I: Reaction of Oxygen With Hydrazine

Temp, deg C	Reaction time, minutes	Hydrazine %, reacted in presence of: 1 mg Mn as MnCl₂	0.1 mg Mn as Mn Cl₂	1 mg Fe as Fe SO₄	1 mg Fe & 0.1 mg Mn	Without addition
20	5	72.5	19.3	3.7	23.5	11.0
20	10	93.5	26.2	9.4	41.8	12.9
20	20	97.8	59.0	16.2	43.8	29.4
60	5	96.3	77.8	29.7	58.5	58.0
60	10	98.0	94.2	37.5	77.0	79.0
60	20	—	97	65.7	97.0	82.0

II: Corrosion Test—Iron-Content Increase (mg Fe)

Time, hr	Condensate without addition	Condensate & 0.6 g Na_2SO_3/l	Condensate & 10 g Na_2SO_3/l	Condensate & 0.6 g hydrazine hydrate	Mg of hydrazine present
0	0.02	0.02	0.02	0.04	364
1	0.06	0.02	0.02	—	—
2	1.2	1.7	0.02	0.04	344
4	9.1	6.4	0.12	—	—
8	24.5	14.0	6.9	0.02	325
24	70.0	47.0	42.0	0.08	282
48	—	—	—	0.18	168

timum pH conditions for the hydrazine-to-oxygen reaction in feedwater, namely 8.5 to 9.0. *Feed temperature at the injection points* was 180 to 190 F. Hydrazine injection took place from Monday to Friday only, so week-end operation of *the boilers brought the system back to* normal conditions, providing reference data for the rest of the week. Further, injection was made only during the *steaming hours of the boilers*, roughly some 16 hours a day.

Test *a*: 700-800% excess hydrazine.

Hydrazine was injected for one week to *give 0.5 to 0.6 ppm in the feed. This* corresponded to 800-1000% excess hydrazine based on the theoretical oxygen requirements.

Almost immediately hydrazine appeared at the feed pump and after a day or two in the surge tank and deaerator, showing it (1) is reasonably stable (2) can withstand the 185-F temperature, existing in the 30-ft length of feed main (3) can pass through the deaerator. No hydrazine could be found *in the steam condensate. This occurrence* of hydrazine, at all points except the steam sample, made analysis more difficult. It took several days to devise, *check and pronounce satisfactory* the modifications required in the analytical technique for the determination of oxygen and ammonia in the presence of hydrazine. It requires very great accuracy to test for oxygen of .01 to .02 ppm or less, and all traces of hydrazine must be removed.

The technique *finally* adopted, wherever hydrazine showed in the sample, was to (1) reduce rapidly the pH of the sample immediately after it had been *taken, thus fixing the hydrazine* (2) determine the ammonia in the usual way. Oxygen was determined by the electrometric method, after first removing the *hydrazine by oxidation with permanganate.*

The hydrazine in the injection solution was determined by direct titration *with potassium* iodate *in acid solution*, in the water after injection by the Pesos and Petit method employing paradimethyl-amino-benzaldehyde reagent.

Results indicated that oxygen was definitely scavenged by hydrazine and, what is more, that oxygen and hydrazine *do not coexist in solution.* When hydrazine appeared at the preinjection point, oxygen contents of condensed steam, feed-pump water and preinjection *water all ran about 0.005 ml per l*, considered the threshold value of the oxygen method of testing. Ammonia in the system did not rapidly increase, as was thought possible, but began to rise after two or three days' operation, becoming as high as 0.9 ppm in the surge tank by the fifth day. A sample of condensed steam, taken when the boiler ceased steaming on Friday, showed ammonia as high as 1.1 ppm. Conductivity of the condensed steam increased to 6-7 units as the ammonia increased.

Test *b*: 150-200% excess hydrazine.

When ammonia in the system dropped back to normal, oxygen tests, carried out before injecting hydrazine, showed a low oxygen level in the steam, despite a normal feedwater oxygen, indicating that oxidation was occurring within the *boiler or feed main, or somewhere after* the feed pump. Possibly it was oxidation of lower iron oxides produced during the hydrazine-injection period.

Concentration of hydrazine was reduced then for Test b's run to about 0.15 ppm in the feed as against Test a's 0.5 to 0.6 ppm. Quite different results developed. No hydrazine recirculation occurred through the surge deaerator system, nor was any significant rise in ammonia concentration detected, although, as has been pointed out, slight decomposition *into ammonia might* be masked by a generally high ammonia content normally present in the system *at that time. A still further difference* was that hydrazine and substantial oxygen concentrations were obtained together at the feed pump, probably *because the greatly reduced hydrazine* excess did not permit the chemical reaction to go to completion at this point.

Oxygen content of the steam was *again reduced to virtually zero*, showing the injection of only 150-200% excess material was apparently satisfactory.

Other Tests. Up to now, we've made *no reference to pH value. A study of* the pH figures shows that these cannot be correlated with ammonia content, also that carbon dioxide ingress must have been playing a variable and active role. This was strikingly borne out at the end of the second week's operation, *that is the end of Test b*, when pH measurements were made on the steam after the boiler was banked. Coincident with a rise in steam, conductivity and ammonia to 8.0 units and 0.44 ppm respectively, pH dropped to 6.8 several hours after the boiler came off load. Some unevaporated, undeaerated make-up water, containing carbon dioxide, was believed to have entered the boilers on shutting down.

Water samples went to the laboratory to confirm ammonia determinations, and to test for albumenoid ammonia. As expected, albumenoid ammonia was nil or very small.

Physical appearance of the boiler waters, after hydrazine injection, was significant. Normally, suspended matter from these boiler waters is large in quantity, *consisting mainly of easily filterable* red ferric oxide. During hydrazine treatment, the quantity of sludge appeared less, and the color, while still red, was less intense. Further, *it was very finely* divided and almost impossible to filter. The hydrazine may have some reducing effect in the boiler or, more probably, there was an absence of oxygen within the boiler, confirming the finding that oxygen removal could still take place within the boiler plant when hydrazine *injection ceased.*

Summary. This three weeks' trial of hydrazine as an oxygen scavenger led to these first indications: (1) Hydrazine is an excellent oxygen scavenger. (2) When equilibrium conditions are established, hydrazine and oxygen do not appear to exist together in solution. (3) *Hydrazine proves more stable than had* been supposed, and does not immediately decompose at temperatures of 185 to 190 F. (4) Main decomposition *product of the excess hydrazine used* is not ammonia under the operating conditions. Ammonia, however, forms under certain circumstances.

Possible hydrazine after effects, and how *they may* influence subsequent tests must be considered. For example, it is possible that hydrazine can behave in a boiler plant in three ways: (1) Primarily it will scavenge free oxygen, giving water and nitrogen as products. (2) Excess hydrazine will then reduce metallic oxides, giving the same products as (1). (3) In *absence* of oxygen or oxides, catalytic or thermal decomposition takes place with the formation of ammonia and nitrogen.

Action (1) is the desirable one, while (2) must occur, especially in old plant where much oxide scale exists. Action (1) may account for various joint leaks, *etc, that occurred in the feed* system of test cases (1) and (2), and also for the water phenomenon.

Action (3), definitely undesirable, *may occur if action (2) reaches* equilibrium, when further excess hydrazine decomposes into ammonia. Ammonia appearance in the trials during the heavy injection of hydrazine supports this view.

Hydrazine is valuable for feedwater treatment, and provided ammonia is not a decomposition product its use does not add impurities to the system. Economically, it compares very favorably with sulfite injection.

Treatment Costs. This statement can be amplified by an example from American practice. In an industrial power plant having nine boilers of 600-psig-design working pressure, where sodium sulfite is used as the deoxygenating agent, cost for sodium sulfite averages $1 per day per boiler.

Calculate equivalent costs for 85% hydrazine hydrate at its present price of $1.55 per lb (one to nine 240-lb drums f.o.b. Niagara Falls, New York) as follows:

	Ppm
Oxygen content of water	0.08
Equivalent hydrazine (N_2H_4)	0.08
Hydrazine residual desired	0.04
	0.12

Since 100,000 lb of water requires 0.012 lb N_2H_4, 0.012 × 24 equal 0.288 lb N_2H_4 per day. Now 85% hydrazine hydrate contains 54% N_2H_4, or 0.288 ÷ 0.540 = 0.533 lb hydrazine hydrate per day. Cost per boiler: *0.533 lb at* $1.55 per lb is $0.83 per day.

Data for this English report supplied by Whiffen & Sons, London, England.

GERMAN REPORT

Degassing Process. There is a definite demand for a chemical degassing agent not affected by the disadvantages of sulfite. In recent years the industrial production of hydrazine points the way to a solution. Hydrazine combines with oxygen dissolved in water in accordance with the equation: N_2H_4 plus O_2 equals N_2 plus 2 H_2O. Thus two perfectly harmless compounds, nitrogen and water, form 32 grams of hydrazine, being able theoretically to bind 32 grams of oxygen, while 252 grams of sulfite are required for 32 grams of oxygen.

Hydrazine, available on the market as a hydrate and added to feedwater in that form, is highly alkaline and, hence, can form salts with acids and also, of course, with any CO_2 that might still be present. Thus, if a certain excess is pres-

(*Continued on page 212*)

HYDRAZINE CHEMICAL AND HANDLING PROPERTIES

HYDRAZINE HYDRATE (85%)

Chemical formula:	$N_2H_4 \cdot H_2O$
Formula weight:	50.05
Grade:	*Technical*
Min active ingredient:	54% N_2H_4
Typical analysis:	N_2H_4 54.6% Cl^- 0.03%
Appearance and form:	Colorless, *mobile* liquid
Pounds per gallon:	8.39 at 25 C
Solubility:	Completely miscible in water and methanol
pH:	9.9 (1% solution at 25 C)
Viscosity:	1.45 centipoises at 25 C
Refractive index:	1.414 n_D^{20}
Surface tension:	75.1 dynes cm at 25 C
Melting point:	Minus 57 C
Boiling point:	119.8 C
Flash point:	193 F, open-cup method
Fire point:	204 F, open-cup method
Storage:	Store in a cool area; keep container tightly closed when not in immediate use. Avoid contact with oxidizing agents
Handling:	Although hydrazine hydrate (85%) is particularly recommended for industrial use because of its lower concentration of hydrazine, the handling precautions may well be considered the same as those applying to hydrazine hydrate (100%) and anhydrous hydrazine In the design of industrial scale equipment for handling anhydrous hydrazine, and the hydrazine hydrates (both 100% and 85%), stainless steel 304 or 347, fabricated by helium-arc welding, is usually suitable. Glass-lined steel is satisfactory, but unsupported glass is not recommended for large equipment because of the possibility of breakage
Availability:	Commercial quantities
Containers:	55 gal (440 lb, net) 30 gal (240 lb, net) Stainless-steel drums, returnable Warning label: White label (corrosive liquid) Also available in 5-pint bottles
Industrial Utility:	Hydrazine has long been recognized as a versatile chemical and its industrial utility has, in many cases, been established It is a powerful reducing agent for both inorganic and organic chemicals. Its ability to reduce metal salts or oxides to the free metal is being utilized, for example, to plate silver on glass, metals and plastics

HYDRAZINE HYDRATE (100%)

Chemical formula:	$N_2H_4 \cdot H_2O$
Formula weight:	50.05
Grade:	Technical
Min active ingredient:	64%, N_2H_4
Typical analysis:	N_2H_4 64.3% Cl^- 0.03%
Appearance and form:	Colorless, *mobile* liquid
Pounds per gallon:	8.61 at 25 C
Solubility:	Completely miscible in water and methanol
pH:	9.9 (1% solution at 25 C)
Viscosity:	1.5 centipoises at 25 C
Surface tension:	74.2 dynes cm at 25 C
Refractive index:	1.4284 n_D^{20}
Melting point:	-51.7 C
Boiling point:	120.1 C
Flash point:	143 F (72.8 C)—open-cup method
Fire point:	166 F (74.4 C)—open-cup method
Handling:	The properties of hydrazine hydrate (100%) are similar to those of anhydrous hydrazine, differing so slightly that the same handling methods and precautions are generally applicable
Availability:	Commercial quantities
Containers:	55 gal (440 lb, net) 30 gal (240 lb, net)
Industrial Utility:	For details covering the utility of hydrazine, refer to heading under *85% hydrazine hydrate*