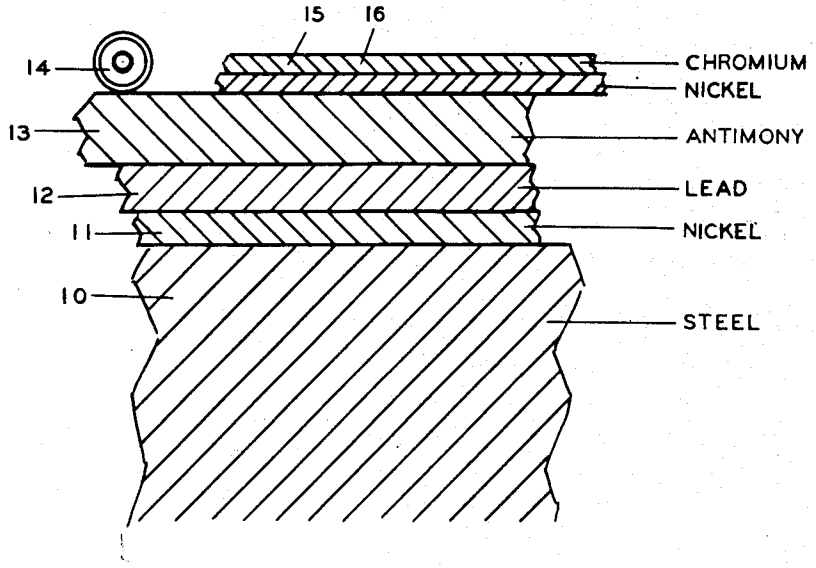
Nov. 10, 1953 A. H. DU ROSE ET AL 2,658,266

LAMINATED COATING

Filed Aug. 7, 1952



A. H. DUROSE *INVENTOR.*
J. D. LITTLE
BY
William H Brown

Patented Nov. 10, 1953 2,658,266

UNITED STATES PATENT OFFICE

2,658,266

LAMINATED COATING

Arthur H. Du Rose, Euclid, and John D. Little, Bay Village, Ohio, assignors to The Harshaw Chemical Company, Cleveland, Ohio, a corporation of Ohio

Application August 7, 1952, Serial No. 303,104

6 Claims. (Cl. 29—196.6)

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This invention relates to the production of protective and decorative electrodeposited coatings on base metals which would otherwise corrode or exhibit an unattractive appearance. More specifically, the invention relates to multiple-layer protective and decorative coatings adapted to be applied over steel or other base metal by electrodeposition successively from different plating solutions.

The most common protective and decorative coating heretofore used consists of chromium over nickel applied directly on the base metal to a thickness of about a thousandth of an inch or more, or chromium over nickel applied over a coating of copper. These nickel or nickel-over-copper coatings, when applied to a sufficient thickness and buffed, or when the nickel is applied from a solution containing a brightening addition agent, are quite satisfactory for chromium plating. Nickel, however, is expensive and sometimes difficult to obtain. A need therefore exists for a protective and decorative coating having substantially the protective and decorative effect of nickel but which can be produced at a lower cost and from materials which are less expensive and less difficult to obtain.

Various metals have been considered as replacements for nickel, but difficulties have always been encountered. Among the other metals which have been considered, lead is attractive from the standpoint of cost, but is soft and difficult to buff to a bright finish. Antimony also has been seriously considered, since it is harder than lead, affords good protection against corrosion, and is readily buffed. Like nickel, antimony will tarnish if exposed to outside atmospheres and should therefore be protected. It was an obvious procedure to try protecting an antimony deposit by applying a chromium deposit thereover in accordance with the practice in nickel plating, chromium over nickel over steel being a very common type of coating for automobile trim, plumbing fixtures and many other uses. When, however, it was attempted to electrodeposit chromium on a bright (image reflecting) antimony surface it was found that the resulting chromium deposit was not bright.

Prior to the present invention it was discovered that a bright chromium deposit can be applied over a bright antimony surface by interposing between such antimony surface and the chromium a very thin nickel (or equivalent) deposit. Such nickel deposit, it was discovered, could be exceedingly thin, for example, as thin as 0.002 mil (0.000002 of an inch) and must not be very thick. The nickel deposit could be produced in any of various nickel plating solutions such as the Watts bath. Deposits from the Watts nickel solution on a bright antimony surface were found

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to be bright up to a thickness of 0.03 mil. A heavier deposit of nickel, for example such as normally used for automobile decoration, that is, a deposit in the order of one mil in thickness, was not satisfactory for use between the antimony and chromium. Such deposits exhibit poor adherence, even tend to flake off after the chromium deposit is applied.

It has now been discovered in accordance with the present invention that in the case of the above described plating sequence, that is, chromium over a nickel flash over bright antimony over lead or equivalent over steel, a markedly increased resistance to corrosion is obtained if a flash of nickel is applied to the steel and then followed in turn by lead, bright antimony, a nickel flash and chromium. In other words, a bright and highly corrosion resistant coating is obtained by the use of chromium over a nickel flash over bright antimony over lead over a nickel flash on a steel object to be coated. The lead layer may be omitted if the steel is roughened before application of the nickel flash thereon, but the conditions are more critical and results not reliable.

Ordinarily, the bright antimony surface will have been produced by buffing and then thoroughly cleaning an electrodeposit of antimony, the production of which as an adherent coating on steel is known to the art. For example, Bloom (U. S. Patent No. 2,389,131) describes a method of etching the steel and plating on the resulting surface from an antimony trifluoride bath containing a monovalent fluoride and operating at a pH somewhat below 6.0. By the use of suitable addition agents bright (as plated) deposits of antimony can be obtained. The particular plating solutions by means of which the antimony and other deposits are produced do not, per se, form any part of the present invention. Lead, nickel, chromium, antimony, etc. plating are well established arts and no novel plating solutions are essential to the realization of the present invention.

If the primary object is to form a protective and decorative coating on steel, brass, copper or the like, a very excellent procedure is to apply first a flash of nickel or cobalt, then an electrodeposit of lead, tin, silver or alloys thereof which are easily applied over nickel. Adherent antimony deposits are easily applied to buffed or unbuffed lead, tin or silver, or lead, tin or silver alloy electrodeposits in the form of adherent coatings which can be readily buffed to a high lustre. On the buffed antimony, there may be then applied a very thin coating of nickel or cobalt, or less desirably, zinc, copper, white brass or iron. Over the resulting thin deposit there is applied an electrodeposited coating of chro-

mium, suitably of a thickness of the order of 0.01 mil, which will not be dull, as in the case where it is plated directly on polished antimony, and which will not cause a separation of the thin nickel (or the like) deposit from the antimony, as when relatively heavy deposits of nickel are applied on the antimony and followed by chromium.

So far as I am aware, no one has heretofore suggested the plating sequence herein disclosed having the protective value as above indicated. It is perhaps surprising that a chromium deposit would not turn out bright when applied over highly polished antimony, but that has been found to be what happens; and while it would be expected from nickel plating practice that a bright chromium deposit could be applied on a bright nickel surface, it is surprising that an ultrathin layer of nickel but not a heavy layer thereof would result in overcoming the tendency of chromium to plate dull over polished antimony and at the same time retain satisfactory adhesion in the case of thin layers (but not in the case of thick layers) of nickel or cobalt. It is surprising also that an ultrathin layer of nickel or cobalt applied between the steel and the lead deposit or between roughened steel and the antimony deposit would result in extraordinarily improved corrosion resistance, far beyond what could be expected merely from the thickness of such a nickel flash itself.

In the accompanying drawing, the figure is a schematic representation of a multiple-layer deposit according to the invention, wherein the thicknesses are greatly exaggerated, and wherein the buffing step is indicated by a schematic representation of a buffing-wheel applied on the surface which is buffed.

In the drawing, the numeral **10** indicates the base metal to be coated, which as indicated, may be steel, copper brass, or the like. Electrodeposited on the base metal body **10** is a thin layer **11** of nickel or cobalt which may be of a thickness from 0.06 to 0.1 mil. This layer can be heavier, say up to .5 mil, but it is not necessary to use any more nickel or cobalt than indicated. Electrodeposited on the nickel flash coating is the optional layer **12** of lead, which, it is to be understood, may be omitted if suitable care is taken to apply a strongly adherent coating of antimony on the nickel or cobalt flash coating. Also the lead coating **11** may be replaced by tin or silver. The antimony deposit **13** must be strongly adherent as it will be if applied over lead, tin or silver, and should be of a thickness great enough that, upon being buffed, there is no danger of cutting through and exposing the underlying layer. The antimony deposit normally may be of a thickness of about 0.3 mil, and preferably is of a thickness of the order of 0.5 to 2.0 mils. A thickness from 0.75 to 1.5 mils should prove adequate for any reasonable amount of buffing. The antimony deposit is buffed to a bright finish, as indicated by the schematic indication of a buffing wheel **14** in contact with its surface, and thereafter there is applied the ultrathin coating **15** of nickel or cobalt (less desirably copper, zinc, iron or white brass). This coating may be of a thickness from .001 to .05 mil, but preferably is from 0.002 to 0.03 mil in thickness. The chromium deposit **16** is applied over the ultrathin coating **15** of nickel, cobalt or the like and may be of a thickness from 0.001 to 0.02 mil.

While the nickel flash under chromium and over bright antimony on lead on steel is not per se a part of the present invention, the fact that its deleterious effect on corrosion resistance can be overcome by a flash of nickel between the steel and the lead is believed not to have known heretofore. The effect is marked and goes beyond any mere additive effect of the thin nickel coating. It was found for example that .01 mil of chromium on 1.0 mil of antimony (buffed) on .2 mil of lead on steel exhibited a salt spray resistance of 100 hours but was not bright. Applying .003 mil of nickel or cobalt over the buffed antimony and under the chromium gave good brightness and adherence but the salt spray resistance was reduced to 40 hours. Applying .06 mil of nickel between the steel and the lead in addition to the nickel flash between the antimony and the chromium, the salt spray resistance went up to 100 hours. This amount (0.06 mil) of nickel on steel as the only coating would resist salt spray only from 2 to 4 hours.

Cobalt in similar thicknesses was found to be the equivalent of nickel for the flash on the steel except for its higher cost.

Plating solutions suitable for the electrodeposition of antimony, lead, nickel, cobalt, zinc, iron, copper and white brass are as follows:

(1)	SbF_3	250 g./l.
	NH_4F	200 g./l.
	pH	4.5
	Temperature	130° F.
(2)	$SbF_3(NH_4)_2SO_4$	400 g./l.
	pH	1.5
	Temperature	130° F.
(3)	$Pb(BF_4)_2$	33.5 oz./gal.
	HBF_4	10.7 oz./gal.
	H_3BO_3	3.0 oz./gal.
	Glue	.03–.06 oz./gal.
	Temperature	Room
(4)	$NiSO_4.6H_2O$	250 g./l.
	$NiCl_2.6H_2O$	35 g./l.
	H_3BO_3	35 g./l.
	pH	4.0
	Temperature	120° F.
(5)	$NiSo_4.6H_2O$	100 g./l.
	$NiCl_2.6H_2O$	15 g./l.
	H_3BO_3	30 g./l.
	pH	3.0
	Temperature	Room

The antimony surface must be well cleaned before nickel is applied.

(6)	$CoCl_2.6H_2O$	100 g./l.
	$NH_4F.HF$	20 g./l.
	pH	3.0
	Temperature	130° F.
(7)	$Zn(CN)_2$	60 g./l.
	NaCN	42 g./l.
	NaOH	79 g./l.
	Na_2S	0.75 g./l.
	Temperature	80° F.
(8)	$FeSO_4.7H_2O$	200 g./l.
	$NaBF_4$	40 g./l.
	pH	3.0
	Temperature	130° F.
(9)	CuCN	22 g./l.
	Free Cyanide	7.5 g./l.
	Water	Remainder
	pH	12
	Temperature	140° F.
(10)	$Zn(CN)_2$	60 g./l.
	$Cu(CN)_2$	14 g./l.
	NaOH	60 g./l.
	NaCN	52 g./l.
	Na_2SO_3	0.48 g./l.
	Temperature	90° F.

Having thus described the invention, what is claimed is:

1. A process comprising electrodepositing on a metallic surface of the class consisting of steel, brass and copper a layer of a metal of the class consisting of nickel and cobalt and mixtures thereof of a thickness from .02 to .2 mil, forming on said layer an adherent coating of a metal of the class consisting of lead, tin and silver, said coating being applied by electrodeposition, forming on said last mentioned coating a bright coating of electrodeposited antimony, forming on said bright antimony coating a film of a metal of the class consisting of nickel, cobalt, zinc, iron, white brass and copper of a thickness from .001 to .05 mil, said film being applied by electrodeposition, and electrodepositing a layer of chromium over said film.

2. A process comprising electrodepositing on steel a layer of nickel of a thickness from .02 to .2 mil, forming on said layer of nickel an adherent coating of lead, said coating being applied by electrodeposition, forming on said last mentioned coating a bright coating of electrodeposited antimony, forming on said bright antimony coating a film of nickel of a thickness from .001 to .05 mil, said film being applied by electrodeposition and electrodepositing a layer of chromium over said film.

3. A process comprising electrodepositing on a metallic surface of the class consisting of steel, brass and copper a layer of a metal of the class consisting of nickel and cobalt and mixtures thereof of a thickness from .02 to .2 mil, forming on said layer an adherent coating of a metal of the class consisting of lead, tin and silver, said coating being applied by electrodeposition, forming on said last mentioned coating a bright coating of antimony, said coating being applied by electrodeposition and then buffed to brightness, forming on said bright antimony coating a film of a metal of the class consisting of nickel, cobalt, zinc, iron, white brass and copper of a thickness from .001 to .05 mil, said film being applied by electrodeposition and electrodepositing a layer of chromium over said film.

4. A process comprising electrodepositing on steel a layer of nickel of a thickness from .02 to .2 mil, forming on said layer of nickel an adherent coating of lead, said coating being applied by

electrodeposition, forming on said last mentioned coating a bright coating of antimony, said coating being applied by electrodeposition and then buffed to brightness, forming on said bright antimony coating a film of nickel of a thickness from .001 to .05 mil, said film being applied by electrodeposition and electrodepositing a layer of chromium over said film.

5. A laminated, metallic, bright, protective coating on a metal base of the class consisting of steel, copper and brass consisting of a firmly adherent layer of a metal of the class consisting of nickel, cobalt and mixtures thereof of a thickness from 0.2 to .2 of a mil, a layer of the class consisting of lead, tin and silver of a thickness from 0.1 to .7 mil overlying and adherent to said last mentioned layer, a firmly adherent layer of antimony on said last mentioned layer and having a bright surface, a film of a metal of the class consisting of nickel, cobalt, zinc, iron, white brass and copper of a thickness from .001 to .05 mil firmly adherent to said bright surface and a layer of fully bright, unbuffed chromium of a thickness from .003 to .03 mil firmly adherent to said film.

6. A laminated, metallic, bright, protective coating on steel consisting of a firmly adherent layer of nickel of a thickness from .02 to .2 mil, a layer of lead of a thickness from 0.5 to .7 mil overlying and adherent to said last mentioned layer, a firmly adherent layer of antimony of a thickness from 0.0003 to 0.002 of an inch on said last mentioned layer and having a bright surface, a film of nickel of a thickness from .001 to .05 mil firmly adherent to said bright surface and a layer of fully bright, unbuffed chromium of a thickness from .003 to .03 mil firmly adherent to said film.

ARTHUR H. DU ROSE.
JOHN D. LITTLE.

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