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The Effects of a Jet Fuel Anti-Icing Additive on Fuel Tank Linings

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Chemistry Division

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The Navy currently is studying the possibility of incorporating an anti-icing additive (AIA) consisting mainly of methyl cellosolve in its jet fuels. A question has arisen as to the effect this additive might have on organic linings now generally used in fuel storage tanks. Test panels coated with the various approved lining materials were immersed for 12 months in a water-fuel mixture containing this anti-icing additive in progressively increasing amounts, ranging from 0 to 100% in the aqueous phase. Results at the end of 12 months indicate that there is significantly less blister formation, both in size and density, of linings exposed to 20 to 40% concentrations of anti-icing additive than of linings exposed to higher and lower concentrations. The concentration limits which the additive would reach in water in normal service are in the 20 to 40% range.

INTRODUCTION

The Navy has constantly endeavored to improve the quality of fuel delivered to aircraft and to this end has actively promoted the idea of coating the interior of aviation fuel storage tanks. This measure not only extends the useful life of the tanks through control of corrosion but also preserves the high quality of the fuel. Tank coatings (linings) are of particular value in providing clean fuels, free of particulate contamination originating from deterioration of the storage vessel and/or transport equipment.

To guard against icing in fuel lines and injectors, an anti-icing additive (AIA), consisting principally of glycerin and ethylene glycol monomethyl ether (methyl cellosolve), is used by the U.S. Air Force in aviation fuels. Similar additives are presently contemplated for use by the Navy. Because methyl cellosolve is a very good solvent for many organic coating materials, a question has arisen as to its effect on tank linings conforming to current Navy specifications. The Bureau of Yards and Docks, which has primary responsibility for the construction of bulk fuel storage facilities, therefore, requested (1) the U.S. Naval Research Laboratory to study the effects of the contemplated additive on tank lining materials currently in use. This is a progress report of the results of this study at the end of 12 months. The AIA used in these tests was UCAR fuel additive 500.*

During an investigation of fuel storage facilities at Ramey Air Force Base, Puerto Rico, personnel of the Fuels Branch of the NRL Chemistry Division obtained samples of water from the bottoms of tanks filled with fuel containing the AIA (2). Analysis of the samples showed an average of 19.5% to 21% additive in the aqueous layer. Samples from other facilities showed similar results (2). Current specifications permit the inclusion of up to 0.15% additive in the fuel, the average apparently being slightly in excess of 0.1%.

It is virtually impossible to keep large underground storage tanks free of water. Fuel-borne water settles out as a result of temperature change when the fuel is transferred from carrier to storage tank. Condensate from air drawn into the tank as fuel is withdrawn continuously accumulates. It can be assumed that additive concentration in the water collecting on the bottom of the tank will be at a maximum. In light of this situation, data on the partition coefficient, solubility, and distribution ratio take on added significance when it is recalled that in most cases tank coating failures have occurred where the coating has been in more-or-less continuous contact with water.

From the partition coefficient of the AIA between JP-5 and water it can be calculated that at ambient temperature (approximately 20°C) a

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*A product of the Union Carbide Chemical Co.

concentration of about 20% AIA in water will be reached when the additive concentration in the fuel is 0.1%. This increases to about 30% at 0°C. Increasing the additive concentration in the fuel increases the above values proportionally. The distribution ratio of AIA between fuel and water is approximately 1/200 at ambient temperature.

EXPERIMENTAL METHOD

Test Method

The standard accelerated test used by NRL (3) for evaluating organic coatings for steel, fuel storage tanks consists of immersing the coated test panel in a vessel containing water, fuel, and vapor phases, approximately equal portions of the panel being exposed to each medium. The vessel is then placed in a 130°F constant-temperature bath for a period of up to 6 months. It has been observed and reported (4,5), however, that coating systems which successfully passed this test developed more extensive blisters at a faster rate when immersed in tap water only, at ambient temperature. It has also been noted that the water/fuel interface is an extremely active area, with initial film failure occurring there more often than not (3).

Taking the results of these various experiences into account, it was decided to immerse coated 3 in. × 6 in. steel Q-Panels* in a water-AIA, JP-5 fuel, and vapor system at 77°F. Blends of water and AIA were prepared at 0, 10, 20, 30, 40, 60, 80, and 100% additive levels of concentration. Although the theoretical maximum concentration of AIA in water (for a static system) is only 40% (based on 0.1% additive in the fuel) it was felt that higher concentrations might yield results which would be indicative of the severity of the test and help discriminate between the inertness of the various coatings.

Test Coatings

A variety of coating types are currently approved by the Navy for use in underground steel tanks (6). The list includes epoxies, phenolic modified epoxies, furan, vinylidene chloride-acrilonitrile copolymers, and polyurethanes (two-package systems). The proprietary coatings shown in Table 1 were selected for this intial study and were applied to steel test panels having a coarse-ground front surface and a sand-blasted back. Surface preparation and coating application were performed in accordance with the manufacturers' recommended procedures.

These coatings were immersed in all the previously described test media for a period of 12 months, except the NRL polyurethane system. Extensive data had been accumulated at this laboratory on plain water and water-fuel immersion of this coating system. Since only five panels coated with this system were available at the start of the test, it was decided to immerse these in media containing 20, 30, 40, 60, and 100% AIA in the water phase.

Test Results

In the most acceptable of the fuel tank linings, failures have manifested themselves in blister formation on those portions of the coating which

TABLE 1
Test Coatings

Coating	Type	No. of Coats
Devran 200 system	Epoxy	5 coats
Thermoline 200	Furan	5 coats
Laminar X500 Tank Lining	Polyurethane	3 coats
NRL (Ref. 3)	Polyurethane	3 coats
Mil-L-18389 (Formula 113/54)	Vinylidene Chloride-acrilonitrile copolymer	5 coats

*Steel test panels purchased from the Q-Panel Co., Cleveland, Ohio.

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are essentially in continuous contact with water. Blister propagation in such instances, regardless of the mode of initiation, has been accredited to an osmotic phenomenon. In general, the results from these tests show that as the concentration of AIA in water is increased from 0% to 40% blister size and density decrease. If the organic additive is considered a solute, then these would be the predicted results on the basis of osmotic theory. As the additive concentration is increased, the water becomes more saturated, and osmotic pressure is reduced. At still higher concentrations, water becomes the solute, and the solvent effects of the additive on the coating start to predominate. Thus, blistering, a water-caused phenomenon, gives way to film softening, and perhaps solution at very high concentrations (80 to 100%) of anti-icing compound.

Tables 2 through 6 show the effects of additive concentrations on each of the five coatings.

DISCUSSION AND SUMMARY

Bureau of Yards and Docks Type Specification TS-T10B Section .3.5.2.1 contains a list of proprietary coatings currently considered acceptable for lining underground, steel, fuel storage tanks. All coatings tested and herein reported are included in this list with the exception of the NRL urethane. The NRL urethane has been accepted (6) and applied satisfactorily as a tank lining, a notable example being the Red Hill tank farm in Hawaii. The primary concern of this study was to determine the effect(s) of the anti-icing additive (methyl cellosolve) used in jet fuels on organic linings used in fuel storage tanks. The more important known facts bearing on this problem, and therefore considered in this evaluation, are: (a) water, either condensate or fuel borne, will collect in the bottoms of storage tanks; (b) the additive under consideration is soluble in water, its JP-5/water distribution ratio being about 1/200 at ambient temperature; (c) most tank coating failures occur where the coating is subject to continuous contact with water.

The results of the test to date indicate that blister formation is retarded when coatings are in contact with water containing from 10 to 40% of the anti-icing additive by comparison with coatings in contact with water containing no AIA. On the basis of results obtained so far, it appears that the use of an anti-icing additive consisting primarily of methyl cellosolve may actually lead to a reduction in tank lining failures attributable to blistering. This encouraging indication warrants continued evaluation of coatings to assure its validity. Results of the tests that have been conducted indicate that at 20, 30, and 40% additive concentrations in water, no blistering has occurred during the first 10 days, with the exception of some Mil-L-18389 (Formula 113) coatings. After 6 weeks the same coatings showed little or no blistering.

The fact that very high concentrations of AIA rapidly destroyed several of these linings further justifies continuation of the test. It is noteworthy that the Devran and Laminar X500 coatings suffered only softening in a test system comprised of 100% AIA, fuel, and vapor. Conversely, all coatings immersed in a three-phase water, fuel, and vapor system containing no AIA showed extensive blistering at the end of 6 weeks. The Formula 113 coatings in three-phase systems containing 10 to 80% AIA displayed a high density of very small blisters which were best observed under magnification. Although slight to moderate softening was observed for some coatings exposed to high concentrations of the AIA, no softening was seen for those exposures in normally encountered concentrations.

Type 53 lining, a blend of Thiokol and Saran Latexes, is the predominant coating used in lining concrete, fuel storage tanks. This coating has only recently been put in test under the same conditions described for the steel tank linings. The Type 53 lining was severely blistered, swollen, and cracked by the 100% anti-icing additive in less than 8 hours. However, at the end of 3 months of immersion, little or no effect is noticeable at lesser concentrations.

Water immersion continues to be potentially degrading to coatings which otherwise are satisfactory tank linings. Therefore, whenever even a minor amount of water is suspected in a tank, it should be removed. This will be two or three times daily when a new shipment of fuel is added to a tank. This removal of water coupled with the apparent retardation of blistering by the AIA should provide many additional years of service from any of the systems tested. Most storage tanks are equipped with sumps and accompanying pumps for the periodic removal of bottom water.

TABLE 2
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure* in Thermoline 200 Coated Panels

Percent AIA in Water Phase	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months
0	10*	10	10	M-4	MD-4; a few corrosion spots, edge and face	MD-4, some edge corrosion
10	10	10	10	10	F-8	MD-8, V.F. corrosion spots; v. sl. softening
20	10	10	10	10	VF-6, F. corrosion spots on face	M-MD-6, F. corrosion spots
30	10	10	10	10	10, F. corrosion spots edges	M-MD-6, F. corrosion spots; v. sl. softening
40	10	10	10	10	MD-4, F. corrosion spots edges	M-MD-4 (low profile), F. corrosion spots; v. sl. softening
60	10	10	M-4-6	MD-4, sl. softening	MD-4, corrosion spots bottoms and edges; sl. softening	D-4, F. corrosion spots bottoms and edges; sl. softening
80	10	10	D-2 (low profile); MD-8 at interface	D-2; MD-8 at interface	0‡	–
100	0†	–	–	–	–	–

*Blistering is rated as per ASTM Method D-714-56 as to size and frequency. An arbitrary scale from 10-0 is used in which 10 represents no blistering. Frequency is described qualitatively as dense (D), medium dense (MD), medium (M), and few (F).
†Severely wrinkled in AIA phase in 13 min; in 40 min coating was dissolved in AIA phase and severely wrinkled in fuel and vapor phases.
‡Fuel phase, MD-8 and soft; vapor phase, MD-8 and soft.

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TABLE 3
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on Laminar X500 Tank Lining Coated Panels

Percent AIA in Water Phase	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months
0	10	10	M-MD-4	MD-4	D-4	D-2 medium low profile
10	10	10	M-6	MD-6	D-4; 1 corrosion spot at bottom edge	D-3
20	10	10	10	M-8	MD-D-6	MD-D-4
30	10	10	10	F-M-8	M-MD-6	MD-4
40	10	10	10	10	F-6 (edges)	F-M-8 F-4 (edges)
60	10	10	10	D-9	F-M-8	F-M-8
80	10	10	10; v. sl. softening	10	MD-8*	MD-8*
100	10	10; v. sl. lifting at edge, fuel AIA interface	10; soft	10; soft	10; soft	10;† soft

*F8 in fuel phase.
†Recovers hardness on overnight exposure to atmosphere.

TABLE 4
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on Devran 200 Coated Panels

Percent AIA in Water Phase	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months
0	10	10	10	MD-6	MD-4	D-3
10	10	10	10	F-M-8	M-MD-4	MD-4
20	10	10	10	MD-8	D-8, F-6	MD-4
30	10	10	10	F-M-8	MD-8	MD-8
40	10	10	10	F-8	F-8	F-8
60	10	10	10; v. sl. softening	F-M-9; sl. softening	F-M-9; sl. softening in all phases	F-M-8; sl. softening in all phases
80	10	10	VF-5; sl. softening	F-4-6; sl. softening	F-2-4; sl. softening in all phases	F-2-4; sl. softening in all phases
100	10	10	10; soft (cheesy)	10; soft	10;* soft	10;*† soft

*Softer than Laminar X500 tank lining coating.
†Recovers hardness on overnight exposure to atmosphere.

TABLE 5
The Effect of Additive Concentration in Water on the
Rate and Degree of Film Failure on NRL Urethane Lining Coated Panels

Percent AIA in Water Phase	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months
0*	10	10	VF-8	F-2-6	M-4 F-M-2	MD-2
20	10	10	10	VF-7	M-4 M-MD-8	M-MD-4
30	10	10	10	10	F-6	M-MD-4
40	10	10	10	VF-8	M-8	M-MD-6 F-4
60	10	10	10	10	MD-D-8	MD-D-8
100	10	†	‡	0	§	§

*Typical values from previous exposures.
†Approximately 15% failed up to 1/4" in from edge.
‡Approximately 85% of coatings failed in aqueous phase.
§Approximately 15% of coatings intact in center of panel in fuel phase. Balance peeled free.

TABLE 6
The Effects of Additive Concentration in Water on the
Rate and Degree of Film Failure in Formula 113 (MIL-L-18389) Coated Panels

Percent AIA in Water Phase	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months
0	10	10	M-4-6 VF-3	M-4-6 VF-3	M-MD-4-6 F-3	M-MD-4-6 F-3
10	10	10	M-8	M-8	MD-8	MD-8 F-5
20	10	10	F-9	M-MD-9	MD-9	D-9 (F-8 fuel phase)
30	10	10	10	D-9	D-9	D-9 (F-8 fuel phase)
40	10	10	10	MD-9	D-9	D-9 (D-9 lower 2/3 of fuel phase)
60	10	10	10	M-9	D-9	MD-D-8-9 (MD-8 and 9 fuel phase)
80	10	10	10	MD-8	MD-D-8 (F-M-9 Fuel phase)	MD-D-6 (M-8 lower 2/3 fuel phase)
100	MD-4*	0	–	–	–	–

*Blisters developed in 1-1/2 hours.

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Research is continuing on a second phase of this project, the development of a blister-resistant polyurethane tank lining. Work thus far has shown that the selection of solvents plays a particularly important role in the ultimate characteristics of urethane coatings. This appears to be much more significant in polyurethanes which cure by chemical reaction between the isocyanate and hydroxyl components than in the more conventional alkyd and oleoresinous-type coatings. It also has been determined that low-solubility, alkaline, inhibitive pigments incorporated into the primer greatly reduce blistering tendencies of two-package urethane coatings.

Currently, evaluations are in progress of several different types of hydroxyl-bearing coreactants for the isocyanate. In addition to polyesters which are used in the NRL polyurethane formulation, castor oils, modified castor oils, and a variety of epoxies are undergoing study. Those formulations which show promise in straight water immersion are being further evaluated in an accelerated test at elevated temperature (130°F), in contact with water-AIA mixtures. Results of this work will be forthcoming in a separate report.

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