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Studies on the electrodeposition of nickel from a Watts' bath in the presence of sodium naphthalene-2-sulphonate and acrylamide additives

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It has been possible to obtain very bright, smooth electrodeposits of nickel from a Watts' bath using a combination of sodium naphthalene-2-sulphonate and acrylamide additives. The electroplates obtained in the presence of sodium naphthalene-2-sulphonate alone and those in the presence of a combination with acrylamide have been examined for their surface roughness, surface topography, sulphur content and various other properties. The results show that the additives modify the structure and surface topography of the deposits to a large extent while producing smooth deposits without a preferred orientation.

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1. Introduction

The electroplating of bright nickel from a Watts' bath in the presence of certain organic additives has been the subject of many studies [1–11]. The conventional classification of these additives into two broad groups, i.e. control agents (or class I brighteners) and levellers (or class II brighteners) rests on their different roles in the bright plating process. It is a well recognized fact that in order to obtain a satisfactory brightening effect a combination of two additives belonging to each of these two groups is necessary. In fact a large number of effective combinations of brighteners belonging to these two classes have been used with satisfactory results [12–22] yielding bright deposits varying in brightness, lusture, and other mechanical and chemical properties. Many recent publications also deal with the role of additives in bright nickel plating from the standpoints of levelling [23], grain size and structural modifications [2, 4, 5, 7–9, 24, 25] and internal stress.

In the present work, we have studied the brightening effect produced on nickel electroplates by a new brightener formulation containing two such additives, i.e. sodium naphthalene-2-sulphonate and acrylamide, a combination which has not been tried previously and which is relatively less costly than conventional combinations. Apart from judging the surface brightness visually, the study also includes measurement of surface roughness of the deposits and examination of the surface topography by scanning electron microscopy (SEM). An attempts has also been made to determine the sulphur content of the deposit by electron microprobe analysis and to examine the effect of these additives on the grain size as well as the preferred orientation of the crystal faces by X-ray studies.

2. Experimental details

The composition and pH of the Watts' bath used, excluding additives, were as follows:

Nickel sulphate ($NiSO_4 \cdot 7H_2O$)	300 g l^{-1}
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	43 g l^{-1}
Boric acid	30 g l^{-1}
Sodium lauryl sulphate	0.25 g l^{-1}
pH	4.3

For preparing the bath, purified chemicals were used and the electrolyte was further purified by low current density electrolysis. Sodium naphthalene-2-sulphonate was prepared by the method of Vogel [26] and was purified by recrystallization from water. Acrylamide (SD laboratory reagent grade) was purified by recrystallization from chloroform. The purified

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compound was stored in a vacuum desiccator in the dark prior to use.

The electroplating cell was a cylindrical vessel of 5 cm diameter. Mild steel rods of 5 mm diameter were used as the cathode and a nickel sheet of 99.5% purity was used as the anode. The anode was held touching the walls of the vessel surrounding the cathode and the cathode was positioned at the centre of the plating cell. The cathode was mechanically polished successively with different grades of emery paper, degreased with benzene and then washed with acetone, tap water and finally distilled water. It was then dipped in 10% hydrochloric acid for a few seconds and then washed successively with tap water and distilled water. It was then immediately mounted into the plating cell.

To obtain electroplates for studying smoothness by profilometer and SEM and for determining the sulphur content by electron microprobe analysis, the samples were plated at 55° C at a current density of 5.2 A dm^{-2} for 30 min. The surface roughness of the electroplates was measured by a type QA Profilometer Amplimeter (Micrometrical Manufacturing Company, Michigan, USA). The surface topography was examined by a model ISI-60 (International Scientific Instruments, Inc., California) scanning electron microscope. The sulphur content of the electroplates was determined by a Map II Electron Microprobe Analyser (Russian make). X-ray diffraction studies were carried out by taking photographs of the diffraction pattern on flat films following the method of Denise and Leidheiser [24] with slight modification. The specimen electroplate was about 32 μm thick, plated on a cylindrical mild steel rod which was slightly flattened on one side parallel to its length. Copper radiation from a Philips X-ray source (type 1008/20 NR D702 made in Holland) was used without any filter [24] and a specimen to film distance of 2 cm was maintained.

3. Results and discussion

The optimum plating conditions for obtaining the brightest deposit was fixed more or less by trial and error. The main factor determining the brightness was the concentration of sodium naphthalene-2-sulphonate in the electrolytic bath; the higher the concentration of this compound, the better the brightening effect. Since the ultimate concentration achievable was limited by the solubility of the compound, a higher bath temperature was desirable. However, the bath temperature was fixed at 55° C which is in the middle of the temperature range (45–65° C) within which a Watts' bath is known to function satisfactorily. At this temperature, the concentration of sodium naphthalene-2-sulphonate in the bath could be increased to 2.3 $\mathrm{g\,l^{-1}}$. Other variables such as the concentration of acrylamide and the current density employed were fixed solely by trial and error. A summary of these experiments is given in Table 1.

It was found from the experimental runs that very bright plating, without any imperfections, were possible only when both the additives were present, and moreover, depending on the relative concentration of each, there was an optimum range of current density which gave the best results, both very low and very high current densities being unfavourable.

The electroplates obtained under these optimum plating conditions (run Nos. 3, 4, 7, 8, 14–16, 22–24, 32, 33) were not only extremely shiny but also smooth. This conclusion was confirmed from a study of the surface topography by SEM (Fig. 1d) and surface roughness measurements (Table 2). These studies further demonstrate the synergetic effect of both the additives whose combined presence produces a very smooth lamellar deposit having a minimum surface roughness. The surface SEM pictures of electroplates obtained under different conditions resulting from the presence and absence of additives (Fig. 1) are quite revealing in spite of the fact that they were taken at relatively low magnification. There are several interesting points about these pictures.

(a) Electroplates obtained from a pure Watts' bath without any additive are rough (Fig. 1a).

(b) When only sodium naphthalene-2-sulphonate is added to such a bath, there is a distinct change in the structure (Fig. 1b and c) which is mostly a field oriented isolation (FI) type spongy growth with a few scattered depressions some of which are quite deep. Fig. 1c shows one such depression with evidence of fresh nucleation. Such a growth pattern obviously does not continue beyond a certain stage. This may be due to the fact that the adsorption of the additive on the projections

Table 1. Exploratory electrodeposition of nickel on mild steel from a Watts' bath using sodium naphthalene-2-sulphonate and acrylamide as additives
Temperature: 55° C; plating time: Variable (19–150 min) adjusted to obtain a constant plating thickness of about 32 μm

Run No.	*Concentration of sodium naphthalene-2-sulphonate* (g l^{-1})	*Concentration of acrylamide* (g l^{-1})	*Current density* (A dm^{-2})	*Nature of the deposit*
1	0	0	5.2	Dull
2	2.3	–	5.2	Brighter than Run 1
3	1.3	0.5	1.1	Very bright without any imperfections
4	1.3	0.5	2.1	Very bright without any imperfections
5	1.3	0.5	3.1	No uniform brightness (mixed with dull areas)
6	1.3	0.5	4.2	No uniform brightness (mixed with dull areas)
7	2.3	0.5	1.1	Very bright without any imperfections
8	2.3	0.5	2.1	Very bright without any imperfections
9	2.3	0.5	3.1	No uniform brightness (mixed with dull areas)
10	2.3	0.5	4.2	No uniform brightness (mixed with dull areas)
11	2.3	0.8	1.1	Bright but black in colour
12	2.3	0.8	2.1	Very bright with occasional black stains
13	2.3	0.8	3.1	Very bright with occasional black stains
14	2.3	0.8	4.2	Very bright without any imperfections
15	2.3	0.8	5.2	Very bright without any imperfections
16	2.3	0.8	6.3	Very bright without any imperfections
17	2.3	0.8	7.3	No uniform brightness (mixed with dull areas)
18	2.3	0.8	8.4	No uniform brightness (mixed with dull areas)
19	2.3	1.2	1.1	Bright but black in colour
20	2.3	1.2	2.1	Very bright with occasional black stains
21	2.3	1.2	3.1	Very bright with occasional black stains
22	2.3	1.2	4.2	Very bright without any imperfections
23	2.3	1.2	5.2	Very bright without any imperfections
24	2.3	1.2	6.3	Very bright without any imperfections
25	2.3	1.2	7.3	No uniform brightness (mixed with dull areas)
26	2.3	1.2	8.4	No uniform brightness (mixed with dull areas)
27	2.3	1.5	1.1	Bright but black in colour
28	2.3	1.5	2.1	Very bright with occasional black stains

Table 1. (Continued)

Run No.	*Concentration of sodium naphthalene-2-sulphonate* (g l^{-1})	*Concentration of acrylamide* (g l^{-1})	*Current density* (A dm^{-2})	*Nature of the deposit*
29	2.3	1.5	3.1	Very bright with occasional black stains
30	2.3	1.5	4.2	Very bright with occasional black stains
31	2.3	1.5	5.2	Very bright with occasional black stains
32	2.3	1.5	6.3	Very bright without any imperfections
33	2.3	1.5	7.3	Very bright without any imperfections

retards the growth of such quick growing areas and result in an FI type of growth which then fills up most of the depression.

(c) When, in addition to sodium naphthalene-2-sulphonate, acrylamide is added to the bath (class II brightener), the surface topography undergoes a striking change; an extremely smooth lamellar deposit results (Fig. 1d).

The sulphur content of the electroplates as studied by electron microprobe analysis is shown

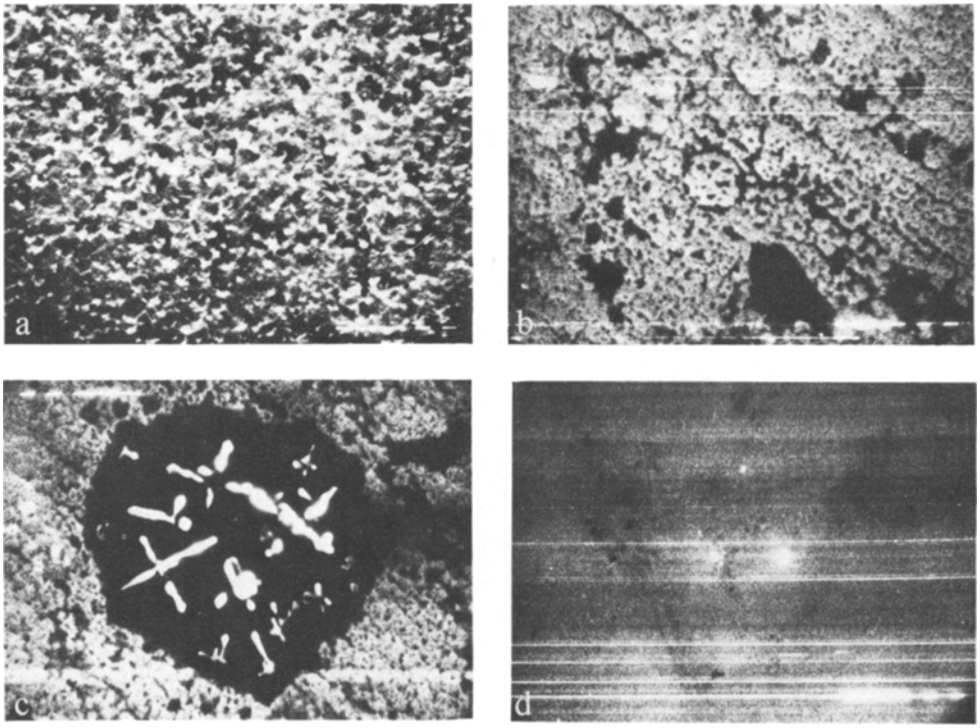

Fig. 1. Scanning electron microscope photographs of the electroplates obtained in the presence and absence of additives from a Watts' bath. (a) Electroplate from a Watts bath with no additives (Run 1). X 1110. (b) and (c) Electroplate from a Watts' bath with sodium naphthalene-2-sulphonate as the additive (Run 2). X 1110. (d) Electroplate from a Watts' bath with sodium naphthalene-2-sulphonate and acrylamide as additives (Run 15). X 1120.

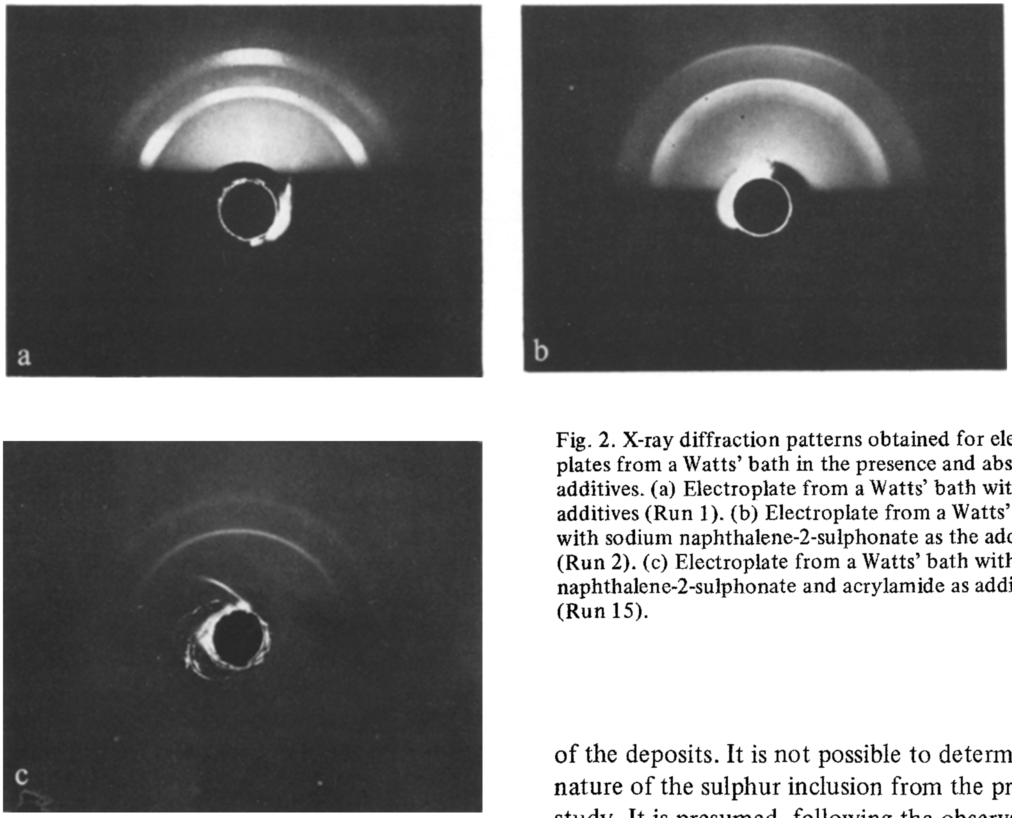

Fig. 2. X-ray diffraction patterns obtained for electroplates from a Watts' bath in the presence and absence of additives. (a) Electroplate from a Watts' bath with no additives (Run 1). (b) Electroplate from a Watts' bath with sodium naphthalene-2-sulphonate as the additive (Run 2). (c) Electroplate from a Watts' bath with sodium naphthalene-2-sulphonate and acrylamide as additives (Run 15).

in Table 3. It is found that the sulphur content of the electroplate increases with the addition of the brighteners, and is at a maximum when both additives are used, a condition which is also necessary for obtaining smooth and bright deposits. These findings are in agreement with similar observations made earlier [27–29] and support the view that some correlation exists between the sulphur content and the smoothness or brightness of the deposits. It is not possible to determine the nature of the sulphur inclusion from the present study. It is presumed, following the observations of Hoekstra and Trivich [30], that the sulphur is present as S^{2-}. The electron microprobe analysis, however, indicates that the sulphur is uniformly distributed. This could be due to the fact, as suggested earlier [25], that the sites of codeposition of 'control agent products' are very close to each other particularly in the presence of the leveller, acrylamide.

Table 2. The surface roughness (rms) values of the electroplates obtained at 55° C with a current density of 5.2 A dm^{-2}

Run No.	*Nature of the bath*	*Surface roughness* (rms) (μm)
1	Watts'	0.356
2	Watts' + sodium naphthalene-2-sulphonate	0.165
15	Watts' + sodium naphthalene-2-sulphonate + acrylamide	0.064

The X-ray diffraction photographs are presented in Fig. 2. Although these were not taken under ideal conditions, they show that there is a distinct change in the grain size as well as the preferred orientation in electroplates obtained in the presence and absence of brighteners. In the absence of any brightener, the diffraction rings are spotty in nature and show intensity maxima in both (1 1 1) and (2 0 0) rings at positions which are in agreement with those obtained by earlier workers [24]. These features indicate a grain size greater than 10^{-2} mm and a (1 0 0) preferred orientation. The addition of sodium naphthalene-2-sulphonate, a class I brightener, results in a diffraction pattern which is not only devoid of spots but is also associated with a marked reduction in the vari-

Table 3. Sulphur content of the electroplates obtained at 55° C with a current density of 5.2 A dm^{-2}

Run No.	*Typical counts*	*Average counts for the standard (FeS)*	*Percentage of sulphur by weight*
1	67, 50, 56, 62, 54, 51	17 906	0.002
2	84, 76, 65, 80, 66	17 906	0.037
15	108, 104, 111, 91, 99, 104, 85, 101, 91, 94	17 844	0.129

ation of intensity over both (1 1 1) and (2 0 0) rings. These are indicative of the fact that there is a reduction in grain size as well as preferred orientation. The presence of both sodium naphthalene-2-sulphonate and acrylamide in the bath brings about a marked change in the structure of the electroplate. Preferred orientation seems to be almost non-existent and the grain sizes are definitely less than 10^{-2} mm.

4. Conclusions

1. It is possible to obtain highly bright and smooth electrodeposits of nickel from a Watts' bath using a combination of sodium naphthalene-2-sulphonate and acrylamide as additives.

2. In agreement with earlier observations in similar systems the additives cause a significant change in the surface topography of the deposit as well as its grain size in addition to the reduction in the preferred orientation of the deposits.

3. The sulphur content of the deposit is found to increase in the presence of the additives but the sulphur seems to be uniformly distributed indicating that its codeposition sites are very close to each other.

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