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METHOD OF PLATING AND ARTICLE PRODUCED THEREBY

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This invention relates to a method of plating and to an article produced thereby, having more particularly reference to the protection of ferrous metals against corrosion by the electrodeposition on the ferrous metal base of composite metallic layers.

It has heretofore been common practice, in the protection of ferrous metals and their alloys against corrosion, to plate over the ferrous metal base with a layer of metal that is more resistant to corrosion than iron, such as nickel or chromium, or nickel and chromium. It has also been customary to apply a coating of copper first directly to the ferrous metal base and then coat over the copper with nickel, or with nickel and chromium. It is well known, however, that deposits of metal, such as nickel and copper protect the underlying ferrous metal base, by which is meant iron and its alloys, such as steel, from corrosion only insofar as the deposits are continuous or non-porous. It has been shown by many researches, starting in particular with that published by E. M. Baker in the Journal of the Society of Automotive Engineers, February, 1924, "Rust Resistance of Nickel-Plated Steel", that it is commercially impossible to produce an absolutely impervious or non-porous deposit, although the porosity may be decreased progressively by increasing the thickness of the deposit. On the other hand, an increase in thickness of the deposit constitutes an increasing expense, because of the longer time which the article must remain in the plating solution, because of the greater consumption of expensive anodes, and because of the cost for power. Furthermore, thick deposits are more difficult and more expensive to buff than are thinner deposits.

Previous workers in the field have proposed to obtain better resistance to rusting by the use of a layer of electrodeposited zinc or cadmium applied directly to the ferrous metal base, on the theory that since zinc and cadmium are electropositive in the electromotive force series toward iron, the iron or iron alloy base will be protected so long as any zinc or cadmium remains in contact therewith. Although rusting is, in fact, retarded by the use of undercoats of zinc or cadmium, another and very serious difficulty is experienced. If there is a hole or pore in the deposit of nickel, and/or chromium, overlying the zinc or cadmium, rapid corrosion of the zinc or cadmium occurs with the formation of a white corrosion product which spreads over the finished surface and greatly mars its appearance. Furthermore, the corrosion product, having a greater volume than the zinc or cadmium from which it was formed, causes the overlying plate to rise or form a blister of non-adherent metal at the point where pores and corrosion occur. For this reason, we have not found it satisfactory or feasible to use a deposit of zinc or cadmium to improve rust resistance.

It has also been suggested that the underplate of copper might be omitted entirely and the nickel plated directly on the ferrous metal base. For steel plated by research methods, this procedure gives excellent results, as it is attested by recent publications from the U. S. Bureau of Standards. In commercial work, however, the use of a single deposit has one very serious objection. Work, after being plated, is almost universally buffed, as by means of wheels made up of disks of cotton cloth and rotated at high speeds. A compound of grease and abrasive is applied to the surface of the wheel. The part to be buffed is held with considerable pressure against the buffing wheel so coated. Careless and inexperienced operators will not infrequently remove all of the plate from very small areas, leaving the ferrous metal base exposed. When this happens, there is, of course, no protection offered at the point where the nickel has been buffed away, but this is not so serious because the completely buffed through parts will be rejected in the plant by the nickel buffing inspector and will be replated. However, when some articles are buffed through clear to the steel, it is evident that many more may be buffed to a point where the nickel is not completely removed, but where it has been reduced to an extremely thin layer. This condition cannot be ascertained by visual inspection and in commercial work the use of a single deposit of nickel presents this great danger of unknowingly shipping plated parts which will have too poor resistance to rusting and which will, therefore, constitute a serious risk of loss of reputation for quality of products.

The use of an intermediate plating of copper obviates this danger of buffing through the plated coating. For instance, if the composite deposit consists of a layer of nickel over the ferrous metal base, then a layer of copper and then another layer of nickel, if the buffer operator buffs through at any point to a depth where the deposit of copper will be reached, this condition is readily found on visual inspection because of the difference in colors of nickel and copper. If the article is not buffed through to the copper, it therefore follows that it is coated with the full

first deposit of nickel, the full first deposit of copper, and at least a portion of the final deposit of nickel.

It is an object of our invention in particular to overcome the disadvantages inherent in all of the above procedures and to utilize their good points in a process of plating. According to our invention, we have substituted a layer of electrodeposited brass for the layer of copper in a composite coating such as above referred to. The color of brass is sufficiently different from that of nickel so that the inspection feature is provided.

Also, according to our invention, we derive the benefit in increased corrosion resistant properties that result from the use of an underplating that has a potential which is higher in the E. M. F. series than that of iron or is only slightly lower than that of iron, since the presence of zinc in the brass plating changes the E. M. F. from that of copper, which is below iron, to one that may be practically the same as that of iron or above. We may vary over a considerable range the composition of the brass deposit, but if the percentage of copper is very high and the percentage of zinc low, the brass deposit will have an E. M. F. which will lie close to that of copper and will not well serve our purpose, because if there is a pore in the deposit, it will, like copper, tend to promote corrosion of the underlying steel but to a less extent than pure copper. As the percentage of copper in the brass is decreased and the percentage of zinc increased, the potential of the brass will become more like the potential of nickel. By so increasing the percentage of zinc, the potential can be brought down to that of nickel, may be made intermediate between the potential of nickel and that of iron, or, on further increase of zinc, may be brought to the potential of iron or may be made intermediate between that of iron and that of zinc.

While, in general, the advantages of our invention can be obtained to a degree with brass deposits of widely varying compositions, best results are obtained when the composition of brass is selected so as to give an electrolytic potential between that of nickel and that of iron, in the "solution", which may be in contact with the article. By the term, "solution" is meant any film of moisture that may be in contact with the plated article. For instance, in the case of automotive bumpers, a film of moisture will form on the bumper on rainy or moist days and may contain dissolved acid gases from the air or dissolved salts which have been splashed up from the street.

In some cases, it may be desirable to make the composition of the brass such that the potential will be close to iron but between iron and zinc. In such case, the galvanic action will be such that the brass deposit will protect the underlying ferrous metal base from corrosion even although there be slight porosity through all of the plated metals. However, the percentage of zinc in the brass should not be increased to a point where corrosion will cause blistering of the deposit and the formation of undesirable white incrustations on the outside surface of the plate.

It is, therefore, an important object of this invention to provide a commercially workable process of plating iron, steel or other ferrous metal alloy with metals having an outer surface of nickel, and/or chromium, and a superior resistance to rusting or corrosion when the plated article is exposed to atmospheric conditions or to accelerated corrosion tests.

Other and further important objects of this invention will become apparent from the following description and appended claims.

Since our invention is especially well adapted for use in the manufacture of an automotive vehicle bumper and the like, it will be described in connection therewith, although it should be understood that the general principles of our invention are of wider application. In the practice of our process in connection with the nickel plating or chromium plating of a steel bar or plate, such as is employed in the manufacture of a vehicle bumper, a bar is first polished on such surfaces as require a bright or image reflecting surface on the finished product. The bar is then thoroughly cleaned in any suitable manner employing for this purpose means and solutions commonly used in the practice of the plating art. For example, the bumper bar may be first immersed in a hot or boiling alkaline solution, such as a solution containing 2 to 4 ounces per gallon of trisodium phosphate or other mixtures of alkaline salts. Electric current may or may not be used to aid the cleaning and in such case, the bumper bar to be cleaned may be made either the anode or the cathode.

After this cleaning operation, the bumper bar may be rinsed in water and may or may not be scrubbed with fine pumice stone and again rinsed. It is good practice to then dip the bumper bar for perhaps 30 seconds in a 10% solution of muriatic acid and to again rinse in water. The bumper bar is then ready for plating. Up to this point, the operations described are those common to the art.

After completion of the foregoing cleaning operations, it is customary to plate the bumper bar with three successive coatings of metal as follows: A first or flash coating of nickel, which, for example, may be 0.0003 inches thick; a second coating consisting of copper, which may be about the same thickness as the first coating of nickel; a third coating consisting of nickel, which may, for example, be twice the thickness of the flash coating of nickel. Any suitable composition of nickel and copper plating baths, respectively, may be used for the nickel and copper plating. After the final nickel plating, the bumper bar is buffed on buffing wheels using an abrasive compound. If the article is to be finished with a top surface of nickel, the operation is then complete. If, however, the article is to be chromium plated, it is subsequently plated with chromium, using procedures commonly employed in the art for that purpose.

The improvement in the art that constitutes this invention is the substitution of a suitable deposit of brass for the deposit of copper. We have found such a deposit of brass to have many advantages over a copper deposit and in addition to have the same advantage of permitting ready visual inspection of the buffed article that copper has. The main advantage, as previously pointed out, in the use of a deposition of brass, rather than copper, is that the composition of the brass may be so selected that its electromotive force lies above that of nickel and preferably between nickel and iron, so that even if there are pores in the nickel layer, the nickel will be protected against corrosion. Furthermore, by using a deposit of brass rather than copper, the ferrous metal base will be protected to a much greater degree, in the event of pores being present in the coated layers, owing to the fact that the electromotive force of the brass deposit is so

much closer to that of the ferrous metal base than is that of copper.

The composition of the brass may be varied through a comparatively wide range, with the copper between 45 and 65% and the zinc between 55 and 35%. Preferably, we employ a composition of brass containing about 60% copper and 40% zinc. Cadmium may be substituted in part or in whole for the zinc in the brass deposit to obtain the advantages of our invention, but we prefer to use zinc because it is a simpler matter to deposit a zinc-copper brass than it is to deposit a cadmium-copper brass.

Our invention contemplates many variations in the number and sequence of the coatings to be applied to the ferrous metal base. These may be indicated as follows:

1. Nickel on brass on nickel on ferrous metal.
2. Nickel on brass on brass on ferrous metal.
3. Nickel on brass on nickel on brass on ferrous metal.
4. Nickel on brass on nickel on copper on ferrous metal.
5. Nickel on brass on copper on ferrous alloy.

The presence of a copper layer would harm rather than help the development of rust resistance, but its presence would not make the layer of brass ineffecive in fulfilling its own function.

Although, as is obvious from the above description, any suitable composition and operating conditions may be used for any and all of the plating operations, for purposes of illustration, we nevertheless give the following compositions of bath and operating conditions which have been found suitable for the practice of this invention.

For the nickel plating bath, we prepare a solution in which the following ingredients are employed in about the proportions stated for each gallon of solution:

32 ounces of nickel sulfate ($NiSO_4.7H_2O$).
8.0 ounces of nickel chloride ($NiCl_2.6H_2O$).
4.0 ounces of nickel boric acid (H_3BO_3).

The pH of the bath is preferably adjusted to between 2 and 3. The proportions above stated may be varied somewhat with comparable results. The solution is heated (as by means of a steam coil) to a temperature of from 100 to 125° F., the best results having been obtained by employing a temperature of about 115° F. For the anodes, substantially pure nickel (at least 99% pure) is employed. With a bath constituted and heated in the manner described, and employing such pure nickel anodes, the work is plated with a current density of approximately 40 amperes per square foot of metal treated, but this may be varied somewhat.

For the brass plating operation, a bath is used containing the following ingredients, preferably in the proportions stated:

	Ounces per gallon
Copper cyanide (CuCN)	4.8
Zinc cyanide ($ZnCN_2$)	2
Sodium cyanide (NaCN)	8 to 12
Sodium carbonate ($Na_2CO_3.10H_2O$)	3
Sodium thiosulfate ($Na_2S_2O_3$)	0.1 to 0.2
Potassium hydroxide (KOH)	0.05
Ammonia solution (28% NH_3)	½ fluid

The amount of ammonia added is determined by the appearance of the deposit and enough ammonia is added to give a clear, bright deposit. Small amounts of cadmium cyanide or other addition agents may be used, if desired, to increase the brightness of the brass deposit.

The solution of the brass plating bath is heated by means of a steam coil to a temperature from 95 to 110° F., preferably to about 105° F., although this temperature is not believed to be critical. Anodes of brass, preferably containing over 99% of copper plus zinc, and preferably containing zinc and copper in the proportion of 60 parts of copper to 40 parts of zinc, are used.

Since the composition of the deposit of brass will, in the long run, tend to become the same as the composition of the anodes, it is obvious that the relative proportions of the copper and zinc in the anodes can be varied over rather wide limits and still obtain satisfactory results.

If there were no loss of zinc or cadmium cyanides from the solution, and if no zinc or cadmium cyanides were added to the solution, the composition of the deposit would eventually become identical with the composition of the anodes. However, some solution is dragged out of the tanks on the work being plated, and this may be compensated for by adding zinc and/or copper cyanides to the solution. If these are not added in the some proportion as they would exist in the solution if there were no loss of solution, then the composition of the deposit will correspondingly be different from the composition of the anodes. It may not be necessary to add copper and zinc cyanides to make up for drag-out loss, because the anode current efficiency will in general be higher than the cathode current efficiency, in which case only sodium cyanide, sodium thiosulfate and ammonia need be added for the continued operation of the solution.

The current density used may be varied considerably, but preferably a current density of 10 to 30 amperes per square foot of surface to be plated is employed. The composition of the anodes and of the bath are so selected and controlled as to give a deposit of brass ranging in composition from 65% copper and 35% zinc to 50% copper and 50% zinc. A more satisfactory range is from 70% copper and 30% zinc to 50% copper and 50% zinc, with the preferred proportions of 60% copper and 40% zinc.

A brass deposit within the foregoing ranges of proportions of copper and zinc will have an E. M. F. between that of nickel and zinc, and if the 60% copper-40% zinc composition is employed, its E. M. F. will lie between nickel and iron.

Since there is some discrepancy between different tables showing the electromotive force series of the metals, the following is given as the approximate single potential of each respective metal toward a solution of normal metal ion concentration or activity, based on the normal hydrogen electrodes:

	Volts
Zinc	0.76
Cadmium	.40
Iron	.34
Nickel	.23
Copper	.33

These figures are quoted from "Principles and Practice of Electroplating and Electroforming", by Blum and Hogaboom, published by McGraw-Hill Book Company, Second Edition, page 407.

Where the composition of the brass deposit is close to the higher limits for the copper, namely, around 80% copper, the brass deposit has an E. M. F. which lies close to that of copper and will, therefore, not possess the advantages of our invention to the maximum extent. A brass plat-

ing of this composition will, like copper, but to a lesser extent, tend to promote corrosion of the underlying ferrous metal or steel. Best results are obtained using the preferred composition of about 60% copper and 40% zinc, since with that composition, the electrolytic potential of the brass layer lies between that of nickel and that of iron. If the zinc is carried too high, say above 50%, corrosion will cause a blistered deposit and the formation of undesirable white incrustations on the outside of the plate.

As previously stated, the finished article may have an exterior coating of chromium, which may be applied in a chromium plating bath of the usual composition and under the conditions now being commonly practiced.

We are aware that numerous details of the process may be varied through a wide range without departing from the principles of this invention, and we, therefore, do not purpose limiting the patent granted hereon otherwise than necessitated by the prior art.

We claim as our invention:

1. A method of plating ferrous metal articles, which comprises electrodepositing directly on the ferrous metal a layer of copper zinc alloy that is higher than nickel in the E. M. F. series and electrodepositing a layer of nickel over said copper alloy layer.

2. In a method of protecting ferrous metals against corrosion, the step of interposing an electrodeposited layer of a brass that is higher than nickel in the E. M. F. series between an exterior plating layer of nickel and the ferrous metal base.

3. In a method of nickel and chromium plating articles having a ferrous metal base, the steps of first protecting the ferrous metal base by electrodepositing directly thereon a layer of brass that is higher than nickel in the E. M. F. series and then electrodepositing nickel directly on said brass layer.

4. As an article of manufacture, a piece of ferrous metal having a composite coating electrodeposited thereon comprising a layer of a brass that is higher than nickel in the E. M. F. series and a layer of nickel thereover.

5. As an article of manufacture, a piece of ferrous metal having a composite coating electrodeposited thereon comprising a layer of a brass that is higher than nickel in the E. M. F. series directly electrodeposited on said ferrous metal and a layer of nickel thereover.

6. As an article of manufacture, a piece of ferrous metal having a composite metallic coating electrodeposited thereon comprising a layer directly superimposed on said ferrous metal of a copper-zinc alloy that is higher than nickel in the E. M. F. series and a layer of nickel directly on said copper-zinc alloy.

7. As an article of manufacture, a piece of ferrous metal having a composite electrodeposited metallic coating thereon comprising an intermediate layer of a brass having a composition of about 60% copper and 40% zinc and a layer of nickel over said brass layer.

8. As an article of manufacture, a piece of steel having a composite electrodeposited metallic coating comprising a layer of nickel over a layer of brass over a layer of nickel directly deposited on said steel, the brass having a potential between that of nickel and iron in the E. M. F. series.

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