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(54) **CONTINUOUS TRIVALENT CHROMIUM PLATING METHOD**

(57) This invention belongs to the field of chemistry and metallurgy and it is specifically related to a process for the electrolytic and electrophoretic production of electrochemical coatings with a bath from trivalent decorative

chromium solutions on a metal or plastic substrate with trivalent chromium ions, sulfate ions, graphite anodes, hexavalent chromium control and false cathode purifications in a continuous industrial operation.

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Description

TECHNOLOGICAL SECTOR

[0001] This invention belongs to the field of chemistry and metallurgy and it is specifically related to a process for the electrolytic and electrophoretic production of electrochemical coatings with a bath from trivalent decorative chromium solutions on a metal or plastic substrate with trivalent chromium ions, sulfate ions, graphite anodes, hexavalent chromium control and false cathode purifications in a continuous industrial operation.

STATE OF THE ART

[0002] Chromium is a very important metal for a large range of industry applications. Over more than 70 years chromate plating decorative and functional process of has been carried out with electrolytes from chromium acid, process with a high content of the Cr+6 ion, considered by the WHO as a carcinogen for operators and personnel entering in contact with companies where it is used which is manifested in ulcers in the nasal septum. Hexavalent chromium has a strong impact in water environment.

[0003] Companies have implemented chromate plating from hexavalent chromium and have to deal with the quality problems related to such process, as the low penetration power leaving yellow areas like holes or angles, milky burnt in high current density zones and stains or veins.

[0004] Within these technologies the most potential and applicable processes are those of trivalent chromium (Cr+3) which has been in development and gaining more attention in the industry.

[0005] Electrochemical coatings of trivalent chromium has been stigmatized throughout the time due to their cost and the process color and stability; these has caused that its implementations is not that popular in large sites or small workshops.

[0006] Trivalent chromate plating baths have been developed from two technologies: sulfate and chloride. Trivalent chromium baths from chloride ions have some disadvantages: a darker color, more sensitivity to metal contaminants and chlorine detachments in the anodes causing safety and occupational health risks, besides of equipment corrosion. Trivalent chromium baths from sulfate ions are more noble, are whiter, close more to the chromate plating from hexavalent ions, are more tolerant to metal and organic contaminants, they do not produce detachment of noxious gases and do not cause safety and occupational health risks.

[0007] Trivalent chromate plating baths from chloride ions work preferably with graphite anode. Anode is produced by the formation of chlorine gas, there is no oxygen production, which causes the formation of Cr+6. Besides, the bath composition may include additives from Br- and HCOO- ions which prevent the evolution of Cr+3 to Cr+6.

[0008] Although the trivalent chromate plating process

from chloride ions mainly uses graphite anodes, the trivalent chromate plating from sulfate ions also uses graphite anodes.

[0009] In the state of the art, the process with graphite anodes in trivalent chromate plating from sulfate ions is unknown. Only the inconvenient of use due to the generation of Cr+6 is known. The Cr+6 is a contaminant of chromate plating baths from trivalent chromium ions and form from anodes by the oxidation of the Cr+3 to Cr+6, causing quality defects on the coating.

[0010] In low concentrations it produces dark color on the coating, veins, efficiency loss and process collapse at high concentrations. First trivalent chromate plating processes from SO_4^{2-} ions, patent 1602404, used a tank with two compartments, in one compartment a Pb anode is immersed in a H₂SO₄ anolyte, which is separated by a permeable membrane, and in the other compartment is a solution with Cr+3 ions that has no contact with the anode and as consequence no oxidation of the Cr+3 to Cr+6 is produced. The disadvantage of this two-compartmental systems is the cost and efficiency in a continuous industrial process.

[0011] Patent US3706639, describes a process for preparing a trivalent chromate plating bath from Cr+6 compounds by using inorganic reducers and platinized graphite and titanium anodes. Besides bath preparations from chromium products are expensive, they do not address the management and evolution of the contaminant Cr+6 during the bath work.

[0012] Patent US 5560815 defines the development of trivalent chromate plating baths from SO_4^{2-} ions, describing the use of anodes coated with iridium and tantalum oxide with the characteristic of a potential lower than the oxygen and as consequence it inhibits the evolution of the Cr+3 to Cr+6. This type of anodes, after a work time in continuous industrial productions, have proven to make easier the formation of Cr+6 in the bath, due to the exhausting of the iridium oxide layer, causing the restriction of the current pass in the anode and defects related to the Cr+6 contaminant.

[0013] Trivalent chromium baths based on SO_4^{2-} available in the market, only work with titanium anodes coated with platinum, iridium oxide, tantalum, niobium, rhodium, etc., this type of anode prevents the formation of the Cr+6 in the bath, but in continuous industrial processes it has a shelf-life depending on the used Direct Current and work volume. Due to the exhausting of the layer or cracking by the excess of DC the anode fails and starts the formation of Cr+6. On the other hand, the price of this type of anodes strongly impacts the final production costs.

Although patent EP0088192 defines a trivalent chromate plating bath different from the chloride ions, it refers to the use of graphite anodes in the trivalent chromate plating processes from sulfate ions and how the release of oxygen in this kind of anodes causes surface erosion and carbon particles release that accumulates in the chromi-

um producing coating defects.

[0014] Patent WO2010051118 refers to the use of manganese ions as additive to inhibit the formation of Cr+6 and increase the shelf-life of insoluble anodes used in the chromate plating process from trivalent and sulfate ions, including lead, lead alloy, platinized titanium anodes or metal anodes that consist of the coating of surface with iridium oxide, ruthenium oxide or mixed iridium/tantalum oxide. Although the shelf-life of this type of anodes increases, they will eventually collapse. In a continuous industrial production 24/6/360, it is difficult to determine the time when they exhaust and the Cr+6 production starts. On the other hand, concentration of Mn ion bath has to be closely controlled due to the risk of an excess that may cause a deposit with chromium changing the coating color and affecting the corrosion resistance.

[0015] Patent US5413646 "HEAT-TREATABLE CHROMIUM" refers to a bath that is part of a hexavalent chromium and an alloy of iridium to reduce it to trivalent chromium through methanol, ammonium formate and sodium sulfate as catalyzer, where the reaction is made from the contaminant hexavalent chromium that reacts in the process with platinum and graphite anodes in order to obtain functional non-uniform chromium. The new invention comes from trivalent chromium, it does not use sodium sulfate as catalyzer but sodium sulfate as a result of the reaction of a crystallization sub process. Iron or alloys can not be used in the new process since iron is a bath contaminant that leaves black veins in the finishing and increases the possibility of corrosion in the final finishing. Likewise, it does not need any temperature changes and the trivalent chromium batch may be applied on plastic or metal for decorative finishing.

[0016] Information about the use of graphite anodes in trivalent chromate plating from SO_4^{-2} ions is not available, and the state of the art only gives information about the dangers of this type of anodes due to Cr+6 contaminants.

[0017] Environmental and safety and occupational health demands with more and more strict rules in the different countries have promoted the interest by the development of trivalent chromate plating with more economic procedures and control. According to the problems described in the state of the art, a trivalent chromate plating process from SO_4^{-2} ions with anodes at reasonable cost and process efficiency is required both quality products and for long-term stability in continuous industrial productions.

[0018] The present invention solves the contamination problem when hexavalent chromium is generated in a low-cost efficient process, proposing a continuous industrial process and corrosion-resistant product with uniform finishing and non contaminant from a bath with trivalent chromium ions, sulfate ions and graphite anodes in a combination appropriate for a continuous industrial operation. With this invention the difficulties of the previous

state-of-the-art are overpassed, such as wear and final collapse of titanium electrodes covered with noble metals, the control and purification of contaminants affecting the process have been eliminated generating a continuous rejuvenation of process, reducing risks, costs and allowing replicating the novelty without technological difficulties.

DESCRIPTION OF THE INVENTION

[0019] The invention proposes a chromate plating process from Cr+3, having SO_4^{-2} ions and preferably using graphite anodes, obtaining a chromium coating with strong adherence to substrate, with mechanical, physical and chemical properties reproducible in continuous industrial productions. The specifications of products of color, thickness and resistance to corrosion and wearing maintains his stability in time and to temperature changes.

[0020] With the developed process, results of variations in work conditions can be predicted. The composition of the bath has proven stability in 24 hours continuous productions with the application of appropriate controls and maintenance. The bath has been noble to changes of temperature, pH, components concentration and tolerant to different contaminants.

[0021] The process of this invention mainly uses graphite anodes that have qualities such as good conductor of electricity, mechanized facility to be adapted to different conformations, good chemical and mechanic resistance, good resistant to anodic corrosion and high relation of surface-volume providing a very good anodic area, they are cost-effective compared to titanium electrodes coated with noble metals. The use of graphite anodes is not limited and also lead and stainless steel anodes are used. With the use of graphite anodes in trivalent chromate plating solutions with SO_4^{-2} ions, a better anode-cathode relation can be used as well as better current density without affecting the electrodes, compared to titanium electrodes coated with noble metal which tend to crack when subjected to high current densities.

[0022] Process starts with a preparation of the trivalent chromium solution with graphite anodes so that bath starts to work. In the process for obtaining the coating the hexavalent chromium is produced over the contaminant limit for which reducer baths of hexavalent chromium are added as explained below. Reducers convert the excess of hexavalent chromium in trivalent chromium releasing the sodium sulfate that must be removed from the bath, and to refine it a crystallization stage is made through the bath cooling.

[0023] Preferably graphite anodes must not have pores, since they cause penetration of the bath solution and an electrical reactions when releasing oxygen that cause an early erosion leaving too much carbon resi-

dues. Graphite anode must be put in acid-resistant fabric bags as those used in the nickel plating process to avoid the pass of anode eroded particles to the solution. In a continuous industrial process the continuous filtration is used at a speed of 4 times to 8 times and preferably from 4 times to 6 times the bath volume per hour. This secures that carbon particles in the batch are controlled and protects the coating quality.

[0024] With the use of graphite anodes in the bath of the present invention, the bath relationship of anode/cathode must be 3:1 and preferable a relation of 2:1, a greater relation and a greater direct current improve the process efficiency, producing a best cathode coating area. The density of current applied must be between 4 dm² to 12 A/dm² and preferable between 5 A/dm² to 8 A/dm².

[0025] The bath prepared for the use with graphite anodes, contains Cr+3 ions, the Cr+3 ions concentration in the bath is between 10g/l to 30 g/l, preferably between 15-g/l to 25 g/l. The $Cr_2(SO_4)_3$ salt is used as the Cr+3 source.

[0026] The bath prepared contains organic and organic chromium complexes that are stable, forming bonds that allow the Cr+3 ion and its reduction to Cr0 in the cathode surface forming a metal sheet with mechanic, physical and chemical properties with strong adherence to the substrate and reproducible in continuous industrial production.

[0027] Chromium complexes of this preparation, also have properties allowing an easier degradation when residual waters treatment is made, with which a reduction of the environmental impacts is assured.

[0028] As the source of products forming complexes with the trivalent chromium organic acids $HCOONa$ / $HCOONH_4$ / $NaCH_3COO$ / NH_3CH_3COO salts; lactate ions $C_3H_5O_3^-$, $(COO)_2^{-2}$, Oxalate ions, malate $C_4H_6O_5$ and glycine NH_2CH_2COOH have been used. This type of compounds are used individually or mixed with C+3 to form complexes. The concentration must be between 50/l to 150 g/l, preferably between 70g/l to 120 g/l.

[0029] It is well known in the technique that the presence of H_3BO_3 in an electrolytic solution, between 40-g/l to 60 g/l, preferably between 45g/l to 50 g/l increases conductivity and acts as a buffer agent and also as an inhibitor of the anode decreasing the attack and detachment of the graphite anode by the presence of B-ions which reduce the O_2 overproduction.

To improve the bath conductivity, the Na_2SO_4 salt is added as a conductor, between 30 g/l to 60 g/l, preferable between 40 g/l to 50 g/l. In the present invention this salt is added only to form the bath since during the process it produces and increases its concentration due to the different reactions of oxide-reduction. The bath of the present invention also includes salts containing Na^+ , K^+ and $(NH)_4^+$ ions.

[0030] The chromium complex discomposes by action of the electrical current and deposits Cr0 on the cathode and releases SO_4^{-2} anion which combines with sodium ions present in the solution forming Na_2SO_4 . Also during the mechanism of reduction from Cr+6 to Cr+3, an increase of acidity is produced by the formation of H_2SO_4 , the control of acidity is made with $NaOH$, Na_2CO_3 , neutralizing the solution with formation of Na_2SO_4 . In this type of bath using graphite anodes, it always tends to become acid.

[0031] pH must be controlled between 3,4 of pH to 4,0. High pH values favor the formation of oxygen and promotes the attack of graphite anode.

[0032] The bath superficial tension must be between 30 dynes to 70 dynes. Adjustment is made by adding moistening agents such as octyl alcohol.

[0033] Process temperature must be between 40°C to 60°C, preferably between 45°C to 50°C. Due to the constant reduction from Cr+6 to Cr+3, bath is concentrating from Na_2SO_4 , and a reduction of temperature may cause the crystallization of this salt.

[0034] To achieve stability in the coating color, electrolytic yield and compliance with the resistance to corrosion specifications and bath penetration, purification with false cathode has been efficient in the control of parasite metals such as Ni, Fe, Cu and Zn, due to that metals do not form strong complexes with the bath strong components. For industrial productions of high capacity which do not allow activities suspension, continuous false application is externally applied to the process with equipment available in the market for this kind of operations, avoiding the progressive contaminants in the bath. When industrial production allow it, false cathode is applied in the tank and regularly with process stopping.

[0035] It has been found that the process of the present invention does not require purification with selective resins allowing a reduction of contaminants produced in the regeneration and a reduction of costs. The use of sequestering agents as EDTA for metal purification is not recommendable in this process because it produces side effects as progressive accumulation by making strong organometallic complexes that affect coating quality and causes problems in the effluent treatment.

[0036] Addition of reducers is made controlling the consumption of amperes-hour and maintaining the Cr+6 between 0ppm to 40 ppm, preferably between 0ppm 20 ppm, rank in which there is no side effect in the coating quality.

[0037] It is very known in the technique the reducer compounds for Cr+6. In our process of trivalent chromate plating from SO_4^{-2} ions, preferably using graphite anodes, where the formation of Cr+6 is obligatory, we used components with SO_3^{-2} anions, mainly $NaHSO_3$, $Na_2S_2O_5$, Na_2SO_3 , $(NH)_4HSO_3$, $Na_2S_2O_4$, and optionally sulfur compounds derived from $S_2O_3^{-2}$, or a

mix thereof. One characteristic of these products is that they do not cause secondary side effects to the bath by decomposition.

Results

[0038] Results obtained at industrial level in continuous operations show the degree of development of this process, several hundredths of thousands of dm² of products for export and local use prove the process stability and quality.

[0039] Results have been obtained with the bath of the present invention from Cr+3 and SO_4^{-2} ions by using graphite anodes, in Hull Cell the penetrations were between 80 % to 92 % even after five trials with the same solution and photometric analysis in presence of diphenylcarbazide with results of Cr+6 between 20ppm to 30ppm, concentration that did not affect coating quality, color was white to almost the hexavalent chromium color without dark veins formation.

[0040] The thickness of coating obtained in decorative coatings from Cr+3, is between 0,3 μm to 2 μm , very similar to those obtained with the process of traditional Cr+6.

[0041] Essays made at industrial level showed that when concentration of Cr+6 has been corrected in the, the < 50 ppm levels are not prejudicial for the coating quality. Concentration levels of Cr+6 between 50-ppm to 150 ppm affect color and produce dark veins. Concentration levels of Cr+6 > 300 ppm strongly decrease the bath efficacy and coating quality.

[0042] It has been found that in the present invention of a trivalent chromate plating bath with SO_4^{-2} ions, preferably working with graphite anodes and purification of continuous false cathode, contaminants concentration maintained within the allowable limits without affecting the coating quality and good process functioning., Cr+6 0ppm to 20 ppm, Ni 30ppm to 150 ppm, Fe 10 ppm to 100ppm. Cu was the contaminant with the less possibility of reaching the trivalent chromate plating bath and with false cathode it was controlled at ranges of <1 ppm

[0043] Inventors could replicate the results in a continuous commercial production with a bath of 1.500 liters of trivalent chromate plating provided by the present invention with SO_4^{-2} ions, preferably working with graphite anodes, controlling the Cr+6 production with the above mentioned reducers, applying crystallization to maintain the Na_2SO_4 contents within the work limits without totally or partially removing the bath since it can be infinitely reused by controlling the hexavalent chromium production in the process.

[0044] The invention is a novelty preparation of a trivalent chromium bath from SO_4^{-2} ions offering the advantage to preferably work with graphite anodes and we have solved the control of Cr+6 generation and control and elimination of the different contaminants, obtaining

a chromium coating with strong adherence to the substrate with excellent mechanical, physical and chemical properties, commercially reproducible in continuous industrial productions. Product specifications of color, thickness, resistance to corrosion and wearing have been stable throughout the time.

[0045] With this invention the difficulties of the previous state-of-the-art have been overpassed, such as exhausting and final collapse of titanium electrodes coated with noble metals, the control and purification of contaminants affecting the process have been simplified, generating a constant process rejuvenation, decreasing risks, costs and allowing applying the novelty without any technological problems.

Claims

1. Process of trivalent chromate plating for decorative coating on a metal substrate or plastic substrate with a thickness coating of 0,3 μm to 2 μm , in which process is a continuous bath containing organic and inorganic chromium complexes from Cr+3 ions taken from salts preferably from $Cr_2(SO_4)_3$ with SO_4^{-2} ions and graphite anodes with an anode-cathode relation of 2:1 resistant to cracking by current density, with control of Cr+6 production with reducers generating sodium sulfate and removal by crystallization of such sodium sulfate generated in the process; and with purification of false cathode for control of parasite metals that have weak complexes in the bath such as Ni, Fe, Cu and Zn for stability in coating color, electrolytic yield and compliance with resistance to corrosion and penetration specifications.
2. Process of trivalent chromate plating as claimed in claim 1 in which it starts with the preparation of a trivalent chromium solution with graphite anodes and in the process of coating obtaining a hexavalent chromium controlled by reducers that convert the excess of hexavalent chromium in trivalent chromium is produced releasing sodium sulfate which is removed in the crystallization stage by bath cooling.
3. Process of trivalent chromate plating as claimed in claim 1 in which the graphite anode must be without pores and put into acid-resistant fabric bags avoiding the pass to the solution of eroded particles of anode in a continuous filtration process at a speed of 4 to 6 times the bath volume per hour to control carbon particles in the bath and protect coating quality.
4. Process of trivalent chromate plating as claimed in claim 1 in which density of applied current must be between 4 dm² to 12 A/dm² and preferably between 5 A/dm² to 8 A/dm².

5. Process of trivalent chromate plating as claimed in claim 1 in which Cr+3 ions concentration is between 10g/l to 30 g/l, preferably between 15-g/l to 25 g/l.

6. Process of trivalent chromate plating as claimed in claim 1 in which the source of products forming complexes in trivalent chromium comes from the $HCOO-Na / HCOONH_4 / NaCH_3COO / NH_3CH_3COO$ organic acid salts; lactate ions, $C_3H_5O_3^-$, Oxalate ions $(COO)_2^{-2}$, malate $C_4H_6O_5$, glycine NH_2CH_2COOH individually or mixed with Cr+3 in a concentration between 50/l to 150 g/l, preferably between 70g/l to 120 g/l.

7. Process of trivalent chromate plating as claimed in claim 1 in which the bath is added as a Na_2SO_4 conductor salt between 30 g/l to 60 g/l, preferably between 40 g/l to 50 g/l only to form the bath and includes salts containing Na^+ , K^+ and $(NH)_4^+$ ions.

8. Process of trivalent chromate plating as claimed in claim 1 in which chromium complex decomposes by the electric current and deposits Cr0 on the cathode and releases SO_4^{-2} anions which combines with sodium ions present in the solution forming Na_2SO_4 and also during the mechanism of reduction from Cr+6 to Cr+3 and increase of acidity is produced by the formation of H_2SO_4 , where control of acidity is made with $NaOH$, Na_2CO_3 neutralizing the solution with the Na_2SO_4 formation.

9. Process of trivalent chromate plating as claimed in claim 1 in which pH is controlled between 3, 4 to 4,0, the superficial tension of the bath must be between 30 dynes to 70 dynes and process temperature must be between 40°C to 60°C, preferably between 45°C to 50°C due to the constant reduction of Cr+6 to Cr+3 in the bath concentrates the Na_2SO_4 and a temperature reduction may cause the crystallization of the concentrated salt to Na_2SO_4 .

10. Process of trivalent chromate plating as claimed in claim 1 in which the adding of reducers is made controlled by the consumption of amperes-hours procuring maintaining the Cr+6 between 0ppm to 40 ppm, preferably between 0ppm 20 ppm, range in which there is no side effects in the coating quality.

REFERENCES CITED IN THE DESCRIPTION

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