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Evaluation of Inhibitors in the Corrosion of AISI 304 Stainless Steel by FC-196 Aqueous Film-Forming Foam Concentrate

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Abstract: An accelerated corrosion test employing rubber band-gridled coupons, the "NRL Rubber Band Test," was used to determine corrosion characteristics of 304 stainless steel in FC-196, a 3-M Company mixture of fluorine-substituted organic compounds used to generate aqueous film-forming foam (AFFF) for fire control on Navy ships. Large variations in corrosive properties among production lots of FC-196 examined could not be explained on the basis of chloride content and pH alone. Of the chemicals and commercial inhibitors tested as preventives against pitting corrosion of 304 stainless steel in FC-196, sodium nitrate was the most effective and should be considered for further testing and possible shipboard use.

INTRODUCTION

Aqueous film-forming foam (AFFF) is a surface-active foam produced by aerating a mixture of water and fluorinated foaming additive. It is one of the most effective agents yet devised for extinguishing liquid fuel fires, and as such is used extensively on Navy aircraft carriers for controlling fires on the flight deck. A recent innovation has been the incorporation of a foaming system with nozzles recessed in the flight deck which may be activated, in the event of a plane crash or fire, to bathe the deck and adjacent regions in fire-suppressing foam.

A separate storage and distribution system of stainless steel is used to contain the foaming additive which is injected by proportioning pumps, at approximately 6% by volume, into the seawater stream at the nozzle head. This auxiliary system has proven troublesome in service because of leaking caused by corrosion. On the *USS America*, pitting corrosion caused the perforation of 1/4-in.-thick walls of CRES 304 stainless-steel tubing in less than 6 months. Subsequent examination revealed that the foaming additive concentrate, an aqueous mixture of fluorine-substituted organic compounds manufactured by the 3-M Company* and designated FC-195, had become contaminated with seawater. The resultant combination of high Cl^- concentration and low pH (FC-195 has a pH of 4.0 to 4.5) was shown through laboratory corrosion tests to be the cause of pitting.

The problem of protecting the foam concentrate system from corrosion was further complicated when FC-195 was superceded by a newer 3-M formulation, FC-196. The new concentrate has the same pH as FC-195 but contains 2000 to 4000 ppm Cl^- whereas FC-195 is essentially chloride-free. The Cl^- content of FC-196 is equivalent to contamination by 10 to 20% seawater, and the experience with FC-195 raised concern that corrosion problems might be encountered with the new additive even in shipboard systems maintained scrupulously free of seawater.

*3-M Company, Minneapolis, Minn.

NRL Problem C05-19; Project S-4643-12081. This is a final report on this phase of the problem; work continuing on other phases. Manuscript submitted October 13, 1971.

A remedy for this problem is being sought by several groups at NRL. One approach, the subject of this report, was to search for a corrosion inhibitor which would forestall Cl^--induced corrosion of 304 stainless steel in FC-196 (and therefore, presumably, in FC-195 also). Although few inhibitors are able to prevent the corrosion of stainless steels in low-pH, high-Cl^- environments, a mixture of compounds is often effective. The best results are often achieved with proprietary formulations developed by companies specializing in corrosion treatment or in the supply of corrosion inhibitors. Accordingly, 30 companies in the corrosion field were requested to recommend inhibitors from their standard products which they thought possibly capable of preventing pitting under the conditions described. Eleven companies responded positively and furnished inhibitor samples for testing. These and a number of chemicals suggested by our own experience were subjected to the laboratory tests described in the next section.

EXPERIMENTAL TECHNIQUE

Earlier work on this problem in the Metallurgy Division showed that ordinary coupon immersion tests do not give results correlating with in-service corrosion experience. However, if a rubber band is stretched around the coupon, more reliable results are achieved, presumably because conditions for pit initiation through crevice corrosion are established. With FC-195 contaminated with saltwater to the Cl^- levels found on the *USS America*, for example, pitting occurs at rhe rubber band/coupon interface in less than 3 days. A standardized test procedure was developed subsequently by Metallurgy Division members which has come to be known as the "NRL Rubber Band Test" (1).

The "NRL Rubber Band Test" uses ten specimen coupons, 1/16 by 1 by 3 in., sheared from AISI 304 stainless-steel sheet. These coupons are degreased in acetone, pickled in 10% HNO_3-H_2O solution for 5 minutes, rinsed with distilled water, and air dried. Each coupon is then girdled lengthwise with a clean, 1/4-in.-wide (size 62) rubber band and placed vertically in a 600-ml beaker (five coupons to a beaker). A 1/4-in. layer of glass beads in the bottom of the beaker stabilizes the coupons and keeps them separated. The beakers are subsequently filled with the test solution to 1/2-in. above the upper edge of the coupons and covered with watch glasses. Test specimens are stored at ambient temperature and examined over a 30-day period (evaporation losses made up as needed) with a 10X binocular microscope, care being taken to disturb the coupons as little as possible during the process. The development of a pit on *any* of the ten specimens within the 30-day interval is considered as failure of the test.

This test was adopted for our investigation essentially as described, except that in some instances, 5 rather than 10 specimens were subjected to the test conditions. At least 10 specimens were used, however, in testing the best inhibitors as well as the various lots of inhibitor-free FC-196 which were to be used as standards. Distilled water and reagent-grade chemicals were employed. The inhibitors were tested normally at 0.01, 0.1, and 1 wt-% concentrations and occasionally at other concentrations, if this was recommended by the supplier.

DISCUSSION OF EXPERIMENTAL RESULTS

Observations Pertaining to the "NRL Rubber Band Test"

Since rubber bands are known to vary considerably from lot to lot, there was concern that these variations, particularly in impurities extractable from the individual rubber bands, might affect the corrosion results. However, no statistically meaningful differences were found in tests which compared acetone-extracted and unextracted rubber bands, nor in those which compared rubber bands (same band size, different lots) varying by approximately 2X in strength. Therefore, these factors were considered not to be crucial in this investigation.

As work progressed with the FC-196 inhibitor mixtures, there were instances where the rubber band swelled and lost tautness. (This was not a problem with FC-196 alone.) Since slackening of the rubber band effectively eliminates the crevice and thereby crevice corrosion, it might well alter the outcome of long-term corrosion tests. However, the mixture which caused swelling and slackening had already failed the corrosion test before this effect was fully developed.

Finally, although it seems necessary to have a rubber band about the coupon for reproducible results, suggesting that crevice corrosion is involved, the first appearance of corrosion on numerous coupons was on the sheared edge at a site well removed from the rubber band. This form of corrosion is marked first by a deposite of white, voluminous corrosion product which increases in size with time, often taking on a rosette-like appearance. The color of the deposit usually darkens as time passes, and portions of it, especially on the outer edges, may become reddish-brown. This corrosion differs from corrosion at the point of contact between the rubber band and coupon, where the corrosion product is very dark or black from its inception. Moreover, while pits are apparent when the deposit at the rubber band/coupon interface is removed as it first appears, pits are found under the whitish sheared edge deposits only after considerable time. If the corrosion product is wiped off in the early stages, no visual sign of attack is evident, even at 30X magnification. However, pits do develop under these deposits, and the occurrence of this type of corrosion must be regarded as a possible initiation of pitting. Therefore, although the original "NRL Rubber Band Test" considered primarily corrosion at the rubber band/coupon contact, we have included corrosion at the isolated sheared edge as an indication of corrosion and failure of the test. This had, in general, only the effect of reducing the time to initial failure, since most specimens showed both types of corrosion, and inhibitors which were effective in delaying the one type of corrosion were also effective in delaying the other.

Difference in Corrosivity between Lots of FC-196

When different lots of FC-196 were subjected to the "NRL Rubber Band Test," they varied greatly in their corrosivity. Figure 1 shows that lot 29 went 30 days without failure whereas

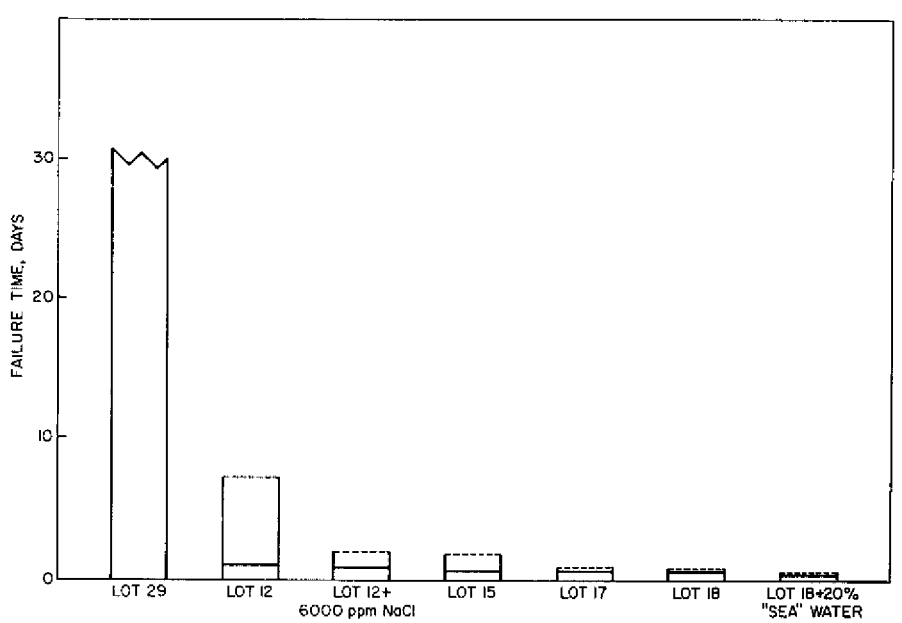


Figure 1 — Variation in the corrosivity of different lots of FC-196. Solid line gives time to failure for first coupon; dotted line, average time to failure for all coupons.

lots 17 and 18 failed in less than 1 day; the other lots failed between these two extremes. Lot 12 plus 6000 ppm NaCl and lot 18 plus 20% "seawater" (3.2% NaCl solution) are two "standard" solutions made up for later inhibitor tests. Analyses of the various lots (Table 1) indicated that although the differences in pH and Cl^- content were small, they were in the right direction (low Cl^- and high pH) to possibly explain the lower corrosiveness of lots 12 and 29. Further experiments proved that this was not the true explanation, however. Increasing the Cl^- content of lot 12 did increase its corrosivity (Fig. 2), but the time to failure at 4300 ppm Cl^- was still considerably greater than that of lot 17, for example, which has a slightly higher pH than lot 12 and only 3200 ppm Cl^-. With lot 29, the addition of HCl and NaCl to yield a pH of 3.5 and a Cl^- content of 5000 ppm was not sufficient to cause failure before 30 days. Lot 29 finally failed at 9000 ppm Cl^- and a 2.5 pH after 24 days. When only Cl^- was added, an addition of 16,000 ppm Cl^- was necessary to reduce the average failure time in lot 29 to 13 days. It seems evident from these results, therefore, that the various lots must contain components other than H_3O^+ and Cl^- which critically affect the corrosion rate.

TABLE 1
Characteristics of Different Lots of FC-196

Lot Number	Chloride Content, Cl^- (ppm)	pH	Average Failure Time (Days)
L12	1850	4.45	7.2
L15	3230	4.59	1.9
L17	3200	4.48	0.9
L18	3850	4.28	0.8
L29	2000	4.46	30+
Lot 12 + 6000 ppm NaCl	5490	4.50	2.0
Lot 18 + 20% "Seawater"	6380	4.30	0.6

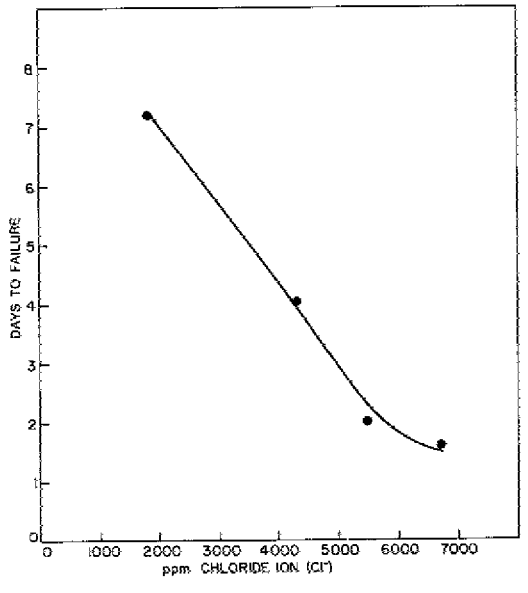


Figure 2 — Average corrosivity as function of Cl^- content in lot 12 FC-196

Evaluation of Corrosion Inhibitors

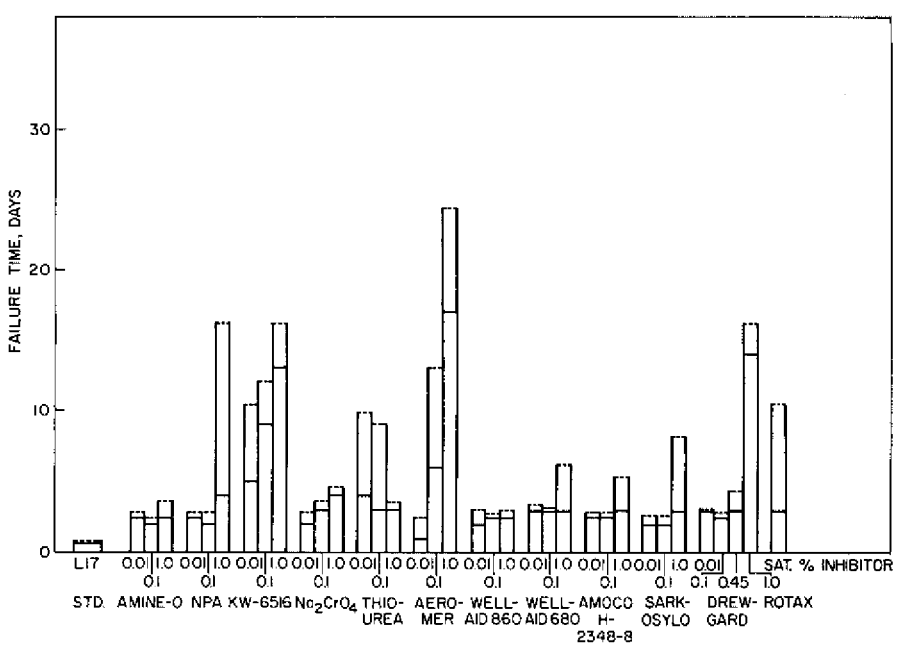
All the inhibitors could not be tested in only one lot of FC-196 because no single lot was available in sufficient quantity. The tests were made, therefore, using lot 17 (Fig. 3), a particularly corrosive lot of FC-196, and lot 12 (Fig. 4) with 6000 ppm NaCl added to make it approximately as corrosive as lot 17. Having to test with two different lots of FC-196 was not considered a disadvantage, since a good inhibitor would have to be effective in either lot. Only 5 coupons were used in these screening tests.

A number of difficulties were encountered. Many of the inhibitors were not totally soluble at the higher concentrations indicated in Figs. 3 and 4. In some cases, such as with Aeromer, some components may have been selectively soluble, since adding more inhibitor results in increased protection of the coupons even after the apparent solubility limit had been exceeded. A few inhibitors had physical properties, e.g., stickiness, which might reduce their effectiveness in some circumstances. Still others, such as sodium chromate, phosphomolybdic acid, and pyrogallol, reacted with FC-196 to form voluminous precipitates. At the concentrations used, some inhibitors, $Na_3PO_4 \cdot 12H_2O$ and Cobratec TT50S, for example, raised the pH of the solution to 7.0 or above, an undesirable effect since FC-196 is stable only in acidic solutions.

It can be seen in Figs. 3 and 4, however, that despite these problems, every inhibitor had a beneficial effect, although only the solutions of 2% and 3% $NaNO_3$, 1% $NaNO_2$, 2% Cobratec TT50S, and 0.5% and 1% $Na_3PO_4 \cdot 12H_2O$ passed the 30-day limit specified in the "NRL Rubber Band Test."

As an auxiliary experiment, the two "next best" inhibitors, Aeromer and KW-6516, were also tested in lot 15 FC-196. A comparison of results shows (Fig. 5) that while the relative efficiency of the two inhibitors remains unchanged, i.e., Aeromer gives the best protection in both lots, the inhibitors are not equally effective in the different lots. Lot 15-1% KW-6516 yields to appreciably quicker failure than Lot 17-1% KW-6516.

With these data in hand, more extensive 10-coupon tests were undertaken with the inhibitors passing the 30-day 5-coupon evaluations. Two other inhibitors were included, Wayhib SF,


FAILURE TIME, DAYS
30
20
10
0
L17
0.01
1.0
0.01
1.0
0.01
1.0

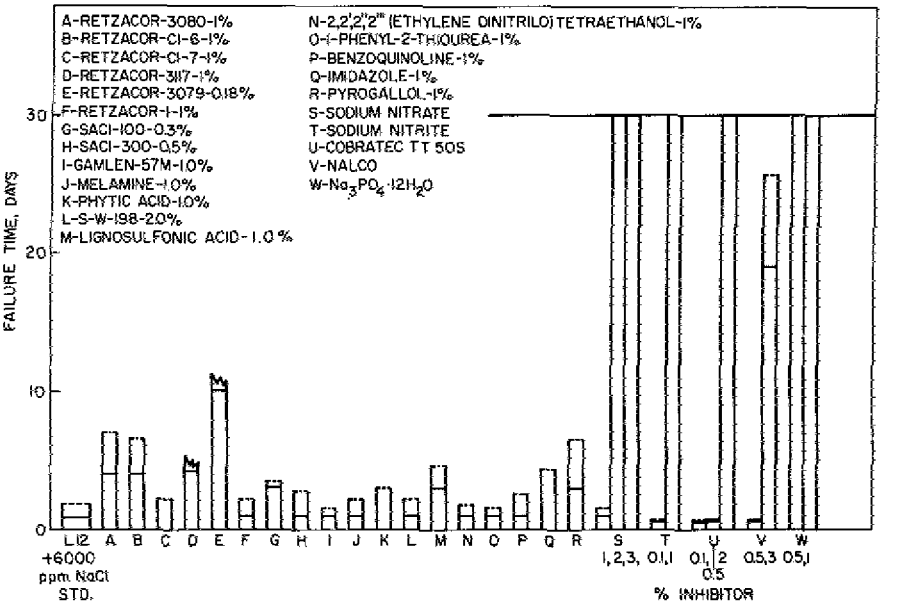


Figure 4 — Corrosivity of lot 12 FC-196 plus 6000 ppm NaCl containing various inhibitors. Solid line gives time to failure for first coupon; dotted line, average time to failure for all coupons.

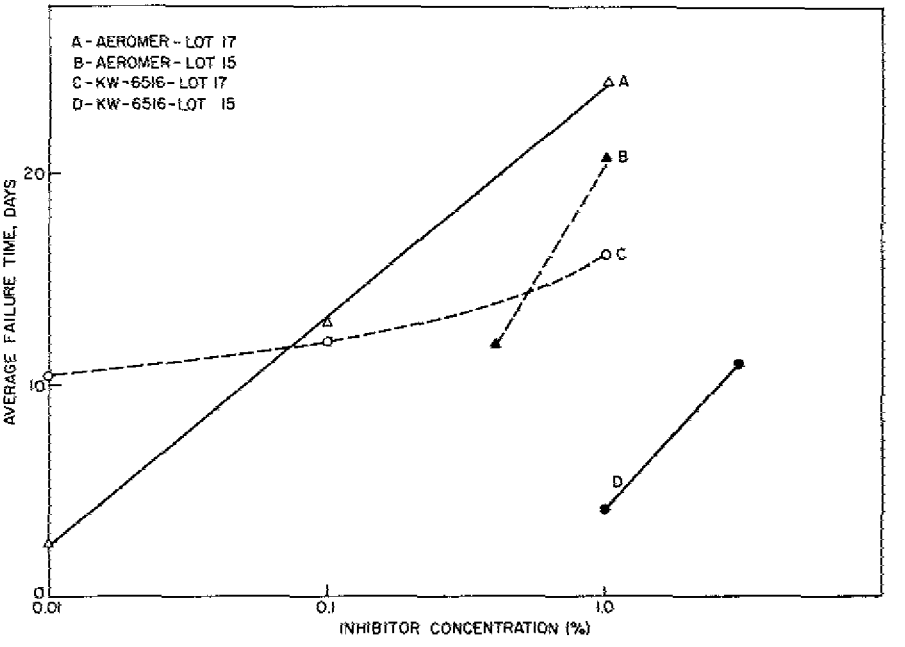


Figure 5 — Effect of inhibitor concentration on corrosion in two different lots of FC-196

not available for the initial tests, and nonylphenoxyacetic acid (NPA), which had shown promise (Fig. 3), although not passing. A mixture of dilute $NaNO_3$, $NaNO_2$, and Cobratec TT50S was tested also to study possible synergistic effects. To bring yet another lot of FC-196 into the program and to include as strongly a corrosive solution as is likely to be encountered in service, these final tests were run in lot 18 and lot 18 plus 20% "seawater," respectively, as well as again in lot 12 plus 6000 ppm NaCl.

The outcome of these tests is given in Table 2 which lists the pH at the start and end of each test with the percent of coupons that passed the 30-day limit without corroding. Two facts are noteworthy. Cobratec TT50S and $Na_3PO_4 \cdot 12H_2O$ were effective in lot 12 plus 6000 ppm NaCl, where they raised the pH to 7 and 8, but they were not effective in lot 18 and lot 18 plus 20% "seawater" where the pH remained lower. Second, only 3% $NaNO_3$ and 1.1% $NaNO_2$ succeeded in giving 100% protection in all three tests in Table 2 (in a subsequent test, however, 1.1% $NaNO_2$ failed also). Since 0.5% $NaNO_3$, 0.2% $NaNO_2$, and 0.5% Cobratec TT50S are largely ineffective, according to Fig. 4, when used alone, the fact that the mixture of the three shows some inhibitive power in Table 2 might indicate a certain amount of synergism. This is difficult to evaluate, however, from such a limited test.

CONCLUSIONS

Although there were complicating factors, all evidence from this investigation indicates that the "NRL Rubber Band Test" is a valid accelerated corrosion test for laboratory study of pitting of 304 stainless steel by FC-196 foaming additive.

The individual lots of FC-196 vary in corrosivity. The variation does not seem to derive from the slight differences in pH and Cl^- content that exist from lot to lot.

There are commercial inhibitors available, e.g., Aeromer, Drewgard, Nalco, RW-6516, and Wayhib SF, which delay the pitting of 304 stainless steel by FC-196. These inhibitors would not guarantee against pitting in shipboard systems containing FC-195 and FC-196, but their use could conceivably result in dollar savings by reducing the amount of corrosion which does occur.

Cobratec TT50S and $Na_3PO_4 \cdot 12H_2O$ are effective inhibitors but are not likely to be usable, because they seem to depend on raising the pH to 7 or higher, which is detrimental to the stability of FC-196. Sodium nitrite is also effective but sodium nitrite itself can cause pitting if its concentration falls below a critical value (2) and its use must be recommended with caution.

Sodium nitrate, at the 3% level, passed every test. This concurs with findings by earlier investigators that sodium nitrate acts as a pitting inhibitor for 18% Cr-8% Ni steel (304 stainless steel) when added in sufficient quantity to Cl^--containing solutions (3,4). Relatively large concentrations are required, but this is not a particular disadvantage here where the corrosive medium is itself a concentrate and used in small quantities.

Sodium nitrate is therefore recommended for further testing as a pitting inhibitor in FC-196.

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E. I. Dupont de Nemours and Company
Geigy Chemical Corporation
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Retzloff Chemical Company
Sherwin Williams Chemicals
Petrolite Corporation

TABLE 2
Inhibitor Evaluation

	Lot 12 + 6000 ppm NaCl			Lot 18			Lot 18 + 20% "Seawater"		
Concentration of Inhibitor	pH at Start	pH at 30 Days	% of Coupons Passed	pH at Start	pH at 30 Days	% of Coupons Passed	pH at Start	pH at 30 Days	% of Coupons Passed
2% $NaNO_3$	4.28	4.43	100	4.24	4.47	100	4.22	4.35	70
3% $NaNO_3$	4.27	4.37	100	4.31	4.41	100	4.33	4.35	100
0.5% $NaNO_2$	4.84	5.18	0	4.80	4.98	80	4.76	5.13	0
1.1% $NaNO_2$	4.65	5.56	100	4.85	5.15	100	4.79	5.31	100*
1% $Na_3PO_4 \cdot 12H_2O$	7.11	7.09	90	5.35	5.85	0	5.32	6.07	0
2% Cobratec TT50S	7.79	7.94	90	–	–	–	–	–	–
3% Cobratec TT50S	7.77	7.91	100	6.60	6.67	20	6.97	7.30	10
3% Wayhib SF	4.48	4.51	80	4.47	4.53	50	–	–	–
3% Nonylphenoxy-acetic acid (NAP)	3.05	3.35	0	3.18	3.40	0	–	–	–
2% Aeromer	4.32	4.48	80	4.37	4.58	10	–	–	–
0.5% $NaNO_3$ + 0.2% $NaNO_2$ + 0.5% Cobratec TT50S	5.40	5.73	40	4.96	5.18	100	4.94	5.09	10

*Subsequent test failed

Bryton Chemical Company
Amoco Chemicals Corporation
Drew Chemical Corporation
Philip and Hunt Chemical Corporation
Nalco Chemical Company

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