Patented May 13, 1952

2,596,307

UNITED STATES PATENT OFFICE

2,596,307

PROCESS OF ELECTROSTRIPPING ELECTRODEPOSITED METALS

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No Drawing. Application November 5, 1947, Serial No. 784,309

18 Claims. (Cl. 204—146)

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The present invention relates to a method for the electro-stripping of electrodeposited metals, and more particularly in relates to a method for the electro-stripping of one or a plurality of various electrodeposited metals in one operation from a base metal.

The removal of the various electrodeposited metals from scrapped, rejected or worn electroplated metal articles in order to recover the base metal articles for replating, has become increasingly important in recent years due to the scarcity of metal and cost of fabrication of the articles. Thus, various electrolytic methods are available for stripping electrodeposited metal layers from such plated articles which articles also comprise a valuable source for the ordinarily valuable deposited metals. In such procedures however, while removal of the deposited metals in the minimum number of steps is one of the primary aims, it is also endeavored to leave the base metal in a condition suitable for re-use, such as replating. Nevertheless, the methods presently available have not combined these two features and are attended by various disadvantages.

Taking decorative chromium plated steel or iron as an example, it is well known that before the chromium deposit is applied, a layer of nickel or layers of copper and nickel, must first be deposited on the iron or steel base metal and the chromium is then deposited on the intermediate layer. The finished article is thus composed of composite layers of chromium and nickel upon the iron or steel base metal, or even composite layers of chromium, nickel and copper upon the base metal. In removing these various layers from rejects or scrapped or worn articles by the electrolytic methods presently available, the plated article is immersed as the anode in an electrolytic cell. The baths heretofore employed as the electrolyte have, however, not been capable of removing or stripping all the plated metals in one operation without seriously attacking the base metal, and in most cases have not been capable of removing all the plated metals in one operation at all. Thus, in many cases separate baths have to be employed—one for stripping off each deposit, or one for stripping off the nickel and chromium layers and another for stripping off the copper layer. The maintaining of several cells containing different baths is obviously cumbersome and costly. A bath that is claimed to be capable of stripping off all these plated metals in one operation, is composed of a mixture of sulphuric and nitric acids. This bath however, readily attacks the base metal. Thus, before all

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the plated metal can be stripped, some of the base metal becomes seriously etched and pitted, requiring extensive polishing operations or in many cases rendering the base article unfit for further use. Various organic acids have also been suggested as the electrolyte. However, these do not strip the various combinations in one operation. Moreover, most shops where stripping is done are called upon to remove different common electrodeposited metals at various times from iron or steel base metals. Heretofore, this has necessitated the maintenance of a plurality of different types of baths, each formulated to remove a specific metal or limited combinations of metals. One inexpensive bath that is capable of removing any of the various common electrodeposited metals and combinations thereof in one simple operation, while leaving the base metal clean and unattacked and ready for replating, has been highly desired. The same difficulties as mentioned above are encountered in electro-stripping composite layers or electrodeposited alloys of other metals.

The primary object of the present invention therefore, is to provide an inexpensive process for electro-stripping a plurality of electrodeposited metals from iron or steel base metals, which requires but one simple operation and which leaves the base metal unattacked.

A further object is to provide an electro-stripping process employing a novel inexpensive electrolyte bath which removes many of the common electrodeposited metals, either as single layers or as combinations, from an iron or steel base metal article.

Another object is to provide a simple, inexpensive electro-stripping process which leaves the iron or steel base metal clean and unattacked and in a condition for direct replating.

A specific object is to remove in one operation all the electrodeposited metals present in common decorative chromium plated iron or steel, leaving the iron or steel base metal clean and ready for replating.

Other objects will be apparent from a consideration of the following specification and the claims.

In accordance with the present invention, the electroplated iron or steel object from which the electrodeposited metal or metals are sought to be removed, is employed as the anode in an electrolytic cell, the electrolytic bath of which compirses as the main effective stripping agent, phosphoric acid. A positive direct current source is connected to the anode and a cathode is pro-

vided to complete the circuit. The current is applied until the electrodeposited metals sought to be stripped have gone into solution. As will be pointed out hereinafter, certain catalytic materials providing cations corresponding to some or all of the metals to be stripped, are preferably present in the electrolyte to facilitate the initial dissolution of the electrodeposited metal.

During the process of the present invention, all the electrodeposited metal becomes dissolved until the iron or steel base metal is exposed. The electrolyte bath employed does not attack the base metal, but in fact leaves it clear and ready for re-use and replating if desired. As a result of the process, electrodeposited metal and especially a plurality of electrodeposited metals such as electrodeposited layers of chromium, nickel and copper may be quickly and easily removed in one operation from iron or steel base metals, leaving the base metal clean, unattacked and ready for replating. One of the primary advantages of the present procedure is that strict time control during the stripping operation is obviated. In fact, the stripped articles may be left in the electrolyte bath over extended periods such as a number of hours, without any apparent damaging effect to the iron or steel base metal. Moreover, by the process of the present invention, a wide variety of the common electrodeposited metals may be removed, obviating the necessity of separate baths for each type of deposited metal.

With respect to the electrodeposited metals that may be stripped in accordance with the present invention, they may be of any metals, composite layers of two or more thereof, or alloys of two or more thereof that are commonly electrodeposited on iron or steel. The metals which are most commonly electrodeposited on iron or steel comprise copper, chromium, gold and silver and combinations of two or more of copper, nickel, chromium, silver and gold and the process is therefore, particularly applicable for the electro-stripping of these metals and combinations thereof. The combinations of metals may be either composite layers or alloys.

One of the principal plated articles that may be treated in accordance with the present invention is so-called decorative chromium plated iron or steel. In such case, the plurality or combination of metals making up the composite electrodeposited layers is either nickel and chromium, or copper, nickel and chromium. Examples of other composite layers of metals are: silver on copper, silver on nickel, gold on copper, gold on nickel, and the like. Examples of combinations of these metals that exist as electrodeposited alloys on iron or steel are: silver-copper alloys, gold-silver alloys, gold-nickel alloys, gold-copper alloys, and the like.

Referring to the electrolyte bath, as stated it is an aqueous solution, the principal effective stripping or dissolving agent of which is phosphoric acid. This means that no other acid is relied upon to aid in the dissolution of the electrodeposited metals, although such other acid may be present in the electrolyte in limited insignificant amounts. The phosphoric acid need not be pure, commercial or technical grades being satisfactory. The concentration of phosphoric acid in the electrolyte may vary widely and generally ranges from about 25% to about 95% by volume, and preferably between about 75% and about 85%, based on the use of the commercial 85% by weight grade of H_3PO_4 solution.

Preferably during the initiation of the process, there are present in the electrolyte a small amount of metal cations corresponding to at least one of and preferably all of the electrodeposited metals sought to be removed. In the claims the term "corresponding to metal sought to be removed" is used to refer to the case where only one electrodeposited metal is to be removed, as well as to the case where a combination of two or more different metals is to be removed, in which case the metal cations correspond to one or more of the metals in the combination. The presence of these cations facilitates the initial dissolution of the metal or metals. These cations may be present in the bath as a result of a previous treatment of plated articles in which the same bath was used, or may be added to the bath at the start of the process in the form of non-etching metal compounds soluble in the phosphoric acid solution. Thus, when the electrodeposited metals to be removed are for example, chromium, nickel and copper, the presence of cations corresponding to at least one of these metals, and especially the presence of chromium ions, nickel ions and copper ions in the electrolyte facilitates the initial dissolution of the respective electrodeposited metals. When the cations are added to the electrolyte, a solution of the proper compound or compounds or the solid compound or compounds may be employed, the only requirement being that the compound used be sufficiently soluble in the phosphoric acid solution to provide the desired cations and does not, in the acid media, cause etching of the base metal. Generally, the oxides and hydroxides of the metal present no problem as to etching. However, certain metal salts do. A simple test to determine whether a metal salt is suitable for the purpose of supplying the desired metal cations without causing etching of the base metal, is to prepare an aqueous solution of phosphoric acid in a beaker or other small container at a concentration within the above defined limits; immerse a small strip of steel as an anode, provide a cathode; add a small amount of the metal salt to the bath, and employ a current density within the range hereinafter set forth. If the surface of the steel strip does not become etched, pitted or otherwise lose its original form, the metal salt is suitable and is termed herein along with the metal oxides and hydroxides as a "non-etching metal compound" capable of supplying metal cations in an aqueous phosphoric acid solution. Examples of some of the non-etching compounds soluble in aqueous phosphoric acid solutions that may be dissolved in the electrolyte to furnish the desired metal cations are: the nickel compounds such as nickel sulfate, nickel carbonate, nickel phosphate, nickel oxalate, nickel ammonium sulfate, nickel oxide, and the like; copper compounds such as copper sulphate, copper phosphate, copper oxalate, copper carbonate, copper ammonium sulphate and the like; chromium compounds such as chromic sulphate, chromic hydroxide, chromic phosphate, chromous sulphate, chromous hydroxide, chromous oxalate, and the like; silver compounds such as silver oxide, silver sulphate, silver phosphate, silver carbonate, silver citrate, and the like; gold compounds such as gold phosphate, gold sulphate, and the like.

The amount of the metal compound dissolved

in the electrolyte to provide the metal ions may vary widely and generally is present in an amount to provide the equivalent of between about 1/64 and about 15 ounces of metal cation per gallon of electrolyte, preferably between about 1/32 and about 1/8 ounce of metal cation per gallon of electrolyte.

The use of a conventional acid inhibitor such as glycerol, diethylene glycol and the like, may be desirable to increase the stable life of the bath. When for example, the concentration of the phosphoric acid diminishes as additional water becomes introduced over a period of use through make-up water, and water adhering to the articles, the presence of the acid inhibitor, insures the advantages to be gained through the use of the present process. The amount of acid inhibitor if employed, will vary depending upon the concentration of the phosphoric acid in the bath, and generally the lower the phosphoric acid concentration, the greater will be the amount of acid inhibitor employed, and the amount employed may range between about 1% and 60% by volume.

In carrying out the process of the invention, the plated article to be treated is immersed as the anode in the above defined bath. The container holding the bath may be any of the conventional containers presently used, such as glass or rubber or lead lined steel tanks and the like. Being the anode, the plated article or "work" will be connected to the positive terminal of a low voltage direct current source such as a storage battery, a rectifier or a direct current generator. Obviously, two or more articles may be treated simultaneously in one electrolyte bath, some or all serving as one anode or each serving as separate anodes. To complete the circuit, a cathode (or cathodes) is provided which may be any conducting material, such as for example copper, lead, iron or steel, of any desired shape, such as for example in rod or sheet form, commonly employed in electrolytic processes. As is common practice, the surface area of the cathode or cathodes should be somewhat comparable to that of the anode or anodes.

Generally, the current density employed will range between about 1/4 and 10 amperes per square inch, preferably between about 1 and about 2 amperes per square inch. The voltage required to obtain these current densities may vary widely depending upon the resistance of the circuit, and is generally between about 5 and about 40 volts.

The temperature of the electrolyte bath may vary from just below its boiling point to room temperature. As is the case with most chemical reactions, the higher the temperature, the greater the rate of reaction. However, since high speed is not the essential factor, for economical reasons the bath is generally maintained between about 120° F. and about 180° F. and preferably between about 140° F. and about 150° F.

No difficulty will be encountered in determining the proper length of time of treatment, since as stated the electrolyte bath will not readily attack the iron or steel base metal. Obviously, the time required will be determined by the thickness and number of metal layers, the type of the electrodeposited metal or metals, and the condition of the bath such as concentration of phosphoric acid, presence or absence of metal cations, temperature, amount of current employed and the like. In any case, the length of time the current is allowed to flow is at least that time required to strip the electrodeposited metal and the point of termination of the process may easily be determined by sight.

After the electrodeposited metal has gone into solution, that is has been stripped, the base metal article is clean and clear and may be directly replated if desired. As it is used, the bath gradually becomes saturated with compounds of the dissolved metal and it may be withdrawn from the cell from time to time to be replenished by fresh electrolyte. The saturated electrolyte bath may be worked in any conventional manner to recover the metal values therein, if desired.

The following examples are illustrative of the process of the present invention and are not intended as in any way limiting.

Example I

A bath is prepared consisting of 225 gallons of an 80% (by volume) phosphoric acid solution, prepared by mixing 80 parts by volume of the commercial 85% by weight H_3PO_4 solution with 20 parts by volume of water, 1.8 lbs. nickel sulfate, 1.8 lbs. copper sulfate and 1.8 lbs. of chromic sulfate. A decorative chromium plated steel article having composite layers of electrodeposited copper, nickel and chromium, with a composite thickness of about .001'' is immersed as the anode in the bath contained in a rubber lined steel tank. Sheet copper cathodes are provided. A current density of 1½ amperes per square inch is employed and the bath is maintained at 150° F. After 12 minutes, all the electrodeposited metals have gone into solution, leaving the base steel article clear and ready for replating.

Example II

The bath consists of 9 gallons of a 60% (by volume) phosphoric acid solution, prepared by mixing 60 parts by volume of the commercial 85% by weight H_3PO_4 solution with 40 parts by volume of water, 1 gallon of glycerin and .3 ounces of silver oxide. The bath is contained in a 10 gallon crock. Five "triple plate" spoons are tied together with iron wire and immersed in the bath as the anode. The spoons are of steel with a composite layer of silver on copper of a composite thickness of about .00075''. A copper cathode is provided. A current density of 1 ampere per square inch is employed and the bath is at room temperature. After 15 minutes, all the electrodeposited metals have gone into solution, leaving the steel base metal clear and bright and ready for replating.

Considerable modification is possible in selecting the ingredients for the electrolyte bath, and other conditions of the system, without departing from the scope of the invention.

I claim:

1. The process for electro-stripping combinations of electrodeposited metals selected from the group consisting of the combinations of two or more of copper, nickel, chromium, gold and silver, from electroplated base metal objects selected from the group consisting of iron and steel objects, which comprises immersing the electroplated object as anode in an electrolytic cell, the electrolyte bath of which consists essentially of an aqueous solution of phosphoric acid, the concentration of said phosphoric acid in said bath being between about 25% and about 95% by volume based on the use of an 85% by weight phosphoric acid solution, and metal cations corresponding to metal sought to be removed in an amount between about 1/64 and about 15 ounces per gallon of electrolyte, and applying an electric

current until the electrodeposited metal is dissolved.

2. The process of claim 1 wherein the temperature of the bath is between about 120° F. and about 180° F.

3. The process of claim 1 wherein the temperature of the bath is between about 140° F. and about 150° F.

4. The process of claim 1 wherein the concentration of phosphoric acid in the bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution.

5. The process of claim 1 wherein the concentration of phosphoric acid in the bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution, and wherein the temperature of the bath is between about 120° F. and about 180° F.

6. The process of claim 1 wherein the concentration of phosphoric acid in the bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution, and wherein said bath is at a temperature between about 140° F. and 150° F.

7. The process for electro-stripping the composite electroplated coatings of chromium, nickel and copper from chromeplated metal objects selected from the group consisting of iron and steel objects, which comprises immersing the chromeplated object as anode in an electrolytic cell, the electrolyte bath of which consists essentially of an aqueous solution of phosphoric acid, the concentration of said phosphoric acid in said bath being between about 25% and about 95% by volume based on the use of an 85% by weight phosphoric acid solution, and metal cations selected from the group consisting of chrome, nickel and copper ions in an amount between about 1/64 and about 15 ounces per gallon of electrolyte, and applying an electric current until the electrodeposited metal is dissolved.

8. The process of claim 7 wherein the bath is at a temperature between about 120° F. and about 180° F.

9. The process of claim 7 wherein the temperature of the bath is between about 140° F. and 150° F.

10. The process of claim 7 wherein the concentration of phosphoric acid in the bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution.

11. The process of claim 7 wherein the concentration of phosphoric acid in the bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution, and wherein the temperature of said bath is between about 120° F. and about 180° F.

12. The process of claim 7 wherein the concentration of phosphoric acid in the bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution, and wherein the temperature of said bath is between about 140° F. and about 150° F.

13. The process for electro-stripping composite coatings of chromium and nickel from chromeplated metal objects selected from the group consisting of iron and steel objects, which comprises immersing the chromeplated object as anode in an electrolytic cell, the electrolyte bath of which consists essentially of an aqueous solution of phosphoric acid, the concentration of said phosphoric acid in said bath being between about 25% and about 95% by volume based on the use of an 85% by weight phosphoric acid solution, and metal cations selected from the group consisting of chromium and nickel ions in an amount between about 1/64 and about 15 ounces per gallon of electrolyte, and applying electric current until the electrodeposited metal is dissolved.

14. The process of claim 13 wherein the temperature of said bath is between about 120° F. and 180° F.

15. The process of claim 13 wherein the temperature of said bath is between about 140° F. and 150° F.

16. The process of claim 13 wherein the concentration of phosphoric acid in said bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution.

17. The process of claim 13 wherein the concentration of phosphoric acid in said bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution, and wherein the temperature of said bath is between about 120° F. and about 180° F.

18. The process of claim 13 wherein the concentration of phosphoric acid in said bath is between about 75% and about 85% by volume based on the use of an 85% by weight phosphoric acid solution, and wherein the temperature of said bath is between about 140° F. and about 150° F.

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