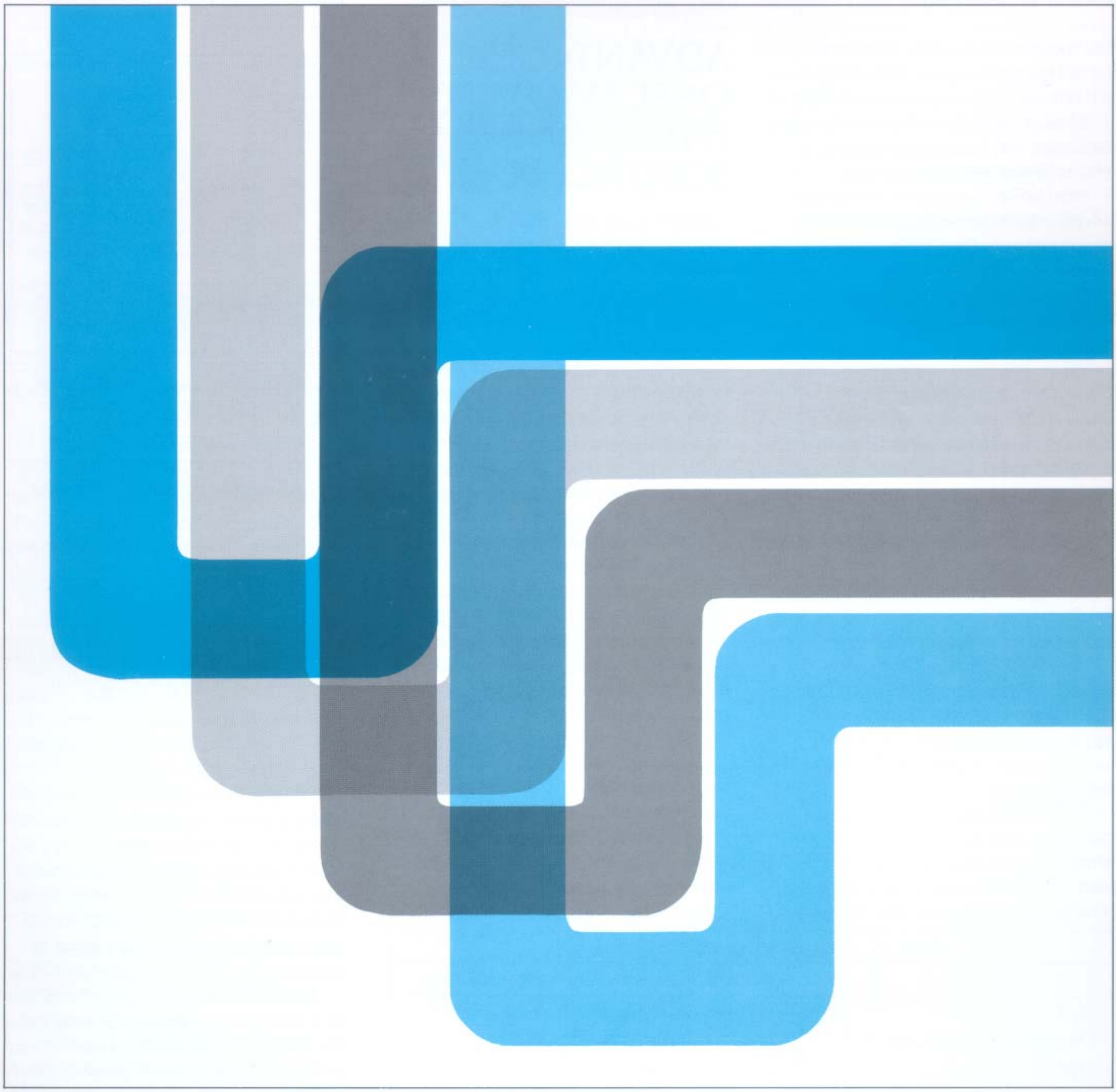
SCAV-OX®

Hydrazine solutions to control oxygen corrosion in boiler systems.



ARCH® CHEMICALS, Inc.

A COMPLETE APPROACH TO OXYGEN CORROSION PROBLEMS

Boiler corrosion is costly. Nationally, the bill for metal repairs, lost energy and time lost because of maintenance shutdowns runs into millions of dollars each year. Yet, corrosion in boilers is relatively inexpensive to prevent.

Most boiler corrosion is due to dissolved oxygen carried into the steam generating system with the feed water. The obvious answer to the problem is to get rid of the oxygen before it can cause damage. In most systems, this is done by both mechanical oxygen removal in deaerators, and by the addition of chemical reducing agents. These agents, which combine rapidly with dissolved oxygen to form harmless reaction products, are known as "oxygen scavengers."

Scav-Ox® 35% hydrazine solution has proved to be an extremely effective oxygen scavenger. At high boiler temperatures it outperforms sodium sulfite, the other most commonly used oxygen scavenger. Arch has broadened the scope of hydrazine's advantages with two 35% hydrazine solutions that have been catalyzed to react rapidly with oxygen at low temperatures: Scav-Ox® II (organic catalyst) and Scav-Ox Plus (organometallic catalyst).

Since mechanical features, physical conditions and water treatment chemistry of various steam generating systems vary, Arch's line is designed to provide the right product for the right purpose. Most important, the two catalyzed products have removed the only significant disadvantage of hydrazine - its slowness, compared with sodium sulfite, in reacting with oxygen at low temperatures. Oxygen scavenger users can thus make full use of hydrazine's many other advantages over sodium sulfite.

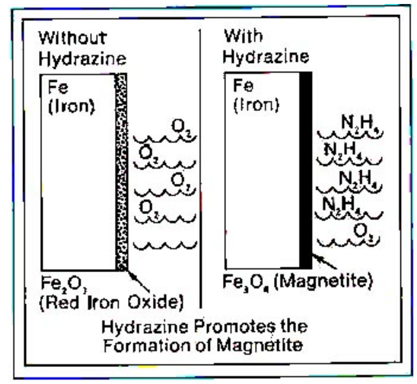
Advantages of Scav-Ox® Hydrazine solutions

Together, Scav-Ox® , Scav-Ox® II and Scav-Ox Plus® offer effective oxygen removal over a wide range of boiler conditions. In addition, all have further important advantages: They form a protective magnetite barrier. They can be used throughout the steam-generating unit. They don't decompose to form corrosive products or solids. They prevent formation of iron and copper oxide deposits. They are compatible with other boiler treatment chemicals. And they help control pH.

Fast oxygen removal. At high boiler temperatures, regular hydrazine scavenges oxygen as fast as sodium sulfite (which can't be used at all at temperatures above 540°F, because it decomposes). At low temperatures, the reaction times of catalyzed hydrazine are comparable to those of catalyzed sodium sulfite. The exact rate of reaction depends on temperature, pH and scavenger concentration.

Magnetite barrier formation. Normally, steel reacts with hot ionized water to form a black iron oxide called magnetite (Fe_3O_4). A thin film of magnetite on the boiler surface acts as an impermeable barrier between the metal and the corrosive agents in the water.

But any dissolved oxygen in the system will attack this barrier. The oxygen reacts with the magnetite, causing the barrier to become uneven. Unchecked, the oxygen attack leads



swiftly to the formation of the destructive red iron oxide, rust (Fe_2O_3).

Hydrazine protects boiler steel by reducing the non-protective red iron oxide back to protective magnetite:

$$N_2H_4 + 6Fe_2O_3 \longrightarrow 4Fe_3O_4 + 2H_2O + N_2$$

A very small residual of hydrazine - a fraction of a ppm - is al l that's needed.

In theory, sodium sulfite could also react with rust to form magnetite:

$$Na_2SO_4 + 3Fe_2O_3 \longrightarrow 2Fe_3O_4 + Na_2SO_4$$

In practice, experiments have shown that this reaction only takes place at 430°F and above (which corresponds to 330 psig in a boiler). By contrast, hydrazine begins reducing rust to magnetite at 250°F. And it promotes the formation of magnetite on non-rusted steel even below the boiling point of water, at temperatures as low as 120°F.

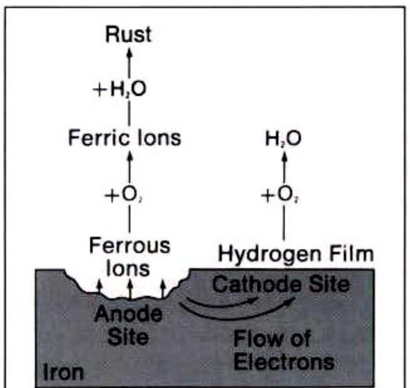
Feed water entry. Scav-Ox® hydrazine solutions can be used throughout the steam generating unit. This is important because even small amounts of dissolved oxygen can cause serious attack in feedwater lines; preheaters, economizers, boilers and condensate return systems.

Table 1 Compositions of Scav-Ox ® Solutions

	Scav-Ox®	Scav-Ox® II	Scav-Ox Plus®
Type	Hydrazine	Hydrazine	Hydrazine
Concentration of N_2H_4 (wt. %)	35.0	35.0	35.0
Type of Catalyst	None	Organic	Organometallic
Amount of Catalyst (wt. %)	0.0	0.2	0.8
Color	Colorless	Light Pink to Light Orange	Pink to Red

THE OXYGEN-IRON CORROSION REACTION

Corrosion is an electrochemical process, analogous to the operation of a battery. Any irregularity in a metal surface is a potential pit-forming anodic site. The metal acts as a conductor of electrons. The water is an electrolyte. But current will not flow if the cathodic site is polarized.



How Oxygen Corrosion Occurs

The reaction between the steel and the water liberates hydrogen, which forms a thin polarizing film on the cathode - unless oxygen is also present. When there is dissolved oxygen in the water, it combines with the hydrogen. The cathodic site is de-polarized, and current flows. When the corrosion current flows, ferrous ions go into solution. These ions may stay in solution as dissolved solids. Or, they ultimately combine with oxygen to form iron oxides, which can be deposited on the metal sur-face as rust. By eliminating dissolved oxygen, the oxygen scavengers permit the hydrogen film to be retained, polarizing the cathodic site and minimizing the corrosion current.

Scav-Ox® and Scav-Ox® II may both be used in systems with high-purity feedwater. (Scav-Ox Plus® is for feedwater with no special purity requirements.). High-purity feed water, however, cannot tolerate addition of sodium sulfite unless it is fed directly to the boiler. But if this practice is followed, feedwater system protection is lost.

No corrosive products or solids.

Hydrazine, a volatile liquid completely miscible with water, reacts with oxygen to form nitrogen and water:

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

No solids are formed, and nitrogen is harmless to the system. Thus neither hydrazine itself nor its reaction products contribute dissolved solids to the system.

In contrast, sodium sulfite reacts with oxygen to form sodium sulfate. In fact, the removal of 1 ppm of oxygen by reaction with sodium sulfite generates 8-9 ppm of sodium sulfate:

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

Sodium sulfate is a soluble salt and therefore increases the total dissolved solids (TDS) in the boiler water. So when sodium sulfite treatment is used, more blowdown is required in order to avoid exceeding permissible TDS specifications for the boiler. This not only consumes additional energy, it also wastes water treatment chemicals scale control agents and dispersants as well as sodium sulfite.

Although hydrazine can be used effectively at temperatures over 500°F, sodium sulfite cannot. Above 540°F (900 psig of saturated steam) the sulfite decomposes to sodium sulfide and sulfur dioxide. Both of these are corrosive, regardless of the presence or absence of oxygen i n a steam condensate system.

Hydrazine, on the other hand, is the only oxygen scavenger used in high temperature, high-pressure systems, such as utility boilers, where no dissolved solids can be tolerated.

At temperatures above 500°F, there is some decomposition of hydrazine into ammonia. However, ammonia helps reduce the corrosion of steel, and small amounts of ammonia in steam condensate will not attack copper in the absence of oxygen. (If oxygen is present, hydrazine at least equivalent to the oxygen will prevent the corrosion of copper in the presence of ammonia.)

Reduced iron and copper pickup.

Feed water often contains dissolved or finely dispersed iron and copper particles and their oxides. Hydrazine not only reduces rust to magnetite, but also reduces cupric oxide to its more passive form, cuprous oxide. Magnetite and cuprous oxide are dense particles, which are readily removed.

In addition, considerable experience has shown hydrazine to be superior to sodium sulfite in controlling iron and copper pickup. Once hydrazine has promoted formation of a magnetite coating, boilers and other water systems remain largely free of metal oxide sludge. Hydrazine-treated boilers contain minimal metal oxide deposits when boilers are taken down for inspection and cleaning.

Table 2 Performance Data of Scav-Ox® Products

	Scav-Ox®	Scav-Ox® II	Scav-Ox Plus®
Reactivity of dissolved O_2 at low temperature	Moderate	Fast	Fast
Percent reduction in feedwater			
corrosion vs. sulfite treatments:			
Carbon steel	6	32	55
Copper	40	60	50
Brass	0	64	68
Admiralty	35	69	51
Pitting test performances	Satisfactory	-	Superior
Dissolved solids (in ppb) resulting from dosage of 1 ppm N_2H_4	None	6	23

Compatibility with other treatment chemicals. Unlike other scavengers, Arch hydrazine's' reaction rates are not hindered by other chemicals such as phosphates, phosphonates, chelants or sludge conditioners, that are normally used in boiler-water treatment programs. This important property assures a more thorough protection of feedwater and boiler systems. It minimizes oxygen carryover to steam and condensate lines.

Control of pH. Water always includes small quantities of hydrogen and hydroxyl ions in equilibrium. With an excess of hydrogen ions present, an acidic condition exists. Iron is dissolved in the water; corrosion results.
The rate of acidic attack is a function of pH. Since hydrazine is a base, it helps to neutralize the acid condition.

WHICH HYDRAZINE TO USE

Whatever type of steam generating system you have, and whatever your operating conditions, there is an Arch hydrazine solution to meet your requirements
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Scav-Ox® suitable for high purity feedwater in systems with no special problems of oxygen corrosion. It contains no catalyst, so while it is free of insoluble solids, it is also slower to react with dissolved oxygen than the catalyzed products. Nevertheless, its reactivity is generally sufficient to protect feedwater systems with well-operated, high-efficiency deaerators and feedwater of about 200°F or more.

Scav-Ox® II is intended for treatment of high-purity feedwater if the system requires a reactive oxygen scavenger due to low feedwater temperature or other oxygen control problems. Scav-Ox II contains a small amount (0.2% by weight) of a partially volatile organic catalyst. Thus, at low temperatures Scav-Ox II reacts more readily with oxygen than Scav-Ox, while leaving an insignificant residue of solids. Only 1.1 to 2.2 parts per billion of catalyst are added to the treated water in a typical dosage of 0.2-0.4 ppm of Scav-Ox II.

Scav-Ox Plus® is a work-horse oxygen scavenger for industrial boilers with no unusual feedwater purity requirements. A portion of the 0.8% of the catalyst in Scav-Ox Plus is a nonvolatile organic complex of cobalt. The catalyst is responsible for the high reactivity of the product as an oxygen scavenger and certain data indicate that it interacts with the surface of carbon steel to inhibit pitting.
Following are facts of general importance regarding your choice of plain or catalyzed hydrazine.

Oxygen corrosion control.
Treatment of a system with a catalyzed hydrazine is recommended if measurements of oxygen residuals and preboiler system corrosion (e.g. economizer pitting) indicate poor control of oxygen corrosion in the plant.
The reasons for poor control may be poor deaerator efficiency, low feedwater temperature, small hold times (high flow rates) and cyclic loads. Whatever the reason, with low feedwater temperature, low pH and high operating rate of a system, the greater the oxygen residual after deaeration, the greater the need for Scav-Ox II or Scav-Ox Plus.

Feed water purity considerations. The use of catalyzed hydrazine solutions may be restricted by feedwater purity requirements. The greater these requirements, the fewer dissolved solids should be introduced with the oxygen scavenger. For instance, feedwater for supercritical units (pressure > 3200 psig) must not contain more than 0.25 ppm total dissolved solids. Only Scav-Ox or Scav-Ox II should be used in such a system.

Boiler pressures. High-pressure systems (900-3200 psig) may require Scav-Ox or Scav-Ox II depending on oxygen problems and feedwater purity required. The small amount of catalyst in Scav-Ox II makes this product suitable for most high-pressure systems. Industrial medium pressure boilers (250-900 psig) have a wide range of feedwater purity requirements, depending on operating pressure, and more importantly on the intended use of the feedwater. For instance, if the feedwater is used to desuperheat steam, it must essentially be free of dissolved solids. Such feedwater should be treated with Scav-Ox or Scav-Ox II. However, feedwater purity specifications in most medium pressure boilers are fully compatible with the amount of catalyst in Scav-Ox Plus at its typical dosages of 0.2 - 1.0 ppm.
Low-pressure boilers (250 psig and less) have the greatest tolerance for dissolved solids and often the greatest need for a highly reactive oxygen scavenger. Scav-Ox Plus is recommended for this type of boiler.
A summary of these recommendations is given in Table 3.

WHEN HYDRAZINE CAN BE USED

Hydrazine can be used successfully at any stage: before startup, when the boiler is in full operation, or when it is down for cleaning or lay-up. For example:

Passivation after cleaning. Before being commissioned, many new boilers are acid cleaned. Acid cleaning is also used in older boilers to remove scale. This cleaning removes the mill scale from new equipment and it removes the carefully built-up magnetite from older units. Without the magnetite, steel surfaces are highly vulnerable to corrosion. Passivation is therefore necessary before startup. This can be accomplished readily by circulating deionized water containing hydrazine. Ammonia can also be added if desired.
Hydrazine is also used as a corrosion inhibitor after cleaning with acidic or alkaline chemicals.

Shutdowns and wet layups. Hydrazine provides excellent corrosion protection during temporary wet layups. Deionized water with 200-400 ppm of hydrazine penetrates all crevices and loose scale-and can be left in the equipment.

Table 3 Recommended Applications for Scav-Ox® Solutions		
Type of System	**Recommended**	**Alternative**
Supercritical (> 3200 psig)	Scav-Ox	Scav-Ox II
High Pressure (900-3200 psig)		
"All volatile treatment"	Scav-Ox	None
Other treatment	Scav-Ox	Scav-Ox II
O_2 control problem	Scav-Ox II	None
Medium Pressure (250 - 900 psig)		
Feed water used in desuperheating	Scav-Ox II	Scav-Ox
Deionized feed water not used in de-superheating	Scav-Ox Plus	Scav-Ox, Scav-Ox II
Softened feed water	Scav-Ox Plus	Scav-Ox, Scav-Ox II
Low Pressure (<250 psig)	Scav-Ox Plus	Scav-Ox II

The use of hydrazine in wet layup leads to clean internal surfaces, purer water, and less blowdown. Note that hydrazine must be used for wet storage of non-drainable superheater tubes because residual solids (such as those associated with sodium sulfite) cannot be tolerated.

WHERE HYDRAZINE CAN BE USED

Hydrazine can be used to provide corrosion protection throughout the steam generating unit- in the preheater, boiler or condensate systems. It can also be utilized effectively in closed circulating hot water heating systems.

Feed water and preheat protection. To protect feedwater and preheat systems, hydrazine can be fed to the storage sections of deaerators or to feedwater storage tanks. Reduced corrosion in these sections will reduce the amount of iron carried in the feedwater. This, in turn, will prolong equipment life and minimize deposits on heat transfer surfaces.

Boiler drums and tubes. Oxygen corrosion in boiler drums and tubes is prevented by normally maintaining hydrazine residuals of 0.03-0.50 ppm in the boiler water. Under like circumstances, sodium sulfite residuals maintained are 10-60 ppm. The higher the pressure the lower the residual maintained, whether hydrazine or sulfite is used.

Steam and condensate systems. Three factors are critical in assuring trouble-free operation: pH, amount of dissolved oxygen, and carryover of dissolved solids. Hydrazine helps to control condensate system corrosion. Fractional amounts of hydrazine vapor may be carried into the steam, depending on residuals in the boiler water and the operating pressures. Boiler water treatment with hydrazine will therefore contribute to condensate system protection.* However, no sodium sulfite will be carried into the steam, except in cases of undesirable carryover of boiler water droplets caused by faulty steam separation.

'Food and Drug Administration regulations require that no hydrazine maybe carried into the steam if the steam may contact food or food products during processing.

Hot water heating. Hydrazine has been shown to be an effective corrosion inhibitor in closed hot water heating systems. Monthly dosages, to bring the hydrazine concentration up to 50 ppm, controlled the corrosion of mild steel and copper alloys in a 170°F laboratory system. (The system was operated for six months with a controlled water loss of 1 % daily to simulate actual operating conditions.)

THE ECONOMICS OF CORROSION PROTECTION

Which is more economical - hydrazine or sodium sulfite?

That is a question, which does not lend itself to a simple answer. On a pound-for-pound basis, sodium sulfite is the more economical. On an application basis, the true economy often lies with hydrazine.

For example, sodium sulfite passivates carbon steel, but less effectively than hydrazine does. To get acceptable protection in a boiler, a much higher residual of sodium sulfite must be maintained. Atypical boiler at 400-600 psig requires a hydrazine residual of only 0.1 ppm - but it requires a sodium sulfite residual of 35-40 ppm, up to 400 times as much.

Neither plain hydrazine nor its reaction products contribute any dissolved solids; catalyzed hydrazines contribute virtually none. But sodium sulfite generates 8-9 ppm of corrosive sodium sulfate for every ppm of oxygen it removes, thus adding substantially to the dissolved solids burden in the system. The greater the dissolved solids, the greater the demand for blowdown. The greater the blowdown, the greater the waste of water treatment chemicals (including the "inexpensive" sulfite) and the greater the consumption of energy.

However, the cost of a premature breakdown of equipment or an unscheduled shutdown in production far outweighs the cost of anti-corrosion chemicals. So, the real question is which will provide the best total corrosion protection. The evidence points clearly to hydrazine.

ARCH AND HYDRAZINE

Arch pioneered the commercial production of hydrazine over 25 years ago. During that time, we have gained considerable insight and experience in the myriad uses this one-time laboratory curiosity now has.

Hydrazine is a powerful reducing agent that reacts readily with oxidants. Pure hydrazine is a colorless liquid that is miscible with water in all proportions. Since hydrazine is a base, solutions of both plain and catalyzed hydrazine are alkaline. (For example, the pH of a 1 % solution of hydrazine is 10.7.)

For water treatment applications, all three types of hydrazine are usually purchased as a 35% solution and further diluted to required concentrations. Some water treatment companies sell special formulations of hydrazine with other necessary boiler water treatment chemicals.

There are no solids to mix when feed solutions are prepared. With simple precautions, hydrazine solutions can be handled in commercial quantities without fear of injury.

FURTHER INFORMATION

Arch offers **Material Safety Data Sheets** (MSDS) containing detailed information on storage and handling, personal protection, first aid, disposal, spill and leak procedures, and toxicological properties. To order an MSDS, call 1-800-511-MSDS.

Individual product bulletins are available for Scav-Ox®, Scav-Ox Plus* and Scav-Ox® II. These bulletins contain more detailed information on the use of these products for boiler water treatment. In addition, information on the safe use of hydrazine is described in the Arch brochure **"Storage and Handling of Aqueous Hydrazine Solutions".** We recommend that anyone handling hydrazine be familiar with its contents. Copies of these bulletins are available on request.

ARCH CHEMICALS, INC.

. Headquartered in Norwalk, CT, Arch is a global specialty chemicals company with approximately $1 billion in annual sales, 3,000 employees worldwide, and leadership positions in four key business segments: Microelectronic Materials, Treatment Products, Performance Products, and Other Specialty Products, which consists of the sulfuric acid business and hydrazine propellants and hydrazine hydrate solutions.

For additional information, please visit our website at : www.hydrazine.com.

Please refer to the Material Safety Data Sheet (MSDS) for complete information on Storage and Handling, Toxicological Properties, Personal Protection, First Aid, Spill and Leak Procedures, and Waste Disposal. To order an MSDS, call the Arch sales office listed below or the MSDS Control Group at (800) 511-MSDS. Before using or handling this product, the MSDS should be thoroughly reviewed.

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