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DECORATIVE METAL PLATING

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Fig. 1.

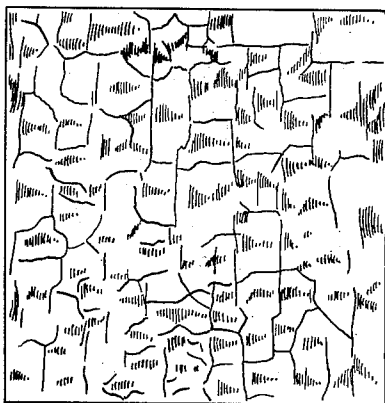


Fig. 2.

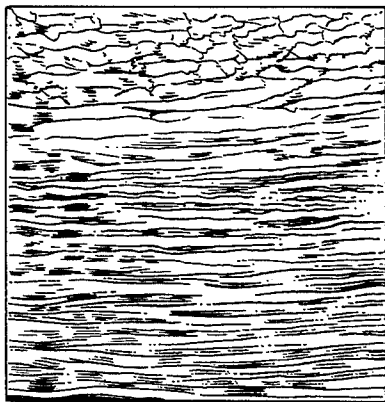
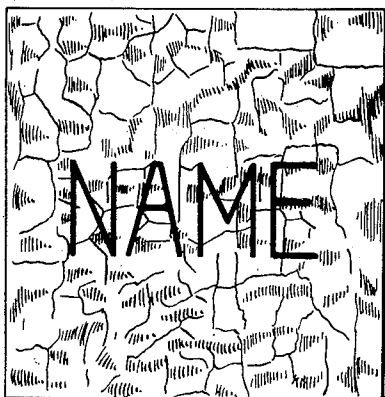


Fig. 3.



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DECORATIVE METAL PLATING

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The present invention relates to a novel metal plating process for producing a decorative electroplated metal finish on metal objects and more particularly to a process wherein a polished and cleaned metal surface is first conditioned anodically to produce an invisible film thereon and then plated in a bright nickel bath whereby a patterned semi-bright nickel plating is produced.

It is an object of the invention to provide a process for the production of a novel decorative finish for metallic electro deposits.

It is a further object of the invention to provide a process whereby the surface of common plated metals is given a pleasing matte-like finish.

It is a further object of the invention to provide a process whereby letters, numbers or other configurations can be easily reproduced on electroplated surfaces.

In accordance with the invention it has unexpectedly been discovered that electroplated decorative finishes can be produced on metal objects, such as, for example, brass, copper and steel, from normal bright nickel plating baths if the articles are preconditioned by an anodic treatment in an alkaline siliceous bath to produce an invisible film thereon before they are electroplated in the bright nickel bath.

The invisible film produced by the anodic preconditioning treatment is one that is invisible to the naked eye and somewhat difficult to detect with the ordinary microscope. However, when nickel is electroplated thereover, patterns of various sized grain structure and different degrees of uniformity are produced in the nickel plate. The intensity of the pattern developed in the nickel coating depends upon the concentration and composition of the nickel plating baths and upon the thickness of the anodic film produced by the preconditioning treatment. The thickness of the anodic film can be controlled by the temperature, time, current density and composition of the conditioning bath.

In carrying out the process according to the invention, the metal object to be given the decorative plating is first given a smooth clean finish, for example, by polishing and cleaning in the ordinary manner to provide a round metallic surface free of grease, dirt and oxide. The cleaning, for example, can be carried out with the usual inhibited alkaline cleaners by soaking therein followed by a cathodic treatment therein or with vapor degreasers such as trichloroethylene. It is also possible to carry out the cleaning of the metal in the same bath as is employed for the anodic preconditioning treatment according to the invention by giving it a cathodic treatment therein before it is made the anode for the anodic treatment. This cleaning method, however, is less preferred than using a separate alkaline cleaning bath, as the dirt removed during the cleaning cycle accumulates in the conditioning bath and shortens its life.

After the metal object has been cleaned, it is then introduced into an alkaline siliceous bath wherein it is made the anode until an anodic film is formed suffi-

cient to provide a patterned effect when such preconditioned object is nickel plated. As the resulting anodic film is invisible, the only way to be certain that the desired film is formed is by routine testing of the preconditioned object by applying a nickel plate thereover. Anodic preconditioning treatments carried out under predetermined conditions, i. e. time, temperature, current density, composition of bath, will give uniform results in the subsequent nickel plating under predetermined conditions.

The essential feature of the preconditioning bath is that it contain a soluble siliceous material such as silicates, metasilicates, colloidal silica gel or hydrated silica and the like and that the pH of such bath is adjusted to a value between 10.25 and 12.2 (electronically).

The quantity of siliceous material employed can be varied considerably, but generally quantities sufficient to provide between about 2 g. and 20 g. of SiO_2 per liter of bath have been found desirable. Generally, the greater the concentration of the siliceous material, the denser will be the pattern produced in the subsequent nickel plate.

In order to provide the proper conductivity and pH of between 10.25 and 12.2, preferably between 10.75 and 12.0, salts, hydroxides or acids can be added. Some salts, however, are less preferred as additions to the conditioning baths as they may tend to have a corrosive action on the metal surface treated and affect the uniformity of the anodic film. For example, sulfates, chlorides, citrates and acetates may give adverse results.

The current densities employed for the anodic preconditioning treatment can, for example, vary between 0.1 ampere per square foot to over 18 amperes per square foot. The best pattern effects were obtained upon subsequent nickel plating when the anodic preconditioning treatment was carried out in the lower range of current densities. Operating voltages of 1 to 3 volts have, for example, been found suitable.

The time of anodic treatment has an effect upon the character of the pattern produced in the subsequent nickel plating. In general the time should be the shorter, the higher the current density employed. Anodic treatments varying from two to sixty seconds have been found suitable for the process according to the invention. Anodic preconditioning treatments at too high a current density and too long a period can result that the subsequent nickel plate is dull and without pattern effects.

The temperatures employed for the anodic preconditioning treatment can vary between room temperature and the boiling point of the preconditioning bath; the best effects, however, have been obtained with a bath operating at a temperature between about 160 to 180° F.

Various siliceous materials have been found suitable for the preparation of the anodic preconditioning baths, such as, for example, sodium or potassium silicates with Na_2O or $\text{K}_2\text{O}/\text{SiO}_2$ ratios ranging from 2:1 to 1:5 as well as colloidal silica gel or hydrated silica, such as, for example, is sold under the tradename Ludox which contains approximately 30% SiO_2 .

Sodium and potassium phosphates, carbonates, borates, hydroxides and phosphoric acid have, for example, been found suitable for adjusting the pH and conductivity of the siliceous preconditioning baths.

After the metal objects have been preconditioned by the anodic treatment in the siliceous bath they should be immediately rinsed with water while still wet and given the usual acid dip and rinse before being introduced into the nickel plating bath. Drying of the preconditioning bath solution upon the preconditioned articles can tend to leave a deleterious dry down pattern which is difficult to risen off either with water or the usual mineral acids.

The nickel plating of the preconditioned metal objects

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can be carried out in any of the usual bright nickel plating baths under usual conditions. The decorative pattern will appear in the nickel plate after a few hundredths of a mil have been plated and becomes pronounced at a thickness between 0.1 and 0.25 mil. With plating thickness over 0.25 mil the pattern tends to become less pronounced.

While the patterned effect according to the invention is only obtained upon the preconditioned metal objects upon subsequent electroplating with nickel, it is possible to produce similar pattern effects in other metallic platings by subjecting the patterned nickel plated object produced according to the invention to further electroplating to produce thin electroplates of other metals such as, for example, gold, copper, chromium and the like thereover from bright metal plating baths.

The patterned electroplatings obtained according to the invention are firmly adherent to the metal base. The patterning effect is not destroyed if a thin coating of clear lacquer is applied thereover should protection of the electroplated surface be desired.

If it is desired to modify the pattern effects obtainable according to the invention, this may be simply done by pressing letters, numbers or words or other configurations into the wet anodic film produced by the preconditioning treatment with a stamp of resilient material, such as a rubber stamp before placing the article into the electroplating bath. Where the film has been touched by the stamp, the subsequent nickel plate will come out bright while the other areas not soon touched will appear with the pattern effect according to the invention. Of course, similar effects could also be obtained with the aid of the usual masking tapes or fluids customarily used in the metal finishing arts.

The accompanying drawings show by way of example several of the pattern effects obtainable according to the invention.

In the drawings:

Fig. 1 shows a metal panel carrying a typical pattern effect obtainable according to the invention,

Fig. 2 shows a metal panel carrying another pattern effect obtainable according to the invention, and

Fig. 3 shows a metal panel in which the patterned effect obtainable according to the invention is interrupted by bright plated areas obtained by pressing the wet anodic film with a rubber stamp prior to the nickel plating treatment. As will be seen from the drawings, the patterned effect obtained according to the invention provided a crackle-like finish which in some respects resembles a brushed finish obtained with rotary brushes. Wide variations in grain size of the pattern can be obtained. For example, the grain size of the pattern can be from about $\frac{1}{32}$ of an inch to about $\frac{1}{2}$ of an inch.

The following examples will serve to illustrate several modifications of the process according to the invention.

Example 1

A brass panel of 30% zinc and 70% copper was buffed to a high degree of luster and then soaked for several minutes in a customarily inhibited alkaline cleaner at 200° F. followed by a power rinse in warm water, and cathodically cleaned in such alkaline cleaner at a current density of 60 amperes per square foot for about 30 seconds at 180° F. The panel was then rinsed with cold water, dipped ten seconds in 10% hydrochloric acid and again rinsed with cold water. The cleaned panel was then transferred to an aqueous solution containing 45 g./l. of a mixture containing 40% of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and 60% of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), where it was given a twenty-five second treatment as the anode at an average current density of 0.6 ampere per square foot. Thereafter, the conditioned panel was rapidly transferred to a cold running water rinse and allowed to remain there for 1 minute. This was followed by a dip into 10% HCl and a cold running water rinse.

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The panel was then immersed carefully into a nickel plating bath of the following composition.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	274.7 g./l.
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	58.6 g./l.
H_3BO_3 -----	40.3 g./l.
Duponal "ME" ¹ -----	0.4 g./l.
Sodium O-benzoic sulfimide ---	1.0 g./l.
H_2SO_4 -----	Sufficient to give a pH between 2.5 and 3.5.

¹ A surface active agent mainly consisting of sodium lauryl sulfonate.

A nickel electrodeposit was formed in ten minutes under a current density of 30 a. s. f. without agitation. After rinsing the nickel solution off, the panel was dipped in a dilute hydrochloric acid solution, rinsed again and then immersed in a chromium plating bath (250 g./l. CrO_3 and 2.5 g./l. of SO_4) for 4 minutes to receive a bright thin chromium plate. A pleasing decorative pattern of decorative value of the type shown in Fig. 1 appeared through the plate.

Example 2

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1 and then transferred to an aqueous anodizing bath containing 18 g./l. of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 27 g./l. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. The panel was anodized therein for 15 seconds at a temperature of 180° F. at an average current density of 0.6 a. s. f. The resulting anodized panel was immediately given a cold running water rinse and then nickel plated in a bright nickel plating bath of the same composition as in Example 1 for ten minutes at 130° F. at an average current density of 30 a. s. f. to produce a nickel plate approximately 0.25 mil thick. The plated panel was rinsed and dried and revealed a uniform decorative pattern.

Example 3

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1 and transferred to an aqueous anodizing bath containing 90 g./l. of a mixture containing 20 hydrated sodium metasilicate and 80% anhydrous di-sodium hydrogen phosphate. The panel was anodized therein for 25 seconds at a temperature of 180° F. and a current density of 0.6 a. s. f. During the anodizing treatment the voltage varied from 1.1 to 1.8 volts to maintain a constant current density. No agitation of the work or solution was employed.

The anodized panel was then immediately rinsed with running cold water for one minute, dipped in 10% HCl for 10 seconds and rinsed again with water.

The rinsed panel was then plated in a nickel plating bath of the following composition.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	G./l. 274.7
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	58.6
H_3BO_3 -----	40.3
Duponal "ME" -----	0.4
Sodium o-benzoic sulfimide -----	2.0

This bath was operated at 130° F. with a cathodic current density of 28-30 a. s. f. until a nickel plating about 0.00025" thick was produced. The thus nickel-plated panel after rinsing was then given a bright chromium plating. The resulting chrome plated finish was rinsed and dried revealing a pattern in the final plate that was semi-lustrous and decorative.

Example 4

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1 and then transferred to an aqueous anodizing bath containing 45 g./l. of a mixture containing 40% of anhydrous sodium carbonate and 60% of Ludox. The panel was anodized therein for 15 seconds under a constant voltage of 1 volt. Thereafter the anodized panel was immediately rinsed with cold water

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and dipped and rinsed again and then given a nickel plate 0.00025" thickness in a nickel plating bath of the same composition as Example 3 at a current density of about 30 a. s. f. The thus nickel plated panel was then given a chromium flash plate of high luster over the nickel plate from a chromic acid sulfuric acid bath of normal concentrations. After rinsing and drying, the finished surface possessed a pleasing decorative pattern.

Example 5

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1, and then transferred to an aqueous anodizing bath of the same composition as that of Example 4. The panel was anodized therein for 20 seconds at 180° F. at a constant current density of 0.6 a. s. f. Thereafter, the anodized panel was immediately rinsed, acid dipped and rinsed again and then given a nickel plate 0.25 mil thick in a nickel plating bath of the same composition as in Example 3. The nickel plated panel was then given a chromium plate as in Example 4. After rinsing and drying the panel has a pleasing decorative pattern similar to that of Example 4, but of slightly smaller grain size.

Example 6

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1 and then transferred to an aqueous anodizing bath containing 45 g./l. of a mixture of 40% of hydrated trisodium phosphate and 60% of sodium silicate "G" (average composition Na_2O 19.4%, SiO_2 62.5%, H_2O 17.5%). The panel was anodized therein for 15 seconds at 180° F. and at a voltage of 1 volt. Thereafter the anodized panel was rinsed, acid dipped and rinsed again, and transferred to a nickel plating bath of the same composition as in Example 3 and allowed to remain therein for 1 minute before applying a current of 30 a. s. f. for 10 minutes. The resulting nickel plated panel was then rinsed, acid dipped and rinsed again and then placed in a chrome plating bath where it was plated for 4 minutes at 104° F. and 100 a. s. f. The pattern developed on the panel was of similar appearance to that of Examples 4 and 5, but had a still smaller grain size.

Example 7

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1 and then transferred to an anodizing bath containing 45 g./l. of a mixture of 20% anhydrous sodium carbonate and 80% Kasil No. 6 (a potassium silicate containing 26.80% SiO_2). The panel was anodized therein for 15 seconds at 1 volt employing a steel cathode. The current density varied between 0.12 and 0.6 a. s. f. decreasing as the time increased. The anodized panel was then immediately rinsed, acid dipped and rinsed again and introduced into a nickel plating bath of the same composition as in Example 1 and plated therein for 10 minutes at 30 a. s. f. A chromium plate followed the nickel plate. The finished nickel and chromium plated panel's surface had a pleasing pattern in which the grains were somewhat elongated as shown in Fig. 2.

Example 8

A buffed brass panel of 30% zinc and 70% copper was cleaned as in Example 1 and then transferred to an anodizing bath containing 9 g. of Kasil No. 6 and 36 g. of anhydrous sodium carbonate per liter. The panel was anodized therein at 180° F. for 15 seconds under a constant voltage of 1 volt. The anodized panel was immediately rinsed and dipped, and rinsed again and given a nickel plate 0.2 mil thick from a nickel plating bath of the same composition as in Example 1. The nickel plated panel was then copper plated in a cyanide bath for 15 seconds and given a clear protective lacquer coating. The resulting lacquered copper plated surface had a pleasing uniform small grained pattern.

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Example 9

A buffed panel of 30% zinc and 70% copper was cleaned as in Example 1 and then transferred to an aqueous anodizing bath containing 45 g./l. of a mixture of 60% sodium silicate "G" and 40% of anhydrous sodium carbonate. The panel was anodized therein for 15 seconds at 180° F. at a voltage of 3 volts without agitation. The anodized panel was then rinsed, acid dipped and rinsed again and transferred to a nickel plating bath of the same composition as in Example 3 wherein it was given a nickel plate 0.2 mil thick. A flash of chromium was plated over the nickel. The finished surface had a very uniform pleasing pattern.

Example 10

A 30:70 brass panel was cleaned and copper plated in a high speed copper cyanide bath and then buffed and cleaned as in Example 1. The cleaned panel was transferred to an aqueous anodizing bath of the same composition as in Example 7 and anodized therein for 15 seconds at 180° F. at 3 volts and a current density of 4-6 a. s. f. The anodized panel was then immediately rinsed, acid dipped, and rinsed again and transferred to a nickel plating bath of the same composition as in Example 1 wherein it was given a nickel plate 0.2 mil thick at 130° F. and a current density of 30 a. s. f. A subsequent plate of chromium was electrodeposited over the nickel plate. The resulting composite coating had a semi-bright luster revealing decorative patterns.

Example 11

A low carbon steel panel (rolled from wire stock) was buffed on one side to provide a high luster and was then cleaned as in Example 1 to provide a sound clean surface. The cleaned panel was transferred to an aqueous anodizing bath containing 45 g./l. of a mixture of 80% sodium silicate "G" and 20% sodium carbonate. The panel was anodized therein for 15 seconds at 180° F. at 1 volt (0.1-0.6 a. s. f.). The resulting anodized panel was then immediately rinsed, acid dipped and rinsed again and given a nickel plate 0.2 mil thick from a nickel plating bath of the same composition as in Example 1. The nickel plated panel was then given a flash of chromium. The surface of the finished panel had a pleasing uniform pattern of somewhat larger grain size than that of the panels produced in the preceding examples.

Example 12

A 30:70 brass panel was buffed and cleaned as in Example 1. The cleaned panel was then immersed in an anodizing solution of the same composition as in Example 11 contained in a steel tank. The panel was attached to the tank by a conductor and permitted to soak without agitation in such solution for 1 minute while being subjected to the galvanic action of steel-brass couple, no outside current being supplied. The resulting anodized panel was rinsed, acid dipped and rinsed again and given a nickel plate 0.2 mil thick in a plating bath of the same composition as in Example 3. The nickel plated panel was then chromium plated for a few minutes. The resulting chromium surface had a pleasing uniformly grained pattern.

Example 13

A 30:70 buffed brass panel was cleaned as in Example 1 and transferred to an aqueous anodizing bath containing 50 g./l. of a mixture containing 71.6% sodium silicate "G," 14.2% of anhydrous sodium carbonate and the remainder hydrated sodium tetraborate. The panel was anodized therein at 180° F. for 60 seconds at a current density ranging from 0.6 to 1.2 a. s. f. The resulting anodized panel was then given a nickel plate 0.2 mil thick from a bath of the same composition as Example 1. The nickel plated panel was then given a flash of chromium. A decorative pattern appeared through the chromium plate.

I claim:

1. A method of producing a decorative finish upon a metal object selected from the group consisting of copper, brass, and steel objects which comprises anodizing such metal object in an alkaline aqueous siliceous solution having a pH of between 10.25 and 12.2 to produce an invisible anodic film thereon and thereafter electroplating such anodized object still carrying such anodic film in a bright nickel plating bath until a patterned nickel plate is produced.

2. The method of claim 1, in which said siliceous solution has a pH of 10.75 to 12.0.

3. The method of claim 1, in which said alkaline aqueous siliceous solution is an aqueous solution of an alkali metal silicate having a pH between 10.25 and 12.2.

4. The method of claim 1, in which said alkaline aqueous siliceous solution is an aqueous solution of a colloidal hydrated silica having a pH between 10.25 and 12.2.

5. The method of claim 1, in which said alkaline siliceous solution contains 2 to 20 grams of SiO_2 per liter.

6. The method of claim 1, comprising in addition electroplating such patterned nickel plated object with another metal from a bright plating bath.

7. A method of producing a decorative finish upon a metal object selected from the group consisting of copper, brass, and steel objects which comprises anodizing such metal object in an alkaline aqueous siliceous solution having a pH of between 10.25 and 12.2 to produce an invisible anodic film thereon, stamping a portion of the

surface bearing the invisible anodic film with a stamp of resilient rubbery material and thereafter electroplating such anodized object still carrying such anodic film in a bright nickel plating bath until a patterned nickel plate is produced.

8. A method of producing a decorative finish upon a metal object selected from the group consisting of copper, brass, and steel objects which comprises polishing and cleaning the surface of such objects to provide a lustrous sound surface, anodizing such metal object in an alkaline aqueous siliceous solution having a pH between 10.25 and 12.2 at a temperature between 160 and 180° F. to produce an invisible anodic film thereon, rinsing the anodized object before the siliceous solution has an opportunity to dry and thereafter electroplating such rinsed anodized object still carrying the anodized film in a bright nickel plating bath until a patterned nickel plate is produced.

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