provide a clean surface thereon, comprising advancing the strip lengthwise at a speed of at least about 500 feet per minute along a path through a treatment zone enclosed closely around the strip and adjacent to its surfaces and filled with hot, acidic electrolyte having an acid content not greater than 35%, while passing direct current between the electrolyte and the strip surfaces at a plurality of localities in the zone spaced lengthwise of the article path, including passing such current from the electrolyte to the surfaces of the strip at one such locality and from said surfaces of the strip to the electrolyte at another such locality, and while advancing said hot electrolyte along the strip surfaces and maintaining turbulence of said electrolyte relative to and throughout said surfaces of the strip in the zone, said current providing a total coulombic charge density affecting said surfaces of the strip in said zone, selected in the range of 0.1 to 3 coulombs per square inch, sufficient to impart clean character to said strip surfaces and insufficient to effect formation on said surfaces of more than 20 milligrams of anodic oxide film per 100 square inches of surface.

15. A method as defined in claim 14, in which said current provides a charge density of not more than 1.5 coulombs per square inch and the passage of said current is effected to provide a current density at the strip surfaces at each of said localities of at least about 600 amperes per square foot.

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