

- (6) *Ibid.*, Vol. II, p. 358, 1965.
 (7) de Maine, P.A.D., Seawright, R.D., *Ind. Eng. Chem.* **55**, 29 (1963).
 (8) Desai, H.N., Naik, D.B., Desai, B.N., *Indian J. Phys.* **8**, 323 (1935).
 (9) El-Aggan, A.M., Bradley, D.C., Wardlaw, W., *J. Chem. Soc.* **1958**, 2092.
 (10) International Critical Tables, pp. 27 (III), 143 (VI), McGraw-Hill, New York, 1926.
 (11) Kraus, C.A., Bishop, J.E., *J. Am. Chem. Soc.* **43**, 1568 (1921).
 (12) Lange, J., *Ann. Physik. Chem.* **A188**, 284 (1941).
 (13) Nazarova, Z.N., Tsumervanik, G.P., *J. Gen. Chem. USSR* **14**, 236 (1944).
 (14) Van Rysselberghe, P., Fristrom, R.W., *J. Am. Chem. Soc.* **67**, 680 (1945).
 (15) Van Rysselberghe, P., Hunt, G., *Ibid.*, **66**, 1488 (1944).
 (16) Vogel, A.I., "Quantitative Inorganic Analysis," 2nd ed., pp. 321, 494 Longmans, Green, London, 1948.

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Stabilization of Monoethanolamine Solutions in Carbon Dioxide Scrubbers

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Monoethanolamine (MEA), the regenerative absorbent used in CO₂ scrubbers aboard nuclear submarines, is now stabilized with a chelating agent, the monosodium salt of *N,N*-diethanolglycine (VFS). This inhibitor is not effective against oxidative degradation at 55° C. in the presence of procatalytic metals, particularly copper. Effective stabilization in the presence of copper is given by tetrasodium (ethylenedinitrilo)tetraacetate (EDTA). At 98° C., with small quantities of typical metal contaminants added, both VFS and EDTA are required for stabilization. The additive combination is ineffective at 138° and 149° C. with limited amounts of oxygen present. Pyrolytic stability of the formulation is adequate at these temperatures. VFS and EDTA are both true anti-oxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA, suggest that their antioxidant activity results from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

AN IMPORTANT specialized use of the regenerative absorbent monoethanolamine (MEA) is in carbon dioxide scrubbers for atmosphere purification aboard nuclear-powered submarines. The present study summarizes the factors influencing MEA degradation under conditions of submarine service, and the beneficial effect of certain chelate formers in reducing such degradation. Pertinent chemical properties of MEA have been reviewed (4).

On the assumption that metal contaminants, particularly iron, catalyzed oxidative breakdown of MEA, a chelating agent, the monosodium salt of *N,N*-diethanolglycine (2) (VFS), is now a required constituent of base stock MEA procured for submarine scrubber use (3).

EXPERIMENTAL

In service, scrubber solutions are in contact with stainless steel, and are exposed to temperatures from about 32° C. in the absorber to 138° C. in the stripper, and possibly 150° C. in contact with the stripper heaters. Experiments simulated a variety of conditions. Most of the aeration tests were conducted in glass cells at 55° C., permitting convenient measurement of the reaction products. At temperatures much above 55° C. corrosive attack on glassware was excessive, so stainless steel (Type 304) was employed. All cells were fitted with standard taper joints to accept water-cooled reflux condensers. The rate of air through the 300-ml. samples was 1 cc. per ml. of solution per minute. Ammonia evolution was monitored by passing the effluent air through 2% boric acid solutions, which were periodically titrated with strong acid. Total nitrogen was determined by Kjeldahl analysis, and peroxides by the iodine-thiosulfate method. All MEA used was redistilled and stored at 5° C. in evacuated sealed vials.

EFFECT OF AIR AND CARBON DIOXIDE

Carbon dioxide-free air passed through 4*N* MEA solutions at 55° C. for several days produced no perceptible degradation. Addition of 1% CO₂ to the air stream to simulate submarine atmospheric conditions, however, resulted in almost instantaneous degradation characterized by the production of ammonia and peroxide (Figure 1, A), the conversion of amine nitrogen to nonbasic forms (possibly cyclic condensation products) as shown in Figure 2, and gross discoloration of the fluid. All further references to MEA in this study imply the carbonated form unless otherwise indicated.

EFFECT OF VFS (NO METALS PRESENT)

Aeration-oxidation experiments at 55° C. with metal-free MEA solutions containing 1.5% VFS revealed no degradation during a 6-week period, indicating that the chelate was an efficient antioxidant in its own right—i.e., it plays a role in which metal deactivation has no part. The long useful life of the amine containing VFS also strongly suggests that VFS is not functioning as a short-term sacrificial additive.

VFS-PEROXIDE REACTION

Air oxidation of many compounds proceeds autocatalytically by a sequence of free radical reactions characterized by the initial formation of peroxides. Efficient antioxidants for such systems function by reacting with, and destroying, the peroxide intermediate, thus interrupting the reaction chain. The presence of peroxides in oxidized MEA solutions

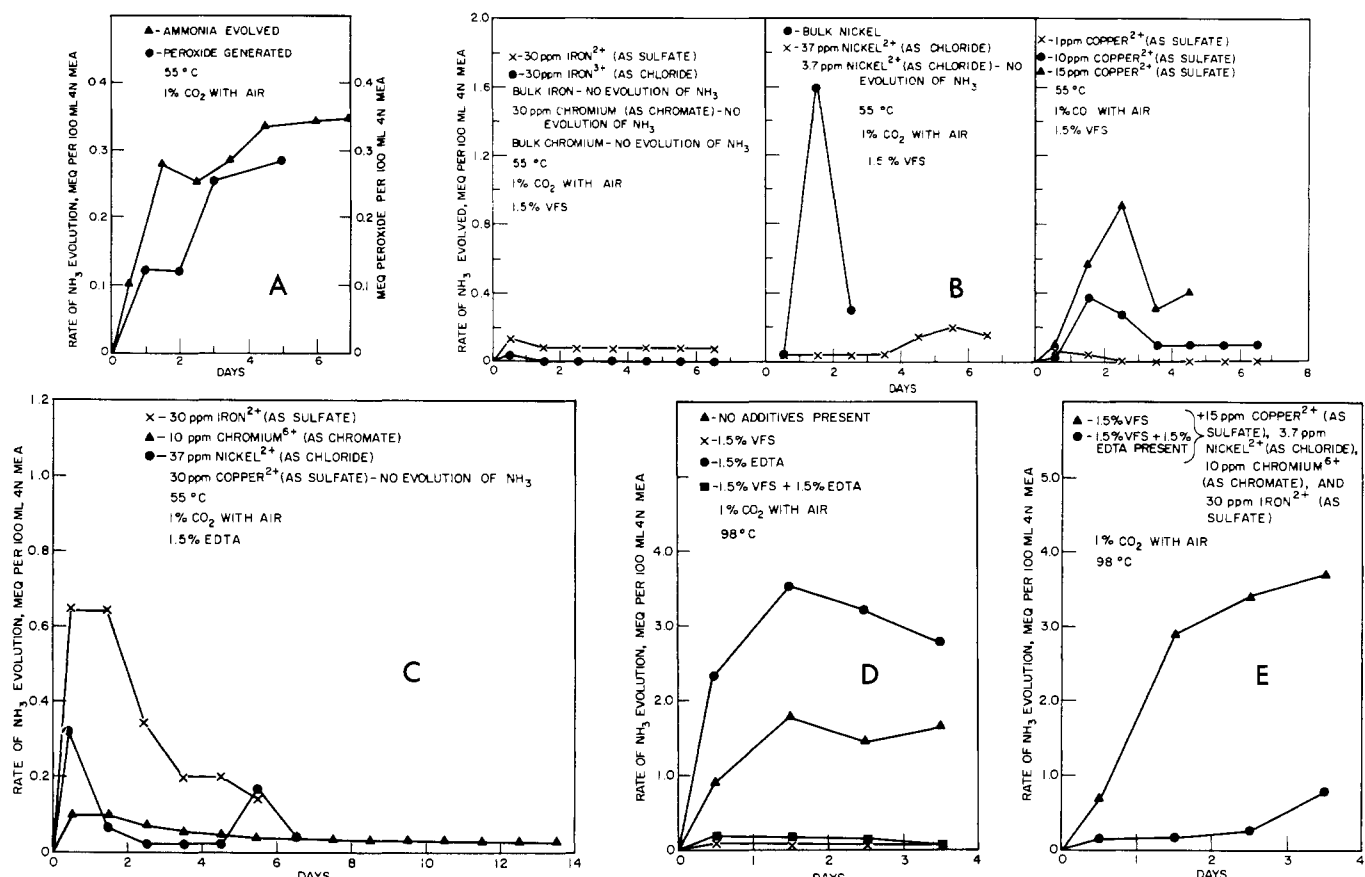


Figure 1. A. Comparison of peroxide formation and ammonia evolution during MEA oxidation. B. Effect of metals on stability of MEA + VFS. C. Effect of copper, iron, nickel and chromium on stability of MEA + EDTA. D. Effect of VFS and EDTA on stability of MEA. E. Effect of additives and metals on stability of MEA

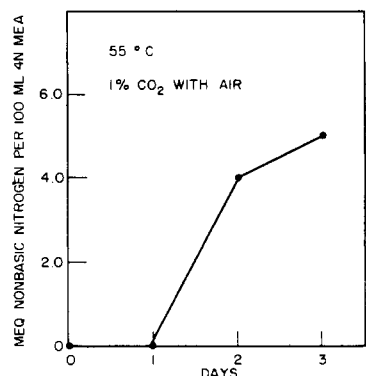


Figure 2. Generation of nonbasic nitrogen-containing compounds in 4N MEA

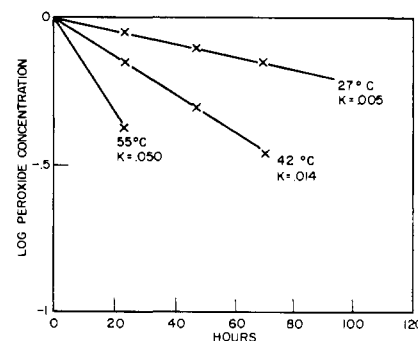


Figure 3. Reaction of VFS with *tert*-butyl hydroperoxide

suggested that oxidation of the amine was peroxide-automated, with the stabilizing role of VFS being the destruction of peroxides and interruption of the oxidation chain.

Such an antioxidant mechanism requires that VFS reduce peroxides, which was verified by reacting equimolar quantities of VFS and *tert*-butyl hydroperoxide in aqueous solution. The reactions were followed by measuring the change in peroxide concentration with time at 27°, 42°, and 55 °C. Figure 3 shows that the peroxide was in fact reduced by VFS. Infrared analysis suggested that the VFS had been oxidized by the peroxide to an amine oxide; the latter possessed no further antioxidant properties.

EFFECT OF VFS IN PRESENCE OF METALS

The procatalytic effect of metals in oxidation reactions is well known. To determine what metals were normally present in the MEA solutions, samples of base stock amine, scrubber solutions, and make-up water whose prior histories and treatment were known were analyzed by emission spectroscopy.

Both the base stocks and used scrubber solutions contained approximately a dozen metals in amounts from less

than 1 part per million, to several hundred parts per million, in the case of sodium derived from VFS. Make-up water samples contained only copper. Of these metals, chromium, nickel, iron, and copper were selected for study—the first three because they comprise the construction material of the scrubber, and copper because it is a well-known degradative catalyst (Table I).

Figure 1,B, summarizes the effect of four metals on MEA-VFS solutions. No deterioration occurred with chromium or with bulk iron. Ferric and ferrous ions produced little deterioration. Nickelous ion (3.7 p.p.m.) was relatively inert, but a tenfold increase caused perceptible activity. Bulk nickel metal corroded rapidly and resulted in severe amine deterioration. Cupric ion (1 p.p.m.) triggered small but perceptible ammonia evolution; at 15 p.p.m., the effect was proportionately more serious.

SCREENING OF MISCELLANEOUS ADDITIVES

Inability of VFS to stabilize MEA in the presence of copper indicated the need for a more effective additive. The optimum characteristics desired in such an additive were that, like VFS, it be an antioxidant in its own right, and a

Table I. Metal Contents of Scrubber Solutions and Make-up Components

Submarine	Source	Copper, P.P.M.	Nickel, P.P.M.	Chromium, P.P.M.	Iron, P.P.M.
Nautilus	Potable water	5.0	None	None	None
	Storage MEA	2.5
	Scrubber (400 hr.)	8.5
	Scrubber (800 hr.)	13.5
Sculpin	Potable water	2.0
	Lean MEA	8.0	10.0
Sea Wolf	No. 1 storage	5.0	2.0	0.4	8.0
	No. 2 storage	3.5	1.8	...	5.0
	Potable water	3.5	None	None	None
	No. 1 scrubber (200 hr.)	9.0	3.0	0.4	15.0
	No. 2 scrubber (168 hr.)	10.0	3.7	0.4	43.0
	No. 2 scrubber (246 hr.)	13.0	3.0	0.6	50.0

^aNo analysis performed.

copper deactivator. Materials selected for study included water-soluble chelating agents, amines, and phenols known to be stabilizers for a variety of systems. Their antioxidant activities in concentrations of 1.5% were first determined in the absence of copper.

The compounds investigated were:

Sodium mercaptobenzothiazole	Propyl gallate
Disalicylalpropylenediamine	Sorbitol
<i>p</i> -Acetylaminophenol	<i>n</i> -Dimethylglycine
<i>o</i> -Aminophenol	Phthaloylglycine
Quinalizarin	Diethylcyclohexylamine
Bisacetylacetone ethylenediimine	Tetrasodium (ethylene-dinitrilo)tetraacetate (EDTA)

Only the last listed of these compounds demonstrated an acceptable degree of antioxidant activity at 55° C., over a 2-week test period, neither peroxide nor ammonia being formed. With all other additives, generation of ammonia was immediate. Three randomly chosen oxidized solutions containing unacceptable additives—i.e., *o*-aminophenol, *p*-acetylaminophenol, and quinalizarin—were examined for their peroxide content; this compound was present in concentrations similar to that found in 4*N* MEA alone. In other experiments, it was determined that, like VFS, EDTA reacted with and destroyed peroxides, probably being converted to an amine oxide (1).

The formation of peroxides in the presence of ineffective additives, as well as the similarity in the reactivities of VFS and EDTA, suggests that the antioxidant activities of both are based on their efficient destruction of chain-propagating peroxide intermediates formed during MEA oxidation.

EFFECT OF EDTA IN PRESENCE OF COPPER

Aeration oxidations with the additive showed no amine breakdown in a 1-week period with 30 p.p.m. of cupric ion present. The additive was less effective than VFS when 30 p.p.m. of ferrous or 10 p.p.m. of chromate ions were added (Figure 1,C). With 37 p.p.m. of nickel, there was little difference between the rather indifferent activities of the additives.

These data suggested that each additive to a large extent complemented the other's effectiveness. Accordingly, a 4*N* MEA solution containing 1.5% each of VFS and EDTA, was subjected to oxidation at 55° C. with cupric, nickelous, ferric, and chromate ions present. To increase the severity

of the test, stainless steel cells replaced those of glass. During a 2-week period there was no evidence of MEA breakdown.

OXIDATION STABILITY OF MEA AT 98° C.

Figure 1,D, shows the rate of ammonia evolution from uninhibited MEA in stainless steel cells to be large at 98° C. Although addition of EDTA did not improve stability, VFS was highly effective. No additional improvement resulted from a combination of 1.5% each of VFS and EDTA.

The stabilizing effect of VFS at 98° C. was nullified by salts of iron, nickel, chromium, and copper (Figure 1,E). Although EDTA did not stabilize the solution at this temperature in the absence of metals, the combination of VFS and EDTA resulted in a substantial improvement in stability with metals present, more in fact than could have reasonably been predicted from the sum of their individual contributions.

HIGH TEMPERATURE STATIC TESTS

To assess the stability of carbonated MEA solutions under stripper conditions, static bomb tests were conducted at 138° and 149° C. in stainless steel cells. The results indicate that, in the absence of oxygen, the solutions are pyrolytically stable. With even limited concentrations of oxygen present, however, oxidative degradation occurs; the VFS-EDTA additive package offers no improvement under these conditions. Thus, the exposure of MEA solutions to temperatures of 138° C. or above in scrubber equipment is feasible to the extent that oxygen can be removed before exposure.

LITERATURE CITED

- (1) Herbst, J.H.E., Barton, S.C., *Tappi* 46, 486 (1963).
- (2) Johnson, W.W., McElwain, R.E., U.S. Patent 3,137,654 (June 16, 1964).
- (3) Military Specification MIL-M-23573 (SHIPS), "Monoethanolamine Chelating Agent Solution," Feb. 12, 1963.
- (4) Scheiman, M.A., "Review of Monoethanolamine Chemistry," U.S. Naval Research Laboratory, Rept. 5746 (June 1962).

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