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FACILITIES ENGINEERING • Maintenance and Repair



USE OF DIETHYLAMINOETHANOL, MORPHOLINE, AND CYCLOHEXYLAMINE FOR CONDENSATE RETURN LINE CORROSION PREVENTION

1. <u>Purpose</u>. This technical note provides a description of and direction for use of three chemicals: diethylaminoethanol (DEAE), morpholine, and cyclohexylamine. These chemicals are used in Army boiler plants to prevent internal corrosion of condensate return lines.

2. <u>Applicability</u>. This technical note applies to all facilities engineering elements responsible for the operation and maintenance of steam generating boiler systems.

3. <u>General</u>. Keplacement costs for underground steam/condensate systems are high. There is also a high cost associated with reduced efficiency while systems are corroding. The use of neutralizing amines, notably DEAE, morpholine, and cyclohexylamine, play a large role in the curtailment of condensate corrosion. This note describes the use and properties of these amines and provides information to simplify the choosing of an appropriate neutralizing amine to give the most economical and effective results in different systems.

4. Discussion.

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a. Condensate Corrosion.

(1) Condensate return line corrosion prevention is an important aspect of boiler water chemistry. Replacement costs for underground steam/condensate systems are expensive, not to mention the cost of the energy in the form of heat in the condensate that is wasted while the corroding system is failing. Also, high makeup rates, due to loss of condensate, often lead to difficulty in maintaining proper boiler water chemistry. Damage to the boilers themselves from scale and corrosion can also occur. Corrosion of return line systems is more common in installations having extensive return systems, such as central energy plants.

(2) Condensate piping corrosion is usually caused by the presence of carbon dioxide, oxygen, or potable water contamination in returning condensate. Oxygen can enter return lines through leaky traps, pumps, valves, and fittings or with boiler feedwater if not completely deaerated and treated with sodium sulfite. Pitting of return piping is indicative of corrosion caused by oxygen or potable water contamination. Corrosion due to oxygen can be prevented by properly treating boiler water and sealing leaks in the system. Corrosion due to contamination can be prevented by stopping leakages of mineralized water into the return system, generally through leaking hot water heater tubes.

(3) Carbon dioxide in condensate originates from boiler makeup water alkalinity. Carbon dioxide causes corrosion in the form of grooving or channeling along the bottom of the condensate return pipe. Since all Army boiler plants use feedwater with at least some alkalinity, corrosion due to carbon dioxide is a serious and common form of condensate corrosion.

(4) Carbon dioxide is produced in boilers because boiler water temperatures cause feedwater alkalinity in the form of bicarbonate to break down into hydroxide and carbon dioxide.

 $HCO_3^{-} - \frac{heat}{2} - - > OH^{-} + CO_2^{-}$ bicarbonate hydroxide carbon dioxide

(5) The hydroxide remains in the boiler water and raises the causticity and pH levels. The carbon dioxide is a gas and leaves the boiler with steam, eventually dissolving in condensed steam. Carbon dioxide dissolved in water is acidic, forming carbonic acid as shown below.

 CU_2 + H_2U - - - - - - - - H₂ CU_3 carbon dioxide water carbonic acid

(6) Carbonic acid, like any other acid, is corrosive. Condensate corrosion due to carbon dioxide can be prevented by minimizing the amount of carbon dioxide produced in the boiler and by treating the residual with "neutralizing" amines, a family of volatile alkaline liquids.

(7) Diethylaminoethanol, morpholine, and cyclohexylamine are the three most widely used neutralizing amines. Historically, only morpholine and cyclohexylamine have been authorized for use in Army boiler plants. Once carbon dioxide is produced in the boiler, its corrosive effects can be minimized by the addition of these amines to neutralize the effect of carbon dioxide by raising condensate pH to a minimum of 7.5. The amines are generally fed separately from other chemicals into the boiler steam drum and go over with steam and dissolve in the condensate.

(8) Each of these amines will not work equally well in all systems. Optimum results are obtained by choosing the appropriate amine on a system by system basis. The following is a description of DEAE, then morpholine and cyclohexylamine and finally a neutralizing amine selection chart.

b. Diethylaminoethanol.

(1) Diethylaminoethanol (DEAE) is a currently available and widely used amine. DEAE has a vapor-liquid distribution of 1.7. This is equivalent to 1.7 parts in steam to every one part in condensate. This means that DEAE will have a relatively uniform distribution throughout return condensate. This makes DEAE ideal for the protection of moderate length systems in between the range of either morpholine or cyclohexylamine used separately. The boiling point of DEAE is 325 °F but it forms an azeotrope (a liquid mixture having a constant minimum boiling point) with water to boil at 210 °F thus enabling DEAE to be used in low pressure systems, especially those having high feedwater bicarbonate and carbonate alkalinity. Morpholine is not suitable for low pressure systems because of its high boiling point and cyclohexylamine may cause problems in systems with high feedwater alkalinity (above 75 ppm).

(2) High feedwater alkalinity produces a high level of carbon dioxide requiring large dosages of amines. The solubility of amines and carbon dioxide together is limited. They form bicarbonate salts, the least soluble of which is cyclohexylamine bicarbonate. When carbon dioxide and cyclohexylamine are present in high amounts, cyclohexylamine bicarbonate deposits out. The likely area for formation of deposits is in low flow areas at the far end of the return system. This problem can be avoided by reducing feedwater alkalinity (dealkalization) or by using DEAE in place of cyclohexylamine in systems with high feedwater alkalinity.

c. Morpholine. Morpholine has a low vapor-liquid distribution ratio of U.4. This is equivalent to U.4 part in the steam to 1.0 part in condensate. Since more morpholine tends to be present in the liquid phase (condensate), it will drop out of steam early making it suitable for protection of short to moderate length condensate return systems. However, since the boiling point of morpholine is 264 °F, it can only be used in high pressure systems, at least 15 psig but best above 50 psig. Because of its high boiling point, very little morpholine is lost in deaerators from returning condensate.

d. Cyclohexylamine. Cyclohexylamine has a high vapor-liquid distribution ratio of 4.7. It is best suited for protection of the far reaches of long systems. In very long systems, it is necessary to also treat with morpholine to protect parts of the system close to the boiler. Cyclohexylamine boils at 273 °F but forms an azeotrope with water to boil at 205 °F. Thus it can be used in low pressure steam systems. Cyclohexylamine also provides good protection in systems without deaerators. However, cyclohexylamine should not be used in systems with a feedwater bicarbonate and carbonate alkalinity of 75 ppm or higher, as explained previously. In addition, care should be used when feedwater alkalinity is above 50 ppm.

e. Morpholine/Cyclonexylamine. A mixture of morpholine and Cyclonexylamine can also be used to provide full protection in medium and large systems. Morpholine will protect the near ends of the system and Cyclonexylamine will protect the far sections. The optimum ratio of each amine in the mixture is determined by performing condensate pH surveys. Une can start with a mixture ratio of 1 part cyclonexylamine to 3 parts morpholine (25/75 percent). The condensate pH survey is then conducted by taking

condensate samples from representative locations in the return system. If samples from far sections have a lower pH than other samples, increase the amount of cyclohexylamine in the mixture and vice-versa. Another pH survey should be conducted whenever the ratio is changed. Eventually, samples taken from points throughout the system should be within the optimum pH range of 7.5 to 8.0 or slightly higher.

f. pH Limits. The recommended pH limit for condensate in all return systems is 7.5 to 8.0. Condensate pH should not be allowed to fall below 7.5 anywhere in a return system. Corrosion rates increase rapidly as pH falls below 7.5. In some systems the pH may reach above 8.0 in some parts of a return system when maintaining the minimum pH of 7.5 throughout the entire system.

g. Chemical Feeding. Feeding of neutralizing amines, including DEAE, is preferably done by means of continuous feed pumps to keep their concentration in the boiler and condensate at a fairly constant level. They can be fed directly into the boiler steam drum or main steam header.

h. Handliny and Safety Measures.

(1) Careful attention must be given to the handling of these chemicals. All neutralizing amines can cause severe burns and are irritating to eyes, skin, and mucous membranes. In concentrated solutions, they are also very flammable. Cyclohexylamine at 98 percent concentration is about as flammable as pure alcohol. When handling amines, personnel will insure that they wear rubber gloves, a face shield, and a rubber apron. If any liquid gets on clothes, the clothes will be changed immediately. An emergency shower and eye wash fountain will be available in the immediate area in case of splashing onto skin or into eyes.

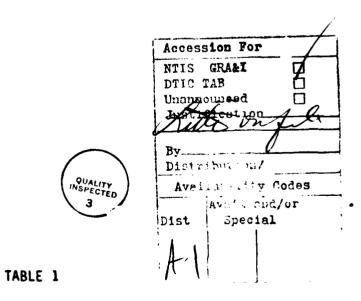
(2) Amines can be purchased in concentrations of approximately 60 percent, or a little less, to greatly decrease the hazards of handling these chemicals. Cyclonexylamine and morpholine can be purchased through the Federal Supply Schedule for Boiler Feedwater and Air-Conditioning Compounds. Cyclonexylamine is available in 60 percent and 98 percent solutions and morpholine is available in 40 percent, 91 percent, and 98 percent solutions through the schedule.

i. Costs. The costs of these amines are approximately the same on a weight basis. The costs of applying these amines differ, however. In water containing 10 ppm of carbon dioxide, it takes 37 ppm of morpholine to bring the pH up to 8.0. If cyclohexylamine is used instead of morpholine, only 15 ppm are required and if DEAE is used, 22 ppm are required. Even though more morpholine is required to treat the same amount of carbon dioxide, less morpholine is lost through deaerators making the cost of treating with morpholine somewhat lower than treating with DEAE or cyclohexylamine. Uverall treatment costs associated with DEAE and cyclohexylamine are about the same.

PHYSICAL AND CHEMICAL PROPERTIES OF NEUTRALIZING AMINES

-		1			
	DEAE	Morpholine	<u>Cyclohexylamine</u>		
Boiling point (100 percent amine)	325° F	264° F	273° F		
Boiling point (Amine/water azeotrope)	210° F		205° F		
Decomposition Temperature	794° F	644° F	626° F		
Vapor/Liquid Distribution ratio	1.7	0.4	4.7		
Specific gravity 100 percent	0.88	1.002	U.86		
pH, 100 ppm solution	10.3	9.7	10.7		
Amount of amine (ppm) required to maintain a pH of 8.0 in water con-	22	37	15		

taining 10 ppm CO₂



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NEUTRALIZING AMINE SELECTION CHART

	Low Pressure High Pressure Systems (above 15 ps			ove 15 psig)
` Amine	(below 15 psi)	Short Dist.	Medium system	Long system
		system length	(<1 mile)**](>1 mile)**
		(<800 ft)**	L	
Morpholine		x		
Morphorne		^		
Cuclobovulaminat	v		1	
Cyclohexylamine*	X		}	
DEAE	x		X	x
	n		Ŷ	Ŷ
Cyclohexylamine/			x	x
Morpholine mixture			^	
			1	

* Not for use in systems having a feedwater alkalinity greater than 75 ppm.

** These systems lengths used for classification are not at all absolute. As an example, a medium length system may have more of the characteristics of a long system if steam distribution lines are poorly insulated or because of the design of the steam system. The characteristics of a steam system are best determined by a condensate pH survey.

TABLE 2

j. Restrictions. No neutralizing amines (including DEAE) are authorized for use in steam supplied for direct contact cooking or humidification (AR 420-49, paragraph 2-26b). A steam-generating heat exchanger will be installed to provide amine-free steam at all such locations.

k. Tables.

(1) Table 1 lists the pertinent physical and chemical properties of the neutralizing amines.

(2) Table 2 is a generalized selection chart to aid in choosing the proper amine for various boiler plant systems.

5. <u>Conclusions</u>. The use of neutralizing amines is an important part of good boiler water treatment. The first step is to select the proper amine to use in each boiler. Proper application of the amine will then provide a large measure of protection against corrosion in condensate return systems.

6. <u>Point of contact.</u> At FESA, contact Nelson Labbe, commercial 703-664-5864, AUTOVON 354-5864. At OCE, contact Jerry Kostos, commercial 202-272-0586, AUTOVON 285-0586.

FOR THE CHIEF OF ENGINEERS:

and T. Wall

EDWARD T. WATLING Chief, Facilities Engineering Division Office of the Assistant Chief of Engineers

PROCUREMENT DATA FOR DIETHYLANINOETHANOL

ATTRIBUTE	RANGE Of Values		TYPICAL Value	test Neteod
	min.	max.		
Form	-	-	liquid	observe
Color (APHA)	-	15	-	Helig Aquatester
Diethylaminoethanol % by weight	99.5	-	-	Gas Chromatogr aph
Water, % by weight	-	0.2	-	Carl Fischer
Distillation Range, ^O C Initial Final	158,0	_ 163.5	-	ASTM D1078
Specific Gravity @ @ 20/20 °C	88.0	0.89	-	ASTM D-87
Flash Point, ^O F	-	-	125	Tagliabue Closed Cup
Viscosity @20°C	-	-	3.5 cps	Brookfield Rotational

Packaging for Shipment

Drums: Chemicals NOIBN

Tank Trucks: Combustible Liquid, NOS; NA1993

Tank Cars: Combustible Liquid, NOS; NA1993 Placarded Combustible; STCC 4913186

Parcel Post, Air Express, Air Freight allowed.