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"IMPROVEMENTS IN OR RELATING TO ELECTROPLATING OF
COPPER ON STAINLESS STEEL".

Council of Six Scientific and Industrial Research, Rafi Marg, New Delhi-1, India, an Indian Registered Body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention:-

This is an invention by Balkurje Anantha Shenoi, Scientist, Ramasubbu Venkatachalam, Senior Scientific Assistant, Srinivasan Chakrapani and Ramachandra Subramanian, Scientist, all of the Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu, India, and all are Indian Nationals.

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This invention relates to improvements in or relating to the technique of electroplating of adherent copper on a stainless steel substrate.

Hitherto it has been proposed to plate copper on stainless steel from an acid copper sulphate bath after activating the surface by one or more than one type of the following treatments to ensure proper adhesion of the electrodeposited copper.

A thin protective oxide film on stainless steel surfaces, which fortifies the surface against attack by most of the chemicals used in plating baths and which has a tendency to reform quickly after stripping, has to be removed completely before electroplating and the surface should be kept active till it is covered with the electrodeposits. This is achieved by :

1 Cathodic treatments

(a) Sulphuric acid (Sp.gr. 1.83):	5-50% by volume
Temperature:	25-32°C
Time:	1-5 minutes
Cathodic current density:	5-25 asf

- 1(b) Hydrochloric acid(Sp.gr.1.12): -5-50% by volume
 Temperature: 25-32°C
 Time: 1-5 minutes
 Cathodic current density: 20 asf
- (c) Immersion in 10-30% hydrochloric acid by volume at room temperature for one minute followed by cathodic treatment in (a).

Immersion treatments

- (a) Sulphuric acid 20-50% by volume at 65°-80°C for one minute after gasing starts.
- (b) Hydrochloric acid: 0.1% by volume
 Sulphuric acid: 1% by volume
 Temperature: 25-32°C
 Time 26 seconds

3 Simultaneous activation and plating treatment

- (a) Nickel chloride: 240 g/l
 Hydrochloric acid: 70 ml/litre
 Temperature: 25-32°C
 Electrode: Nickel
 First anodic current density: 20 asf for 2 minutes followed by cathodic current density: 20 asf for 6 minutes
- (b) Nickel chloride: 240 g/l
 Hydrochloric acid: 100 ml/litre
 Temperature: 25-32°C
 Electrode: Nickel
 First cathodic current density: 50-200 asf for 2-4 minutes followed by anodic current density: 15-50 asf for 15-30 minutes
- (c) Nickel chloride: 30-300 g/l
 Hydrochloric acid: 12-120 ml/litre
 Temperature: 25-32°C
 Nickel anode
 Cathodic current density: 5-100 asf
 Time: 1/2-5 minutes
- (d) Copper sulphate: 0.375 g/l
 Hydrochloric acid(conc.): to one litre
 Temperature: 25-32°C
 Anode: Nickel
 Cathodic current density: 40-60 asf
 Time: 1-5 minutes
- (e) A combination of more than one type of the above treatments to secure best adhesion.

The articles is then quickly rinsed and carried over to acid copper sulphate bath for plating copper and in practice to secure best adhesion of the electrodeposit a strike plating in any one of the baths under simultaneous activation and plating treatment is necessary to secure good adhesion, or copper can be plated in a cuprous chloride hydrochloric acid bath upto a maximum of 10 thou. It is claimed that the bath is protected against atmospheric oxidation by an oil layer.

This is open to the following objections:

Baths (a), (b) and (c) use nickel as the 'strike metal' in which case the transfer from the strike bath to the copper plating bath through the intermediate rinsing operation is critical. The rinsing should be thorough and efficient to prevent the carryover of the chloride ion in the sulphate copper plating bath. At the same time, the time of dwelling in rinse water should be as short as possible to prevent passivation of nickel surface and to ensure perfect adhesion of subsequent thick deposits of copper or other electro deposited metals. In the case of cuprous chloride baths (Indian Patent No.113473) when they are used strike copper plating prior to further build of copper or other electrodeposits, the carry over of oil layer, especially from complex shaped articles, will introduce contamination in the plating baths which will lead to rough deposits and if purification is resorted to, this will load the purification system; thereby increase the cost. However, since the copper deposit from the strike bath will not be passivated, the rinsing can be through the time of rinsing is not critical. Even though this electrolyte could be used as a plating bath to build up copper deposits up to 200 to 250 micron thick the conventional methods with special advantages as described in the patent No.113473, further thickness build up for example 500 micron as required for plating copper on stainless steel heating utensils, the bath suffered from the disadvantages that the deposit tended to be rough and powdery the cause of which could not be established by us so far. So, it was imperative that subsequent build up of copper beyond 200

microns thick has to be done in the conventional copper electrolytes, which has no special advantages. Further, the carry over of oil into the plating bath is a serious disadvantage.

With the bath (d) namely copper sulphate 0.375 g/l conc. hydrochloric acid one litre, the concentration of copper sulphate is so low and critical that the control of strike plating is very difficult and the strike deposit will tend to become powdery and non-adherent.

The object of this invention is to obviate these disadvantages by eliminating the nickel strike entirely by use of cupric chloride-hydrochloric acid bath as a strike bath. By having the copper in the divalent stage, this bath does not suffer from the disadvantage of atmospheric oxidation and hence the use of oil layer needed for protecting the cuprous chloride from oxidation is dispensed with.

The bath described in this present invention is so formulated that the concentration of cupric ion in the electrolyte is not so low as to make control very critical.

During the course of our investigations, we found that the presence of cuprous ion in this cupric electrolyte or cupric ions in cuprous chloride electrode showed a tendency to form powdery non-adherent deposits and it was absolutely necessary to have the copper either in the cupric or cuprous state alone. Thus, the use of copper anodes in the cupric chloride electrolyte is not possible as it will dissolve only in the cuprous state both chemically and electrochemically.

The use of nickel anodes in this electrolyte ushers in nickel ions in solution which virtually becomes of nickel chloride solution on prolonged use and the deposits from such a continued electrolyte was not satisfactory from the adhesion viewpoint. This difficulty was overcome by use of carbon or graphite anodes either in the form of sheets or rods.

To these ends, the present invention broadly consists in giving a flash strike plating in cupric chloride-hydrochloric acid electrolyte using graphite or carbon sheets or rods as insoluble anodes, followed by build up of copper to required thickness in an acid electrolyte like copper sulphate sulphuric acid or copper fluoborate fluoboric acid baths, after thorough rinsing of the work to free from chloride ions, which ensures the absence of carry over of chloride ions into the plating baths.

The initial deposit of copper from the said cupric chloride electrolyte may also form the starting surface for further plating of other metals such as nickel, cadmium, chromium, zinc tin from suitable electrolytes.

The concentration of the constituents in the electrolyte used for strike plating lies in the following ranges:

Copper as cupric copper:	8 g/l - 16 g/l
Hydrochloric acid(10 N):	400-700 ml/l
Glue, gelatin or gum arabic	up to 1 g/l

and is operated in the range

Temperature:	30°-60°C
Anodes:	Insoluble graphite or carbon sheets or rods
Cathode current density:	0.5 Asdm - 5 ASdm
Anode current density:	0.5 Asdm - 5 Asdm
Anode to cathode area ratio:	3:1 to 1:1
Time of strike plating:	2 minutes to 10 minutes

Activation of the surface

The electrolyte itself will activate the surface to be plated if the work is kept without current for 5 to 10 minutes in the electrolyte. However, the activating treatments recommended below may also be used to ensure very good adhesion time and again:

Cathodic treatments

(a) sulphuric acid(Sp.gr. 1.84):	5-50% by volume
temperature:	25-32°C
time	1-5 minutes
cathode current density	0.5-10 asdm
anodes	lead or graphite
(b) hydrochloric acid(Sp.gr. 0.18)	5-25% by volume
temperature:	25-4=°C
time:	1-5 minutes
cathode current density:	0.2-5 asdm
anodes:	graphite or carbon

anodic treatments

(c) Hydrochloric acid(sp.gr. 1.18):	5-20% by volume
temperature	25-35°C
time	1-5 minutes
anodic current density ..	6-8 asdm
cathode	stainless steel or graphite

After activating the surface to be plated by adopting any one of the above procedures, the work is carried over to the strike plating bath without rinsing and cathodically treated in the said electrolyte for 2 to 10 minutes, the operating conditions being as described earlier. Then the work is rinsed thoroughly in running water or by counter current rinsing and carried over to the plating electrolyte to build up the required electrodeposit to the predetermined thickness. For example, the work is plated with copper to a thickness of 500 microns, in an acid copper sulphate bath. The adhesion of this thick copper is so good that it breaks only at the copper and not at the copper-stainless steel interface, as shown by the shear adhesion tests.

Thus, to electrodeposit copper adherently on a stainless steel surface to thicknesses in the range 25 to 625 microns or to electroplate other metals like nickel, cadmium, tin, zinc or chromium adherently on stainless steel articles, the process is carried out

1. Degreasing with an organic solvent like benzene, kerosene, trichlorethylene to remove organic films or buffing compounds by swabbing, soaking or vapour phase treatments.
2. Cathodic cleaning in alkaline electrolyte in the conventional manner to saponify and remove the soap residues from the buffing operation and to make the surface clean.
3. Activating the surface to be plated in any of the electrolytes as described substantially hereinbefore under "Activation of Surface".
4. Strike plating: The activated surface is carried over to the cupric hydrochloric acid electrolyte and a thin deposit of copper is formed on the surface by making it cathodic in a manner substantially described for strike plating.
5. Rinsing: The work now carrying a thin adherent deposit of copper from the said electrolyte obtained in a manner as described hereinbefore, is washed thoroughly with running water or by counter current rinsing or by spraying or by a combination of these to remove the chloride ions striking to the work and jigs.
6. Acid dip: The surface is then given a simple immersion dip in a suitable acid the concentration of which is 5 to 10% by volume, the acid chosen being sulphuric acid or fluoboric acid depending on the anions in the subsequent plating bath.
7. Rinsing: The work is ~~is~~ thoroughly rinsed in running water or by counter current rinsing or by spraying.
8. Plating: The work is then made the cathode in an electroplating bath which is preferably to be an acid type of electroplating bath and the required thickness of the desired metal is plated on the surface carrying the thin deposit of copper obtained as described hereinbefore.

It has been established that when the process is carried out as described substantially hereinbefore the failure of deposit during adhesion testing occurred only at the top metal surface and never at the interface of stainless steel copper.

The following typical examples are given to illustrate the invention:

EXAMPLE 1

1. The sauce pans (stainless steel 18:8 type) to be plated are suitably stopped off exposing only the area to receive the deposit of copper.

2. The surface of metal exposed is then degreased with trichloroethylene and cathodically cleaned in the electrolyte :

Sodium carbonate:	25 g/l
Sodium hydroxide:	35 g/l
Temperature:	70-80°C
Current density:	15 asdm
Anode	Mild steel
Time:	2 minutes
Anode area:	20 dm ²
Cathode area:	20 dm ²

3. Rinsed in water

4. Activated by keeping the work immersed in the strike bath of the following composition:

Copper carbonate:	40 g/l
Hydrochloric acid:	600 ml/l
Gum arabic:	0.05 g/l
Temperature:	35°C
Time:	5 minutes
Anode area:	30 dm ²
Cathode area:	20 dm ²

'Striking'

5. In the same electrolyte, the work is made the cathode, graphite sheet electrode is used as anode and strike plating is performed as follows:

Cathode current density:	2 asdm
Time	5 minutes

7. The work is thoroughly rinsed and plated in the following bath to get a deposit of copper 500 microns thick.

Copper fluoborate:	200 g/l
Fluoboric acid(40%):	30 ml/l
Glue:	0.05 g/l
Temperature:	35°C
Current density:	1.8 asdm
Time:	20 hours
Cathode anode	Copper
cathode	work with strike copper

8. Rinsed

9. The stop-off removed

10. Dried and machined to remove the nodules and buffed.

EXAMPLE 2

1. The stainless steel sheet (stainless steel containing more than 12% Cr) to be plated with copper and chromium is carried through the sequences 1 to 3 as in example 1.

2. Then the surface is activated in the following electrolyte as described below :

Hydrochloric acid (1.18):	20% by volume
Water:	80% by volume
Graphite:	cathode
Work	anode
anodic current density	7.0 asdm
temperature	30°C
time:	3 minutes

5. Without rinsing the work is given a strike plating of copper in the following electrolyte as described below:

CuSO ₄ .5H ₂ O	50 g/l
Hydrochloric acid(10W):	700 ml/l
Anode:	graphite or carbon rod
Cathode:	work
cathode current density:	4 asdm
time:	2 minutes
Anode area:	20 dm ²
Cathode area:	20 dm ²

6. Rinsed

7. Copper plating in

Copper sulphate:	250 g/l
sulphuric acid(1.84):	40 ml/l
gelatin	0.02 g/l
phenol sulphonic acid:	1.0 g/l
current density:	0.9 asdm
time	50 minutes

8. Rinsed

9. Chromium plating in the bath containing

chromic acid:	400 g/l
sulphuric acid:	4 g/l
temperature:	40°C
cathode current density:	21.5 asdm
time:	10 minutes

10. Rinse and dry

EXAMPLE 3

1. Degrease the stainless steel(304 type) work to be plated in trichlorethylene.

2. Cathodically clean in the alkaline electrolyte as in Ex. 1

3. Rinse

4. Activate in the following electrolyte as follows :

Sulphuric acid:(sp.gr. 1.84):	20% by volume
temperature:	30°C
cathode:	work
anode:	lead
cathode current density:	10 asdm
time:	5 minutes

5. Without rinsing, make the work cathodic in the following electrolyte:

Cupric chloride:	20 g/l
Hydrochloric acid:	400 ml/l
Water:	600 ml/l
Anodes:	carbon rods
Cathode current density:	1.0 asdm
Time:	15 minutes

6. Rinse thoroughly

7. Nickel plate in the following electrolyte:

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	240 g/l
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	50 g/l
Boric acid:	30 g/l
pH	5.0
Anodes	Nickel
Cathode	work to be plated
Cathode current density	2.0 asdm
time	45 minutes

8. Rinse

9. Bright chromium plating

Chromic acid	250 g/l
Sulphuric acid:	2-5 g/l
Temperature:	55°C
Cathode current density:	30 asdm
Time:	3 minutes

10. Rinse and dry

The following are among the main advantages of this invention:

1. The nickel strike and the subsequent critical rinsing step are eliminated.
2. The unstable cuprous chloride electrolyte with an oil layer is dispensed with.
3. The use of cupric ions in wider range is made possible in the strike bath thereby minimising the careful control of cupric ions in the electrolyte to get good adhesion of subsequent deposits.
4. Copper or for that matter any other metal can be build up on this strike copper substrate to any desired thickness upto 25 microns from the conventional electroplating baths with very good adhesion and surface structure.

Subd this 7th day of October, 1955

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THE PATENTS ACT 1970

COMPLETE SPECIFICATION

(See Section 10).

"IMPROVEMENTS IN OR RELATING TO ELECTROPLATING OF
COPPER ON STAINLESS STEEL".

Council of Scientific and Industrial Research, Rafi Marg,
New Delhi-1, India, an Indian Registered Body incorporated under
the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and
ascertains the nature of this invention and the manner in which
is to be performed:-

This is an invention by Balkunje Anantha Shehoi, Scientist,
Ramasubbu Venkatachalam, Senior Scientific Assistant, Srimivasan
Chakrapani and Ramachandra Subramanian, Scientist, all of the
Central Electrochemical Research Institute, Karaikudi-6, Tamil
Nadu, India, and all are Indian Nationals.

The invention relates to improvements in or relating to the technique of electroplating of adherent copper on a stainless steel substrate.

Hitherto it has been proposed to plate copper on stainless steel from an acid copper sulphate bath after activating the surface by one or more than one type of the following treatments in order to ensure proper adhesion of the electrodeposited copper.

A thin protective oxide film on stainless steel surface, which fortifies the surface against attack by most of the chemicals used in plating baths and which has a tendency to reform quickly after stripping, has to be removed completely before electroplating and the surface should be kept active till it is covered with the electrodeposite. This is achieved by:

1. Cathodic treatments:

- | | | |
|-----------------------------------|---|-----------------------------|
| a) Sulphuric acid (Sp.gr. 1.84) | : | 5.50% by volume |
| Temperature | : | 25-32°C |
| Time | : | 1-5 minutes |
| Cathodic Current Density | : | 0.5 - 2.5 A/dm ² |
| b) Hydrochloric acid (Sp.gr.1.18) | : | 5 - 50% by volume |
| Temperature | : | 25-32°C |
| Time | : | 1 - 5 Minutes |
| Cathodic Current Density | : | 2.0 A/dm ² |

- c) Immersion in 10-30% hydrochloric acid by volume at room temperature for one minute followed by cathodic treatment as in 1 (a).
2. Immersion treatments:
- a) Sulphuric acid 20 - 50% by volume at 65-80°C for one minute after gasing starts.
- b) Hydrochloric acid : 0.1% by volume
Sulphuric acid : 1% by volume
Temperature : 25 - 32°C
Time : 26 seconds
3. Simultaneous activation and plating treatment:
- a) Nickel chloride : 240 g/l
Hydrochloric acid : 70 ml/litre
Temperature : 25-32°C
Electrode : Nickel
First anodic current density 2.0 A/dm² for 2 minutes
followed by cathodic current density 2.0 A/dm² for 6 minutes.
- b) Nickel chloride : 240 g/l
Hydrochloric acid : 100 ml/l
Temperature : 25-32°C
Electrode : Nickel
First cathodic current density 5.0-20.0 A/dm² for 2-4 minutes
followed by anodic current density 1.5-5.0 A/dm² for 15-30 min.
- c) Nickel chloride : 30-300 g/l
Hydrochloric acid : 12-120 ml/l
Temperature : 25-32°C
Anode : Nickel
Cathodic current density : 0.5-10.0 A/dm²
Time : 30 secs - 5 minutes
- d) Copper sulphate : 0.375 g/l
Hydrochloric acid : to one litre
Temperature : 25-32°C
Anode : Nickel
Cathodic current density : 4.0 - 6.0 A/dm²
Time : 1-5 minutes
- e) A combination of more than one type of the above treatments to secure best adhesion.

The article is then quickly rinsed and carried over to acid copper sulphate bath for plating copper and in practice to secure best adhesion of the electrodeposit, a strike plating in any one of the baths under simultaneous activation and plating treatment is necessary to secure good adhesion or copper can be plated in a cuprous chloride hydrochloric acid bath upto a maximum of 250 microns. It is claimed that the bath is protected against atmospheric oxidation by an oil layer.

This is open to the following objections:

Baths (a), (b) and (c) use nickel as the 'strike metal' in which case the transfer from the strike bath to the copper plating bath through the intermediate rinsing operation is critical. The rinsing should be thorough and efficient to prevent the carryover of the chloride ion to the sulphate copper plating bath. At the same time, the time of dwelling in rinse water should be as short as possible to prevent passivation of nickel surface and to ensure perfect adhesion of subsequent thick deposits of copper or other electrodeposited metals. In the case of cuprous chloride baths when they are used to strike copper plating prior to further build of copper or other electrodeposits, the carryover of oil layer, especially from complex shaped articles, will introduce contamination in the plating baths which will lead to rough deposits and if purification is resorted to, this will load the purification system thereby increasing the cost. However, since the copper deposit from the strike bath will not be passivated, the rinsing can be thorough and the time of rinsing is not critical. Even though this electrolyte could be used as a plating bath to build up copper deposits up to 200 to 250 micron thick, the conventional methods with special advantages as described in the Patent No. 113473 further thickness build up for example 500 micron as required for plating copper on stainless steel heating utensils, the bath suffered from the disadvantages that the deposit tended to be rough and powdery. So, it was imperative that subsequent build-up of copper beyond 200 microns thick has to be done in the conventional copper electrolytes, which has no special advantages. Further, the carry-over of oil into the plating bath is a serious disadvantage.

With the bath (d) namely copper sulphate 0.375 g/l conc. hydrochloric acid one litre, the concentration of copper sulphate is so low and critical that the control of strike plating is very difficult and the strike deposit will tend to become powdery and non-adherent.

The object of this invention is to obviate these disadvantages by eliminating the nickel strike entirely. We have found that this can be done by the use of a cupric chloride-hydrochloric acid bath as a strike bath. By having the copper in the divalent stage, this bath does not

suffer from the disadvantage of atmospheric oxidation and hence the use of oil layer needed for protecting the cuprous chloride from oxidation is dispensed with.

We have developed a bath which is so formulated that the concentration of cupric ion in the electrolyte is not so low as to make control very critical.

During the course of our investigations, we found that the presence of cuprous ion in this cupric electrolyte or cupric ions in cuprous chloride electrolyte showed a tendency to form powdery non-adherent deposits and it was absolutely necessary to have the copper either in the cupric or cuprous state alone. Thus, the use of copper anodes in the cupric chloride electrolyte is not possible as it will dissolve only in the cuprous state both chemically and electrochemically.

The use of nickel anodes in this electrolyte ushers in nickel ions in solution which virtually becomes nickel chloride solution on prolonged use and the deposits from such a continued electrolyte was not satisfactory from the adhesion viewpoint. This difficulty has been overcome by use of carbon or graphite anodes either in the form of sheets or rods. According to the present invention, there is provided a process for the production of copper plated stainless steel heating vessels and processing vessels by (i) surface preparation and cleaning of the surface to be plated, followed by (ii) acid dip to make the surface active and (iii) subsequent plating in conventional electroplating baths at standard operating conditions characterised in that after step(i) and before step (iii) above, the cleaned surface is (a) activated in hydrochloric acid solution, and (b) subjected to strike copper plate in a cupric chloride-hydrochloric acid electrolyte using graphite or carbon anodes.

Thus the activation may be done under the following conditions:

Hydrochloric acid (Sp. Gr. 1.18) :	5-25% by vol.
Temperature	: 1-5 minutes
Anodic current density	: 6-8A/sq.dm
<i>Cathode</i>	: Graphite or stainless steel

A flash copper strike plating electrolyte comprising:

Copper as cupric copper	: 8-16 g/l
Hydrochloric acid (Sp.Gr: 1.18)	: 400-700 ml/l
Glue, gelatin or gum arabic	: upto 1 g/l

may be operated in the following range of conditions:

Temperature	: 30-60°C
Cathodic current density	: 0.5-5 A/dm ²
Anodic Current density	: 0.5-5 A/dm ²
Anode to cathode area ratio	: 3:1 to 1:1
Time of plating	: 2 minutes - 10 minutes

Thus, a flash strike plating is given in cupric chloride-hydrochloric acid electrolyte using graphite or carbon sheets or rods as insoluble anodes, followed by build-up of copper to required thickness in an acid electrolyte like copper sulphate sulphuric acid or copper fluoborate fluoboric acid baths, after thorough rinsing of the work to free from chloride ions, which ensures the absence of carry-over of chloride ions into the plating baths.

The initial deposit of copper from the said cupric chloride electrolyte may also form the starting surface for further plating of other metals such as nickel, cadmium, chromium, zinc and tin from suitable electrolytes.

The concentration of the constituents in the electrolyte used for strike plating lies in the following ranges:

Copper as cupric copper	: 8-16 g/l
Hydrochloric acid (Sp.Gr:1.18)	: 400-700 ml/l
Glue, gelatin or gum arabic	upto 1 g/l
and is operated in the range	
Temperature	: 30-60°C
Anodes	: Insoluble graphite or carbon sheets or rods
Cathodic current density	: 0.5-5 asdm
Anodic current density	: 0.5-5 asdm
Anode to cathode area ratio	: 3:1 to 1:1
Time of strike plating	: 2 minutes to 10 minutes

Activation of the surface:

The electrolyte itself will activate the surface to be plated if the work is kept without current for 5 to 10 minutes in the electrolyte. However, the activating treatments recommended below may also be used to ensure very good adhesion:

Cathodic treatment:

(a) Sulphuric acid (Sp. gr: 1.84)	: 5-50% by volume
Temperature	: 25-32°C
Time	: 1-5 minutes
Cathodic current density	: 0.5-10 asdm
Anode	: lead or graphite
(b) hydrochloric acid (Sp. gr: 1.18)	: 5-25% by volume
Temperature	: 25-40°C
Time	: 1-5 minutes
Cathodic current density	: 0.2-5 asdm
Anodes	: Graphite or carbon

Anodic treatment:

(c) Hydrochloric acid (Sp. gr: 1.18)	: 5-25% by volume
Temperature	: 25-35°C
Time	: 1-5 minutes
Anodic current density	: 6-8 asdm
Cathode	: Stainless steel or graphite

After activating the surface to be plated by adopting any one of the above procedures, the work is carried over to the strike plating bath without rinsing and cathodically treated in the said electrolyte for 2 to 10 minutes, the operating conditions being as described earlier. Then the work is rinsed thoroughly in running water or by counter current rinsing and carried over to the plating electrolyte to build up the required electrodeposit to the predetermined thickness. For example, the work is plated with copper to a thickness of 500 microns in an acid copper sulphate bath. The adhesion of this thick copper is so good that it breaks only at the copper and not at the copper-stainless steel interface, as shown in the shear adhesion tests.

Thus, to electrodeposit copper adherently on a stainless steel surface to thicknesses in the range 25 to 625 microns or to electroplate other metals like nickel, cadmium, tin, zinc or chromium adherently on stainless steel articles, the process is carried out as described substantially hereunder:

1. Degreasing with an organic solvent like benzene, kerosene, trichloroethylene to remove organic films or buffing compounds by swabbing, soaking or vapour phase treatments.
2. Cathodic cleaning in alkaline electrolyte in the conventional manner to saponify and remove the soap residues from the buffing operation and to make the surface clean.

3. Activating the surface to be plated in any of the electrolytes as described substantially hereinbefore under "Activation of Surface".
4. Strike plating: The activated surface is carried over to the cupric hydrochloric acid electrolyte and a thin deposit of copper is formed on the surface by making it cathodic in a manner substantially described for strike plating.
5. Rinsing: The work now carrying a thin adherent deposit of copper from the said electrolyte obtained in a manner as described hereinbefore, is washed thoroughly with running water or by counter current rinsing or by spraying or by a combination of these to remove the chloride ions striking to the work and jigs.
6. Acid dip: The surface is then given a simple immersion dip in a suitable acid the concentration of which is 5 to 10% by volume, the acid chosen being sulphuric acid or fluoboric acid depending on the anions in the subsequent plating bath.
7. Rinsing: The work is thoroughly rinsed in running water or by counter current rinsing or by spraying.
8. Plating: The work is then made the cathode in an electroplating bath which is preferably to be an acid type of metal is plated on the surface carrying the thin deposit of copper obtained as described hereinbefore.

It has been established that when the process is carried out as described substantially hereinbefore the failure of deposit during adhesion testing occurred only at the top metal surface and never at the interface of stainless^{steel} copper.

The following typical examples are given to illustrate the invention:

EXAMPLE-1

1. The sauce pans (stainless steel 18:8 type) to be plated are suitably stopped off exposing only the area to receive the deposit of copper.
2. The surface of metal exposed is then degreased with trichlorethylene and cathodically cleaned in the electrolyte:

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Sodium carbonate	:	25 g/l
Sodium hydroxide	:	35 g/l
Temperature	:	70-80°C
Current Density	:	15 asdm
Anode	:	Mild steel
Time	:	2 minutes
Anode area	:	20 dm ²
Cathode area	:	20 dm ²

3. Rinsed in water

4. Activated by keeping the work immersed in the strike bath of the following composition:

Copper carbonate	:	40 g/l
Hydrochloric acid	:	600 ml/l
Gum arabic	:	0.05 g/l
Temperature	:	35°C
Anode area	:	30 dm ²
Cathode area	:	20 dm ²

5. 'Striking'

6. In the same electrolyte, the work is made the cathode, graphite sheet electrode is used as anode and strike plating is performed as follows:

Cathode current density	:	2 asdm
Time	:	5 minutes

7. The work is rinsed and then immersed in 5% by volume fluoboric acid for few seconds.

8. The work is thoroughly rinsed and plated in the following bath to get a deposit of copper 500 microns thick.

Copper fluoborate	:	200 g/l
Fluoboric acid (40%)	:	30 ml/l
Temperature	:	35°C
Glue	:	0.05 g/l
Current density	:	1.8 Asdm
Time	:	20 hours
Anode	:	Copper
Cathode	:	Work with strike copper

9. Rinsed

10. The stop-off removed

11. Dried and machined to remove the nodules and buffed.

EXAMPLE-2

1. The stainless steel sheet (stainless steel containing more than 12% Cr) to be plated with copper and chromium is carried through the sequences 1 to 3 as in Example 1.

4. Then the surface is activated in the following electrolyte as described below:

Hydrochloric acid (Sp.gr : 1.18)	: 20% by volume
Water	: 80% by volume
Graphite	: Cathode
Work	: Anode
Anodic current density	: 7 asdm
Temperature	: 30°C
Time	: 3 minutes

5. Without rinsing the work is given a strike plating of copper in the following electrolyte as described below:

Copper sulphate	: 50 g/l
Hydrochloric acid	: 700 ml/l
Anode	: Graphite or carbon rod
Cathode	: Work
Cathodic current density	: 4 asdm
Time	: 2 minutes
Anode area	: 20 dm ²
Cathode area	: 20 dm ²

6. The work is rinsed and immersed in 10% by volume sulphuric acid and then rinsed.

7. Copper plating in -

Copper sulphate:	: 250 g/l
Sulphuric acid (1.84)	: 40 ml/l
Gelatin	: 0.02 g/l
Phenol sulphonic acid	: 1.0 g/l
Current density	: 0.9 asdm
Time	: 50 minutes

8. Rinsed

9. Chromium plating in the bath containing

Chromic acid	: 400 g/l
Sulphuric acid	: 4 g/l
Temperature	: 40°C
Cathodic current density	: 21.5 asdm
Time	: 10 minutes

10. Rinse and dry

1. Degrease the stainless steel (304 type) work to be plated in tri-chlorethylene

2. Cathodically clean in the alkaline electrolyte as in Ex. 1

3. Rinse

4. Activate in the following electrolyte as follows:

Sulphuric acid (Sp.gr: 1.84)	:	20% by volume
Temperature	:	30°C
Cathode	:	Work
Anode	:	Lead
Cathodic current density	:	10 asdm
Time	:	5 minutes

5. Without rinsing, make the work cathodic in the following electrolyte:

Cupric chloride	:	20 g/l
Hydrochloric acid	:	400 ml/l
Water	:	600 ml/l
Anode	:	Carbon rod
Cathodic current density	:	1 asdm
Time	:	15 minutes

6. The work is rinsed and immersed in 5% by volume sulphuric acid and then rinsed.

7. Nickel plate in the following electrolyte:

Nickel sulphate	:	240 g/l
Nickel chloride	:	50 g/l
Boric acid	:	30 g/l
pH	:	5.0
Anode	:	Nickel
Cathode	:	Work to be plated
Cathodic current density	:	2 asdm
Time	:	45 minutes

8. Rinse

9. Bright chromium plating

Chromic acid	:	250 g/l
Sulphuric acid	:	2 to 5 g/l
Temperature	:	55°C
Cathodic current density	:	30 asdm
Time	:	3 minutes

10. Rinse and dry.

The following are among the main advantages of this invention:

1. The nickel strike and the subsequent critical rinsing step are eliminated.
2. The unstable cuprous chloride electrolyte with an Cu layer is dispensed with.
3. The use of cupric ions in wider range is made possible in the strike bath thereby minimising the careful control of cupric ions in the electrolyte to get good adhesion of subsequent deposits.
4. Copper or for that matter any other metal can be built up on this strike copper substrate to any desired thickness up to 625 microns from the conventional electroplating baths with very good adhesion and surface structure.

WE CLAIM...

1. A process for the production of copper plated stainless steel heating vessels and processing vessels by (i) surface preparation and cleaning of the surface to be plated, followed by (ii) acid dip to make the surface active and (iii) subsequent plating in conventional electroplating baths at standard operating conditions characterised in that after step (i) and before step (iii) above, the cleaned surface is (a) activated in hydrochloric acid solution, and (b) subjected to strike copper plate in a cupric chloride-hydrochloric acid electrolyte using graphite or carbon anodes.
2. A process as claimed in claim 1 wherein a flash copper strike plating electrolyte comprising:

Copper as cupric copper	: 8.16 g/l
Hydrochloric acid (Sp.gr:1.18)	: 400-700 ml/l
Glue, Gelatin or Gum arabic	: upto 1 g/l

is operated in the following range of conditions:

Temperature	: 30-60°C
Cathodic current density	: 0.5-5 A/dm ²
Anodic current density	: 0.5-5 A/d m
Anode to cathode area ratio	: 3:1 to 1:1
Time of plating	: 2 minutes - 10 minutes

3. A process as claimed in claim 1 or 2 wherein the activation is done under the following conditions:

Hydrochloric acid (Sp.gr. 1.18)	: 5-25% by vol.
Temperature	: 1-5 minutes
Anodic current density	: 6-8A/sq.dm
Cathode	: Graphite or stainless steel

4. A process for the production of copper plated stainless steel heating vessels and processing vessels substantially as herein before described.

Dated this 30th day of December, 1975

Sd/-

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