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METHOD OF ANODIC CLEANING

Gilbert H. Orozco, Euclid, Ohio, assignor to Gilbert H. Orozco and Roland A. Whitbeck, partners, doing business as Gilron Products Company, Cleveland, Ohio

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This application is a continuation-in-part of my prior application Serial No. 383,982, filed March 18, 1941, and abandoned subsequent to the filing of the present application.

The invention relates to a method of cleaning metal articles and particularly articles made from carbon steel, preparatory to plating and to a composition for use in connection with the method.

Most articles which are to be plated are subjected to certain manufacturing operations during which they become coated with oils, greases, waxes and stearic acids, the stearic acids and waxes being present in buffing and polishing compounds which are applied to the articles during buffing, polishing and like operations.

It is common practice to remove such films by electrolysis of the articles in certain hot aqueous alkaline cleaning baths.

The alkaline cleaning baths, while effective for removing the greater portion of such films from the articles do not entirely remove the films. This is because the water commonly used in cleaning baths usually contains calcium and magnesium which, in the presence of alkaline cleaning agents, combine with the oil, grease, and wax films to form deposits of very light calcium and magnesium colloidal soap films or emulsions on the articles. Calcium and magnesium are often present in the buffing and drawing compounds so that they are introduced into the cleaning bath even though the water used is originally free from such materials.

The colloidal films thus formed are insoluble in water, have a high affinity for the metal and adhere tightly thereto, the tenacity of the soap films increasing in a rather direct proportional relationship to the increase in the pH of the alkaline bath.

Alkaline cleaning baths and electrolytic processes heretofore used do not remove these films in their entirety but leave a very slight but tenacious film which renders the surfaces of the articles unsuitable for subsequent plating. These slight films are customarily removed by the relatively expensive steps of brushing, scrubbing, high pressure spraying, and other mechanical operations after subsection of the articles to electrolytic cleaning. Due to the very high affinity for metal of the colloidal or soapy films and particularly those formed by heavy metal soaps, even these mechanical steps are not as effective as could be desired.

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When films such as discussed above are subjected to so-called hot or vapor degreasing treatment in a cleaning bath containing chlorinated solvents such as trichloroethylene and dichloroethylene only the oily and greasy substances and light metal soaps are usually removed. Such treatment because it will not remove heavy metal soap films is not therefore fully effective or dependable as a means for preparing articles for plating and particularly articles made from high carbon steel. Similarly the degreasing process mentioned and others discussed above are not completely effective in removing colloidal clays and the like used in manufacturing processes. Those leave light pigment films which although practically imperceptible interfere with subsequent plating.

Most metals, and particularly high carbon steel, cleaned by the prior methods, although apparently very clean, are found upon handling to have very light films and surface deposits of foreign matter, commonly referred to as "smut films" and in the case of carbon steel "graphitic films" and "carbon smut", all of which are detrimental in subsequent plating processes.

One of the objects of the present invention is to remove all of the films and deposits such as hereinbefore described from the surface of metal articles by dissolving the films chemically while concurrently subjecting the articles anodically to electrolytic cleaning at a high current density.

Another object is to prepare the surface of the articles by subjecting the articles to an aqueous solution which either prevents the formation of the colloidal films and other films originally, or removes them after formation, or so conditions them that they are removed in the usual rinsing and acid dipping which precedes the actual plating operation.

Other objects and advantages will become apparent from the following specification wherein a preferred embodiment of the present invention is disclosed for purposes of illustration.

The present method has to do essentially with the cleaning operation which precedes the usual water rinse and acid dip which are commonly employed subsequent to cleaning in the plating art, and would not in most cases displace the water rinse and/or acid dip in those instances in which such are generally required.

In accordance with the present invention, the article to be cleaned, without presoaking, is subjected anodically to a bath containing sodium or

potassium acetate, or a combination thereof, and, in addition thereto, an alkaline salt which imparts to the bath a pH greater than 11. The bath is purposely maintained free from silicates and borates such, for example, as metasilicate, waterglass, orthosilicate, borates, and other water soluble calcium precipitants. Borates or silicates have been used in alkaline cleaning baths heretofore because of their detergent properties, but I have found that the borates or silicates themselves are hard to rinse off and produce detrimental micro-films.

The piece is immersed in the bath in a tank which is a cathode, the piece itself being supported on a suitable rack which is the anode of a high current density plating circuit, as distinguished from the method generally used in plating wherein the piece forms the cathode and the tank the anode and a low current density circuit is employed. A current density of at least 35 amperes per square foot of surface of the piece to be cleaned is preferred and the term "high current density" as used hereinafter signifies at least 35 amperes per square foot of surface. With this high density current anodically applied to the article while the article is in the bath described, complete cleaning in about 30 to 60 seconds in the case of non-ferrous metals and 1 to 5 minutes in the case of ferrous metals is obtained.

By subjecting the piece to the current anodically the so-called "hydrogen effect" on the metal piece or article and which results in cathodic cleaning by release of hydrogen at the piece is eliminated. Instead the oxygen is released at the piece or anode and, therefore, there is no "hydrogen effect" on the piece. The so-called "hydrogen effect" on the surface of an article to be plated is such that after plating the article, there is a tendency for the plating to peel after exposure in air for lack of proper bond to the piece and appears to be due to the hydrogen inclusion or the plating out of metallic impurities in the bath.

Example I

A suitable dry mix, by weight, for forming an effective bath to be used in connection with the high current density anodic cleaning of metals such as copper or low carbon steel may comprise the following:

		Preferred	Range
		Per cent	Parts
1	Sodium (anhydrous) or potassium acetate about.....	10	5 to 50
2	Sodium or potassium hydroxide about.....	16.5	10 to 55
3	Sodium carbonate about.....	20	10 to 40
4	Alkaline phosphate salt, such as tetrasodium pyrophosphate or sodium or potassium metaphosphate about.....	28	5 to 55
5	Trisodium phosphate, about.....	25	
6	A wetting agent (e. g. a sodium salt of an alcohol sulphuric acid) about.....	.5	-----

The dry mixture is dissolved in water in the ratio of about eight ounces of the dry mix for each gallon of water. A current density of 80 to 100 amperes per square foot of surface of the metal article to be cleaned is used and with the work constituting the anode.

Example II

A bath which is particularly useful in connection with the cleaning of high carbon steel may comprise the following dry mix, by weight, mixed with water in about the concentration above recited:

		Preferred	Range
		Parts	Parts
1	Sodium acetate (anhydrous).....	15	5 to 50
2	Sodium hydroxide.....	45	10 to 55
3	Sodium carbonate.....	29	10 to 40
4	An alkaline (e. g. potassium or sodium) phosphate salt having the properties of disintegrating magnesium or calcium soaps, such for example, as one or more of the group comprising tetrasodium pyrophosphate, sodium metaphosphate, potassium pyrophosphate or potassium hexametaphosphate.....	10	5 to 55
5	A wetting agent, if desired about.....	1	1 to 2

In the event, in either Example I or II, a formulation is chosen that uses the upper range of either the acetate or phosphate components of the cleaner, the increase would be balanced by employing the indicated lower percentages of sodium carbonate in the mixture.

The sodium acetate is extremely effective for removal of graphitic films from steel such as tend to form particularly on high carbon steels of the type commonly used, for example, as automobile bumper stock. Sodium acetate or potassium acetate, one or the other or an equivalent thereof or mixture of the two are essential ingredients in the bath particularly in that they augment the action of the phosphates of the bath in rendering the surfaces of the articles uniformly clean and free from smut and superficial films. The pH of a sodium acetate solution is below about 9 and therefore is not in the pH range of optimum detergency. Hence the sodium acetate must be augmented by stronger alkaline salts when used in a cleaning bath. In practicing the present invention the pH of the bath is maintained above 9 at all times, and the acetate should not be below 5% of the solute.

The sodium or potassium hydroxide impart electrical conductivity to the solution. Since the hydroxyl anion has about twice the equivalent conductivity of any other anion, it is apparent that an addition of caustic soda or caustic potash will impart twice the conductivity of any other alkaline salt that could be added.

The sodium carbonate, which is formed in sodium hydroxide solutions exposed to air, is likewise a conducting salt. Its properties in softening hard or temporarily hard water high in calcium or magnesium bicarbonates are well known.

As an illustration of the value of electrical conductivity in the present cleaner, it was found that a prior art cleaner containing twelve ounces per gallon of a proprietary material produced an average anode current density of 35 to 45 amperes per square foot at 200° F. at a pressure of six volts. Using the identical cleaner tank but substituting twelve ounces per gallon of the preferred composition in Example II for the prior art material, an average anode current density of 60 to 90 amperes per square foot was obtained at an identical voltage and temperature. Since commercial plating generators are made at 6, 9, or 12 volts it can be seen that the optimum range of high anode current density can only be obtained for a given spacing of the electrodes by a cleaner of high conductivity.

The alkaline phosphate salts, for example tetra-sodium pyrophosphate, hexametaphosphate or the like, are varied in amount depending upon the condition of the water and of the articles. They effectively prevent the formation of magnesium and calcium soaps and are an effective conditioner of the bath. While the pyro and

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metaphosphates are the preferred materials in this invention because of their superior sequestering action, it should be pointed out that the orthophosphates are also effective. It is well known that aqueous solutions of both the pyro and metaphosphates tend to hydrolize or revert to the orthophosphate under heating in the presence of free alkali-hydroxides. I have found, however, that such hydrolysis does not interfere materially with the operation of the present cleaner composition or at least render it inoperative.

The concentration of the solution is preferably increased in the case of extremely hard water and decreased toward the lower limit in the case of softer water.

By maintaining the bath free from water soluble silicates or borates, micro-films which would be caused by the silicates or borates are eliminated.

The current density of the work is dependent upon the conductivity of the solution which in turn is proportional to the concentration and temperature of the cleaning bath. I have found that the higher concentrations and temperatures are to be preferred. The method is practiced preferably with a bath temperature about 150° F. up to the boiling point of the particular bath.

The combination of anodic application of current of high density to an article while the article is in an alkaline cleaning bath of a character described, effectively cleans the article and removes any and all films and foreign matter so that the article is made ready for plating in all instances by the simple subsequent step of water rinse and acid dip.

I claim:

1. The method of cleaning and preparing metal articles for plating, which comprises removing carbonaceous film by subjecting the articles anodically to a current density greater than 35 amperes per square foot of surface of the article while the article is immersed in an aqueous alkaline cleaning bath consisting essentially of water as a solvent and a dry solute of ingredients as follows, by weight:

	Parts
A substance selected from the group consisting of sodium acetate and potassium acetate.....	5 to 50
Sodium hydroxide.....	10 to 55
Sodium carbonate.....	10 to 40

and said bath being substantially free from silicates and borates.

2. The method of cleaning and preparing metal articles for plating, which comprises removing carbonaceous film by subjecting the article anodically to a current density greater than 35 amperes per square foot of surface of the article while the article is immersed in an aqueous alkaline cleaning bath consisting essentially of water as a solvent and a dry solute of ingredients as follows, by weight:

	Parts
A substance selected from the group consisting of sodium acetate and potassium acetate.....	5 to 50
Sodium hydroxide.....	10 to 55
Sodium carbonate.....	10 to 40
An alkaline phosphate salt from the class consisting of tetrasodium pyrophosphate, sodium metaphosphate, potassium pyrophosphate, potassium hexameta-	
phosphate	5 to 55

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and said bath being substantially free from silicates and borates.

3. The method of cleaning and preparing metal articles for plating, which comprises removing carbonaceous film by subjecting the article anodically to a current while immersed in an aqueous alkaline cleaning bath consisting essentially of water as a solvent and a dry solute of ingredients as follows, by weight:

Parts

A substance selected from the group consisting of sodium acetate and potassium acetate.....	5 to 50
Sodium hydroxide.....	10 to 55
Sodium carbonate.....	10 to 40

and said bath being substantially free from silicates and borates.

4. The method of cleaning and preparing metal articles for plating, which comprises removing carbonaceous film by subjecting the article anodically to a current while immersed in an aqueous alkaline cleaning bath consisting essentially of water as a solvent and a dry solute of ingredients as follows, by weight:

Parts

A substance selected from the group consisting of sodium acetate and potassium acetate.....	5 to 50
Sodium hydroxide.....	10 to 55
Sodium carbonate.....	10 to 40
An alkaline phosphate salt from the class consisting of tetrasodium pyrophosphate, sodium metaphosphate, potassium pyrophosphate, potassium hexameta-	
phosphate	5 to 55

and said bath being substantially free from silicates and borates.

GILBERT H. OROZCO.

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