

# Anodic Synthesis of Sulfur-Bridged Polyaniline Coatings onto Fe Sheets

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## Synopsis

Sulfur-bridged polyaniline coatings are obtained onto Fe anodes by electrolyzing a basic solution of one aniline and ammonium sulfide. Their sulfur content ranges from 7% to 17%, depending on the substituents on aniline. Various substituted anilines may be polymerized in this way and coating pollution by azobenzene formed in a side reaction is almost completely avoided. Sulfur probably enters the polymer chains through a free radical mechanism, HS<sup>-</sup> intermediates being formed by both homogeneous and anodic oxidation of HS<sup>-</sup> anions. Coatings from *N*-allylaniline, being thermally curable, show satisfactory physical properties.

## INTRODUCTION

The anodic synthesis of polyaniline coatings onto Fe sheet has recently been presented in this journal.<sup>1</sup> Although aniline oxidation (chemical or electrochemical) to polymeric products (aniline black) is usually better achieved in sulfuric acid,<sup>2,3</sup> the process described was performed in alkaline water-methanol solutions. The use of aggressive acid media was in fact precluded since the main aim of the work was the *in situ* formation of corrosion protective films for Fe substrates. On the contrary, aniline oxidation was allowed at Fe anodes when natural passivation of Fe in an alkaline medium was further strengthened by the presence in solution of suitable Fe corrosion inhibitors such as allylamine or potassium chromate.<sup>1</sup> In this way, coherent homogeneous polyaniline films were obtained; however, the alkaline medium involved some disadvantages with regard to the chemical constitution of the products. Oxidative coupling of aniline to polymers was always paralleled by azobenzene formation: When using aniline as monomer, azobenzene content in the films might reach 10–20%, but with most nitrogen or ring substituted anilines (excluding nitroanilines) head-to-head coupling of anode radical intermediates prevailed over head-to-tail reaction (polymerization), practically inhibiting any *in situ* film formation.

The present work describes how, on simply performing aniline (and substituted anilines) anodization in the presence of sulfide ions, not only is the by-production of azobenzene removed, but remarkable favorable implications occur both in formation kinetics and in the chemical constitution of the films.

## EXPERIMENTAL

All the monomers used in this study, aniline and substituted anilines, were commercially available reagent grade chemicals. The electrolytic reaction

medium consisted of water-methanol mixtures containing fixed amounts of allylamine (0.50 mol/L) and cellosolve (ethyleneglycol monoethylether) (0.30 mol/L) and variable monomer and ammonium sulfide concentrations. The coating process was initially investigated on microscale by controlled potential techniques using either a rotating Fe disc (area = 0.031 cm<sup>2</sup>) or, for cyclic voltammetry, a stationary Fe microelectrode of the same area: in each case the reference electrode was an SCE. The coating runs were conversely performed by constant voltage (two electrodes) in an undivided cell, previously described,<sup>1</sup> using Fe sheet samples as anodes having useful dipped area = 25 cm<sup>2</sup>.

For determining the chemical constitution of the films, the material was recovered from the samples by suitable organic solvents and then submitted to various instrumental methods, including pyrolysis coupled with mass spectrometry.<sup>4</sup>

The physical properties of the films were determined according to ASTM procedures.

## RESULTS

### Voltametric Data

The behavior at rotating Fe ( $\omega = 1000$  r/min) of aniline (0.16 mol/L) in water-methanol (1:1 by vol) with allylamine (0.50 mol/L), cellosolve (0.30 mol/L), and KOH (0.10 mol/L), either in the presence (plain curve) or in the absence (dashed curve) of (NH<sub>4</sub>)<sub>2</sub>S (0.05 mol/L), is shown in Figure 1. It can be observed that, for the same sweep rate (83 mV/s), in both cases the current attains a maximum followed by fast decrease; the fact is related to the formation of insulating films, but the filming rate (or electric resistance of the forming film) is much higher in the presence of (NH<sub>4</sub>)<sub>2</sub>S. This datum is confirmed by Figure 2, which shows that on polarizing the Fe electrode at +1.0 V vs. SCE and re-

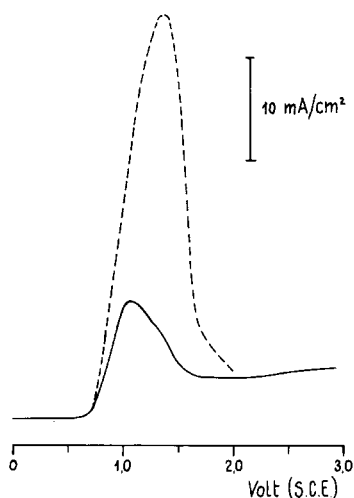


Fig. 1. Voltametric curves obtained at rotating Fe by anodizing aniline either in the presence (—) or in the absence (---) of sulfide ions.

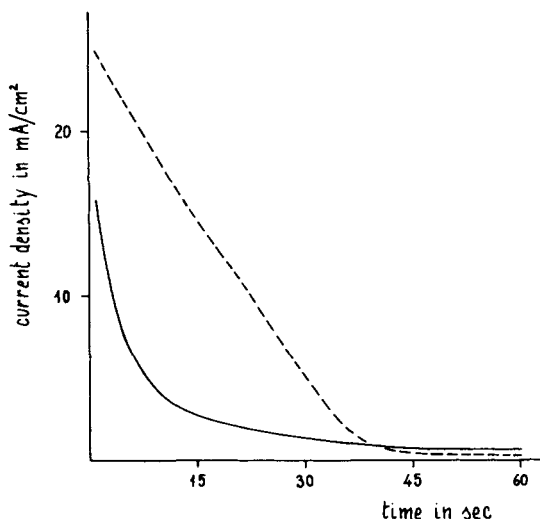


Fig. 2. Filming kinetics of a rotating Fe electrode polarized at +1.0 V (SCE) either in the presence (—) or in the absence (---) of sulfide ions.

current decrease against electrolysis time, a much faster drop is obtained when  $(\text{NH}_4)_2\text{S}$  is present in solution.

Figure 3 shows cyclic voltammetry patterns (sweep rate = 200 mV/s) obtained at stationary Fe using a water-methanol (1:1 by vol) solution containing aniline (0.54 mol/L), ammonium sulfide (0.087 mol/L), and allylamine (0.40 mol/L). The first anodic peak (from  $-0.40$  V on) is due to sulfide ions; in fact, this peak increases with ammonium sulfide concentration and its potential corresponds to data in the literature on sulfide oxidation at Fe in alkaline medium.<sup>5,6</sup> The

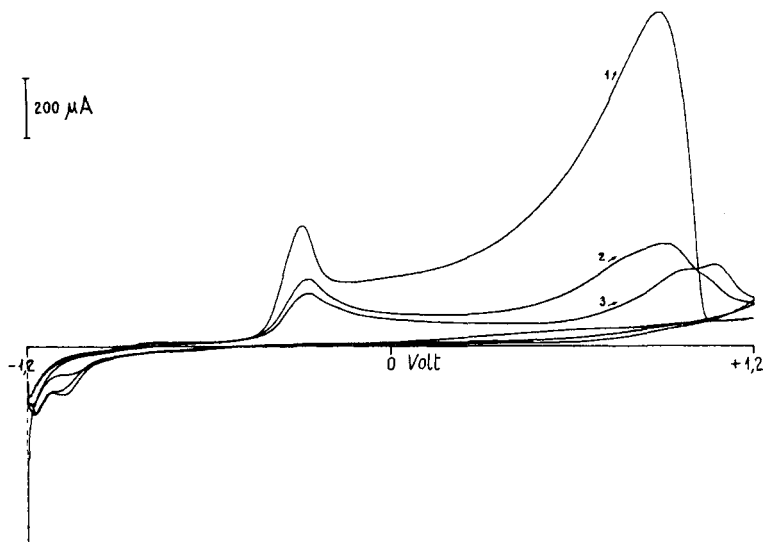


Fig. 3. Cyclic voltammetry patterns obtained at Fe from an aniline/ $(\text{NH}_4)_2\text{S}$  solution. (1) First potential scan; (2 and 3) subsequent potential scans without cleaning the electrode.

subsequent peak at a much more anodic potential is related to aniline oxidation. Although sulfides clearly oxidize before aniline, the insulation of the Fe electrode achieved by running successive potential scans (curves 2 and 3) in any case indicates very efficient organic filming.

### Coating Runs

The process of coating Fe sheets by anodizing aniline/ $(\text{NH}_4)_2\text{S}$  system exhibits some peculiarities with respect to the process using aniline alone. As well as faster insulation kinetics also resulting for the macroscale process (see Fig. 4), the following points must be made:

—Coating is not paralleled by formation of other colored products (e.g., azobenzene and tar) diffusing into the solution, which instead keeps stable and clear. (This holds true during repeated coating runs.)

—The films generally tolerate higher voltages better, although some black pits may form when potential differences  $\geq 8$ –10 V are applied. At the highest voltages,  $\text{H}_2\text{O}$  discharge may also become relevant.

—The films are pale in color.

—Coherent filming is obtained in any case by most substituted anilines, when at least one ortho or para position of the ring is free. For substituted anilines, filming kinetics are very close to those shown by aniline.

With regard to the coulombic yields (weight of material per charge passed), this ranges from 0.2 to 0.3 mg/C for the system aniline (0.54 mol/L) and ammonium sulfide (0.087 mol/L) by electrolysis voltages = 4–5 V. Such values generally decrease either for higher voltages applied or ammonium sulfide concentrations above 0.1 mol/L. Similar data are obtained using substituted anilines. Although the coulombic yields attained are about double those resulting in the absence of sulfide ions,<sup>1</sup> they do not reach 50% of the theoretical stoichiometry of head-to-tail aniline anodic coupling polymerization.

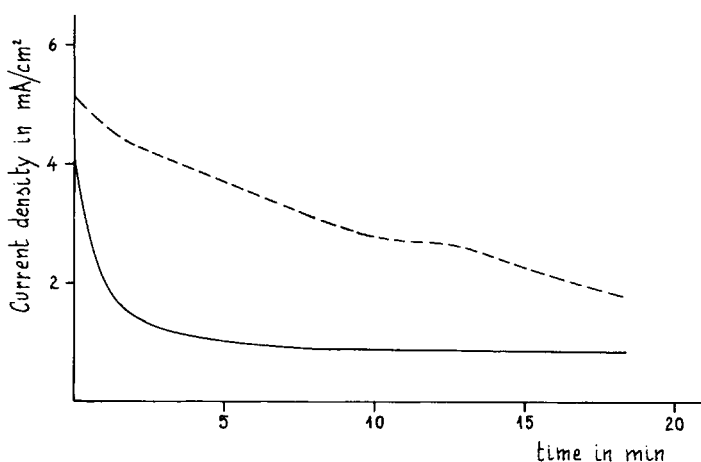


Fig. 4. Current decrease during anodization at Fe sheet anodes, under constant voltage applied (6.0 V), of aniline (0.54 mol/L) either in the absence (---) or in the presence (—) of  $(\text{NH}_4)_2\text{S}$  (0.087 mol/L).

### Constitution of the Coatings

**Elemental Analysis—Molecular Weight:** The coating material obtained from either aniline or substituted anilines is much more stable than the corresponding aniline black and may be handled without causing irreversible modifications. Thus it may be recovered by dissolution (acetone, DMF) from the sheet samples and then precipitated again by water: Such operations may be repeated without crosslinking or insolubilization of the product. Traces of entrapped sulfur were removed from the precipitates by washing with ammonium sulfide solutions (soluble polysulfides are formed this way<sup>7</sup>) and then distilled water. Having submitted the purified materials to elemental analysis and molecular weight determinations (by vapor pressure osmometry) the data reported in Table I were obtained. It is interesting to note here the following points:

—The oxidation product of mesidine was identified as 2,4,6,2',4',6'-hexamethylazobenzene on the basis of the data in Table I and its mass spectrum (electron impact, positive ions, 70 eV; 266 =  $M^+$  100%; 119 =  $C_9H_{11}$  80%; 147 =  $C_9H_{11}N_2$  25%; 223 25%; 251 18%).

—In contrast, all other coating samples are oligomeric in nature and contain variable amounts of sulfur. The presence of sulfur in the polymer network is the main reason for the discrepancies between the experimental and theoretical (based on monomer —2H, i.e., azo-derivative or polyaniline) compositions. A small oxygen content, already observed and interpreted in a previous paper as due to possible hydrolysis of imino groups,<sup>1</sup> also contributes to the overall compositions.

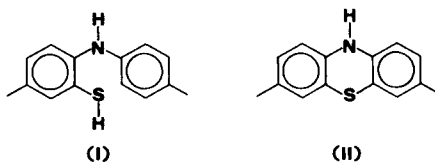
—The *N,N*-dimethylaniline oxidation product has the largest sulfur content among the coating samples analyzed.

—The sulfur content in the polymer is, at least for aniline, largely independent of sulfide concentration in solution. In other words, the entrance of sulfur into the polymer chains seems to take place very fast.

**Mass Spectra:** The mass spectrum of a sample obtained from the anodization of the aniline/ammonium sulfide system is shown in Figure 5. Many peaks are in common with those given by a polyaniline synthesized in the absence of sulfides; the main ones are the following:

$$\begin{array}{ll} m/e = 78 + n \cdot 91 & \text{with } n = 0, 1, 2, 3, 4 \\ m/e = 93 + n \cdot 91 & \text{with } n = 0, 1, 2, 3, 4 \\ m/e = 194 + n \cdot 91 & \text{with } n = 0, 1, 2, 3 \end{array}$$

However, most of these are coupled here to peaks having 30 or 32  $m/e$  units more, probably due to structures I and II:



On the contrary, for the same pyrolysis and mass fragmentation conditions (210°C, 70 eV), a mechanical mixture of aniline black and sulfur only gives signals typical of either polyaniline alone or elemental sulfur ( $m/e = n \cdot 32$  with  $n = 1-8$ ).

TABLE I  
Elemental Analysis and Molecular Weight Data of Coating Samples

Monomer	Monomer/sulfide in the electrolytic solution	Experimental composition			Theoretical composition <sup>a</sup>			$\bar{M}_n$
		C	H	N	C	H	N	
Aniline	6.2	70.12	5.02	13.06	79.12	5.49	15.38	510
Aniline	62.0	69.83	4.92	13.19	79.12	5.49	15.38	450
4-Toluidine	6.3	69.61	6.10	10.52	80.00	6.67	13.33	460
2,6-Dimethylaniline	16.6	72.51	6.91	10.05	80.67	7.56	11.76	560
3,5-Dimethylaniline	11.3	71.68	6.48	9.11	80.67	7.56	11.76	980
Mesidine	7.5	80.95	8.12	10.91	81.20	8.27	10.53	250
<i>N,N</i> -dimethylaniline	2.8	62.11	6.09	9.75	80.67	7.56	11.76	1400

<sup>a</sup> Calculated on composition of monomer-2H.

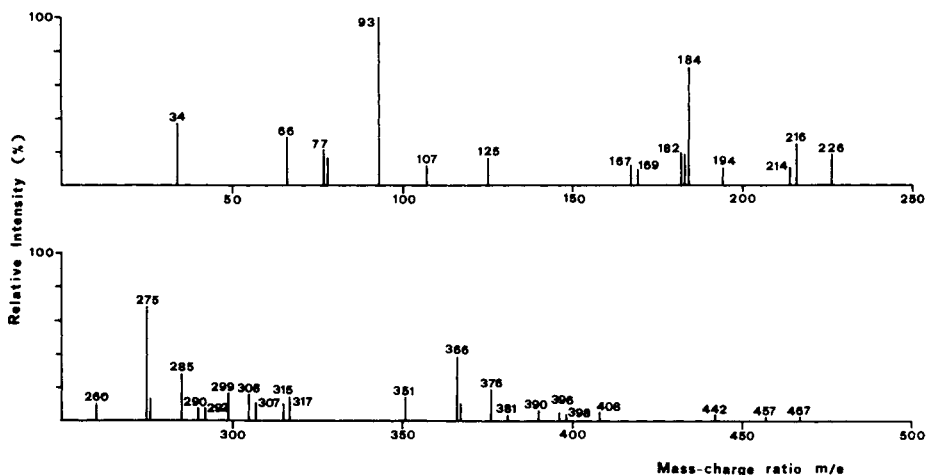


Fig. 5. Pyrolysis-mass spectrum of coating material obtained from aniline/ $(\text{NH}_4)_2\text{S}$  system.

It must, moreover, be mentioned that, fractionating a coating sample by adsorption chromatography over silica gel some characteristic products may be separated and then identified individually by mass spectrometry. Some of those were:

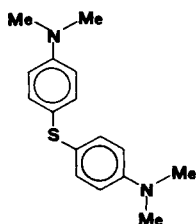
- (a) Very small amounts of azobenzene (from initial hydrazobenzene through air oxidation),
- (b) anilinoazobenzene:  $\text{M}^+$  at  $m/e = 273$ , intense peaks at 196 and 168.
- (c) the tetramer



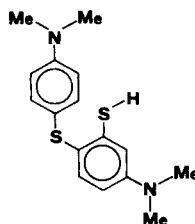
$\text{M}^+$  and  $m/e = 364$ ; intense peaks at 259 and 167; methastable peaks at 184.2 and 107.6.

The films given by substituted anilines generally lead again to similar pyrolysis-mass spectrometry fragmentation products which need not be discussed further. However, the data given by the oxidation product of *N,N*-dimethylaniline are peculiar: Figure 6 shows the mass spectrum. Here  $m/e = 240$  may be ascribed to tetramethylbenzidine, whereas any fragment for  $m/e > 250$  contains sulfur.

The following structures may therefore be identified:



$m/e = 272$



$m/e = 304$

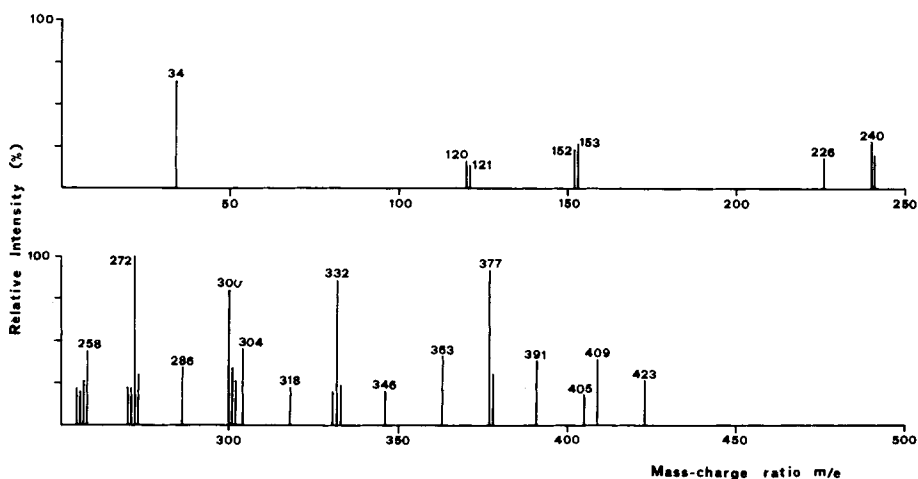
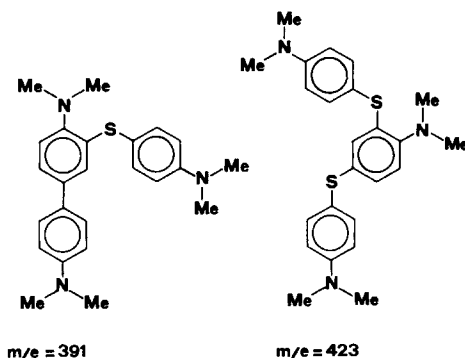


Fig. 6. Pyrolysis-mass spectrum of coating material obtained from *N,N*-dimethylaniline/ $(\text{NH}_4)_2\text{S}$  system.



All other peaks might come from these structures through successive transfers of methyl groups caused by pyrolysis.<sup>8</sup>

**Physical Properties:** As mentioned above, the color of films obtained from aniline and substituted anilines is not so deeply black as that typical for aniline polymers. The colors may range from pale brown (aniline) to yellow (*N,N*-dimethylaniline) or green (*N*-allylaniline). Most of the films are very soluble in organic solvents even when oven-dried at 100°C, although they generally darken on heating (oxidation of aniline units to quinoneimines). Higher insolubility is generally achieved with higher curing temperatures.

For aniline, as may be deduced from the fast current drop of Figure 4, indicating relatively low amounts of charge passed, film thickness achieved in 5–10 min is not more than 1–1.5  $\mu\text{m}$ . When dried in oven at  $\geq 120^\circ\text{C}$  for 20 min, these films exhibit some microporosity, fair adhesion, 3H hardness, and salt fog corrosion resistance ranging between 15 and 20 h. However, better results are obtained from *N*-allylaniline: here in fact allyl groups allow oxidative crosslinking with large molecular weight increase<sup>9</sup> at 150°C, whereupon the films become completely insoluble in any solvent. The film then exhibits reduced microporosity, 6H hardness, good adhesion, and salt fog corrosion resistance close to 80 h.



### Chemical Runs

To clarify better the reactivity of sulfides with anilines during the anodic process, some runs were performed to see both how these ions affect aniline oxidation performed by a chemical catalyst and how they interact with aniline oxidation intermediates.

**Polymerization of Aniline by CuCl/O<sub>2</sub> in the Presence of Ammonium Sulfide:** The well-known CuCl/O<sub>2</sub> redox couple,<sup>10</sup> according to the literature,<sup>11</sup> quantitatively converts aniline into azobenzene. Indeed by operating in pyridine at 70°C we obtained in this way azobenzene yields >90%.

Conversely, on dissolving 3 mL aniline and 0.088 g CuCl in 30 mL pyridine and refluxing this system at 70°C under O<sub>2</sub> with periodical additions of ammonium sulfide (in total 1.8 g), it turned out that the final production of azo- or hydrazobenzene (after 48 h) was not greater than 1%. In this way a tar was obtained which, once freed from elemental sulfur, gave the following composition: C = 58.69%, H = 4.22%, N = 10.42%, S = 13.76%. Its IR spectrum exhibits the main bands of an electrochemical sample: 1590s, 1510s, and 1490s (C=C stretching); 1130 m (Ph—N stretching); 110m; 1030m; 820m, 745s, and 690s (o.o.p. C—H bending). Mass spectrum instead gave only low *m/e* values, as often happens for compounds of relatively high molecular weight. An  $\bar{M}_n$  = 660 resulted from vapour pressure osmometry in DMF. However, deviations observed during this determination at high dilution suggest that the compound may bear many ionizable groups. Taking into account the probably high oxygen content, it also seem that some aniline-bound SH groups were further oxidized during polymerization. A successive oxidation run was carried out under the previous conditions but in the presence of hydrazobenzene (0.606 g) too: Table II shows how both aniline and hydrazobenzene disappeared during this run. The polymeric product obtained is similar to that resulting from the first experiment.

**Interaction of Ammonium Sulfide with *N,N'*-Diphenyl-*p*-Quinonediimine:** *N,N'*-diphenyl-*p*-quinonediimine, an intensely red molecule, may be used as a model compound for quinoneimine moieties of aniline black structure. Its quinone ring may be suitable for adding nucleophilic species through the mechanism typical of quinones.<sup>12</sup> Therefore, on dissolving this compound in ethanol-pyridine, it was observed that the addition of a water solution of ammonium sulfide caused the quantitative precipitation of a white compound. Its elemental composition (C = 82.40, H = 5.86, N = 10.66, S = 1.01) fits theoretical provisions, apart from a minor sulfur content, of dianilinobenzene (C = 83.07, H = 6.15, N = 10.77). An authentic sample of this compound exhibited the same IR (strong bands at 3380, 1595, 1520, 1510, 1490, 1310, 1225, 1180, 820, 745, 740

TABLE II  
Kinetics of Aniline and Hydrazobenzene Consumption during a Chemical Polymerization Test

Reaction time (h)	Unreacted aniline (%)	Unreacted hydrazobenzene (%)
15	67	97
28.5	41	82
37	30	70
53	2	8

and  $690\text{ cm}^{-1}$ ) and mass spectrum ( $260 = M^+$  100%, 183 17%; 167 15%;  $130 = M^{++}$  7%) of the reaction product which, in addition, showed, when heated at  $170^\circ\text{C}$ , a low intensity peak at  $m/e = 292$  corresponding to a sulfur atom entering the molecule.

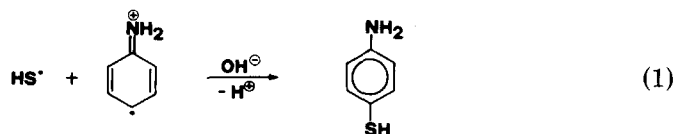
It may thus be concluded that interaction between sulfide ions and quinoneimine moieties mainly develops through an oxidoreduction process, although a nucleophilic attack by  $\text{HS}^-$  to quinone rings cannot be completely discarded.

## DISCUSSION

The data reported above show that sulfide anions interact with oxidation of anilines at different stages. Thus one can outline sulfide intervention either on anilinium free radicals directly formed by anode reaction or on the more stable products of the coupling process.

Let us consider the first interaction type. As an anodic potential is applied to a Fe electrode dipped in an alkaline sulfide solution, surface Fe oxides are partly dissolved, but Fe is passivated again by a Fe sulfide layer,<sup>5,6</sup> on which some sulfide oxidizes to elemental sulfur<sup>5,6</sup>: this last process clearly involves the formation of  $\text{HS}^\cdot$  radicals.

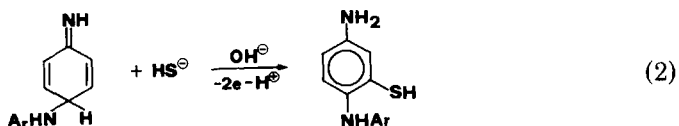
On the other hand, aniline also oxidizes on the passivated Fe surface with the initial product of free radical intermediates of further chemical coupling steps. For aniline and *N*-monosubstituted anilines, coupling reactions involve *N*—*N* and *N*—*C* bond formation, but in the presence of  $\text{HS}^\cdot$  radicals the following process must also be considered:



(Clearly, such an addition may also occur on free ortho positions of the ring.)

Other than accounting for the large amount of sulfur bonded to the aromatic ring resulting from both elemental analysis and mass spectral data, reaction (1) is supported by the following points:

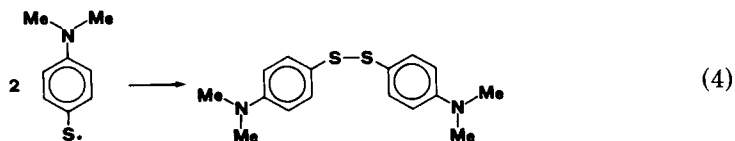
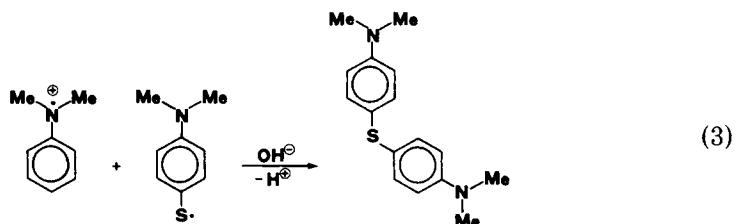
(1) an anionic addition mechanism of  $\text{HS}^-$  to electrophilic meta positions of quinoneimine radicals according to the schema



is unlikely here as, on blocking meta positions of aniline (i.e., by using 3,5-dimethylaniline) no decrease of sulfur content in the polymer was tested. On the other hand, a possible addition of  $\text{HS}^-$  to quinoneimine intermediates of further polymer growth stages has very low weight, as tested by the redox reaction of  $\text{HS}^-$  anions with *N,N'*-diphenyl-*p*-quinonediimine.

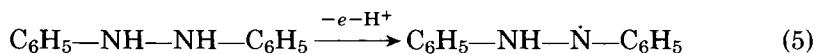
(2) Absence of sulfur in the oxidation product from mesidine. Here, in fact, blocking ortho and para positions of the aniline ring hinders any possible radical coupling according to reaction (1), and only allows *N*—*N* bond formation.

Furthermore it must be noted that  $\text{HS}^\cdot$  entering the aromatic rings leads to formation of thiophenol groups which are probably anode-reactive to form the corresponding thiophenyl radicals, and these may well share further coupling reactions. Evidence of this fact is given by the product obtained by oxidation of *N,N*-dimethylaniline. Actually the mass spectrum in Figure 6 clearly shows that bonding of more than two *N,N*-dimethylaniline units always implies intervention by sulfur. Moreover, the unusually high sulfur content (corresponding to 0.75 S atoms per monomer unit) and the quite high  $\overline{M}_n$  obtained from *N,N*-dimethylaniline, a monomer unable to couple through N atom, both strongly suggest sulfur atoms as responsible for the bridging of aromatic units. The following C—S and S—S coupling steps could be envisaged. (On investigating anode oxidation of amino thiophenols as model intermediates of the process described,<sup>13</sup> S—S dimers formation has been tested. Such reaction occurs very easily at potentials well below those required by amino group oxidation.)

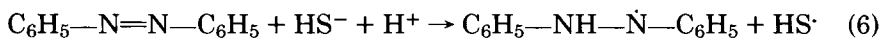


Let us now consider sulfide ions interaction with the products of the N—N coupling reaction.

It has been known for a long time<sup>14</sup> that sulfides reduce azo groups to the corresponding hydrazo: but what about the absence of any free hydrazobenzene from either films or electrolyzed solution? The results obtained from chemical oxidation runs show that hydrazobenzene may copolymerize with aniline. Therefore, hydrazobenzene has to form free radical intermediates by anodic and/or chemical oxidation



The same radicals may also originate from azobenzene reduction by ammonium sulfide:



It is true that also in the absence of sulfides, such hydrazo radicals may form at the anode during aniline oxidation, although their further oxidation to azobenzene prevails over engagement into polymerization. However it is only in the presence of sulfide ions that all azobenzene diffusing from the electrode is immediately reduced and thus recycled again to the anode and forced towards polymerization. Therefore, through processes shown by schemes 1 and 3–6

(which satisfactorily account for experimental data) aniline-sulfur copolymers are obtained by simply anodizing aniline and sulfide ions together. Clearly the structure of such polymers is random as polymer molecules are formed through N—C, N—N, S—C, and S—S coupling reactions: the prevalence of each is mainly related to the type of aniline monomer. These facts deeply change the nature of polymeric films with respect to aniline black: the high conjugation of such compound turns out to be broken here and the oxidation degree is strongly reduced.

First, the consequences for the films obtained here are increased stability and higher electric resistance. With reference to this, the protective properties of the films and possible technological interest of the described process should be mentioned here. The present stage undoubtedly represent an improvement on previous results<sup>1</sup>: as well as insulating properties (which grant higher throwing power to in situ deposition) mention must also be made of faster deposition times, solution stability, absence of by-reactions wasting the monomers, and the wide range of utilizable monomers. However, the high resistance of the films whereby relatively low thickness (1–3  $\mu\text{m}$ ) is generally achieved narrows any utilization to either technologies requiring thin films or Fe corrosion pre-treatment. A second major limitation is the low molecular weight of the polymers which constitutes a handicap as regards resistance to chemicals, solvents and aggressive environments; obviously further research effort will be aimed at making the film suitable for thermosetting curing. The results obtained here with *N*-allylaniline indicate the soundness of such a research line.

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