

Effect of the structure of aromatic disulphides on some physico-mechanical properties of electrodeposited copper coatings

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The effect of a series of disulphides (diphenyl, dibenzyl, dinaphthyl and di(naphthylmethyl) with sulpho, dimethylamino, hydroxy or oligoethoxylated hydroxy substituents) on the physico-mechanical properties (ductility, tensile strength, microhardness, brightness and levelling) of copper coatings deposited from sulphuric acid electrolytes has been studied. The amount of codeposited carbon and sulphur was also measured. The aromatic disulphides generally gave coatings of better quality than those obtained in the presence of aliphatic disulphides studied previously. Strongly enhanced ductility (up to 40%) and reflectivity (~80%) were achieved in the presence of dimethylamino derivatives. The ductility of the coatings, in contrast to the tensile strength, appears to be correlated to the amounts of codeposited carbon and sulphur.

1. Introduction

The addition of organic compounds to sulphuric acid copper electrolytes can have a very substantial effect on the properties of the deposits. Mirror-brightness, high levelling, low internal stress of the coatings, as well as stability on use, are among the properties sought. Organic disulphides containing hydrophilic substituents have proved to be among the most widely used components of brightening agents [1-5].

Recently the requirements towards physico-mechanical properties such as ductility, tensile strength and microhardness have become more demanding and this has led to a search for new and more effective organic addition agents. Simpler and cheaper electrolytes, as well as regard for environmental factors, are now under consideration and scrutiny.

This work is concerned with the effect of a series of diaryl or diarylmethyl disulphides, listed in Scheme 1, on the ductility, tensile strength, microhardness, reflectivity and levelling of copper coatings, as well as the inclusion of carbon and sulphur. The compounds chosen comprise benzene and naphthalene derivatives with anionic (sulpho), cationic (dimethylamino) and neutral substituents (hydroxy or oligoethoxylated hydroxy). The possibility of using these compounds as alternative components to dyes in brightening agents, has also been discussed.

2. Experimental details

2.1. Materials

All inorganic reagents were of AR grade and were used without further purification. Commercial poly-

ethyleneglycol (m.w. 3000) was used. The sodium salt of m-benzenedisulphonic acid was prepared according to [6]. The preparation and purity of the disulphides is described in [4] and [7].

2.2. Physico-mechanical properties

Samples of the coatings were obtained in a bath of 7 dm⁻³ electrolyte containing 80 dm⁻³ of CuSO₄ · 5H₂O, 180 g dm⁻³ of sulphuric acid, 0.05 g dm⁻³ sodium chloride, 1 g dm⁻³ of m-benzenedisulphonic acid and 16 g dm⁻³ of polyethyleneglycol, further designated as the basic electrolytes, BE, to which 0.022 g dm⁻³ of the aromatic disulphide studied were added. The cathode current density was 2.5 A dm⁻² and the electrolyte was kept at room temperature. Elliptical (70 mm × 35 mm) phosphor (0.04-0.07%) alloyed copper bars were used as anodes.

A copper coating, 40 μm thick, was deposited on a stainless steel cathode (180 mm × 85 mm). The coating could be readily sheared and its reflectivity (*B*) and its microhardness (*HV*) were determined. The tensile strength (*σ*) and the relative elongation (ductility) were measured on twelve spade-shaped foil samples at a stretch rates of 100 mm min⁻¹ and *P* of 50 kg. The same foil was also used to obtain samples for carbon and sulphur analysis by means of an automatic LECO IR 32 (USA) spectroscope-analyser by a standard procedure [8].

2.3. Levelling

The levelling capacity (*L*) was measured by means of a profilograph-profilometer 'Perthen' (Germany) on 20 μm thick copper coatings deposited on a cathode

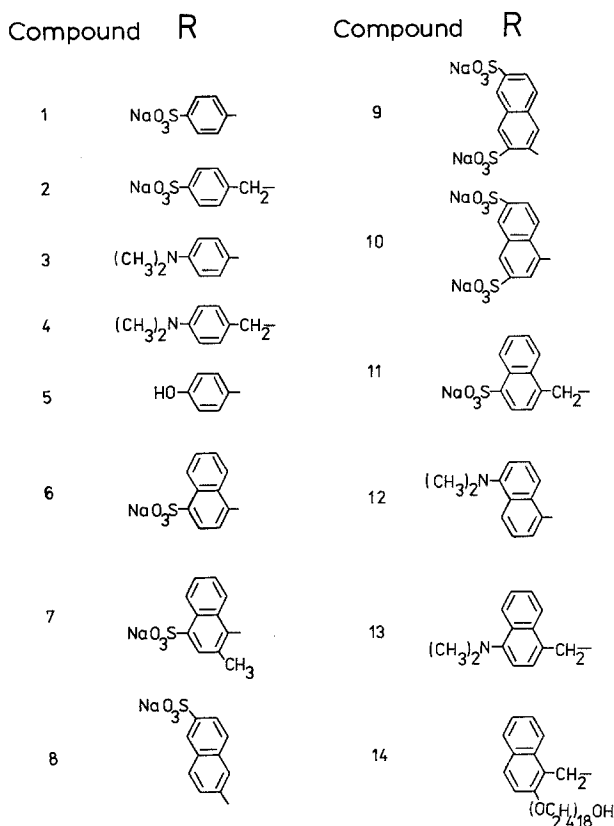


Fig. 1. Scheme showing list of aromatic disulphides, R_2S_2 . (R = compound displayed).

(20 mm \times 10 mm), cut from an unmodulated nickel gramophone-record matrice with troughs 30 μ m deep with an edge angle of 90°. L was obtained as the mean of five measurements over intervals 5 mm long and calculated as

$$L = \frac{d_2 - d_1}{h} \times 100$$

where d_2 and d_1 are the thickness of the copper coating at the bottom of the trough and on the flat portion of the matrix, respectively, and h is the the initial depth of the trough.

3. Results and discussion

The data obtained on the properties of the coatings deposited in the presence of the disulphides of the Scheme (listed in Fig. 1) are presented in Table 1. Comparison of the effect of these compounds on the ductility of the coatings with that of samples obtained only in the presence of dialkyl disulphides or in the presence of additives containing both dialkyl disulphides and phenazine dyes, studied previously [9], showed that most of the diaryl disulphides give rise to greater residual elongations. Further, while combinations of dialkyl disulphides and dyes gave bright coatings of good quality, in the presence of $(NaO_3S(CH_2)_n)_2S_2$, with $n = 1$ to 4, alone, the coatings were not only opaque, but also uneven, roughly crystalline and with a considerable variation in thickness. In the cases of less accessible zones, such as the holes in printed circuits, no coating was observed.

A general survey of the data in Table 1 indicates that the introduction to the electrolyte of diaryl or diarylmethyl disulphides can give rise to properties of the deposits which are of interest to microelectronics and other branches of industry. Another point of interest is that there is a correlation between the properties of the deposits and the amounts of included carbon and sulphur.

Thus the residual elongation of the foil obtained in the BE is 3% and this value remains practically unchanged in the presence of dialkyl disulphides (for example 3,3-dithiobispropanensulphonic acid). With the disulphides studied this value ranged from 3 to 16%.

Certain behaviour patterns show some regularity. With the two sulphonic acids 1 and 2, *p*-sulphophenyl and *p*-sulphophenylmethyl, respectively, the introduction of the methylene group in the second leaves the ductility unchanged, but some properties change abruptly: hardness is doubled, brightness is lost and the sulphur content increases considerably; tensile strength and levelling change to some extent in opposite directions. With the naphthalenesulphonic acids 6 and 11 the difference is again only the 'intermediate' methylene group and the same change in properties is observed though less evidently. The series of five naphthalenesulphonic acids, 6–10, indicated no significant sensitivity to the position of the disulphide bridge, α or β , not to the position or number of sulpho groups. Compared to the benzenesulphonic acid 1, improved brightness, but poorer ductility (except 9) is obtained.

As far as applications are concerned, of greatest interest are the properties of the deposits obtained in the presence of the positively charged dimethylamino derivatives, 3 and 4 in the benzene series and 12 and 13 in the naphthalene series. With the former of each pair, the aromatic ring is directly attached to the disulfide bridge and these give deposits of very high residual elongation, 12 and 16%, respectively, accompanied by high microhardness. The introduction of an intermediate methylene group in 4 and 13, while not very favourable with regard to ductility, gives rise to brightness of the deposits which normally can only be achieved by the addition of dye components in such compositions. (It may be noted that the same structural change had the opposite effect on brightness with the sulphonic acids.)

Examples of aromatic disulphides with neutral substituents are the *p*-hydroxyphenyl derivative, 5, and the polyethoxylated naphthol derivative, 14. The former appeared very similar to the parent phenol, while in the latter the rather long polyglycol chain, necessary for solubility in water, dominated its properties.

A noteworthy observation is that increased $\Delta l/l$ in all cases is accompanied by increased C and S content (Fig. 2a), while no such relationship is observed between the tensile strength of the coatings and included carbon and sulphur (Fig. 2b).

In a previous paper [10] we studied the effect of the

Table 1. Properties of copper deposits obtained in the presence of 22 mg dm^{-3} diaryl or diarylmethyl disulphides

Compound	$\Delta l/l$ (%)	σ (kg mm^{-2})	HV (kg mm^{-2})	B (%)	L (%)	C (%)	S (%)
BE	3	9	115	6	4	9	4
phenol	7	4.2	132	27.7	-13.8	27	4
1	8	19.6	115	60.5	5	12	1.5
2	8	13.4	230	0	19	19	12
3	12	17.7	215	0	28	62	18
4	8	9.7	110	79.7	50	20	9
5	5	10.9	113	27.6	7	21	9
6	3	6.4	125	45.2	23	22	5
7	4	8.9	140	35.0	12	17	5
8	5	11.9	118	78.1	17	18	2
9	8	25.0	115	31.8	5	-	-
10	4	12.6	89	37.5	3	-	-
11	3	4.7	152	1.3	30	15	2
12	16	19.5	283	31.1	42	46	19
13	4	16.0	231	89.5	54	20	6
14	5	17.3	230	65.2	54	21	7

structure of the same disulphides on their electrochemical behaviour. The manner of their adsorption on copper and the degree of coverage of the cathode surface, in particular, depending on the kind of aromatic nucleus, type of substituent, or the presence of an intermediate methylene group, stand in a definite relationship to the physico-mechanical properties of the copper coatings.

Combinations of the above disulphides offer very good possibilities for improving the physico-mechanical properties of the copper coatings. Thus, for example, addition to the BE of di(5-dimethylaminonaphthyl) disulphid (12) and di(4-dialkylamino-1-naphthylmethyl) disulphide in certain ratios allows deposition of coatings with a residual elongation of 40%, retaining a mirror brightness (over 80%) and a levelling of about 60%, which is suitable for printed circuits. Similar combinations also give very high values of tensile strength ($38\text{--}40 \text{ kg mm}^{-2}$) and HV (over 250 kg mm^{-2}).

4. Conclusion

The organic sulphur compounds discussed in the present paper are promising materials for the preparation of sulphuric acid electrolytes used in the deposition of functional of functional copper coatings. The results indicate that with certain aryl or arylalkyl disulfides it is possible, contrary to the experience with alkyl disulphides, to obtain bright and reasonably level deposits without the addition of organic dyes. At the same time these compounds have favourable effects on other physico-mechanical properties of primary importance in microelectronics and other branches of industry: $\Delta l/l$, σ , HV . They permit values of these parameters to be obtained which cannot be achieved with commonly used brightening agents.

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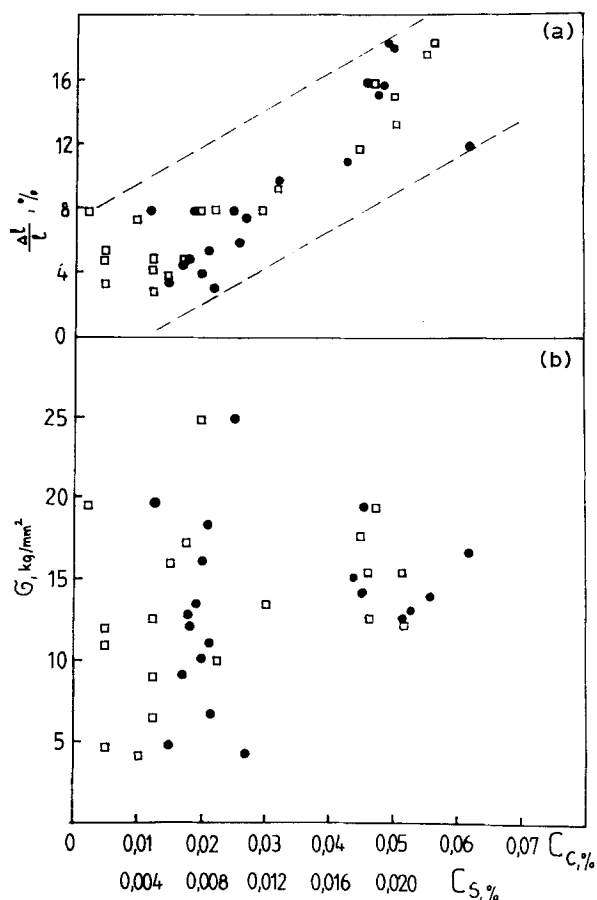


Fig. 2. (a) Dependence of the relative elongation, $\Delta l/l$, of copper coatings on the amount of codeposited carbon (●) and sulphur (□). (b) Dependence of the tensile strength, σ , of the copper coatings on the amount of codeposited carbon (●) and sulphur (□).

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