May 18, 1937. J. E. STARECK 2,081,121

DECORATING METALS

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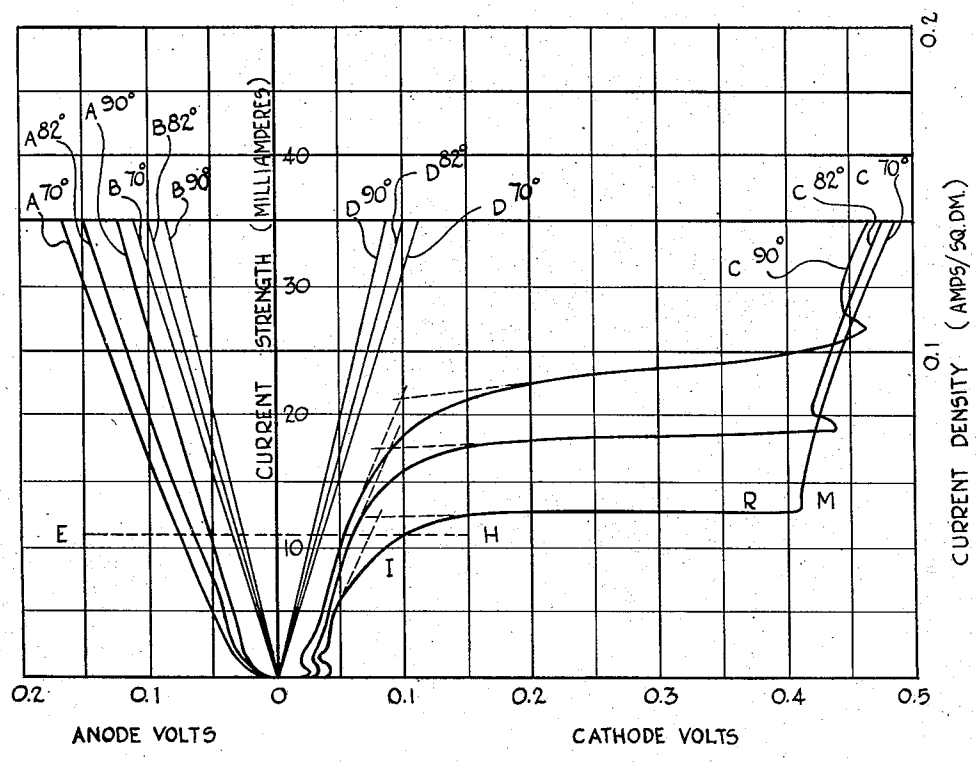


Fig. 1

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DECORATING METALS

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This invention relates to decorating metals; and it comprises a method of producing decorative colored coatings on metal articles wherein such an article is made a cathode in an aqueous bath containing in solution a complex salt of cupric copper and a potential is imposed thereon sufficient to produce cuprous oxide but insufficient to cause formation of metallic copper, thereby producing coatings of cuprous oxide, these coatings being often thin, translucent and transparent, exhibiting characteristic thin film or interference colors; and it further comprises a metal article carrying an electrically deposited colored coating of cuprous oxide, this coating being often thin and transparent and exhibiting characteristic thin film colors; certain other metals sometimes being employed in lieu of copper; and the invention further comprises novel baths for use in such processes; all as more fully hereinafter set forth and as claimed.

In the arts handling metal articles, a cheap, simple and ready method of providing colored decorative, protective coatings is a desideratum. Various processes looking to this end are known in the prior art; many involving electrolytic operation. Mostly, these are anodic processes, as in decorating lead articles with iridescent lead oxid films, in providing aluminum with an oxid coating which can be dyed, etc. Cathodic processes producing protective, thin film coatings having characteristic thin film colors are a desideratum.

The present invention provides a method of decorating any metal with colored coatings of cuprous oxide, the article being made a cathode in a copper solution. While it may be used in making relatively thick coatings having an inherent color, this color being reddish shades, it will be more particularly described with reference to producing thin colored films of ornamental character. The method may be used on all sorts of shaped and formed articles, as for example, ash trays and ornamental electric fixtures; or on large plates and sheets to be stamped or otherwise worked up. The article to be decorated may be of any metal; iron, steel, copper, brass, etc. The metal article or sheet is made a cathode in an alkaline bath comprising dissolved salts, or complexes, containing cupric copper, and a potential is imposed across the bath between cathode and anode at a voltage adjusted to plate or deposit on the cathode a regular coating, of uniform thickness, of cuprous oxide. This coating may be thick enough to display the characteristic inherent color of cuprous oxide but it may also advantageously, for certain purposes, be made thinner; too thin to exhibit inherent or "pigmentary" color. In this embodiment of the invention the thin transparent coating may exhibit brilliant interference ("thin film", "rainbow", or "soap-bubble") colors. The particular hue developed depends on the thickness of the coating, which in turn depends on the time of plating for any given bath and operating conditions. Almost any desired hue may be secured. All spectral colors and hues are readily obtainable. In these thin films the inherent color of the cuprous oxide is subordinated to the brilliant coloring due to optical interference of light on reflection through the thin film. The colors develop in the order yellow, orange, red, purple, blue, blue-green, silver, yellow, gold, peach, rose, violet, green and green-yellow.

In these thin film coatings the colors are due to the physical structure, of the coating and not to pigment, dyes or stains, and the color is as permanent as the coating itself; it does not fade. The coating is derived from the reagents in the bath and the surface of the article is not attacked.

Knowledge that electrodeposited metal oxide films give colors through light "interference" has existed for many years. Such knowledge however appears to have remained largely a matter of academic interest.

For the prior state of knowledge on color effects from thin metal-oxide films, reference may be made to such publications as: Field & Bonney, "The Chemical Coloring of Metals and Allied Processes", Chapman & Hall, Ltd. London (1925), and Hirons, "Metal Coloring and Bronzing", Macmillan & Co., London, (1929). A very recent publication is Field & Weill's "Electroplating", Pitman Publishing Company, New York, (1935).

Notwithstanding such prior knowledge, a practical and commercially available process of electroplating metal oxide coatings does not appear to have been known heretofore, and I am not aware of any use heretofore of an electrolytic process for depositing such oxide coatings for obtaining color effects which was capable of satisfying actual commercial requirements. Such attempts as have been made have always given uncertain, unsatisfactory and unreliable results, and have resulted in ultimate failure as a reliable or satisfactory commercial process.

The present invention of electrodepositing metal oxide coatings upon a metal article used as a cathode provides a process or processes which is practicable, commercial and continuous, and by which adherent coatings giving uni-

form color effects can be reliably obtained not only on flat surfaces but also on recessed and irregular objects; articles of all shapes. The colors are non-fading.

The invention further provides novel baths for use in such process or processes, and articles comprising novel combinations of coatings by which desired modifications of the hues obtainable from the effect of light on the metal oxide coatings are obtained.

According to the present invention, I first prepare a bath containing ions of a metal, the valence of which is capable of being decreased by partial reduction at the cathode to form a metal oxide, and in which bath the metal oxide which is deposited on the cathode from the bath is sparingly soluble, or insoluble. Copper is a metal the ions of which, in suitable baths, can be partially reduced, i. e. from the cupric to the cuprous stage; and cuprous oxide deposited on a cathode from such baths is practically insoluble therein.

The two above-mentioned requirements give a wide choice in the preparation of the bath. The presence of ions of the metal in appropriate concentrations may be initially obtained by putting into or forming in the bath a soluble complex compound which dissociates to provide and maintain an adequate but not excessive supply of said metal ions, and by making the bath alkaline, or decreasing the acidity, the insolubility of the metal oxide deposit is obtained.

Such soluble complex compounds may be obtained by putting into or forming in the bath a compound of the metal together with appropriate quantities of certain other organic or inorganic substances with which the metal forms a soluble complex compound or mixture of compounds. Examples of these complex-forming substances are alkali-metal salts of organic acids such as lactic, citric, glycolic, tartaric and salicylic; non-acid organic compounds such as cane sugar and glycerol, alkali-metal salts of inorganic acids, such as pyrophosphoric, carbonic and tetraboric; alkali-metal hydroxides. I prefer in most cases to use organic rather than inorganic substances to obtain the aforesaid complex compounds or mixture of compounds.

In making up the baths, acids of the above salts, such as lactic, citric, salicylic, etc., acids, may be used, the alkali salts being formed by reaction in the bath with enough alkali hydroxide to give to the bath the desired alkalinity. Other derivatives of the acids or forms of the salts may be used. In these baths the compound of the metal reacts to form a complex compound with the above named inorganic or organic substances, said complex compound containing the metal as part of a complex anion. By deduction based on my knowledge of electrochemistry, I conclude that the complex anion further dissociates to give the metal cation and a simpler anion.

Specific examples of the make-up constituents of baths suitable for use in my process, are as follows:

I—Lactate

$CuSO_4.5H_2O$	100 g/1
Lactic acid (85%)	150 cc/1
NaOH	112 g/1

II—Citrate

$CuSO_4.5H_2O$	100 g/1
Citric acid	355 g/1
NaOH	246 g/1

III—Glycollate

$CuSO_4.5H_2O$	100 g/1
Glycollic acid	128 g/1
NaOH	112 g/1

IV—Tartrate

$CuSO_4.5H_2O$	100 g/1
Rochelle salt	125 g/1
NaOH	35 g/1

V—Salicylate

$CuSO_4.5H_2O$	24 g/1
Salicylic acid	56 g/1
NaOH	42 g/1

VI—Sugar

$CuSO_4.5H_2O$	50 g/1
Cane sugar	100 g/1
NaOH	50 g/1

VII—Glycerol

$CuSO_4.5H_2O$	100 g/1
Glycerol	125 cc/1
NaOH	50 g/1

The sodium hydroxide in the foregoing examples is present in sufficient amount to convert the organic acids, lactic, citric, glycollic, and salicylic, to their respective sodium salts; to react with the copper sulphate; and to leave an excess of free alkali.

VIII—Pyrophosphate

$CuSO_4.5H_2O$	100 g/1
$Na_4P_2O_7 \cdot 10H_2O$	275 g/1

IX—Caustic

$CuSO_4.5H_2O$	15 g/1
NaOH	400 g/1

X—Tetraborate

$CuSO_4.5H_2O$	15 g/1
Borax	150 g/1

These specific examples are merely illustrative. These proportions and concentrations can be widely varied in preparing suitable baths from which to electrodeposit the insoluble metal oxide.

To electrodeposit a metal-oxide coating, the article to be coated after appropriate preliminary treatment is suspended as a cathode in a bath of the character described, and an electric current is passed thereto through the bath from a suitable anode, preferably of the same metal as the metal of the oxide to be deposited on the cathode. A potential is applied across the anode and cathode, adjusted so as to cause cathodic reduction to be limited to that forming a metal oxide. The cell voltage that is employed is primarily determined by the range of cathode single electrode voltages within which the current remains substantially constant.

The cell voltage is employed to overcome the following resistance factors; the external resistance of the circuit; the internal resistance of the bath solution; the resistance between the anode and the solution inter-face, and the resistance between the cathode and the solution inter-face. When the cell voltage overcomes these resistances and causes a current to pass through the bath from the anode to the cathode, the related or corresponding factors or parts of the indicated or cell voltage (the voltage reading of a voltmeter connected at the cell across the anode and cathode bus-bars) are: the external resistance voltage (which is usually so small as to be negligible with conductors of adequate size

and with good connections between the conductors and the anode and cathode); the internal bath resistance voltage; the anode single electrode voltage; and the cathode single electrode voltage. Each of these factors of the cell voltage, and consequently of the resistance, will differ for different conditions. Temperature, size of conductors and character of connections at joints will vary the resistance of the external part of the circuit. The conductivity of the electrolyte and distance between anode and cathode will change the bath internal resistance voltage. The conductivity of the electrolyte will be affected by bath composition and temperature. Polarization and the nature of the anode will affect the anode single electrode voltage. The nature of the cathode, the deposit on the cathode, and polarization will affect the cathode single electrode voltage.

The actual cell voltage to be employed is equal to the external resistance voltage plus the measured internal resistance voltage plus the measured anode single electrode voltage plus the measured cathode single electrode voltage. The external resistance voltage is usually so small, as already stated, that it may be ignored as negligible or estimated approximately without affecting the accuracy of determination of the total or cell voltage.

The internal resistance voltage, the anode single electrode voltage and the cathode single electrode voltage are measured simultaneously or concurrently by the following procedure. The plating bath of chosen ingredients is made up and preferably aged or stabilized by passing a current through it, or by allowing it to stand, or by other practices or means. A representative sample of this solution that is to be used for the electrodeposition, is poured into a Haring cell and a chosen temperature maintained. This cell and its electrical connections and the method of employing it are illustrated and described in the paper by Stareck and Taft, entitled "The Use of a Modified Haring Cell in Detecting Electrode Reactions", published in Transactions of the Electrochemical Society (1935), Vol. LXVII, pp. 357–374. The anode and cathode that are used in this Haring cell are taken of the same materials as those to be employed in the industrial bath. An insoluble anode will require a considerably higher anode single electrode voltage to overcome the resistance between the anode and the solution inter-face than a soluble anode and I prefer generally for the measurement in the Haring cell and for the industrial bath, an anode of the metal, the oxide of which is to be deposited. The back of the anode and, particularly, the back of the cathode in the Haring cell (but not in the industrial bath) are insulated by use of a stop-off lacquer or other suitable means.

Referring to page 361 of the article by Stareck and Taft, the apparatus assembly discloses a modified Haring cell containing an anode and cathode of equal areas with two equidistant screens between them in the solution, a battery, a rheostat which must be very sensitive for the present measurements, an ammeter which should be a milliammeter, a voltmeter which should be a high resistance centivoltmeter and a potentiometer, which latter is not necessarily required for the present measurements.

The electrical connections to the electrodes are made as shown and the resistance of the rheostat is decreased until the milliammeter just begins to indicate a flow of current. This reading of milliamperes is noted and the corresponding voltage is measured on the centivoltmeter. By means of the switches, as shown, the centivoltmeter measures the internal resistance voltage of the solution for the five centimeter spacing between the two screens (the middle compartment voltage), or the anode single electrode voltage plus the internal resistance voltage (the anode compartment voltage), or the cathode single electrode voltage plus the internal resistance voltage (the cathode compartment voltage). Subtraction of the already measured internal resistance voltage from the anode and cathode compartment voltages gives the anode and cathode single electrode voltages respectively.

The resistance of the rheostat is diminished by small amounts and after each diminution of resistance, measurements are made of simultaneous or corresponding values of milliamperes of current and of each of the said anode, middle, and cathode compartment voltages for the five centimeter spacing of the electrodes. This is continued until the deposition of metal or of organic matter upon the cathode has begun. Thus is obtained a tabulation of data from which the internal resistance voltage of the bath, the anode single electrode voltage, and the cathode single electrode voltage can be computed and ascertained, corresponding to definite currents of electricity expressed in milliamperes for the chosen temperature, or calculated to current density. These tabulated results are represented best when plotted on cross section paper, where the current in milliamperes (or as current density) is the axis of ordinates and the voltage for each of the three sources is the axis of abscissae.

In the accompanying illustration is shown a typical graph illustrating the relations described.

In the showing the graph is that obtained by the procedure outlined above, using in the Haring cell, a lactate bath having the make-up constituents of Bath I of the specific examples of baths given in the foregoing part of this specification, at a temperature of 70° F., is shown in Figure 1. Simultaneous values of the three aforesaid voltages (anode single electrode, cathode single electrode and internal resistance voltages) are those which correspond to the same height on the milliampere axis. For example, at the height of the dotted line EH, the current is 11.0 milliamperes, the anode compartment voltage is 0.075 volt the cathode compartment voltage is 0.100 volt, and the middle compartment voltage is 0.035 volt. From these figures the anode single electrode voltage is found to be 0.040 volt, or the distance on the graph between the intersection of EH on OA 70° and OB 70°. The cathode single electrode voltage in a similar manner is found to be 0.065 volt or the distance on the graph between the intersection of EH on OD 70° and OC 70°. The internal resistance or middle compartment voltage is 0.035 volt represented on the cathode side of the graph by OD 70° and on the anode side by OB 70°. The cell voltage at the indicated value of current for a distance of ten centimeters between anode and cathode is the sum of the anode single electrode voltage (0.040 volt), the cathode single electrode voltage (0.065 volt), and the internal resistance voltage (0.070 volt), or $0.040+0.065+0.070=0.175$ volt. This number (0.175) is the cell voltage for the conditions given above, and the method of ob-

taining it can be followed for obtaining the voltage of the industrial cell.

For the actual spacing of the anode to the cathode to be employed in the industrial cell, if it be greater or less than 10 centimeters, the internal resistance voltage can be computed from the internal resistance voltage found in the Haring cell; such voltage being directly proportional to the distance between anode and cathode, other conditions remaining the same.

Curves for the anode single electrode voltage, cathode single electrode voltage, and internal resistance voltage, obtained by the same procedure in the modified Haring cell as already described, the bath being also the same, but temperature being raised and thereby the conductivity increased, are also given on the graph, Fig. 1. Curves O—$A^{82°}$, O—$A^{90°}$ are the curves for the anode single electrode voltage at 82° F. and 90° F. respectively. Curves O—$C^{82°}$, O—$C^{90°}$ are the curves for the cathode single electrode voltage at 82° F. and 90° F. respectively. The internal resistance voltage is measured between O—$B^{82°}$ and O—$D^{82°}$ for the bath at 82° F. and between O—$B^{90°}$ and O—$D^{90°}$ at 90° F. The cathode current density, in amperes per square decimeter is given at the right of the chart.

A study of the three cathode single electrode voltage curves O—$C^{70°}$, O—$C^{82°}$, O—$C^{90°}$ shows that they have as common characteristics, a portion of a horizontal character between two essentially upward or rising portions, thus exhibiting a characteristic "plateau". A study of many other cathode single electrode voltage curves, for various baths and for various conditions shows that they likewise have the same common characteristics. The place on each of the curves where the horizontal or substantially horizontal portion abruptly bends upwardly is the place where the character of the electrodeposition changes and metal or organic matter begins to be deposited. Below the plateau or horizontal or substantially horizontal portion of the curves, (that is, in the initial upward portion) the cathode is incompletely covered, or unevenly covered or of non-uniform color, especially when the cathode has an irregular, or recessed surface to be covered, such as is the rule in articles of commerce.

The greater the length or range of the horizontal or substantially horizontal portion of the cathode single electrode voltage curve, and the more said portion approximates true or absolute horizontality, the better adapted are the baths and operating conditions which give such type of curves, to the production of uniform metal oxide coatings over the entire surface to be covered in the range of the so-called "interference" colors, particularly of recessed or irregular articles (cathodes). Where colors beyond the so-called "interference" stage are to be produced advantage can be taken of the greater rate of deposition obtainable when operating under conditions which give high current-densities in the cathode single electrode voltage range, even though the horizontality of the range may be of a less degree.

Referring again to the curves on the graph, Fig. 1, the point where the metal or organic matter deposits and where, consequently spotted deposits begin and where the curve bends sharply upward is indicated by the letter M. As a working rule, the beginning of the plateau or the substantially horizontal portion of the cathode single electrode voltage curves may be fixed or approximated at the point of intersection of a prolongation of the flatter part of the curve lying intermediate the essentially upward portions, as indicated by the line IM, and an initial substantially upward portion of the curve as indicated by the line OI. However, the precise determination of the point I is not of first importance from an operating standpoint since it is desirable to electrodeposit beyond I and toward M within the range IM.

Within the range of cathode single electrode voltage the corresponding range of cell voltage is found by summation as already explained, and the actual cell voltage that is employed industrially must be set, regulated and maintained within this range (other conditions remaining constant).

As the substantially horizontal portion of the cathode single electrode voltage curve (IM) approaches absolute horizontality, a remarkable phenomenon becomes more and more pronounced; i. e., while the electro-deposition continues, a relatively large increase in the cathode single electrode voltage (and, therefore, in the cell voltage) produces a relatively small increase in the current used. Indeed, in the upper part of the substantially horizontal portion of the curve, in the vicinity of the point R, the current used for a considerable variation of the cathode single electrode voltage (and, therefore, of the cell voltage) on both sides of said point R, remains practically constant. Said phenomenon has the practical advantage that in industrial color plating the cell voltage need not be rigorously kept constant since there exists a permissible variation (while still within the critical range) without apparent effect upon the deposit.

Associated with this novel phenomenon of practically equal flow of current for different voltages, is another phenomenon of great practical value; the electrodeposition of the metal oxide on the cathode is uniform and equal all over the cathode, even upon the recessed and remote parts. The current density as evidenced by the results is uniform all over the cathode surface, or, expressed differently, there is practically perfect throwing power. This is unique in electrolytic deposition so far as I am aware. In electroplating processes, it is well known that the thickness of the electrodeposit varies at different parts of the article, being thicker on high-spots and on edges, and thinner (or even absent) on central areas, on recessed parts and on remote parts of the surface of the cathode. This ordinary inequality of deposition has been explained by Lukens in an article in Transactions of The Electrochemical Society, p. 29, Vol. LXVII (1935), entitled "The Mechanism of Conductance". The deposits which may be produced in accordance with the present invention do not have this fault since, within the aforesaid cathode single electrode voltage range, especially in its optimum part the current flowing to all parts of the article (cathode) is substantially the same, notwithstanding potential differences at different parts of the article (cathode) within the aforesaid range of cathode single electrode voltage, and, as shown by the results, an oxide coating of uniform thickness giving a uniform color effect is obtained.

The appositeness of this phenomenon to the desired result, i. e. coatings giving the effects of uniform color, especially on irregular and recessed articles of commerce, will be clearly appreciated from the following considerations: The color being in greater or less degree obtained by the effect (so-called "interference") of light passing through the metal oxide-coating and being reflected back to the eye, the coating must be of very nearly the same thickness (within a frac-

tion of a wave-length of light) over the entire surface of the article, in order to obtain the same "interference" color.

The two concurrent phenomena of practically equal flow of current for different voltages, and uniform distribution of current on all parts of the cathode may be conveniently called "isorhea". The process of color plating herein described is carried out under isorheic conditions. The isorheic range is on the plateau of the single electrode voltage curve IM and its optimum location is beyond I and toward M.

The hereinbefore referred to range of cathode single electrode voltage will differ for different plating solutions and for different solution temperatures. In plating solutions having different concentrations or different proportions of the same ingredients, the range may also differ, but the definite method of determining each appropriate range has been given above.

For example, for baths having the specific make-up constituents hereinbefore given, the aforesaid ascertained ranges of cathode single electrode voltage, as determined by the modified Haring cell method heretofore described, are as follows:

Bath	Temperature °F.	Range of cathode single electrode voltage	Amperes /dm²
Lactate	70	0.04–0.36	0.052
Citrate	71	0.05–0.45	0.036
Cane sugar	64	0.08–0.63	0.024
Glycollate	69	0.11–0.49	0.128
Salicylate	71	0.07–0.34	0.024
Glycerol	69	0.06–0.34	0.008
Tartrate	72	0.10–0.39	0.024
Caustic	64	0.05–0.27	0.012
Pyrophosphate	70	0.08–0.20	0.016
Tetraborate	61	0.5 –0.27	0.004

Note: On the graph Fig. 1, the cathode single electrode voltage range is obtained by subtracting the internal resistance voltage of the cathode compartment from the numerals on the "Cathode volts" side of the graph.

In order that the process of electrodeposition of metal oxides at the cathode shall be isorheic to the highest degree, I have found not only that the optimum vicinity in the substantially horizontal portion of the curve, such as the vicinity of the point R, Figure 1, should be chosen, as I have already explained, but also that the range as indicated by IM, Figure 1, should be wide and that it should have an extensive portion that is virtually horizontal. These last two conditions are favored by low temperature and also by moderate conductivity of the bath. The measurements with the modified Haring cell and the plotting of the results as described in reference to Figure 1 show the width of the range, the extent of its horizontality, and the position of its optimum part.

In practicing the process, it is generally necessary to regulate the cell voltage during the deposition. This may be done automatically or by manually adjusting a resistance regulator. It is advisable to adjust the cell voltage so that the cathode single electrode voltage will be at a point in the higher part of its range as already pointed out.

Temperature has an effect on the conductivity of the solution, and makes the deposition proceed faster as the temperature is increased, and slower as it is decreased. It also affects the cathode single electrode voltage-range, by shifting it in the direction of higher voltages with increasing temperature. Excessively high temperatures should be avoided in baths containing organic ingredients, as above certain temperatures the complexes appear to be destroyed. Room temperatures are generally satisfactory. In baths of inorganic ingredients the temperatures may be considerably higher than for organic. In practical operation the temperature should be closely regulated so that it remains practically constant and uniform throughout the bath. Since temperature is one of the factors which determines the isorheic range, it is desirable that the temperature remain nearly constant after determination of the appropriate voltage for operation.

Small changes in the composition do not in themselves have much effect on the herein referred to cathode single electrode voltage range. Excessive quantities of organic salt or compound in relation to the metal compound, however, will decrease the solution conductivity and the cathode single electrode voltage range with the result that the bath loses part of its covering ability. The optimum proportion of the lactate to the copper is normally about five molecular weights of lactate to one molecular weight of copper. Sodium hydroxide, on the other hand, does not appreciably affect the cathode single electrode voltage range, but does markedly increase the conductivity and rate of deposition of the bath; the anode efficiency is also increased. The sulfate ion concentration does not appear to have a marked effect on the plating characteristics of the bath. The carbonate ion, resulting either from carbon dioxide absorbed from the air or from that added as sodium carbonate, is a stabilizer of the bath. Certain oxidation products of the organic constituents, as well as small amounts of other organic or inorganic buffer agents, tend to act as stabilizers and to increase the cathode single electrode voltage range.

The composition of the solution is regulated for continuous operation by adjustment of the essential constituents therein. Where soluble anodes of a metal which corresponds to the metal which is deposited in the form of its oxide can be used, the metal constituent can be furnished by the dissolution of the anode during the working of the process, such additional quantities as may be required being supplied to the bath by adding thereto a suitable compound of the metal.

I have found, however, that under some conditions soluble anodes will become passive, and show an abrupt or abnormal increase in the anode single electrode voltage. This condition of the anode will generally be indicated on the ammeter by a considerable fall of current compared with normal, and as a rule may be eliminated by renovating the anodes and by increasing the alkalinity of the bath. In general, passivity of the cathode and abnormal resistance at the cathode solution interface may be regulated or eliminated by proper preliminary treatment of the cathode as by cleaning in alkaline and acid solutions, the last cleaning solution being advantageously an alkaline solution, such as a sodium carbonate solution at room temperature, followed by water rinsing, and a prompt transfer to the plating solution. Having the cathode at the temperature of the bath before immersion is desirable.

As the electrodeposition progresses at a given voltage, after an initial rise in current which sometimes takes place, a gradual fall of the current (amperes) will be observed on the ammeter. This is due to the increase of resistance at the

solution interface of the cathode, partly as a result of the change of the cathode surface from metal to metal-oxide at the initial stage of the deposition, and the increase of the thickness of the metal-oxide deposit during deposition. If a graph is prepared on which amperes are plotted against time in minutes while cell voltage, temperature, and bath composition are kept constant the curve obtained will usually have a decided initial slope, followed by a very gradual downward trend.

It is advantageous to employ and observe an ammeter during operation. The strength of the current for the particular plating solution, temperature, and previously ascertained voltage used in an indicator of the proper working of the process.

Good adherent deposits are obtained directly on a wide choice of metals, among which may be mentioned the noble metals, iron and steel, copper and copper alloys. By appropriate preliminary treatments adherent deposits may be obtained directly on a number of other metals and alloys. Metals and alloys on which adherent deposits cannot be obtained directly can be first plated with other metals and then with the said metal oxide coating.

To obviate shade or tone modifications of the hue obtained by the interference effect of light traversing the oxide coatings, especially the very thin coatings, due to color-absorptive differences of the surfaces on which the oxide coatings are deposited, it is advantageous to provide the article or articles with a coating of a uniform constitution before electrodepositing the transparent (or nearly transparent) oxide coating, as previously described. Such a preparatory coating is particularly advantageous in production work where uniformity of color on pieces of different base metal is sought, and may be conveniently obtained in the bath used for color plating by (1) raising the initial voltage to electrodeposit metal, or preferably by (2) electrodepositing an oxide coating through about one spectral cycle (ordinarily requiring about one to two minutes), removing the article from the bath, and reducing the oxide to metal, as by immersing it in a sodium carbonate solution and subjecting it to the action of current while connected in an electrical circuit as cathode. The article, after the oxide coating thereon is reduced to metal, is then replaced in the plating bath, and the coating electrodeposited on the reduced oxide metal coating in the same manner as previously described.

A number of variations of specific hues may also be obtained by varying the type of finish of the surface to be coated or by changing the color of the surface prior to coating with the said metal oxide. The former effect may be obtained by well known methods of buffing, scratch brushing, sandblasting, etc. The latter effect, however, may be obtained by taking advantage of the partial transparency of the metal oxide coating, the color effect of which, as a result of this exceptional property, is affected by the shade and intensity of color of the base metal or immediate undercoating. Differences of shade and intensity of color of the base metal surface may be obtained by coating the article with various metals, alloys, or other conducting substances, the shade of which will produce the predetermined desired final effect. Dark surfaces, such as grey, bronze, or black, give more intense hues of interference colors and deeper shades of pigmentary colors, while light colored surfaces, such as white, yellow, or reddish-yellow, generally give pastel shades of interference colors and lighter shades of pigmentary colors.

A gloss finish on the surface underlying the metal oxide coating such as is obtained by buffing adds brightness to the effect of color obtained from the metal oxide coatings on such surfaces. A dull finish on the surface underlying the metal oxide coating, such as is obtained by scratch-brushing or sand-blasting, gives a soft shade of a pearly character.

An important factor in the electrodeposition of metal oxides at the cathode is the plating time. Since the interference color obtained is a function of the thickness of deposit which, in turn, is proportional to the elapsed plating time, the control of time is of primary importance. For a bath of a selected composition, operating under isorheic conditions, at a given constant temperature, the color of the deposit can be predetermined for a given plating time.

In a representative specific embodiment of the invention the procedure was as follows: A lactate bath having the solution make-up hereinbefore given was put into a hard-rubber lined tank, a stone-ware tank, an iron tank, or other suitable tank which does not react with the bath, and was stabilized. The desired temperature was maintained closely constant at 70° F. by suitable means, as by coils in the tank connected to water and steam pipes the valves of which are controlled by a thermostatic regulator. It is favorable to agitate the solution. This was done. Clean copper anodes having a surface area approximately equal to the surface area of the article or articles to be coated were hung from bus-bars in the bath. The articles to be coated were thoroughly cleaned prior to immersion in the bath, by successive immersion in alkali and acid cleaning solutions. The final cleaning was done in a solution of sodium carbonate at room temperature, followed by water rinsing, this being favorable. The articles at approximately the temperature of the bath, (mounted on a rack), were immersed in the bath and connected to a live cathode-bus-bar. The resistance regulator was adjusted so as to maintain the cell voltage within an indicated range of 0.16 to 0.48 volt (at about .4 volt) on the scale of a centivoltmeter connected across the tank to the anode and cathode bus-bars with an anode to cathode spacing of 10 cm. The design of the electrical circuit was such that the voltage required to overcome the resistance of the external part of the circuit included within the voltmeter connections, the resistance of the bath solution, and the anode resistance at the solution interface of the anode amounted to about 0.12 volt. An additional 0.08 volt must be added to this figure for each succeeding 10 cm. of distance between anode and cathode when operating under the specific conditions given. The cathode single electrode voltage range, for the bath solution and temperature used (70° F.), within which the amperes passing to the cathode at different voltages are substantially the same, being 0.04 to 0.36 volt, corresponded to the range 0.16 to 0.48 volt on the cell centivoltmeter scale.

The interference color or hue for a given set of conditions which the electrodeposited coating given by the action thereon of light being a function of the time of electrodeposition, the time which the article remains in the bath was carefully watched, and, after the elapse of a length of time which previous trials of the bath have

shown to be required for depositing a thickness of coating for producing the particular hue desired, the cathode articles were disconnected and removed from the solution. Thereafter, the articles were washed and dried. A clear lacquer may be applied, if desired. With a clear lacquer the color and appearance of the article produced by the coating process are not substantially altered and the cuprous oxide is protected against atmospheric changes. Exposed to air cuprous oxide, and particularly in thin films, has a tendency to change. For electrodepositing oxide coatings having a pigmentary color, the length of time of deposition does not have to be so carefully watched.

The typical form of the voltage-current curve (plotted as hereinbefore described) for the lactate bath given in the above description of a specific mode of procedure is shown by the curves in Figure 1.

Proceeding according to the specific mode of procedure hereinbefore described, and with a properly stabilized bath, using on the article to be coated an undercoat of reduced copper oxide, I have found the color-sequence as the electrodeposition progressed, to be as follows:

First cycle

Seconds	20	40	60	80	110
Color	Orange	Red	Purple	Blue	Light green

Second cycle

Seconds	140	170	200	230	260
Color	Yellow	Gold	Pink Red	Purple Blue	Dark green

As the cycles progress, the hues become more and more modified by the pigment color of the copper oxide, and when the progression has gone through about nine cycles, no further interference variation is perceptible to the eye and the oxide coating begins to approach a rich deep red opalescent pigment color, which does not vary periodically through further cycles. For intervals of time intermediate to those listed above, oxide coatings are obtained which give numerous intermediate hues, the hues being in the nature of blends of adjacent colors in the preceding list.

In the preceding example, a lactate bath was used. Some electrolytes require a higher voltage. For a cane sugar bath (Bath VI) a maximum voltage between anode and cathode of 0.75 results (at a spacing of 10 cm.) at room temperature; this voltage being the sum of the value 0.63 volt (see the table of cathode single electrode voltages for different baths, ante) and the 0.12 volt required to overcome the various resistances. With higher voltages at the bus bars and ordinary resistances in the circuit and bath, metallic copper or hydrogen, either or both, is formed.

In a specific embodiment of the present invention, decorating brass ash trays with brilliant thin film colors, the trays were pickled and cleaned and connected to a source of direct current as cathodes in a decorating bath. This particular bath was made up by dissolving copper sulfate in commercial liquid lactic acid and making it alkaline with caustic soda. The amount of commercial crystallized copper sulfate used was 0.8 pound per gallon. The amount of lactic acid (85 per cent) was 0.5 to 0.6 quart per gallon and the amount of caustic soda (NaOH) per gallon was 0.8 to 0.9 pound. A copper anode was used and a potential of 0.25 volt was applied across anode and cathode at a current density of 0.05 ampere per square decimeter of cathode surface. Colors immediately appeared, the hue gradually changing with time. In this particular operation a rather thick green coating was wanted and current was allowed to pass long enough to give the described alternation of colors three times, the hues following the cycle stated. At the end of 8 minutes the ash tray took on a fine pea-green color and the tray was removed, washed and dried. The color was unchanged on washing and drying and was uniform over the entire surface. In this particular operation, the dried tray was finally spray coated with a thin film of a clear nitrocellulose lacquer to shield the cuprous oxide from the air.

For depositing thin oxide coatings producing color effects primarily by "interference", it is advantageous to work with a bath having a moderate rate of deposition. Such a bath may be obtained by noting the rapidity with which the colors change from one hue to another during operation. If the rate of deposition is too high for conveniently stopping when the desired hue is reached, then the rate of deposition of the solution may be decreased, for example by lowering the alkalinity thereof, or lowering the operating temperature, or diluting the solution, or by using a combination of these factors.

While it is possible to use a bath having a moderate rate of deposition (such as the lactate bath heretofore described) to deposit pigment-colors, it is advantageous, from the standpoint of shortening the plating time, to use a bath having a high rate of deposition. Such a bath may be obtained for example by increasing the alkalinity, raising the operating temperature, increasing the concentration of the solution ingredients, or by a combination of these factors.

An example of a lactate bath having a high rate of deposition, is one made up as follows and operated at a temperature of 70° F. Its rate of deposition may be further increased by increasing the temperature.

$CuSO_4.5H_2O$	100 g/l
Lactic acid (85%)	150 cc/1
NaOH	176 g/1

The conducting characteristic of the bath is of consequence in obtaining desirable coatings. From the standpoint of carrying out the process in the most expeditious manner, it is desirable to have the cathode current density as high as is consistent with the ability of the operator to stop the plating at a time when the deposit reaches a thickness corresponding to a desired hue in the "interference" range. With a number of the baths herein disclosed, the time of plating through a cycle in the "interference" range may be a matter of a few minutes. From a number of baths given herein, cathode current densities of about .02 ampere per square decimeter or more can be obtained, and from these a progression through the initial cycles in the "interference" range can be obtained in about two to four minutes. In the specific example of the process given herein, the time for progression through the first cycle in the "interference" range is about 2 minutes, and the cathode current density is about .05 ampere per square decimeter. For the expeditious deposits of coatings of thickness in the pigmentary range, the cathode current

density and rate of deposition can be much higher.

If desired, polychrome effects may be obtained by removing the article when a desired hue is obtained and blocking out portions with a suitable "stopping varnish" and then resuming operation. Paraffin or beeswax may be employed as the stopping off material.

The removed article after washing and drying usually shows no substantial change in hue. The decorative coating is brilliant and regular. The coating can be made of uniform hue all over the surface of the article, unless some parts have been intentionally blocked out, and the hue changes but little under different angles of view. The throwing power of the bath is excellent and there is little or no difference in hue in different parts. However, by manipulation rainbow or iridescent effects may be obtained. The finish withstands atmospheric corrosion and relatively high temperatures, and it may be cleaned by ordinary methods. It may be lacquered, varnished or waxed in the usual ways. It is often convenient to spray on a thin coating of transparent lacquer.

The coating is durable, handsome and satisfactory. The process is economical. The coating is thin and the current consumption is small. Ordinary or room temperatures are used. The method is well adapted for either batch or automatic operation.

In obtaining the hue desired, the particular cycle in which the deposition is stopped is important. The greens and reds obtained in the second cycle are particularly brilliant. It is often desirable in obtaining these colors that the operation be stopped at this point. The reds and greens obtained in similar portions of the succeeding cycles are different in shade.

As stated, by subjecting different portions of the article to the electrolytic treatment for different lengths of time, polychrome effects can be secured. Continuously graduated or blended color effects (rainbow effects) can be secured by gradually withdrawing the article from the bath during plating, so that the time of plating varies for different portions of the article. This can be done with the aid of a hydraulic lift or equivalent device arranged to raise from the bath the articles, or rack on which the articles are mounted, with a continuous or intermittent movement, during the coating operation.

Cuprous oxide films produced according to the invention exhibit unilateral conductivity and photoelectric properties and are useful in rectifier elements and photoelectric cells. For such purposes films thick enough to show body color of cuprous oxide are ordinarily most useful. Although the films produced are substantially anhydrous the electrical properties are often improved by a slight baking. The films are well adapted for such uses, as they are regular and very uniform in thickness. Highly compact types of rectifiers can be made up of a stack of copper foils plated with cuprous oxide in accordance with the present invention. The principle of the invention may be employed to advantage in voltage control rectifier units, in which the cuprous oxide film is employed to control its own deposition. The metal oxide is an excellent undercoat for varnishing, painting and enameling.

This case is a continuation-in-part of my prior application, Serial No. 721,398, filed April 19, 1934.

What I claim is:

1. In the production of decorative non-metallic coatings on metal articles, the process which comprises making such an article a cathode in an alkaline solution of a copper salt and passing current between such cathode and an anode until the desired color results, the cathode current density being of the order of one or more hundredths of an ampere per square decimeter, and the potential difference between an active and non-passive copper anode and a cathode, at a spacing of 10 centimeters and at room temperature, between about 0.16 and 0.75 volt, the voltage being greater with greater anode to cathode spacing and with increase of temperature and the current density being greater with increase of temperature.

2. In the decoration of metallic articles, the method which comprises making such an article a cathode in an alkaline bath containing a soluble organic compound of copper, applying a voltage between the anode and cathode terminals of the order of 0.16 to 0.48 volt with an anode to cathode spacing of the order of 10 centimeters and continuing the passage of current until a uniform bright hue is obtained on the article.

3. In the decoration of metallic articles, the method according to claim 2 wherein the areas of anode and cathode are substantially equal.

4. A method of electrodepositing cuprous oxide coatings useful for decoration and other purposes, comprising passing an electric current between an anode and an article to be coated, as a cathode, through an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insoluble, at a cathode single electrode voltage within an ascertained range throughout which the flow of current for a given area of cathode becomes substantially constant for different voltages in said range, and depositing a cuprous oxide coating of uniform hue.

5. A method of electrodepositing cuprous oxide coatings useful for decoration and other purposes, comprising passing an electric current between an anode and an article to be coated, as a cathode, through an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insoluble, at a cell voltage which produces the condition of isorhea at the cathode with deposition of cuprous oxide and depositing a cuprous oxide coating of uniform hue.

6. A method of electrodepositing cuprous oxide coatings useful for decoration and other purposes, comprising passing an electric current between an anode and an article to be coated, as a cathode, through an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insoluble, at a cathode single electrode voltage ascertained or predetermined as lying on the substantially horizontal portion of a curve thereof, obtained by plotting corresponding voltages and currents, as abscissae and ordinates respectively and depositing a cuprous oxide coating of uniform hue.

7. A method of electrodepositing cuprous oxide coatings useful for decorative and other purposes, comprising passing an electric current between an anode and an article to be coated, as a cathode, through an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insolu-

ble, at a cathode single electrode voltage ascertained or predetermined as lying on the substantially horizontal portion of a curve thereof, obtained by plotting corresponding voltages and currents, as abscissae and ordinates respectively, and in the higher-voltage part of said substantially horizontal portion and depositing a cuprous oxide coating of uniform hue.

8. A method of electrodepositing copper oxide coatings useful for decorative and other purposes, comprising passing an electric current between an anode and an article to be coated, as a cathode, through an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insoluble, at a cathode single electrode voltage within a range throughout which the flow of current for a given area of cathode is substantially constant for different voltages, and regulating said voltage to maintain it within said cathode single electrode range or at a desired part of said range and depositing a cuprous oxide coating of uniform hue.

9. A method according to claim 4, further comprising maintaining the solution during the operation at a substantially constant temperature.

10. A method according to claim 4, further comprising maintaining the composition of the bath substantially constant.

11. A method according to claim 4, further comprising bringing the cathode-articles to substantially the temperature of the solution at or before passing current thereto for depositing said cuprous oxide coating.

12. A method of electrodepositing cuprous oxide coatings useful for decorative and other purposes, comprising passing an electric current between an anode and an article to be coated, as a cathode, through an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insoluble, at a cathode single electrode voltage within an ascertained range throughout which the flow of current for a given area of cathode is substantially constant for different voltages, regulating said voltage to maintain it within said cathode single electrode range or at a desired part of said range, and maintaining the temperature of said solution substantially constant and depositing a cuprous oxide coating of uniform hue.

13. A method according to claim 4, wherein the electrolytic solution at 70° F. at said voltage, gives a cathode current density of .02 ampere per square decimeter, or more.

14. A method according to claim 4, wherein said electrolytic solution contains copper in the form of an ionized or ionizable complex-molecule.

15. A method according to claim 4, wherein said electrolytic solution contains copper in the form of an ionized or ionizable copper-citrate molecule.

16. A method according to claim 4, wherein said electrolytic solution contains copper in the form of an ionized or ionizable copper-glycollate molecule.

17. In the production of decorative polychrome cuprous oxide coatings on metallic surfaced articles, the process which comprises making such an article a cathode in an electrolytic solution capable of yielding copper ions and in which the cuprous oxide deposited therefrom is substantially insoluble at a cathode single electrode voltage within an ascertained range throughout which the flow of current becomes substantially constant for different voltages in said range, and partially withdrawing the article from the bath during the operation, to cause different portions of the article to be subjected to the electrolytic action for different lengths of time.

18. A method according to claim 4, wherein said electrolytic solution contains copper in the form of an ionized or ionizable copper-lactate molecule.

19. A method according to claim 4, wherein the anodes are copper, and are active and non-passive.

20. In a method of electrodepositing cuprous oxide coatings useful for decoration and other purposes, determining or ascertaining (1) the internal resistance voltage, (2) the anode single electrode voltage, and (3) the cathode single electrode voltage range for cuprous oxide deposition, for the bath composition and temperature to be used, and passing current between the anode and cathode at a voltage which is the sum of the ascertained internal resistance voltage, the ascertained anode single electrode voltage, and a cathode single electrode voltage within the substantially isorheic part of the ascertained cathode single electrode voltage range for cuprous oxide deposition, and depositing cuprous oxide in a bath of the composition and at the temperature for which the voltage was ascertained as aforesaid.

21. A shaped or formed article of manufacture having a metallic surface prepared to give it a characteristic appearance, said surface carrying a layer of electrolytically deposited cuprous oxide, said oxide being deposited under the conditions set forth in claim 4 and being thin enough to be translucent and permit the effect of the underlying metal surface to be visible therethrough and the production of a compounded appearance, and a transparent coating film shielding the cuprous oxide against the action of air.

22. A decoratively colored article of manufacture comprising a base, a layer or coating of electrolytically deposited cuprous oxide, a layer of a metal beneath the cuprous oxide layer and above the surface of the base, said cuprous oxide layer and the layer immediately beneath it coacting to produce a desired hue-quality unobtainable from a layer of cuprous oxide directly on the surface of the base, and a transparent coating-film shielding the cuprous oxide against the action of air.

23. An article according to claim 22, wherein the surface of the base is of one color and the surface of the layer over the base and beneath the cuprous oxide layer is of another color, one being dark and the other light.

24. A decoratively colored article of manufacture, comprising a base, a layer of cathodically deposited cuprous oxide, said base having a matte finish, said cuprous oxide layer and the surface immediately beneath it coacting to produce a pearl quality of hue, and a transparent coating-film shielding the cuprous oxide against the action of air.

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