



ORGANIC CHEMICALS

MDEA

Proven Technology for Gas Treating Systems



**MDEA
Gas Treating
Systems from
Arkema solve
problems to
save money...
sure and simple.**

Whether you have excessive foaming, heat stable salts or CO₂ in your amine system, Arkema has an elegant means of addressing typical problems in gas treating facilities today. Our state-of-the-art n-Methyldiethanolamine (MDEA) product line, unique computerized diagnostic programs, and expert services combine to address your system problems and *save you money*.

WITH ARKEMA MDEA PRODUCTS AND SERVICES:

- **You're sure** — we deliver timely response, comprehensive analysis and accurate diagnosis of system efficiencies without black magic - we find the problem and address it.
- **It's simple** — in most cases, our MDEA products **do not** require investment in additional equipment. Our amine formulas are compatible with most gas treating systems and are simple drop in replacements.
- **You save and save** — we minimize your losses and your savings continue over the long term due to reduced corrosion, foaming losses, and amine make-up. Repeated doses of additives are not necessary.
- **We're state-of-the-art** — Arkemas' computerized diagnostic systems can identify performance robbing parameters. And we can set up a program of ongoing system management assistance to help you maintain optimum performance.



**MDEA TECHNOLOGY IS PROVEN.
ARKEMA MAKES IT EVEN BETTER.**

The benefits of MDEA in gas treating are well known. Most notable are:

- Higher absorption capability and selectivity for H₂S as compared with other amines.
- Increased acid gas scrubbing or sweetening capacity and lower circulation rates.
- Lower operating temperature equates to additional economies not available with alternative systems.



As a global international chemical company with facilities in every industrialized region around the world, Arkema has been supplying refineries with chemical products and processing aids for decades. Over the years we have perfected a simple, yet effective approach to gas treating systems.



Our specialized formulas fine tune MDEA's benefits to address such specific operating problems as Heat Stable Salts, foaming, and CO₂ accumulation. Our customized technology offers you:

MDEA-ACT— An activated MDEA-based solvent developed for high efficiency CO₂ removal in natural gas, synthetic gas and sponge iron applications. It is formulated to minimize or eliminate foaming and corrosion in amine units.

MDEA-LF™ — A formulated “Low Foaming” MDEA solvent that minimizes foaming without carbon filtration. Losses due to foaming are typically reduced by 25 to 40% compared to other MDEA products. This product selectively removes H₂S in the presence of CO₂ allowing CO₂ to slip through the system.

MDEA-HST — A formulated “Low Foaming” MDEA solvent, developed for high capacity sulfur removal from refinery gas and liquid streams. This product selectively removes H₂S in the presence of CO₂. In addition, this product is formulated to be resistant to degradation and buildup of Heat Stable Salts (HSS). This feature makes MDEA-HST well-suited for refinery fuel gas scrubbing where HSS buildup is often encountered.

Custom Engineering — Arkemas' MDEA products and services are designed to address the typical as well as unusual difficulties in gas treating systems. Any of our formulas can be modified to custom fit your needs.

■ **EXPERT SERVICE. GLOBAL RESOURCES.**

The professionals at Arkema offer you decades of refinery expertise. We provide the technical knowledge and assistance you need, backed by the resources of one of the largest chemical companies in the world.

You'll find comprehensive technical information on MDEA for gas sweetening on the pages that follow including selectivity, MDEA gas plant design, and analytical procedures for gas scrubbing solutions. This literature represents just one small example of how ATOFINA Chemicals aims to give you more for your MDEA needs.

Allow us to demonstrate how MDEA products and services can handle your system problems and save you money. For more information contact Arkema.



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■ INTRODUCTION

In gas sweetening, one of the most significant advantages of the last twenty years has been the development of technology for the use of N-methyldiethanolamine (MDEA) in amine treaters. MDEA is the only amine used for gas sweetening which has the flexibility for efficient use in both bulk acid gas (H₂S and CO₂) removal or selective H₂S scrubbing. The low foaming properties of MDEA ensure that it is the most cost-effective gas sweetening agent for a variety of conditions.

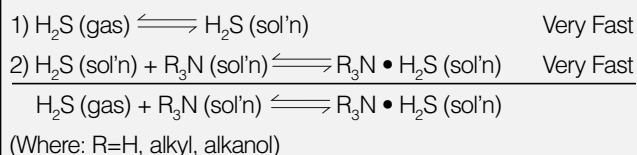
■ SELECTIVITY

One of the most important considerations in designing gas scrubbing units is the degree of H₂S/CO₂ selectivity compatible with the raw gas composition and the specifications for the treated gas. Within the limits set by these two parameters, maximizing selectivity is usually desirable, as the size of the gas treating plant can be kept relatively small. This may result in reduced capital costs. Because additional CO₂ does not have to be stripped in the regenerator, energy usage is reduced. If desired, the CO₂ may be removed in a downstream unit for such uses as enhanced oil recovery (EOR). By increasing the H₂S content of the acid gas feed, Claus sulfur recovery units can be operated with greater efficiency and lower cost.

Of all the amines currently used by the gas treating industry, MDEA is the most selective for H₂S. MDEA does not react with CO₂ to form a stable carbamate.

■ CHEMICAL BASIS FOR SELECTIVITY

Regardless of the nature of the amine (primary, secondary, or tertiary), a common mechanism applies for the reaction of the amine with H₂S:

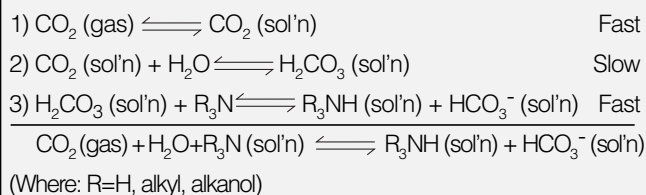


The reaction in Step 2 is extremely rapid (it is often referred to as "instantaneous") and, as a result, the rate of absorption of H₂S is controlled by the rate of diffusion of H₂S from the vapor to the liquid phase (Step 1). The net effect is that, for H₂S, the absorber operates close to equilibrium and the rich H₂S loading is set by the absorber temperature, H₂S partial pressure, and the amine concentration.

The absorption of CO₂ proceeds by two parallel reaction schemes.

The first involves slow hydration of CO₂ to form carbonic acid, which is then neutralized by the amine to give the bicarbonate salt:

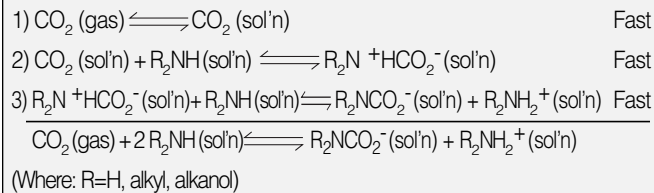
The rate of CO₂ absorption via the carbonic acid mechanism is limited by the relatively slow hydration of CO₂ (Step 2).



The second mechanism consists of direct reaction of the amine and CO₂ to form a zwitterionic intermediate which reacts with a second mole of amine to form the amine carbamate:

Only primary and secondary amines such as MEA, DEA, and DGA can react via the carbamate mechanism. With these classes of amines, carbamate formation is rapid and the bulk of the CO₂ is absorbed in this way.

In the carbamate mechanism, two moles of amine are consumed for each mole of CO₂ absorbed. Thus, primary and secondary amines have a maximum practical CO₂ loading of 0.5 mole/mole. (Amine degradation and corrosion considerations lower this upper limit to less than about 0.2 mole/mole in most applications).



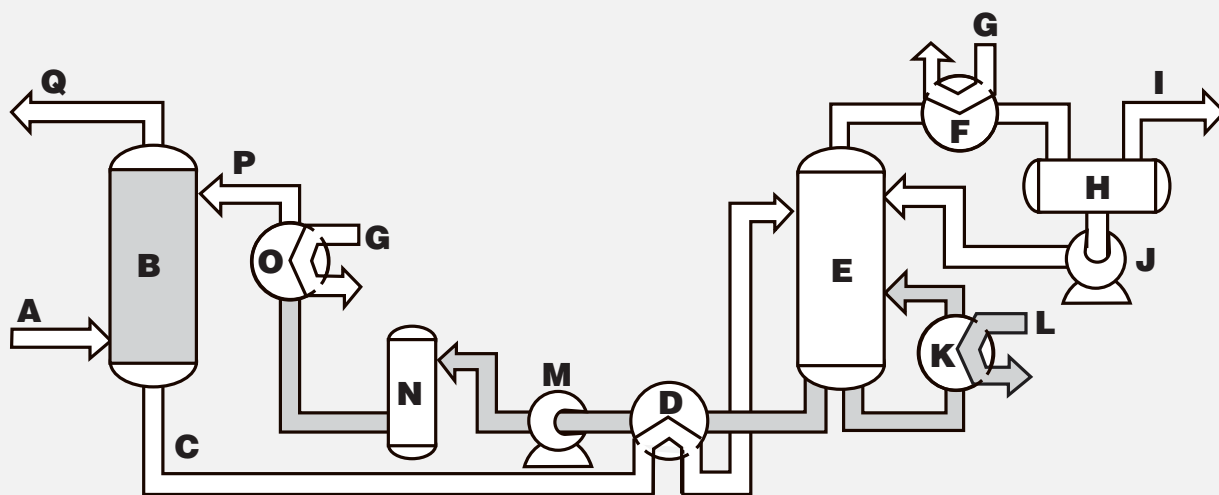
Because the carbamate reaction is so rapid, primary and secondary amines are not selective at all (except for DIPA which shows some selectivity due to steric hindrance of propanol groups). MDEA has the highest level of selectivity.

MDEA GAS PLANT DESIGN

MDEA plant configuration is similar to that used in traditional amine plants. The basic concepts of acid-gas removal by absorption, and solution regeneration by heat stripping, are identical to other systems. MDEA systems require new sizing and flow estimation techniques as they introduce the new generation of cost-effective, energy-efficient sweetening. **Each plant must be specifically tailored to the range of conditions it will encounter in the field.**

The following information is given for gaining preliminary estimates of unit sizing and operation. A much more rigorous engineering treatment is required to obtain a well-designed unit. A standard unit is shown in Figure 1.

Figure 1: Diagram of amine-scrubbing unit.



- | | | |
|--------------------------------------|------------------|-------------------------|
| A) Sour feed gas | G) Cooling water | M) Lean-solution pump |
| B) Absorber | H) Reflux drum | N) Solution filter |
| C) Rich/lean solution | I) Acid gas | O) Lean-solution cooler |
| D) Rich/lean solution heat exchanger | J) Reflux pump | P) Lean MDEA |
| E) Regenerator | K) Reboiler | Q) Sweet-treated gas |
| F) Condenser | L) Steam | |

UNIT BASICS

In the standard MDEA unit, the sour gas enters the absorber (contractor) at the bottom and flows countercurrently to the MDEA. The liquid entering the top is known as the "lean" solution. As the solution passes down through the trays or packing, it absorbs H₂S and CO₂ from the gas stream, producing sweet gas that exits the top. When the MDEA gets to the bottom of the tower, the stream is called the "rich" solution (rich in acid gases).

The rich MDEA must be regenerated for reuse in the closed system. It is preheated in the lean/rich heat exchanger and passed from the base of the contactor to a point near the top of the stripper (regenerator or still). There, heat is continually provided from a reboiler at the base to drive H₂S and CO₂ overhead. A stream of lean MDEA is drawn from the still bottoms, passed through the lean/rich heat exchanger and the lean solution cooler and returned to the contactor. This completes the cycle.

INITIAL CIRCULATION RATE CALCULATION

The start of an estimate is the calculation of liquid circulation rate. Knowing some basic unit-operating parameters can give a quick flow rate using the following formula:

$$\text{Liquid Circulation Rate (in GPM)} = \frac{25.5 \times \text{GF} \times \Delta\text{AG}}{\text{ML} \times \text{MDEA} \%}$$

Where GF = Gas flow rate in MM scf per day
 ΔAG = Acid gas (AG) removed in volume %
 (%-AG in sour stream minus %-AG in sweet (stream))
 ML = Mole loading of AG in the rich amine minus
 Mole loading of AG in the lean stream
 MDEA = Concentration of MDEA in liquid stream in weight %

This method only applies to "ball park" comparisons. Computer simulation incorporating the specific design parameters of your unit is needed for final design.

SAMPLE CALCULATION

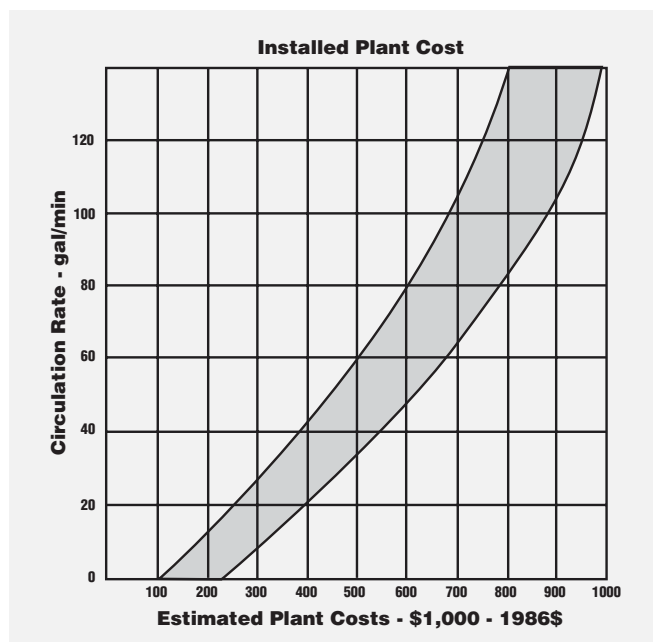
A high-pressure gas feed is entering at 50 MM scf/day with 3% CO₂ and 200 ppm H₂S. For an exit gas having 1.5% CO₂ and 1 ppm H₂S, approximately 1.5% AG is removed. Standard MDEA units are designed using a 25 to 50 wt% working solution with 0.3 to 0.6 mole loadings. Assuming a 40 wt% MDEA solution is used with an ML of 0.50, the required circulation rate would therefore be:

$$\text{GPM} = 25.5 \times 50 \times 1.5 / (0.5 \times 40) = 95.6 \text{ GPM}$$

Essential to this calculation is the contactor design and operation. This will determine how much of the CO₂ can be slipped with the sweet gas stream and the mole loadings achieved in the rich solution.

From the initial conditions and flow rates, a rough estimate of the capital investment required for an MDEA plant can be made. Figure 2 gives the relationship between the circulation rate and the cost of turn-key operation. There has been a trend in recent years to the off-the-shelf packages that some major engineering firms offer. These tend to be lower in price and well-suited for smaller gas plants requiring relatively little engineering, however, you should conduct a thorough analysis of your requirements before using such a package.

Figure 2



■ OTHER EQUIPMENT

Filtration is an essential operation in maintaining solution integrity for MDEA. The major problems (foaming and corrosion) that hamper amine-plant operation can be minimized with filtration. Two-stage filtration has been shown to give the best results. The solution first goes through a standard particulate filter. Care should be taken to ensure that the filter elements are of virgin cotton or inert polymer fibers. Treated fibers tend to lose their coating into the MDEA system, causing foaming. Both slip-stream and full-stream filtration may be used. The second stage is activated carbon filtration to remove organic components that can cause foaming or corrosion. Generally, slip streams of 5-15% of the amine stream are used to maintain clean solutions. The carbon used mostly is a heavier type to avoid material loss which fouls the system. Velocities are designed at 8-10 gpm/ft² to ensure proper filtration. A good filter system can help prevent foaming and corrosion, therefore reducing solution loss and extending equipment life. Another solution to foaming problems is our MDEA-LF. It is specially formulated to combat foaming problems without the need for carbon filtration.

The lean-amine/rich-amine heat exchanger is a primary piece of equipment used to decrease energy consumption. Optimum design will decrease the heat load on the still reboiler and decrease cooling requirements for the lean-amine stream.

The regenerator is the major energy user within the MDEA unit. Rich amine enters the column near the top, generally in the second to fourth tray, and is stripped of H₂S and CO₂ using a bottoms reboiler for heating. The reboiler is operated at 230-275°F (most often at 240-250°F) to ensure adequate stripping. On the other end of the column, the reflux ratio is adjusted to limit energy usage while providing a well-stripped lean-amine stream.

Cooling Water is generally used to bring the lean amine back to acceptable temperatures before going back into the contactor. To maintain pipeline quality gas, MDEA solutions should not be run above 110°F when entering the contactor.

■ DESIGNING FOR SELECTIVITY

In designing an MDEA gas-scrubbing unit, a number of factors influence the degree of selectivity that is desired and that can be achieved. The first step in designing for selectivity is to obtain a thorough knowledge of the inlet gas parameters and the sweet gas specifications, both at startup and allowing for any anticipated changes over the design life of the plant. A number of the factors which must be taken into consideration are listed on Table 1.

Table 1
Design Factors in MDEA Plants

Inlet Gas Conditions	Outlet Gas Requirements
Inlet Temperature	Natural Gas Plants:
Acid Gas Partial Pressure	H ₂ S Specifications
Acid Gas Mole Fraction	CO ₂ Specifications
H ₂ S/CO ₂ Mole Ratio	Tail Gas Plants:
Projected Composition Changes	Sulfur Emissions Regulations

High inlet temperatures and high acid-gas partial pressures affect the degree of selectivity that can be achieved by limiting the performance of the amine. If the inlet gas temperature is above 110°F and/or the acid-gas partial pressure is under about 10 psi, it is difficult to treat a gas stream effectively, and the engineer might not be able to design for selectivity if the outlet gas is to meet design specifications, however, this may be achieved with a specifically formulated MDEA.



The factors that affect selectivity are adsorber pressure and $\text{CO}_2/\text{H}_2\text{S}$ ratio. Selectivity increases at lower adsorber pressure. The higher the $\text{CO}_2/\text{H}_2\text{S}$, mole ratio is in the inlet gas, the easier it is to design for selectivity.

In practice, gas-scrubbing plants are not designed to just meet the sweet-gas specifications. Instead, more conservative designs are generally used to account for variations in the inlet gas composition, and to allow the plant to meet design specifications even during minor process upsets.

The single most important restriction on the amount of selectivity which can be built into a gas-treating plant is the sweet-gas specification. For the design engineer, the first consideration must be that the plant produces on-spec gas over the anticipated range of process conditions.

For natural-gas plants, two sets of specifications apply. For "pipeline quality" gas, the maximum H_2S content is limited to 0.25 Grain/100scf or 4 ppmv. This standard is almost always used in North America, although some individual contracts may set stricter limits. The allowable CO_2 content of the sweet gas is often not directly specified, but is in practice limited by the contract specification for the heating value of the gas. The typical contract specification of about 1,000 BTU/scf limits the CO_2 content of the gas to around 1-2%, depending on the hydrocarbon mix of the gas and nitrogen content.

In treating the tail gas from a sulfur recovery unit (SRU) such as a Claus reactor, the only specification that must be met is the maximum allowable sulfur emission limit for the plant. Here, as much CO_2 as possible should be slipped to the flare while still meeting the sulfur emissions limit.

Other design situations include the scrubbing of synthesis gas in ammonia plants where complete CO_2 removal is required and two-stage scrubbing where CO_2 is to be used for enhanced oil recovery. In the latter case, MDEA can be used in the first-stage scrubber to remove H_2S with maximum selectivity and to remove the remaining CO_2 in the second stage.

Because the nature of MDEA's H_2S selectivity is kinetic, as the amine contact time in the absorber decreases, selectivity increases. Reducing the amine contact time can be achieved by moving the lean-amine inlet in the absorber to a lower tray.

Reducing the amine-circulation rate also increases selectivity. To aid in optimizing the design of multiple-flow schemes and in deciding on the most cost-effective option, many engineers are turning to commercially available amine process simulation programs. These programs allow the design engineer to compare alternative designs under anticipated process conditions quickly and cheaply, and to design the most efficient plant for the desired application.

CORROSION

Of all the amines used in gas treating, MDEA has the highest chemical and thermal stability. Unlike MEA, DEA, DGA and DIPA, MDEA does not react with CO_2 , COS or CS_2 to form degradable products. As a result, properly operated MDEA plants are expected to show little or no corrosivity towards carbon steel, however, contamination with heat stable salts and understripping will increase corrosion. Copper and copper alloys such as brass or Admiralty metal are severely corroded by all amines and should never be used with MDEA.

With proper design and maintenance, MDEA systems can be operated with minimal corrosion. Excessive acid gas loadings in the rich amine should be avoided. Field experience has shown that the maximum MDEA concentration that can be used safely is about 50 wt.%.

Erosion corrosion, caused by suspended solids and/or excessive fluid velocities (especially in pipe elbows), is also a potential problem in amine scrubbing units. Efficient operation of a particulate filter, coupled with good design, will minimize problems resulting from erosion corrosion.

A major cause of corrosion in MDEA plants is contamination. In particular, a concentration of heat-stable salts above several percent of the MDEA charge is strongly linked to corrosion problems.

Because of the potential for contamination caused by SO_2 breakthrough, tail-gas cleanup plants require careful operation to avoid corrosion problems. SO_2 breakthrough is avoided by

proper reactor control and maintaining excess H₂. An efficient quench tower is vital for maintaining solution integrity. Brine entrainment in natural gas and use of untreated well water for makeup are potential sources of highly corrosive chlorides. MDEA-HST is effective in preventing corrosion from chloride contamination.

In the past, Heat Stable Salts have been “eliminated” by adding caustic until the free amine and total assays are made



equivalent. All that is accomplished by this approach is to convert amine salts to sodium salts:

The corrosive anions are not removed from the solution. The only certain method of controlling corrosion caused by heat stable salts is by replacing at least a portion of the solution with fresh amine. MDEA-HST, on the other hand, does not require replacement.

It is important to maintain solution quality to avoid both corrosion and foaming. MDEA is not easily reclaimable as MEA, DIPA and DGA are. It is good practice to have a virgin cotton particulate filter and a sidestream charcoal filter to remove contaminants. Although, in certain cases, the charcoal filter can be eliminated by using a formulated product such as MDEA LF.

As wet CO₂ is extremely corrosive, care must be exercised to avoid uncontrolled releases of CO₂ into the vapor space particularly above the rich amine. The site most prone to CO₂ caused corrosion is the lean/rich heat exchanger. The maximum exchanger outlet temperature of the rich amine should be about 20°F below the reboiler temperature. Adequate reboiler heat duty is necessary for adequate stripping to avoid corrosion. This is especially true when sour gas volumes are significantly below design. If the amine circulation rate is too high, H₂S/CO₂ selectivity will be lost. A good protective measure for dealing with minor upsets is to maintain about 0.5% MDEA in the reflux overhead.

Flashing of acid gases can occur anywhere the rich amine is heated and/or there is a large pressure drop. Sites that are prone to corrosion, in addition to the lean/rich heat exchanger, are the inlet to the regenerator and the downstream sides of orifices. Careful monitoring is necessary, especially when operat-

ing at rich-amine loadings of 0.5 mole/mole.

Oxygen contamination of sour gas can lead to serious corrosion problems. Rarely present in natural gas, oxygen contamination usually occurs in sulfur recovery units where oxygen may be present in excess during the initial H₂S burn.

Oxygen contamination can cause operating problems by two mechanisms. First, corrosion of the scrubber internals can occur due to direct oxidation of the steel surfaces. The iron oxides formed are then sloughed off into the rich-amine stream where they react with H₂S to give iron sulfides. In addition, oxygen reacts with H₂S to form sulfur acid. If no H₂S is present, O₂ reacts with amine or hydrocarbons to form carboxylic acids. These acids cause the buildup of Heat Stable Salts, and an increase in the effective molar loadings.

Corrosion monitoring can be carried out in several ways. Some operators track the dissolved-iron content of the solution. Iron concentrations above 5-15 ppm generally indicate corrosion is occurring. This is somewhat unreliable as the iron will be precipitated by the H₂S in the rich amine and removed in the particulate filter, indicating a misleadingly low dissolved iron concentration. In addition, localized corrosion will go undetected. A high rate of fouling of the particulate filter or the plugging of pipes, valves or orifices with iron sulfide indicates a corrosion problem. Localized corrosion is somewhat easier to detect based on the site of fouling. One method of detecting localized corrosion is placing monitoring coupons of the material of construction in selected sites where the likelihood of corrosion is significant, such as the lean/rich heat exchanger, regenerator inlet, reboiler and reflux condenser.

We offer an enhanced level of analytical service which detects even low levels of corrosion without the need for coupons, probes or other installed equipment. When this is used in combination with the other monitoring techniques previously described, the operator can generally detect corrosion problems before serious damage occurs and take appropriate action.

■ FOAMING

When gaseous and liquid phases are mixed, as, for example, in the absorber in a gas-treatment plant, some of the gas may be retained in the liquid phase, forming a stable emulsion or foam. The presence of foam can lead to severe operating problems in gas-treating systems. Loss of scrubbing efficiency, solution losses due to carryover into the lean gas stream, fouling of downstream equipment, and increased pressure drop across the absorber are some of the symptoms of foaming problems.

Field experience indicates that the foaming tendency varies with amine concentration. Adjusting the amine strength (either up or down) often corrects the problem.

In most cases, solution contamination can be identified as the cause when foaming occurs. The most common source of contamination is the presence of "wet" hydrocarbons (C_3+) in the sour-gas stream. Condensation of these hydrocarbons in the absorber to give a third organic phase will often cause severe foaming. Trace amounts of heavy organics can dissolve in the lean-amine solution. As the solvent recirculates, hydrocarbon buildup occurs and, after a critical concentration is reached, foaming begins.

In addition, numerous other causes of foaming are possible. For example, using an improper coating for the inside of a storage tank can cause severe organic contamination and foaming. The quality of makeup water must be carefully monitored. Use of hard water should be avoided to prevent precipitating insoluble sulfides and carbonates in the amine. Steam condensate is an excellent source of makeup water, provided that high concentrations of filming amines are not present. Boiler feed water should not be used as it contains filming amines.

Heat Stable Salts indirectly contribute to foaming by causing corrosion. Particulate corrosion products can provide a nucleation site for foaming to occur.

With foaming, the best cure is prevention. To minimize heavy hydrocarbon contamination, it is imperative to install a gas/liquid separator and operate it as efficiently as possible. Although the extensive solution reclaiming required for MEA, DGA and DIPA can be avoided with MDEA, passing a sidestream through an

activated charcoal bed should be done to maintain solution quality. A particulate filter of virgin cotton or inert polymer fibers should also be used. When replacing the elements in the particulate filter, the cotton must not be treated with linseed oil. This treatment, a common practice, will cause foaming immediately after startup.

If foaming does occur, the problem may be controlled with an antifoam to keep the plant running until the cause is isolated and corrected. Both silicone and alcohol-based antifoams have been used successfully. Routine addition of antifoam does not cure foaming problems, it is only a short-term solution. We provide recommendations of products.

New and converted units require special attention before startup. Foaming problems can usually be avoided by thoroughly cleaning the system to remove harmful surface deposits. The final wash in the cleaning sequence should be 2-5% aqueous MDEA to remove contaminants that could foul the amine during startup.

■ ANALYTICAL PROCEDURES FOR GAS SCRUBBING SOLUTIONS

To operate a gas scrubbing plant at peak efficiency, the condition of the amine solution must be carefully monitored. The analytical procedures in this section are those used by Arkemas' Analytical Chemistry Department and have either been developed by Arkema or adapted from standard procedures in the open literature. (NOTE: Proper safety precautions such as always wearing safety glasses and other protective equipment should always be observed.)

The analytical procedures listed below are intended as a general guide for the operator in setting up an in-house analytical laboratory. Occasionally, the need arises for more sophisticated analytical techniques that are not routinely available to the individual operator. In those instances, Arkemas' Analytical Chemistry and Organic Chemicals R&D Departments at our King of Prussia, Pa., research facility are available to offer state-of-the-art analytical and consultation services as part of our commitment to customer services.

MDEA ANALYSIS

Among the most important analyses for ensuring the proper operation of MDEA scrubbing units are total amine, free amine, and, when practical, amine purity by gas chromatography (GC).

Total amine is determined by non-aqueous titration using perchloric acid in glacial acetic acid. This method is non-specified and gives the total base concentration (in millequivalents/gram [mEq/g]).

The total anion content of the solution is obtained by titration with tetrabutylammonium hydroxide in 2-propanol. Because any H₂S and CO₂ present are included in this total anion concentration, this determination should be run on the lean solution (where the H₂S and CO₂ content is negligible) for a true indication of the Heat Stable Salt content.

The "free" amine is calculated as the difference between the total amine and total anion concentrations.

DETERMINATION OF AMINES AND AMINE SALTS IN GAS SCRUBBING SOLUTIONS

Apparatus:

200 mL Tall Form Beakers (2).
25 mL Burets (2).

Reagents:

Perchloric Acid, 0.1N glacial acetic acid, standardized with 1,3-diphenylguanidine.

Tetrabutylammonium Hydroxide, 0.1N in 2-propanol, standardized with benzoic acid.

(Indicator Solution) 0.1% Quinaldine Red in glacial acetic acid.

(Indicator Solution) 0.1% Thymol Blue in N,

N-dimethylformamide (DMF).

Procedure:

Weigh about 300 mg to +0.1 of the sample solution into a 200 mL tall form beaker, add 50-100 mL of glacial acetic acid, and three or four drops of Quinaldine Red indicator solution. Titrate to the complete disappearance of the of the red color with 0.1N perchloric acid in glacial acetic acid. Record mL of titrant as "A".

Weigh about 500-1,000 mg to +0.1 of sample solution into a 200 mL tall form beaker, add 50-100 mL of 2-propanol, and three or four drops of Thymol Blue indicator solution. Titrate with 0.1N tetrabutylammonium hydroxide to the color change from yellow to blue. Record mL of titrant as "B".

Calculations:

1. Total Amine (mEq/g) = ("A") $\frac{\text{Normality of HClO}_4}{\text{Grams of Sample}}$
2. Total MDEA (Wt%) = (Total Amine (mEq/g)) (11.917)
3. Total Anion (mEq/g) = ("B") $\frac{\text{Normality of Bu}_4\text{u NOH}}{\text{Grams of Sample}}$
4. Free Amine (mEq/g) = Total Amine (mEq/g) - Total anion (mEq/g)
5. Free MDEA (wt%) = (Free Amine (mEq/g)) (11.917)

Gas chromatography (GC) is an extremely useful tool for the analysis of MDEA gas scrubbing solutions. Total MDEA can be rapidly determined using a packed column and thermal conductivity detector; it can be determined even more quickly if a capillary column is used. In addition to giving the total MDEA concentration, the gas chromatograph also detects the presence of volatile impurities such as other amines, glycols, hydrocarbons and degradation products. By using a flame-ionization detector (FID), which does not detect water, amine purity can be measured with greater sensitivity by using an internal standard. Method #1999-10-25:2307_07662 is available upon request. Robbins and Bullin have developed a method for the simultaneous determination of total MDEA, acid-gas loadings and hydrocarbons by GC (Robbins, G. D., Bullin, J. A. American Institute of Chemical Engineers - 1984 Spring National Meeting; May 20-23, 1984, Paper 60E). The major disadvantage of GC is that it cannot be used to determine the total anion content of the solution. This is a particularly serious drawback in the analysis of tail-gas treaters on sulfur recovery units where contamination by SO₂ is a primary operating consideration.

Ion chromatography (IC) and liquid chromatography (LC) method can be used to identify and quantify respectively specific anionic and weak organic acid impurities in gas scrubbing solutions. Method #1999-10-25:2307_07663 is available upon request.

ACID GAS LOADINGS

The efficiency of an amine unit is determined by its cyclic capacity (i.e., the difference between the rich and lean loadings). To help meet design specifications for the treated gas while minimizing the amine circulation rate and reboiler steam usage, reliable data on the rich and lean amine loadings are needed.

Hydrogen sulfide and carbon dioxide may be determined simultaneously by evolution. A sample of the amine solution is acidified and purged with nitrogen while being heated to liberate the acid gases. The gas stream is then passed through two scrubbers, the first of which contains excess 0.1N KI₃ for the scrubbing of H₂S while the second contains excess 0.1 Ba(OH)₂ for the scrubbing of CO₂. Both acid gasses are determined by back-titrating the respective unreacted scrubbing agent.

If a sample has been contaminated with SO₂ (as in a tailgas unit), the H₂S loading cannot be determined accurately. (If SO₂ contamination is suspected, the total anion content of the solution should be determined.)

Calculations:

1. $\frac{\text{Ref. Vol. \#2-A) Normality HCl} (2.201)}{\text{Grams of Sample}} = \% \text{CO}_2$
2. $\frac{\text{(Ref Vol. \#1-B) (Normality of Na}_2\text{S}_2\text{O}_3) (1.704)}{\text{Grams of Sample}} = \% \text{H}_2\text{S}$
3. $\text{CO}_2 \text{ Loading (moles/mole MDEA)} = \frac{(\% \text{CO}_2) (2.71)}{(\% \text{MDEA (Total)})}$
4. $\text{H}_2\text{S Loading (moles/mole MDEA)} = \frac{(\% \text{H}_2\text{S}) (3.51)}{(\% \text{MDEA (Total)})}$

As mentioned above, H₂S and CO₂ may also be determined by gas chromatography.

Apparatus:

Gas Evolution Apparatus. Drawing 1.

Nitrogen Source (preferably a cylinder of prepurified N₂) with appropriate regulators.

Heat Source (Bunsen burner, heated oil bath, heating mantle, etc.).

25 mL Mohr Pipets(2)

125 mL Stoppered Erlenmeyer Flask(1)

250 mL Stoppered Erlenmeyer Flask(1)

25 mL Burets(2)

Reagents:

Hydrochloric Acid, 1.0N. Dilute 82.5 mL of concentrated reagent to one liter with distilled water.

Iodine, 0.1N. Dissolve 13.0 grams of iodine crystals into 100 mL of water containing 25 grams of potassium iodide. Stir to dissolve and make up one liter with distilled water.

Barium Hydroxide, 0.1N. Dissolve 8.6 grams to +/- 1 mg of reagent grade barium hydroxide in carbon dioxide-free distilled water and make up one liter.

Sodium Thiosulfate, 0.1N. Dissolve 24.8 grams to +/- 1 mg of reagent grade sodium thiosulfate, pentahydrate, in distilled water and make up one liter.

Hydrochloric Acid, 0.1N. Dilute 8.2 mL of concentrated reagent to one liter with distilled water. Standardize against tris(hydroxymethyl)aminomethane (TRIS).

Starch, 0.2%. Add a slurry of one gram of soluble starch in 20 mL of distilled water to 480 mL of boiling distilled water.

Barium Chloride, saturated.

Procedure:

Purge apparatus (Drawing 1) with a stream of nitrogen for about five minutes while empty. Stop the nitrogen flow and add exactly 15.0 mL of 0.1 iodine solution to the first scrubber (#1) and add exactly 15.0 mL of barium hydroxide to the second scrubber (#2). Connect both scrubbers to the reaction flask. Add 25 mL of water to the reaction flask, followed by one gram sample and 10 mL of 1.0N HCL through the Teflon® stopcock at the top of the evolution apparatus. The stopcock must be turned

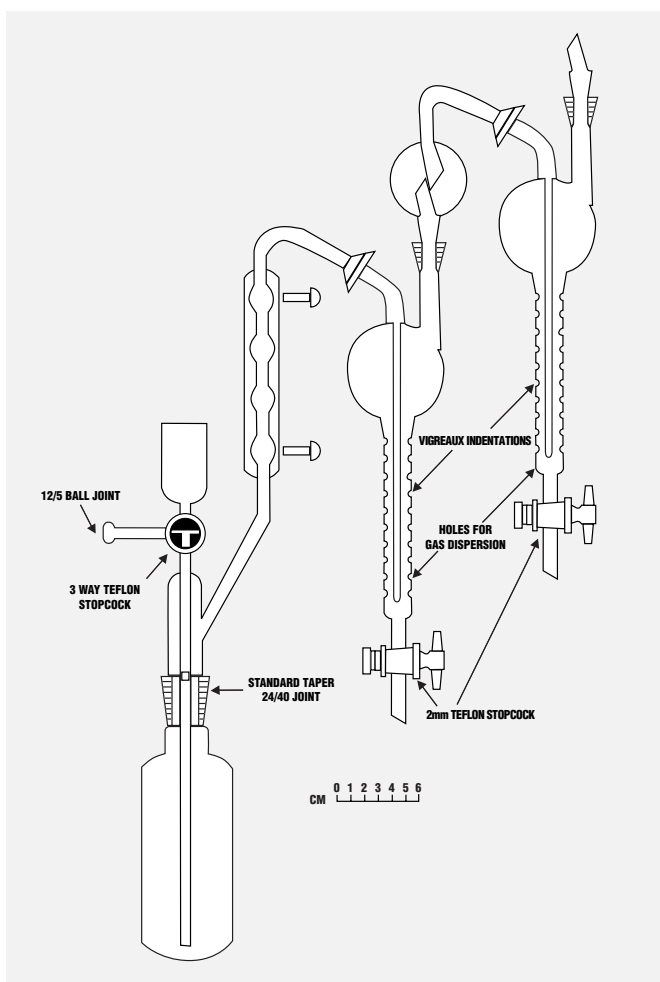
into the proper position for entry into the reaction flask. Turn the stopcock to the "Nitrogen Purge" position and boil the sample/HCL solution gently for ten minutes. Remove from heat and sweep with nitrogen for an additional fifteen minutes.

Disconnect the scrubber system and drain the contents of scrubber #2 into a stoppered 125 mL Erlenmeyer flask. Rinse and add the washings to the flask. Quickly add 15mL of saturated barium chloride solution, a few drops of phenolphthalein solution and titrate with 0.1N HCl to the colorless end point. Record the volume of 0.1N HCL used as "A".

Rinse the contents of scrubber #1 into a 250 mL stoppered Erlenmeyer flask, add enough distilled water to produce a volume of 75-100 mL and titrate with 0.1 sodium thiosulfate to the starch end point. Record the titrant volume as "B".

Perform a reference titration on 15 mL of each of the above solutions and record the titration volume for each scrubber solution.

Gas Evolution Apparatus



OTHER ANALYSES

Chloride

Chloride contamination of MDEA solutions can lead to serious corrosion problems, particularly in the reboiler. Improper demister operation, contamination from brackish cooling water and the use of untreated well water for makeup are all possible chloride sources. Titration with mercuric nitrate is a suitable method of analysis.

Apparatus

200 mL Tall Form Beakers

Magnetic Stirrer, with Teflon[®]-covered stirring bars.

10 mL Buret

Reagents:

2-Propenol (reagent grade)

sym.-Diphenylcarbazone, 1.5% in ethanol.
Fisher Scientific Company D-86.

Bromophenol Blue, 0.05% in ethanol.

Nitric Acid, 10% aqueous v/v.

Mercuric Nitrate, 0.01N. Dissolve 1.7 grams of mercuric nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 500 mL of distilled water that contains 2 mL of concentrated nitric acid. Make up to one liter with distilled water. Using a pH meter, adjust the pH to 1.7 with nitric acid.

Potassium hydroxide, 45% (w/v)

Standardization:

Weigh 400 mg to +/- 0.1 mg of KCl and make up one liter with water. Into a 200 mL tall form beaker, pipet 10 mL of the standard chloride solution (10 mL = 4.0 mg KCl). Add 50 mL of 2 propanol, 25 mL of water, and 3 drops of bromophenol blue indicator solution. Add one drop of 45% KOH, and then add dilute nitric acid until indicator turns yellow. Add three drops excess. Add eight drops of diphenylcarbazone indicator and titrate slowly with the mercuric nitrate solution. Vigorous stirring should be maintained at all times. The end point is the first permanent

color change from yellow to magenta. Record mL of mercuric nitrate solution used and set beaker aside to use as a comparison color.

$$\text{Normality} = \frac{\text{mg of KCl taken}}{(74.555) (\text{mL of Hg(NO}_3)_2)}$$

Procedure:

Weigh about 1.0 gram to +/- 0.1 mg of sample into a 200 mL tall beaker. Add 50 mL of 2-propanol, 25 mL of water, three drops of bromophenol blue indicator, and a Teflon®-covered stirring bar. Add dilute nitric acid until the solution turns yellow. Add three drops nitric acid. Add eight drops of the diphenylcarbazone indicator and titrate slowly dropwise until the magenta end point is obtained. Vigorous stirring must be maintained.

Calculation:

$$\text{ppm Chloride} = \frac{(\text{mL of Hg(NO}_3)_2) (\text{Normality}) (35.45) (10^3)}{\text{Grams Sample}}$$

Reference:

Dirscherl, A., Zur Mikrobestimmung Geringer Chlorgehalte in Organischen Verbindungen, *Mikrochim. Acta*, 1968, 316-320.

Metals

The presence of high concentrations (5 ppm) of metals (especially iron) in MDEA gas-scrubbing solution is a strong indication of a corrosion problem. A low metals concentration does not indicate an absence of a corrosion problem, as corrosion may be localized with only a small area of metal attacked. In addition, dissolved metal ions tend to be precipitated as the sulfides by reacting with H₂S in the rich solution.

Nevertheless, the metals content of the solution should be tested if a corrosion problem is suspected. Because the concentrations of any dissolved metals will generally be low (<50ppm), atomic absorption spectroscopy (AA) or Inductively Coupled Plasma (ICP) are the methods of choice. Unfortunately, most gas plants do not have access to these particular instruments and so must use other methods of analysis. For iron, the metal of most interest to operators, the best alternative is a colorimetric one based on complexation with orthophenanthroline, after reduction to the ferrous state with hydroxylamine. By measuring its absorption at 510nm, the concentration of the complex can be determined through use of a calibration curve and the iron content of the sample can be calculated.

COLORIMETRIC DETERMINATION OF IRON IN MDEA

Apparatus:

Spectronic 20 Genesys spectrophotometer or equivalent.
100 mL Volumetric Flasks (6).
1 mL Volumetric Pipet (1).
10 mL Mohr Pipet (1).
150 mL Beaker (1).
Hot Plate (1).

Reagents:

10% Aqueous Hydroxylamine Hydrochloride.
1:1 NH₄OH. Dilute concentrated NH₄OH with an equal volume of distilled water.
Orthophenanthroline solution, 0.1 g dissolved in 75 mL warm water, cooled and made up to 100mL.

Standard Curve:

Weigh exactly 1.000 g pure iron wire. Transfer to a beaker and add 50 mL water and 25 mL 1:1 H₂SO₄. Warm on a hot plate until dissolved. Cool and transfer to 1000 mL volumetric flask and dilute to volume with water (1 mL = 1 mg Fe). Pipet volumes of 1, 2, 5, 8, and 10 mL of the 10 ug Fe/ mL diluted standard into individual 100 mL volumetric flasks, add 10 mL 1:1 H₂SO₄, 10 mL orthophenanthroline solution, and dilute to volume. Read the absorbance at 510 nm. Plot the absorbance versus µg Fe. The standard curve should be checked about every six months.

Procedure:

1. Accurately weigh samples expected to contain 10 to 100 μg Fe to suitably sized beaker.
2. Warm the sample on a medium heat to evaporate the MDEA to dryness.
3. Take up the residue in water, and add 2 mL 10% hydroxylamine hydrochlorine solution.
4. Adjust the pH to 3-6 with 1:1 NH_4OH or 1:1 H_2SO_4
5. Transfer the solution to a 100 mL volumetric flask, diluting to about 70 mL with water, then add 10 mL orthophenanthroline solution.
6. Dilute to volume, mix thoroughly, and read absorbance at 510 nm.
7. Read μg Fe from standard curve.

Calculation:

$$\text{ppm Fe} = \frac{\mu\text{g Fe}}{\text{g sample}}$$

Extractive Techniques

The presence of small amounts of nonpolar impurities such as heavy hydrocarbons and glycols in an amine solution can cause major operating problems, particularly foaming.

Confirming the presence of such impurities is the first step in correcting the problem. The combination of solvent extraction and infrared spectroscopy (IR) allows the determination of non-polar impurities to be made quickly and reliably. If only a single impurity is present, the determination can be semi-quantitative. GC can also be used to analyze the concentrated extract.

Before extraction, the sample is acidified with 6N HCl to retain the MDEA in aqueous phase. Suitable solvents for the extraction step are methylene chloride, ether and hydrocarbon solvents such as hexane or toluene. For most applications, methylene chloride is preferred as it does not have bands in the IR that interfere with the identification of glycols (as would ether) or wet hydrocarbons (as would hexanes or toluene).

The recommended sample size is 100-250 g of solution. Thus an extractable impurity present at 10 ppm would yield 1-2.5 mg of extract. The size of the sample used can be adjusted up or down depending on the sensitivity desired.

SOLVENT EXTRACTION OF MDEA GAS-SCRUBBING SOLUTIONS

Reagents:

Hydrochloric Acid, 6N.

Methylene Chloride, Reagent Grade

Apparatus:

Perkin Elmer 1310 IR Spectrophotometer (or equivalent)

1 L Separatory Funnel

1 L Erlenmeyer Flasks (2)

Stirring Hot Plate with Teflon®-coated magnetic stirrers

Procedure:

Weigh out 100-250 g of sample. Carefully add 6N HCl to pH 1-3. (Safety Note: The amine solution should be chilled in an ice-bath and the acid should be added slowly with stirring during the procedure to control the strongly exothermic neutralization reaction.) After neutralization, transfer the sample, which should be at or below room temperature, to a 1 L separatory funnel and extract 2-3 times with equal volumes of methylene chloride. Evaporate the combined methylene chloride extracts to dryness (under nitrogen if possible) in a tared container and obtain the weight of the residue.

The isolated residue may then be analyzed by standard IR and/or GC techniques as appropriate.

Calculations:

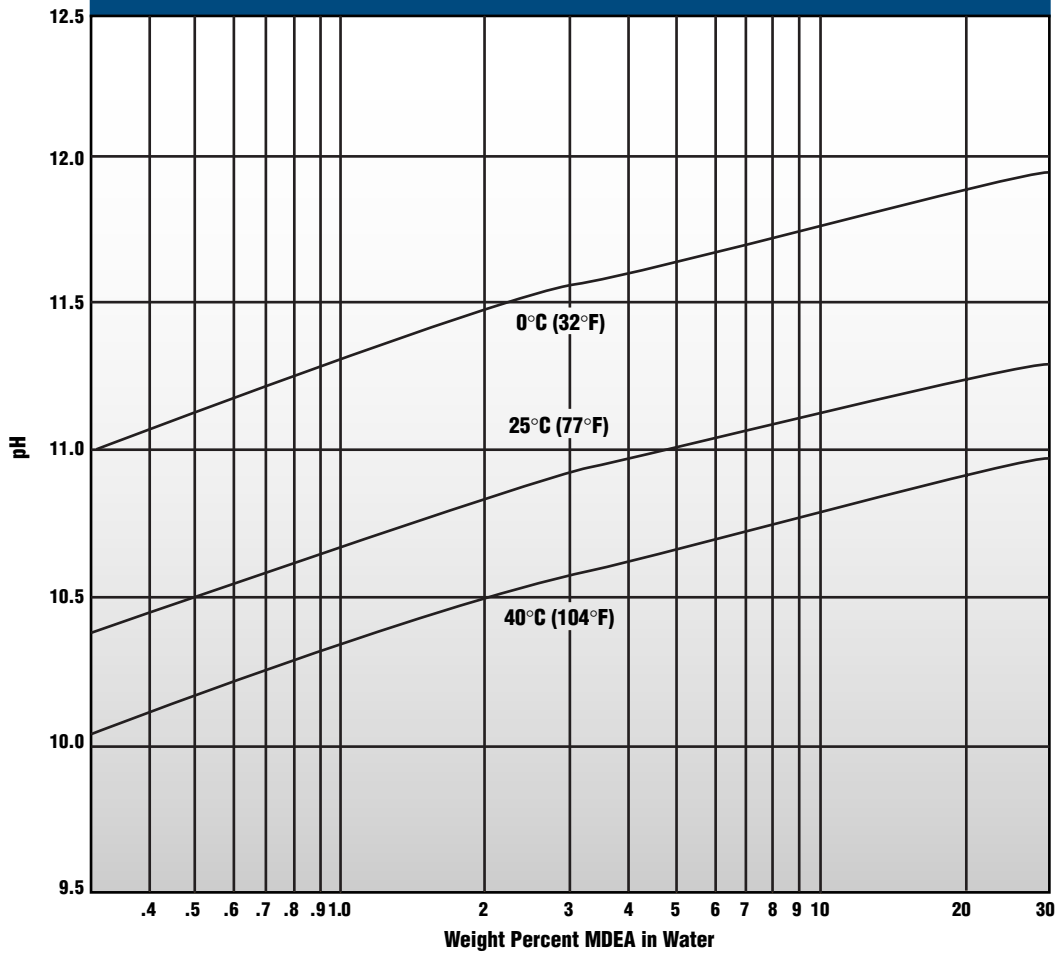
$$\text{ppm Extractables} = \frac{(\text{mg residue}) (1.000)}{(\text{g sample})}$$

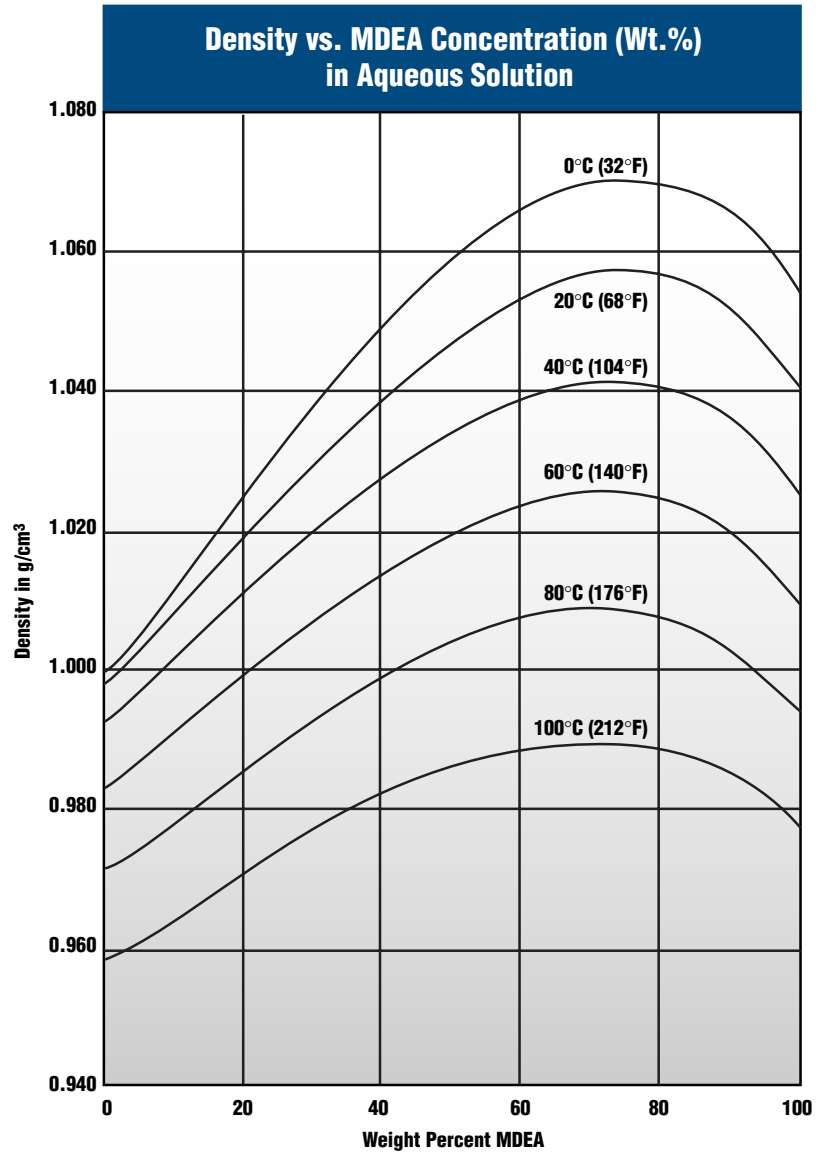
PHYSICAL PROPERTIES OF AQUEOUS MDEA SOLUTIONS

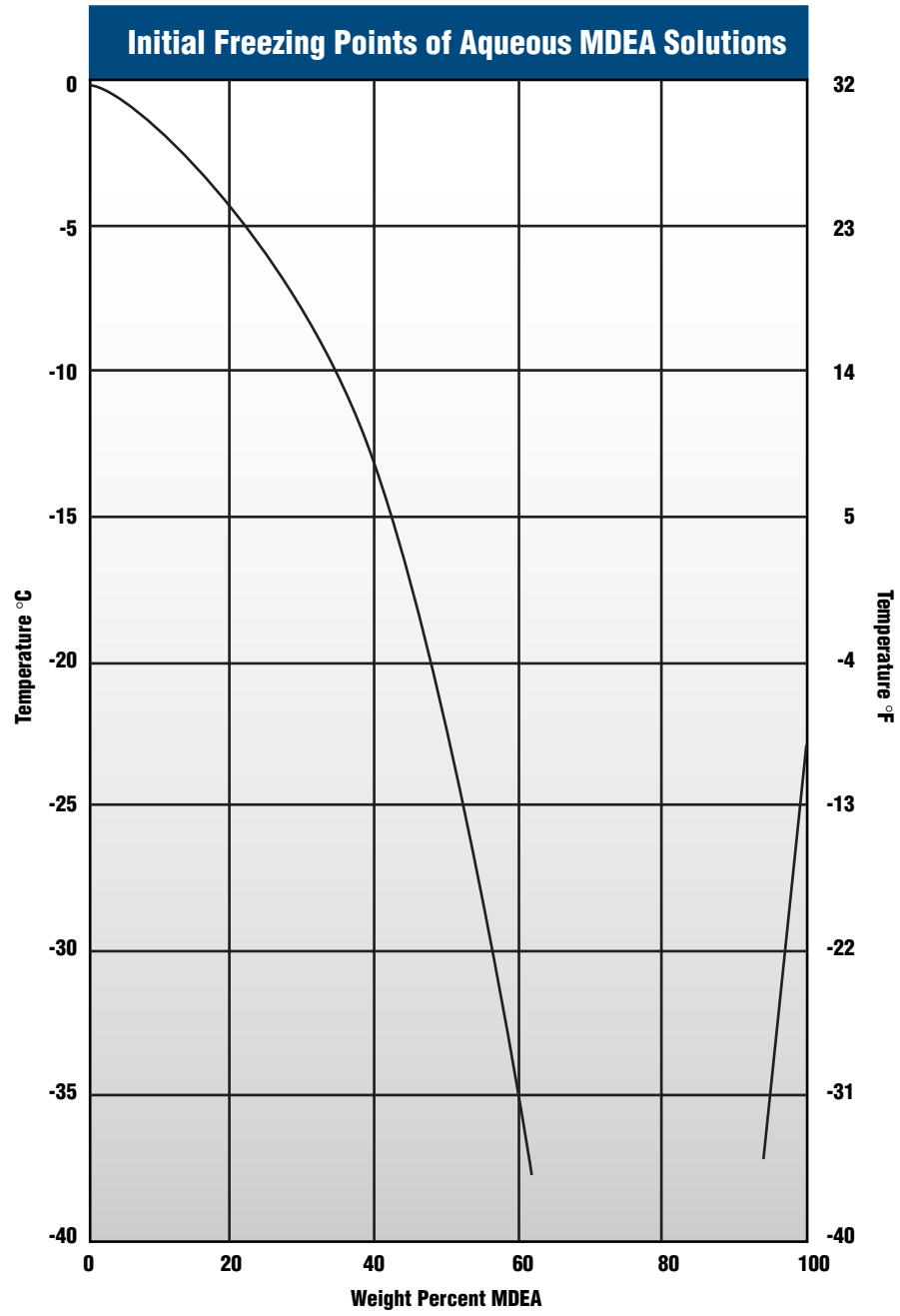
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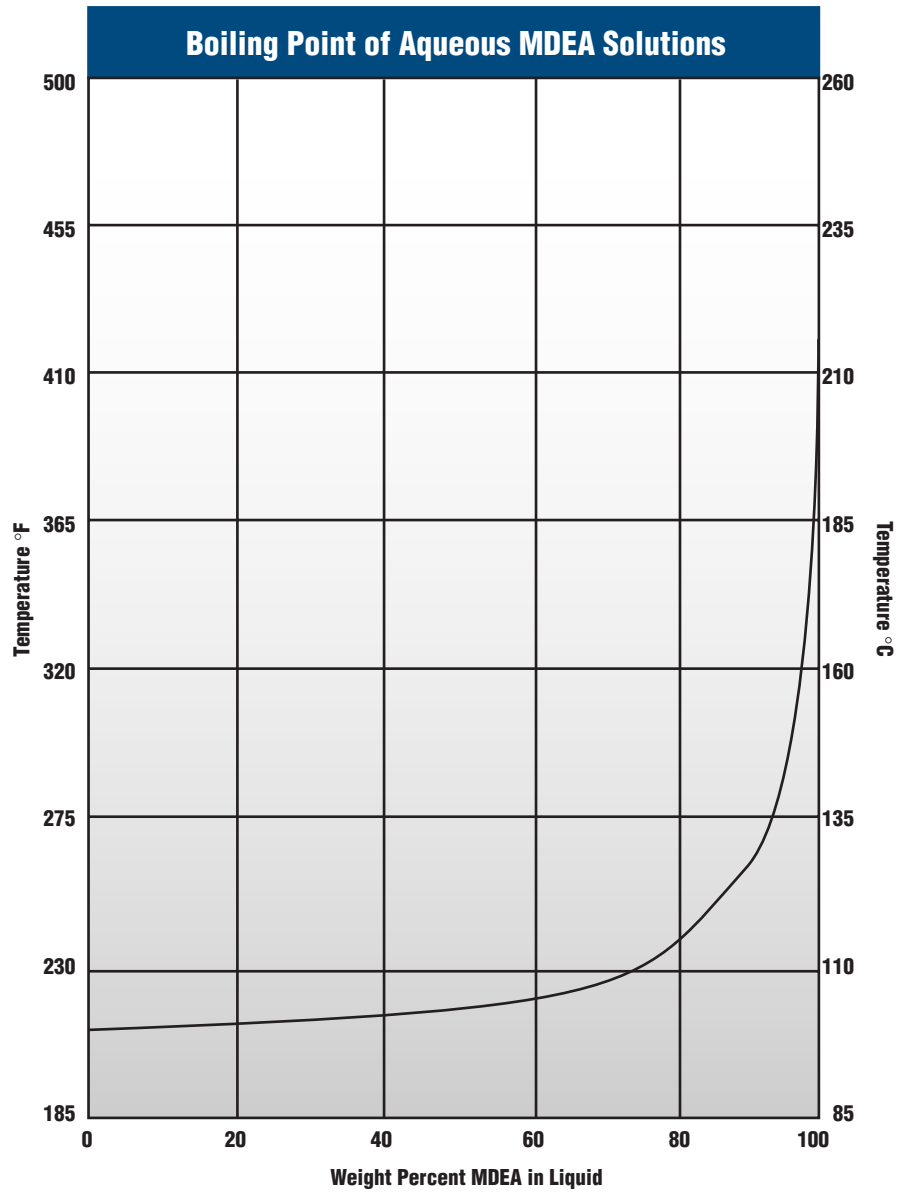
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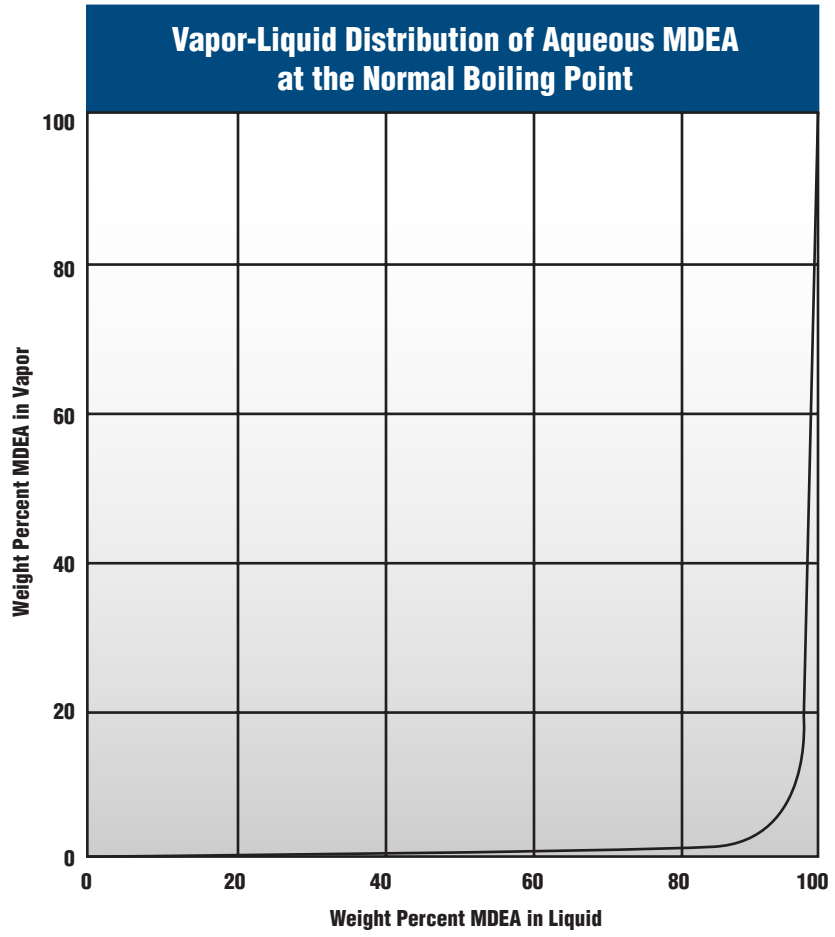
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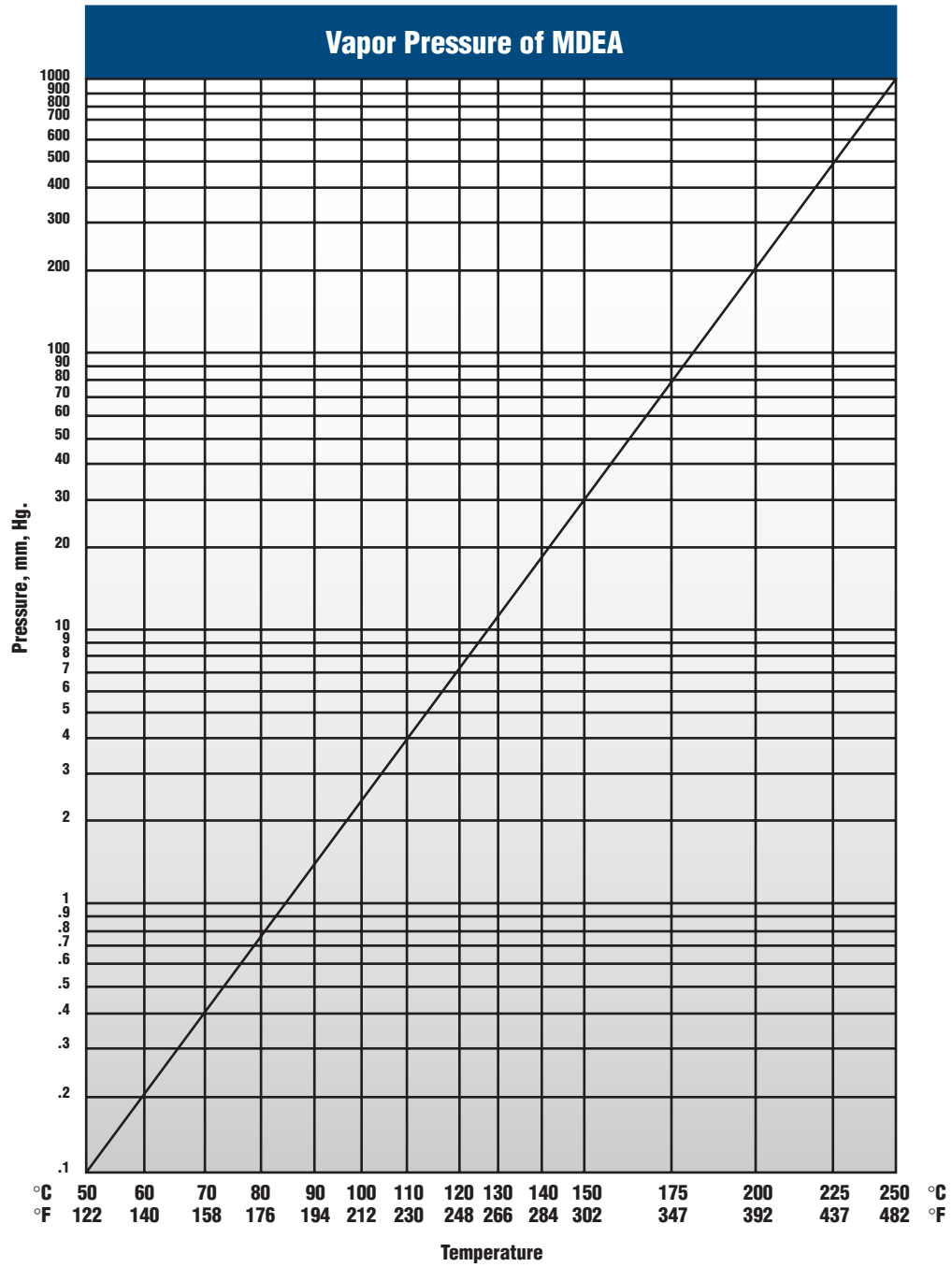


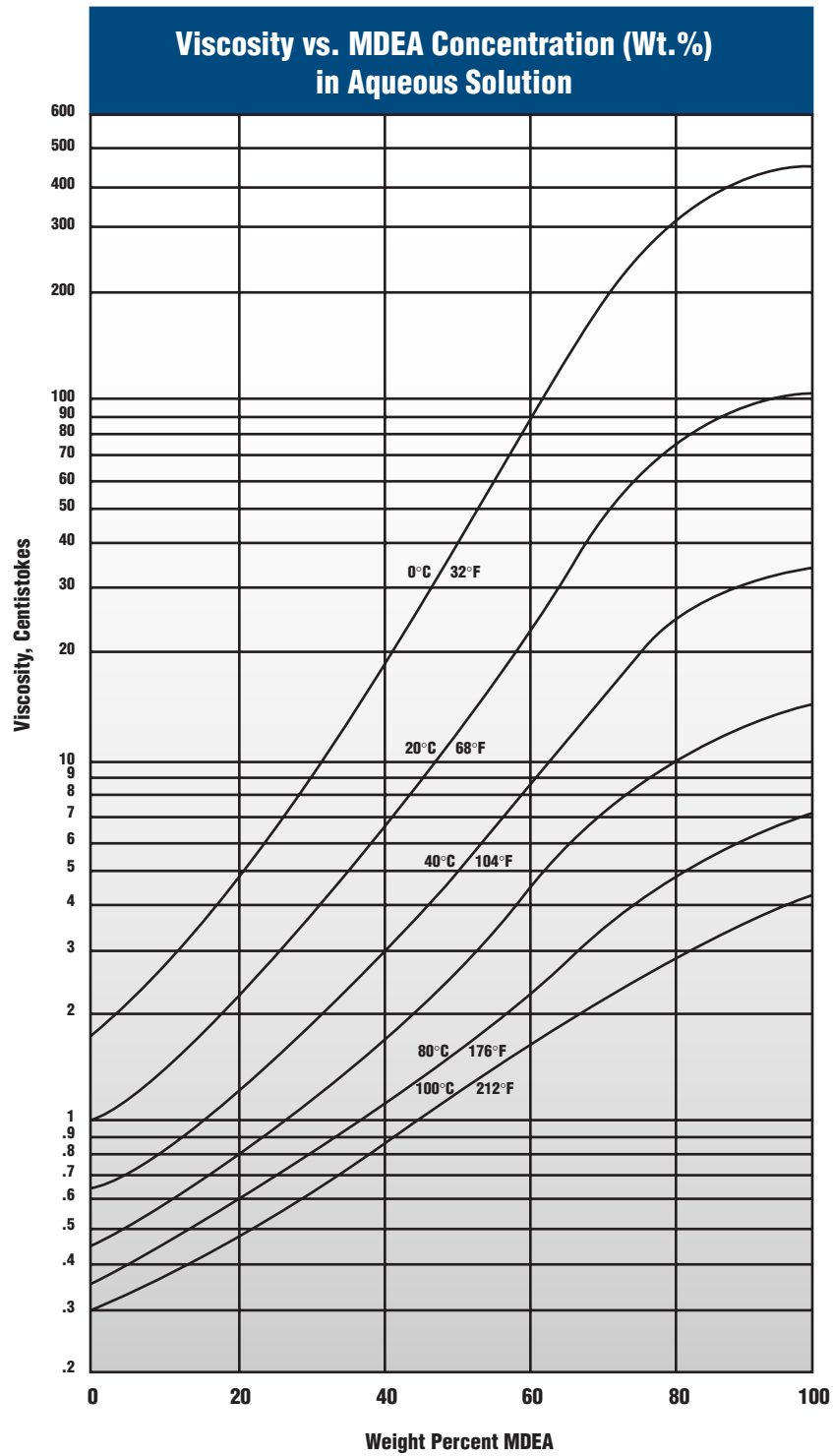


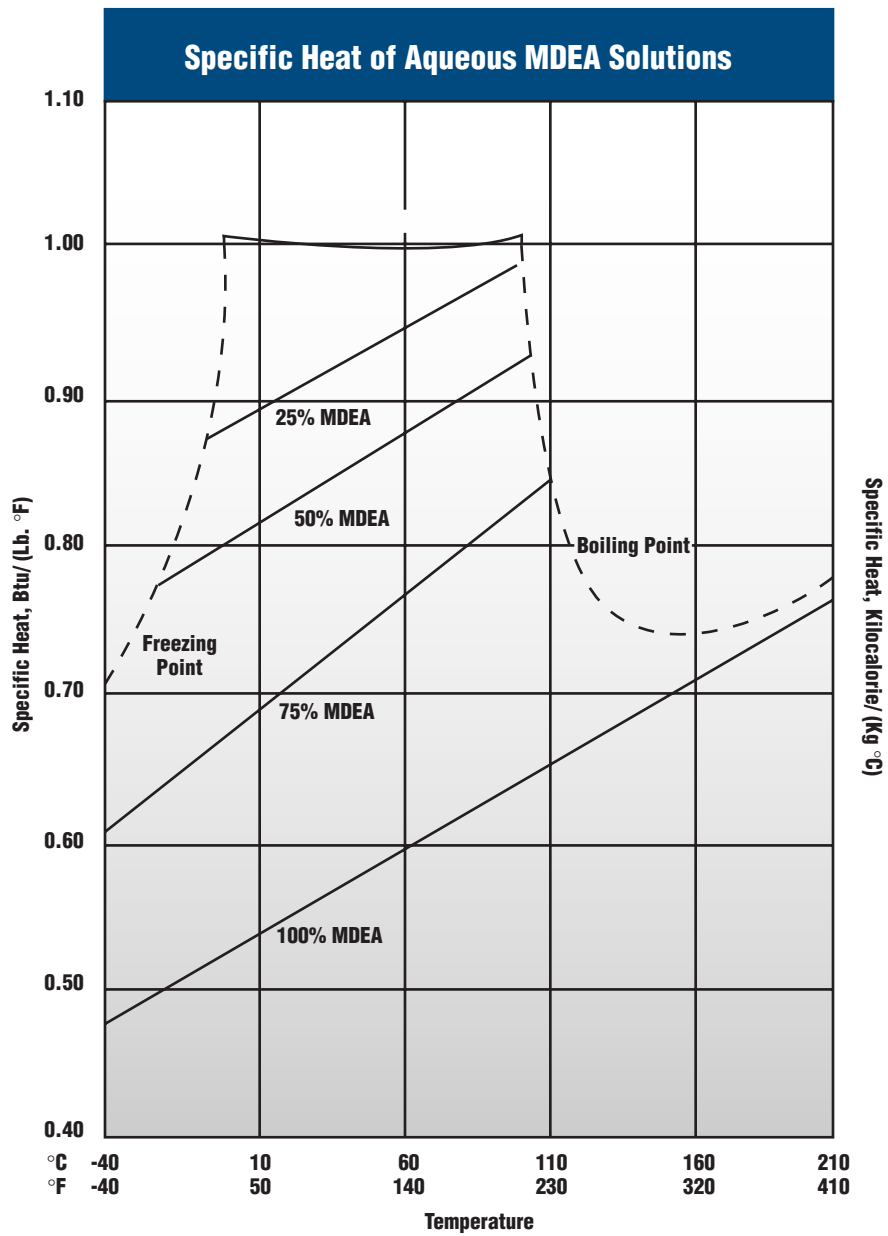


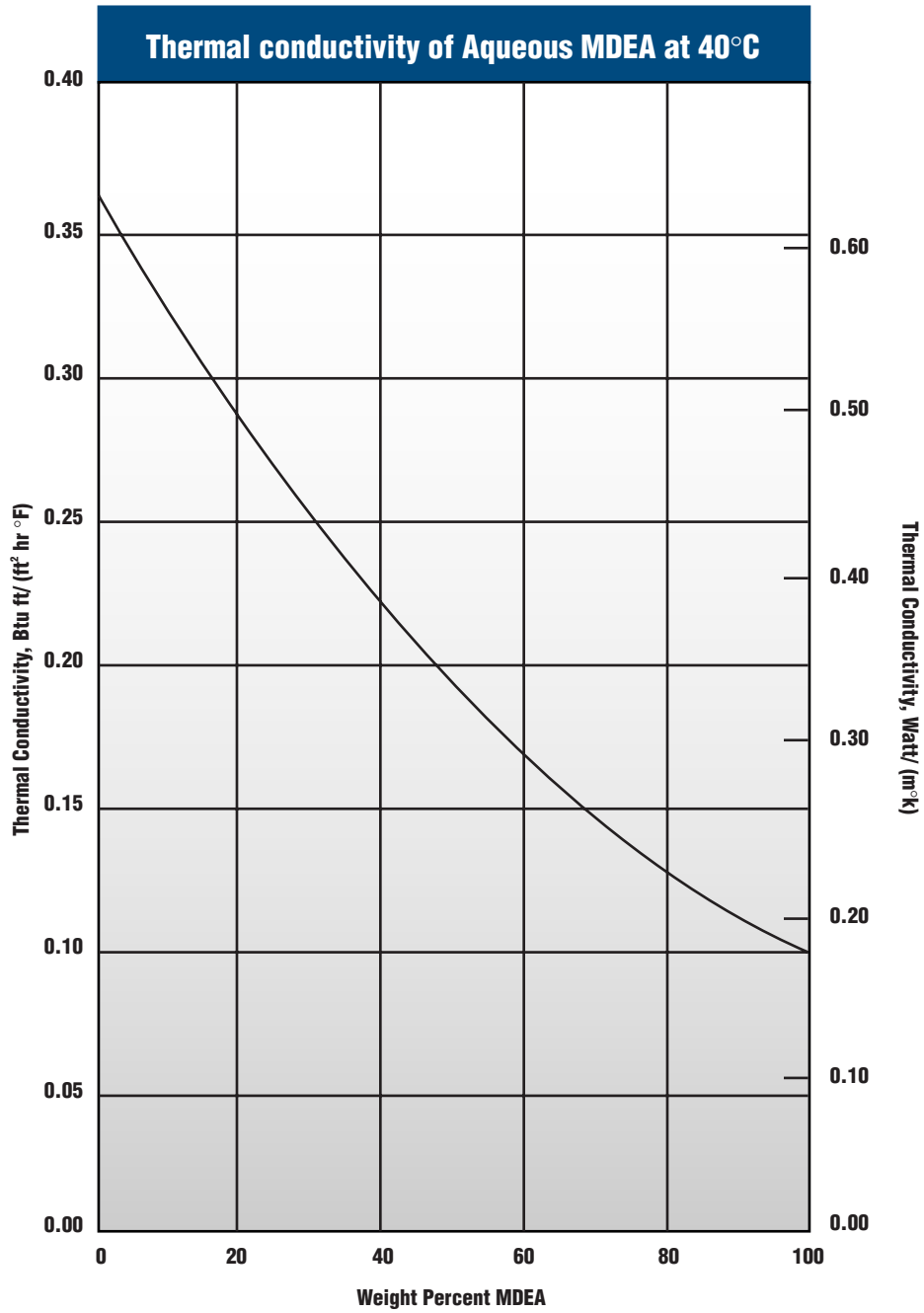














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