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2,989,446

ELECTROPLATING

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This invention relates to electroplating and more particularly to a novel process and the plated product produced thereby.

In plating ferrous articles and other basic metal members with electro-deposits of nickel-zinc alloy, it is desirable to apply a predetermined thickness of alloy of proportions which we can term zinc-rich as used now and hereinafter to mean more than 50% zinc and less than 50% nickel. Preferably the nickel content is about 13% to about 24% nickel and the balance is zinc. This alloy deposit is highly suited as a plating on both ferrous and non-ferrous articles, the latter including brasses and die castings particularly. In connection with the former, the zinc-rich alloy deposit has remarkable properties in increasing the corrosion resistance of the ferrous base article, and the advantages of using this deposit and some explanations advanced therefor are more completely disclosed in Schantz Patent No. 2,419,231. The Schantz patent further discloses an electroplating bath of specified compositions which have proved very satisfactory in producing the zinc-rich deposit on the article.

The bath employed in the present invention is very similar to the just mentioned plating bath according to the Schantz teaching which employs unidirectional direct current only therein to continuously cathodically plate a ferrous article with an alloy deposit which is zinc-rich, containing approximately 85% zinc and 15% nickel. The zinc-rich deposit offers good corrosion resistance on iron or steel as already mentioned, but has the deficiency of being practically impossible commercially of taking a chromium plate or a nickel plate thereover which will have good adherence to the zinc-rich deposit. The difficulty with nickel-zinc alloy which is zinc-rich is that it dissolves in electrolyte baths generally used in commercial chrome plating or nickel plating, and continues to do so in spots at least, even when the plating current is flowing.

In the present invention we retain the advantages of corrosion proofing generally according to Schantz Patent 2,419,231, but in doing so we produce a composite form of deposit to which a chrome plate or nickel plating readily adheres. In accordance with our invention, in a first step we generally follow the teachings of unidirectional plating current in the alloy plating bath of the Schantz patent to produce a zinc-rich deposit on the article and thereafter in a subsequent step two we employ periodic reversal of current to apply upon the zinc-rich alloy a nickel-rich alloy deposit of a particular character to which nickel or chromium plate will satisfactorily adhere. The feasibility of producing this nickel-rich alloy comes from our present discovery that in one bath, merely by controlling the current density, the current duration, and the current direction, we can produce the unexpected and unusual result that nickel-rich alloy commences to over coat the zinc-rich alloy which had previously come from the same bath. In distinction to the term zinc-rich which is already defined, we intend the term nickel-rich to mean more than 50% nickel and less than 50% zinc. In distinction to ordinary cathodic unidirectional plating (D.C.), we intend the term "periodic reversal" (P.R.) to mean the utilization of the direct current in one direction for a short period in which the article is anodic, followed by a short period in which the current is switched in reverse to make the article cathodic,

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followed by another short period in which the current is again reversed to make the article anodic, and continuing to switch the current until completion of the period desired.

It is not clear why the proportions of the alloy deposit being plated onto the article become changed incident to P.R. switching so that the zinc-rich layer is over coated with the nickel-rich layer and vice versa, nor is it clear why the resulting nickel-rich layer will receive and offer particularly good adherence to a subsequent chrome plate or nickel plate. However, some tests have indicated a provisional or working hypothesis. When an article to be plated is immersed in an electrolytic bath which under normal current density such as 50 amps. per sq. ft. will plate out a zinc-rich alloy deposit thereon, and when the current density employed is below approximately 20 amps. per sq. ft. for some articles, the alloy deposited thereon results in being nickel-rich varying from about 50% to 100% nickel, depending on other variables, with the balance being zinc. Further, when that article is cathodically plated with the alloy for a period which is interrupted with a reversal of current to give the article a short anodic treatment resulting in its polarization, and when the cathodic treatment is immediately or subsequently resumed so as to depolarize and restart plating of the article at normal current density, the effective proportion of the current density immediately available for actual plating is considerably lower for the initial part of the period in which all or a large part of the electrical energy is being consumed in the immediate problem of depolarization, that is, dispelling gas bubbles from the passive surface of the article in order to reactive it and to resume normal cathodic plating. Thus, the effective part of the normal current density during the initial cathodic phases of P.R. plating may be so low that only nickel-rich deposits initially occur and these normal total current densities of 50 amps. per sq. ft. referred to are conventional in bumper plating work, for instance, in which automobile bumpers with an average area of 10 sq. ft. are subjected to 500 amps. current input on the meter. Longstanding suspicions have existed in the art with regard to polarization effects, and criticisms of their harmful qualities in electroplating work, particularly reverse current operations, have been suggested heretofore as in Holt Patent 1,534,709. The disadvantages of polarization are explicitly set forth in the Holt patent which teaches periodic current reversal to combat and eliminate those disadvantages, whereas instantly it would appear that the polarization effects are actually being harnessed to produce the result presently intended. In any case, the theory of reversal of proportions as a result of unidirectional current followed or preceded by polarization effects of P.R. current treatment, and the further theory of an alloy deposit of metals which is produced by applications of P.R. current in a manner so as to take chrome plate or nickel plate directly thereover where not previously commercially possible, are used in this specification only as convenient bases for explaining the invention.

In the present invention and, generally in accordance with the teachings of the mentioned Schantz Patent 2,419,231, we employ a bath containing:

	gm./l.	oz./gal.
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	240-300	32-40
ZnCl_2	90-120	12-16

The bath also contains 1-3% by volume of glacial acetic acid or other suitable buffer, for instance, the buffer may be salts of acetic acid and also formic, citric, boric, or tartaric acid or the salts thereof. The bath

further contains by volume 1% of a wetting agent of composition not specifically known, but commercially available as the Udylyte (Detroit, Michigan), No. 22 nonpitter. The contents of the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and the ZnCl_2 are equivalent respectively to 8–10 ozs. per gal. of nickel metal and 6–8 ozs. per gallon of zinc metal. The latter zinc metal may be present in the bath in the form of zinc sulfate instead of or with the zinc chloride but at least 50% of the total of the nickel and zinc salts must be chlorides. The pH of the bath is 1 to 3 and preferably 2.0–2.5. The bath temperature range is 70° F.–165° F., and preferably the bath is between about 135° F. and 145° F. The cathode current density is 20–600 amps. per sq. ft., but preferably the cathode current density is 50–60 amps. per sq. ft. The article itself constitutes the cathode (literally anode during the anodic phases of the current reversal cycle) and the anodes themselves may take several satisfactory forms, but in any case the electrolyte is kept in circulation in well-known manner while the articles are being treated, except when plating upon wire or strip moving through the electrolyte such circulation may not be necessary.

Preferably, nickel anodes are used or else separate nickel and zinc anodes are used having their surface areas relatively proportioned on the same ratio as the nickel and zinc in the desired zinc-rich alloy. In the latter case it is desirable to employ a plurality of the zinc anodes and a plurality of the nickel anodes and to position them properly on the anode support in a spaced relationship to get the current distribution desired. Instead of using the separate zinc and nickel anodes, cast or rolled alloy anodes may be used having the metals in about the same proportions as in the zinc-rich alloy being plated out or, if desired, having the metals in substantially equal proportions. When nickel anodes only are being used, zinc must be added to the bath from time to time to strengthen the zinc salts and replace the zinc plated out. When it is possible to use zinc anodes alone the nickel is replenished in the nickel salts of the above character by adding nickel to the bath from time to time. Insoluble anodes may be used in some instances in the baths, but even when such electrodes are satisfactory the bath requires the constant addition of both zinc and nickel to replenish the metal concentration which has been depleted by being plated out of their salts.

During the P.R. cycles in the bath, the periods of cathodic current last at least about 3 seconds apiece, but never longer than for about 30 seconds' duration. The companion anodic pulses during the P.R. cycle are intentionally shorter than the cathodic pulses, particularly when the anodic current intensity used exceeds the strength of the cathodic current used, but in any case the coulombs applied to the bath during each cathodic pulse exceed the coulombs during the subsequent anodic pulse to insure that the thickness plated each time exceeds the amount depleted. Thus, a succession of net deposits is consistently accumulating from being cyclically plated out of the solution and gradually building up as microscopically thin parallel plated increments on the article. The coulombs of each anodic pulse are between about 20% and about 80% of the coulombs of the adjacent cathodic pulse for best results.

In instances where the cathodic current intensity and the anodic current intensity of the P.R. period are each equal to approximately 50 amps. per sq. ft., the preferred plating cycles have had the proportions in the range between 12 seconds cathodic–9 seconds anodic (anodic coulombs 75% of cathodic) to about 10 seconds cathodic–2 seconds anodic (anodic coulombs 20%) and the 12-second cathodic–8-second anodic (anodic coulombs 66⅔%) and 13 seconds cathodic–9 seconds anodic (anodic coulombs 69%) cycles within that range have proved very satisfactory for the P.R. process. In this range the alloys deposited have been between about 56% and 96% nickel and the balance zinc.

In the following examples all baths, current densities, and temperatures are mainly the same. During each period captioned D.C. plating (direct current alloy plating) and likewise during each period captioned P.R. plating (periodic reverse current alloy plating), the plating bath contained with minor variations:

	g./l.	oz./gal.
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	260	35
ZnCl_2	96	13

The bath was buffered by 2½% glacial acetic acid by volume. The respective amounts of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and the ZnCl_2 were the equivalents of 65 grams per liter of nickel metal and 50 grams per liter of zinc metal. The bath also contained 1% of Udylyte nonpitter No. 22. The bath had a pH of 2.2 and a temperature of 135° F. Nickel anodes were used.

As a general guide regarding the nickel-zinc alloy deposits, it is to be kept in mind in the examples below that the D.C. plating current and that the P.R. current in both directions is very satisfactory in the range of 50–60 amps. per sq. ft. although the P.R. currents in one direction, for example to make the article cathodic, is not necessarily equal to, but may for instance, be one-half the strength of the P.R. current in the anodic direction. Except as otherwise pointed out below the zinc-rich alloy applied during the D.C. plating period is at least 0.1 mil thick, but preferably 0.4 mil thick and good results have been obtained with between 0.6 mil and 1.2 mils thickness. In fact, there seems to be no readily ascertainable upper limit to the thickness of deposits which uniformly show good adherence. Except as otherwise pointed out below the P.R. period for applying the nickel-rich alloy lasts at least approximately 3 minutes and although the thickness can be slightly more or very substantially more, we preferably use a 10-minute P.R. period which insures sufficient thickness that the deposit will adhere properly and without being porous as it would be if extremely thin.

The difficulty with porosity in the nickel-rich deposit is that it will admit chrome plating electrolytes and nickel plating electrolytes to contact the zinc-rich alloy under coat and in case such an article is immersed to be nickel plated or chrome plated, the electrolyte will immediately commence to dissolve out the Zn-rich alloy under coat and thus undermine the nickel-rich over coat in spots at the same time at which a nickel plate or chrome plate is presumably being applied over the entire surface.

The following examples illustrate various ways in which our process can be carried out.

Example I

A formed steel automobile bumper of suitable dimensions, for instance with a developed width and length of 17" x 110", is subjected to the following steps, the bumper being bare steel or if desired, having a coating of nickel or copper plate.

Step one, a 29-minute period of D.C. plating: The purpose of this step was to produce a zinc-rich alloy deposit. A current density of 50 amps. per sq. ft. was used and a buffered chloride bath of the foregoing constituents was employed. The zinc-rich alloy consisted of approximately 85% zinc and 15% nickel and the deposit was generally homogeneous and was 1.2 mils (0.0012") thick.

Step two, a 10-minute period of P.R. plating: The purpose of this step was to produce an over coat of nickel-rich alloy deposit and to do so the article remained in the same bath as in step one. The periodic reverse cycle was so arranged that this article was 8 seconds anodic–12 seconds cathodic, 8 seconds anodic–12 seconds cathodic, etc., recurrently for the duration of the 10-minute period. The current density was 50 amps. per sq. ft. and the thickness of the alloy deposit was 0.2 mil (0.0002"). The

nickel-rich deposit was generally homogeneous consisting of 80% nickel and 20% zinc.

Step three, buffing period: In this period buffing compounds were abraded against the article to make it bright and also to remove any oxide coating remaining on the article and thereby reactivate its surface following plating.

Step four, removal of the buffing compound: The buffing compound was removed by employing a cathodic cleaning step in which the article was made cathode in an alkaline cleaner, for example, an aqueous solution of 4-6 oz. per gallon caustic soda or sodium carbonate.

Step five, water rinse: In this step the article was rinsed in water to remove the buffing compound cleaner.

Step six, acid dip: The article was dipped in a 10% solution of hydrochloric acid to reactivate the surface.

Step seven, water rinse: This step of water rinsing the article insured the removal of any traces of the hydrochloric acid.

Step eight, chrome plating period: A chromium sulfate plating bath was used as the electrolyte which contained:

Chromic acid ----- 45 oz. per gal. (CrO_3)
Sulfate ----- 0.45 oz. per gal. (SO_4)

The chrome plating bath was maintained at a temperature of 118° F. and the cathode current density was 100 amps. per sq. ft. The composition of the resulting product was chromium upon nickel-rich deposit upon zinc-rich deposit upon the base ferrous article. The period for depositing the chromium lasted time-wise purely according to the thickness desired which in this particular case was 0.015 mil (0.000015") thick. The foregoing method upon elimination of the chrome plate produced in step eight, with or without the elimination also of the buffing produced in step three, nevertheless produces more than a mere transitory stage intermediate article. Such article, sheathed in the outer coat of 80% nickel-rich alloy of step two, satisfies a specific object of this invention of making it possible to electroplate high nickel-zinc alloys on a commercial basis, and such nickel-rich electrodeposition of this 80% character named or to slightly higher or lower proportions has not to our knowledge been previously done successfully. The bare nickel-rich deposit greatly improves corrosion resistance and, in the approximate thickness specified, is not porous as evidenced by the fact that it effectively insulates the zinc-rich under coat from its natural tendency of dissolution in chrome plating baths or other chemical agents which might attack it. The nickel-rich deposit manifestly offers corrosion proofing plus brightness utility when applied as the outer coat to articles lacking the immediately adjacent intermediate surface of zinc-rich alloy, but when the article is ferrous and also has a satisfactory thickness of the intermediate zinc-rich deposit under the nickel-rich outer coat, then a particularly useful and corrosion resistant, smooth and bright article results.

Example II

The steps in this example are the same as in Example I above, except that following the completion of step two thereof and prior to beginning buffing step three, a light nickel electrodeposit was applied to the nickel-rich deposit on the bumper. In the known method, the nickel is applied in a manner to have dull semi-bright, or bright finishes optionally. The thickness of nickel deposit is preferably between 0.050 mil and 0.750 mil and in the present instance was approximately 0.1 mil (0.0001") thick. The nickel plate bath had a pH of 3.5 and contained, per gallon thereof:

45 oz. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
5 oz. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
5.5 oz. boric acid

and the traces of this bath were then removed from the article by a conventional water rinse following the nickel plating. The resulting article was essentially the same as

in Example I, the buffing step removing some, but not all of the intermediate nickel coat from the article which therefore consisted of chromium upon nickel upon nickel-rich alloy upon zinc-rich alloy upon the base ferrous article. The nickel protects the nickel-rich alloy from the effects of buffing by forming a tough intermediate sheath which very satisfactorily holds up against the abrading effect of the buffing step and does so much more effectively than the 0.2 mil deposit of nickel-rich alloy does alone in its bare form as its results from step two in the Example I foregoing. The method of Example II, upon elimination of the chrome plate with or without the elimination of the nickel coat and also the buffing procedure, nevertheless produces more than a mere transitory stage intermediate article. Such article is of evident utility if the nickel coat is the outermost coat and, with the nickel outermost, this article has utility even if no zinc-rich layer is present below the nickel-rich alloy deposit.

Example III

Step one, a 29-minute period of D.C. plating: The purpose of this step was to produce a zinc-rich alloy deposit on the bumper. A current density of 60 amps. per sq. ft. was used and a buffered chloride bath of the foregoing constituents was employed. The zinc-rich alloy consisted of approximately 85% zinc and 15% nickel and the deposit was generally homogeneous and 1.5 mils (0.0015") thick.

Step two, a 10-minute period of P.R. plating: The purpose of this step was to produce an over coat of nickel-rich alloy deposit on the article which remained in the same bath as in step one. The periodic reverse cycle was so arranged that this article was 8 seconds anodic, 12 seconds cathodic, 8 seconds anodic, 12 seconds cathodic, etc., recurrently for the duration of the 10-minute period. The current density was 50 amps. per sq. ft. and the thickness of the plate was 0.2 mil (0.0002"). The nickel-rich deposit was generally homogeneous consisting of 80% nickel and 20% zinc.

Step three, a 1-minute period of D.C. plating: The purpose of this precautionary step was to depolarize the surface of the article through the application of a thin zinc-rich alloy deposit. The interposition of this deposit prevents an oxide film from forming on the article which would otherwise tend to form in some instances when it is initially exposed to the air following its polarization in the bath.

Step four, acid dip: The article was dipped in a 10% solution of hydrochloric acid to remove the thin zinc-rich deposit which at this point had fulfilled its entire purpose inasmuch as thereafter no oxide film has a tendency toward forming when the article is reexposed to air.

Step five, water rinse: In this step the article was rinsed in water to remove the hydrochloric acid.

Step six, buffing period: In this period buffing compounds were abraded against the article to make it bright and smooth.

Steps seven-eleven complete the article and were identical with and in the same order as the last five steps (steps four-eight) of Example I, namely, removal of buffing compound, water rinse, acid dip, water rinse, and chrome plating period. The resulting article was essentially the same as in Example I, being composed of chromium upon nickel-rich deposit upon zinc-rich deposit upon the base ferrous article. The bond between the chromium and the nickel-rich deposit was highly effective and tenacious owing to the effect of the temporary sheath of zinc-rich alloy which during the process of its application and subsequent complete removal served the very effective purpose of insulating the article from the formation of any oxide film over the nickel-rich deposit, prior to the subsequent application of the chrome electrodeposit directly to the nickel-rich alloy deposit. It is equally advantageous to employ this zinc-rich temporary sheath when the nickel-rich under coat therebeneath is to

Example IV

Step fifteen, water rinse: This step of water rinsing the article was to remove the hydrochloric acid.

Example V

Step six, 29-minute period of continuous D.C. plating: This die casting was electroplated in a buffered chloride bath of the foregoing constituents to produce a zinc-rich

alloy deposit at a current density of 50 amps. per sq. ft. The thickness was 0.0012" (1.2 mils) of simultaneously deposited zinc and nickel in the proportions 80% zinc and 20% nickel.

Step seven, buffing step: This step is optional, and requires that the article be temporarily removed from the foregoing buffered chloride bath.

Step eight, alkaline cleaning step employing electro-cleaning operation with appropriate alkaline cleaner to remove the buffing compound of the preceding optional step from the die casing: This step is, of course, optional depending solely on whether the optional buffing step was used.

Step nine, acid dip: The article was subjected to an acid dip in a proper bath to neutralize the alkaline treated surface thereof.

Step ten, 2-minute step of continuous D.C. plating: This optional step reconditions the buffed surface of the article to essentially the status of what that immediate surface would have possessed had steps seven-nine been omitted following the D.C. plating step six. This step ten is highly desirable where the buffing and dipping steps seven-nine are employed, and, of course, involves the reintroduction of the article into the same or equivalent bath as the buffered chloride bath of step six from which it was temporarily removed.

Step eleven, 10-minute P.R. step: The article was subjected to 50 amps. per sq. ft. current density employing the P.R. cycle in the same bath as in the step six preceding, the intervening steps seven-ten being omitted or not as optional. The co-deposited nickel-rich nickel-zinc was in the proportion 80% nickel, 20% zinc to a thickness of 0.2 mil (0.0002").

Step twelve, 1-minute step of continuous D.C. plating: This step prevents the formation of oxides when the article is first exposed to air upon removal from the bath following step eleven.

Step thirteen, acid dip: The article was subjected to an acid dip in a bath having a concentration of 10% HCl to remove the zinc-rich deposit formed in step eight thereby making the external nickel-rich coating acid to receive a deposit and actively bond thereto in the following step.

Step fourteen, nickel plate: The article was nickel plated either semi-bright or bright to a thickness of 0.0003" (0.3 mil) or 0.0004" (0.4 mil). The bath employed had a pH of 3.5 and contained per gallon thereof:

	Oz.
Nickel chloride -----	5
Nickel sulfate -----	45
Boric acid -----	5.5

Step fifteen, buffing step: The article was buffed in the case of the semi-bright nickel plate of the preceding step although buffing is unnecessary with the bright nickel plate option of the preceding step fourteen.

Step sixteen, chrome plate step: The article was chrome plated to a thickness of 0.010 mil (10 millionths of an inch) and the chrome plating electrolyte consisted of:

	Oz./gal.
Chromic acid -----	45
SO ₄ -----	0.45

The resulting article was chrome plate upon nickel plate upon nickel-rich alloy upon zinc-rich alloy upon the base article which was a zinc die casting. The purpose of the P.R. step six was to enable the nickel plate according to step fourteen to adherently bond to the zinc die casting without the necessity for a cyanide copper over coat in order to properly take the bright nickel plate.

The multiple step procedures and the respective products of the preceding examples are not exhaustive. In many cases the plating current employed will be satisfactory under various ranges of impressed voltage

depending upon the spaced relationship of the anodes and the articles treated, and relatively low plating and deplating voltages were actually employed which were in the range between 6 and 24 volts and preferably the plating and deplating voltages were each about 10 volts D.C. In each case the anodes were nickel, but the plating and deplating can be accomplished satisfactorily according to this invention with electrodes of other compositions.

The electrodeposits produced by the invention are particularly applicable to automobile bumpers, hardware, and the like which are subject to abrasion and exposure to moisture and deleterious gases. The electrolyte may be agitated and distributed in accordance with well-known practices in plating. It has been found desirable to maintain a clean electrolyte, for example, by filtering or the like, inasmuch as the electrodeposits have such a smooth and highly polished surface that any solid impurities from the electrolyte deposited on the plated work are much more apparent than in ordinary electroplating.

Variations within the spirit and scope of the invention described are equally comprehended by the foregoing description.

We claim:

1. In a method of plating articles which comprises passing an electric current through the article and through the electrolyte which, under substantial and satisfactory current density and sustained conditions of current in a direction to make the article continuously cathode, plates out a zinc-rich alloy thereupon, said electrolyte comprising a bath having a pH between about 1 and 3 and temperature between about 70° F. and 165° F. in which salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gal. and a zinc metal content of 6 to 8 ozs. per gal., at least 50% of the total of the nickel and zinc metal concentration in the electrolyte being in the form of chlorides, the improved steps comprising passing current through the article and the electrolyte for a time period within which the current flow is being periodically reversed to make the article once anodic and next cathodic in that bath to deposit a nickel-rich alloy on the article, wherein the current density is of a value between 20 and 600 amps./sq. ft. in each direction and wherein on alternate anodic and cathodic pulses the anodic flow is sustained for at least 2 seconds, with the cathodic flow being sustained for a duration sufficient to apply to the bath coulombs in excess of the anodic flow but not over 30 seconds and repeating said anodic and cathodic reversal of current flow at least several times in the duration of said time period to plate nickel and zinc simultaneously on the article until a desired thickness of the nickel-rich deposit has been electroplated with good adherence to the article from that bath.

2. In a method of plating articles which comprises passing an electric current through the article and through the electrolyte which, under substantial and satisfactory current density and sustained conditions of current in a direction to make the article continuously cathode, plates out a zinc-rich alloy thereupon from the electrolyte bath, said electrolyte comprising a bath having a pH between about 1 and 3 and temperature between about 70° F. and 165° F. in which the salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gal. and a zinc metal content of 6 to 8 ozs. per gal., at least 50% of the total of the nickel and zinc metal concentration in the electrolyte being in the form of chlorides, the improved steps including successively passing cathodic currents of uniform strength and duration through the article and the electrolyte so as to follow the period of each one of the cathodic pulses with a next cathodic pulse, but interrupted by an intervening step of reversal of flow of the current in the anodic direction for a period of lesser duration than the cathodic periods but sufficient to deplate the article of an amount of the nickel-zinc co-

deposit substantial enough to polarize the article just prior to receiving said next successive cathodic pulse, wherein the current density is of a value between 20 and 600 amps./sq. ft. in each direction and wherein on alternate anodic and cathodic pulses the anodic flow is sustained for at least about two seconds, with the cathodic flow being sustained for a duration sufficient to apply to the bath coulombs in excess of the anodic flow but not over 30 seconds and repeating said interruptions to cause the successive cathodic codeposits of nickel and zinc to accumulate to a desired thickness but with the nickel predominating for at least the initial phase of each cathodic step and thus accumulating a homogeneous nickel-rich deposit composed of a plurality of microscopically thin, parallel plated increments.

3. In a method of plating articles which comprises passing an electric current through the article and through the electrolyte which, under substantial and satisfactory current density and sustained conditions of current in a direction to make the article continuously cathode, plates out a zinc-rich alloy thereupon from the electrolyte, said electrolyte comprising a bath having a pH between about 1 and 3 and temperature between about 70° F. and 165° F. in which the salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gal. and a zinc metal content of 6 to 8 ozs. per gal., at least 50% of the total of the nickel and zinc metal concentration in the electrolyte being in the form of chlorides, the improved steps comprising electroplating the article in contact with the electrolyte by means of current flow which is being periodically reversed to make the article once anodic and next cathodic in that bath to deposit a nickel-rich alloy on the article, wherein the current density is of a value between 20 and 600 amps./sq. ft. in each direction, and wherein on alternate anodic and cathodic pulses the anodic flow is sustained for at least approximately a two second time duration and each cathodic pulse is sustained between about 3 and 30 seconds and of sufficient duration to apply coulombs to the bath in excess of the anodic pulse and repeating said anodic and cathodic reversals of current flow continuously for the duration of a complete period of at least approximately 3 minutes to plate nickel and zinc simultaneously on the article so as to produce a substantial nickel rich deposit with good adherence to the article.

4. In a method of plating articles in an electrolyte bath having a pH between about 1 and 3 and a temperature between about 70° F. and 165° F. in which the salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gal. and a zinc metal content of 6 to 8 ozs. per gal., at least 50% of the total of the nickel and zinc metal concentration in the bath being in the form of chlorides, the improved steps comprising causing electric current for a period of at least approximately 4 minutes to flow therethrough while the article is in contact with the electrolyte and with the current unidirectional to make the article continuously cathode for electroplating thereon a zinc-rich deposit from the bath, and interrupting said cathodic period of unidirectional current flow by switching to a second period of periodically reversed current flow, in which the article is once anodic and next cathodic in that bath to deposit a nickel-rich alloy on the article, wherein the current density is of a value between 20 and 600 amps./sq. ft. in each direction and wherein on alternate anodic and cathodic pulses the anodic flow is sustained for at least 2 seconds, with the cathodic flow being sustained for a duration sufficient to apply to the bath coulombs in excess of the anodic flow but not over 30 seconds with a repetition of said anodic and cathodic reversals of current flow at least several times through the duration of said second period until a desired thickness of the nickel-rich deposit has been electroplated on the zinc-rich deposit on the article from that bath.

5. In a method of plating articles in an electrolyte having a pH between about 1 and 3 and a temperature between about 70° F. and 165° F., in which salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gal. and a zinc metal content of 6 to 8 ozs. per gal., at least 50% of the total of the nickel and zinc metal concentration in the electrolyte being in the form of chlorides, the improved steps comprising causing electric current for a period of at least approximately 4 minutes to flow therethrough while the article is in contact with the electrolyte and with the current unidirectional to make the article continuously cathode for electroplating thereon a zinc-rich deposit from the electrolyte, and interrupting said cathodic period of unidirectional current flow by switching to a second period of at least about 48 seconds of periodically reversed current flow in which the article is once anodic and next cathodic in the electrolyte to deposit a nickel-rich alloy on the article, wherein the current density is of a value between 20 and 600 amps./sq. ft. in each direction, and wherein on alternate anodic and cathodic pulses the anodic flow is sustained for at least approximately a two second time duration and each cathodic pulse is sustained between about 3 and 30 seconds and of sufficient duration to apply coulombs to the bath in excess of the anodic pulse and repeating said anodic and cathodic reversals of current flow continuously for the duration of the 48-second period to electroplate a nickel-rich deposit on the article from said electrolyte.

6. In a method of plating articles in an electrolyte bath having a pH between about 1 and 3 and a temperature between about 70° F. and 165° F. in which the salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gal. and a zinc metal content of 6 to 8 ozs. per gallon, at least 50% of the total of the nickel and zinc metal concentration in the electrolyte being in the form of chlorides, the improved steps comprising causing electric current for a period of at least approximately 4 minutes to flow therethrough while the article is in contact with the electrolyte and with the current unidirectional to make the article continuously cathode and electroplate thereon a zinc-rich deposit from the electrolyte, and interrupting said cathodic period of unidirectional current flow by switching to a second period of at least about 3 minutes of periodically reversed current flow, in which the article is once anodic and next cathodic in the electrolyte to deposit a nickel-rich alloy on the article, wherein the current density is of a value between 20 and 600 amps./sq. ft. in each direction and wherein on alternate anodic and cathodic pulses the anodic flow is sustained for at least about two seconds, with the cathodic flow being sustained for a duration sufficient to apply to the bath coulombs in excess of the anodic flow but not over 30 seconds and repeating said anodic and cathodic reversals of current flow continuously for the duration of the 3-minute, second period to electroplate a nickel-rich deposit on the article from said electrolyte.

7. In a method of plating articles in an electrolyte bath having a pH between about 1 and 3 and a temperature between about 70° F. and 165° F. in which the salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ozs. per gallon and a zinc metal content of 6 to 8 ozs. per gallon, at least 50% of the total of the nickel and zinc metal concentration in the electrolyte being in the form of chlorides, the improved steps comprising passing an electric current cathodically through the electrolyte during a first period of electrolytic treatment of the article for a time sufficient to deposit thereon a zinc-rich alloy cumulative to thickness of at least 0.1 mil net, and thereafter subjecting the article to repetitive reversals of current in that electrolyte for the duration of a second period lasting at least 4 minutes wherein there

are alternate periods of anodic and cathodic treatment of the article such as to deposit from said electrolyte a nickel-rich alloy of proper thickness to prevent porosity, and wherein the cathodic current has a density of 20-600 amps. per sq. ft. and the cathodic periods are each between about 3 and 30 seconds duration, and wherein the time employed during the anodic treatment periods being at least two seconds is of sufficient duration to deliver at least about 20% but less than about 80% of the coulombs consumed in the cathodic deposition time occurring in said second period.

8. A method according to claim 7 wherein said first period deposition comprises the initial step of passing electric current through the article and through the electrolyte in a direction to make the article continuously cathode for at least about 4 minutes to deposit zinc-rich alloy on it, a next step of periodically reversing the direction of flow of the electric current over a lesser period than said 4-minute period to make the article alternatively anodic and cathodic so as to deposit a nickel-rich alloy thereon, and then repeating said 4-minute cathodic deposition step and said periodic reverse deposition step several times to form alternating strata of the reversed proportions aforesaid of the nickel-zinc alloy deposit.

9. A method according to the steps of claim 7 including the further steps of making the article continuously cathode for a period sufficient to deposit further zinc-rich alloy thereupon for proper depolarization purposes to prevent formation of a gas film or of oxides upon subsequent exposure to air, and then subjecting the article to acid treatment to remove the zinc-rich deposit produced by the last named continuous cathode period so as to reactivate the surface of the article and thereafter electrolytically depositing on said surface a layer of metal selected from the group of chromium and nickel.

10. A method according to the steps of claim 7 including the further steps of bright buffing the article for a period sufficing to eliminate surface impediments thereon and then subjecting the article to acid treatment to reactivate the surface for further plating with a metal selected from the group consisting of chromium and nickel.

11. A method of adapting metal articles to receive a chromium layer, the steps comprising first inserting said metal article in an electrolytic bath having a pH between 1 and 3 and a temperature between about 70° F. and 165° F. in which salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ounces per gallon and a zinc metal content of 6 to 8 ounces per gallon, and passing an electric current of sufficient density and sustained direction through said electrolyte and said article to make the article continuously cathode for a time duration of not more than 30 seconds to produce a thin layer of zinc-rich alloy thereon, then periodically reversing the current flow through said electrolyte while said metal article remains in the bath for a sufficient time period in which the duration being at least 2 seconds for the anodic cycle of the reversing current is substantially less than for the cathodic cycle producing a nickel-rich alloy deposit upon said first mentioned zinc-rich deposit on said metal article, said anodic and cathodic reversal of current flow being repeated several times during said time period until a desired thickness of the nickel-rich deposit has been plated upon said zinc-rich deposit; and subsequently chromium plating said metal article in a known manner over the last mentioned nickel-rich deposit; said nickel-rich deposit being provided to prevent the process of chromium plating from dissolving at least part of the first zinc-rich deposit.

12. In a method of nickel-chromium plating metal articles the steps comprising first inserting said metal article in an electrolytic bath having a pH between 1 and 3 and a temperature between about 70° F. and 165° F. in which salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte a nickel metal content of 8 to 10 ounces per gallon and a zinc metal

content of 6 to 8 ounces per gallon, and passing an electric current of sufficient density and sustained direction through said electrolyte and said article to make the article continuously cathode for a time duration of between 3 and 30 seconds to produce a thin layer of zinc-rich alloy thereon which generally contains more than 50% zinc and less than 50% nickel, and secondly while using the same bath providing a layer of nickel-rich alloy which generally contains more than 50% nickel and less than 50% zinc over the zinc-rich alloy deposit by periodically reversing the direction of said current, the anodic pulses in the periodic reverse cycle applying less coulombs than the cathodic pulse, and third, chromium or pure nickel plating the such prepared metal article over said first and second deposit, said second deposit effectively preventing the dissolving, at least in part, of said first zinc-rich deposit.

13. A method of adapting metal articles to receive a chromium layer, the steps comprising first inserting said metal article in an electrolytic bath having a pH between 1 and 3 and a temperature between about 70° F. and 165° F. in which salts of nickel and zinc have been dissolved in sufficient amount to give to each gallon of electrolyte nickel metal content of 8 to 10 ounces per gallon and a zinc metal content of 6 to 8 ounces per gallon, and passing an electric current of sufficient density and sustained direction through said electrolyte and said article to make the article continuously cathode for a time duration of not more than 30 seconds to produce a thin layer of zinc-rich alloy thereon, then periodically reversing the current flow through said electrolyte while said metal article remains in the bath for a sufficient time period in which the duration of anodic pulses is at least 2 seconds and is sufficiently shorter than the cathodic pulses so that the amount of coulombs applied to the bath during the cathodic pulse exceeds that during the anodic pulse and a nickel-rich alloy is thereby deposited on the said first mentioned zinc-rich deposit on said metal article, said anodic and cathodic reversal of current flow being repeated several times during said time period until a desired thickness of the nickel-rich deposit has been plated upon said zinc-rich deposit; and subsequently chromium plating said metal article in a known manner over the last mentioned nickel-rich deposit; said nickel-rich deposit being provided to prevent the process of chromium plating from dissolving at least part of the first zinc-rich deposit.

14. In an electroplating process wherein an object placed in an electrolyte is coated with a first zinc-rich layer by passing direct current through said object and said electrolyte and coated secondly with a nickel-rich alloy, the improvement comprising the step of depositing said second coating on the object by periodically reversing said current while the object remains in the same electrolyte, each cathodic pulse not more than 30 seconds in the reverse current period delivering coulombs to the electrolyte and object in excess of the anodic pulse being at least 2 seconds.

15. A method according to the steps of claim 7 including the further step of plating the article directly upon its outermost nickel-zinc alloy deposit with a metal selected from the group consisting of chromium and nickel.

16. In an electroplating process wherein an object placed in an electrolyte is coated with a first zinc-rich layer by passing direct current through said object and said electrolyte and coated secondly with a nickel-rich alloy, the improvement comprising the step of depositing said second coating on the object by periodically reversing said current while the object remains in the same electrolyte, each cathodic pulse being not more than 30 seconds in the reverse current period delivering coulombs to the electrolyte and object in excess of the anodic pulse being no less than 2 seconds, whereby said periodic reverse current provides the object with a cathodic pulse from between about 3 seconds to 30 seconds and an anodic pulse

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for at least 2 seconds and the current density is of a value of 20 to 600 amps./sq. ft. in each direction.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,989,446

June 20, 1961

Milton B. Hammond et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 33, for "reactive" read -- reactivate --;
column 6, line 10, for "its", second occurrence, read -- it --;
column 9, line 11, for "casing" read -- casting --.

Signed and sealed this 24th day of April 1962.

(SEAL)

Attest:

ESTON G. JOHNSON
Attesting Officer

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Commissioner of Patents