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PROCESS FOR ELECTROPLATING A SINTERED FERROUS ARTICLE

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This invention relates to a method of preparing sintered metal articles for electroplating. Specifically this invention relates to a method which comprises (1) subjecting a sintered metal article to the action of a basic solution, (2) subjecting the resulting article to the action of an acid cleaning solution and (3) electrolytically depositing a metallic coating on the surface of the cleaned article using an acid electroplating bath. More specifically this invention relates to a method of preparing a sintered metal article for electroplating which comprises subjecting said article, e. g., a sintered ferrous article, to the action of a basic solution, and thereafter to the action of an acid cleaning solution prior to electrolytically depositing a metallic coating, e. g., a chromium coating, on the surface of the sintered metal article.

An object of my invention is to prepare a sintered metal article for the step of electroplating the surface of said article with a metallic coating so as to prevent a so-called pitted or "sinking" effect of the metallic coating deposited by the plating process on the surface of the sintered metal article. A further object is to prevent, in some cases, deterioration of the deposited metallic surface on exposure to the air, e. g., rusting, caused by improper treatment of the sintered metal object prior to the electroplating operation.

In many cases it has been desirable to coat the sintered metal article with another, perhaps harder and smoother, metallic coating. This metallic coating is usually deposited on the surface of the sintered metal article by an electrolytic plating process. However, great difficulty has been experienced in obtaining smooth, permanent finishes of these electroplated metallic coatings. The common procedure in preparing the sintered article for the step of electroplating in an acid solution has been to immerse the sintered article in a cleaning solution, which is usually a strongly acidic bath (also referred to as a "pickling" solution), and thereafter to place the article in the acid electroplating bath for deposition of the desired metallic coat on the surface of the sintered metal article.

When the above procedure is followed, examination of the surface of the plated sintered metal article reveals that the article is unequally plated. In addition, a "sinking" effect is noted, i. e., the deposited coating appears to have sunk into the tiny pores found on the surface of sintered metal articles. This "sinking" effect results in undesirably rough finishes on the sintered metal

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article and, in addition, if the sintered metal article comprises a ferrous material, any breaks in the surface of the metallic coating, as a result of this "sinking" effect, will cause rusting of the article on exposure to the oxidizing effects of the air. Metallic articles prepared by other methods such as, for example, by casting of molten metal or by machining from unsintered metal blanks, do not exhibit the degree of porosity shown by sintered metal articles prepared from metal powders and therefore this "sinking" effect usually is not encountered after electroplating such metal articles with a metallic coating.

Attempts have been made to overcome the aforementioned "sinking" of the plated metallic surface by grinding or buffing the surface of the sintered metal article to reduce the porosity of the surface prior to the electroplating step. This has been successful to a limited degree. However, best results are obtained when grinding or buffing of the sintered article is followed by immersion in a basic solution prior to the pickling step.

According to my invention, this "sinking" effect of the plated coating on the sintered metal article, with its attendant disadvantages, is prevented by immersing the sintered metal article in a basic solution before cleaning or pickling the article in an acid bath in preparation for the electroplating operation. I have found that by first subjecting the sintered article to the action of a basic solution in the absence of an electric current, the pores of the sintered article are filled with small amounts of the basic material thereby tending to neutralize any of the acid from the cleaning solution or electroplating solution which may later become occluded in the honeycomb passages underneath the electro-deposited metallic coating. Without this prior treatment in the basic solution, the trapped acid tends to attack or dissolve the electroplated metallic coating, causing the previously described "sinking" effect and subsequent deterioration of the deposited metallic surface.

The basic solutions employed in practicing my invention may be prepared from materials having a neutralizing effect on the acids encountered in the cleaning or pickling solutions and in the electroplating baths. Among the basic compounds that may be used in preparing the basic solution are the inorganic bases, e. g., ammonium hydroxide, the alkali-metal hydroxides, such as sodium hydroxide, potassium hydroxide, etc., alkaline-earth metal hydroxides, e. g., calcium hydroxide, barium hydroxide, etc., the soluble car-

bonates and bicarbonates of such bases (both hydrous and anhydrous forms), e. g., sodium carbonate, potassium carbonate, calcium bicarbonate, sodium bicarbonate, potassium bicarbonate, etc., and organic bases, for instance trimethyl amine, tributyl amine, dimethyl aniline quinoline, etc. Mixtures of two or more of the aforementioned basic materials also may be employed. I prefer to use sodium carbonate as the basic material in preparing the basic solution.

The basic solution may be in the form of an aqueous solution or other solution medium, as for example, an alcohol solution. Preferably, it is desirable to use an aqueous solution because of the solubility of a greater number of the basic materials in such a medium. In addition, the economy involved recommends the use of water as a solvent. However, due to poor solubility of some of the basic materials in the above-mentioned solvents, it may be necessary to dissolve the basic material in solvents other than water or alcohol. Among these may be mentioned benzene, toluene, xylene, etc.

The strength or degree of basicity of the basic solution may also be varied. The percentage by weight of basic material or materials based on the total weight of the basic solution may vary from about 0.5% to about 20 to 30%. Though higher strengths may be employed, no useful purpose is served thereby, since the small amount of basic material necessary to neutralize the minute amounts of occluded acid makes it desirable that dilute solutions of the basic material be employed. Thus, in many instances, solutions or baths containing, by weight, from about 1 to 6 or 8 parts of the basic material (e. g., sodium carbonate) per hundred parts of solvent, e. g., water, have been found adequate.

The sintered metal article may be immersed in the basic solution under a variety of temperature and pressure conditions, for instance at normal or at elevated temperatures of the basic solution and at atmospheric or superatmospheric pressures. I prefer that the basic solution be heated to boiling or near-boiling temperatures before contacting the sintered metal article with the basic solution. The higher temperatures assist in better impregnating the pores of the sintered article with the basic solution.

The length of time that the sintered metal article may be immersed in the basic solution may vary, e. g., from about 1 minute to 2 hours, depending on such influencing factors as, for example, the temperature of the solution, size and composition of the sintered metal article, etc. I have found that when boiling or near-boiling basic solutions are employed, the sintered metal article need only be immersed for a short period of time, of the order of about 2 to 10 minutes, or as little as 4 to 6 minutes.

The cleaning or pickling treatment of the sintered metal article, following treatment in the basic solution, may take place in any of the strong acid solutions and mixtures of acid solutions well known in the art and used for that purpose. Thus the cleaning or pickling solution may be a 50% aqueous hydrochloric or sulfuric acid bath, or a mixture of aqueous hydrochloric and sulfuric acid solutions. Other acids or mixtures of acids in varying concentrations may be employed in the cleaning solution, depending on the desired strength and acidity of the cleaning solution. Among the acids which may be mentioned are the inorganic acids including hydrochloric, sulfuric, nitric, phosphoric acids, etc.; organic acids, e. g., acetic acid (glacial), etc., as well as other types of acids represented by such compounds as ethyl phosphoric acid, ethyl sulfuric acid, etc. The cleaning solution may be heated if desired.

The time of immersion of the sintered metal article in the cleaning solution may be varied depending, for example on the concentration and temperature of the solution, type of acid or acids employed, composition of the sintered metal article, etc. I have found that immersion in cleaning solutions consisting of 50% sulfuric acid or hydrochloric acid, from 30 seconds to 2 minutes is a sufficient length of time. The cleaned article may be rinsed in water after removal from the acid cleaning solution.

The electroplating step may consist of any of the methods well known in the art for electrolytically depositing coatings of metals on the surface of metallic articles. Among the coatings which may be deposited electrolytically are chromium, copper, nickel, indium, iron, lead, palladium, tin, zinc, etc., and alloys of two or more of these and other metals.

After removal of the plated sintered metal article from the acid electroplating bath, it is desirable to rinse the article in water and immerse it again for a short time in the same basic solution used prior to the electroplating operation in order to neutralize any acid remaining on the surface of the plated article. This latter step serves to neutralize any acidic material remaining on the surface of the plated article which might interfere with the permanence of the finish. The article is then washed and dried.

It is also desirable, but not necessary, in practicing my invention, to grind or buff the surface of the sintered metal article prior to immersion in the basic solution preceding the acid cleaning and electroplating steps. Surface-grinding assists in decreasing the number and size of the pores on the surface of the sintered metal objects.

In order that those skilled in the art may better understand how the present invention may be practiced, the following example is given by way of illustration and not by way of limitation:

A sintered iron plate (manufactured by compacting and molding iron powder at high pressures in a mold and thereafter sintering the preformed article at elevated temperatures) which had been surface-ground, was immersed for 5 minutes in a boiling solution of a 3% aqueous sodium carbonate solution. Thereafter the plate was washed in water and immersed for 1 minute in a 50% aqueous hydrochloric acid pickling solution. The iron plate treated in this manner was then plated electrolytically at 6 amperes per square inch for 20 minutes in a chromium electroplating bath containing the following ingredients:

33 ounces chromium oxide (CrO_3) per gallon of water

0.33 ounce sulfuric acid (specific gravity 1.84) per gallon of water

The iron plate was removed from the electroplating bath, rinsed with water, immersed again for about a minute in the 3% aqueous sodium carbonate solution, rinsed and dried. The sample showed no "sinking" effect of the deposited chromium. The surface was shiny, smooth and even. The surface remained in this condition indefinitely without any noticeable change.

When another sample of the surface-ground, sintered, iron plate was treated exactly as above,

except that the plate was not immersed in the basic solution prior to dipping in the pickling solution, the chromium surface exhibited the previously described pitted, "sinking" effect. Upon exposure to the air, rusting of the surface soon occurred. This rusting became more pronounced as the time of exposure to the oxidizing effect of the air continued. No rusting whatsoever was noticed, even after long service use, of the surface of the plated, sintered iron plate which had been immersed in the sodium carbonate solution prior to the electroplating operation.

My method of treating sintered metal articles whereby such articles are subjected to the action of a basic solution prior to the pickling and electroplating operations is not to be confused with methods in existence in the art for cleaning metal parts by treating the parts with a strongly caustic solution, or treating the parts first with a strongly caustic solution and then with a strongly acid solution for the purpose of merely cleaning said metal parts.

The strengths of the basic solutions employed in practicing my invention are usually of such an order that little, if any, cleaning of the sintered metal article is accomplished. The basic solution used in carrying my invention into effect impregnates the pores of the sintered metal article and provides a neutralizing agent for any acid which later may become occluded in its pores as a result of cleaning the article in the acid cleaning or pickling solution. Its function is also to neutralize any acid which may become trapped in the pores of the sintered article as a result of the electroplating operation in the acid electroplating solution.

My invention is applicable to sintered metal objects manufactured from metallic powders which have been compacted, preformed and molded under high pressures, and then sintered at elevated temperatures to cause flow and cohesion of the particles of metal powder whereby strong, homogeneous articles are formed. Articles prepared in this manner exhibit the type of surface porosity which heretofore has proved difficult to electroplate properly with another metallic coating. However, my invention may be applied to metal objects wherein the porosity of the metal base prevents the deposition of smooth coatings of metallic materials by the usual electrolytic plating processes. Articles prepared by casting of molten metals or by machining of unsintered metal blanks do not usually present the problem of porosity found in the case of sintered metal articles.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The process for electroplating a sintered ferrous article containing a multitude of microscopic pores on its surface thereby to obtain a metallic coating free of a pitted, "sinking" effect, which process consists essentially of (1) surface-grinding the sintered ferrous article, (2) immersing the said sintered article in the absence of an electric current so as to impregnate it in a heated 0.5 to 30 per cent aqueous alkaline solution maintained at around its boiling point thereby to occlude small amounts of the alkaline solution within the pores of the sintered article, (3) removing the article and washing it with water, (4) immersing the washed article in and subjecting it to the action of an acid cleaning solution, (5) removing the article from the acid cleaning solution and electrolytically depositing a chromium coating on the surface of the cleaned article using an acid electroplating bath, (6) removing the electroplated article and rinsing it with water, (7) immersing the article again in the aforementioned alkaline solution to neutralize any acid remaining on the surface of the plated article, and (8) rinsing the article with water and drying it.

2. The process as in claim 1 wherein the aqueous alkaline solution employed in step 2 for impregnating the pores of the sintered article comprises, by weight, from about 1 to 8 parts of the alkaline material per 100 parts of water solvent.

3. The process as in claim 1 wherein the aqueous alkaline solution comprises an aqueous sodium carbonate solution containing, by weight, from about 1 to 8 parts of sodium carbonate per 100 parts of water solvent.

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