

subject to local depletion of chromate, much lower concentrations may be employed.

ACKNOWLEDGMENT

The author is indebted to O. F. Tarr for many helpful suggestions in the planning and interpretation of results, and to R. L. Costa and E. A. Roche of the Research Department, Mutual Chemical Company of America, for assistance in the preparation and exposure of test panels. Depth of pitting was measured by R. L. Costa by optical methods. The author wishes to take this opportunity of thanking F. N. Speller and G. W. Seagren for their review of this report.

LITERATURE CITED

- (1) Aluminum Co. of Am., "Alcoa Aluminum and Its Alloys", 1942.
- (2) Am. Soc. of Refrig. Engrs., *Circ.* 10 (1930).
- (3) Atwill, A. H., *Refiner Natural Gasoline Mfr.*, 21, 130-2 (1942).
- (4) Brown, R. H., *A.S.T.M. Bull.* 126, 21-6 (1944).
- (5) Brown, R. H., and Mears, R. B., *Trans. Electrochem. Soc.*, 74, 495 (1938).
- (6) Burns, R. M., *A.S.T.M. Bull.* 126, 17-20 (1944).
- (7) Burns, R. M., and Schuh, A. E., "Protective Coatings for Metals", New York, Reinhold Pub. Corp., 1939.
- (8) Darrin, Marc, *Am. Soc. Refrig. Engrs. Corrosion Rept.*, pp. 21-7 (1944).
- (9) Darrin, Marc, *IND. ENG. CHEM., ANAL. ED.*, 13, 755-9 (1941).
- (10) Evans, U. R., "Metallic Corrosion, Passivity and Protection", London, Edward Arnold & Co., 1938.
- (11) Finney, W. R., and Young, H. W., *Natl. Petroleum News*, 19, 81-6 (1927).
- (12) Friend, W. Z., *Heating, Piping, Air Conditioning*, ASHVE J: Sec., 13, 788 (Dec., 1941).
- (13) Greenburg, L., and Bloomfield, J. J., U. S. Pub. Health Service, *Pub. Health Repts.*, 47, 654-75 (1932).
- (14) Hall, G. L., Md. State Dept. Health, *Bur. Sanitary Eng., Ann. Rept.* 1940, 180-2 (1941).
- (15) Holler, H. D., *Chem. & Met. Eng.*, 49, 171 (1942).
- (16) Kendall, V. V., and Speller, F. N., *IND. ENG. CHEM.*, 23, 735-42 (1931).
- (17) Mears, R. B., and Brown, R. H., *Ibid.*, 33, 1001-10 (1941).
- (18) Mears, R. B., and Eldredge, G. G., *Trans. Electrochem. Soc.*, 83, 403-17 (1943).
- (19) Mutual Chemical Co. of Am., "Chromium Chemicals, Their Uses and Technical Properties", 1941.
- (20) Remscheid, E. J., *Elec. Eng.*, 60, 173-8 (1941).
- (21) Skeen, G. R., and Ward, A. L., *Gas J.*, 219, 537-41 (1937).
- (22) Speller, F. N., "Corrosion: Causes and Prevention", New York, McGraw-Hill Book Co., 1935.
- (23) Sterne, C. M., *Proc. Am. Soc. Testing Materials*, II, 35, 261-71 (1935).
- (24) Tarr, O. F., Darrin, Marc, and Tubbs, L. G., *J. Am. Chem. Soc.*, 66, 929-30 (1944).
- (25) Ulmer, R. C., and Decker, J. M., *Combustion*, 10, 31-3 (1928).
- (26) Van Brunt, C., and Remscheid, E. J., *Gen. Elec. Rev.*, 39, 128-30 (1936).

[End of Symposium]

Sodium Nitrite as Corrosion Inhibitor for Water¹

A. WACHTER

Shell Development Company, Emeryville, Calif.

SODIUM nitrite is a good corrosion inhibitor for water and under many conditions can completely suppress the corrosion of steel. The concentrations of nitrite needed for pronounced inhibition vary with the severity of conditions and the pH and composition of the water. Sodium nitrite can completely prevent corrosive attack on steel in sodium chloride solutions and in aqueous alcohol solutions. It is also effective on steel which is covered with rust scale. Corrosion of many of the common ferrous and nonferrous metals is either inhibited or not adversely affected by the presence of nitrite.

SODIUM nitrite is a highly effective corrosion inhibitor capable of preventing corrosion of steel by water and oxygen under many conditions. Although the mechanism by which sodium nitrite functions as an inhibitor is not known with certainty, evidence (3) indicates that it acts as an oxidizing agent to produce a very thin tenacious film of ferric oxide on anodic areas, and does not remove oxygen in the manner of sodium sulfite. Many references to this substance are found in patents, but there are remarkably few discussions in scientific literature. An earlier paper (3) described characteristics of sodium nitrite as an inhibitor with particular regard to its application for preventing internal corrosion by water in pipe lines for gasoline and other petroleum products. This application (1, 2) has proved singularly effective, and at present such inhibition is being employed in over 32% of the total gasoline pipe line mileage in the United States. Sodium nitrite, incorporated into a mucilaginous-base

coating composition (4), also provides efficient protection against corrosion by moisture in steel drums containing gasoline. Since many other practical applications are probably possible, it is considered worth while to present data here which may be of general interest.

INHIBITION OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

Sodium chloride may be taken as a common corrosion-enhancing constituent in water. Experiments have been made to determine the corrosion inhibiting behavior with respect to steel of sodium nitrite in sodium chloride solutions. The method was described previously (3). Figure 1 shows typical results for low chloride concentrations. Concentrations of nitrite needed to completely suppress corrosion under these conditions are extremely low; 0.005% suffices for distilled water, 0.03% for a 0.05% sodium chloride solution, and 0.06% for a water sample from a gasoline pipe line.

Figure 2 indicates the minimum concentrations of sodium nitrite needed to prevent corrosion of steel by solutions containing up to 10% of sodium chloride. The corrosion rates for the sodium chloride solutions with no added nitrite under these conditions were about the same within the limits of experimental uncertainty, the average value being 6.7 mils per year with maximum deviations of ± 0.4 . No attempt was made to control the hydrogen ion concentration; however, pH measurements were made before and after each experiment. Initial pH values of the nitrite-chloride solutions were between 6.2 and 7.2, usually slightly below 7. Final pH values were as high as 9 to 11 in ex-

¹ Based on discussion by the author at the Symposium on Corrosion Inhibitors, presented in the preceding pages.

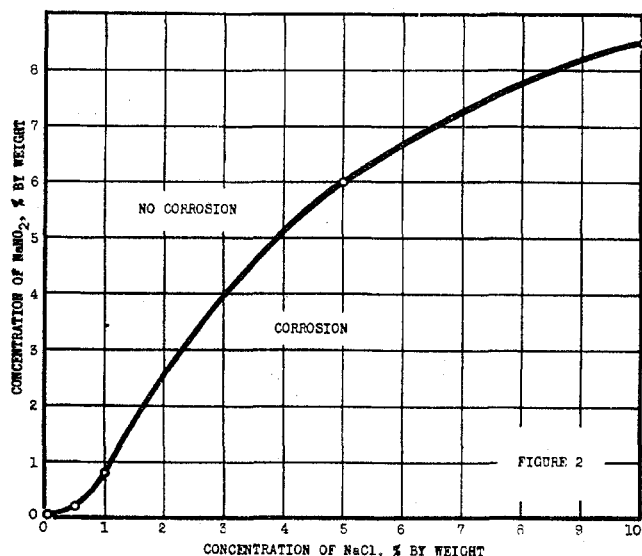
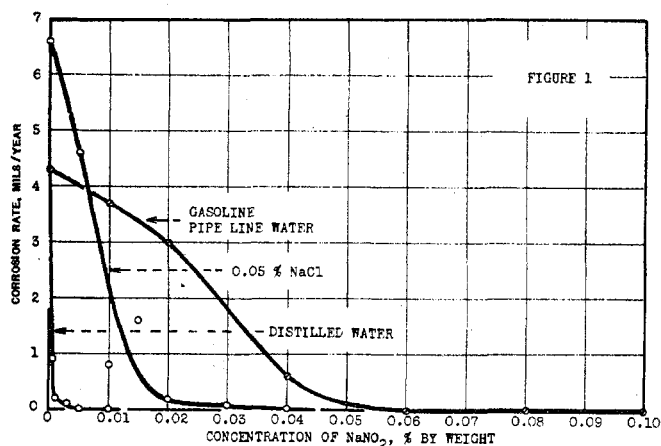


Figure 1. Influence of Sodium Nitrite Concentration on Corrosion of Steel by Some Waters

Figure 2. Minimum Concentrations of Sodium Nitrite for Preventing Corrosion of Steel by Sodium Chloride Solutions

Conditions for Figures 1 and 2: Sandblasted low-carbon steel strip, $\frac{3}{8}$ by $5\frac{1}{2}$ inches, in 120-ml. bottle containing 20 ml. aqueous solution of sodium nitrite and sodium chloride, 70 ml. gasoline, and 30 ml. air space. Bottle rotated end over end at 60 r.p.m. for 14 days at room temperature (approximately 25°C). Fresh air introduced into air space every second day.

periments with less than completely inhibiting concentrations of nitrite but were only slightly over 7 when no corrosion occurred. In these experiments it was judged that no corrosion occurred when the rate of attack was less than 0.1 mil per year; the specimen appeared bright and the liquid was clear.

Sodium nitrite requirements increased markedly as sodium chloride concentration increased. For example, although 0.005% and 0.2% sodium nitrite sufficed to prevent corrosion in distilled water and in 0.5% sodium chloride solution, respectively, at least 4% sodium nitrite was needed to prevent rusting under these conditions in 3% sodium chloride. It should be kept in mind that less severe corrosive conditions would require lower concentrations of sodium nitrite and correspondingly more severe conditions would require higher concentrations.

INFLUENCE OF pH

On several occasions it has been observed that sodium nitrite does not inhibit corrosion in acidic water. For example, a pH of at least 6 is required for 0.06% sodium nitrite to be effective for water in a particular gasoline pipe line (3). Figure 3 gives results

Table I. Efficacy of Inhibitors with Slightly Rusted Steel

Preconditioning period A: Sandblasted SAE 1015 steel rods ($\frac{1}{4}$ by 5 inches) were rusted equally by alternate dipping in 0.05% NaCl solution, immersion for about 20 hours in gasoline, and hanging in air for about 8 hours; the cycle was repeated several times over a period of 5 days.

Period B: Rusted rod prepared as in A, fastened in a 4-ounce bottle containing 20 ml. of inhibitor solution (pH 9.0 to 9.5) or water, 70 ml. of gasoline, and 30 ml. of air space. Bottle rotated end over end at 60 r.p.m. and room temperature. Fresh air introduced into air space every second day. Corrosion rates calculated from weight loss of cleaned specimens.

| Aqueous Soln. | Corrosion Rate ^a , Mils/Year | |
|--------------------------------|---|---------------------------|
| | 7-day expt. ^b | 14-day expt. ^c |
| Water | 8.8 \pm 0.5 | 9.1 \pm 0.3 |
| 1.2% Na_2CrO_4 | 4.2 \pm 0.2 ^d | 3.0 \pm 0.3 |
| 1.2% NaNO_2 | 0.7 \pm 0.6 | 0.9 \pm 0.3 |

^a Average values during period B and average deviation from mean.

^b Each solution tested in triplicate. From 3 rods average weight of rust formed during period A was 161 \pm 18 mg. and average weight loss of steel was 110 \pm 12 mg., corresponding to a corrosion rate of 15 mils/year.

^c Each solution tested in quadruplicate. Average weight loss of 4 rods in period A was 128 \pm 11 mg.

^d 1.0% Na_2CrO_4 solution used in this experiment.

Table II. Effects of Sodium Nitrite with Different Metals

Conditions: Metal strip, $\frac{3}{8}$ by $5\frac{1}{2}$ inches, fastened in a 120-ml. bottle containing 25 ml. of aqueous solution (in distilled water). Bottle rotated end over end at 60 r.p.m. for 14 days at room temperature (about 23°C). Air in bottle replenished every second day. Corrosion rates calculated from weight loss of cleaned specimens.

| Metal | Corrosion Rate, Mils/Year | |
|--------------------------------------|---------------------------|---|
| | 0.05% NaCl soln. | 0.05% NaCl + 0.2% NaNO_2 soln. |
| Low-carbon steel | 17.6 | 0.0 |
| Tin-plated steel | 5.0 ^a | 0.2 ^b |
| 13% chromium steel | 0.2 | 0.0 |
| 18-8 stainless steel | 0.0 ^c | 0.0 ^d |
| Aluminum (52-S) | 5.5 | 0.2 |
| Muntz metal (60 Cu, 40 Zn) | 0.3 | 0.3 |
| Admiralty brass (70 Cu, 29 Zn, 1 Sn) | 0.3 | 0.1 |
| Red brass (85 Cu, 15 Zn) | 0.5 | 0.3 |
| 70 copper-30 nickel | 0.1 | 0.1 |
| Monel | 0.0 | 0.0 |
| Nickel | 0.0 | 0.0 |

^a Attacked principally on steel at exposed edges.

^b Slight effects on plate.

^c Slight tarnish.

^d Bright, unaffected.

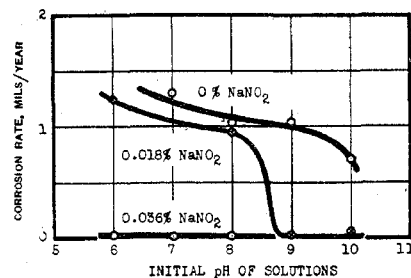


Figure 3. Influence of pH on Inhibition with Sodium Nitrite

Conditions: Polished low-carbon steel strip, $\frac{3}{8}$ by 3 inches, in 120-ml. bottle containing 50 ml. aqueous solution, 20 ml. gasoline, and 50 ml. air space. Each aqueous solution contained 0.02% by weight of a buffer mixture consisting of H_2PO_4^- , H_2BO_3 , CH_3COOH , NaOH . Bottles rotated end over end at 60 r.p.m. for 16 days at room temperature. Fresh air introduced into air space every second day.

from a series of experiments with nitrite-containing water at different pH values, obtained by a low concentration of a buffering mixture. The buffered water without nitrite is only mildly corrosive under the test conditions; a corrosion rate of 1.3 mils per year is found with water of pH 7. It is evident that pH has a marked influence on corrosion in the range 6 to 10 when insufficient nitrite is present, gives only slight inhibition at 6 to 8, and provides complete inhibition at 9 and 10. When ample sodium nitrite was present (0.036% for this water), pH changes had little or no effect in the range 6 to 10, all corrosion rates being

substantially zero. In general, maximum effectiveness of the sodium nitrite is achieved in definitely alkaline solutions.

EFFICACY WITH VARIOUS METALS

Inhibitors are often applied in equipment which has already rusted. Table I summarizes experiments to test the behavior of sodium nitrite on rusted steel; marked reduction of corrosion,

INHIBITION OF ALCOHOL SOLUTIONS

Although sodium nitrite is a fairly strong oxidizing agent, apparently it can be used safely in the presence of many organic compounds in water. For example, an aqueous solution of sodium nitrite is successfully used in gasoline pipe lines in contact with about two hundred thousand times its volume of gasoline. Many references to its use as a corrosion inhibitor in alcohol and

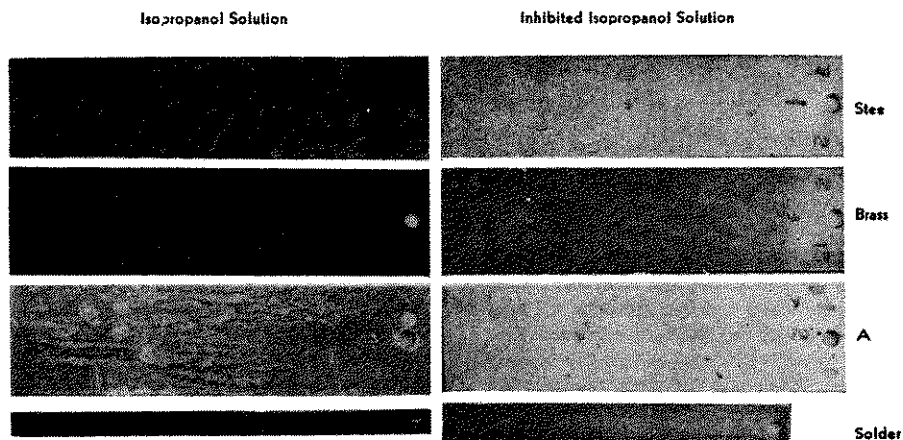


Figure 4. Corrosion Inhibition of Metals in Isopropanol Solution (Table V)

superior to that obtained with sodium chromate, was achieved. Nitrite is effective on rusted steel probably because it has little or no depolarization effect at cathodic areas.

Preliminary experiments with different metals indicate that sodium nitrite protects several from corrosion by water. Results with different solutions are summarized in Tables II, III, and IV, and with an isopropanol solution in Table V. Although nitrite had no marked effect with various brasses at room temperature, significant reduction of attack occurred at elevated temperatures. Results of the same nature were observed with Monel. Sodium nitrite also achieved marked reduction of attack on aluminum. Although measurements have not been made with zinc or galvanized iron, it is believed from observations in other experiments that zinc would not be protected by sodium nitrite and that attack might even be somewhat increased.

glycol antifreeze compositions are found in patent literature. Tables V and VI summarize results of experiments with sodium nitrite in aqueous solutions of isopropyl and methyl alcohols. Figure 4 shows the appearance of the metal specimens at the termination of the experiment in isopropanol solution. Sodium nitrite effectively inhibits corrosion of steel and also tends to protect other metals in these solutions.

LITERATURE CITED

- (1) Smith, S. S., *Oil Gas J.*, Sept. 24, 1942; Smith, S. S., and Schulze, R. K., *Ibid.*, p. 62, Nov. 25, 1943.
- (2) Wachter, A. (to Shell Development Co.), U. S. Patent 2,297,666 (Sept. 29, 1942).
- (3) Wachter, A., and Smith, S. S., *IND. ENG. CHEM.*, 35, 358 (1943).
- (4) Wachter, A., and Stillman, N., *Oil Gas J.*, March 25, 1943.

Table III. Effects of Sodium Nitrite with Different Metals

Conditions: Polished strips, $\frac{1}{4}$ by 3 inches, immersed in 1500 ml. of tap water solutions, stirred, exposed to air at 50° C. for 7 days. Corrosion rates calculated from weight loss of cleaned specimens.

| Metal | Corrosion Rate, Mils/Year | |
|---------------------|---------------------------|--------------------------------|
| | Water | Water + 0.1% NaNO ₂ |
| Admiralty brass | 1.5 | 0.8 |
| Red brass | 1.7 | 0.8 |
| 70 copper-30 nickel | 0.7 | 0.4 |
| Monel | 4.5 | 0.1 |

Table IV. Effects of Sodium Nitrite with Different Metals

Conditions: Polished strips, $\frac{1}{4}$ by 3 inches, immersed in 1500 ml. of salts in distilled water, stirred, exposed to air for 48 hours; pH of solutions adjusted to 8.1 with NaOH; 2 strips of each metal and 4 of steel in each solution. Corrosion rates calculated from weight loss of cleaned specimens.

| Metal | Temp., °C. | Corrosion Rate, Mils/Year | |
|------------------|------------|---------------------------|--|
| | | 0.1% NaCl soln. | 0.1% NaCl + 0.1% NaNO ₂ soln. |
| Low-carbon steel | Room | 11.2 ± 0.6 | 0.5 ± 0.1 |
| | 80 | 37.2 ± 1.1 | 8.7 ± 0.7 |
| Red brass | Room | 1.8 ± 0.1 | 2.0 ± 0.1 |
| | 80 | 12.3 ± 0.2 | 6.6 ± 0.5 |
| Monel | Room | 0.9 ± 0.1 | 0.2 ± 0.0 |
| | 80 | 10.0 ± 0.4 | 0.5 ± 0.1 |

Table V. Corrosion Inhibition of Isopropanol Solution

Conditions: Metal strips, each $\frac{1}{4}$ by 3 inches except solder, immersed in 750 ml. aqueous solution aerated by blowing air through an immersed porous thimble, at room temperature for 112 hours. Corrosion rates calculated from weight loss of cleaned specimens.

| Metal | Corrosion Rate, Mils/Year | |
|-----------------------|---------------------------------|--|
| | 30% by wt. isopropanol in water | 30% isopropanol in water + 0.03% NaNO ₂ + 0.015% oleic acid |
| Low-carbon steel | 32.0 | 0.03 |
| Aluminum (52S) | 0.4 | 0.04 |
| Brass (70 Cu, 30 Zn) | 0.5 | 0.00 |
| 50 lead-50 tin solder | 0.07 | 0.07 |

Table VI. Sodium Nitrite Inhibition of Methanol Solution

Conditions: Polished SAE 1015 steel rod, $\frac{1}{4}$ by 6 inches, fastened in a 120-ml. bottle containing 20 ml. of a 67% by weight aqueous solution of methanol, 70 ml. of gasoline, and 30 ml. of air space. Rotated end over end at 60 r.p.m. for 15 days at room temperature.

| Salts in Aqueous Methanol Soln. | Corrosion Rate, Mils/Year |
|--------------------------------------|---------------------------|
| 0.06% NaCl | 3.1 |
| 0.03% NaNO ₂ + 0.06% NaCl | 0.1 |
| 0.55% NaNO ₂ + 0.06% NaCl | 0.1 |