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(54) **An electroplated plastics object and a process for the manufacture thereof.**

(57) The present invention provides an electroplated plastics object that will withstand severe conditions without the electrodeposit separating from the substrate. It comprises a substrate of directly plateable plastics material on top of which is electrodeposited successively (i) a nickel-based alloy layer consisting of either 5 to 50% iron and 0 to 20% cobalt or 10 to 60% cobalt, the balance being nickel which must be at least 50% in the iron-containing alloy, (ii) a layer of pure nickel or of nickel-cobalt alloy, and (iii) a layer of chromium. Further intermediate layers may also be included.

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An Electroplated Plastics Object and a Process for the Manufacture thereof

The present invention relates to electroplating plastics material for use in testing conditions.

It is known from US Patent No 3,865,699 and an article in Products Finishing, January 1978, pages 78 to 80 that certain plastics compositions can be directly electroplated without the need for complex and numerous pre-plating steps which are necessary when electroplating conventional plastics, for example ABS (acrylonitrile-styrene butadiene copolymer). However, the use of that simple electroplating process has been hampered by the fact that the electrodeposit of a Group VIII metal tends to lift away from the plastics material when chromium is electrodeposited on top. A solution to this problem, disclosed in British Patent Specification No 1,534,638, is (i) to age the plastics object prior to plating to allow the free-radicals present to dissipate and (ii) to isolate the layer of the Group VIII metal from the chromium plating bath using a barrier that is imperveous to hydrogen.

We have now discovered the surprising fact that it is not necessary to use the two steps specified in British Patent Specification No 1,534,638 when certain nickel-based alloys are used as the layer of Group VIII metal.

In accordance with the present invention, there is provided a chromum-plated object which comprises a substrate made of, or having a surface composed of, directly plateable plastics material, a strike layer of an alloy of a metal of Group VIII of the Periodic Table electroposited directly on the substrate, a layer of corrosion-resistant nickel, and a layer of electrodeposited chromium characterised in that the strike layer is a nickel-based alloy consisting of, by weight, either from 5 to 50% iron and from 0 to 20% cobalt or from 10 to 60% cobalt, the balance in each case being, except from incidental elements or impurities, nickel, which must be present in an amount that is not less than 50% when the strike layer contains iron.

The present invention also provides a process of electroplating a substrate made of, or having a surface composed of, a directly plateable plastics material with chromium, which process comprises electro-depositing directly on the substrate a strike layer composed of an alloy of a metal of Group VIII of the Periodic Table and subsequently electrodepositing a layer of corrosion-resistant nickel and a layer of chromium characterised in that the strike layer is a nickel-based alloy consisting of, by weight, either from 5 to 50% iron and from 0 to 20% cobalt or from 10 to 60% cobalt, the balance in each case being, except for incidental elements or impurities, nickel, which must be present in an amount that is not less than 50% when the strike layer contains iron.

The deposit can generally withstand service conditions SC3 and SC 4 of ANSI/ASTM specification B 604-75 which are severe service and very severe service respectively. SC 3 is given in that specification as:

> "Service Condition No SC 3 (Severe) -- Exposure that is likely to include occasional or frequent wetting by rain or dew or strong cleaners and saline solutions and temperature extremes; for example, conditions encountered by porch and lawn furniture, bicycle and perambulator parts, and hospital furniture and fixtures."

and SC 4 is given as:

> "Service Condition No SC 4 (Very severe) -- Service conditions that include likely damage from denting, scratching, and abrasive wear in addition to exposure to corrosive environments and temperature extremes; for example, conditions encountered by exterior components of automobiles and by boat fittings in salt water service."

In order to discover the service conditions that a particular coating can withstand it is subjected to CASS tests, in which a coating is deemed to be able to withstand

SC 3 and SC 4 if it can withstand two and three 16 hour thermal cycles respectively. A thermal cycle for SC 3 and SC 4 involves subjecting a deposit to a high limit of 85°C and a low limit of -30 and -40°C respectively.

As used herein the term "directly plateable plastics material" (DPP) is a material, as disclosed in British Patent Specification No 1,480,522, that has a volume resistivity of less than 1000 ohm-cm and comprising (i) carbon black, (ii) elemental sulphur or a sulphur-containing compound, and (iii) on organic polymer, with the polymer and the elemental sulphur or at least part of the sulphur of the compound being capable of chemically bonding together. Before plating with a metal of Group VIII, the surface of the substrate must not be subjected to a treatment that would destroy the capability of the organic polymer and the sulphur or the sulphur of the compound for chemically bonding together. A particularly useful directly plateable plastic has a composition within the following ranges:

INGREDIENT	% BY WEIGHT
Carbon black	25 - 41
Elemental sulphur	0-15 - 1.5
MBT or MBTS	0.2 - 1.5
ZnO	0 - 7
Polymer*	Balance
S/MBT or MBTS	0.5 - 6.0

*The polymer is from the group of ethylene-propylene copolymers, propylene and ethylene homopolymer, and propylene and ethylene homopolymers or copolymers in admixture with a saturated rubber flexibilizer said admixture having a weight ratio of rubber to homopolymer or copolymer of up to 1.

Compositions of matter within the foregoing ranges in the melt-blended and cooled condition generally have volume resistivities below about 200 ohm-cm.

The corrosion-resistant layer of nickel is put on because the chromium layer is usually very thin as a result of its slow plating rate and low cathode efficiency and is usually porous. Thus, the layer below the chromium must be corrosion-resistant. If the corrosion-resistant layer were not present, the nickel-iron strike layer in particular would corrode in service conditions 3 and 4. In the case of the nickel-cobalt strike layer, the high cost of cobalt means that the strike layer should preferably be as thin as possible, and may be as thin as 0.1 µm, and, in order to provide an adequately thick plating deposit on the plastics substrate, a layer of corrosion-resistant nickel may be added. However, the thickness of the electrodeposit may be made up by nickel or a nickel alloy and corrosion-resistant nickel may be deposited on top of that. The corrosion-resistant nickel may be pure nickel or a nickel-cobalt alloy and optionally contains small amounts of sulphur and/or other residuums from brightening and/or stress releiving agents in the plating bath.

Since there is no need to provide more than minimal ageing the plastics substrate prior to plating, it can be plated soon after it is moulded, thereby giving considerable saving in production costs.

The amount of iron in the iron-containing strike alloy is preferably within the range of from 6 to 25% by weight, and more preferably about 20% by weight.

In the case of the nickel-cobalt alloy, the cobalt is preferably within the range of from 30 to 60% by weight.

In a preferred case, the nickel-cobalt strike layer is very thin (0.1 to 0.5 µm thick) and a layer composed of nickel or a nickel-based alloy at least 0.9 µm thick is electrodeposited on top. That layer of nickel or nickel-based alloy can be the layer of corrosion-resistant nickel.

The plated plastic product of the present invention may be made by molding a DPP into any desireable shape and, after at most a minimal ageing, inserting the molded object as a cathode into a plating bath capable of depositing the strike layer onto the substrate. The cathode potential may initially be maintained at a low level and gradually increased in order to allow the plastic object to be completely covered with metal without burning. Full voltage can ordinarily be applied after a few minutes and thereafter plating can proceed normally to deposit the strike layer of nickel alloy, a superimposed layer or layers of corrosion resistant nickel and a top layer of chromium.

We have no explanation why the coating produced by the process of the present invention does not peel during thermal cycling. That the nickel alloy might itself be acting as a hydrogen barrier, is disproven by the fact that it is ineffective as a means of retaining bond strength unless it is directly adhered to the DPP. While the examples in the present specification show that a hydrogen barrier is not necessary in the electrodeposit of the invention, it has been found advantageous in some instances to include in the plating operation a step of providing a flash layer of Watts (or other pure) nickel over the nickel-iron or nickel-cobalt alloy flash and a subsequent step of providing a copper layer under the corrosion-resistant nickel and chromium toppings. The purpose of this copper layer is not as a hydrogen barrier, since such a layer is not necessary, as shown by the examples in the present specification, but rather this copper layer serves the same purposes that it does in conventional deposits on conventional plastics.

The present invention is especially concerned with electroplated plastic objects suitable for service conditions at least as severe as service conditions SC 3, for example, exterior automotive usage where the plated object is subjected in use to corrosion and a wide range of service temperatures, ie, from frigid arctic to tropical conditions. Several processes according to the present invention will now be described in greater detail, by way of example only.

Table I identifies a number of patent specifications which disclose baths from which, and methods by which, satisfactory nickel-iron alloy strike layers can be deposited.

TABLE I

US PATENT NO	INVENTOR
3,878,067	Tremmel
3,922,209	Passal
3,969,198	Law et al.
3,974,044	Tremmel
4,002,543	Clauss et al.
4,010,084	Brugger et al.
4,014,759	McMullen et al.
4,036,709	Harbulak
4,053,373	McMullen et al.

In carrying the invention into practice, nickel-iron plating baths used in the Udylite NIRON (Registered Trade Mark) bright ferro-nickel plating process have been employed. Such baths are disclosed in US Patent Speificiations Nos 3,974,004 and 4,002,543. As disclosed in technical literature distributed by Udylite Division of OXY METAL INDUSTRIES CORPORATION, air-agitated baths for use in the NIRON process may contain the ingredients set forth in Table II.

TABLE II

	Optimum	Range
Total Nickel Content	39 g/l	30-60 g/l
Total Chloride Content	18 g/l	11-30 g/l
Nickel Sulphate ($NiSo_4.6H_2O$)	105 g/l	49-150 g/l
Udychlor 67 ($NiCl_2.3\text{-}1/2\ H_2O$)	48 g/l	30-90 g/l
Boric Acid (H_3BO_3)	45 g/l	40-56 g/l
Total Iron (Fe)	2 g/l	1-4 g/l
% Ferric Iron (Fe^{+3})	Less than 40% of total iron up to a maximum of 1 g/l (0.13) oz/gal)	
NIRON* STABILIZER NF	20 g/l	15-49 g/l
NIRON* BRIGHTENER FN-1	2.5%	2-3%
NIRON* FN-2 INDEX**	1.6	1.2-2.5

*Trademark
**An arbitrary index not equivalent to concentration providing a relative guide to brightening effect of Udylite FN-2s brightener.

The optimum bath composition set forth in Table II gives electrodeposits of alloy containing about 20% iron, the balance being essentially nickel. The ratio of iron to nickel was varied from the optimum in a number of instances as discussed hereinafter.

Strike plating of directly plateable plastic in any of the baths disclosed in the aforelisted patents in Table I, or the baths of Table II should be done in accordance with normal practice as taught in the art except that voltage ramping is normally used in order to achieve complete coverage of the plastic object. Ramping can be conveniently done by applying a voltage of one volt for 1 minute, 2 volts for a second minute and 3 volts for a third minute. Other ramping sequences can also be used. Full amperage is thereafter applied for such time as is necessary to complete a strike deposit about 10 to about 50 µm thick. Thereafter plating can be carried out in any fashion desired with no necessity for any hydrogen barrier layer to be present in the total plate.

A series of tests were conducted for the purpose of determining minimum amount of iron which would be effective to prevent destruction of a metal-polymer bond when a fully plated nickel-chromium test plaque is subject to 85°C for 16 hours. For the purposes of these tests, the following materials and procedures were used:

Directly plateable plastics material comprising in percent by weight about 30.5% carbon black, about 0.6% each of elemental sulfur and mercaptobenziazole, about 2.86% zinc oxide, about 4.76% mineral oil with the balance being essentially ethylene-propylene copolymer was used. This composition was molded into 7.62 x 10.16 cm test plaques which were aged either 4 days or 6 days prior to plating.

The test plaques were initially strike plated with a number of different baths and then uniformly were plated with about 20 µm of semi-bright nickel from a PERFLOW bath, about 7.6 µm bright nickel from a UDYLITE 66 bath and about 0.38 µm regular chromium from a non-proprietary bath containing 250 g/litre CrO_3 and 2.5 g/litre of sulphate ion. Strike platings were made from the following baths:

- A 100% Ni Watts bath
- B 100% Ni NIRON bath containing all addition agents of the NIRON baths as discussed above in Table II but free from iron
- C 65% Ni - 35% Fe NIRON* electrodeposit from a bath containing 6.0 g/litre of Fe
- D 94% Ni - 6% Fe NIRON* electrodeposit from a bath containing 0.6 g/l of Fe made by mixing 9 parts of bath B with 1 part of bath C
- E 87% Ni - 13% Fe NIRON* electrodeposit from a bath containing 1.6 g/l of iron made by mixing about 27 parts of bath C with 73 parts of bath B
- F 80% Ni - 20% Fe NIRON* electrodeposit from 3.1 g/l of iron made by mixing about 52 parts of bath C with 48 parts of bath B

G 75% Ni - 25% Fe electrodeposit from a bath (without brighteners) prepared by adding ferrous sulphate (5 g/litre of iron), an iron stabilizer (20 g/litre NIRON* Stabilizer NF) and a stress reducer (2 vol % NIRON* Additive FN-1) to a Watts bath.

H 100% iron - made up by dissolving 238 grams of ferrous sulphate heptahydrate in water to provide a litre of solution, adjusting the pH to about 2.8 to 3.5 and the surface tension to 40 dynes/cm.

*Trademark

Approximately the same procedure was used for depositing the Ni and Ni-Fe strike coatings. This involved voltage "ramps" of 1 V for 30 sec., 2 V for 30 sec., 3 V for 30 sec., and 5.3 A/dm^2 for 4 minutes. Generally, additional time at 3 V was required for complete metal coverage prior to the 4 minutes final strike coating.

The 100% iron deposit required a voltage "ramp" of 1 V for 30 sec., 2 V for 2 minutes, and 2.7 A/dm^2 for 5 minutes.

Following completion of plating with nickel and chromium, plaques were exposed at 85°C for 16 hours and then tested for coating adhesion in a qualitative peel test. Plate adhesion was rated on a scale of 0-5 (5 = best) as follows:

0 - Coating separated from plastic on cooling.

1 - Slight flexing of panel resulted in coating separation.

2 through 4 - Increasing difficulty to peel coating from plastic.

5 - Could not peel coating from plastic.

It would appear that peel ratings greater than 3 are needed for a practical strike coating.

Results of the tests are set forth in Table III.

TABLE III

Test No	Plaque Age (Days)	Strike Bath	Highest Peel Rating
1	4	A	0
2	4	B	1
3	4	C	5
4	4	F	5
5	4	E	5
6	4	D	3
7	6	A	1
8	6	B	1
9	6	C	5
10	6	F	3
11	6	E	4
12	6	D	4
13	6	G	4
14	6	H	1

Table III shows that Strike Baths A (100% nickel Watts bath), B (100% nickel with NIRON additives), and H (100% iron) are unsuited for depositing a strike layer under an all-nickel (topped with chromium) plate on directly plateable plastic when service conditions require resistance to damage caused by heating to 85°C (Service Conditions 3 and 4). While these particular tests did not include subjecting specimens to thermal cycles, they did involve exposure of the specimens to 85°C for longer than normally tested and showed (test No 6 wherein a strike layer containing 6% iron was used) that minimum amounts of iron are required in strike alloys to give thermal stability to the strike alloy-plastic bond when the strike alloy is adjacent metal containing hydrogen produced during chromium deposition.

All-nickel/chromium plated directly plateable plastic objects having a strike of nickel-iron alloy plated from a NIRON plating bath as set forth in Table II were subjected to combined thermal cycle - CASS tests as specified by two major US automotive manufactures. Table IV sets forth results from ten specimens subjected to three test cycles, each cycle consisting of 2 hours at 85°C, 2 hours at room temperature, 2 hours at -30°C, 2 hours room temperature and 16 hours of CASS testing.

TABEL IV

ASTM RATINGS AND DEFECTS AFTER

1st cycle		2nd cycle		3rd cycle	
9/9	sB, sS	9/8	sB, sS	9/8	sB, sS
9/9	sB, sS	9/8	sB, sS	8/7	sB, sS, sSp
9/9	spR	9/8	sB, sS	8/8	sB, sS, sSp
9/9	spR	9/9	sB, sS	9/8	sB, sS, sSp
9/9	SB, sS	8/7	isB, sS	7/6	isB, lB, sS, sSp
9/9	sB, sS	7/6	isB, sS	6/6	isB, lB, sS, sSp
10/10		10/10		10/9	sS
9/9	sB, sS	9/9	sB, sS	8/7	sB, sS, sSp
9/9	sB, sS	8/8	sB, sS	8/7	sB, sS sSp
10/10		10/10		10/9	vsB, sS

The numbers in the left-hand column are the ratings given in B537 ASTM 70. The abbreviations used are as follows and conform to that ASTM standard.

Types of failure

B = blistering

R = the plastic or underlying copper is visible

pR = the plastic or underlying copper is visible through pinhole corrosion

S = staining or spots

Sp = surface pits that do not extend all the way through to the plastic

Degree or extent of all failures except blisters

vs = very slight amount

s = slight amount

i = moderate amount

is = intermediate amount of small failures

Degree or extent of blisters

vs = very small size

s = small size

i = intermediate size

l = large size

is = intermediate amount of small blisters

TABLE V sets forth the results of testing ten specimens in the following manner; 22 hours of CASS testing followed by four thermal cycles each cycle consisting of 2 hours at 85°C, 2 hours at room temperature, 2 hours at $-30^{o}C$ and 2 hours at room temperature, and after completion of four such cycles a second 22 hour CASS test.

TABLE V

ASTM RATINGS AND DEFECTS AFTER

1st 22 hr. CASS		4th Thermal cycle		2nd 22 hr. CASS	
9/8	sB, sS	9/8	sB, sS	8/8	sB, sS
8/8	sB, sS	8/8	sB, sS	8/8	sB, sS
9/9	sB	9/9	sB, sS	8/8	sB, sS
9/9	sRs	9/9	sB, sS	9/9	sB, sS
9/9	sB, sS	8/7	sB, sS	7/7	sB, sS
8/8	sB, sS	7/6	sB, lB, sS	6/6	isB, isS, lB
10/10		10/9	vsB	10/9	vsB
8/8	sB, sS, spR	7/7	sB, sS	7/7	sB, sS
9/9	sSp, sS	9/9	sB, sS	8/7	sB, isS, sSp
10/10		10/10		10/9	vsB

Additional tests for thermal stability of directly plateable plastic objects having nickel-iron alloy strike deposits indicate that the bond between the directly plateable plastic and the alloy strike is exceptionally stable to thermal degradation. Contrarywise, when the alloy deposit is separated from the directly plateable plastic by a layer of nickel and the total deposit is topped with chromium and no copper or other hydrogen barrier layer is present, the plated deposit completely exfoliates after exposure to $85^{o}C$ for 16 hours.

Table VI identifies a number of documents which disclose baths from which, and methods by which, nickel-cobalt alloy electrodeposits can be made.

TABLE VI

US PATENT NO	INVENTOR
2,963,784	Chester
3,093,557	Cope et al.
3,111,463	Tan et al.
3,922,209	Passal
4,010,084	Brugger et al.
4,036,709	Harbulak
4,053,373	McMullen et al.
4,069,112	Harbulak

Electrodeposition of Alloys A. Brenner Academic Press 1963.

Nickel-cobalt alloys have been produced from baths which are essentially Watts nickel baths modified by the replacement of part of the nickel with cobalt. Similar results can be obtained using all-chloride, all-sulphate or all-sulphamate nickel plating baths. Operable ranges of composition and operating conditions of such modified Watts baths are set forth in Table VII.

TABLE VII

INGREDIENT	RANGE	DESIREABLE
Ni	2 - 80 g/l	4.6 g/l
Co	1 - 10 g/l	4.5 g/l
$SO_4^{=}$	90 - 120 g/l	108.2 g/l
Cl^-	4 - 30 g/l	15.6 g/l
H_3BO_3	20 - 60 g/l	41.9 g/l
pH	2.0 - 5.0	3.7
Temperature	25 - 75 ^oC	57 ^oC
Surface Tension	29 - 45 dynes/cm	34 Dynes/cm
Cathode Current Density	0.16 - 6.0 a/dm^2	0.65 a/dm^2
Co/Ni	0.02 - 0.12	0.07

It is important to note that the alloy deposited from baths, the compositions of which are set forth in Table VII, is not necessarily the same as the ratio of metal ions in the bath. Generally speaking the cobalt content of the deposited alloy increases (a) with the cobalt content in the bath, and (b) as the cathode current density decreases.

Strike plating of directly plateable plastic in any of the baths disclosed in the aforelisted documents in Table VI, or the baths of Table VII should be done in accordance with normal practice as taught in the art except that voltage ramping is normally used in order to achieve complete coverage of the plastic object. Ramping can be conveniently done by applying a voltage of one volt for 1 minute, 2 volts for a second minute and 3 volts for a third minute. Other ramping sequences can also be used. Full or higher amperage is then after applied for such time as is necessary to complete a strike deposit about 1.0 to about 5.0 µm thick taking care that the plating bath is switched at the appropriate time when only a very thin initial nickel-cobalt deposit is desired. Thereafter plating can be carried out in any fashion desired with no necessity for any hydrogen barrier layer to be present in the total plate.

In accordance with a most preferred aspect of the present invention only the initial portion of a deposit is nickel-cobalt alloy. Specifically, the nickel-cobalt alloy directly deposited on DPP can be about 0.1 to about 0.5 μm thick followed by a layer of a nickel electrodeposit, for example, a Watts nickel electrodeposit. If, except for a surface chromium layer, the electroplate on DPP is all-nickel or nickel-based alloy, the ultra-thin nickel-cobalt alloy layer (ie, about 0.1 to 0.5 μm layer) overlayed with Watts nickel, semi-bright nickel, etc will suffice. If however the total plate is to contain copper, it is necessary for a layer thickness of about 1 to 5 μm to be built up with a layer of nickel before copper is deposited. In other words, there must be a nickel deposit at least about 0.9 μm thick between the strike alloy and the copper. Failure to build up the full thickness with nickel will usually result in a depletion of nickel-cobalt stike deposit in recessed areas during subsequent copper plating.

A series of tests were conducted for the purpose of determining minimum amounts of cobalt which would be effective to prevent destruction of a metal-polymer bond when a fully plated nickel-chromium test plaque is subjected to 85^{o}C for 16 hours. For the purpose of these tests, the following materials and procedures were used:

Directly Plateable Plastic comprising in percent by weight about 30.5% carbon black, about 0.6% each of elemental sulphur and mercaptobenxothiazole, about 2.53% zinc oxide, about 4.76% mineral oil with the balance being essentially ethylene-propylene copolymer was used. This composition was moulded into 7.62 x 10.16 cm test plaques which were aged either 4 days or 6 days prior to plating.

The test plaques were initially strike plated with a number of different baths and then uniformly were plated with about 20 μm of semi-bright nickel from a PERFLOW bath, about 7.6 μm bright nickel from a UDYLITE 66 bath and about

0.38 µm regular chromium from a non-proprietary bath containing 250 g/litre CrO_3 and 2.5 g/litre of sulphate ion. Strike platings and their associated plating baths were as follows:

A 100% Ni Watts bath

B 100% cobalt - made up by dissolving about 400 grams of cobalt sulphate heptahydrate, about 37 grams of boric acid and about 20 grams of cobalt chloride hexahydrate in water to provide a litre of solution and adjusting the pH with sulphuric acid to about 4.0

C 65% Ni - 35% cobalt* prepared by adding cobalt sulphate to a Watts bath to obtain a cobalt content of 6.2 g/litre

D 75% Ni - 25% cobalt* prepared by adding cobalt sulphate to a Watts bath to obtain a cobalt content of 2.4 g/litre

E 87% Ni - 13% cobalt* prepared by adding cobalt sulphate to a Watts bath to obtain a cobalt content of 0.6 g/litre

F 92% Ni - 8% cobalt* prepared by adding cobalt sulphate to a Watts bath to obtain a cobalt content of 0.25 g/litre.

*Alloy compositions are nominal and were determined on the basis of platings on foil done in simulation of strike plating conditions.

Approximately the same procedure was used for depositing all the strike coatings. This involved voltage "ramps" of 1 V for 30 sec., 2 V for 30 sec., 3 V for 30 sec., and 5.3 A/dm^2 for 4 minutes. Generally, additional time at 3 V was required for complete metal coverage prior to the 4 minutes final strike coating.

Following completion of plating with corrosion-resistant nickel and chromium, the plaques were exposed at 85°C for 16 hours and then tested for coating adhesion in a qualitative peel test. Plate adhesion was rated on a scale of 0-5 (5 = best) as follows:

0 - Coating separated from plastic on cooling.

1 - Slight flexing of panel resulted in coating separation.

2 through 4 - Increasing difficulty to peel coating from plastic.

5 - Could not peel coating from plastic.

It would appear that peel ratings greater than 3 are needed for a practical stike coating.

Results of the tests are set forth in Table VIII.

TABLE VIII

Test No	Plaque Age (Days)	Strike Bath	Highest Peel Rating
1	4	A	0
2	6	A	1
3	6	B	No adhesion after strike
4	6	C	4
5	6	D	5
6	6	E	5
7	6	F	3

Table VIII shows that Strike Baths A (100% nickel Watts bath), and B (100% cobalt) are unsuitable as a basis for chromium plate on directly plateable plastic when service conditions require resistant to damage caused by heating to 85°C (Service Conditions SC 3 and SC 4). While these particular tests did not include subjecting speciments to thermal cycles, they did involve exposure of the specimens to 85°C for longer than normally tested and showed (test No 7 wherein the strike layer containing 8% cobalt was used) that a minimum amount of cobalt is required in strike alloys to give thermal stability to the strike alloy-plastic bond

Table IX sets forth additional bath compositions and operating conditions for strike baths.

TABLE IX

Bath No	1	2	3	4	5	6	7
Ni (g/l)	80.4	64.4	64.4	62.5	63.3	74.6	64.4
Co (g/l)	----	0.03	0.54	1.3	2.5	4.5	12.0
$SO_4^=$ (g/l)*	110.7	89.8	90.7	88.7	91.9	108.2	110
Cl^- (g/l)	15.4	11.5	11.5	11.5	11.6	15.6	11.5
H_3BO_3	38.3	41.5	41.5	36.2	44.1	41.9	30.5
pH	3.7	3.8	3.7	3.7	3.7	3.7	3.7
Temp. °C	57	57	57	57	57	57	57
Surf. Tens. dynes/cm	34	34.5	34	34	34	34.5	34

*Calculated value

Using Bath No. 6, the average amount of cobalt in an electrodeposit of Ni-Co alloy was measured and compared to the cathode current density used in making the electrodeposit. The resultant data, set forth in Tabel X shows lowering of cobalt content with increase in cathode current density.

TABLE X

Current Density (A/dm^2)	Co (%)
0.32	39.0
0.65	35.1
1.29	31.4
2.58	24.1
5.16	16.4

The data in Table XI shows that, given a particular cathode current density, the cobalt content of an alloy electrodeposit increases with concentration of cobalt in the plating bath.

TABLE XI

Bath No	Co Conc. g/l	Co as % total Ni + Co in Bath	% Co in deposited Alloy @ 0.65 a/dm^2	@ 5.16 a/dm^2
3	0.54	0.8	9.8	3.6
4	1.3	2.0	18.4	7.7
5	2.5	3.8	30	16
6	4.5	5.7	35.1	16.4
7	12.0	15.7	48	32

Accordingly in light of the teachings of Tables X and XI, those skilled in the art will appreciate the need for correlating bath composition and deposition cathode current density in order to maintain a deposited nickel-cobalt stike alloy within the operable composition range disclosed herein.

Bath No 6 was used, along with or in part or total substitute for a Watts nickel bath (Bath 1), to provide strike deposits on wheel spinners moulded of DPP the composition of which is set forth hereinbefore. The wheel spinners are in the shape of a "pilgrim's hat" about 5.7 cm from brim to crown and about 7.6 cm in diameter at the brim exclusive of five equally spaced lugs, each having a mounting hole, around the outside of the brim. The wheel spinners were moulded from the DPP which had been pre-heated for 4 hours at 118°C prior to moulding and were then aged from 2 to 6 days after moulding and before plating in batches of 12. Details of the plating are set forth in Table XII.

TABLE XII

RACK	A	B	C	D	E	F
Initial Strike						
Type	Ni-Co	Ni-Co	Watts	Ni-Co	Ni-Co	Watts
Thickness (μm)	1.25	0.25	0.28	0.29	0.18	0.26
Max. Av. CD (a/dm^2)	1.35	0.60	0.60	0.66	0.41	0.60
Thickness Watts @ 0.66 a/dm^2 (μm)	---	---	---	---	0.19	---
Thickness Watts @ 5.5 a/dm^2 (μm)	---	4.32	4.32	---	---	4.32
Thickness Bright Acid Copper @ 4.5 a/dm^2 (μm)	---	---	---	11.4	11.4	---
Thickness Semi Bright Ni @ 5.5 a/dm^2 (μm)	21.1	18.0	18.0	11.2	11.2	18.0
Thickness Bright Ni @ 5.5 a/dm^2 (μm)	5.3	5.3	5.3	5.3	5.3	5.3
Thickness Dur Ni @ 5.5 a/dm^2 (μm)	2.8	2.8	2.8	2.8	2.8	2.8
Thickness Cr @ 12.4 a/dm^2 (μm)	0.43	0.43	0.43	0.43	0.43	0.43
Total thickness (μm)	31.0	31.2	31.2	21.5	31.5	31.2
Days aging before Plating	2	2	3	3	6	25

The plated wheel spinners from racks A to F were subjected to thermal degradation and CASS corrosion testing with results as set forth in Table XIII.

TABLE XIII

RACK	A	B	C		E	F
Therm. Deg. Test Failure of Spinner bodies						
85°C - 16 hours	0	0	all 12 failed	0	0	not run
cool to room temp. plus -30°C - 2 hours	0	0	not run	0	0	not run
CASS Corrosion Test 4-16 hour cycle total 64 hours (Rating)	9.2/7.8	9.8/8.0	not run	10/7.0	10/8.8	10/5.8
Superimposed on Thermal Degradation Test	Yes	Yes	--------		Yes	No

The data in Tables XII and XIII shows that initial striking of the DPP surface with nickel-cobalt alloy provides good nickel-chromium deposits resistant to thermal degradation and corrosion regardless of whether a copper interlayer is present. The presence of a copper layer in the samples of racks D and E improves somewhat on the good corrosion resistance ratings exhibited by the samples of racks A and B.

Spinners, as described hereinbefore, were moulded out of dried (8 hr) DPP and plated the day after moulding. The strike bath used in plating these spinners was Bath 6 as set forth in Table IX. Twelve spinners were struck in Bath 6 at 1 volt for one minute, 2 volts to complete coverage (about 2 minutes) and 1.8 volts at 0.54 A/dm^2 for 1.5 minutes. Plating was completed, in sequence, with 2.03 μm of Watts nickel, 14.2 μm of bright acid copper, 10.7 μm of semi-bright nickel, 6.4 μm of bright nickel, 2.03 μm of Durnickel and 0.25 μm of chromium for a total deposit thickness of 34.8 μm. Table XIV sets forth the result of thermal degradation tests in terms of plate-to-plastic bond failures in the spinner body (out of 12) and in the spinner lugs (out of 60).

TABLE XIV

	First Cycle 85°C - 16 hrs -30°C - 2 hrs		Second Cycle 85°C - 16 hrs -30°C - 2 hrs		Third Cycle 85°C - 16 hrs -30°C - 2 hrs	
	85°C	-30°C	85°C	-30°C	85°C	-30°C
Body	0	0	0	0	0	1*
Lugs	0	0	0	0	0	0

*Isolated spot near crown of the spinner about 2.5 mm in diameter and primarily plastic delamination.

The data in Table XIV shows that by using a nickel-cobalt alloy strike there is no need for aging molded DPP more than 1 day after molding to avoid failure under reasonable thermal degradation testing.

Sixty additional spinners were given nickel-cobalt alloy strikes in baths set forth in Table XI at a cathode current density of about 0.65 A/dm^2 by holding a 1 volt for 1 minute, 2 volts for 2 to 2.5 minutes for complete coverage and 1.8 volts for 1.5 minutes. Twelve additional spinners were struck in a cobalt-free Watts bath in the same manner. The 72 spinners were then finish plated by depositing, in sequence, 2.03 µm of Watts nickel, 14.2 µm of bright acid copper, 10.7 µm of semi-bright nickel, 6.4 µm of bright nickel, 2.03 µm of Durnickel and 0.25 µm of chromium for a total deposit thickness of 34.8 µm. Table XV sets for the results of thermal degradation tests on these 72 spinners.

TABLE XV

Estimated % Co in Strike Deposit	First Cycle 85°C - 16 hrs -30°C - 2 hrs		Second Cycle 85°C - 16 hrs -30°C - 2 hrs		Third Cycle 85°C - 56 hrs -30°C - 2 hrs		
	Failures after 85°C	-30°C	Failures after 85°C	-30°C	failures after 85°C	-30°C	-48°C*
0	1	1	1	1	3	7	9
9.8	2	2	2	3	3	9	12
18.4	0	0	0	0	0	0	1
30	0	0	0	0	0	0	0
35	0	0	0	0	0	0	0
48	0	0	0	0	0	0	0

*Cooled 3 hours then held at -46 to -50°C for 1.5 hours.

Table XV shows the advantage in using very thin (ie, about 0.1 µm to about 0.6 µm) cobalt-nickel alloy strike deposits which, on the average, contain greater than about 30% cobalt, eg, about 30% to about 60% cobalt, balance nickel. None of the 36 spinner samples struck with such an alloy deposit failed in the extremely severe thermal degradation test comprised of the three cycles as set forth in Table XV.

Examination of lug areas on the samples tested as reported in Table XV showed 151 failures out of 180 possibles with samples struck with either pure nickel or nickel-cobalt alloy estimated to contain less than 20% cobalt. Of those samples struck with nickel-cobalt alloy estimated to contain from 30% to 50% cobalt, there were only 10 failures out of 180 samples tested.

A second set of spinners was plated in a manner similar to manner in which the aforementioned sixty spinners were plated. These additional spinners were tested under conditions as set forth in Table XVI.

TABLE XVI

Estimated Cobalt in Strike Deposit	Failure of Lugs 100°C for 16 hrs -30°C for 2 hrs		Failure of Body 100°C for 16 hrs -30°C for 2 hrs	
	% Failures after		% Failures after	
	100°C	-30°C	100°C	-30°C
0 %	53%	77%	0%	83%
9.8%	0%	96%	0%	0%
18.4%	0%	20%	0%	0%
30 %	0%	0%	0%	0%

The data in Table XVI shows again the highly advantageous results obtained when nickel-cobalt alloy strike layers contain about 30% cobalt.

1. A chromium-plated object which comprises a substrate made of, or having a surface composed of, directly plateable plastics material, a strike layer of an alloy of a metal of Group VIII of the Periodic Table electroplated directly on the substrate, a layer of corrosion-resistant nickel, and a layer of chromium characterised in that the strike layer is a nickel-based alloy consisting of, by weight, either from 5 to 50% iron and from 0 to 20% cobalt or from 10 to 60% cobalt, the balance in each case, being, except for incidental elements and impurities, nickel which must be present in an amount that is not less than 50% when the strike layer contains iron.

2. An object as claimed in claim 1, characterised in that the amount of iron in the strike layer is in the range of from 6 to 25%.

3. An object as claimed in claim 2, characterised in that the amount of iron in the strike layer is about 20%.

4. An object as claimed in claim 1, characterised in that the amount of cobalt in the strike layer is in the range of from 30 to 60%.

5. An alloy as claimed in claim 1 or claim 4, characterised in that the strike layer is iron-free and has a thickness in the range of from 0.1 to 0.5 μm and there is deposited directly on top of the strike layer a layer of nickel that is at least 0.9 μm thick.

6. A process of electroplating a substrate made of, or having a surface composed of, a directly plateable plastics material with chromium, which process comprises electrodepositing directly on the surface a strike layer composed of an alloy of a metal of Group VIII of the Periodic Table and subsequently depositing a layer of corrosion-resistant nickel and a layer of chromium characterised in that the strike layer is a nickel-based alloy consisting of, by weight, either from 5 to 50% iron and from 0 to 20% cobalt or from 10 to 60% cobalt, the balance in each case being, except for incidental elements and impurities, nickel which must be present in an amount that is not less than 50% when the strike alloy contains iron.

7. A process as claimed in claim 6, wherein the substrate is electroplated immediately after it has been moulded.

8. A process as claimed in claim 6 or in claim 7, which is substantially as hereinbefore defined.