United States Patent Office 3,843,495
Patented Oct. 22, 1974

3,843,495

CORROSION RESISTANCE OF DECORATIVE CHROMIUM ELECTROPLATED OBJECTS

Thomas P. Malak, Garfield Heights, Ohio, assignor to Kewanee Oil Company, Bryn Mar, Pa.

No Drawing. Continuation of application Ser. No. 206,893, Dec. 10, 1971, which is a continuation-in-part of application Ser. No. 850,657, Aug. 15, 1969, both now abandoned. This application Nov. 1, 1973 Ser. No. 411,604
Int. Cl. C23b 5/50; C23f 17/00
U.S. Cl. 204—35 R 5 Claims

ABSTRACT OF THE DISCLOSURE

The corrosion resistance of decorative chromium plated objects having chromium plated over a layer of nickel, cobalt or an alloy thereof, is improved by treatment of the layer which underlies the surface chromium layer by impingement of solid particulate matter so as to form micronicks in the underlying layer. These micronicks cause an equivalent number of micropores to form in the chromium layer electrodeposited thereover. The number of micropores per square inch should exceed 3,000 and preferably be in the range of 40,000–200,000 per square inch for decorative chromium plated objects depending on the type, size, and density of the particle and momentum at impingement. The treated nickel or cobalt layer should be sufficiently thick to prevent the micronicks formed therein from penetrating completely through to the substrate. Likewise, multiple layers of nickel or cobalt can be used and other underlying metal layers such as copper can be interposed between the substrate and the layer or layers of nickel or cobalt.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation of earlier copending application Ser. No. 206,893, filed on Dec. 10, 1971, now abandoned, which in turn is a continuation-in-part of application Ser. No. 850,657, filed on Aug. 15, 1969 and now abandoned.

BACKGROUND OF THE INVENTION

In the recent past, it has been discovered by various workers in the field, that decorative chromium plated articles can be improved with respect to corrosion resistance by forming micropores in the chromium layer. U.S. Pat. No. 3,298,802 and U.S. Pat. No. 3,449,223 illustrate examples of such decorative articles of improved corrosion resistance. In U.S. No. 3,298,802 an object which may or may not be electrodeposited with other metal coatings, receives a continuous bright nickel electrodeposit. This bright nickel electrodeposit is followed by a thin electrodeposit of nickel which incorporates various solid non-conductive particles into said thin nickel layer. Thereafter, chromium is electrodeposited on the particulate containing nickel layer. The particles in the nickel layer interfere with the flow of current during electrodeposition of the chromium layer and result in the formation of a microporous chromium deposit. U.S. No. 3,449,223 discloses a similar process which calls for a particulate containing bright nickel layer being plated directly on a substrate without the need for an underlying particle-free bright nickel layer.

BRIEF DESCRIPTION OF THE INVENTION

It is an object of the present invention to produce a decorative chromium plated article having improved resistance to corrosion.

Another object is a treatment for improving the corrosion protection of a metallic or non-metallic article provided by an electrodeposit of decorative nickel, cobalt or alloys thereof, and a surface layer of chromium.

Yet another object is the production of a metallic or non-metallic article with a duplex electrodeposit comprising a first decorative layer of nickel, cobalt or alloys thereof and a thin surface layer of chromium, providing improved corrosion protection for the article, said duplex layer treated by contacting the decorative layer with solid particulate material with a force and for a period of time sufficient to form at least 3000 micronicks per square inch on the surface of the nickel, but insufficient to cause dulling of the surface, and thereafter depositing a thin chromium layer thereover.

DETAILED DESCRIPTION OF THE INVENTION

In more detail, the present invention relates to an improvement in the corrosion protection of a metallic article, at least a portion of which is covered with a duplex layer comprising a first electrodeposit of decorative nickel, cobalt or alloys thereof and a second electrodeposit of chromium. The improved protection is achieved by forming micronicks in the decorative layer of the nickel, cobalt or alloys thereof and thereafter depositing a thin layer of chromium thereover. The micronicks are formed by impacting solid particles against the decorative layer with sufficient force and intensity to form at least 3000, and preferably between 40,000 and 200,000 micronicks per square inch. These micronicks extend into, but not through, the decorative layer. For purposes of the present invention, the decorative layer shall comprise a bright or semi-bright layer of nickel, cobalt or alloys thereof deposited directly on all or a portion of a metallic or non-metallic substrate or on one or more layers of copper, zinc or other materials previously deposited thereon. These previous layers may be either electroless or electrolytically deposited. The decorative layer is typically deposited to a thickness of 0.3 to 1.5 mils. The layer of chromium deposited thereover is substantially thinner than the decorative layer and is typically between about 5 and 20 millionths of an inch in thickness.

Various particulate materials have been used with success in the instant process. These include round Ottawa sand (30–35 mesh), jagged sand (35 mesh), lead powder, polyethylene pellets ⅛ x 1/16 x 1/16" (Goodrich Geon Vinyl No. 8814 white), magnesium filings, glass beads (Blastolite BLXN–16 General Steel Industries, St. Louis, Mo.), polystyrene pellets (.05" diameter), iron powder, nickel powder and powdered silicon (320 mesh). Any solid particulate material would be useful in the practice of the present invention which has sufficient hardness to withstand the impact with the surface of the decorative layer at least to the extent of altering said surface in the formation of a micronick.

If small particulate matter is used in the practice of the present invention, such as for example, a powdered silica of 320 mesh size, such powdered silica must be given an extremely high velocity so that it possesses sufficient force at impact to form micronicks. Such powdered silica can be successfully used in the practice of the instant invention when air conveyance is the method of impinging said particles on said nickel or cobalt surface. Merely dropping such powdered silica on to such a surface would not result in sufficient momentum to effect such nick formation as required by the instant invention. If, on the other hand, rounded Ottawa sand was utilized in an air conveyance method as contemplated by the instant invention, the momentum would be too great assuming the particles reached the same speed as the powdered silica previously discussed and would result in dulling or destruction of the surface of the decorative layer unless the impacts were precisely controlled which would not be commercially feasible Should lead of the same mass be substituted for the sand, the velocity of the lead particle would have to be somewhat above the velocity of the

sand in order to accomplish the same results, this being due to the fact that lead is more malleable than sand and would absorb more of the force of the impact on the nickel surface.

Another factor which would influence the size, hardness and velocity of the particle is the decorative layer itself. More ductile deposits would require less velocity for a given particle of a given size since micronicks would be more easily formed therein. Likewise as the electrodeposit becomes more ductile, the particle used may be of decreased hardness to achieve the same result.

The size of the particles impinging upon the surface of the decorative layer so as to produce the micronicked condition as indicated previously may vary widely. However, generally the particles would be in the size range of 15–400 mesh although larger or smaller particles could effect the same result under appropriate conditions.

In the practice of the instant invention, particulate matter is made to contact a decorative layer of the object to be thereafter electroplated with chromium. Particles of the appropriate size are impinged against the surface of the layer with enough force and for a sufficient period of time to form nicks in the surface of the layer. To achieve appreciable increase in corrosion resistance, the minimum number of micronnicks formed should be at least approximately 3000 per square inch, although lesser numbers of nicks so formed effect some improvement in corrosion resistance. The preferable nick density is in the range of 40,000 to 200,000 per square inch. Each nick should extend into, but not through the decorative layer. The nick size at the surface of the layer can be anything up to approximately 8 microns. The shape of the nick is not critical and can be circular, jagged, elongated, etc. The only upper limit on the nick density is that the nick formation should cease before the electrodeposit shows dulling to the human eye, although the creation of a slight haze which does not otherwise reduce the brightness of the deposit is acceptable. Quantitatively, the treatment should not increase the diffuse reflectance of the surface as measured on a spectrophotometer by more than about 1%. The pores do not normally cover more than about 1.5% of the total surface of the electrodeposit, whereas a more severe treatment such as sand blasting, hammering or the like affects a much greater amount of the surface.

In some manner the nicks thus formed in the electrodeposited layer result in the formation of micropores in the chromium layer deposited thereover. The number of micropores which extend through the chromium layer are approximately equivalent to the number of nicks in the underlying nick layer. In some instances, however, a smaller number of micropores have apparently resulted with the same improvement in corrosion resistance. It is theorized in these cases that micropores were actually present but went undetected in the test method using to determine the same, or the pores did not go entirely through the chromium a the time of testing for same by the Dubpernell method but quickly extend therethrough on corrosion testing to give equivalent results. In determining the microporosity of the chromium layer, use is made of the "Dubpernell" test in which the composite electroplate including the top layer of chromium is made cathodic in an acidic copper sulfate solution, preferably with a cell potential of about 0.2–0.3 volts. Copper is thus deposited only at the pores and not on the bulk of the surface where it is believed the chromium is covered by an oxide film. The frequency of microporosity is determined by using a microscope at 100–400 magnification.

The brightness of the finished article, that is, after electrodeposition of the final chromium layer, depends on the number, size and depeth of the nicks in the underlying decorative layer. This could be determined by extensive laboratory work. However, this would appear to be an unnecessary expenditure of time and effort since visual observation of the treated decorative layer foretells the finish one could expect on the final chrome plated product. If the treated layer appears dull, a satin finish thus results upon chromium electrodeposition, whereas if it is bright, a decorative chromium finish will result. Thus, according to the instant invention, impingement of solid particulate matter on a bright layer should be stopped before the surface of the layer shows dulling to the human eye.

Any method which is capable of causing particulate matter to strike the surface with the required force may be utilized in the practice of the instant invention. Numerous methods have been used with great success. For example, sand or other particulate matter can be dropped on to the surface to effect the requisite porosity. Vibratory finishing machines containing various particles as the media have also been used with great success. As previously mentioned air conveyance or the like can also be utilized to achieve the desired results. Another method would be to suspend the particulate material such as sand in a liquid medium, the liquid medium being agitated sufficiently so that plated articles placed therein would be struck by sand particles with sufficient force to effect the desired porosity in the surface thereof.

One important object which must be kept in mind in the practice of the instant invention is that the micronicks should not extend entirely through the decorative layer unless, of course, another layer of nickel or the like underlies said created layer. Likewise, additional metallic layers such as copper, nickel or the like can be interposed between the base material and the decorative layer to further improve corrosion resistance and the like.

The present invention is applicable to all electroplated composites composed of a decorative layer and chromium layer, inasmuch as an improvement in corrosion resistance results in each and every case over the equivalent untreated composite.

In determining the corrosion resistance, suitable accelerated tests which correlate well with longer service tests on commercial articles of manufacture were used. These include the Copper Accelerated Salt Spray (CASS) and Corrodkote tests. Using these accelerated tests, the enhancement of the corrosion resistance by the practice of the instant invention has been dramatically shown.

It should be noted that when corrosion tests are made, two types of corrosive attack generally result. With conventional systems composed of chromium and a decorative layer, pinhole rusting occurs in which rapid penetration to the substrate generally occurs. If the substrate for the electrodeposited coatings is steel, rust will become evident in the pinhole points of attack although the remaining bulk surface of the object may remain bright and show little attack.

Where a decorative layer-chromium surface has been treated according to the instant invention, few if any pinhole rust spots will develop over long periods for normal thicknesses. However, shallow surface attack will occur at the pores in the chromium and the test object will tend to appear dull and stained in varying degree due to corrosion of the decorative layer at the pores. However, this stain can be removed by simple washing.

The following examples illustrate the practice of the instant invention.

EXAMPLE I

4" x 6" flat steel panels (three per set) were plated with 0.4 mils semibright nickel onto which were subsequently plated 0.2 mils of bright nickel. These electroplating baths used to plate the nickel were standard commercial baths and provided typical deposits well known to those skilled in the art. After the panels had been plated with the two layers of nickel, they were treated by pouring Ottawa Sand (30–35 mesh) from a height of 10" over the surface of the panels to provide impingement of the sand on the panels at a 45° angle so as to form micronicks in said nickel surface. In all, 250 cc.'s of Ottawa Sand were poured as uniformly as possible over the surface of 4" x 6" panel. The panels were then chromium

plated. The chromium deposit was 10 millionths of an inch thick and was deposited from a conventional chromium electroplating bath having a CrO_3/H_2SO_4 ratio of 100:1. One panel per set was Dubpernell tested and the pore count for the set determined. The remaining two panels were corrosion tested 48 hours Cass, then 20 hours Corrodkote. Corrosion test results are given below for the sand treated panels as well as untreated control panels and numbers given under the corrosion test headings refer to pinhole rust spots. All panels resulted in a decorative chromium finish with the surface being fully bright.

Test material	Appearance (Dubpernell)	Pores per sq. in.	Rust spots 32 hrs., Cass	48 hrs., Cass	20 hrs., Corrodkote
Sand treated Ni then Cr plated	Medium porosity	35,000	4	10	10
		45,000	0	3	12
Untreated controls	Edge macrocracking		19	100	200
			33	100	200
			9	100	200
			2	48	100
			4	60	200
			33	100	200

EXAMPLE II

This example illustrates another method of securing impingement of solid particles on a plated object. In this instance, a vibratory finishing machine was used, specifically one sold under the trade name Vi-Brader by Rampe Manufacturing Co., Cleveland, Ohio, Model COF9. This vibratory finishing machine consists of a semi-cylindrical, plastic lined tub mounted on a motor driven eccentric arm such that the tub is vibrated, giving a circular motion to the sand or other medium contained in the tub. Vibration of the tub can vary between 900–1800 orbits per minute. Parts placed in the tub move in a circular direction along with the medium which was a fine sand in this test. For this test 1½" x 6" steel panels were used which had a rounded recess ⅝" deep and 2" across. These panels were electroplated with successive layers as follows:

	Flat area, mil	Recess area (bottom), mil
Semi bright nickel	0.5	0.2
Bright nickel	0.3	0.1
Chromium	0.014	0.004

The nickel-plated steel panels (3 per set) were treated in the Vi-Brader prior to the final chromium electrodeposition. One panel was Dubpernell tested while the other two panels per set were Cass tested. The results were as follows:

	Tumbling time, seconds	Appearance (Dubpernell)	Rust spots 36 hrs. Cass-recess	52 hrs. Cass-flat surface
Vibration rate (orbits/min.):				
1,800	30	Slight uniform microporosity.	30	6
1,800	30	do	29	9
1,800	15	do	6	8
1,800	60	do	9	1
Control			100	35
Do			100	38

Note that because of the thin deposits in the recess of the panels, a considerable number of rust spots were noted after 36 hours of testing.

EXAMPLE III

1½" x 6" steel panels with rounded recesses as described in Example II above, were electroplated as follows:

	Flat area, mil	Recess area (bottom), mil
Semi bright nickel	0.5	0.2
Bright nickel	0.3	0.1
Chromium	0.017	0.005

Prior to electrodeposition of the chromium layer, the underlying bright nickel layer was treated in a Vi-Brader as described in Example II supra. The Vi-Brader was run at 1800 orbits per minute using a ground corncob media. One panel was allowed to tumble freely in the Vi-Brader for a period of 60 seconds while another panel was held stationary while the Vi-Brader was operated for 60 seconds. After such treatments with the Vi-Brader, the panels were chromium plated and corrosion tested with the following results:

Treatment	Rust spots 48 hrs., recess	Cass flat	60 hrs., recess	Cass flat
Vibratory-tumble	100	0	100	1
Vibratory-hold	100	2	100	2
Control	200	17	200	22

Another use of the instant invention is in conjunction with the processes as described in the aforementioned U.S. Pat. Nos. 3,298,802 and 3,449,223. As discussed earlier, these patents call for a process wherein decorative chromium has a microporous finish resulting in improved corrosion resistance. In such patents the microporous chromium layer is formed due to the fact that electrically non-conductive particles are embedded in the nickel layer underlying said surface chromium layer. If in the practice of these processes this underlying nickel containing non-conductive layer is found to possess insufficient particulate material to produce the desired corrosion resistance, then the instant invention, i.e., the impingement of particulate matter on the nickel surface may be used as a supplemental treatment which has the same effect as if increasing the amount of particulate material entrapped in said nickel layer. Thus, if the nickel plating bath of this prior art process was operated with insufficient amount of particulate matter in the plating bath, the parts plated thereby could be brought up to specification with respect to corrosion resistance by treatment according to the instant invention.

Another problem also exists with these prior art processes in that if the chromium layer is defectively deposited on said nickel particulate containing layer, such plating parts are defective and it has been found that after stripping the defective chromium therefrom, new chromium electrodeposited directly on the surface from which the prior chromium was stripped lacks equivalent corrosion resistance. The exact reason for this is not known with certainty but in some manner the particulate containing nickel layer does not yield nearly the corrosion protection when the subsequent chromium layer is deposited thereon after stripping of a prior chromium deposit. Commercially, when such electroplated parts have been stripped of chromium, they have been recycled back to the nickel plating bath and a second layer of particulate containing nickel is deposited thereon followed by the

final chromium electrodeposition. In accordance with the instant invention, the need for this second layer of particulate containing nickel is avoided and equivalent corrosion resistance is obtained by impinging particulate matter on said particle containing nickel layer after stripping of the defective chromium followed by the appropriate chromium electrodeposition. In this instance as well as the instance previously discussed regarding particulate containing nickel deposits, the treatment is, of course, much less severe than the treatments required to produce equivalent corrosion protection in non-particulate containing nickel layer systems since the particulate matter in the nickel layer acts equivalently to the micronicks formed by the impingement of solid materials.

What I claim is:

1. A method of improving the corrosion protection of a base metal comprising the successive steps of:

(a) electrodepositing a decorative layer of nickel, cobalt or an alloy thereof over the base metal;

(b) impinging a solid particulate material against the decorative layer to form at least 3000 micronicks per square inch extending into, but not through, said decorative layer without visably dulling the same, the size of said micronicks not exceeding about 8 microns at the surface of said layers; and

(c) depositing a layer of chromium to a thickness of at least about 5 millionth of an inch over said decorative layer, said chromium layer being substantially continuous but being characterized by the presence of discontinuities coinciding with the micronicks in the decorative layer.

2. The method of claim 1 wherein one or more layers of metal are depositetd upon the base metal prior to electrodeposition of the decorative layer.

3. The method of claim 1 wherein between 40,000 and 200,000 micronicks per square inch are formed in said decorative layer by impingement.

4. The method of claim 3 wherein the micronicks cover no more than about 1.5% of the total surface of the decorative metal.

5. The method of claim 1 wherein the decorative layer is deposited to a thickness of between about 0.3 and about 1.5 mils.

References Cited

UNITED STATES PATENTS

1,813,842	7/1931	Fink et al.	204—41
1,835,636	12/1931	Corbit	204—36 X
1,835,664	12/1931	Merten	204—36 X
3,388,049	6/1968	De Castelet	204—29
3,428,441	2/1969	Du Rose et al.	204—41 X
3,545,996	12/1970	Duncan	117—8
3,787,191	1/1974	Duncan	204—35 RX

GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

204—29, 36, 41