

UNITED STATES PATENT OFFICE

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CHROMIUM PLATING

No Drawing.

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Our discovery relates to chromium plating.

The prevailing chromium plating baths are the chromic acid baths founded on the so-called Sargent's solution, with certain modifications. The chromic acid bath, however, is very deficient in throwing capacity, and great difficulty is experienced in properly chromium-plating irregular articles. This often requires special shaped anodes, and even then the recesses are often not plated at all, or are very thinly plated.

In our prior applications, Serial No. 198,689 filed June 13, 1927, and Serial No. 264,952 filed Mar. 26, 1928, we have described and claimed a process of chromium plating, and a bath which employs chromium chloride and various conducting salts of alkaline metal earths. This bath has been very successful in plating nickel-plated articles, but it is subject to some short-comings on account of its cost and because it does not deposit a heavy film on the cathode.

Our new process is a bath which employs ingredients that are easily obtained on the market, and are relatively cheap. It also has a very high throwing capacity, and deposits a relatively heavier film of chromium than is the case with our previous chromium chloride processes.

We employ a bath of bichromate of soda, hydrochloric acid and oxalic acid. For example, we take 240 grams of bichromate of soda dissolved in one-half liter of warm water; to this is added 154 grams concentrated hydrochloric acid; to this is added 3.75 grams of hydrated oxalic acid. We then add enough water to bring the bath up to one liter. The bath is then completely stirred up. It will be obvious that for larger or smaller baths the proportions will be varied accordingly.

This bath is operated preferably anywhere from room temperature up to 160 degrees Fahrenheit, and the higher the temperature the better the conductivity of the bath, but

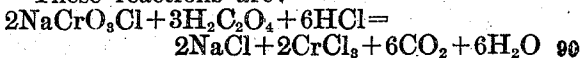
higher temperature lowers the polarization of the cathode, and consequently lowers the throwing ability of the bath. This bath is preferably operated at a voltage of from 4 to 13 volts. The amperage of this bath will be anywhere from 100 amperes to 500 amperes per square foot of cathode. The amperage will vary substantially directly as the voltage.

The above bath is what we call a rapid bath,—that is, the deposits are much faster than a bath made up as given in the example below, which we call a slow bath. Such a slow bath may be made up by dissolving 360 grams bichromate of soda in half a liter of warm water; to this is added 77 grams hydrochloric acid, and then 240 grams oxalic acid. Water is then added to make the bath up to one liter. The bath can be operated at room temperature, up to 160 degrees F. and with a voltage of from 4 to 13, and a corresponding amperage of 100 to 500 amperes per square foot of cathode. In this bath, however, the deposit will be relatively slower than the previous bath. This is due to a larger percentage of trivalent chromium, to wit: chromium chloride. There is a higher alkalinity at the cathode than in the other bath, due to less hydrochloric acid.

We find that the above baths can be operated successfully without the use of oxalic acid, although we much prefer to use the oxalic acid as it aids in reducing the hexavalent chromium to the trivalent form.

The bichromate of soda, $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{HCl}$ (hydrochloric acid) in solution, reacts to form $2\text{CrO}_3\text{ClONa} + \text{H}_2\text{O}$, the first ingredient being chlorochromate of soda plus water. To this the oxalic acid is added, which reacts to form chromium chloride, which in turn reacts with the chlorochromate to form chromium chromate.

These reactions are:



	NaCl-----	Sodium chloride (common salt)	acetic acid, phosphoric acid, and others, as the main purpose of the free acid is to prevent alkalinity at the cathode, and also as a conductor.	
	CrCl ₃ -----	Chromium chloride		
	CO ₂ -----	Carbon dioxide		
	H ₂ O-----	Water		
5	NaCrO ₃ Cl--	Sodium chlorochromate	What we claim is:	70
	$\text{NaCrO}_3\text{Cl} + 2\text{CrCl}_3 + 3\text{H}_2\text{O} = \text{XCr}_2\text{O}_3 \cdot \text{YCrO}_3 + \text{NaCl} + 6\text{HCl}$		1. A chromium plating bath including when ready for operation, chlorochromate of soda, chromium chromate, hydrochloric acid, and water.	
	NaCrO ₃ Cl-----	Sodium chlorochromate	2. A chromium plating bath which when ready for operation includes an alkaline metal chlorochromate, and chromium chromate and an acid.	75
10	H ₂ O-----	Water	3. A chromium plating bath, which when ready for operation includes an alkaline metal chlorochromate, chromium chromate, and hydrochloric acid.	80
	CrCl ₃ -----	Chromium chloride	4. A chromium plating bath which when ready for operation includes one of the alkaline metal or earth metal chlorochromates.	85
	XCr ₂ O ₃ ·YCrO ₃	Chromium chromate	5. A chromium plating bath which is made up solely of bichromate of soda, hydrochloric acid, water and a reducing agent.	
	NaCl-----	Sodium chloride (common salt)	6. A chromium plating bath which is made up solely of bichromate of soda, hydrochloric acid, oxalic acid and water.	90
15	HCl-----	Hydrochloric acid	7. A chromium plating bath which is made up solely of an alkaline metal or earth metal bichromate, hydrochloric acid, and a reducing agent.	95
	From reading the above reactions it will be seen that carbon dioxide passes off as a gas, and chromium chloride is formed, and sodium chloride and water. The above reaction of course is in only part of the bath, and the chromium chloride thus formed in the last reaction then reacts with the chlorochromate forming chromium chromate		In testimony whereof we have affixed our signatures.	
20	(XCr ₂ O ₃ ·YCrO ₃).		JOHN F. K. McCULLOUGH.	
25	The final constituents of the bath are therefore: chlorochromate of soda, chromium chromate, common salt, and water, and some excess hydrochloric acid that has not reacted with the other ingredients.		BENJAMIN W. GILCHRIST.	100
30	We find that a bath so constituted has great throwing power. The throwing power depends upon the polarization of the cathode, the conductivity of the bath, and the cathode efficiency. All of these are high in a bath made in accordance with the above directions and consequently the throwing power is very good.			
35	Bichromate of soda may be easily procured and it is the cheapest salt of chromium obtainable. Hydrochloric acid and oxalic acid are both relatively cheap and easily obtainable. Furthermore, carbon dioxide is the only gas given off in quantity, and this is comparatively inoffensive. The free hydrochloric acid that remains in the final bath renders the conductivity of the bath relatively good.			105
40	In this bath we use soluble chromium anodes or insoluble graphite or magnetite anodes. Care must be taken in proportioning the amount of chromium anodes to insoluble anodes, due to the fact that the chromium anode dissolves in three valencies and the trivalent chromium would thereby lower the efficiency of the solution.			110
45	The bichromate of soda may be replaced by the chromates or bichromates of the alkaline metal or alkaline earth metals, such as ammonium and potassium of the alkaline metal group, and barium, strontium, and calcium, of the alkaline earth metal group.			115
50	The free hydrochloric acid in the bath may be replaced by numerous other acids, such as			120
55				125
60				130