

UNITED STATES PATENT OFFICE.

EMILE PLACET AND JOSEPH BONNET, OF PARIS, FRANCE.

PROCESS OF ELECTRODEPOSITION OF CHROMIUM.

SPECIFICATION forming part of Letters Patent No. 526,114, dated September 18, 1884.

Application filed August 20, 1892. Serial No. 443,640. (No specimens.) Patented in France November 12, 1890, No. 209,459, and July 17, 1891, Nos. 214,940, 214,941, 214,942, and 214,943; in Belgium November 18, 1890, No. 92,775; in England November 27, 1890, No. 19,344, and December 31, 1891, No. 22,855; in Sweden November 29, 1890, No. 4,257; in Norway December 4, 1890, No. 2,283; in Germany December 5, 1890, No. 66,099; in Spain March 3, 1891, No. 11,537, and in Austria-Hungary March 24, 1891, No. 53,381 and No. 8,074.

To all whom it may concern:

Be it known that we, EMILE PLACET and JOSEPH BONNET, citizens of the Republic of France, and residents of Paris, France, have invented new and useful Improvements in the Electrolysis of Chromium, of which the following specification is a full, clear, and exact description.

The said improvements have been, wholly or in part, patented to us in the following-named countries: France, dated November 12, 1890, No. 209,459, and July 17, 1891, Nos. 214,940, 214,941, 214,942, and 214,943; Belgium, dated November 18, 1890, No. 92,775; England, dated November 27, 1890, No. 19,344, and December 31, 1891, No. 22,855; Germany, dated December 5, 1890, No. 66,099; Austria-Hungary, dated March 24, 1891, No. 53,381 and No. 8,074; Spain, dated March 3, 1891, No. 11,537; Sweden, dated November 29, 1890, No. 4,257, and Norway, dated December 4, 1890, No. 2,283.

In a former application, filed December 10, 1890, Serial No. 374,184, we have described a general electrolytic process particularly applicable to metals which are very difficult to obtain by electrolytic action, such for example as iron and chromium. The present invention, while applicable to other metals, relates more particularly to the electrolysis of chromium which, so far as we are aware, has not been obtained in this manner prior to our invention. By our processes, as hereinafter set forth, we obtain electro-deposited chromium of great purity, in coherent masses of sufficient size for various industrial uses, and of different colors, as may be desired. In these processes we use salts and compounds of chromium which heretofore have never been used or proposed for use for the purpose in view, and from which, in the manner hereinafter pointed out, metallic chromium is produced in sufficient quantity, and with sufficient economy to constitute an industrial process, very different from the result of laboratory experiments, by which the production of minute specimens of metallic chromium has been heretofore attempted.

In the following detailed description we have given the salts or compounds from which metallic chromium can be obtained commercially, specifying the proportions and compositions of the baths, and indicating the variations desirable with different compounds. The most important of these compounds is chromic acid, either the commercial acid, or chromic acid obtained from chromate or bichromate of an alkali metal. The method of using chromic acid is described under paragraph first, below.

In paragraphs second to eleventh, we have described the employment of a series of chromic compounds, as sulphate of chromium, chrome-alum, or other salt of the sesqui-oxide of chromium, azotate of chromium, and other compounds which are equivalents for the purposes of the invention, and in connection with all of which we employ an alkaline sulphate or alkaline earth-metal to increase the deposition. Finally under paragraphs thirteenth and fourteenth we describe the procedure when heat is employed.

We will now describe in detail the principal baths which we have actually used and from which the results referred to have been obtained.

First. A solution of chromic acid in water. This solution may be very little concentrated. One to two grams of chromic acid in one hundred grams of water are sufficient. However, the more the solution is concentrated, the more abundant is the deposition. We vary the shade of the metal deposited by adding to the solution a small quantity (for example—five to ten grams per liter) of one of the following acids: The phosphoric, sulphurous, oxalic, benzoic, formic, gallic, pyrogallie, picric, phenic, salicylic, and other analogous acids, give very white depositions of chromium. The acetic, hydro-fluosilicic, &c., acids give brilliant deposits, but deeper. Boric acid gives dim grayish depositions, but very abundant. Finally sulphuric, azotic, chlorhydric, arsenious, tartaric, citric, lactic, tannic, &c., acids give depositions of a more or less deep shade, according to the quantity employed.

To prepare our solution of chromic acid, we make use of chromic acid obtained by the ordinary processes, or else, we produce chromic acid in the bath itself, in proportion as the deposition of chromium is made. In this case we employ as a bath, a solution of an alkaline bichromate, and we pour into this solution, in small successive quantities, an acid (sulphuric acid, nitric acid, hydrofluosilicic, or any other acid) which in combining with the alkaline base, sets the chromic acid free, or else, we prepare the chromic acid by putting in suspension oxide of chromium hydrated in a solution of oxalic acid, or of any other organic acid, and passing through it a current of electricity. At the end of a very short time, under the influence of the electricity, the oxide of chromium is found transformed into chromic acid, according to the formula $2(\text{Cr}_2\text{O}_3 + 6\text{O} = 4(\text{CrO}_3)$. The best results, however, are obtained by using chromic acid produced by means of electricity in the following way: We prepare, first, a solution of chromate or bichromate of an alkali metal and insert therein a porous vessel containing the same solution, or simply pure water, and containing also an electrode of carbon, platinum, or other conductor which will not be attacked. In the external solution is placed another suitable electrode with which is connected the positive pole of an electric generator. After the electric current has passed for some time all of the alkali will have passed into the porous vase, leaving chromic acid in solution in the vessel containing the positive electrode. This chromic acid is absolutely pure, and suitable not only for the further operation of obtaining chromium, but for various industrial uses. We obtain directly by electrolysis mixtures or alloys of chromium and of different metals, by dissolving, in our baths of chromic acid, oxides or carbonates which do not decompose the chromic acid; such as the oxides or the carbonates of copper, of iron, of aluminium, of magnesium, of tungsten, of molybdenum, of nickel, of silver, &c. We also obtain electrolytic deposits of chromium by employing the following baths:

Second. A solution of ten, fifteen or twenty grams of sulphate of chromium in one hundred grams of water. We add to this solution sulphuric acid until no more oxide of chromium is deposited at the negative pole. When the deposit of oxide ceases it will be known that the bath is sufficiently acidulated.

Third. Instead of sulphate of chromium we employ by preference, chrome alum (double sulphate of chromium and of potash, of soda or of ammonia); because the chrome-alum is more easy to prepare. We acidulate it likewise by means of sulphuric acid. To facilitate the deposition, we find it advantageous to add to our baths, ten to fifteen per cent. of an alkaline sulphate or alkaline earth-metal, or of a mixture of them.

Fourth. Instead of sulphuric acid to acidu-

late our baths, we may also employ azotic, phosphoric, chlorhydric, hydrofluosilicic acids; and the organic acids, or a mixture of these acids. It is thus we have composed the following bath: ten to fifteen grams chrome alum; ten to fifteen grams sulphate of potash, of soda or of ammonia; five grams oxalic acid, or other organic acid; and one hundred grams of water. We heat this solution, which is green, until it becomes violet; and we obtain a bath which gives magnificent depositions of chromium.

Fifth. We dispense with acidulating our baths, by employing for their foundation, salts very acid by themselves, such as the bisulphates, the bi-phosphates, the bi-acetates, &c. The acid which is found combined in these salts in definite proportions, acts (for the end we propose) in much better conditions than when we add the acid directly to the bath. We name for example, fifteen to twenty grams of chrome-alum, five to ten grams of neutral or alkaline sulphate, five to ten grams of alkaline bi-sulphate, and one hundred grams of water.

Sixth. To a solution of chromic acid, of chromate or bi-chromate of an alkali metal, we add a small quantity of any acid (sulphuric acid, chlorhydric, phosphoric, or other.) We add, further, a sulphate, a chloride, or other alkaline salt; and we obtain a bath which is very easily reducible by electricity. We take for example—ten to fifteen grams of an alkaline bi-chromate, five to ten grams of any suitable acid, fifteen to twenty grams of chrome-alum, and one hundred grams of water. We add sometimes a little alcohol or any other reducing body, to render the reaction more rapid.

Seventh. In a solution of chrome-alum, or any other salt of sesqui-oxide of chromium, we pour a solution of an alkaline bi-carbonate and obtain a violet precipitate. In plunging into the liquor, which holds in suspension this violet precipitate, the two electrodes of a battery, we obtain a deposition of chromium at the negative pole.

Eighth. We may add to our baths a solution of soda or of potash; of cyanides or of alkaline sulpho-cyanides, holding in solution or in suspension oxide of chromium or cyanide of chromium.

Ninth. Instead of chrome-alum in the bath above, we sometimes find it advantageous to employ the salts of chromium, using a suitable acid solvent when required.

Tenth. The roseo-chromic salts or compound chrome-ammoniacs (formula: $\text{Cr}_2\text{O}_3 \cdot 4\text{NH}_3$) give us likewise electrolytic baths. We will indicate, as an example, only the most simple of these baths. We take hydrate of sesquioxide of violet chrome, and we dissolve it in ammonia, or in a mixture of ammonia and of an ammoniacal salt, (such as chlorhydrate of ammonia, sulphate of ammonia, or other ammoniacal salt.) Under the influence of electricity this bath gives at the negative

pole a magnificent deposit of chromium. In adding to this bath an acid (chlorhydric acid, or sulphuric acid, azotic, &c.) a series of baths is obtained which give depositions of chromium under the influence of an electric current.

Eleventh. Instead of alkaline sulphates—as we have indicated above—as an example, to facilitate the deposition of chromium—we employ likewise—the alkaline nitrates, phosphates, pyrophosphates, fluorides, fluosilicates, borates, chlorides, chlorates, sulphurets, benzoates, oxalates, tartrates, citrates, acetates, sulphites, bi-sulphites, &c., or alkaline earths. For example:—fifteen to twenty grams of chrome-alum or of fluosilicate of chromium, ten to fifteen grams of fluosilicate of potash or soda or of ammonia, five to ten grams of hydrofluosilicic acid or any other suitable acid, and one hundred grams of water. We maintain the composition constant in our baths, either by means of a soluble anode, or by the addition of oxide of chromium, or of salts similar to those which compose these baths, or by means of a methodic circulation of solutions more or less concentrated. The baths that we have just indicated may generally be mixed with each other, and the recovery of the substances which compose them may vary within very great limits, according to the quality of the metal it is desired to obtain. Small quantities of alcohol, of gelatine, of sugar, of glycerine, or of other analogous matters, added to these baths produce a favorable action on the quality of the metal deposited. These and analogous organic substances improve the quality of the deposited metal, as shown by actual results. This action may be due to a better grouping of the molecules, which is in some way favored by the presence of the above named substances. The explanation of the action is obscure, but the effect certain.

Twelfth. We obtain, directly by electrolysis, alloys of chromium of various metals; aluminium, magnesium, nickel, cobalt, tin, zinc, antimony, silver, palladium, platina, &c., by mixing with our baths salts or oxides of the metals we wish to alloy. The baths being the one acid, the others alkaline, we can exactly choose the mixture of salts or of oxides which suit the best for the deposition of the alloys that we wish to obtain. We obtain likewise alloys in employing, in our baths of chromium, soluble anodes, as ferro-chrome, nickel, iron, aluminium, zinc, copper, silver, &c. By taking baths of copper, of zinc, of iron, of aluminium, nickel, lead, tin, silver, gold, &c., and in adding a certain quantity of one of the baths of chromium, that we have just indicated, we obtain deposits of copper, of zinc, of iron, aluminium, nickel, &c., which are found to be considerably improved by the presence of a certain quantity of chromium which is deposited at the same time as the principal metal. Finally we obtain alloys by

depositing alternately superposed layers of chrome and of the metal that we wish to alloy, and melting the whole.

Thirteenth. We work generally at the ordinary temperature. However, we find it often advantageous to heat our baths; which gives us more rapid and more abundant depositions. In certain cases, even, we heat our baths to aqueous fusion and the igneous fusion of the salts that we employ. This is in effect how we work in certain cases. We take for example—ten to fifteen grams of bisulphate of potash, one hundred grams of chrome-alum, and one hundred grams of water. We heat it to the dissolution of the salts; and we pass through it the electric current. The chromium is deposited immediately at the negative pole. We maintain the baths by means of chrome-alum alone, or by means of a concentrated solution of chrome-alum and of alkaline bisulphate. The bath is thus constantly renewed, and can consequently last indefinitely. One can, moreover, suppress water in the formation of the bath, and prepare the bath by heating, immediately, the mixture of the salts to their fusion. We add sometimes to these fused baths a suitable salt of an alkaline earth metal.

Fourteenth. The fusion of chromium demands a very high temperature, and we therefore employ generally the electric current to effect this fusion. Often to effect this fusion instead of using electrodes of pure carbon, we employ electrodes composed of carbon, oxide of chromium, of chrome-salts, or of flour of chrome, the whole previously agglomerated with a solvent (borax, phosphate lime, fluoride, &c.) and a reducer (zinc, magnesium, aluminium, &c.)—so that we effect at the same time the reduction and the fusion of the metal. We may put into the composition of these electrodes foreign metals, copper, aluminium, zinc, nickel, silver, &c., or oxides of these metals in order to obtain immediately the alloys of chrome and of these other metals. Finally, we find it advantageous to introduce in the crucible where we effect this fusion, inert gases or reducing gases, such as hydrogen, carburated gases, gases containing the dust of zinc, of aluminium, &c.; and we introduce these gases by the help of a tuyere, or simply by the interior itself of the electrodes which in this case are hollow.

We would observe in conclusion that, as we are well aware, Bunsen in 1854 experimented with protochloride of chromium to obtain by electrolysis infinitesimal particles of metallic chromium. The protochloride of chromium (CrCl) is an extremely rare and expensive compound costing now about one hundred and fifty dollars per kilo, and moreover very unstable, decomposing instantly upon exposure to air. This is very different from the sesquichloride (Cr_2Cl_3) which it is erroneously supposed by uninformed persons was used by Bunsen and which is in fact insoluble.

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 ble *per se*. The protochloride has not been
 and could not be used save for a labora-
 tory experiment, and is essentially different
 in character and in results from chromic
 5 acid or the equivalents thereof employed
 in our processes. It has also been proposed
 to separate metals (chromium among oth-
 ers) from each other by transforming the
 metals into double oxalates and using solu-
 10 tions of these in electrolytic baths. This
 method of analysis is of no value for and can-
 not be adapted to the extraction of chromium
 by electrolysis, because, first, the metal de-
 posited at the negative electrode is of very
 15 bad quality, impure and commercially worth-
 less, being very different from the pure chro-
 mium obtained by our process; and second,
 because the oxalates, as well as all compounds
 of organic acids, are too costly to be used com-
 20 mercially. We disclaim compounds formed
 with organic acids. It has also been pro-
 posed to deposit chromium on the surface of
 metallic objects from a bath of chromium dis-
 solved in a double chloride of soda and am-
 25 monia. It is impossible to dissolve chromium
 in this manner and to plate other metals
 therewith. Though this method was pro-
 posed in 1852, it is well known that no arti-
 cles electroplated with chromium were ever

produced until our present invention was car- 30
ried into practice.

We claim as our invention or discovery—

1. The process herein described of produc- 35
 ing electrolytic deposits of metallic chromium,
 by passing an electric current through an
 electrolytic bath composed essentially of a
 soluble chromic compound, such as chromic
 acid, in aqueous solution as set forth.

2. The process herein described of produc- 40
 ing metallic chromium, by passing an electric
 current through a bath containing a chromic
 compound, as specified, in aqueous solution,
 and a salt of an alkali or alkali earth metal.

3. The described process of obtaining elec- 45
 trolytic deposits of chromium by forming a
 bath of a salt or compound of chromium,
 such as hereinbefore specified, and a salt of
 an alkali earth metal, heating the bath, and
 passing an electric current through the sam- 50
 e, substantially as described.

In testimony whereof we have signed this
specification in the presence of two subscrib-
ing witnesses.

EMILE PLACET.
JOSEPH BONNET.

Witnesses:

ROBT. M. HOOPER,
JOSEPH JOURNIER