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ELEMENTS FOR USE IN THE ELECTRODEPOSITION OF CHROMIUM

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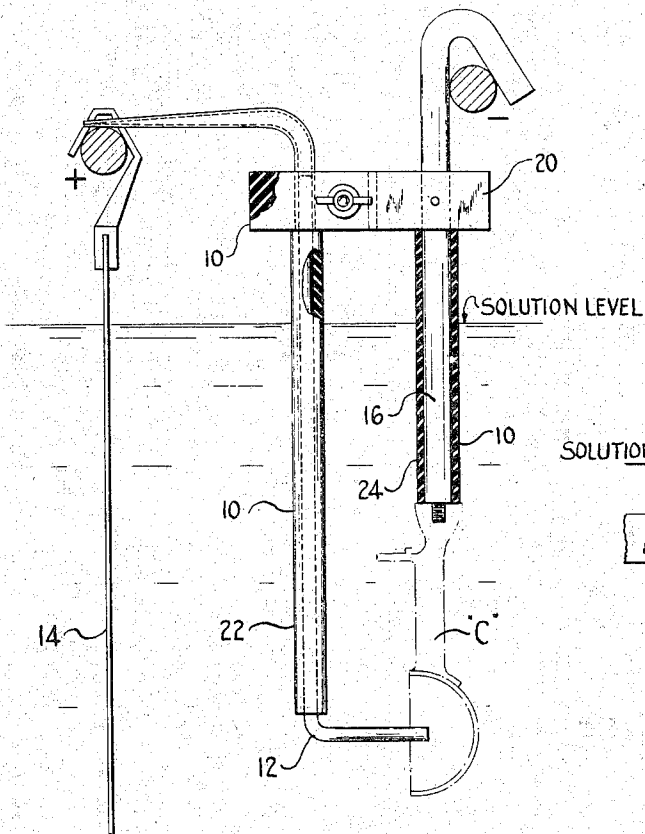


Fig. 1

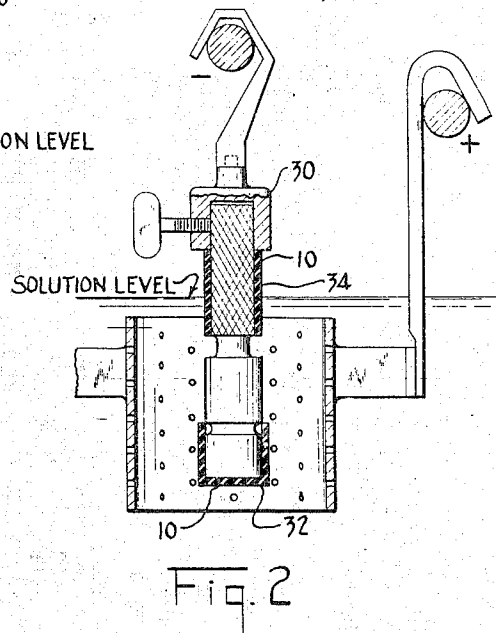


Fig. 2

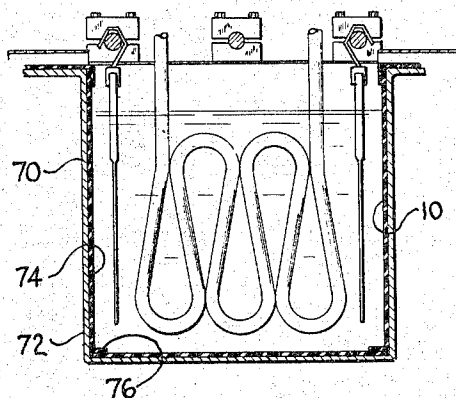


Fig. 4

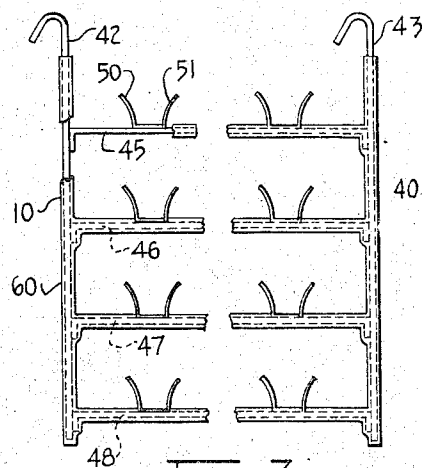


Fig. 3

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ELEMENTS FOR USE IN THE ELECTRO-
DEPOSITION OF CHROMIUMGeorge K. Herzog, New Rochelle, N. Y., assignor
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7 Claims. (Cl. 204—5)

This invention relates to a method, apparatus and elements thereof for use in the electrodeposition of chromium and provides improvements therein.

As is well recognized in the art of chromium deposition, a want has existed for an electrical insulator which would be highly resistant to plating solutions containing chromic acid and be more satisfactory and serviceable than those heretofore used. Insulators, or coatings thereof are used in the art of chromium plating, for example, to hold conducting parts of opposite polarity in spaced relation in or above the solution, to insulate parts of conductors and racks immersed in the solution, to "stop" or inhibit the flow of plating current to parts of cathodes on which it is desired not to have a plate, for lining containers to hold the plating solution, etc. The most satisfactory insulators heretofore discovered and now used are glass, ceramics, certain rubber products, "Bakelite"* condensation-resin, and cellulose products.

*The word "Bakelite" is understood to be a trade-mark of the corporation making and selling the resin, which resin is a condensation product formed from phenol and formaldehyde.

Glass and ceramics are of limited application because they are difficult to work, and are fragile. Rubber reacts with the plating solution, disturbing its composition in several ways, the rubber reducing the chromic acid to various trivalent chromium compounds and fouling the solution, and the sulphur increasing the acid-radical content by being oxidized to sulphuric acid radical. "Bakelite" is very brittle, difficult to work and therefore of limited application. When fillers are incorporated in the "Bakelite" to reduce brittleness and increase workability, the resulting product is readily attacked by the plating solution, causing fouling of the solution and destroying the insulator. Films of "Bakelite" or of cellulose compounds resulting from the drying of liquid coats of the dissolved materials also react with the plating solution, reducing the chromic acid and fouling the solution; the films are brittle and swell and increase in brittleness after exposure to chromic acid solution, and the parts of conductors and racks to which these coatings are applied have to be recoated at frequent intervals, the practice in many plants being to apply coats of the solution on weakened areas of the racks at the end of each day preparatory to use the next day. Furthermore, it is common practice in production to remove any films of grease or dirt on articles to be chromium plated by first racking them and then immersing the racks containing the work to be cleaned into hot alkaline solutions. Bakelite films break down very rapidly when immersed in hot alkaline solutions. Cellulose products and

films thereof behave similarly to "Bakelite" and have the same shortcomings.

The most satisfactory containers heretofore used for plating solutions containing chromic acid are lead or lead-alloy lined containers, and glass or ceramic containers. The lead-lined containers are conducting and some current will flow to them resulting in objectionable stray current effects. A disadvantage of stray currents, for instance, is the "shading" effect which occurs when an article is placed too close to the conducting lining, some of the current intended for plating going to the lining, and not enough going to the article, so that the part of the article adjacent to the lining is not plated or is improperly plated. Lead is also very heavy and is subject to attack by the solution, lead chromate being formed, which results in failure of the linings and in the formation of an undesirable sludge in the solution. Certain lead-alloys overcome the attack to a considerable extent. Glass and ceramic containers are heavy, fragile, and expensive, and they are principally used where the bath is of small capacity.

By the present invention I provide apparatus and elements thereof of an insulating character, or having insulating parts, which are highly resistant to attack by warm or cold chromium plating solutions containing chromic acid, which give superior service as insulation in the special use with these chromium-plating solutions, and which allow the plating process to be carried out without the composition of the solution being affected or the solution fouled; and the invention also provides a method of applying such insulation.

By the present invention I furthermore provide containers, etc. which are highly resistant to attack by warm or cold plating solutions containing chromic acid, which are of reduced weight as compared with metal, glass or ceramic containers, and which enable the process of plating to be carried out without the disadvantages of stray current effects.

One of the usually given properties of chromic acid is that of its attack on, and reduction by, organic substances.* It is therefore a surprising

*Hoppe & Freeman, "Electroplating with chromium, copper and nickel", Prentice-Hall, 1930 pg. 118, 195; Merck's Index, Merck & Co., Inc., 1930, pg. 167 under "Chromium trioxide"; Smith "Introduction to Organic Chemistry", The Century Company, 1917, pg. 880 under "Chromic anhydride".

discovery that organic substances formed by the polymerization of vinyl compounds (vinyl-compounds being characterized by the double bond group—CH=CH₂) should, when applied as insulators in any of the ways hereinbefore indicated, or as a container, etc., withstand the oxidizing action or other attack of warm or cold plating baths containing chromic acid. The vinyl com-

pound polymers which I have found suitable are those which from the physical standpoint are solid and tough. As most of the polymerization products of the common vinyl compounds are either too soft or too brittle, the desired physical properties may be obtained in the conjoint polymerization product of two different vinyl compounds (by which is meant polymerization of two or more compounds while in mutual contact); one compound (a vinyl halide, as vinyl chloride, for example, or vinyl benzene (styrene), for example) being one which, when separately polymerized, forms a "hard" resin, and the other compound (an ester of a lower aliphatic acid, as vinyl acetate, vinyl propionate, vinyl butyrate, for example) being one which, when separately polymerized, forms a "soft" resin.

These conjoint polymerization products or resins are made and sold by Carbide & Carbon Chemicals Corporation, 30 East 42nd Street, New York city. However, those conjoint polymerization products in which the proportion of the vinyl ester of the "soft" resin forming type is too great, may tend to hydrolyze, or are less resistant for some other reason, and therefore the vinyl ester of the "soft" resin forming type should be about equal to, and preferably less than, the vinyl compound of the "hard" resin forming type. That is, the range of the proportions of the two types of compounds in the conjoint polymerization product (calculated as the monomeric compounds however present in the resin) should be 50 to 95 parts of the vinyl compound of the "hard" resin forming type to 50 to 5 parts of the vinyl ester of the "soft" resin forming type. The optimum conjoint polymerization resin is one having 85 to 87 parts, of a total of 100 parts, of the vinyl compound of the "hard" resin forming type, and 15 to 13 parts of the vinyl ester of the "soft" resin forming type, calculated as explained above; and when "parts" of one or the other vinyl compounds are referred to herein, the word will be understood as being used in the sense explained above.

According to my invention, I make apparatus and elements, and the insulating parts thereof, to be used in contact with chromium plating solutions of a conjoint polymerization resin as herein described.

Embodiments of the invention are illustrated in the accompanying drawing, wherein;

Fig. 1 is a view principally in side elevation, but with parts in section, illustrating the invention in the form of a rack with an auxiliary anode.

Fig. 2 is a view partly in side elevation and partly in section, illustrating the invention in the form of a rack or fixture for plating an article with "stops" applied thereto.

Fig. 3 is a view in side elevation illustrating the invention in the form of a rack for holding a number of articles to be plated.

Fig. 4 is a view in cross-section of a plating tank according to the present invention.

Referring to said drawing, numeral 10 designates insulation of conjoint polymerization resin according to the present invention applied in a variety of ways to apparatus and elements, and to parts thereof.

Referring to Fig. 1, numeral 12 designates an auxiliary anode (conducting) which may be, as here shown, connected to the same anode bus-bar as the normal anode 14. 16 designates a conducting-rod which is connected to the cathode bus-bar and which supports the article C to be plated, the article being illustrated as a part of an ice-cream scoop, and as connected to a threaded stud

18 projecting from the rod 16. The position of the auxiliary anode 12 with relation to the cathode-article C is a more or less precise one, and so as to avoid the labor and care of positioning the auxiliary anode 12 for each plating operation, the auxiliary anode 12 and the cathode-rod 16 are mounted in fixed relation in a block 20. The block 20, connecting the parts 12 and 16 of opposite polarity, is made of insulation of the herein described kind. The rack or fixture shown in Fig. 1, when used for plating in a chromium plating installation, projects partly below the surface of the plating bath, the immersed part being below the "solution level" indicated in the figure. The parts 12 and 16 being conductors having opposite polarity, the parts below the solution level should be insulated so that current will not flow directly from one part to the other. To prevent such current flow, insulation of the herein described kind in the form of a tube or sleeve 22 is applied to the vertical length of the auxiliary anode 12, and insulation of the herein described kind in the form of a tube or sleeve 24 is applied to the rod 16. The parts of the rack above the solution level also come into contact with the solution, as the gas arising from the bath as a spray carries with it some of the plating solution which wets the parts of the racks above the solution-level of the bath.

The chromium plating solution is one containing chromic acid, and, to resist the action of the plating solution, I make the insulating block 20 and tubes 22 and 24 of molded or extruded conjoint polymerization resin hereinbefore described. Blocks, tubes, and also the coatings hereinafter described, of the hereinbefore described conjoint polymerization resin are not attacked by chromium plating solutions containing chromic acid, such conjoint polymerization resins having the characteristic of not being wetted by the plating solution, and hence do not require frequent renewals. They are also strong and non-brittle.

In Fig. 2 a fixture 30 for re-plating the "no-go" portion of a "go no-go" gauge is illustrated. The "go" portion of the gauge is "stopped" by having applied thereto a moulded cap 32 of the hereinbefore described conjoint polymerization resin which is fitted closely over the "go" portion of the gauge. A sleeve 34 of the hereinbefore described polymerization resin is also preferably applied to the handle part of the gauge to "stop" plating thereon.

In Fig. 3 is illustrated a conventional form of rack 40 for holding a plurality of articles for chromium plating at one time. The rack 40 comprises the side-rods (conducting) 42 and 43, to which are connected a series of cross-rods (conducting) 45, 46, 47, 48, and on these cross-rods are sets of spring-fingers (conducting) 50, 51, which press and hold the articles (not shown) to be chromium plated. The rack 40 is suspended in the chromium plating solution from a cathode-bus-bar by hooks 55. Insulation 10 of the hereinbefore described kind is applied to the rods 42, 43, 45, 46, 47, 48, to prevent current from passing directly from the anodes to the said rods. The insulation 10 is here shown as a coating 60 resulting from the successive application of films or coats of the hereinbefore described conjoint polymerization resin in solution, and drying. In applying the coating 60 to the metal surface (copper for example) the metal should first be thoroughly cleaned. A priming coat should then be applied. The priming coat consists of a solution of the hereinbefore described conjoint polymerization resin containing a suitable pigment (as

blue-lead*) for stabilizing the resin during subsequent baking.

*See page 38, "Useful information about lead" published by Lead Industries Association, New York city, 1931.

The priming coat is then baked on at a suitable temperature. Thereafter successive coats of the hereinbefore described conjoint polymerization resin are applied by applying successive coats of a solution of the aforesaid resin, and drying.

An example of the method of applying the resin as a built-up coating, is as follows:—

1. Spray one coat of primer consisting of a solution of the hereinbefore described conjoint polymerization resin containing blue lead as a stabilizer.

2. Dry $\frac{1}{2}$ hour in air, then bake one hour at 350° F.

3. Apply one coat by dipping in a clear solution containing about 20% of the hereinbefore described conjoint polymerization resin dissolved in a suitable solvent.

4. Dry $\frac{1}{2}$ hour in air, then force dry one hour in an oven at 150° F.

5. Apply one coat by dipping in said clear resin solution.

6. Dry $\frac{1}{2}$ hour in air; then force dry one hour in an oven at 150° F.

7. Apply one coat by dipping in said clear resin solution.

8. Dry $\frac{1}{2}$ hour in air, then force dry 4 hours in an oven at 150° F.

Instead of dipping in the solution of the hereinbefore described conjoint polymerization resin, it may be applied with a brush, or by spraying the solution on the rack.

In Fig. 4 is illustrated a tank or container 70 for a plating solution containing chromic acid, forming part of an installation for chromium plating. The tank 70 may be of welded steel 72 having the insulation 10 of the herein described kind applied thereto in the form of a lining or coating 74. The coating may be a coating which is built up by spraying or otherwise applying coats or films of the hereinbefore described resin solution, and drying, as heretofore described, or it may be composed of moulded sheets of the conjoint polymerization resin hereinbefore described. The joints 76 may be closed in suitable manner, as by heating the lapped portions of the sheets of the hereinbefore described conjoint polymerization resin to soften them somewhat and then pressing the lapped portions together; or the hereinbefore described conjoint polymerization resin in the form of a powder may be warmed and applied as a putty to the joint; or a thick solution of the hereinbefore described conjoint polymerization resin may be applied to the joint and subsequently dried. The tank or tank-lining 60 may also be a molded monolith of the hereinbefore described conjoint polymerization resin. With a tank so constructed straying of current to the sides of the tank will be avoided and the "shading" effect on articles suspended in the solution, near the sides for plating, will be avoided. Also there will be no attack on the lining by the plating solution which contains chromic acid, and consequently no sludge formation such as results from the attack of chromic acid on the lead linings of lead-lined tanks. Moreover, with a tank such as here provided, there is no metal contamination of the plating solution, such as results when solutions containing chromic acid come into contact with iron, copper, etc. The tanks accord-

ing to this invention are lighter in weight than heretofore, strong, and non-fragile.

The conjoint polymerization resins as herein described, applied as herein described, will hold their form, and maintain their resistance to the action of chromium plating solutions containing chromic acid in the usual warm baths (temperatures of $35-55^{\circ}$ C.) as well as in the cold baths.

Chromium plating solutions usually contain from about 150 to 500 grams per liter of chromic acid (CrO_3) and catalysts in the form of an acid radical or radicals, such as sulphate-radical, fluoride-radical (silico-fluorides, boro-fluorides), etc. Such solutions may also sometimes contain other radicals, such as the chloride-radical, etc. Reference is made to Fink Patent #1,581,188 and Fink & McLeese Patents #1,844,751 and #1,928,284, concerning the composition, etc. of chromium plating baths and methods.

Racks provided with insulation according to this invention have the further advantage that they may be immersed in the usual hot alkaline cleaning solutions frequently employed preliminary to chromium plating, without being destroyed by such solutions or liquids.

The invention may receive various other embodiments than those herein specifically illustrated and described.

What is claimed is:

1. An element or part of a chromium plating installation which is in contact with a solution containing chromic acid and has insulating properties, consisting essentially of a conjoint polymerization resin which does not hydrolyze and does not react with such a plating solution, containing a vinyl compound of the "hard" resin forming type (consisting of the group vinyl halides, styrene) and a vinyl compound of the "soft" resin forming type (consisting of the group of esters of a lower aliphatic acid) the range of the proportions of the two types of compounds in the conjoint polymerization product (calculated as the monomeric compounds however present in the resin) being 50 to 95 parts of vinyl compound of the "hard" resin forming type to 50 to 5 parts of the vinyl compound of the "soft" resin forming type.

2. An element or part of a chromium plating installation, according to claim 1, in which the range of the proportions of the two types of vinyl compounds is 85 to 87 parts of the vinyl compounds of the "hard" resin forming type and 15 to 13 parts of vinyl compounds of the "soft" resin forming type, calculated as such however present.

3. A container for a chromium plating solution containing chromic acid, comprising a surface portion in contact with the chromic acid solution consisting essentially of a conjoint polymerization resin which does not hydrolyze and does not react with such a plating solution, containing a vinyl compound of the "hard" resin forming type (consisting of the group vinyl halides, styrene), and a vinyl compound of the "soft" resin forming type (consisting of the group of esters of a lower aliphatic acid) the range of the proportions of the two types of compounds in the conjoint polymerization product (calculated as the monomeric compounds however present in the resin) being 50 to 95 parts of vinyl compound of the "hard" resin forming type to 50 to 5 parts of the vinyl compound of the "soft" resin forming type.

4. A container for a chromium plating solution containing chromic acid, according to claim 3, in which the range of the proportions of the

two types of vinyl compounds is 85 to 87 parts of the vinyl compounds of the "hard" resin forming type and 15 to 13 parts of vinyl compounds of the "soft" resin forming type, calculated as such however present.

- 5 5. A rack forming an element of a chromium plating installation, comprising insulation on parts thereof in contact with solutions containing chromic acid consisting essentially of a con-
- 10 joint polymerization resin which does not hydrolyze and does not react with such a plating solution, containing a vinyl compound of the "hard" resin forming type (consisting of the group vinyl halide, styrene) and a vinyl compound of the
- 15 "soft" resin forming type (consisting of the group of esters of a lower aliphatic acid) the range of the proportions of the two types of compounds in the conjoint polymerization product (calculated

as the monomeric compounds however present in the resin) being 50 to 95 parts of vinyl compound of the "hard" resin forming type to 50 to 5 parts of the vinyl compound of the "soft" resin forming type.

- 5 6. A rack forming an element of a chromium plating installation, according to claim 5, in which the range of the proportions of the two types of vinyl compounds is 85 to 87 parts of the vinyl compounds of the "hard" resin forming type and 15 to 13 parts of vinyl compounds of the "soft" resin forming type, calculated as such however present.
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7. A rack forming an element of a chromium plating installation, according to claim 5, in which the insulation consists of built-up films or layers of the said resin.
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