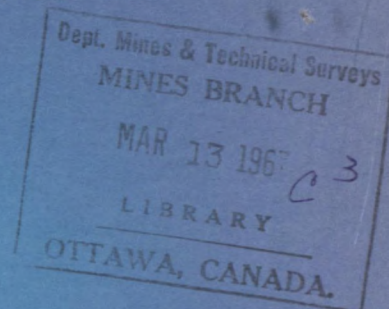




DEPARTMENT OF
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*ADDITIVES PREVENT LOW
CARBON STEEL CORROSION
IN SULFUROUS ACID*

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Reprinted from *Materials Protection*, Volume Five,
December 1966, Number Twelve, pp.28 and 29

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1967

Additives

PREVENT LOW CARBON STEEL CORROSION IN SULFUROUS ACID

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Mild steel in contact with an aqueous solution of sulfurous acid can be protected from corrosion by the use of an inhibitor consisting of ammonium oxalate and hexamine. The experimental results leading to this discovery are described in this article.

WHEN MILD STEEL is in contact with a sulfurous acid solution containing hexamine and ammonium oxalate, a dark solid film is produced on it. This film protects the steel from corrosion by the acid.

This discovery resulted from laboratory research which was a continuation of the authors' study on sulfurous acid corrosion of low carbon steel, which already has been reported.¹

Early in these present studies it was found that hexamine⁽¹⁾ alone gives fairly good protection under certain circumstances although no solid film is produced. However this protection decreases as time goes on, possibly due to a reaction taking place between the sulfurous acid and hexamine.

Later it was found that ammonium oxalate, (NH₄)₂C₂O₄, gives fairly good protection by producing a solid film on the steel. Unfortunately this film is soft, adheres poorly and has a somewhat erratic rate of formation.

Eventually it was learned that a combination of these two additives produces a solid film which is hard, adherent to the steel, fairly free from pores and gives good protection to the low carbon steel in the sulfurous acid.

Experimental Procedure

Low carbon steel specimens (5.0 x 1.5 x 0.1 cm) were blasted with a mixture of No. 100 fused alumina grain and water (450 g of alumina/litre of water) until clean. They then were scrubbed, rinsed in water, dipped rapidly in hydrochloric acid, rinsed again, dried and weighed. Finally each one was completely immersed in 200 cc of a solution produced by dissolving in distilled water the desired amount of sulfur dioxide (8 g/l), the desired amount of additive and sufficient sodium hydroxide to produce the desired pH.

The solutions in each series of experiments were adjusted to the same pH so that any difference in protection could be attributed to the additive alone. At the end of each series the specimens were scrubbed clean with a mild abrasive material, rinsed, dried and reweighed. The protective value (P)

of the additive under the conditions of each experiment in the series was calculated using the formula

$$P = \left(1 - \frac{\text{corrosion rate with additive}}{\text{corrosion rate without additive}}\right) \times 100 \text{ per cent}$$

The temperature was 21 ± 3 C in each experiment. In certain experiments the thicknesses of the protective films were determined by means of the Aminco-Brenner Magne-Gage.

Amine-Type Compounds Found Useful

It is known that certain acids become less corrosive to steel when they contain small proportions of arsenic. Early in this research low carbon steel was placed in sulfurous acid containing arsenic trioxide or antimony trioxide as an additive. Neither compound appeared to dissolve in the acid and no inhibiting effect was observed.

None of the organic chemicals investigated gave sufficient corrosion inhibition to be of interest as an additive to sulfurous acid until amine-type compounds were tried. Hexamine showed particular promise.

TABLE 1—Protective Value of Hexamine in Sulfurous Acid Solutions

HEXAMINE CONCENTRATION g/l	PROTECTIVE VALUE %		
	3 DAY TEST	6 DAY TEST	9 DAY TEST
0	0	0	0
1.2	50	40	-
2.5	86	-	58
3.7	97	90	78
5.0	98	94	92

As shown in Table 1, the protection obtained when 3.7 or 5.0 g/l of hexamine was added was excellent (97 and 98%) in a three-day test. However that obtained with the same concentrations of hexamine at the end of nine days, was considerably less (78 and 92%). Evidently this chemical cannot be relied upon to give good protection over an extended time. No visible film was produced on the steel surface during these experiments.

Experiments with Oxalates

Later, since ferrous oxalate is one of the most insoluble of the ferrous compounds, it was thought that a soluble oxalate might be useful as an additive to sulfurous acid. Accordingly the effect of adding corrosion-inhibiting oxalic acid, sodium oxalate or ammonium oxalate was investigated.

TABLE 2—Protective Values of Oxalates in Sulfurous Acid Solutions

ADDITIVE CONCENTRATION g/l	PROTECTIVE VALUE %					
	OXALIC ACID		SODIUM OXALATE		AMMONIUM OXALATE	
	5 DAY TEST	21 DAY TEST	6 DAY TEST	21 DAY TEST	5 DAY TEST	21 DAY TEST
0	0	0	0	0	0	0
1.2	10	30	22	39	25	82
2.5	75	85	55	75	42	93
3.7	80	88	88	91	72	95
5.0	84	91	93	95	88	96

The results of these experiments are shown in Table 2. It will be noted that the protection afforded by each of these oxalates was particularly good, the two salts being even more effective than the acid itself; also that the protection was still increasing after twenty-one days of test. When used at a concentration of 5.0 g/l ammonium oxalate gave a protection of 96% and sodium oxalate one of 95%, at the end of the twenty-one days.

When an oxalate was used as additive a dark-colored solid film was produced on the steel. A small amount of yellow material observed on these films, was found to be ferrous oxalate by X-ray diffraction.

(1) Tertiary Amine Hexamethylenetetramine (CH₂)₆N

TABLE 3—Film Thickness at Various Treatment Durations

DURATION OF TREATMENT DAYS	FILM THICKNESS cm x 10 ⁻⁴	
	OXALATE SOLUTION	OXALATE-HEXAMINE SOLUTION
0	0	0
2	20.5	5.6
6	25.1	10.4
8	35.0	11.2

When ammonium oxalate (5.0 g/l) was used as the additive, the variation of the film thickness with time was as shown in Table 3. The thickness increased rapidly during the first two days, and then more slowly during the next six days. The rate of formation was erratic, the film was soft and easily crumbled, and its adherence was not particularly good when scrubbed with a nylon brush. The outer part of the film appeared to be more porous than the inner part.

Since these three soluble oxalates proved to be particularly good additives it was decided to experiment with succinic and sebacic acids whose formulas bear some resemblance to that of oxalic acid. Contrary to expectation, these materials proved to be unattractive. The succinic acid gave negligible protection and the latter only 13% protection.

Hexamine and Ammonium Oxalate Combined

Since ammonium oxalate and hexamine were found to be useful additives when used separately, and since the mechanism of protection obviously was different in the two cases, it seemed possible that a combination of the two might be more effective than either one separately.

Various combinations of these two materials were investigated, each experiment lasting fourteen days. The results showed that such combinations can give an even higher degree of protection against sulfurous acid corrosion, than either compound alone.

TABLE 4—Protective Values of Ammonium Oxalate-Hexamine Combinations in Sulfurous, Sulfuric and Sulfurous-Sulfuric Acids (14 day test)

AMMONIUM OXALATE g/l	HEXAMINE g/l	PROTECTIVE VALUE %		
		SULPHUROUS ACID	SULPHUROUS and SULPHURIC ACIDS	SULPHURIC ACID
0	0	0	0	0
1.0	3.5	97.5	95	58
1.5	3.5	98	-	68
2.0	3.5	98	96.5	75
2.5	3.5	98	97	77

In all of the experiments with combinations of these two additives the solutions had a pH of 2 at the beginning and the partially spent solutions were replaced by fresh ones every three days.

As shown in Table 4, a combination of 1 g/l of ammonium oxalate and 3.5 g/l of hexamine had a protective value of 97.5% when present in sulfurous acid solution of the concentration used in all of the previous experiments (8 g of sulfur dioxide in one litre of the acid). A combination of 2 g/l of the oxalate and 3.5 g/l of hexamine had a protective value of 98% and appeared to be the most attractive of any investigated.

In Table 3 it is shown that the thickness of the film produced by the last-mentioned combination of additives was much less than that produced by the oxalate additive alone. However its rate of growth appeared to be less erratic. The thinness of the film may have been due to its becoming nonporous at a fairly early stage of the experiment.

Usefulness of Additives in Sulphuric Acid

According to Nelson² sulfuric acid is the most widely used reagent in the chemical industry, and it far outpaces its closest competitor. Accordingly it seemed worth while to determine the usefulness of a hexamine-ammonium oxalate

combination in inhibiting the corrosion of low carbon steel by this acid. Experiments of this type were performed, the SO₂ content of the acid being the same as in the case of the sulfurous acid solutions already referred to, i.e., 8 g/l.

As shown in Table 4, a protective value of 77% was obtained when the ammonium oxalate and hexamine contents were 2.5 and 3.5 g/l respectively. In other words, although perfect protection of the steel was not obtained, the corrosion rate was considerably less when these two additives were present in the acid.

Additional experiments performed with a combination of sulfurous and sulfuric acids, the SO₂ content of each acid being 4 g/l, showed that the protective value was 97% when the ammonium oxalate and hexamine contents were 2.5 and 3.5 g/l respectively (Table 4). In other words, comparatively large amounts of sulfuric acid can be present in the sulfurous acid without materially changing the protective value obtained with the latter alone.

Summary

An extensive study was made of the use of additives in combatting the corrosion of low carbon steel by aqueous solutions containing sulfurous acid at room temperature. The great majority of the additives studied had little or no practical value.

It was found that hexamine gives good temporary protection and that ammonium oxalate gives good protection of a more permanent nature. However a combination of the two materials is much superior to either one alone. The solid film produced by the combination is harder and much more adherent to the steel than that produced by ammonium oxalate alone.

Finally it was shown that large amounts of sulfuric acid can be present in the sulfurous acid without materially changing the protective value obtained with the latter alone; also that the presence of a combination of hexamine and ammonium oxalate in sulfuric acid alone will considerably reduce the corrosion rate of low carbon steel in that acid.

This discovery may have many applications in connection with the use of steel in sulfurous acid environments. It has been tested extensively on a laboratory scale and now awaits testing in the field.

Acknowledgment

The authors express their appreciation to Messrs. S. Kaiman and M. R. Hughson for identifying ferrous oxalate by X-ray diffraction analysis.

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