

# Accelerating Effect of NaNO<sub>2</sub> on the Polymer Plating of 6-Substituted-1,3,5-Triazine-2,4-Dithiol Mono Sodium Salts

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**ABSTRACT:** Organic polymer plating properties of 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salts were investigated in the presence of various supporting electrolytes. Among these, the NaNO<sub>2</sub> supporting electrolyte greatly accelerated the film formation rate in polymer plating. The accelerating effect of NaNO<sub>2</sub> was further confirmed by comparing plating potentials in the presence of NaNO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>. The potentiostatic polymer plating of DAN in the presence of the NaNO<sub>2</sub> supporting electrolyte took place in the potential range of 1.65–1.8 V (compared against saturated calomel electrode reference). Film formation was influenced by such factors as the pH of solution and both the chemical structure and the concentration of triazine dithiol. In polymer platings, NO<sub>2</sub><sup>-</sup> anions are thought to be electrochemically oxidized to yield NO<sub>2</sub> radicals and these radicals react with DAN to yield new thiyl radicals. The thiyl radicals in the DAN molecules couple with each other by means of disulfide bonds, resulting in the growth of polymer film. Organic polymer plating films are shown to contain disulfide bonds, monosulfide bonds obtained by the reaction between allyl groups and thiyl radicals, and network chains. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2300–2309, 2001

**Key words:** polymer plating; 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salts; thiyl radical; polymer thin films

## INTRODUCTION

The formation of polymer thin films on metal surfaces is a topic of considerable interest from the standpoint of industrial applications and functional surface control. In our previous study,<sup>1</sup> the electrochemical polymerization of 6-diocetyl-amino-1,3,5-triazine-2,4-dithiol in 0.1M Na<sub>2</sub>CO<sub>3</sub> aqueous solution was proposed as an effective technique for the formation of polymer thin films. We called this technique “polymer plating” because it is a new and effective way of coating metals, similar to the formation of coatings in metal plating.

Polymer plating using 6-substituted-1,3,5-triazine-2,4-dithiols has attracted a great deal of attention because of its ability to provide an effective surface treatment for metal mold<sup>2</sup> that requires a high releasing property to plastics, metal parts that require a better adhesive property<sup>3,4</sup> to plastics or rubbers, and metal products with anticorrosive properties.<sup>5,6</sup> To develop new applications and expand the potential applications for polymer platings, it is necessary to further investigate the unknown factors involved in this new plating technique. The purpose of this study is to investigate various factors in the polymer plating of 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salt in NaNO<sub>2</sub> aqueous solution and to elucidate the mechanism involved in the formation of polymer plating.

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## EXPERIMENTAL

6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salts were obtained by reacting cyanuric trichloride, amines (substituted groups), and NaSH, according to the method reported in a previous study.<sup>7</sup> The polymer plating of 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salts was carried out using a potentiostat/galvanostat (Hokuto Denko HA-20) with a linear scanner (Hokuto Denko HB-103) and X-Y recorder (Riken Denshi F-3DP) as previously described.<sup>1,8</sup> The electrolytic cell was equipped with a working electrode (steel plate:  $0.2 \times 30 \times 60$  mm), counter electrode (Pt plate:  $0.2 \times 30 \times 60$  mm), and reference electrode [saturated calomel electrode (SCE); voltage potentials are reported throughout this study in reference to SCE values]<sup>1</sup> and filled with electrolytic solution containing 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salts and electrolytes in water. The steel plates (average roughness less than  $0.02 \mu\text{m}$ ) were polished to a mirrorlike surface with diamond paste ( $0.2 \mu\text{m}$ ). Polymer weight was determined from the difference in plate weight before and after polymer plating, using a Mettler AT250 electronic scale (measurement accuracy:  $\pm 0.005$  mg).

FTIR spectra were measured with a Nippon Denshi FTIR, IR-5500 (Nippon Denshi Co.) by high-performance reflection absorption spectroscopy (IR-RAS) using the Johnson and KBr methods. Raman spectra were obtained with a Nippon Denshi Raman Spectrograph.

## RESULTS AND DISCUSSION

### Electrolytes

The electrolytic solution system was composed of three components: solvents, supporting electrolytes, and triazine dithiols. The electrolytes generally promote electric current flow during the electrochemical reaction in an aqueous solution. Table I shows the effect of electrolytes on film weight in the polymer plating of 6-diallylamino-1,3,5-triazine-2,4-dithiol mono sodium salt (DAN) on steel plates. The pH of solutions was adjusted to approximately 10.2 with  $0.01M$  NaOH and  $H_2SO_4$  aqueous solutions; the pH of DAN– $NaNO_2$  aqueous solution was 6.5 before adjustment. The pH of the  $Na_2CO_3$  aqueous solution was not adjusted because the initial pH of 11.2 was shown in a previous study<sup>1</sup> to give the best polymer plating.

**Table I** Effect of Electrolyte on Film Weight in the Organoplatin of DAN on Steel Plates<sup>a</sup>

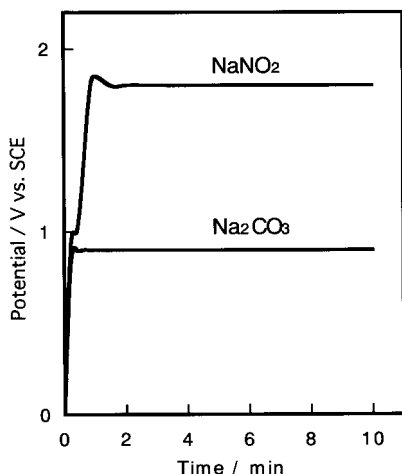
Electrolyte ( $10 \text{ mol m}^{-3}$ )	pH	Film Weight ( $\text{g m}^{-2}$ )
NaCl	10.2	—
$Na_2SO_4$	10.2	—
$Na_2SO_3$	10.2	0
$Na_2S_2O_3$	10.2	0
$NaNO_3$	10.2	0
$NaNO_2$	10.2	0.219
$Na_2CO_3$	11.2	0.020
$Na_2B_4O_7$	10.2	0
$Na_2MoO_4$	10.3	0.025
$Na_3SiO_3$	12.0	0.015
$NaH_2PO_4$	10.2	—
$(NaPO_3)_6$	10.2	0

<sup>a</sup> DAN:  $5 \text{ mol m}^{-3}$ ; current density:  $2 \text{ A m}^{-2}$ ; time: 10 min; temperature:  $30^\circ\text{C}$ .

Supporting electrolytes such as NaCl,  $Na_2SO_4$ , and  $NaH_2PO_4$  caused the weight of the plate to decrease during the polymer plating of DAN and in some cases to completely inhibit the formation of polymer film because the steel was corroded by the electrolytic solution during plating. Salts such as  $Na_2SO_3$ ,  $Na_2S_2O_3$ ,  $NaNO_3$ ,  $Na_2B_4O_7$ , and  $(NaPO_3)_6$  always gave the same weight before and after plating. In these cases, the polymer plating did not occur on the steel surface<sup>1</sup> in the electrolytic solution. In electrolytic solutions containing  $NaNO_2$ ,  $Na_2CO_3$ ,  $Na_2MoO_4$ , and  $Na_2SiO_3$  a polymer film was deposited on the steel surface. In particular, the solution with  $NaNO_2$  yielded markedly higher polymer weight on steel surface than did other solutions. The reason is that  $NaNO_2$  exerted a remarkable accelerating effect on the formation of polymer film on the steel surface.  $NaNO_2$  is thus thought to play a particular role in the formation of polymer film in addition to its role as an electrolyte.

### Potential in Polymer Plating

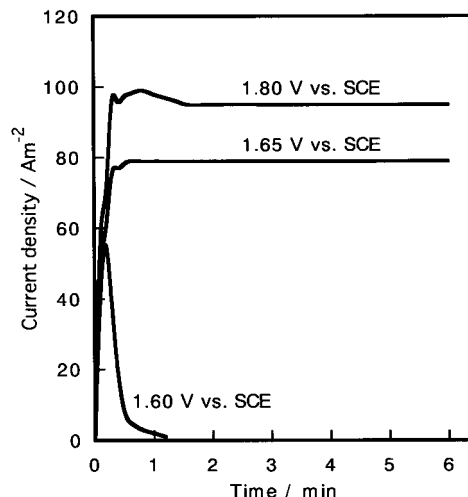
To determine the particular role that  $NaNO_2$  plays in the polymer plating of DAN, a potential that resulted in polymer film at a high rate on steel was investigated. Figure 1 shows changes in the potential of polymer plating of DAN in  $0.01M$   $NaNO_2$  and  $Na_2CO_3$  aqueous solutions in the galvanostatic method. In  $0.01M$   $Na_2CO_3$  aqueous solution, the potential of polymer plating increased rapidly up to about 0.85 V after the switch was



**Figure 1** Polymer plating potential of DAN ( $5 \text{ mol m}^{-3}$ ) in the presence of  $\text{NaNO}_2$  or  $\text{Na}_2\text{CO}_3$  ( $10 \text{ mol m}^{-3}$ ) at  $30^\circ\text{C}$ . Current density:  $2 \text{ A m}^{-2}$ .

turned on and a similar value was maintained for 10 s. The potential at 0.85 V is probably that needed to allow polymer film to grow continuously on the polymer thin film. The actual potential required to cause polymer film to form directly on the steel surface is probably less than 0.85 V. In  $0.01\text{M}$   $\text{NaNO}_2$  aqueous solution, the potential for polymer plating increased rapidly up to 0.90 V, was maintained briefly around 0.90 V, and after 10 s increased rapidly again up to 1.8 V and was maintained at that same value from that point onward. The initial increase in potential is attributed to the formation of polymer films on the steel surface and the subsequent growth of polymer film.  $\text{NaNO}_2$  seems to have no influence on extending the period of polymer film formation because the potential in this case is close to that in  $0.01\text{M}$   $\text{Na}_2\text{CO}_3$  aqueous solution.  $\text{NaNO}_2$  is thought to markedly accelerate the formation of polymer films at a potential of 1.8 V.

Figure 2 shows the relation between current density and time when potentials were set up at fixed values. Comparing 1.65 V to 1.85 V, the current density became constant, although below 1.65 V it decreased to around zero after the potential had initially increased rapidly. It is very difficult to grow polymer films with a high rate below 1.65 V or over 1.85 V. The former is attributed to the fact that  $\text{NaNO}_2$  does not show an accelerating effect; the latter, to the fact that the dissolution of metals occurs after the peeling of polymer film. Figure 3 shows the relation between film weight and potential in the polymer plating of DAN in  $0.01\text{M}$   $\text{NaNO}_2$  and  $\text{Na}_2\text{CO}_3$  aqueous

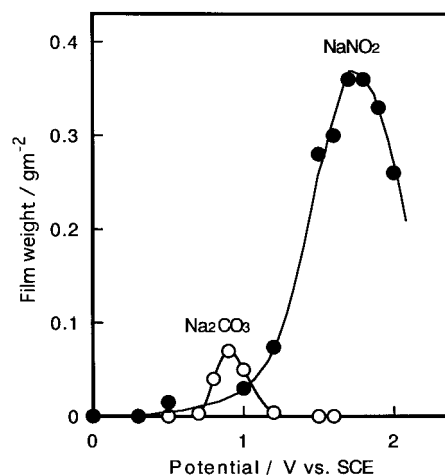


**Figure 2** Relation between current density and time in the potentiostatic polymer plating of DAN ( $5 \text{ mol m}^{-3}$ ) in the presence of  $\text{NaNO}_2$  ( $10 \text{ mol m}^{-3}$ ) at  $30^\circ\text{C}$ .

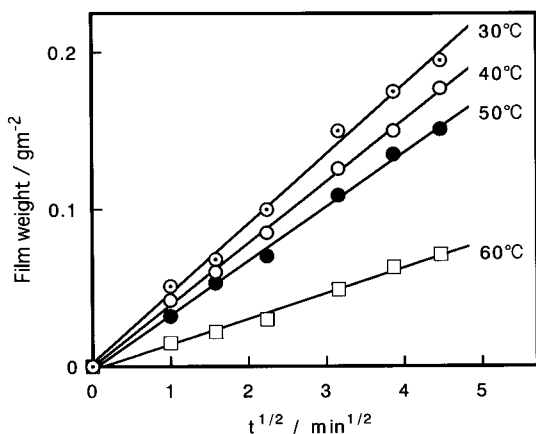
solutions. Film weight showed the highest value at 1.85 V in the case of  $0.01\text{M}$   $\text{NaNO}_2$  aqueous solution and at 0.85 V in the case of  $0.01\text{M}$   $\text{Na}_2\text{CO}_3$  aqueous solution. In both the potentiostatic and galvanostatic methods, the optimum potential for the formation of polymer film appears to be the same.

### Conditions in Polymer Plating

Conditions affecting the polymer plating of DAN were investigated to clarify the effect of various



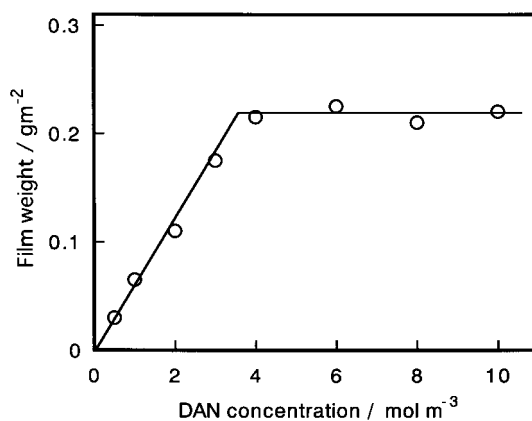
**Figure 3** Effect of potential on film weight in the potentiostatic polymer plating of DAN on steel plates in the presence of different electrolytes. DAN:  $5 \text{ mol m}^{-3}$ ;  $\text{NaNO}_2$  or  $\text{Na}_2\text{CO}_3$  concentration:  $10 \text{ mol m}^{-3}$ ; time: 5 min; temperature:  $30^\circ\text{C}$ .



**Figure 4** Effect of temperature on film weight in the galvanostatic polymer plating of DAN ( $5 \text{ mol m}^{-3}$ ) on steel plates in  $10 \text{ mol m}^{-3}$   $\text{NaNO}_2$  aqueous solution. Current density:  $2 \text{ A m}^{-2}$ .

factors on the formation of polymer film. Figure 4 shows the effect of temperature on the relation between film weight and time in the polymer plating of DAN. Film weight increased with the square root of time ( $t$ ) but decreased with temperature. A parabolic relationship appears to exist between film weight and time in the polymer plating of DAN. The polymer plating of DAN contains a diffusion process at a rate-determining step; DAN diffuses in the region of the interface neighborhood on the metal surface during polymer plating. A decrease in the formation rate of polymer film occurred with temperature ( $30\text{--}60^\circ\text{C}$ ) in the DAN- $\text{NaNO}_2$  aqueous solution. In the DAN- $\text{Na}_2\text{CO}_3$  aqueous solution system, the formation rate of polymer film increased with temperature. Decreases in the rate in the DAN- $\text{NaNO}_2$  aqueous solution are therefore related to the presence of  $\text{NaNO}_2$ ; thus  $\text{NaNO}_2$  is thought to function increasingly as an oxidant to steel as the solution temperature increases.

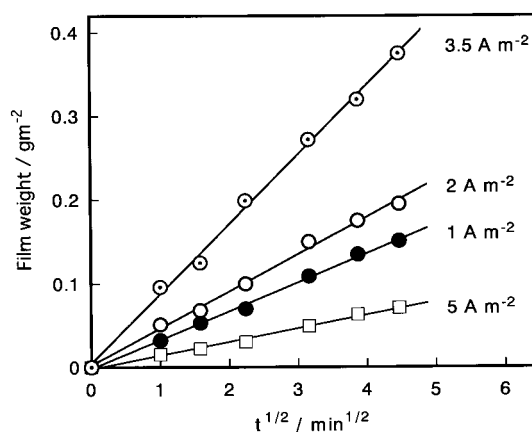
Figure 5 shows the relation between film weight and DAN concentration in polymer plating. The film weight increased up to a DAN concentration of  $4 \text{ mol m}^{-3}$  and then became constant.<sup>1</sup> This increase in film weight with increasing the DAN concentration means that the DAN concentration at the interface between the steel plate and aqueous solution exerted a significant influence on film growth. Within the DAN concentration range up to  $4 \text{ mol m}^{-3}$ , the film formation rate was proportional to the first power of DAN concentration, which is the same as the case for radical polymerization of vinyl compounds. The



**Figure 5** Effect of DAN concentration on film weight in the galvanostatic polymer plating of DAN in  $100 \text{ mol m}^{-3}$   $\text{NaNO}_2$  aqueous solution at  $30^\circ\text{C}$  for 20 min. Current density:  $2 \text{ A m}^{-2}$ .

fact that film weight remains constant at DAN concentrations above  $4 \text{ mol m}^{-3}$  shows that film formation is not influenced by the concentration. The polymer film is considered to be formed mainly by a two-dimensional reaction. DAN thiolate anions are arranged on the steel substrate surface in an electric bilayer immediately following voltage application.<sup>1</sup> The thiolate anions become instantly situated in an electric bilayer by polarization in the two-dimensional plane. Polymer formation resulting from the two-dimensional reaction is a special feature of the proposed polymer plating.<sup>1</sup>

Figure 6 shows the effect of current density on film weight in the polymer plating of DAN. For each current density, a parabolic relationship was

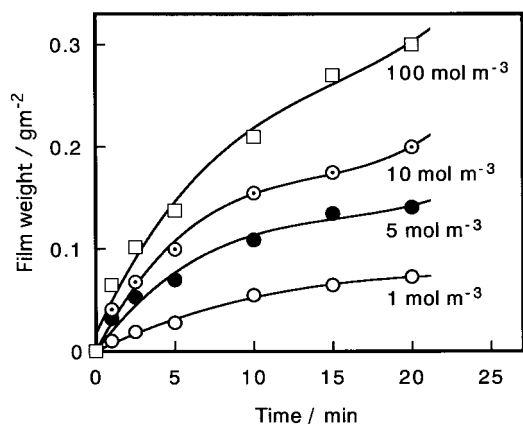


**Figure 6** Effect of current density on film weight in the polymer plating of DAN ( $5 \text{ mol m}^{-3}$ ) on steel plates in  $10 \text{ mol m}^{-3}$   $\text{NaNO}_2$  aqueous solution at  $30^\circ\text{C}$ .

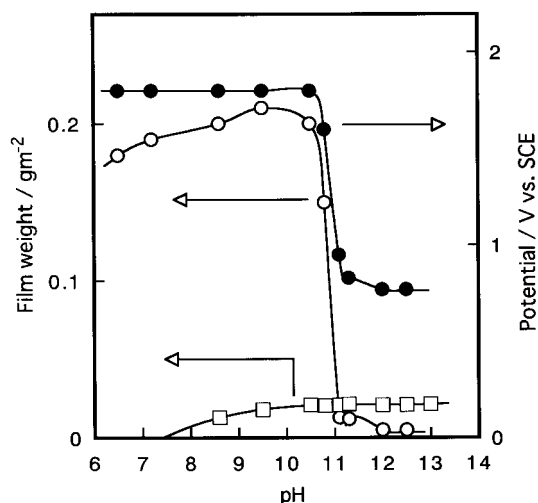
seen between film weight and time in the polymer plating of DAN. There was an optimal current density that gives the highest film weight; that is, the accelerating effect of  $\text{NaNO}_2$  was dependent on current density. At a current density of  $3.5 \text{ A m}^{-2}$ , the accelerating effect of  $\text{NaNO}_2$  was exhibited.

Figure 7 shows the effect of  $\text{NaNO}_2$  concentration on film weight in the polymer plating of DAN on steel plates. The film weight increased with  $\text{NaNO}_2$  concentration. In this figure, the relationship between film weight  $W$  and time  $t$  is described by the equation  $W = kt^{1/2}$ , where  $k$  is a rate constant. Thus in polymer plating accelerated in the presence of  $\text{NaNO}_2$ , the diffusion process of DAN is a rate-determining step. Furthermore, the plots of  $\ln[k]$  and  $\ln[\text{NaNO}_2]$  were linear with a slope of 0.3. The value represents the participation order number that reflects the molar number<sup>9</sup> of  $\text{NaNO}_2$  involved in the formation of  $1M$  polymer units. The participation order number (0.3) obtained is thought to be sufficiently large, considering the reaction at the interfacial area. Based on the results, the polymer plating of DAN in the presence of  $\text{NaNO}_2$  can be expressed as  $R_p = k[\text{DAN}]^1[\text{NaNO}_2]^{0.3}$ , where  $R_p$  is the growth rate of polymer film and  $k$  is a rate constant.

The effect of pH in the DAN aqueous solution on film weight was investigated to elucidate the accelerating effect of  $\text{NaNO}_2$  on polymer plating and is shown in Figure 8. In  $\text{NaNO}_2$  aqueous solution, film weight increased gradually from pH 6.5 to 10.5, dropped drastically between pH 10.5 and 11.1, and then decreased gradually with in-



**Figure 7** Effect of  $\text{NaNO}_2$  concentration on film weight in the polymer plating of DAN on steel plates. DAN:  $5 \text{ mol m}^{-3}$ ; current density:  $2 \text{ A m}^{-2}$ ; temperature:  $30^\circ\text{C}$ .



**Figure 8** Effect of electrolyte pH on film weight and potential in the galvanostatic polymer plating of DAN on steel plates in the presence of different electrolytes at  $30^\circ\text{C}$  for 10 min. DAN:  $5 \text{ mol m}^{-3}$ ;  $\text{NaNO}_2$  concentration:  $10 \text{ mol m}^{-3}$ ; current density:  $2 \text{ A m}^{-2}$ . (O, ●): in the presence of  $\text{NaNO}_2$ ; (□): in the absence of  $\text{NaNO}_2$ .

creasing pH. The potential was maintained around 1.85 V between pH 6.5 and 10.5, dropped sharply to 0.85 V between pH 10.5 and 11.3, and afterward became constant. In  $\text{Na}_2\text{CO}_3$  aqueous solution, the film weight increased gradually from pH 6.5 to 10.5 and became constant beyond pH 10.5. As shown by the results, the accelerating effect of  $\text{NaNO}_2$  was exhibited between pH 6.5 and 10.5. The drastic drop of film weight between pH 10.5 and 11.1 results from the decomposition of water that occurs at the lower-potential side than 1.8 V for decreasing the overpotential at a pH greater than 11 in the presence of  $\text{NaNO}_2$ . As a result, the polymer plating on the metal surface is suppressed because oxygen gas is generated at the interface of electrode decomposing water.

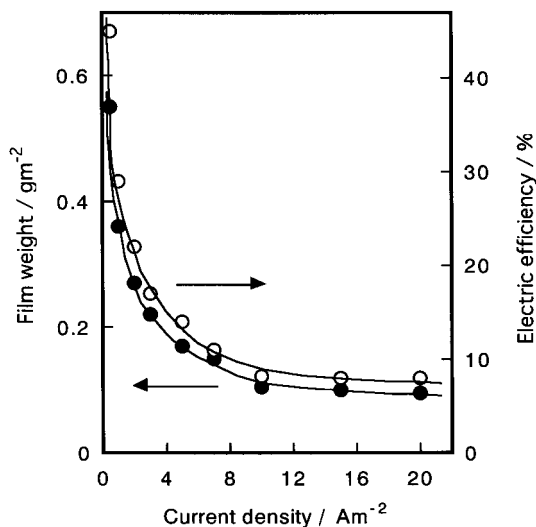
Figure 9 shows the effect of current density on the film weight and electric efficiency in the polymer plating of the DAN- $\text{NaNO}_2$  system. The film weight decreased exponentially with current density in the range of  $0.3\text{--}20 \text{ A m}^{-2}$  when the electric quantity is 3 C. Electric efficiency in the polymer plating of the DAN- $\text{NaNO}_2$  system also decreased exponentially with current density. Polymer film is formed most effectively at low current density ( $0.3 \text{ A m}^{-2}$ ), although in this case electric efficiency is not high, with approximately 45% being the best value. At a high current density, the coupling of thiyl radicals is considered to be suppressed by  $\text{HNO}_2$  generated at the inter-

face of the electrode [see eqs. (4) and (6) in Fig. 12].

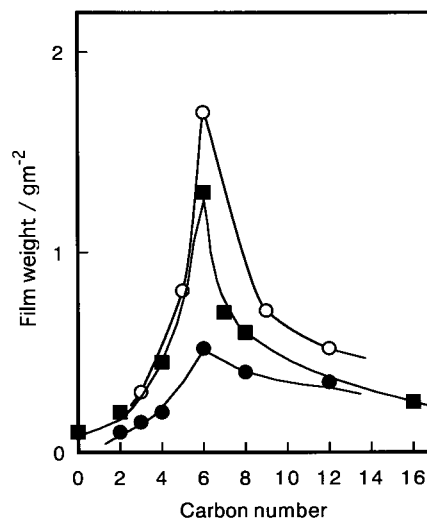
### 6-substituted-1,3,5-Triazine-2,4-dithiol Mono Sodium Salts

To elucidate the accelerating effect of  $\text{NaNO}_2$ , it is important to thoroughly investigate the effect of the 6-substituted groups in 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salts. Figure 10 shows the effects of substituted groups and types on film weight. The substituted groups are expressed by the carbon number of the 6-substituted groups. Three types were used for the substituent:  $-\text{N}(\text{R})\text{CH}_2\text{CH}=\text{CH}_2$ ,  $-\text{N}(\text{R})_2$ , and  $-\text{NHR}$ , where R is an alkyl group with a carbon number of 0 to 16 and an allyl group. For all substituted types, a carbon number of 6 yields the highest film weight. The increase in film weight with carbon numbers up to 6 is ascribed to the aggregation of the 6-substituted-1,3,5-triazine-2,4-dithiolate anion and the degree of dissociation of the thiols. The decrease in film weight with carbon numbers greater than 6 is attributed to an increase in the steric hindrance of the 6-substituted groups, which prevents the formation of thiyl radicals.<sup>10</sup> An increase in steric hindrance to thiyl radical attributed to the 6-substituted groups markedly suppresses the intermolecular coupling reaction.

Film weight, which is influenced by the types of 6-substituted groups, increased in the order of



**Figure 9** Effect of current density on film weight in the galvanostatic polymer plating of DAN ( $5 \text{ mol m}^{-3}$ ) on steel plates in  $10 \text{ mol m}^{-3}$   $\text{NaNO}_2$  aqueous solution at  $30^\circ\text{C}$ . Electric quantity: 3 C.

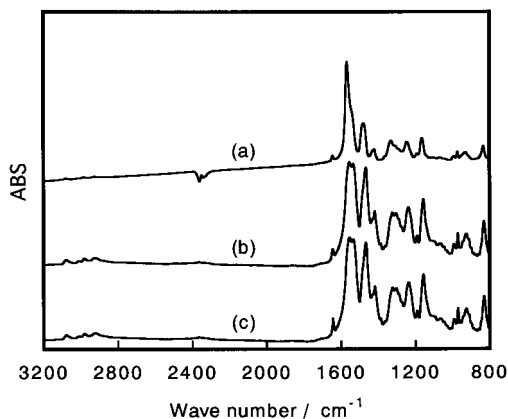


**Figure 10** Effect of substituted groups on film weight in the galvanostatic polymer plating of 6-substituted (X)-1,3,5-triazine-2,4-dithiol mono sodium ( $5 \text{ mol m}^{-3}$ ) on steel plates in  $10 \text{ mol m}^{-3}$   $\text{NaNO}_2$  for 20 min at  $30^\circ\text{C}$ . Current density:  $2 \text{ A m}^{-2}$ . (○): X =  $-\text{N}(\text{CH}_2\text{CH}=\text{CH}_2)\text{R}$ ; (■): X =  $-\text{N}(\text{R})_2$ ; (●): X =  $-\text{NHR}$ ; R = alkyl groups.

$-\text{NHR} < -\text{N}(\text{R})_2 < -\text{N}(\text{R})\text{CH}_2\text{CH}=\text{CH}_2$ . Given that allyl groups react easily with thiyl radicals, triazine dithiol derivatives with a  $-\text{CH}_2\text{CH}=\text{CH}_2$  group gave the highest film weight. The increase in functional groups in an intermolecule increases the chances for polymer formation to increase. Among the 6-substituted groups,  $-\text{N}(\text{R})_2$  has a higher aggregating property for intermolecules and reactivity than that of the  $-\text{NHR}$  groups. It is thought that the proton in  $\text{RNH}^+$  groups attracts thiyl radicals, thus reducing reactivity.

### Structure of Polymer Film

Film formed on steel in the plating of DAN is easily estimated to be a polymer because it is insoluble in strong alkali aqueous solutions with high pH and in methanol; DAN is easily soluble in alkali aqueous solutions and methanol. Figure 11 shows the FTIR spectra of (a) polymer film on steel, which was prepared by polymer plating; (b) polymer powders prepared from the polymer film in (a); and (c) specially prepared polymer powder. The polymer powders (b) were produced by shaving the polymer film from the steel surface. Polymers (a) and (b) are therefore the same substance chemically but the shapes, thin film versus powders, are different. Polymer powder (c), poly(6-diallylamino-1,3,5-triazine-2,4-disulfide), was prepared by the reaction of 6-diallylamino-1,3,5-



**Figure 11** FTIR spectra of polymer film measured by RAS method on steel (a), polymer powder by the Johnson method (b), and specially prepared polymer powder by the KBr method (c).

triazine-2,4-dithiol with benzothiazyl disulfide.<sup>11</sup> The FTIR spectrum of polymer (a) was measured by the RAS method, and those of (b) and (c) were measured with the Johnson method and KBr method, respectively. Spectra (a), (b), and (c) all exhibit absorption peaks at the same wave number as a matter of course but were different with respect to the absorption intensity in each peak.

The three compounds appear to be roughly the same, although differences in the wave shapes show detailed differences in chemical and steric structure. Polymer film (a) has a basic chemical structure similar to that of polymer powder (c) (poly 6-diallylamino-1,3,5-triazine-2,4-disulfide). The presence of disulfide bonds could not be determined from the FTIR spectra because the SS bond is inactive with respect to infrared rays. The Raman spectra of both polymers (b) and (c) indicated an absorption peak at  $540\text{ cm}^{-1}$ , which is based on the SS bond. The differences between polymers (a), (b), and (c) are attributed to the difference between anisotropic films and isotropic powders. The spectra of (b) and (c) showed the same absorption peaks and wave numbers, except for the absorption intensity of the C=C band at  $1643\text{ cm}^{-1}$ . The absorption intensity of the C=C band in the former is smaller than that in the latter. The C=C group content in polymer powder (b) as well as polymer film (a) was smaller than that in polymer powder (c). These results suggest the presence of  $\text{-C-S-C-}$  groups because the formation of thiyl radical ( $\text{-C-S}\cdot$ ) is estimated. The presence of  $\text{-C-S-C-}$  groups is associated with the formation of three-dimensional films during polymer plating.

Table II shows the tetrahydrofuran (THF)-insoluble parts of polymer film obtained under various polymer plating conditions. The THF-insoluble part is a measure of the extent of three-dimensionalization. During plating in  $\text{NaNO}_2$  and  $\text{Na}_2\text{CO}_3$  aqueous solutions, polymers that were insoluble in THF were formed as thin films on the steel surface. The  $\text{NaNO}_2$  aqueous solution gave a considerably higher THF-insoluble fraction than did the  $\text{Na}_2\text{CO}_3$  aqueous solution.  $\text{NaNO}_2$  aqueous solution results in the generation of numerous thiyl radicals, compared with  $\text{Na}_2\text{CO}_3$ . The THF-insoluble fraction increased gradually with plating time and became constant after a certain time. This suggests that the top surface layer of the polymer film has a lower THF-insoluble fraction than the inner layer near the interface between the formed film and the steel substrates.

### Mechanism

The polymer plating of 6-substituted-1,3,5-triazine-2,4-dithiol mono sodium salt in  $\text{NaNO}_2$  aqueous solution is thought to be basically similar to the above-noted polymer plating of 6-dioctylamino-1,3,5-triazine-2,4-dithiol mono sodium salt.<sup>1</sup> In  $\text{NaNO}_2$  aqueous solution, various plating behaviors different from those in the case of  $\text{Na}_2\text{CO}_3$  aqueous solution were observed as described below. The effect of  $\text{NaNO}_2$  aqueous solution has the effect of accelerating polymer plating.

$\text{NaNO}_2$  dissociates into  $\text{Na}^+$  and  $\text{NO}_2^-$  at pH values over 6.5. When the potential is greater than 1.65 V,  $\text{NO}_2^-$  is transformed to  $\text{NO}_2\cdot$ , transferring electrons to the anode, as shown in Figure 12 [see eq. (1)]. The reaction occurs mostly at 1.85 V because the decomposition of water occurs violently at a potential over 1.85 V.  $\text{NaNO}_2$ , how-

**Table II** THF-Insoluble Fraction in Polymer Plating of DAN on Steel Plates<sup>a</sup>

Time (min)	THF-Insoluble Fraction (%)	
	$\text{NaNO}_2$	$\text{Na}_2\text{CO}_3$
0	0	0
1	70	0
3	75	20
5	81	25
10	85	30
30	85	32

<sup>a</sup> DAN:  $5\text{ mol m}^{-3}$ ;  $\text{NaNO}_2$  or  $\text{Na}_2\text{CO}_3$  concentration:  $10\text{ mol m}^{-3}$ ; temperature:  $30^\circ\text{C}$ ; current density:  $2\text{ A m}^{-2}$ .

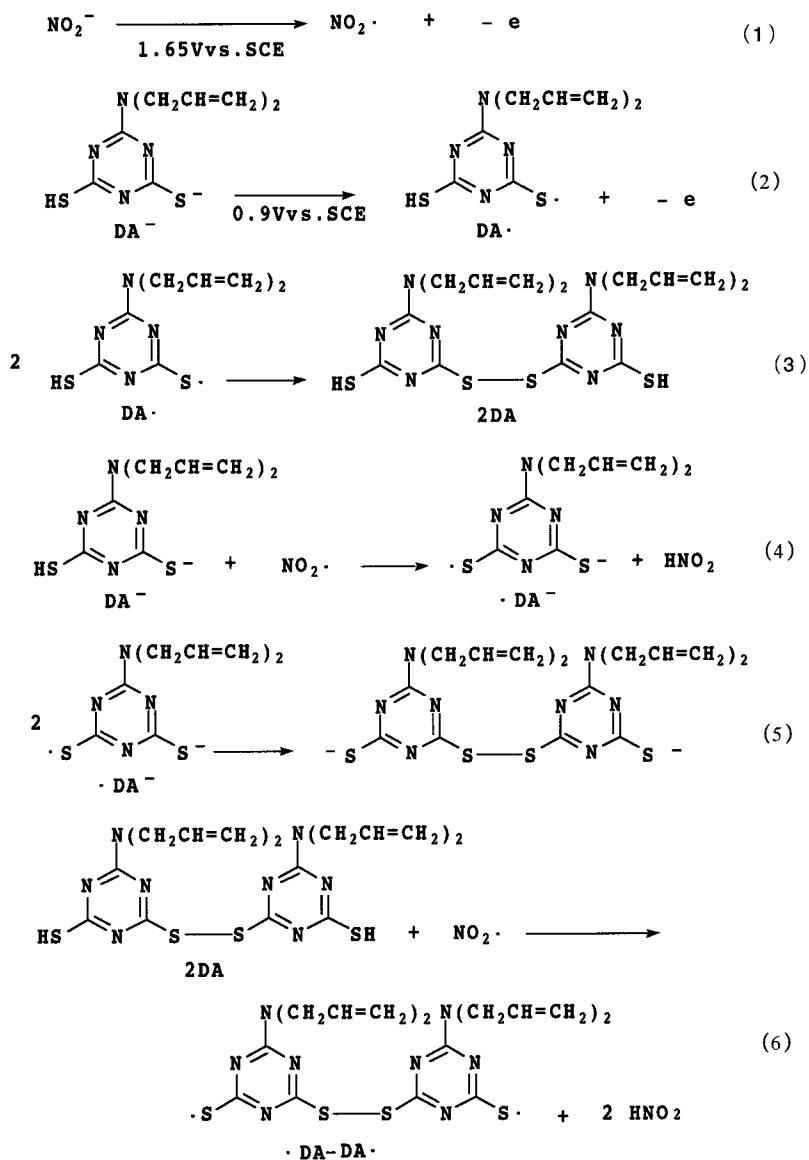
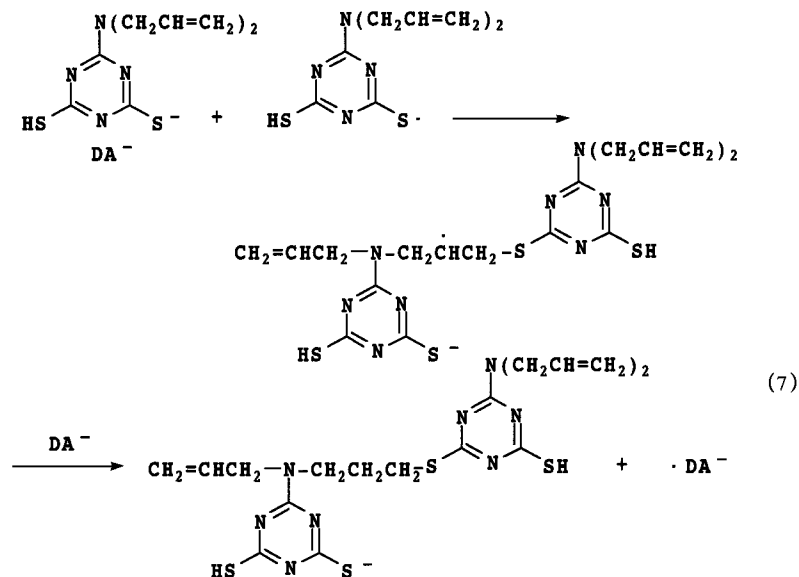


Figure 12 Cationoid reactions in the presence of DAN and NaNO<sub>2</sub>.

ever, does not participate in the formation of the first layer of polymer film because the polymer plating of DAN occurs at 0.85 V. At this potential, the anion (DA<sup>-</sup>) of 6-substituted-1,3,5-triazine-2,4-dithiol (DA) transfers an electron to the anode to give the monothyl radical of DA (DA<sup>·</sup>) and these radicals react to give the dimer (DA-DA) of DA as shown in eqs. (2) and (3) (Fig. 12). The telomer film formed during this initial period causes the potential to rise to 1.85 V and simultaneously allows the potential for the decomposition of water to shift over 1.85 V to the anode side. The SH terminal groups in the dimer film react with NO<sub>2</sub> to give the bithyl radical terminal

groups (‘DA-DA’) and HNO<sub>2</sub>, and then they react with each other to give the polymer of DA, as shown in eq. (6) (Fig. 12). It is possible that the bithyl radical terminal is formed through another pathway as follows. The anion of DA reacts with NO<sub>2</sub> to generate a radical anion (‘DA<sup>-</sup>’) and HNO<sub>2</sub>, as shown in eq. (4) (Fig. 12). The coupling reaction of ‘DA<sup>-</sup>’ allows the dimer dianion (‘DA<sup>-</sup>-DA<sup>-</sup>’) of DA to form, in response to the bithyl radical terminal, as shown in eq. (5) (Fig. 12). HNO<sub>2</sub> changes easily to NO<sub>2</sub><sup>-</sup> in NaNO<sub>2</sub>, proceeding to NO<sub>2</sub> at potentials over 1.65 V. Thus, NO<sub>2</sub><sup>-</sup> functions repeatedly as NO<sub>2</sub> in the neighborhood of the interface between the substrate and aque-





**Figure 13** Crosslinking reaction during organic polymer plating of DAN on steel.

ous solution. This is the reason that  $\text{NaNO}_2$  shows an accelerating effect in the polymer plating of DAN.

The polymer film of DAN was insoluble in THF because it was composed of network polymer. The mechanism by which the network chain is formed is shown in Figure 13. The thiyl radical terminal further reacts with the  $\text{C}=\text{C}$  bond in the allyl groups to yield a monosulfide  $-\text{SC}-$  bond between the DA polymers. The reaction occurs between layers above and below. Numerous pathways are available for forming network chains. For example, the network chain in the polymer plating of DAN can be formed when the thiyl radical terminal of an upper layer reacts with the allyl groups of a lower layer.

## CONCLUSIONS

The effect of  $\text{NaNO}_2$  on accelerating the electrochemical polymerization of 2-diallylamino-1,3,5-triazine-4,6-dithiol mono sodium (DAN), in polymer plating was investigated.

1.  $\text{NaNO}_2$  has the dual functions of supporting electrolytes and acting as an accelerator. Many of the supporting electrolytes used in this study, for example,  $\text{Na}_2\text{CO}_3$ , had no accelerating effect in the polymer plating of DAN.
2. In the case of the  $\text{Na}_2\text{CO}_3$  supporting elec-

trolyte, the galvanostatic polymer plating of DAN occurred at a potential of 0.85 V but in the presence of the  $\text{NaNO}_2$  supporting electrolyte, it occurred continuously at 1.8 V. The potentiostatic polymer plating of DAN in the presence of the  $\text{NaNO}_2$  supporting electrolyte took place in the potential range of 1.65–1.8 V (compared against saturated calomel electrode reference).

3. In the presence of  $\text{NaNO}_2$ , the polymer plating of DAN decreased with temperature. A parabolic relationship was seen to apply between film weight and time. The formation rate of polymer film was shown to be proportional to the 0.3 power of  $\text{NaNO}_2$  concentration and the first power of the DAN concentration. The accelerating effect of  $\text{NaNO}_2$  was exhibited in the pH range of 6.5 to 10.5. Electric efficiency in the polymer plating of DAN in the presence of  $\text{NaNO}_2$  decreased with current density in the range of  $0.3 \text{ A m}^{-2}$  (45%) to  $20 \text{ A m}^{-2}$  (8%).
4. In the case of 6-substituted groups in triazine dithiols, film weight increased in the order of  $-\text{NHR} < -\text{N}(\text{R})_2 < -\text{N}(\text{R})\text{CH}_2\text{CH}=\text{CH}_2$ . In all substituted types, a carbon number of 6 showed the highest film weight.
5. The chemical structure of polymer film was estimated to be a three-dimensional polymer consisting of mono- and disulfide

bonds, which were formed by the reaction between thiols and allyl groups.

6. Nitrite anions changed to nitrite radicals through an anodic reaction. Nitrite radicals reacted with triazine dithiols to give triazine bithiyl radicals. Thus a three-dimensional polymer is thought to be formed by a coupling of bithiyl radicals and the reaction of bithiyl radicals with allyl groups.

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