

PATENT SPECIFICATION

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 (72) Inventor WILLIAM RONALD WEARMOUTH



(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF HARD, HEAT-RESISTANT NICKEL-BASE ELECTRODEPOSITS

- (71) We, INCO EUROPE LIMITED (formerly known as International Nickel Limited), a British company, of Thames House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the production of hard, heat-resistant nickel-base electrodeposits by electro-deposition techniques which are particularly suitable for use in electroforming, and to articles consisting of, or having as an outer surface, electrodeposits so produced. The term 'electrodeposit' as used herein is to be understood to include electroforms.
- As is well known, the production of electroforms involves building up deposits of adequate thickness on a mandrel, which in turn requires that the stress in the deposit should not be so high as to cause premature separation of the deposit from the mandrel. As is further known, the electroformability and hardness of nickel can be improved by electrodepositing the nickel from an electrolyte containing addition agents which introduce sulphur into the resulting electrodeposit. However whilst the sulphur improves electroformability by reducing the stress in the electrodeposit it does so at the expense of its ductility, and sulphur contents in excess of approximately 0.005% will cause the electrodeposit to embrittle when exposed to temperatures in excess of approximately 200°C. This temperature embrittlement is particularly disadvantageous in articles consisting of or including electrodeposits requiring exposure to elevated temperatures, either in use such as moulds and dies, or in manufacture such as screen printing cylinders which may be subjected to localised heating by brazing, welding or by the use of heat curable glues, or during surface masking using heat curable lacquers.
- We have now found that embrittlement of a hard sulphur-containing nickel base electrodeposit on exposure to temperatures exceeding 200°C is lessened if the electrodeposit is formed by codeposition of nickel, sulphur and manganese.
- Accordingly the present invention provides an article consisting of, or having as an outer surface, a hard sulphur-containing nickel electrodeposit exposed in use or manufacture to temperatures exceeding 200°C, the electrodeposit containing, by weight, from 0.007 to 1% sulphur and sufficient manganese, in the range of from 0.02 to 5%, in excess of the stoichiometric amount necessary to form manganese sulphide with the sulphur, to improve embrittlement resistance of the electrodeposit at temperatures exceeding 200°C.
- The mechanism by which the embrittlement is reduced is not understood, but surprisingly it appears that when the manganese containing electrodeposit is exposed to temperatures in excess of 200° harmful brittle grain boundary films of nickel sulphide are not formed. Possibly this may be due to the formation of less harmful manganese sulphides in preference to nickel sulphides at temperatures greatly in excess of 200°C but at temperatures up to about 400°C significant amounts of manganese sulphide are unlikely to form and yet surprisingly grain boundary nickel sulphides are not formed either. Nevertheless the amount of manganese in the electrodeposit must be in the range of from 0.02 to 5% by weight and in excess of the stoichiometric amount necessary to form manganese sulphide with the 0.007 to 1% by weight sulphur present in the electrodeposit. This means that in the electrodeposit the manganese content must be more than 1.71 times the sulphur content. Moreover it is found that the presence of manganese with the nickel and sulphur in the electrodeposit does not detrimentally increase the stress in the electrodeposit such as to prevent electroforming. This is surprising as the presence of manganese alone in a nickel electrodeposit does raise the stress

sufficiently to make electroforming very difficult if not impossible.

Whatever the mechanism behind the reduction of embrittlement, the electrolyte used to form the electrodeposit in the article of the invention contains a source of nickel ions, preferably in the form of nickel sulphate or sulphamate, with or without other conventional additions such as nickel chloride and/or boric acid. Suitable electrolytes include sulphate-chloride electrolytes of the conventional Watts or high-chloride types, conventional sulphamate electrolytes or high sulphamate electrolytes such as described in the Specification of our Patents Nos. 999,117, 1,081,308 and 1,101,093. One such high sulphamate electrolyte widely used for the electroforming of nickel and known as the "Ni-Speed" electrolyte, contains from 550 to 650 g/l (grammes per litre) of nickel sulphamate, from 5 to 15 g/l of nickel chloride and 30 to 40 g/l of Boric acid.

The electrolyte also contains a source of sulphur and a source of manganese ions. The source of sulphur conveniently is a sulphur bearing organic compound, preferably an aryl compound containing a functional sulphonate group. A suitable source of sulphur is O-benzoic sulfimide or the sodium salt of naphthalene tri-sulphonic acid and more preferably it is O-benzoic sulphimide sodium salt, herein termed "saccharin sodium". Optionally the electrolyte may contain a secondary brightener such as 2 butyne 1:4 diol, herein termed "butyne-diol".

Preferably the source of sulphur is present in the electrolyte in an amount sufficient to introduce more than 0.02% by weight sulphur into the resulting electrodeposit. Advantageously no more than 0.065% sulphur should be introduced into the electrodeposit. When the source of sulphur is saccharin sodium it is preferably added to the electrolyte in an amount in the range of from 0.1 to 0.4 g/l, e.g. 0.25 g/l, to provide a range of available sulphur in the electrolyte of from 0.01 to 0.065 g/l.

The source of manganese ions preferably is one or more of manganese sulphamate, sulphate, and chloride and other soluble manganese compounds compatible with the electrolyte. Moreover to facilitate incorporation of the desired amount of manganese in the electrodeposit, the concentration of the manganese ions in the electrolyte preferably is related to the current density used in the electrodeposition process. To this end the current density preferably should be in the range of 2.7 to 20 A/dm² (amperes per square decimetre), preferably in the range of 4.3 to 12.9 A/dm² for example 6, 8 or 10 A/dm², with the manganese ion concentration in the electrolyte preferably being in the range of from 12 to 20 g/l (grammes per litre).

In general increasing the concentration of

manganese ions in the electrolyte facilitates the incorporation of manganese in the electrodeposit. Advantageously from 0.03 to 3.5% manganese, preferably from 0.07 to 0.35% and more preferably from 0.1 to 0.25% manganese, should be incorporated in the electrodeposit. Conveniently at least 0.07% and more preferably at least 0.1% manganese should be incorporated together with from 0.02 to 0.065%, preferably from 0.025 to 0.040%, sulphur to minimise embrittlement of the electrodeposit on heating.

As aforesaid, in electrodeposits according to the invention the manganese content of from 0.02 to 5% must be greater than the stoichiometric amount necessary to form manganese sulphide (MnS). Preferably the amount of manganese present should exceed the stoichiometric amount by at least 0.03%. Advantageously the manganese content should not be more than 0.08% in excess of twice the stoichiometric amount.

Preferably electrodeposits produced according to the invention contain, excluding impurities, only nickel, manganese and sulphur. However some of the nickel present may optionally be replaced by iron and/or cobalt. Normal impurities which may be present include carbon and cobalt, usually present only in trace amounts.

Examples of the methods of producing electrodeposits of the present invention will now be given.

Example 1.

A conventional "Ni Speed" electrolyte was used containing in aqueous solution:

Nickel Sulphamate		
$\text{Ni}(\text{SO}_4\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$	560 g/l	
Nickel Chloride		
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	8 g/l	105
Boric Acid		
H_3BO_3	33 g/l	

Manganese was added to portions of this electrolyte in the form of manganese sulphamate or manganese sulphate and sulphur was added in the form of saccharin sodium. Electrodeposits were formed by plating from the electrolyte at a temperature of 60°C on stainless steel cathodes, as foils with a thickness of approximately 200 microns for samples A, B, C, 1 and 2 using manganese sulphamate as a source of manganese in the electrolyte, and on stainless steel mandrels, as cylinders 35 mm (millimetres) long, 30 mm in diameter and 100 microns thick for samples 3 to 6 and D using manganese sulphate as a source of manganese in the electrolyte. The samples were stripped from the cathodes or mandrels and hardness measurements made on the samples on a Vickers diamond pyramid indentation machine at a load of 1.0 Kg (kilo-

gramme) at room temperature both as-plated and after heating for various temperatures and times with the results shown in the following Table 1 in which samples A to D are outside the invention and samples 1 to 6 according to the invention. The samples were also analysed for manganese and sulphur content with the results shown in Table 1, and the ductility of the samples after stripping was measured at room temperature, on strips 12 mm wide cut therefrom, after heating for various times at various elevated temperatures, as the number of reverse bends through 90° before fracture. Internal stress of the as-plated samples was measured using a modified Brenner-Senderoff spiral contractometer.

TABLE 1

Sample	Mn concentration in electrolyte (g/l)	Saccharin concentration in electrolyte (g/l)	Current Density A/dm ²	Electrodeposit		Electrodeposit Hardness (Hv)			Ductility		Stress N/mm ²
				wt%Mn	wt%S	As-plated	After 22 hours at 450°C	After 18 hours at 600°C	After 22 hours at 450°C	After 18 hours at 600°C	
A	0	0	6.5	<0.02	0.001	245	145	87	33	11	-35
B	0	0.25	6.5	<0.20	0.020	473	182	124	0	0	-58
C	20	0	6.5	0.10	0.005	200	N.D.	N.D.	9	N.D.	+240
1	20	0.25	2.7	0.03	0.017	389	158	98	2	1	-62
2	20	0.25	6.5	0.15	0.032	498	215	140	11	15	-48
D	14	0.25	4.3	0.03	0.018	398	169	100	0	0	-86
3	14	0.25	6.5	0.06	0.022	405	177	100	3	0	-80
4	14	0.25	8.6	0.10	0.023	405	183	100	4	2	-91
5	14	0.25	10.8	0.11	0.023	410	197	100	4	5	-62
6	14	0.25	12.9	0.17	0.026	443	193	100	8	20	+36

N.D.—Not determined—Internal Stress too tensile for satisfactory plating of foil
 negative stress is compressive positive stress is tensile
 N/mm²=Newtons per square millimetre

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As can be seen from the results of Table 1, the pure nickel electrodeposit sample A, outside the scope of the present invention, had a moderate hardness of 245 Hv as-plated with a compressive internal stress just adequate to permit both general and cylinder electroforming. The hardness was retained quite well at temperatures up to 450°C and the ductility was retained reasonably at temperatures up to 600°C. The sulphur containing nickel electrodeposit sample B, outside the scope of the present invention, had a better as-plated hardness than sample A, better retained hardness and compressive internal stress such as to permit cylinder electroforming but not general electroforming, but embrittled catastrophically as indicated by zero ductility after heating at 450°C. The manganese containing electrodeposit sample C, also outside the scope of the present invention, had poorer as-plated hardness than the pure nickel sample A, better resistance to embrittlement than sample B but an internal stress too highly tensile for satisfactory foil formation or commercial electroforming or for anything but limited property measurements to be effected.

In contrast to these results the manganese and sulphur containing nickel electrodeposit samples 1 to 6 made according to the present invention, all had higher as-plated and retained hardnesses than samples A and C, and similar or better resistance to embrittlement at elevated temperatures than sample B, coupled with internal stress values permitting satisfactory cylinder electroforming and in some instances general electroforming.

Furthermore increasing the content of the manganese source in the sulphur-containing electrolyte and increasing the current density utilised, tended to increase the amount of manganese in the electrodeposit, tended to increase the as-plated and retained hardnesses, improved the resistance to embrittlement at temperatures in excess of 200°C and maintained the internal stress generally suitable for cylinder electroforming. Sample D, which contained slightly less manganese than the stoichiometric amount necessary to form man-

ganese sulphide with all the sulphur present and which is outside the invention, in general had lower as-plated and retained hardnesses and poorer retained ductility than the samples 1 to 6 made according to the invention.

With the conventional "Ni-Speed" electrolyte, the electrodeposit of the present invention preferably is made at current densities greater than 6.5 A/dm² with manganese concentrations in excess of 14 g/l and saccharin sodium concentrations of approximately 0.25 g/l to introduce at least 0.1% manganese into the electrodeposit.

An electrolyte more commonly employed than the Ni Speed electrolyte is the Watts type electrolyte which uses commercially available manganese sulphate as the source of manganese ions rather than manganese sulphamate which usually has to be prepared experimentally. A Watts type electrolyte was used in the following Example II.

Example II.

A conventional Watts type electrolyte was used containing in aqueous solution:

Nickel Sulphate NiSO ₄	285 g/l
Nickel Chloride NiCl ₂	29 g/l
Boric Acid H ₃ BO ₃	40 g/l
Saccharin Sodium	0.25 g/l

Manganese was added to this electrolyte in the form of a solution of manganese sulphate to give a manganese content in the electrolyte of 16 g/l. Nickel was electrodeposited from the electrolyte at a pH of 4 and a temperature of 60°C at different manganese and sulphur concentrations and different current densities, onto a stainless steel mandrel as cylinders 35 mm long and 30 mm diameter x 100 microns thick. The electroformed samples were separated from the mandrel and hardness values were measured at room temperature together with the manganese and sulphur contents, the internal stress and ductility after heating, using the techniques of Example I, with the results shown in the following Table II.

TABLE II

Sample	Current Density (A/dm ²)	Wt. %Mn	Wt. %S	Hardness (HV)			Ductility		Stress (N/mm ²)
				as-plated	22 hours at 450°C	18 hours at 600°C	22 hours at 450°C	18 hours at 600°C	
E	4.3	0.03	0.024	240	136	113	0	0	-43
F	6.5	0.05	0.030	274	140	136	0	0	-62
7	8.6	0.16	0.033	408	200	147	3	4	-59
8	10.8	0.20	0.034	418	200	144	5	4	-56
9	12.9	0.22	0.035	437	210	163	6	6	-53

negative stress is compressive positive stress is tensile.

As can be seen from the results of Table II the conditions used to produce the samples 7 to 9 according to the present invention, and samples E and F outside the invention, gave satisfactory cylinder electroforms. However Samples E and F with less manganese than the stoichiometric amount necessary to form manganese sulphide with the sulphur present had low as-plated and retained hardness and poor retained ductility. Optimum results were obtained with samples 7 to 9, by increasing the sulphur and manganese contents to an optimum in excess of about 0.1% manganese and about 0.03% sulphur and by using a current density preferably of at least 8.6 A/dm², whereupon increasing as-plated and retained hardness values and increasing ductility values after heating to 450 and 600°C were obtained with increasing current density and increasing manganese and sulphur contents.

The effect of varying the saccharin sodium, which is a primary brightener, concentration together with the effect of the presence of a

secondary brightener such as butyne diol, in an electrolyte of Example II is shown in the following Example III.

Example III.

A conventional Watts type electrolyte was used containing in aqueous solution:

Nickel Sulphate NiSO ₄	285 g/l	30
Nickel Chloride NiCl ₂	26 g/l	
Boric Acid H ₃ BO ₃	37.7 g/l	
Manganese Sulphate as Mn ²⁺	15 g/l	35
Saccharin Sodium	0.25 g/l	

Butyne diol was added to the electrolyte in various quantities and metal was electrodeposited onto a stainless steel mandrel as foil 50 mm x 50 mm x 100 microns thick at a current density of 4.3 A/dm², under the conditions and the results shown in the following Table III, in which samples 10 and 11 were made according to the invention. All conditions and methods of measurement were as in Example II.

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TABLE III

Sample	Butyne Diol concentration (g/l)	Wt. %Mn	Wt. %S	Hardness (HV)			Ductility		Stress (N/mm ²)
				as-plated	22 hours at 450°C	18 hours at 600°C	22 hours at 450°C	18 hours at 600°C	
10	0.10	0.06	0.021	289	191	82	3	5	+31
11	0.25	0.30	0.061	577	245	191	10	9	+55

negative stress is compressive positive stress is tensile.

As can be seen from the results of Table III additions of from 0.10 to 0.25 g/l butyne diol to electrolytes containing 0.25 g/l saccharin sodium had the effect of allowing greater amounts of manganese to be deposited with the same current densities than were necessary in the absence of butyne diol. For example with 0.10 g/l butyne diol and 0.25 g/l saccharin sodium the sample 10 electrolyte form obtained at 4.3 A/dm² contained 0.06% manganese and 0.021% sulphur in comparison with sample E of Example II, obtained from a butyne diol free electrolyte at 4.3 A/dm², which contained 0.03% manganese and 0.024% sulphur. Comparison of the results in Table II and Table III for samples E, 10 and 11 show that in general butyne diol additions increased the as-plated hardness, the retained hardness and ductility after heating at 450 and 60°C and the stress in a tensile direction. Preferably with butyne diol additions saccharin sodium additions should be at least 0.25 g/l. Furthermore increasing butyne diol additions increased the hardness values as-plated and after heating at 450 and

600°C and increased the ductility after heating at 450 and 600°C.

Another suitable electrolyte is the conventional sulphamate electrolyte as used in the following Example IV.

Example IV.

A conventional sulphamate electrolyte was used containing in aqueous solution:

Nickel Sulphamate
 $\text{Ni}(\text{SO}_4\text{NH}_4)_4\text{H}_2\text{O}$ 280 g/l
 Nickel Chloride NiCl_2 5 g/l
 Boric Acid H_3BO_3 35 g/l
 Saccharin Sodium 0.25 g/l

Manganese was added to this electrolyte in the form of manganese sulphate to give a manganese content in the electrolyte of 13 g/l. Experimental details were the same as for Example I and the electroformed samples G, H and 12 to 14 in the form of cylinders 35 mm long, 300 mm in diameter and 100 microns thick, of which samples 12 to 14 were according to the invention, gave the results recorded in the following Table IV.

TABLE IV

Sample	Current Density (A/dm ²)	Wt. %Mn	Wt. %S	Hardness (HV)			Ductility		Stress (N/mm ²)
				as-plated	22 hours at 450°C	18 hours at 600°C	22 hours at 450°C	18 hours at 600°C	
G	4.3	0.02	0.040	295	136	136	0	0	-95
H	6.5	0.06	0.037	333	140	82	0	0	-98
12	8.6	0.10	0.040	378	177	93	0	1	-100
13	10.8	0.12	0.033	420	170	93	1	10	-94
14	12.9	0.18	0.031	420	190	139	6	15	+17

negative stress is compressive positive stress is tensile.

As can be seen from the results of Table IV the best hardness properties as-plated and after heating to 450 and 600°C and the best ductility properties were obtained with manganese contents of at least 0.1% using current densities of at least 8.6 A/dm². The samples G and H which both contained less manganese than the stoichiometric amount necessary to form manganese sulphide with the sulphur present had low as-plated and retained hardness and poor retained ductility.

A further suitable electrolyte is the high chloride electrolyte used in the following Example V.

Example V.

A conventional high chloride electrolyte was used containing in aqueous solution:

Nickel Sulphate NiSO ₄	280 g/l	20
Nickel Chloride NiCl ₂	75 g/l	
Boric Acid H ₃ BO ₃	40 g/l	
Saccharin Sodium	0.25 g/l	
Manganese Sulphate as Mn ²⁺	12 g/l	

Experimental details were the same as for Example II and the electroformed samples 15—17 made according to the invention and J and K outside the invention gave the results shown in the following Table V.

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TABLE V

Sample	Current Density (A/dm ²)	Wt. %Mn	Wt. %S	Hardness (HV)			Ductility		Stress (N/mm ²)
				as-plated	22 hours at 450°C	18 hours at 600°C	22 hours at 450°C	18 hours at 600°C	
J	4.3	0.03	0.027	274	130	122	0	0	-42
K	6.5	0.05	0.030	410	174	95	0	0	-55
15	8.6	0.09	0.030	420	185	100	2	7	-46
16	10.8	0.08	0.029	424	185	100	3	7	-49
17	12.9	0.14	0.032	432	169	142	5	10	-32

negative stress is compressive positive stress is tensile.

As can be seen from the results for samples 15 to 17 in Table V, at constant manganese and saccharin sodium concentrations, the manganese in the electroform, hardness as-plated and after heating at 450 and 600°C, and resistance to embrittlement when heated at 450 and 600°C, all improved with increasing current density reaching an optimum at current densities of at least 8.6 A/dm² and at manganese contents of at least 0.1%. The samples J and K containing less manganese than the stoichiometric amount necessary to form manganese sulphide with the sulphur present, had generally poorer retained hardnesses and ductility than the samples 15 to 17.

As can be seen from the results of Examples 1 to V satisfactory resistance to embrittlement at temperatures in excess of 200°C is obtained with articles according to the invention, con-

sisting of or including electrodeposits made from electrolytes operated in the range of 4.3 to 12.9 A/dm², preferably 6.5, 8.6 or 10.8 to 12.9 A/dm², with the manganese ion concentration conveniently in the range of from 12 to 20 g/l. In general increasing the manganese concentration in the electrolyte allows satisfactory manganese contents, preferably at least 0.1% to be incorporated in the electrodeposit at lower current densities whilst still obtaining satisfactory resistance to embrittlement at temperature in excess of 200°C.

Although the invention allows the production of articles consisting of, or having as an outer surface, electrodeposits, for any application in which resistance to abrasion, to wear and to embrittlement at temperatures in excess of 200°C, is desirable, such as for electroformed dies and moulds for the production of aluminium and zinc die castings, the in-

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vention is particularly suitable for the production of electroformed screen printing cylinders. Customarily screen printing cylinders are electroformed so that a nickel coating, nominally 100 to 200 microns thick, is applied to a cylindrical mandrel part immersed and rotated in the electrolyte. To improve the hardness and thereby the abrasion resistance of the cylinder and to enable it to be removed from the mandrel organic stress reducing agents have to be used which introduce sulphur into the electroform. This sulphur content causes the electrodeposit to have a compressive stress which facilitates separation from the mandrel but leads to embrittlement if the cylinder is heated to temperatures in excess of 200°C.

Because of this lack of resistance to embrittlement such cylinders must be fabricated at temperatures considerably below 200°C and this restricts the type of photoresist masking lacquers suitable and prevents end pieces being attached in any way other than by gluing. On the contrary screen printing cylinders produced according to the invention have lessened embrittlement when exposed to temperatures in excess of 200°C. Because of this such cylinders can safely be subjected to higher furlishing temperatures, allowing the use of more effective lacquers with higher curing temperatures, of more effective glues with higher curing temperatures, or even allowing the end plates to be attached by welding or brazing. Furthermore such cylinders can be repaired using welding and brazing techniques.

Other applications of the invention are for the production of hard resistant nickel coatings which require to be readily repairable by welding or brazing, such as mould or die faces.

WHAT WE CLAIM IS:—

1. An article consisting of, or having as an outer layer, a hard sulphur-containing nickel electrodeposit exposed in use or manufacture to temperatures exceeding 200°C, the electrodeposit containing, by weight, from 0.007 to 1% sulphur and sufficient manganese, in the range of from 0.02 to 5%, in excess of the stoichiometric amount necessary to form manganese sulphide with the sulphur, to improve embrittlement resistance of the electrodeposit at temperatures exceeding 200°C.

2. An article according to claim 1, in which the electrodeposit contains from 0.03 to 3.5% manganese.

3. An article according to claim 1 or claim 2, in which the electrodeposit contains from 0.07 to 0.35% manganese.

4. An article according to any one of claims

1 to 3, in which the electrodeposit contains from 0.1 to 0.25% manganese.

5. An article according to any one of claims 1 to 4, in which the electrodeposit contains from 0.02 to 0.065% sulphur.

6. An article according to any one of claims 1 to 5, in which the electrodeposit contains manganese in an amount at least 0.03% in excess of the stoichiometric amount.

7. An article according to any one of claims 1 to 6, in which the electrodeposit contains iron and/or cobalt.

8. An article according to claim 1, in which the electrodeposit is substantially as hereinbefore described with reference to any one of Examples I to V.

9. An article according to claim 1 in the form of a screen printing cylinder.

10. Method of producing the electrodeposit of the article according to claim 1, in which sulphur, nickel and manganese are co-deposited from an electrolyte containing a source of nickel ions, a source of sulphur and a source of manganese ions.

11. Method according to claim 10, in which the source of nickel ions is nickel sulphate or nickel sulphamate with or without nickel chloride.

12. Method according to claim 10 or claim 11, in which the source of sulphur is an aryl compound containing a functional sulphonate group.

13. Method according to any one of claims 10 to 12, in which the source of sulphur is O-benzoic sulfimide sodium salt.

14. Method according to any one of claims 10 to 13, in which sufficient source of sulphur is used to give a free sulphur content in the electrolyte of from 0.01 to 0.065 grammes per litre.

15. Method according to any one of claims 10 to 14, in which the electrolyte contains 2 butyne 1:4 diol.

16. Method according to any one of claims 10 to 15, in which the source of manganese ions is one or more of manganese sulphamate, manganese sulphate and manganese chloride.

17. Method according to claim 16, in which the electrolyte contains sufficient of the source of manganese ions to give a manganese ion content of 12 to 20 grammes per litre.

18. Method according to any one of claims 10 to 17, in which the electrolyte is operated at a current density in the range of from 2.7 to 20 amperes per square decimetre.

19. Method according to any one of claims 10 to 18, in which the electrolyte is operated at a current density in the range of from 4.3 to 12.9 amperes per square decimetre.

20. Method according to claim 10, substantially as hereinbefore described with reference to any one of Examples I to V.

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vention is particularly suitable for the production of electroformed screen printing cylinders. Customarily screen printing cylinders are electroformed so that a nickel coating, nominally 100 to 200 microns thick, is applied to a cylindrical mandrel part immersed and rotated in the electrolyte. To improve the hardness and thereby the abrasion resistance of the cylinder and to enable it to be removed from the mandrel organic stress reducing agents have to be used which introduce sulphur into the electroform. This sulphur content causes the electrodeposit to have a compressive stress which facilitates separation from the mandrel but leads to embrittlement if the cylinder is heated to temperatures in excess of 200°C.

Because of this lack of resistance to embrittlement such cylinders must be fabricated at temperatures considerably below 200°C and this restricts the type of photoresist masking lacquers suitable and prevents end pieces being attached in any way other than by gluing. On the contrary screen printing cylinders produced according to the invention have lessened embrittlement when exposed to temperatures in excess of 200°C. Because of this such cylinders can safely be subjected to higher furbishing temperatures, allowing the use of more effective lacquers with higher curing temperatures, of more effective glues with higher curing temperatures, or even allowing the end plates to be attached by welding or brazing. Furthermore such cylinders can be repaired using welding and brazing techniques.

Other applications of the invention are for the production of hard resistant nickel coatings which require to be readily repairable by welding or brazing, such as mould or die faces.

WHAT WE CLAIM IS:—

1. An article consisting of, or having as an outer layer, a hard sulphur-containing nickel electrodeposit exposed in use or manufacture to temperatures exceeding 200°C, the electrodeposit containing, by weight, from 0.007 to 1% sulphur and sufficient manganese, in the range of from 0.02 to 5%, in excess of the stoichiometric amount necessary to form manganese sulphide with the sulphur, to improve embrittlement resistance of the electrodeposit at temperatures exceeding 200°C.

2. An article according to claim 1, in which the electrodeposit contains from 0.03 to 3.5% manganese.

3. An article according to claim 1 or claim 2, in which the electrodeposit contains from 0.07 to 0.35% manganese.

4. An article according to any one of claims

1 to 3, in which the electrodeposit contains from 0.1 to 0.25% manganese.

5. An article according to any one of claims 1 to 4, in which the electrodeposit contains from 0.02 to 0.065% sulphur.

6. An article according to any one of claims 1 to 5, in which the electrodeposit contains manganese in an amount at least 0.03% in excess of the stoichiometric amount.

7. An article according to any one of claims 1 to 6, in which the electrodeposit contains iron and/or cobalt.

8. An article according to claim 1, in which the electrodeposit is substantially as hereinbefore described with reference to any one of Examples I to V.

9. An article according to claim 1 in the form of a screen printing cylinder.

10. Method of producing the electrodeposit of the article according to claim 1, in which sulphur, nickel and manganese are co-deposited from an electrolyte containing a source of nickel ions, a source of sulphur and a source of manganese ions.

11. Method according to claim 10, in which the source of nickel ions is nickel sulphate or nickel sulphamate with or without nickel chloride.

12. Method according to claim 10 or claim 11, in which the source of sulphur is an aryl compound containing a functional sulphonate group.

13. Method according to any one of claims 10 to 12, in which the source of sulphur is O-benzoic sulfimide sodium salt.

14. Method according to any one of claims 10 to 13, in which sufficient source of sulphur is used to give a free sulphur content in the electrolyte of from 0.01 to 0.065 grammes per litre.

15. Method according to any one of claims 10 to 14, in which the electrolyte contains 2 butyne 1:4 diol.

16. Method according to any one of claims 10 to 15, in which the source of manganese ions is one or more of manganese sulphamate, manganese sulphate and manganese chloride.

17. Method according to claim 16, in which the electrolyte contains sufficient of the source of manganese ions to give a manganese ion content of 12 to 20 grammes per litre.

18. Method according to any one of claims 10 to 17, in which the electrolyte is operated at a current density in the range of from 2.7 to 20 amperes per square decimetre.

19. Method according to any one of claims 10 to 18, in which the electrolyte is operated at a current density in the range of from 4.3 to 12.9 amperes per square decimetre.

20. Method according to claim 10, substantially as hereinbefore described with reference to any one of Examples I to V.

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For the Applicants,
R. J. BOUSFIELD,
Chartered Patent Agent,
Thames House, Millbank,
London, S.W.1.

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