

AD609888

NRL Report 6189

The Stabilization of Monoethanolamine Solutions for Submarine Carbon Dioxide Scrubbers

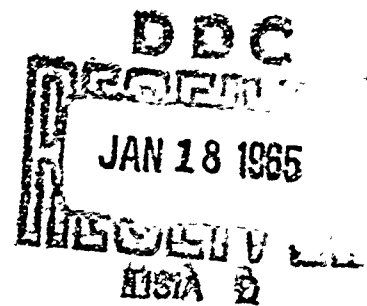
C. H. BLACHLY AND H. RAVNER

*Surface Chemistry Branch
Chemistry Division*

December 4, 1964

COPY	<u>2</u>	OF	<u>3</u>	<u>R</u>
HARD COPY	\$. 1 . 0 0			
MICROFICHE	\$. 0 . 5 0			

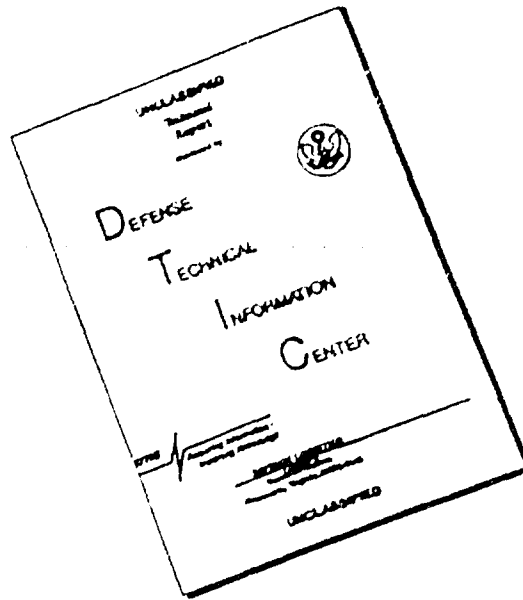
15 P



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

ARCHIVE COPY

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL APPARATUS AND TEST CONDITIONS	1
EFFECT OF AIR AND CARBON DIOXIDE	2
EFFECT OF VFS (NO METALS PRESENT)	2
VFS-PEROXIDE REACTION	2
EFFECT OF VFS IN THE PRESENCE OF METALS	4
SCREENING OF MISCELLANEOUS ADDITIVES	6
EFFECT OF EDTA IN THE PRESENCE OF COPPER	7
OXIDATION STABILITY OF MEA AT TEMPERATURES ABOVE 131° F	8
HIGH-TEMPERATURE STATIC TESTS	10
CURRENT STATUS OF VFS-EDTA ADDITIVE PACKAGE	12
SUMMARY AND CONCLUSIONS	12
RECOMMENDATIONS	13
REFERENCE	13

ABSTRACT

Monoethanolamine (MEA), the regenerative absorbent used in all CO₂ scrubbers aboard nuclear submarines, is at present stabilized with a chelating agent, the monosodium salt of N, N-diethanolglycine (VFS). In dynamic tests at 131° F the additive, although effective in metal-free solutions, did not prevent oxidative degradation of the amine when copper was present in the concentrations usually found in scrubber solutions. Effective stabilization in the presence of copper was given by the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA). At 208° F in the presence of several metal contaminants, a combination of VFS and EDTA was required for stabilization.

Both VFS and EDTA were shown to be true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA suggested that their antioxidant activity resulted from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

Static tests to simulate stripper operation revealed the amine to be reasonably stable against thermal degradation at 280° and 300° F. Some oxidative breakdown occurred with a limited quantity of air present; more serious degradation occurred when oxygen gas replaced air. A combination of VFS and EDTA did not prevent oxidation of the amine at these temperatures when small amounts of oxygen were present.

It was recommended that contamination by copper be curtailed to increase the service life of CO₂ scrubber solutions, that a combination of VFS and EDTA be used as a stabilizing additive package, and that additional engineering data be obtained from dockside scrubber tests.

PROBLEM STATUS

This is a final report on this phase of the problem; work is continuing on other phases.

AUTHORIZATION

NRL Problem C08-05
BuShips Problem SF-013-08-03-4092,4093,4094,4095

Manuscript submitted September 28, 1964.

THE STABILIZATION OF MONOETHANOLAMINE SOLUTIONS FOR SUBMARINE CARBON DIOXIDE SCRUBBERS

INTRODUCTION

Carbon dioxide is the major contaminant of nuclear submarine atmospheres, and its continuous removal must be efficient and reliable. The regenerative absorbent now used in the CO₂ scrubbers on nuclear submarines is a formulation based on monoethanolamine (MEA); its continued use by the Navy reflects a generally acceptable, but not necessarily optimum, level of performance. Degradation of the amine is manifested to ship personnel by the generation of the toxic irritant ammonia, by darkening of the solution which interferes with the determination of normalities by color indicator titrations, by decreased efficiency of CO₂ removal, and by excessive requirements for makeup amine. The storage of adequate replacement stocks of MEA on board preempts valuable space on the submarine.

The need to improve the stability of MEA scrubber solutions, for the reasons enumerated became apparent during early nuclear submarine operations. MEA degraded under service conditions but additives, particularly certain chelate-formers, gave beneficial effects in reducing such degradation. The progress of this work is contained in the annual summary of the NRL habitability program (1) and in communications with BUSHIPS. Also a comprehensive literature survey of the properties of MEA (2) was carried out for better understanding of its reactions.

A significant portion of the initial program to develop suitable stabilizers was carried out at the Mare Island Naval Shipyard (3,4). On the assumption that oxidative breakdown of the amine was catalyzed by metal contaminants, particularly iron, additives of the chelating type received special attention. The most effective of those studied was the monosodium salt of N,N-diethanolglycine (3,4).^{*} On the basis of the Mare Island results, VFS is now a required constituent of the base stock MEA procured for scrubber use (5). (Although VFS is an effective stabilizer of scrubber solutions, it does not chelate with iron ions to any significant extent at the alkaline pH of the scrubber solution.)

In service, scrubber solutions are in contact with the stainless steel from which the scrubbers and their components are fabricated. The temperatures to which the solutions are exposed range from about 90° F in the absorber to 280° F in the stripper (although skin temperatures of the immersion heaters may be of the order of 300° F). In the absorber, the solution is in intimate contact with an abundance of air, and is presumably close to saturation with respect to both air and CO₂ at the time it is drawn off to be cycled through a heat exchanger to the stripper. The only air available to the amine after it leaves the absorber is that carried in solution.

EXPERIMENTAL APPARATUS AND TEST CONDITIONS

Oxidation of unstabilized MEA occurs in all compartments of the scrubber system at rates which are dependent both on temperature and oxygen supply. Despite the abundance of oxygen in the absorber the reaction rate is slow because of the relatively low temperature. As the solution is pumped to the stripper the initial increase in rate due to the

^{*}The name is usually abbreviated to VFS, the initials of a commercial trade name for this material.

temperature rise is offset to an undetermined extent by the depletion of the available oxygen supply. Since there is no one set of conditions of temperature and oxygen supply which completely describes the environment of the solution, the laboratory experiments were designed to simulate a variety of conditions. The majority of aeration tests were conducted in glass cells at 131°F (55°C), at this temperature the oxidation rate permitted convenient measurement of the reaction products. At temperatures much above 131°F, corrosive attack by the amine on laboratory glassware was excessive, and stainless steel (type 304) cells were employed. Use of these cells had the additional advantage of permitting exposure of the solutions to simulated scrubber wall conditions. All cells accommodated 300 ml samples and were fitted with standard taper joints to accept water-cooled reflux condensers. The rate of airflow through the samples was 1 cc per ml of solution per minute. Unless otherwise indicated, 1% of CO₂ was added to the air to approximate submarine atmospheric conditions. 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 conventional Kjeldahl analysis, and peroxides by iodine-thiosulfate method.

Laboratory-grade MEA was generally so contaminated as to be unsuitable as a reference material. All MEA used in this study, therefore, was redistilled and stored at 40°F in evacuated sealed vials until needed.

EFFECT OF AIR AND CARBON DIOXIDE

When CO₂-free air was passed through 4N MEA solutions at 131°F for several days, no perceptible degradation occurred. Addition of 1% CO₂ to the air stream, however, resulted in almost instantaneous onset of degradation characterized by the evolution of ammonia and the generation of peroxide (Fig. 1); the conversion of amine nitrogen to non-basic forms, possibly cyclic condensation products (Fig. 2); and gross discoloration of the fluid. All further references to MEA in this report will imply the carbonated form of the amine unless otherwise indicated.

It will be seen in subsequent experiments that the pattern of ammonia evolution from oxidized MEA solutions containing procatalysts often differs from that in Fig. 1 in that the rate increases rapidly to a maximum and then falls off sharply. Since in these latter instances oxidation of the amine proceeds despite any subsequent reduction in ammonia evolution (e.g., by conversion of amine nitrogen to nonbasic forms), it is believed that the catalysts promote secondary oxidative reactions which do not necessarily lead to ammonia evolution.

EFFECT OF VFS (NO METALS PRESENT)

Aeration-oxidation experiments conducted at 131°F with metal-free MEA solutions containing 1.5% VFS revealed no evidence of degradation during a six-week period, i.e., there was no generation of ammonia, peroxides, or nonbasic nitrogen-containing compounds. Apart from the practical importance of these results, their quite unexpected significance was that the chelate was evidently a true antioxidant in its own right, a role in which metal deactivation played no part.

VFS-PEROXIDE REACTION

The generation of peroxides in oxidized unstabilized MEA solutions, and the absence of peroxides when VFS was present suggested the nature of the stabilizing role of the additive. In both aqueous and nonaqueous media, air oxidation of many compounds proceeds by a sequence of reactions characterized by the initial formation of peroxides.

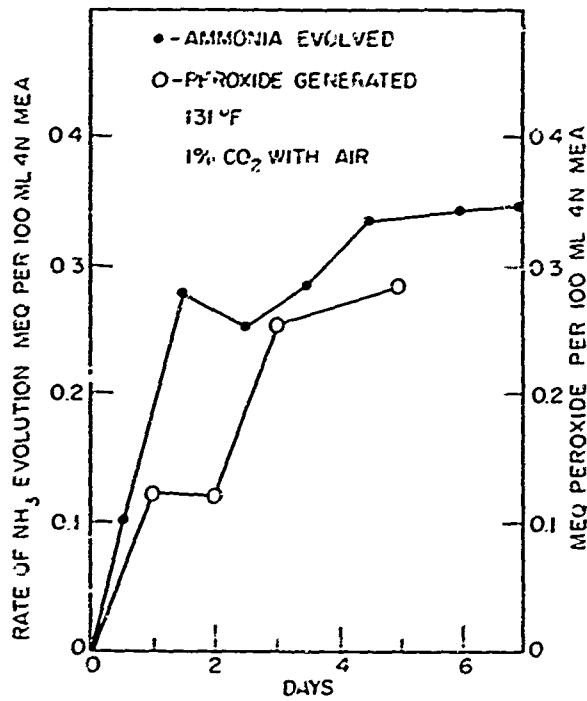
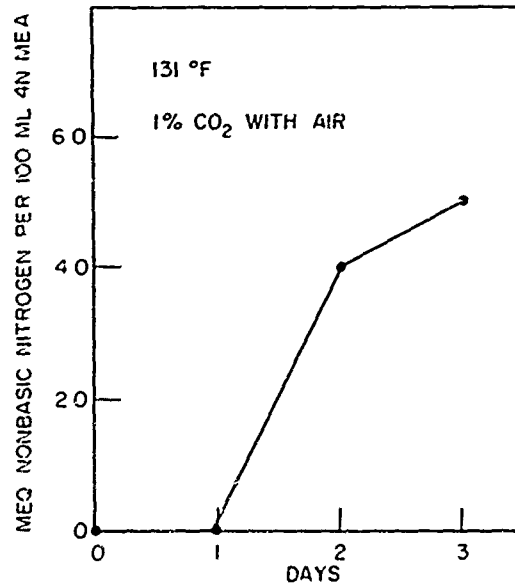


Fig. 1 - Dynamic test of MEA stability with no additive present

Fig. 2 - Dynamic test of generation of nonbasic nitrogen-containing compounds with no additive present



Subsequent oxidation of the parent material is autocatalyzed by the decomposition of the peroxide, producing free radical chain carriers. The most 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 indicated the possibility that oxidation of the amine was peroxide-autocatalyzed, with the stabilizing role of VFS being the classic one of destruction of peroxides and interruption of the oxidation chain.

Such an antioxidant mechanism requires that the VFS be capable of reducing peroxide. This capability was verified by reacting equimolar quantities of VFS and tertiary butyl

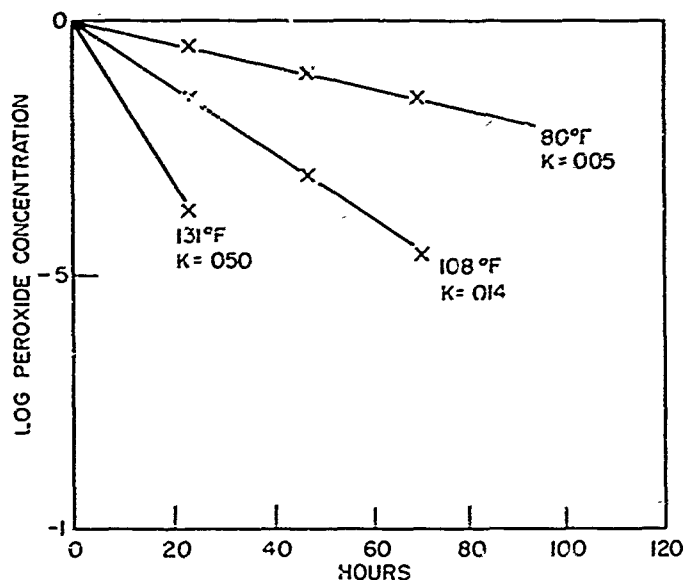


Fig. 3 - Reaction of VFS with tert-butyl hydroperoxide

hydroperoxide in aqueous solution under static conditions. The reactions were followed by measuring the change in peroxide concentration with time at 80°, 108°, and 131° F. Figure 3 shows that the peroxide was reduced, the activation energy of the reaction being 16.5 Kcal. These results, together with additional data presented in a later section, support the suggested role of VFS in the stabilization of MEA. It is of interest to note that oxidation by the peroxide converted the VFS to an amine oxide which possessed no further antioxidant properties. This reaction is probably one of several modes by which the additive is depleted in use.

EFFECT OF VFS IN THE PRESENCE OF METALS

The procatalytic effect of metals in oxidation reactions is well known, and its occurrence in MEA solutions would not be unexpected. As was noted previously, the Mare Island investigation was predicated on the assumption that iron was a major degradative catalyst (3). To determine what metals were in fact normally present in scrubber solutions, emission spectrographic analyses were made of samples which had been obtained earlier for another investigation. The initial results proved to be sufficiently interesting to warrant a more comprehensive study. Arrangements were therefore made with Submarine Squadron Ten to secure samples of base stock amine, used scrubber samples, and makeup water whose prior histories and treatment were known (6).

Both the base stocks and used scrubber solutions consistently contained approximately a dozen metals whose concentrations ranged from less than 1 ppm to, in the case of sodium derived from VFS, several hundred ppm. Of these metals, chromium, nickel, iron, and copper are known to catalyze many oxidation processes. These four were therefore selected for a study of their effect on MEA stability (Table 1). Makeup water samples contained only one of these metals, copper.

The plausible source of the iron, chromium, and nickel contents of the amine solutions is stainless steel, the material of construction of the scrubbers and presumably of much of the processing equipment for the MEA. However, in laboratory experiments in which MEA solutions were contained in stainless steel cells at 131° F for as long as six weeks and at 300° F for several days, no pickup of these metals occurred. Nevertheless

Table 1
Metal Contents of Scrubber Solutions and Makeup Components

Submarine	Source	Copper (ppm)	Nickel (ppm)	Chromium (ppm)	Iron (ppm)
NAUTILUS	Potable water	5.0	*	*	*
	Storage MEA	2.5	†	†	†
	Scrubber (400 hrs)	8.5	†	†	†
	Scrubber (800 hrs)	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	*	*	*
	No. 1 Scrubber (200 hrs)	9.0	3.0	0.4	15.0
	No. 2 Scrubber (168 hrs)	10.0	3.7	0.4	43.0
	No. 2 Scrubber (246 hrs)	13.0	3.0	0.6	50.0

*No metal present.

†No analysis for metal.

debris from attrition of pump components and other moving parts of processing or operating equipment could readily accumulate in both base stock and operating amine solutions in sufficient amounts to account for the metal content. The source of the copper present in base stock MEA could not readily be determined; presumably it was present in the MEA as received from the supplier. The copper content of the makeup water undoubtedly results from use of copper tubing in the potable water distribution system of the submarine. The steady buildup of copper in scrubber solutions is caused in part by additions of makeup water and base stock amine. Another source may be airborne copper fines which enter the solutions via the scrubber air inlet port.

Figures 4-6 summarize the effects of chromium, iron, nickel, and copper on the stability of MEA-VFS solutions, as measured by the evolution of ammonia. In Fig. 4, the effects of the chromium and iron are shown. No deterioration occurred with chromium as bulk metal or as the chromate, or with bulk iron. Deterioration due to 30 ppm of ferric ion was very small; that from 30 ppm of ferrous ion was somewhat larger but nevertheless of relatively low order.

In a concentration of 3.7 ppm, nickelous ion was relatively inert but a tenfold increase in concentration caused a rise in activity comparable to that caused by ferrous ion (Fig. 5). The presence of bulk nickel metal resulted in rapid deterioration of the amine and extensive corrosion of the metal specimen. Although the quantity of nickel dissolved would by itself have been sufficient to account for the deterioration of the amine, the etched metal surface may also have had an additional degradative effect. These results would indicate that although the concentrations of soluble nickel shown in Table 1 can reasonably be tolerated by MEA-VFS solutions, the presence of significantly larger amounts could be detrimental. The use of nickel or nickel plate in the scrubber is obviously precluded.

The effect of copper in the concentrations found in operational scrubber solutions is serious. Even 1 ppm of the metal as cupric ion triggered the evolution of small but perceptible quantities of ammonia; as the copper content was increased to 15 ppm, the effect was proportionately more serious (Fig. 6). Copper was the only one of the four metals studied which, in concentrations consistently found in scrubber solutions, had an unacceptably high level of catalytic activity.

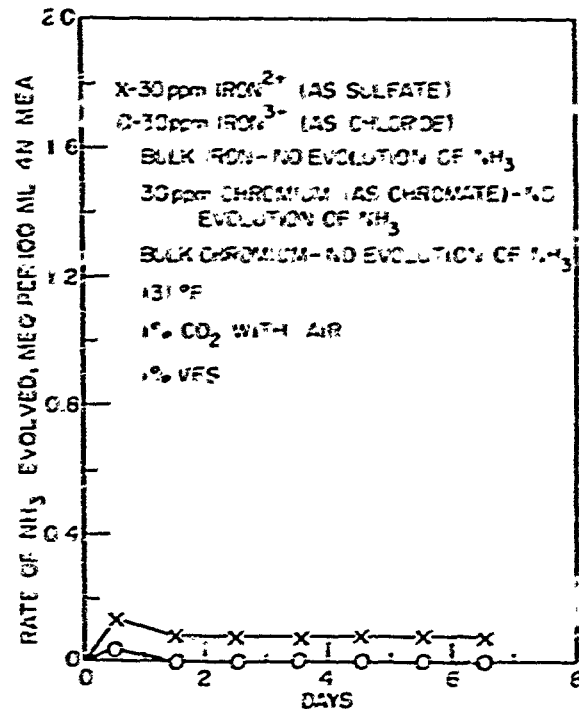


Fig. 4 - Dynamic test of MEA-VFS stability with iron and chromium present

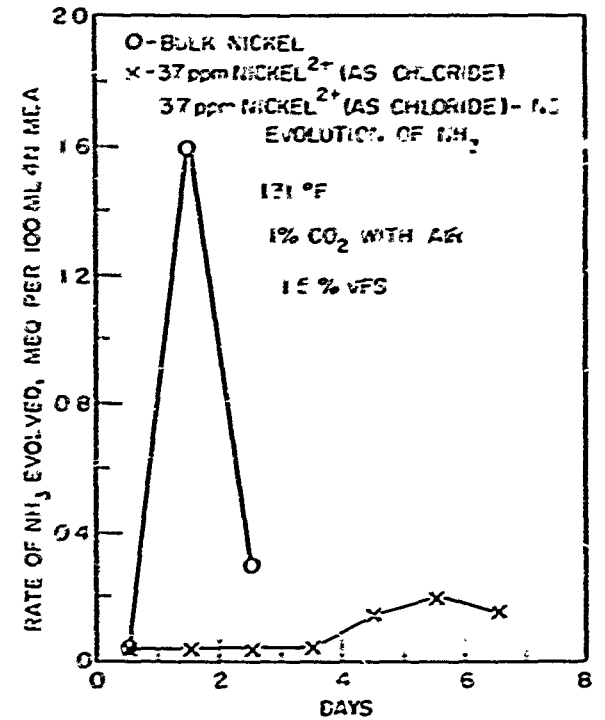


Fig. 5 - Dynamic test of MEA-VFS stability with nickel present

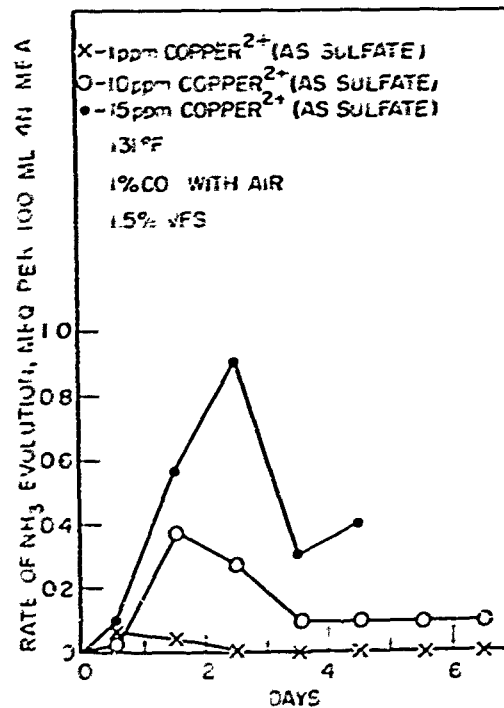


Fig. 6 - Dynamic test of MEA-VFS stability with copper present

SCREENING OF MISCELLANEOUS ADDITIVES

The inability of VFS to stabilize MEA effectively when copper is present prompted a search for a more effective additive. The optimum characteristic of such an additive was that like VFS it be an antioxidant in its own right, and in addition, a copper deactivator.

Materials selected for study included water soluble chelating agents, amines, and phenols known to be stabilizers for a variety of systems (Table 2). Their antioxidant activities in concentrations of 1.5 percent were determined in the absence of copper.

Table 2
Compounds Studied as Additives for MEA

Sodium mercaptobenzothiazole
Diethylcyclopropylenediamine
p-acetylaminophenol
o-aminophenol
Quinalizarin
bis acetylacetonediimine
Propyl gallate
Sorbitol
n-dimethylglycine
Phthaloylglycine
Diethylcyclohexylamine
Tetrasodium ethylenediaminetetraacetic acid (EDTA)

Only EDTA demonstrated an acceptable degree of antioxidant activity in 4N MEA at 131°F, i.e., prevented the evolution of ammonia over a two-week test period. The solutions containing three of the unacceptable additives, o-aminophenol, p-acetylaminophenol, and quinalizarin, were examined for peroxide content; it was found that peroxides were generated simultaneously with ammonia. With EDTA, however, no peroxides were found. In other experiments, it was determined that, like VFS, EDTA reacted with and destroyed peroxides, while simultaneously being converted to an amine oxide (7). The activation energy of the reaction (16.2 Kcal) was about the same as that of VFS and peroxide.

The failure of the inefficient additives to prevent the formation of peroxides as well as the similarity in the reactivities of VFS and EDTA lend weight to the belief 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 THE PRESENCE OF COPPER

EDTA is an efficient chelating agent for copper in alkaline media, and a determination of its stabilizing activity in copper-containing MEA solutions was therefore of considerable interest. Aeration oxidations in which EDTA replaced the VFS of previous experiments showed no evidence of amine breakdown in a one-week period with 30 ppm of cupric ion present. As seen in Fig. 7, however, the additive was less effective than was VFS when 30 ppm ferrous or 10 ppm chromate ions were added to the solution. With 37 ppm nickel, there was little difference between the rather indifferent activities of the additives.

These data showed that each additive to a large extent complemented the other's effectiveness, and an evaluation of the efficiency of a mixture of the additives in the presence of the four metals was indicated. Accordingly, a 4N MEA solution containing 1.5% each of VFS and EDTA, was subjected to oxidation at 131°F in the presence of 15 ppm cupric, 3.7 ppm nickelous, 30 ppm ferric, and 10 ppm chromate ions. To increase the severity of the test, stainless steel cells replaced those of glass. During the two-week test period there was no evidence of MEA breakdown such as ammonia evolution, production of non-basic nitrogen-containing compounds, or solution discoloration. The mixture of additives thus appeared to have considerable merit.

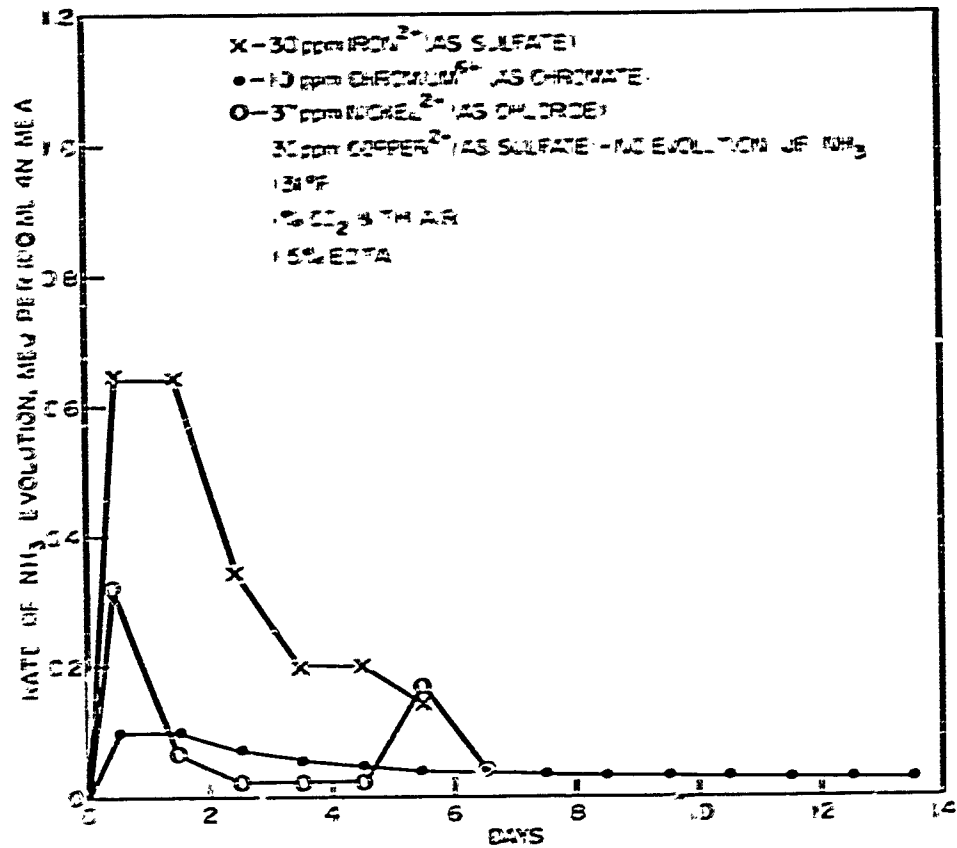


Fig. 7 - Dynamic test of MEA-EDTA stability with copper, iron, nickel, and chromium present

OXIDATION STABILITY OF MEA AT TEMPERATURES ABOVE 131°F

As was previously indicated, the 131°F oxidation experiments provide a useful, but arbitrary, set of conditions under which to study MEA stability. Aeration tests at higher temperatures may be equally unrealistic as far as reproducing scrubber operations, but they nevertheless provide useful data on the stability of the MEA-additive system under more severe conditions. Tests were therefore conducted at 160°F (71°C) and 208°F (98°C) using stainless steel cells; other experimental conditions were unchanged.

At 160°F, with no metal catalysts present, MEA solutions containing 1.5% VFS evolved a minor quantity of ammonia during the first two days of the run, after which the rate diminished to a very small value (Fig. 8). Essentially the same results were obtained with VFS and EDTA present.

The data from oxidation experiments conducted in stainless steel cells at 208°F are illuminating. Figure 9 shows the rate of ammonia evolution from uninhibited MEA to be large. The addition of 1.5% EDTA to the solution resulted in no improvement in stability; VFS, on the other hand, provided a high order of stability, the ammonia evolution being only 10% of that when no additive was used. No additional improvement resulted from a combination of 1.5% each of VFS and EDTA.

The excellent stabilizing effect of VFS at 208°F was completely nullified by the addition of salts of iron, nickel, chromium, and copper (Fig. 10). Because of the inability of EDTA to stabilize the solution at this temperature in the absence of metals, its effectiveness with metals present was assumed to be equally poor. However, the combination of VFS and EDTA resulted in a substantial improvement in the stability of the amine in the

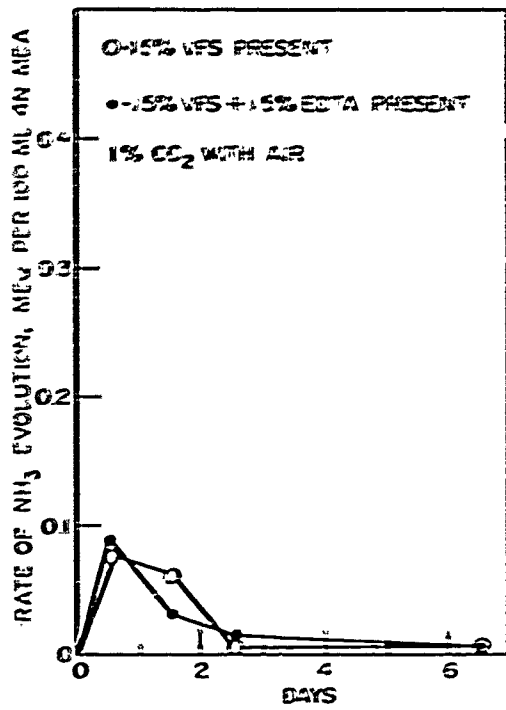


Fig. 8 - Dynamic test at 160°F of effect of additives on MEA stability in stainless steel cells

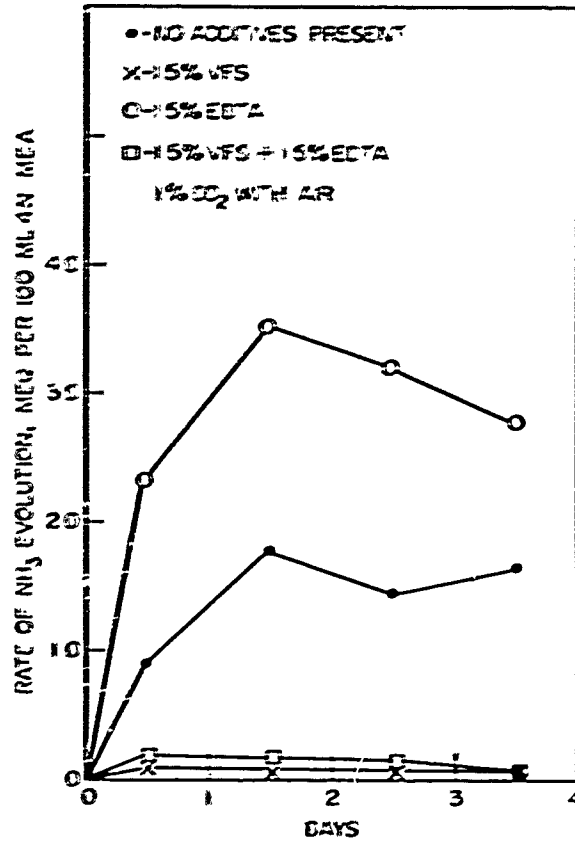
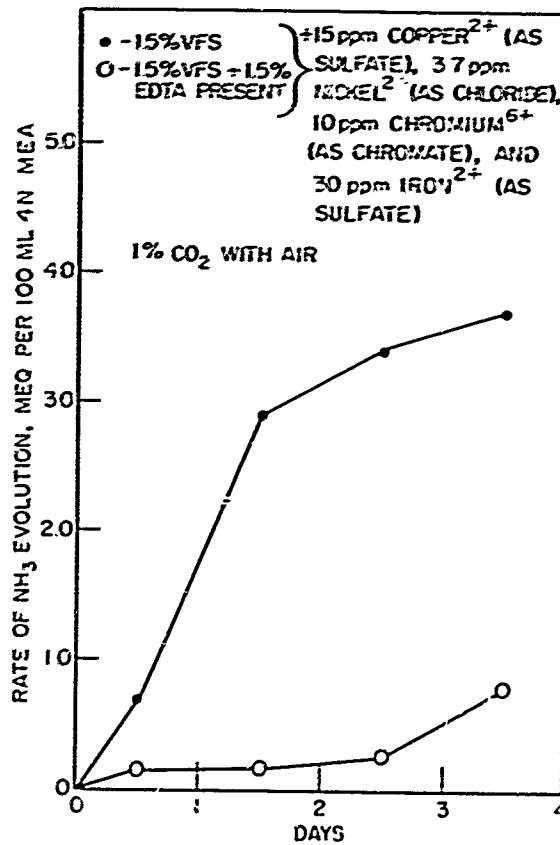


Fig. 9 - Dynamic test at 208°F of effect of additives on MEA stability in stainless steel cells

Fig. 10 - Dynamic test at 208°F of effect of additives and metals on MEA stability in stainless steel cells



presence of metals – more, in fact, than could have reasonably been predicted from the sum of their individual contributions.

HIGH-TEMPERATURE STATIC TESTS

The possibility of raising stripper temperatures from 280° to 300°F is receiving engineering consideration in order to promote scrubber efficiency. As was pointed out earlier, when the amine solution is cycled from the absorber to the stripper, it is close to saturation with respect to both carbon dioxide and air. While data on carbon dioxide contents are available, reliable figures are lacking for air. To devise an adequate laboratory test to obtain data on air content, and to determine the thermal and oxidative stabilities of the amine under realistic stripper conditions pose major engineering difficulties. Therefore, to obtain a reasonable indication of both the thermal stability of MEA at 280° and 300°F and its sensitivity to oxidation at these temperatures with only limited quantities of oxygen present, some simple static tests were devised. Cylindrical stainless steel cells of 90-ml capacity were filled with 50-ml samples of amine treated as described in Table 3, sealed with neoprene stoppers, and autoclaved. Because neoprene deteriorates if exposed under these conditions for excessive periods, 280°F tests were limited to three days and 300°F to two days. At the conclusion of the test period, the cells were cooled to room temperature and uncapped. A stream of highly purified nitrogen gas was immediately passed through the samples for one hour, the effluent gas passing into a boric acid trap to permit ammonia determinations. The quantity of nonbasic nitrogen formed was estimated from normality changes.

Table 3
Preparation of Monoethanolamine Samples for High-Temperature
Stability Experiments*

Runs 1 and 5	A 4N solution was treated by passing through it for three hours a vigorous stream of purified nitrogen containing 1% CO ₂ .
Runs 2 and 6	Same as Run 1, but with air substituted for the nitrogen.
Runs 3 and 7	A 4N solution containing 1.5% each of VFS and EDTA was saturated with 1% CO ₂ .
Runs 4 and 8	Same as Runs 3 and 7, but with oxygen substituted for air.

*No metal specimens were added to any of the runs.

The results of the 280°F experiments are shown in Table 4. Run 1 served to evaluate the thermal stability of the solution since its oxygen content was nil. During three days, a small quantity of ammonia was evolved (3.2×10^{-4} meq/ml) but no nonbasic nitrogen-containing compounds were formed. When the duration of the run was increased to six days, ammonia evolution rose 75%. If reasonable significance is assigned to these ammonia values, the thermal degradation rate was minor. It should be understood, however, that the effect on MEA stability of three days of continuous exposure at 280°F may not be equivalent to that which would result from intermittent exposure of the solution to 280°F for the same aggregate length of time during scrubber operation.

The experimental conditions of Runs 2 and 3 deviated from those of operating scrubbers not only in the manner of exposure to 280°F as described in Run 1, but also in that in the scrubber each portion of the amine entering the stripper is nearly saturated with air and CO₂, whereas in the test cells the available oxygen depleted by reaction with the amine was not replenished. Both runs evolved somewhat more ammonia than did Run 1.

Table 4
Static Tests of High-Temperature MEA Stability at 280°F for 3 Days

Solutions*	Run	Test Period (Days)	Meq Nonbasic Nitrogen Formed	Meq NH ₃ Evolved per ml
MEA-CO ₂ -N ₂	1	3	none	3.2 × 10 ⁻⁴
		6	none	5.6 × 10 ⁻⁴
MEA-CO ₂ -Air	2	3	none	5.0 × 10 ⁻⁴
MEA-CO ₂ -Air-EDTA-VFS†	3	3	none	8.8 × 10 ⁻⁴
MEA-CO ₂ -O ₂ -EDTA-VFS†	4	3	0.04	13 × 10 ⁻⁴

*CO₂ in 1% concentration.

†VFS and EDTA each in 1.5% concentration.

It thus appears that the additives do not offer much antioxidant protection under these severe test conditions; they may in fact break down themselves. Because of its higher oxygen content (fivefold that of Run 3), the MEA in Run 4 suffered the greatest degradation; although the amount of ammonia evolved was larger than that of any previous run, it was small in comparison with the quantity of nonbasic nitrogen-containing compounds formed.

Results of the 300°F experiments are shown in Table 5, Runs 5 to 8. Although the data are not directly comparable to those at 280°F because of the difference in test periods, it would appear that no catastrophic increase in the rate of thermal breakdown resulted from the higher temperature.

Oxidation of the amine would be expected to proceed faster and probably further at 300°F than at 280°F, in accord with the rule-of-thumb that the reaction rate doubles with every 20°F rise in temperature. Since a 300°F stripper temperature implies heater skin temperatures of 325°F or higher, service results might be even more severe. The 300°F oxidation data in Table 5 are almost identical with those for 280°F, a probable consequence of the fact that the same limited quantity of oxygen was available in both runs.

The high-temperature experiments indicate that the thermal stability of MEA appears to be acceptable at 280° and 300°F, although the effect of a heater skin temperature of 325°F cannot be readily estimated. Oxidation stability and the effect of additives under

Table 5
Static Tests of High-Temperature MEA Stability of 300°F for 2 Days

Solutions*	Run	Meq Nonbasic Nitrogen Formed	Meq NH ₃ Evolved per ml
MEA-CO ₂ -N ₂	5	none	4.8 × 10 ⁻⁴
MEA-CO ₂ -Air	6	none	5.6 × 10 ⁻⁴
MEA-CO ₂ -AIR-EDTA-VFS†	7	none	8.0 × 10 ⁻⁴
MEA-CO ₂ -O ₂ -EDTA-VFS†	8	0.06	14 × 10 ⁻⁴

*CO₂ in 1% concentration.

†VFS and EDTA each in 1.5% concentration.

stripper conditions are a function of oxygen content, other things being equal. The laboratory tests described do not sufficiently reproduce these conditions to enable firm conclusions to be drawn; well-monitored dockside scrubber experiments are required to obtain these data (8).

CURRENT STATUS OF VFS-EDTA ADDITIVE PACKAGE

The finding that the useful life of CO₂ scrubber solutions as now formulated is materially shortened by the presence of copper, and to a lesser degree by reasonable amounts of nickel and iron, is of obvious practical significance. The important sources of copper are as particulate matter in the air intake, and as contaminants of the base stock amine and the makeup water supply. Significant reduction in copper content can be most conveniently achieved by substituting battery-grade for potable makeup water, and incorporating a copper-limitation requirement in the MEA procurement specification (9). Use of the VFS-EDTA additive package would ameliorate the effect of the remaining copper. With the possibility in mind that the additive package will cope with copper contamination from all sources, BUSHIPS has directed that use of potable water be continued for makeup purposes (10). Sea trials of an MEA-VFS-EDTA formulation are now underway.

SUMMARY AND CONCLUSIONS

1. MEA solutions (4N) in which no metals are present oxidize rapidly in air containing 1% CO₂ at 131°F (55°C). Among the degradation products are ammonia, nonbasic nitrogen-containing compounds, and peroxides.
2. In the presence of the currently used MEA stabilizer, the sodium salt of N,N-diethanolglycine (VFS), none of the above oxidation products are formed.
3. The effect of VFS in MEA solutions is consistent with that of an antioxidant which functions by reacting with and destroying peroxides, thus interrupting the autocatalytic oxidation of the amine. Less effective additives did not prevent the generation of peroxides in oxidized MEA.
4. A variety of metals are found in used scrubber solutions; those investigated for their catalytic effect on the degradation of MEA solutions were iron, chromium, nickel, and copper. All but chromium had some adverse effect on MEA-VFS solutions under certain conditions, that of copper being the most serious. In a concentration of only a few ppm, copper greatly accelerated the degradation of MEA solutions.
5. The tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) eliminated the adverse effect of copper. Like VFS, EDTA reacted with and destroyed peroxides, and in its own right was an antioxidant for MEA when no catalytic metals were present.
6. In dynamic tests a combination of 1.5% each of VFS and EDTA gave complete protection against the oxidative degradation of MEA in glass cells at 131°F when iron, nickel, chromium, and copper were present in amounts usually found in operating scrubber solutions. At 208°F the combination provided excellent protection to MEA against degradation in stainless steel cells with similar quantities of the metals present; the effect appeared to be synergistic under these conditions.
7. Static tests in stainless steel cells at 280° and 300°F revealed that in the absence of air, thermal degradation of MEA, as evidenced by ammonia evolution, was slight. With air present, with or without the addition of VFS and EDTA, there was some increase in

ammonia evolution. When oxygen gas replaced air, nonbasic nitrogen-containing compounds were formed at both temperatures. There is some preliminary indication that increasing the scrubber stripping temperature to 300° F so as to increase operating efficiency may not cause excessive thermal breakdown of the amine; however, additional work is required to gauge the effect of other factors, e.g., heater skin temperatures of 325° F and above, and the effect on oxidation stability of cycling the solution through the stripper with its oxygen content renewed at each pass.

RECOMMENDATIONS

1. The procurement specification for MEA should be revised to include a limit on copper content.
2. The specification should also be revised to include the combination of the tetrasodium salt of ethylenediaminetetraacetic acid and the presently-used sodium salt of N-diethanolglycine, in amounts which will give 1.2 to 1.5% of each when the amine concentrate is diluted to give a 4N solution.
3. If technically feasible, battery-grade water should replace potable makeup water to reduce the amount of copper entering scrubber solutions.
4. Well-monitored dockside scrubber tests should be carried out to obtain data relating oxygen content of the absorber effluent to its thermal and oxidative stability in the stripper.

REFERENCES

1. Carhart, H.W., and Piatt, V.R., Editors, "Third Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," NRL Report 6053, Dec. 31, 1963
2. Scheiman, M.A., "A Review of Monoethanolamine Chemistry," NRL Report 5746, June 1, 1962
3. Johnson, W.W., McElwain, R.E., and Lew, M., "Stabilization of Monoethanolamine with Chelating Agents," Mare Island Naval Shipyard R and D Report No. 7116-59 SF 013-11-05 (1960)
4. Johnson, W.W., and McElwain, R.E., U.S. Patent 3137654 (June 16, 1964)
5. Military Specification "Monoethanolamine Chelating Agent Solution," Mil-M 23573 (Ships), Feb. 12, 1963
6. Parker, C.A., Wiseman, P., and Hatchard, C.G., "The Degradation of Monoethanolamine by the Action of Air and Carbon Dioxide," Admiralty Materials Laboratory Report No. B/105(M), July 1955
7. Herbst, J.H.E., and Barton, S.C., Tappi 46:486 (1963)
8. Blachly, C.H., and Ravner, H., "Effect of the Tetrasodium Salt of Ethylenediaminetetraacetic Acid on the Stabilization of Monoethanolamine Solutions," NRL Ltr rpt 6170-82 HR:eb, Feb. 24, 1964
9. Blachly, C.H., and Ravner, H., "The Effect of Trace Amounts of Copper on the Stability of Monoethanolamine Scrubber Solutions," NRL Memorandum Report 1482, Dec. 1963
10. BuShips ltr S13N616/9380, Ser 649G2-817, May 19, 1964

BLANK PAGE

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Naval Research Laboratory Washington, D.C.		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE THE STABILIZATION OF MONOETHANOLAMINE SOLUTIONS FOR SUBMARINE CARBON DIOXIDE SCRUBBERS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) A final report on one phase of the problem.			
5. AUTHOR(S) (Last name, first name, initial) Blachly, C.H. Ravner, H.			
6. REPORT DATE December 4, 1964		7a. TOTAL NO. OF PAGES 19	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. NRL Problem C08-05		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6189	
b. PROJECT NO. BuShips SF 013-08-03-4092, 4093, 4094, 4095		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES Unlimited availability			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Bureau of Ships)	
13. ABSTRACT Monoethanolamine (MEA), the regenerative absorbent used in all CO ₂ scrubbers aboard nuclear submarines, is at present stabilized with a chelating agent, the monosodium salt of N,N-diethanolglycine (VFS). In dynamic tests at 131°F the additive, although effective in metal-free solutions, did not prevent oxidative degradation of the amine when copper was present in the concentrations usually found in scrubber solutions. Effective stabilization in the presence of copper was given by the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA). At 208°F in the presence of several metal contaminants, a combination of VFS and EDTA was required for stabilization. Both VFS and EDTA were shown to be true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA suggested that their antioxidant activity resulted from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA. Static tests to simulate stripper operation revealed the amine to be reasonably stable against thermal degradation at 280° and 300°F. Some oxidative breakdown occurred with a limited quantity of air present; more serious degradation occurred when oxygen gas replaced air. A combination of VFS and EDTA did			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Submarine Habitability Monoethanolamine (MEA) Stabilization of MEA Additives for MEA Chelate-formers Peroxides Ammonia formation MEA degradation products Carbon dioxide scrubbers Monosodium salt of N,N-diethanolglycine (VFS) Ethylenediaminetetraacetic acid (EDTA) Toxic irritants Nonbasic nitrogen-forming compounds						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

DOCUMENT CONTROL DATA - R & D
(Continuation Sheet)

Report 6189

Unclassified

13.

not prevent oxidation of the amine at these temperatures when small amounts of oxygen were present.

It was recommended that contamination by copper be curtailed to increase the service life of CO₂ scrubber solutions, that a combination of VFS and EDTA be used as a stabilizing additive package, and that additional engineering data be obtained from dockside scrubber tests.

UNCLASSIFIED

contaminants, a combination of VFS and EDTA was required for stabilization. Both VFS and EDTA were shown to be true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA suggested that their antioxidant activity resulted from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

Static tests to simulate stripper operation revealed the amine to be reasonably stable against thermal degradation at 280° and 300°F. Some oxidative breakdown occurred with a limited quantity of air present; more serious degradation occurred when oxygen gas replaced air. A combination of VFS and EDTA did not prevent oxidation of the amine at these temperatures when small amounts of oxygen were present.

It was recommended that contamination by copper be curtailed to increase the service life of CO₂ scrubber solutions, that a combination of VFS and EDTA be used as a stabilizing additive package, and that additional engineering data be obtained from dockside scrubber tests.

UNCLASSIFIED

UNCLASSIFIED

contaminants, a combination of VFS and EDTA was required for stabilization. Both VFS and EDTA were shown to be true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA suggested that their antioxidant activity resulted from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

Static tests to simulate stripper operation revealed the amine to be reasonably stable against thermal degradation at 280° and 300°F. Some oxidative breakdown occurred with a limited quantity of air present; more serious degradation occurred when oxygen gas replaced air. A combination of VFS and EDTA did not prevent oxidation of the amine at these temperatures when small amounts of oxygen were present.

It was recommended that contamination by copper be curtailed to increase the service life of CO₂ scrubber solutions, that a combination of VFS and EDTA be used as a stabilizing additive package, and that additional engineering data be obtained from dockside scrubber tests.

UNCLASSIFIED

UNCLASSIFIED

contaminants, a combination of VFS and EDTA was required for stabilization. Both VFS and EDTA were shown to be true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA suggested that their antioxidant activity resulted from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

Static tests to simulate stripper operation revealed the amine to be reasonably stable against thermal degradation at 280° and 300°F. Some oxidative breakdown occurred with a limited quantity of air present; more serious degradation occurred when oxygen gas replaced air. A combination of VFS and EDTA did not prevent oxidation of the amine at these temperatures when small amounts of oxygen were present.

It was recommended that contamination by copper be curtailed to increase the service life of CO₂ scrubber solutions, that a combination of VFS and EDTA be used as a stabilizing additive package, and that additional engineering data be obtained from dockside scrubber tests.

UNCLASSIFIED

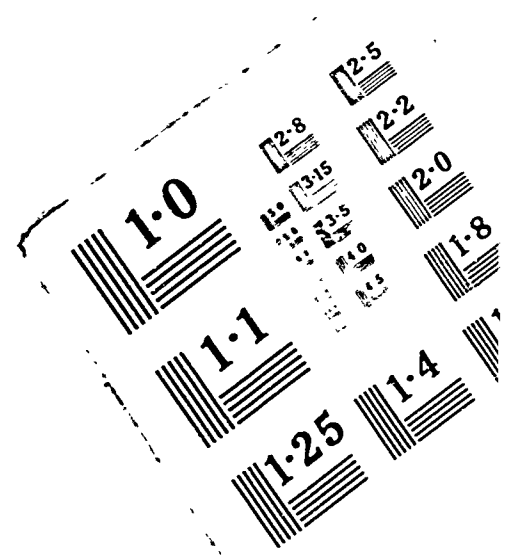
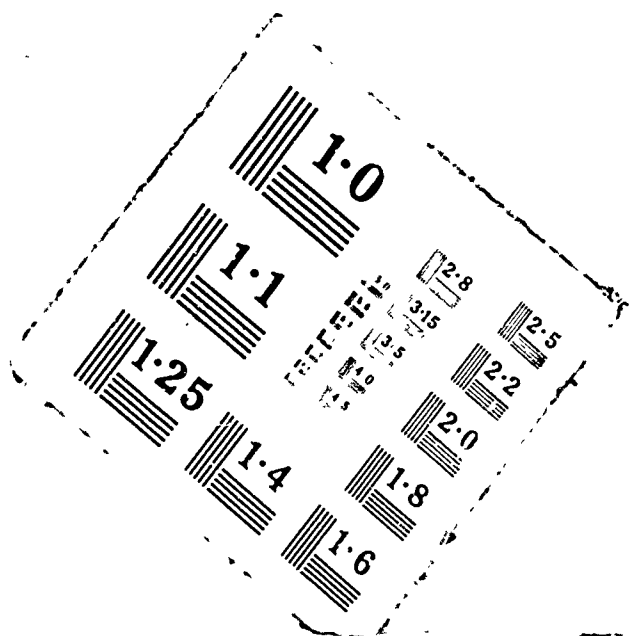
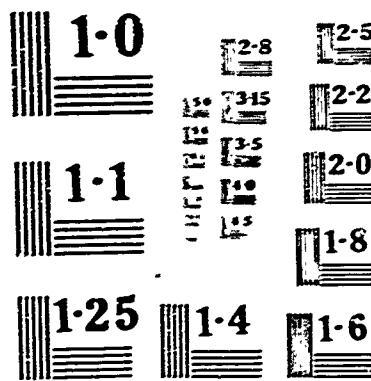
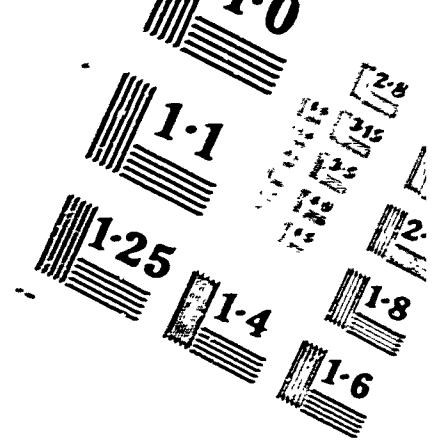
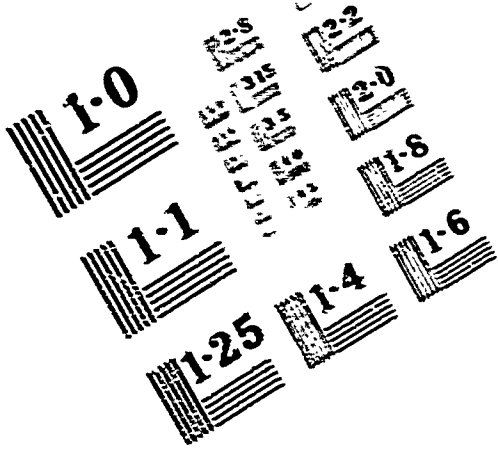
UNCLASSIFIED

contaminants, a combination of VFS and EDTA was required for stabilization. Both VFS and EDTA were shown to be true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA suggested that their antioxidant activity resulted from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

Static tests to simulate stripper operation revealed the amine to be reasonably stable against thermal degradation at 280° and 300°F. Some oxidative breakdown occurred with a limited quantity of air present; more serious degradation occurred when oxygen gas replaced air. A combination of VFS and EDTA did not prevent oxidation of the amine at these temperatures when small amounts of oxygen were present.

It was recommended that contamination by copper be curtailed to increase the service life of CO₂ scrubber solutions, that a combination of VFS and EDTA be used as a stabilizing additive package, and that additional engineering data be obtained from dockside scrubber tests.

UNCLASSIFIED





U. S. NAVAL RESEARCH LABORATORY
WASHINGTON 25, D. C.

IN REPLY REFER TO
2000-24: ESR: br
SER: 300
12 February 1965

From: Director, U.S. Naval Research Laboratory, Washington, D.C. 20390
To: Distribution List

Subj: NRL Report 6189, "The Stabilization of Monoethanolamine Solutions for Submarine Carbon Dioxide Scrubbers"; corrections to

1. Page 2, 4th paragraph, 5th line of subject report should read as follows:

evolution (e.g., by conversion of amine nitrogen to nonbasic forms (6)), it is believed that the

2. Page 4, 2nd paragraph of subject report. Delete "(6)" at end of this paragraph.

M. E. Jansson

M. E. JANSSON
Director

ARCHIVE COPY