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Ethylene Sulfide Graft on Polyamine as a Nonfouling Anticorrosion Agent

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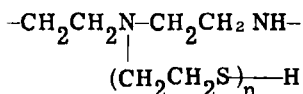
ABSTRACT

Graft copolymers of ethylene sulfide on polyalkylenimines have been shown to be both corrosion inhibitors and antifoulants. Laboratory results were confirmed in a mill test in which iron equipment was used for scrubbing gas with aqueous ethanolamine in order to remove carbon dioxide and hydrogen sulfide. Means have been found for controlling the solubility of the graft.

Polyethylenimine has been patented as a corrosion inhibitor in gas conditioning [1]. The patent specified a minimum molecular weight of 800 and covered numerous derivatives. It did not teach a clear purpose for alkylating or acylating the polymer and no comparative performance information was given. Polymers of ethylene sulfide have been cited as anticorrosion agents [2]. The grafting of propylene sulfide on polyethylenimine has been studied by Levine [3] and by Lautenschlager and Zieman [4].

We have described previously the preparation of a random copolymer of ethylene sulfide and ethylenimine [4, 5]. It was found to be effective as an anticorrosion agent in a laboratory test involving the

exposure of iron test specimens to hot aqueous ethanolamine heated in an atmosphere of carbon dioxide and hydrogen sulfide. We then prepared a graft of an equal weight ratio of ethylene sulfide on polyethylenimine for the same purpose. When such a graft was made in water or aqueous methanol, it was mainly insoluble. X-Ray diffraction showed the presence of crystallinity of the same nature as in poly(ethylene sulfide), but superimposed on the spectrum of amorphous material. The ethylene sulfide had polymerized in the form of pendant oligomeric chains with terminal SH.



While a slurry of the insoluble graft had some anticorrosion value, we desired a dispersible material for greater ease of continuous feeding to a sour gas-scrubbing operation. The soluble graft had a foaming tendency, but this was controlled by the addition of an anti-foamer.

We found that we could prepare a soluble graft by conducting the graft polymerization in a nonionizing solvent. For example, an equal weight graft made from a 30% solution of polyethylenimine in dioxane was sticky and opalescent. It contained 3.72 mmole/g thiol, which corresponds to approximately $n = 2$ (DP = 2). The method of assay for thiol was the quenching of the color of the carbonium ion of bisdimethylaminobenzhydrol. When the grafting was carried out in aqueous dioxane, the use of 8% water gave some insoluble graft; 20% water gave mostly insoluble graft. Graft made in chloroform was recovered as a colorless turbid viscous resin.

The grafts had a stench which could be reduced by steam distillation. In the case of a graft made with propylene sulfide the stench was even worse. Presumably there is some amine-catalyzed rearrangement to thioaldehyde in this case. The addition of 30% propylene sulfide to the ethylene sulfide prior to grafting on polyethylenimine (in methanol) did not prevent precipitation of an insoluble graft. Evidently the base-initiated copolymerization is not random, and crystallization still occurs.

The low molecular weight polyethylenimine (PEI-6) used in most of this work had a GPC maximum at 1850. PEI 600 which was used also had a molecular weight maximum at 6000 and gave a noticeably more stringy graft. Polypropylenimine having a molecular weight peak at 14,000 but a very broad distribution gave a graft similar to that of PEI 600.

Other substrates were used, for example, tetraethylenepentamine, polyethylene polyamine, polypropylenimine, and partially hydrolyzed

polyethyloxazoline. The production of relatively long graft chains on randomly chosen sites of a low molecular weight substrate necessarily leads to exaggerated heterogeneity in composition. Polyethylene polyamine was a satisfactory substrate. It contained 8-9% pentamer, 30-36% hexamer, and higher oligomers, some of which are branched and some cyclic. The graft on this substrate was nevertheless highly heterogeneous. For example, a graft made with 43 mole % ethylene sulfide was mainly a white filterable solid containing 44 mole % ethylene sulfide, but the mother liquid contained a soluble graft having 10 mole % ethylene sulfide.

The structure of polyethylenimine is branched. While it is known to initiate the polymerization of ethylene sulfide with highly nucleophilic tertiary amine nitrogens, those in polyethylenimine do not become quaternary and are evidently noncompetitive.

Polyethyloxazoline was hydrolyzed to the extent of 65%, and the resulting linear polyethylenimine (partially in the propionamide form) was grafted in aqueous dioxane (30% water) to give a product dispersible in aqueous acetic acid.

Because ethylene sulfide is hydrophobic, it is convenient to add an organic solvent in order to make the reaction mixture initially homogeneous. When we used acetone as the solvent, we encountered a special effect. When an acetone solution of polyethylenimine was allowed to stand several days at room temperatures before the addition of ethylene sulfide, a reaction occurred. The solution became progressively darker and eventually gelled. Not all of the amino groups reacted with acetone. When the ethylene sulfide was added before the solution gelled, a graft was obtained which could be rendered soluble by hydrolyzing and removing part of the combined acetone. The hydrolysis was done by heating in a mildly acidic solution (Table 1).

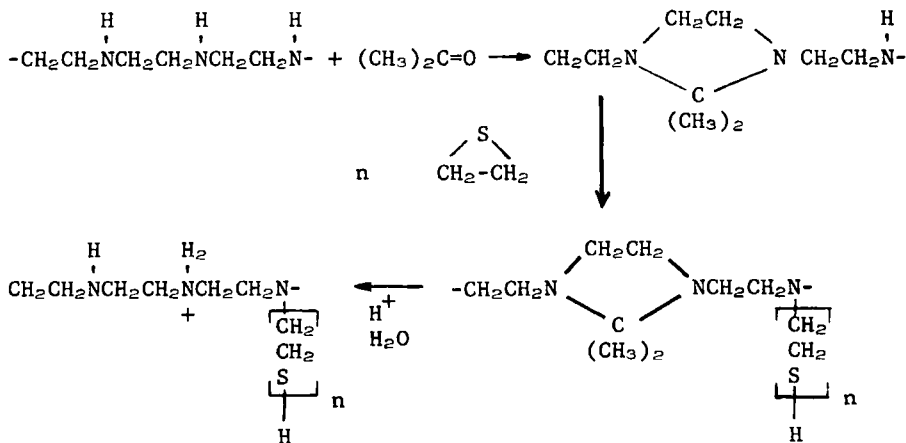


TABLE 1. Acetone Graft Solubility as Function of Aging Time of PEI-6 Solution in Acetone at Room Temperature

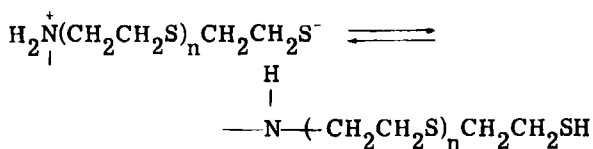
Aging time (days)	Feed ES/PEI (mole ratio)	Insolubles (%)
9	1.0	21
1	0.74	10
6	0.74	8
7	0.74 (slow addn.)	1
9	0.40	0

One might have expected that by restricting the number of sites in this way, one would have generated longer and more easily crystallized graft side chains. On the other hand, acetone, being a non-hydroxylic solvent, favors short and multiple grafting. Equal weights of ethylene sulfide and polyethylenimine were used.

If the graft made in acetone was not post-hydrolyzed and acidified, it crosslinked on standing, especially if allowed to dry as a film. The acidified hydrolyzed graft was vacuum dried to a water-soluble solid.

Whereas grafting in methanol normally gave crystalline, insoluble graft, the acetone derivative was transferred from acetone to methanol and then grafted to give a soluble graft.

The graft polymer exhibited a ceiling temperature for solubility in water provided the pH was in the 8-9.5 range, as it is in aqueous ethanolamine, a common sour gas-scrubbing reagent. This pH region is the isoelectric region for the graft and the ceiling temperature results from hydrolysis of the terminal mercaptide ion at the higher end of the isoelectric region. The random copolymer exhibited no cloud point nor did graft samples lean in ethylene sulfide show one. The addition of salt lowered the cloud temperature and carbonation of the solution eliminated it (Table 2).



A similar amine, N-methylmorpholine, produced cloud temperatures lower than those in ethanolamine solutions. The rate of

TABLE 2. Cloud Points of Graft in Ethanolamine (MEA) Solutions

Substrate	Graft		Cloud point in ethanolamine (°C)	
	Mole ratio ES/PEI	Reaction solvent	10%	30%
PEI-6	0.7	Acetone	40	45
PEI-3	1.08	Dioxane	50	45
PEI-600	0.7	Acetone	55	60
PEI-6	0.7	Acetone, hydrolyzed	70	80
PEI-6	1.08	Dioxane	40 ^a	90

^a45°C in pH 9.5 water.

re-resolution of the polymer after clouding out and cooling was dependent on amine concentration. In ethanolamine solution the clarification of the cooled solution was faster at the lower amine concentration (10%); in N-methylmorpholine, at the higher amine concentration (30%).

In the case of the graft on the higher molecular weight PEI-600 substrate, the graft solution gelled at the cloud point in 30% ethanolamine. Thermoreversible gelling was observed also in the case of the hydrolyzed acetone graft. With this material the gel in 30% ethanolamine was strong and translucent; that in 10% ethanolamine was soft and opaque.

A test was made in which the substrate (PEI-6) was partially premethylated. The graft no longer exhibited cloud point behavior and was less effective as an anticorrosion agent. Quaternization of 10% of the amino groups had occurred during the methylation, and the grafting was conducted with the derivative only swelled with dioxane. The grafting level was not high (weight ratio of S/N = 0.5) in this case.

The property of the graft copolymer which was of interest was that of inhibiting corrosion of iron in an aqueous amine containing acidic substances extracted from sour gas. Laboratory tests were set up for dispersible and/or soluble additives and also for more insoluble additives. The former were tested in a pressure vessel containing bottles of amine solution and immersed coupons and pressured with carbon dioxide and/or hydrogen sulfide. The tests were carried out at 125°C and 30 psi for 16 hr and the loss in coupon

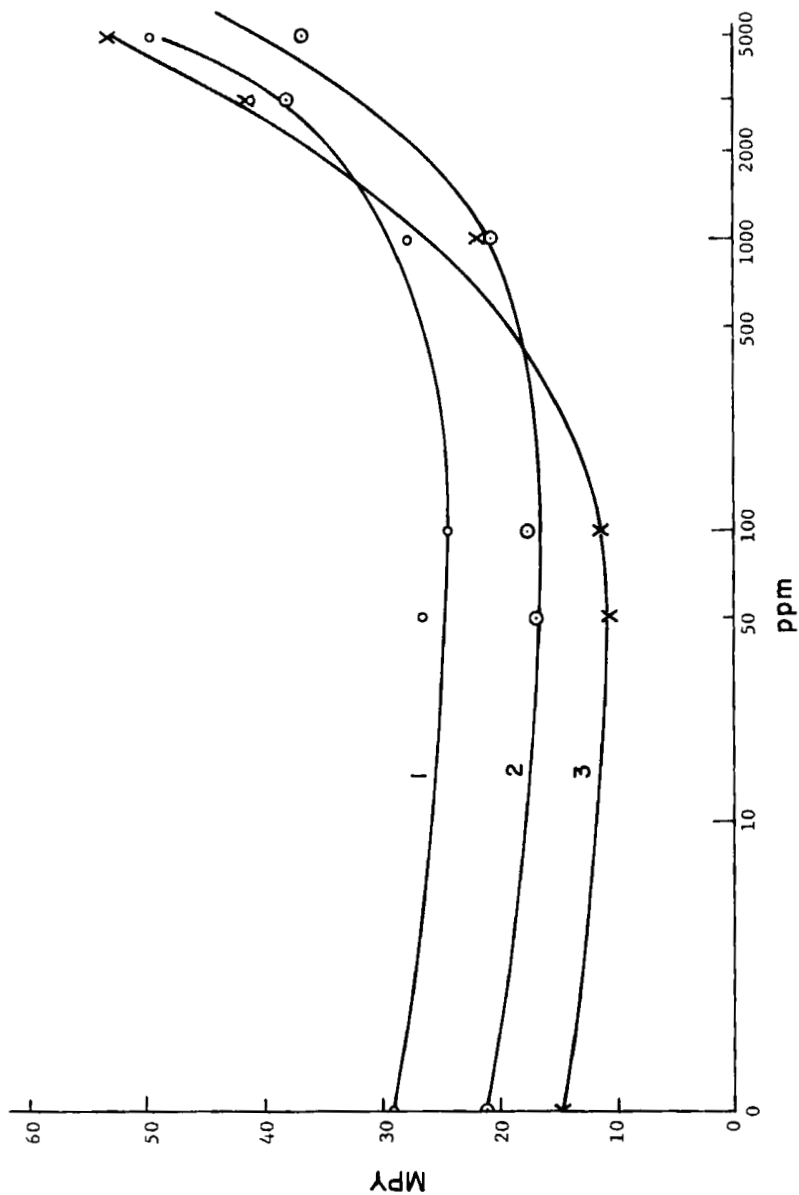


FIG. 1. Corrosion rate in mils per year (mpy) vs. concentration of polyethylenimine: (1) 33% MEA; (2) 20% MEA; (3) 12% MEA. PEI-6; CO₂ only.

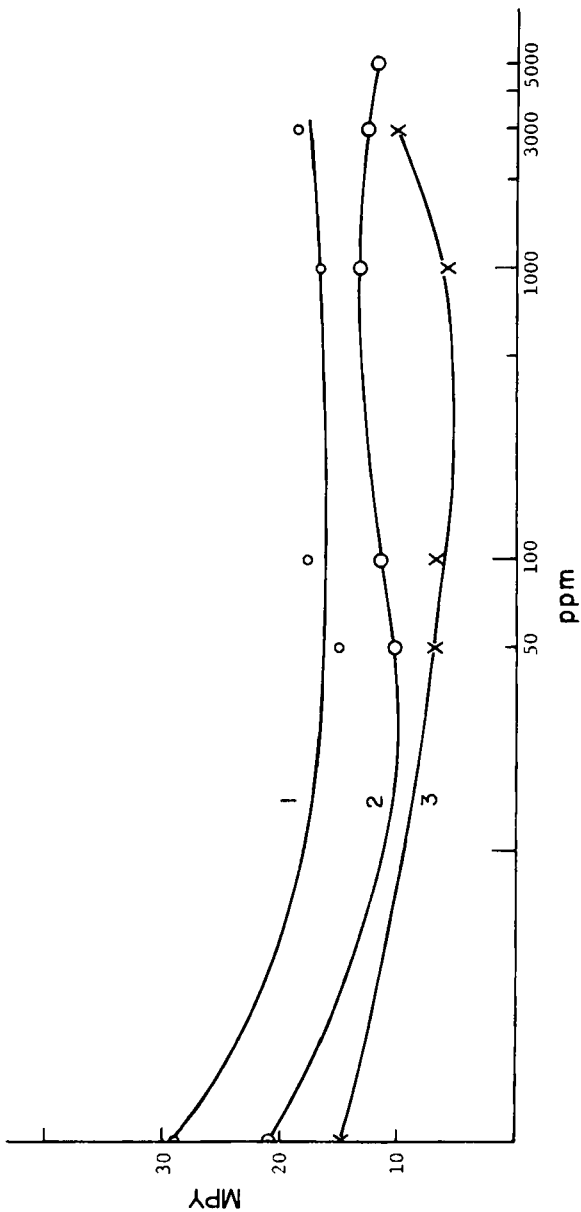


FIG. 2. Corrosion rate vs. concentration of soluble graft made in acetone: (1) 33% MEA; (2) 20% MEA; (3) 12% MEA. Graft; CO₂ only.

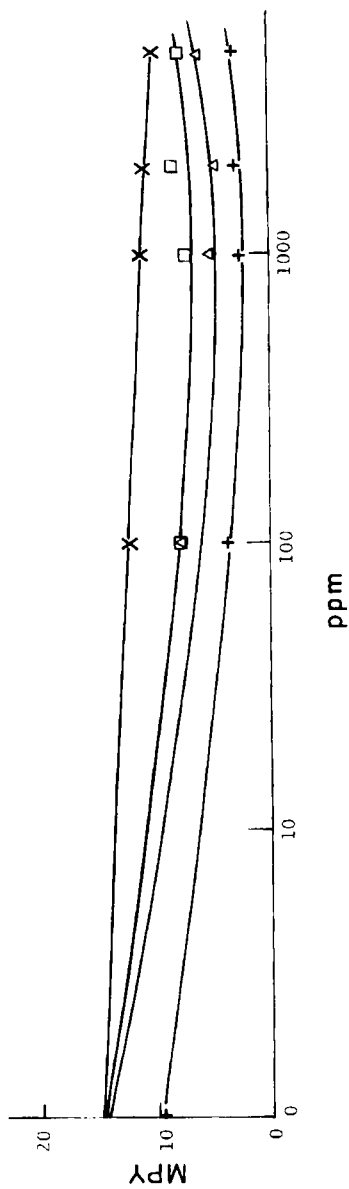


FIG. 3. Comparison of graft and polyethylenimine in the presence of H_2S ($CO_2/H_2S = 9$): (x) graft (acetone), 30% MEA; (\square) PEI-6, 30% MEA; (\triangle) PEI-1000, 30% MEA; (+) PEI-6, 20% MEA.

TABLE 3. Laboratory Corrosion Rates in mils per year (mpy) in Several Ethanolamine Concentrations Containing 100 and 1000 ppm of Graft Made in Acetone

Ethanolamine (%)	Corrosion rate (mpy)					
	CO ₂ only			CO ₂ /H ₂ S		
	Blank	100 ppm	1000 ppm	Blank	100 ppm	1000 ppm
15	20	7.5	7	13	13	11
20	28	16	10	10.5	--	11
30	37	11	11	14.5	5.7	11

weight was measured. The corrosion was general, without pitting. The more insoluble graft was loaded on filter paper in a cartridge and the solution circulated through it. A further test which was of a less practical nature but was informative was to observe the corrosion potential at room temperature using acetic acid as a substitute for carbon dioxide and mercaptoethanol as a substitute for hydrogen sulfide.

The laboratory tests showed that, with CO₂ and without H₂S in aqueous ethanolamine, polyethylenimine was a corrosion inhibitor at low concentration and a corrosion promoter at high concentration (Fig. 1). The dispersible graft was effective as corrosion inhibitor for CO₂ and improved in performance as concentration was increased (Fig. 2). Effectiveness vs. H₂S was limited to lower ethanolamine concentrations (10-15%) (Table 3), but extended to high concentrations in more weakly basic amines, such as diethanolamine or N-methylmorpholine (Fig. 3).

As a test of the effect of changing length of the side chain, a graft (sample 14) was made in dioxane, yielding an opalescent viscous polymer having a mole ratio of 0.69 and another (sample 12) in dioxane containing 7.7% water yielding a paste having a mole ratio of 0.65. In corrosion tests with 12% ethanolamine and with carbon dioxide only, graft 14 was slightly more of a corrosion promoter than graft 12 at high additive concentration, but not nearly as much as was polyethylenimine. The graft made in acetone was not a corrosion promoter at any concentration. With hydrogen sulfide present, it was the other way around; graft 14 was slightly better than 12 in 12% ethanolamine.

A test with oligomeric polyamines showed a correlation of effectiveness with ferrous iron chelate constants (Fig. 4) and molecular weight in the case of polyethylenimine (Figs. 3 and 5). Also the grafts of

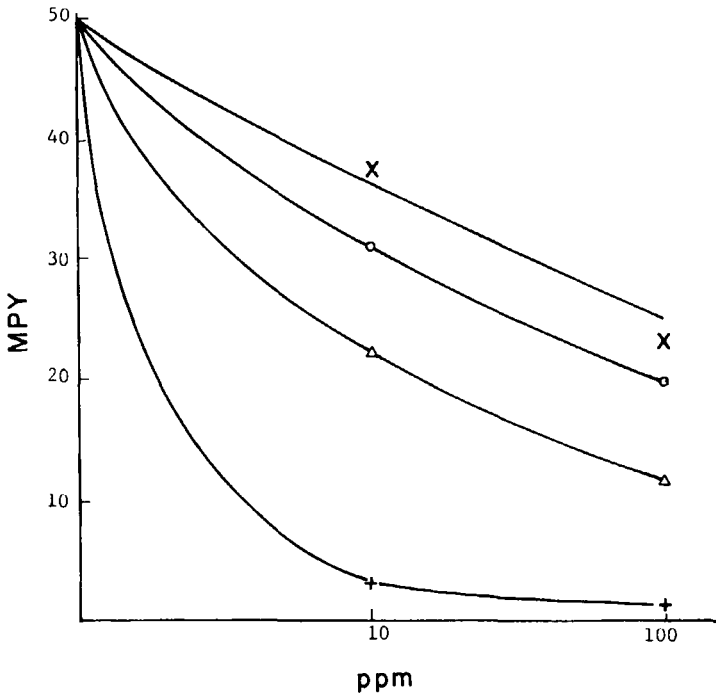


FIG. 4. Comparison of corrosion rate of polyamine oligomers: (x) en4, $\log K = 4.28$; (o) tri tetra, $\log K = 6.23$; (Δ) tetra penta, $\log K = 7.80$; (+) PEI-3, $\log K = 11.20$ [tetrakis(aminoethyl)ethylene-diamine]. Data of Bjerrum et al. [6]; 50% DEA; $\text{CO}_2/\text{H}_2\text{S} = 1/9$; Fe^{2+} .

ethylene sulfide on polyethylene polyamine, PEI 3, 6, and 600 were similar in performance.

It was found [7] that sulfur was synergistic with polyethylenimine, and the addition of sulfur tended to eliminate the corrosion-promoting effect at high polyethylenimine concentration when CO_2 was the sole gas (Table 4).

The blanks showed that corrosion increased with increasing amine concentration and when a substantial amount of hydrogen sulfide was present (Fig. 6).

The recirculating test loop showed in three tests that the cartridge containing the less dispersible graft reduced the corrosion rate to 1.44 mpy (5 day run), 0.74 mpy (3 day run), and 0.85 (3 day run). The gas was 9/1 $\text{CO}_2/\text{H}_2\text{S}$ and the amine, 30% ethanolamine.

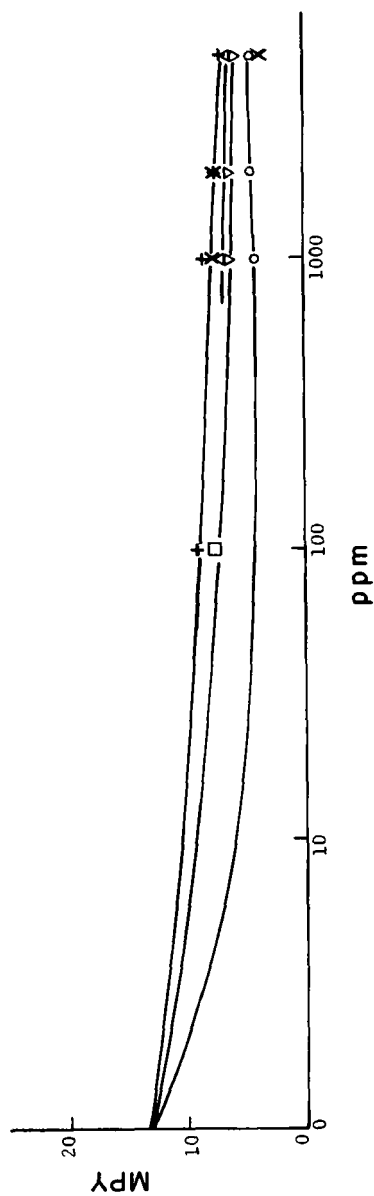


FIG. 5. Comparison of corrosion rates of grades of polyethylenimine: (□) PEI-1000; (+) PEI-600; (x) PEI-400; (Δ) PEI-18; (▽) PEI-12; (○) PEI-6. 30% MEA; CO₂/H₂S = 9/1.

TABLE 4. Sulfur Synergism with PEI; Inhibited Rate in $\text{CO}_2/\text{H}_2\text{S} = 9/1$

MEA (%)	S (ppm)	Inhibited rate (% of control)			
		100 ppm PEI-6	1000 ppm PEI-6	2000 ppm PEI-6	5000 ppm PEI-6
15	---	26, 43	14, 58	27, 14	-13, -24
15	500	62, 15	22, 60	68, 54	58, 3
15	1000	66, 65	44, 65	68, 65	65, 66
15	5000	64, -4	27, 57	53, 45	69, 66

Some observations were made of potential changes shown by steel coupons immersed at room temperature in ethanolamine (1.6 M) solutions containing acetic acid (0.5 M) and the corrosion inhibitors (100 ppm). Under these conditions, the corrosion rate was very low (< 1 mpy) without the inhibitor. The addition of the graft made in acetone produced a potential shift from the -0.4 V (relative to silver-silver chloride) passive value to an active potential of -0.75 V which indicated a bare surface. A diffusion-limited reduction current was observed. When oxygen was added to the argon atmosphere, the potential returned to that of the passive surface. Upon standing, the solution lost its ability to cause this cathodic shift. It lost also the foaming tendency which it initially had. This result indicates that the thiol group may have become consumed in the act of removing rust, and perhaps oxygen as well. The graft was examined also in sodium acetate buffer at pH 8-9 and the rapid cathodic shift again observed. On standing overnight, the diffusion-limited cathodic current was lost. Polyethylenimine gave a similar cathodic shift but only very slowly (overnight) (Fig. 7). This result is consistent with the known tendency of concentrated polyethylenimine solutions to detach scale from a rusty container.

The presence of 1000 ppm of the post hydrolyzed acetone graft gave a rapid cathodic shift to -0.75 V. The passive current was higher and a diffusion limited type reduction current was observed, indicating possible electroactive behavior. Upon standing in air, the solution lost its ability to undergo the cathodic shift and lost also a tendency to foam.

A mill trial was then made in a plant in which ethane containing 2% carbon dioxide and 35 ppm hydrogen sulfide was conditioned with aqueous ethanolamine. Almost immediately after the addition of 100 ppm of the dispersible graft, the level of soluble iron in the recirculating

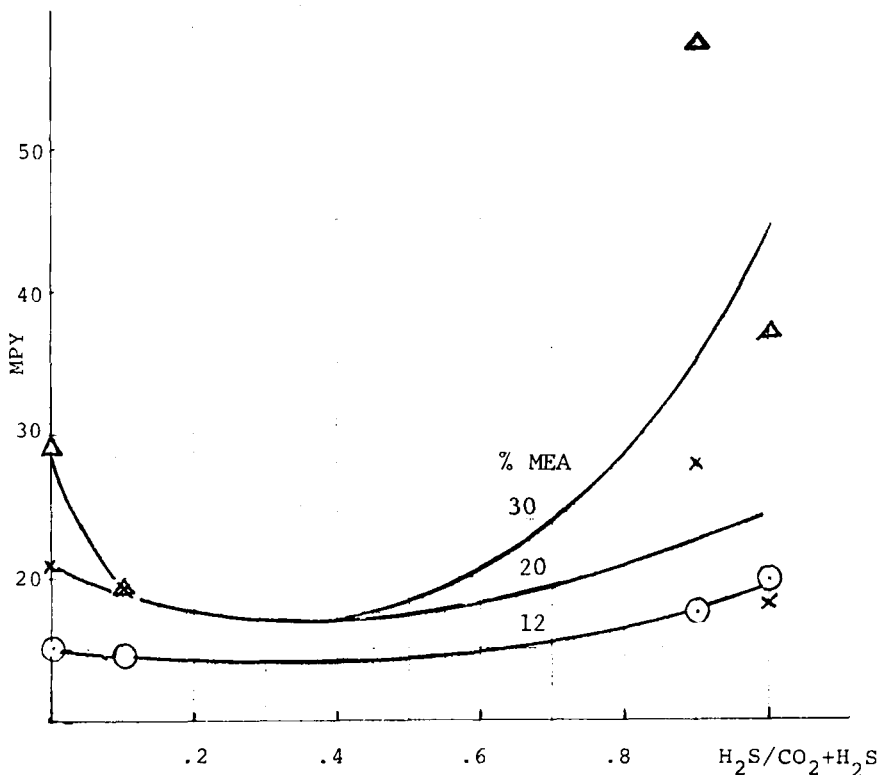


FIG. 6. Corrosion rate of controls vs. H_2S/CO_2 ratio: (○) 12% MEA; (×) 20% MEA; (△) 30% MEA.

stream was reduced from 5-6 ppm to 2-3 ppm. Coupon corrosion in the reboiler where the solvent is stripped fell from 14.9 mpy to 6 mpy; in fact, within a week the corrosion rate fell to 0.4 mpy. During the test the pressure increase that was normally experienced due to scale buildup in the heat exchangers was stabilized, thus allowing several fold increase in the on-stream time. This is called an antifoulant effect.

The ethanolamine concentration was then increased from 13 to 18%, and the graft no longer functioned as an anticorrosion agent. Polyethylenimine was substituted and it functioned in part. It was a corrosion inhibitor, but it actually increased the level of soluble iron and did not act as an antifoulant.

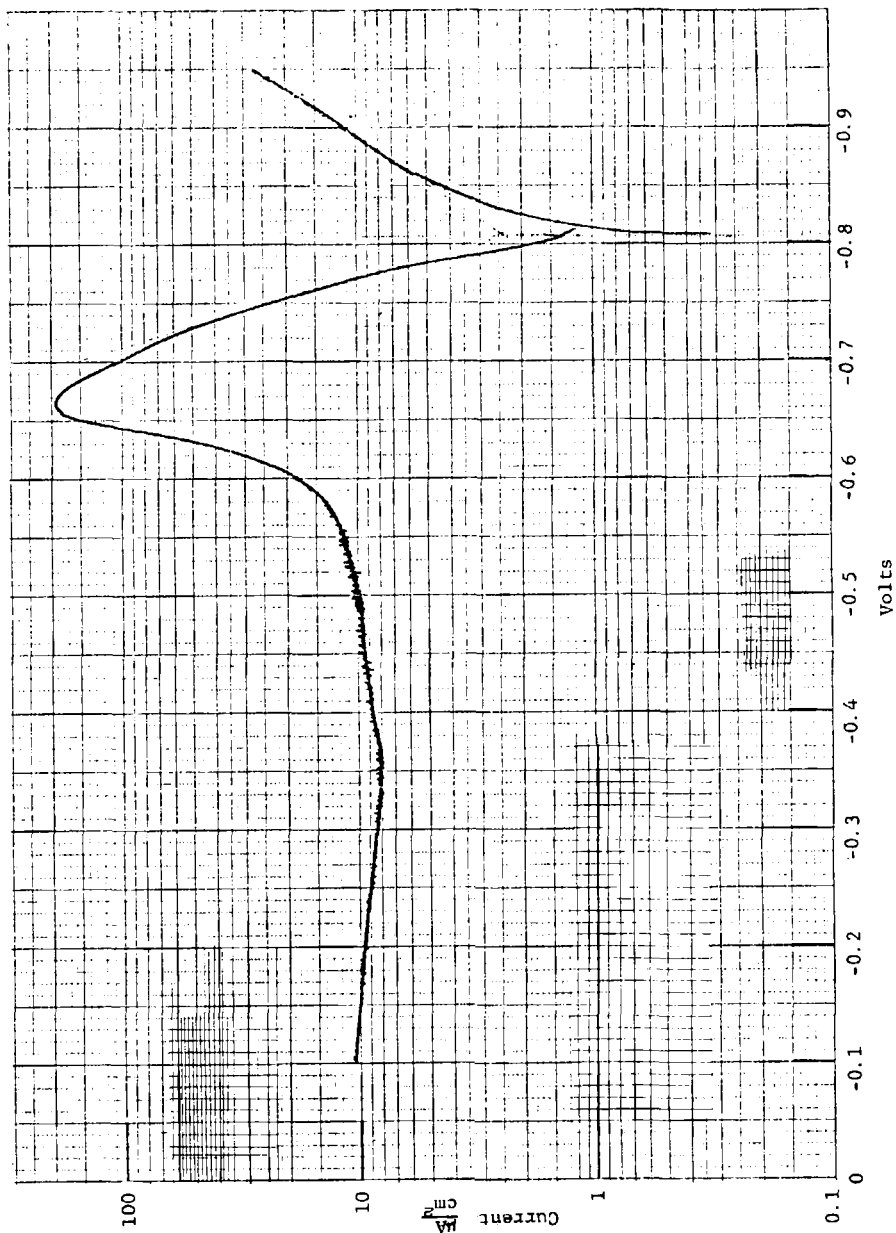


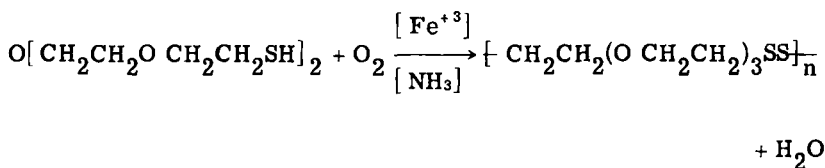
FIG. 7. Tafel plot for 10% ethanalamine, one third neutralized with acetic acid, 850 ppm PEI-6.

The cartridge loaded with less soluble graft was also tested in the mill and it was effective, but tended to load up with scale. It was necessary then to change it, but the graft contained in it had not been exhausted.

DISCUSSION

The mechanism of corrosion in a gas conditioning plant is at least in part protonic. Hydrogen is evolved in the corrosion of iron while conditioning gas containing carbon dioxide. If the corrosion mechanism were exclusively protonic, it would be hard to explain why the corrosion rate increased with increasing amine concentration. Aqueous ethanolamine saturated with CO_2 at room temperature and pressure and then heated in the open to 100°C had a pH of 8 in 10% ethanolamine and 9 in 23% ethanolamine. Water is more acidic. Air is not supposed to be present, but the scale recovered from the plant in which the mill test that was run was a mixture of oxides and sulfides. Freshly precipitated ferrous sulfide is readily oxidized to sulfur and ferric oxide. It seems possible that dithiocarbamate or sulfur synergism may be involved in the laboratory tests with polyethylenimine and hydrogen sulfide. The mechanism of the synergism is presumed to be the known reaction of sulfur with secondary amines to form disulfide and trisulfide bridges and thus crosslink the polyethylenimine in situ.

The role of thiol groups present in the graft is likewise believed to be one of crosslinking. It was found by Nummy [8] that a particular dithiol having chelating properties with iron could be readily cured with air in the presence of a catalytic amount of ferric ion and ammonia. A nonchelating dithio such as hexamethylenedithiol was relatively inactive.



Insoluble films on test compounds were formed during the laboratory test of the graft made in dioxane and during electrolytic oxidation of the graft. The insoluble film was a protective coating against air oxidation initiated with a trace of hydrogen chloride. It had toughness and a degree of water resistance.

The ability of polyethylenimine to transport iron is shown by the

fact that it dissolves freshly precipitated ferrous hydroxide in aqueous ethanolamine. The graft had little tendency to do so provided the ethylene sulfide to polyethylenimine weight ratio was at least 1:2.

The graft did clean the coupon in the polarization studies, but it lost the capability of doing so, presumably when the thiol group was consumed. It formed a visible coating. This is no doubt the important factor in the effectiveness. The cathodic current in the electrochemical tests may be due to disulfide. Some regeneration of thiol was observed in the mill run.

The graft reduced copper salts, if present, and caused the plating of copper, but so did polyethylenimine.

EXPERIMENTAL

Acetone Derivative of Polyethylenimine

Amine bending absorptions in the $750\text{--}950\text{ cm}^{-1}$ region remain strong after 3 hr, but are largely gone after a day. The NH_2 wag and twist absorption in the $850\text{--}950\text{ cm}^{-1}$ region and the NH_2 anti-symmetric stretching band at 3360 cm^{-1} disappear, also. Some of the NH bending absorption at 770 cm^{-1} and NH stretching (and NH_2 symmetric stretch) at 3300 cm^{-1} persist. The dimethylimidazolidine structure should have a doublet at 7.25 and $7.3\text{ }\mu\text{m}$, but a single methyl band at $7.25\text{ }\mu\text{m}$ was observed. There was a slow development of a band at $6.25\text{ }\mu\text{m}$ as the color deepened from yellow to brown over the period of a week. The color bodies were not extractable from the polymer. Unless it had been heated as a dry material, the polymer was soluble in warm tetrahydrofuran. It dissolved in warm acetone or chloroform and did not precipitate on cooling. The neutral equivalent was 100.

The amine infrared bands reappeared on hydrolysis, but the nitrogen content did not increase all the way to that of polyethylenimine.

ANAL. Found: N, 25.3% (acetone derivative); N, 27.6% (hydrolyzed acetone derivative). Calcd: N, 32.5% (polyethylenimine).

Separation of Graft Sample by Extraction

A solution of polyethylenimine (PEI-6, 63.4 g) in water (45.4 g) and acetone (416 g) was aged 5 days. To a portion (308 g) was added ethylene sulfide (39 g). The product was slightly turbid, but could be clarified by reducing the pH below 8.5. The turbid solution was diluted with water and acetone distilled under reduced pressure.

The unacidified graft was extracted with water giving a soluble fraction (9.5%) which had a neutral equivalent of 10.55 meq/g and gave no cloud point. A second extraction was made with aqueous trimethylamine. The soluble portion (28% of original) had a neutral equivalent of 6.3 meq/g and gave cloud points of 80 and 90°C in 10 and 30% ethanolamine, respectively. The remainder had a neutral equivalent of 4.5 meq/g. Only a portion was soluble in 10% ethanolamine and it gave a cloud point of 75°C and the turbid solution clarified slowly on cooling. This portion was hydrolyzed with hydrochloric acid, regenerated with anion exchange to give in 34% yield a product of neutral equivalent 9.1 meq/g, having cloud points of 70 and 80°C in 10 and 30% ethanolamine, respectively.

The insoluble portion was hydrolyzed with hydrochloric acid and then the solution adjusted to pH 8 with Dowex 1 (hydroxide form) anion exchange resin. The solution was concentrated under reduced pressure and a viscous residue obtained. The yield of hydrolyzed polymer was 26.4 g; the neutral equivalent was 8.8 meq/g. The S/N atomic ratio was 0.84.

Grafting in Solvents Other than Acetone

To a solution of polyethylenimine (PEI-6) (14.4 g) in methanol (30 ml) was added ethylene sulfide (12 g). The solution became cloudy and warm and within a minute had formed a white cake. The product was partially soluble in methanol.

ANAL. Found (insoluble portion): N, 20.0%; S, 17.9%; (soluble portion): N, 16.9%; S, 5.4%.

Polyethylenimine (PEI-6), 50 g) was dissolved in dioxane (75 g) and ethylene sulfide (52 g) added gradually while the mixture was stirred in a 70°C bath. The product contained a white precipitate. It was concentrated to an opalescent sticky mass, yield 78 g.

ANAL. Found: N, 13.95%; S, 22.0%.

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