

NRL Report 6445

AD644563

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

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October 7, 1966

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ABSTRACT

Ethylene glycol monomethyl ether (methyl cellosolve), a good solvent for organic polymers, has been evaluated by the Navy as a jet fuel anti-icing additive. The effect(s) which such an additive might have on organic coatings applied to the interior of large underground fuel storage tanks could influence any decision on its adoption. Steel and concrete panels coated with lining materials currently used by the Navy were exposed to aqueous solutions of the anti-icing additive in the presence of JP-5 for up to two years. Results indicate that 20 to 60% additive concentrations in the water phase inhibited blister size and/or density by comparison with water immersion alone. Although the presence of additive in the test media resulted in a slight softening of the Type 53 lining for concrete tanks, there is no significant difference in adhesion of this film to concrete when immersed in water alone or with additive concentrations up to 60%. No adverse effect of the additive on linings applied to steel or concrete is anticipated in the normally encountered concentrations of 20 to 40%. It is concluded that the presence of this anti-icing additive in concentrations normally to be encountered could extend the service life of the coatings.

PROBLEM STATUS

This is a final report on this phase of the project. Work is continuing on the general investigation and development of tank linings.

AUTHORIZATION

NRL Problem C03-06
Project Y-F015-01-001

Manuscript submitted June 6, 1966.

FINAL REPORT ON THE EFFECTS OF A JET FUEL ANTI-ICING ADDITIVE ON FUEL TANK LININGS

INTRODUCTION

This is the second and final report on laboratory tests performed to determine the effect(s) of a jet fuel anti-icing additive (AIA) (UCAR 500)* on organic fuel tank linings. The AIA consists of 99.6% ethylene glycol monomethyl ether (methyl cellosolve)* and 0.4% glycerine. Methyl cellosolve, a moderately high boiling material (124.6°C), is a good solvent for many organic polymers. Since an organic lining must remain intact on the tank walls in order to protect the tank and the quality of the contained fuel, it must not be rapidly dissolved or degraded by the fuel or any of its components. Therefore, this work was undertaken to assess the potentially deleterious effects of an additive consisting mainly of such a powerful solvent as methyl cellosolve on existing tank linings.

Only the composite additive, and not its individual components or composition variations, was evaluated. The additive was evaluated by immersing the linings in three-phase media: a water phase containing various concentrations of the AIA, a liquid phase of JP-5 and the equilibrium concentration of AIA, and the vapor phase above these liquids.

The initial report (1) contained results of the first 12 months' study, and this report covers 13 additional months. Proprietary linings of several organic polymer types approved in Navy Bureau of Yards and Docks Type Specification TS-T10c and currently in use by the Navy have been observed during 25 months of immersion. In addition the Type 53 lining for concrete tanks (NavDocks Spec. 47Yb) and some experimental urethane systems for steel tanks were exposed to the same test media during the last 13 months. The tank linings listed in TS-T10c are of two types: (a) one-package systems in which the coating is cured by solvent evaporation and (b) two-package systems in which the cure is effected by a chemical reaction, the catalyst being added to the pigmented base just prior to application.

SUMMARY OF PRIOR RESEARCH

As was reported in Ref. 1, steel Q-panels,† 3 in. x 6 in. with one ground face and one sandblasted face, were coated with Navy-approved proprietary tank linings according to the individual manufacturer's recommendations. Enough panels with each type of coating were prepared to allow a series of tests in different concentrations of the AIA. The coated panels were then immersed in the three-phase test media such that approximately equal areas were exposed to each phase. Since the distribution ratio of AIA between fuel and water is approximately 1/200 at ambient temperatures, most of the additive remains in the water phase. The composition of this phase was varied to include 0, 10, 20, 30, 40, 60, 80, and 100% of the AIA, and separate panels with identical coatings of each type were exposed to each concentration. Previous studies of linings (2) revealed that film failure in the form of blistering occurred faster in water at ambient temperature (77° F) than at the elevated temperature (130° F) of the standard test (3). In view of this observation, the current studies initially reported in Ref. 1 were carried out at 77° F.

*Product of the Union Carbide Corporation.

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

At 75° F an additive concentration in fuel of 0.1% will equilibrate with a 22% concentration in a water phase; at 15° F it will equilibrate with a 45% concentration in a water phase (4). Therefore, additive concentrations of 10 to 40% in water were of great practical interest, since these concentrations are equivalent to those encountered in normal service. During the first 12 months (the reporting period covered by Ref. 1) no adverse effects could be attributed to the presence of the additive at these concentrations. Higher concentrations were employed in an effort to accelerate any damaging effects upon the coatings. The anticipated increase in severity of the test generally did not develop until the water phase was completely replaced with AIA. At 100% AIA concentrations, linings composed of saran and furan dissolved and one polyurethane film was rendered unserviceable. Another polyurethane and an epoxy coating were severely softened but did not lose film integrity. In reduced concentrations of AIA in water the solvent effect was considerably less. In fact, coatings immersed in the aqueous concentrations of 10 to 40% AIA normally to be expected blistered less readily than identical coatings in water alone.

RESULTS OF CONTINUED IMMERSION

Tables 1 through 5 cover the complete test period of 25 months and show the effects of various additive concentrations in the water phase upon the rates and degrees of film failure of the five coatings designed for steel tanks. All of the coatings appearing in these five tables have performed satisfactorily in the field when used in tanks containing aviation gasoline (AvGas) or JP-5. The second year of continuous immersion of these materials has yielded results which substantiate the conclusions reported in Ref. 1.

As the concentration of AIA in the water phase is increased from 0 to 60%, a general reduction in blister size and/or density is observed. The specific AIA concentration at which a minimum blister size and density occur differs slightly from coating to coating. Although concentrations in excess of 40% AIA in the water phase should not be encountered in the field, immersion results obtained in the higher concentrations may be useful for the prediction of long-term solvent effects of the additive upon a lining. Thus, there was a slight softening of the films produced from two-package coatings when exposed to additive concentrations of 40-80%, but the effect was not sufficiently severe to adversely affect the role of the linings. The beneficial effect of retarded blister formation at these concentrations more than offsets concern about the softening effect.

The effects of high AIA concentrations upon one-package coatings were more pronounced. These systems, such as saran and furan, depend upon solvent evaporation to form the protective film, whereas two-package systems, such as epoxies and polyurethanes, undergo extensive chemical reactions as the films form. The furan coating (Table 1) was severely affected by the higher additive concentrations, and it failed completely in 80% AIA. The saran lining (Table 5) developed a high blister density in the higher additive concentration. It appears that the solvent effect of the methyl cellosolve is more pronounced on those coatings which cure by solvent evaporation than on those cured by chemical reaction.

The results of immersion-test evaluations of the Type 53 lining system for concrete fuel storage tanks are included in Table 6. This system, a blend of Thiokol (polysulfide) and saran latexes, has performed very satisfactorily in the field. No blistering of the coating was observed over the additive concentration range 0-60%. However, the undiluted methyl cellosolve severely attacked the lining and rendered it unserviceable after 4 days' immersion. A general trend of increasing softness of the Type 53 lining was observed during the course of the 12-month immersion period, and the degree of softness was more pronounced in the higher AIA concentrations. At the end of twelve months, the coatings immersed in 0, 20, 30, 40, and 60% AIA concentrations were tested destructively for hardness and adhesion. The results of the Shore "A" durometer hardness tests are recorded in Table 7. A softening effect due to the additive is revealed; however, in the

20-40% concentration range it is not so severe as to impair the function of the lining. Adhesion of the Osnaburg-reinforced lining to the concrete substrate was evaluated by measurement of the force (in pounds) required to separate a 1-inch width at a uniform rate. The test was performed immediately after removal of the samples from the immersion media. There was no significant difference in the adhesion of the lining whether it was exposed to 20-60% additive concentrations or to JP-5 and water without additive.

EFFECT OF 20% AIA IN WATER ON EXPERIMENTAL COATINGS

The observation that film failure of tank linings by blister formation appeared to be retarded by the presence of normally expected concentrations of AIA in the immersion media was made early in the program. In order to establish whether or not this observation was valid, panels coated with four experimental polyurethane formulations as well as the standard formulation were subjected to immersion in three separate test media. The primer coatings of the test formulations were produced from different hydroxyl-bearing coreactants and a common isocyanate. The intermediate and top coatings were those of the standard NRL urethane system (Table 4). The test media were: (a) water at 77° F, (b) water/AvGas*/vapor at 130° F, and (c) water (20% AIA)/JP-5/vapor at 77° F. All of the coating formulations had previously performed well in one or both of the first two media. The test results are given in Table 8, in which the coatings are designated according to the primer resins. With regard to these systems, the observation was confirmed, since blister development was retarded in water containing the AIA.

DISCUSSION

An anti-icing additive consisting mainly of methyl cellosolve is being considered for use in Navy JP-5. Although the concentration of the additive in the fuel is low (0.1-0.15%), its distribution ratio between fuel and water at ambient temperature is high (1/200). The water which collects in fuel tank bottoms has an average AIA concentration of 20-30%. The purpose of the immersion tests described in this report was to determine the effect(s), if any, the presence of the additive might have on the organic coatings currently in service on the interior of fuel storage tanks. All of the coatings evaluated have demonstrated excellent resistance to fuels. When failures have occurred, they have usually been blister formations on those portions of the coating which are in more or less continuous contact with water, which is always present in varying amounts in tank bottoms. In tests, coatings in contact with water containing from 10 to 60% AIA have fewer and/or smaller blisters than the same coatings in contact with water having no additive content.

Figures 1-3 illustrate the effect the presence of the AIA has on the extent of film degradation. The panels in Fig. 1 were coated with the standard NRL urethane tank lining system. Figure 1a shows the coating after 7 months' immersion in tap water at 77° F. Figures 1b, 1c, and 1d show the same coating after 20 months' immersion in mixed test media whose respective aqueous phases contained 20, 40, and 60% AIA. The arrow indicates the location of the water/fuel interface. It is readily apparent that the blisters are large in the absence of additive (Fig. 1a) but are small in the presence of the additive (Figs. 1b, 1c, and 1d). The panels in Figs. 2 and 3 have been coated with two different experimental urethane primers plus the standard NRL urethane intermediate and top-coats. The new primers were based on a linear polymer of the glycidyl ether of Bisphenol A (Fig. 2) and a polyester (Fig. 3) as the isocyanate coreactants. Figure 2b shows a reduction in blister density in comparison with Fig. 2a; Fig. 3 shows an increase in blister density in comparison with Fig. 3a but a more significant reduction in blister size.

*115/145 grade.

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Table 1
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on Thermoline 200 Coated Panels (One-Package Furan-Type Coating - see the final sentence of the Introduction)

AIA in Water (%)	Size and Frequency of Blistering* After Various Time Periods at 77° F						
	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months	25 Months
0	10	10	10	M, 4	MD, 4	MD, 4	MD, 4
10	10	10	10	10	F, 8	MD, 8 (very slight softening)	MD, 6
20	10	10	10	10	VF, 6	M-MD, 6	MD, 6
30	10	10	10	10	10	M-MD, 6 (very slight softening)	MD, 6-8
40	10	10	10	10	MD, 4	M-MD, 4 (low profile; very slight softening)	MD, 4
60	10	10	M, 4-6	MD, 4 (slight softening)	MD, 4	D, 4 (slight softening)	MD-D, 3
80	10	10	D, 2 (low profile) MD, 8 (at interface)	-	0 (MD, 8, softening in fuel and vapor phases)	-	-
100	0 (severely wrinkled in 13 min; dissolved in 40 min)	-	-	-	-	-	-

*Blistering is rated as per ASTM Method D-714-56 as to size and frequency. An arbitrary scale from 10 to 0 is used in which 10 represents no blistering. Frequency is described qualitatively as dense (D), medium dense (MD), medium (M), few (F), and very few (VF).

Table 2
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on Laminar X-500 Tank Lining (Two-Package Polyurethane Coating)

AIA in Water (%)	Size and Frequency of Blistering After Various Time Periods at 77° F						
	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months	25 Months
0	10	10	M-MD, 4	MD, 4	D, 4	D, 2	D, 2
10	10	10	M, 6	MD, 6	D, 4	D, 3	D, 3
20	10	10	10	M, 8	MD-D, 6	MD-D, 4	D, 4
30	10	10	10	FM, 8	M-MD, 6	MD, 4	MD, 4
40	10	10	10	10	F, 6	F-M, 8 F, 4	F, 6
60	10	10	10	D, 9	F-M, 8	F-M, 8	F, 8
80	10	10	10 (very slight softening)	10	MD, 8 (F, 8 in fuel phase)	MD, 8	M, 8
100	10	10	10 (softening)	10	10	10	10

Table 3
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on Devran 200 System Lining (Two-Package Epoxy System)

AIA in Water (%)	Size and Frequency of Blistering After Various Time Periods at 77° F						
	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months	25 Months
0	10	10	10	MD, 6	MD, 4	D, 3	D, 3
10	10	10	10	F-M, 8	M-MD, 4	MD, 4	MD, 4
20	10	10	10	MD, 8	D, 8 F, 6	MD, 4	MD, 4
30	10	10	10	F-M, 8	MD, 8	MD, 8	MD, 8
40	10	10	10	F, 8	F, 8	F, 8	F, 8
60	10	10	10 (very slight softening)	F-M, 9	F-M, 9 (Slight softening in all phases)	F-M, 8	F-M, 8
80	10	10	VF, 5 (slight softening)	F, 4-6	F, 2-4 (slight softening in all phases)	F, 2-4	F, 2
100	10	10	10 (softening)	10	10	10	F, 8

Table 4
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on NRL Urethane Lining (Two-Package Coating)

AIA in Water (%)	Size and Frequency of Blistering After Various Time Periods at 77° F						
	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months	25 Months
0*	10	10	VF, 8	F, 2-6	F-M, 2 M, 4	MD, 2	MD, 2
20	10	10	10	VF, 7	M, 4 M-MD, 8	M-MD, 4	M, 3 M, 8
30	10	10	10	10	F, 6	M-MD, 4	MD, 4
40	10	10	10	VF, 8	M, 8	M-MD, 6 F, 4	F, 4 M, 6
60	10	10	10	10	MD-D, 8	MD-D, 8	MD-D, 8
100	10	15% failed	85% failed	0	-	-	-

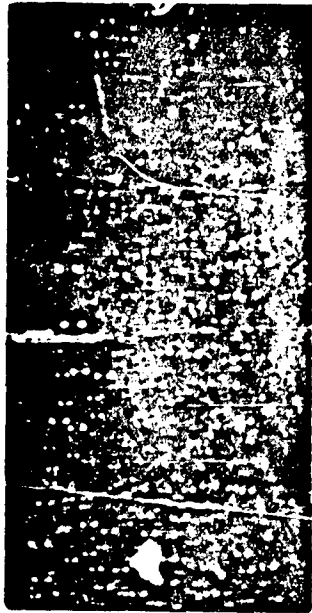
*Typical values from previous exposures.

Table 5
The Effect of Additive Concentration in Water on the Rate and Degree of Film Failure on Formula 113 (Mil L-18389) (One-Package Saran-Type Coating)

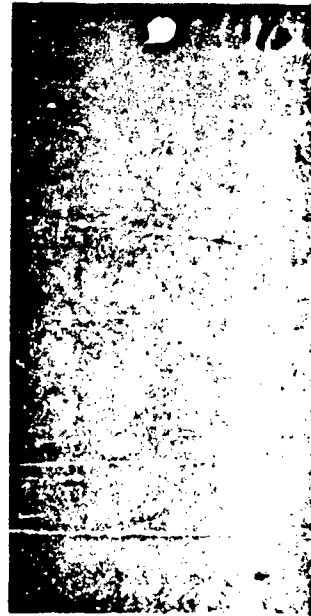
AIA in Water (%)	Size and Frequency of Blistering After Various Time Periods at 77° F						
	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months	25 Months
0	10	10	M, 4-6 V-F, 3	M, 4-6 V-F, 3	M-MD, 4-6 F, 3	M-MD, 4-6 F, 3	MD, 6 F, 3
10	10	10	M, 8	M, 8	MD, 8	MD, 8 F, 4	M-MD, 8 F, 4
20	10	10	F, 9	M-MD, 9	MD, 9	D, 9 (F, 8 in fuel phase)	MD, 8
30	10	10	10	D, 9	D, 9	D, 9 (F, 8 in fuel phase)	MD, 8
40	10	10	10	MD, 9	D, 9	D, 9 (in lower two-thirds of fuel phase)	D, 9
60	10	10	10	M, 9	D, 9	MD-D, 8-9 (MD, 8-9 in fuel phase)	MD-D, 8
80	10	10	10	MD, 8	MD-D, 8 (F-M, 9 in fuel phase)	MD-D, 6 (M, 8 in lower two-thirds of fuel phase)	MD-D, 6
100	MD, 4	0	-	-	-	-	-

Table 6
The Effect of Additive Concentration in Water on the Rate and Degree of Failure of Osnaburg Reinforced Type 53 Lining on Cement Blocks

AIA in Water (%)	Size and Frequency of Blistering After Various Time Periods at 77° F					
	8 Hours	24 Hours	10 Days	6 Weeks	6 Months	12 Months
0	10	10	10	10	10	10
20	10	10	10	10	10	10
30	10	10	10	10 (very slight softening)	10 (very slight softening)	10 (very slight softening)
40	10	10	10	10 (very slight softening)	10 (very slight softening)	10 (slight softening)
60	10	10 (very slight softening)	10	10 (slight softening)	10 (slight softening)	10 (slight softening)
100	10 (severe softening)	F, 4	0 (at 4 days)	-	-	-



(a) Immersed in water for 7 months



(b) Immersed in water (20% AIA)/JP-5/vapor for 20 months



(c) Immersed in water (40% AIA)/JP-5/vapor for 20 months



(d) Immersed in water (60% AIA)/JP-5/vapor for 20 months

Fig. 1 - NRL urethane linings after immersion at 77°F in water and various concentrations of anti-icing additive



(a) Immersed in water



(b) Immersed in water (20% AIA)/JP-5/vapor

Fig. 2 - Experimental urethane tank lining based on a linear polymer of glycidyl ether and Bisphenol A after immersion for 13 months at 77°F

Table 7

The Effect of Additive Concentration in the Water Phase on the Film Hardness of Type 53 Linings (Osnaburg Reinforced) Applied to Concrete

AIA Concentration (%)	Film Hardness in Different Test Media Measured With a Shore Durometer "A" Gauge			AIA Concentration (%)	Film Hardness in Different Test Media Measured With a Shore Durometer "A" Gauge		
	Water	JP-5	Vapor		Water	JP-5	Vapor
0	82	83	87	40	69	75	79
20	75	82	85	60	65	73	70
30	71	80	82	100	35	45	40

SUMMARY

Methyl cellosolve is a very effective solvent for many organic polymers. This solvent effect was in evidence when high concentrations (80-100%) of the additive were present in the test media. The effect was more pronounced on coatings which cured by solvent evaporation than on the chemically cured, two-package systems. However, the marked difference in the degree of failure between coatings exposed to concentrations of 0% additive and 100% additive indicates that a moderate dilution of the AIA with water retards the solvent effect. At normally encountered concentrations, the solvent effect is

Table 8
Rate and Degree of Film Failure of Experimental Urethane Tank Linings as a
Function of AIA Content and Testing Conditions and Primer Hydroxyl Component

Test Media	Size and Frequency of Blistering			
	2 Weeks	6 Weeks	6 Months	12 Months
Epoxidized Castor Oil				
Water at 77° F	VF-F, 6-8	VF-F, 8	VF, 8	VF, 8
Water/AvGas/vapor at 130° F	F, 4	F, 6	M, 2-4	-
Water (20% AIA)/ JP-5/vapor at 77° F	VF, 8	VF-F, 6-8	VF, 8	VF, 8
Linear Glycidol Ether-Bisphenol A				
Water at 77° F	VF, 8	VF, 8	VF, 6	VF-F, 6
Water/AvGas/vapor at 130° F	10	10	VF, 3-4	-
Water (20% AIA)/ JP-5/vapor at 77° F	10	10	VF, 6-8	VF, 4
Medium Functionality Polyester				
Water at 77° F	F, 6	F-M, 4 and 8	F-M, 2-4	M, 4; M-MD, 2
Water/AvGas/vapor at 130° F	VF, 6	F-M, 4 clusters	F-M, 4	-
Water (20% AIA)/ JP-5/vapor at 77° F	10	F-M, 6	F-M, 4	F, 4
High-Molecular-Weight Epoxy				
Water at 77° F	F, 6-8	F-M, 6	F-M, 6	F-M, 4-6
Water/AvGas/Vapor at 130° F	VF-F, 8	F-M, 6	F-M, 2-3	-
Water (20% AIA)/ JP-5/vapor at 77° F	10	F, 8	F, 6	F, 4-8
Standard NRL Urethane				
Water at 77° F	VF, 8	M-MD, 4	MD, 2-3	MD, 2
Water/AvGas/Vapor at 130° F	10	10	F-M, 8 at interface	-
Water (20% AIA)/ JP-5/vapor at 77° F	10	F-M, 8	M, 4; M-MD, 8	M-MD, 4



(a) Immersed in water



(b) Immersed in water
(20% AIA)/JP-5/vapor

Fig. 3 - Experimental urethane tank lining based on a medium functionality polyester after immersion for 13 months at 77°F

not expected to contribute to premature film failure. Furthermore, tank linings exposed to water often fail as the result of blistering, but the presence of methyl cellosolve in the water phase at normally encountered concentrations even reduces the blister size and/or density.

CONCLUSION

It is concluded, on the basis of the results from 25 months of immersion, and observation, that the addition of the methyl cellosolve anti-icing additive should have no adverse effect on the fuel tank lining systems currently specified in Navy Bureau of Yards and Docks Type Specifications TS-T10c (steel tanks) or 47Yb (Type 53 lining for concrete tanks). On the contrary, indications are that it could extend the service life of the coatings.

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Security Classification

DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1 ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a REPORT SECURITY CLASSIFICATION Unclassified
		2b GROUP
3 REPORT TITLE FINAL REPORT ON THE EFFECTS OF A JET FUEL ANTI-ICING ADDITIVE ON FUEL TANK LININGS		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) A final report on one phase of the problem		
5 AUTHOR(S) (Last name, first name, initial) Rohl, G.E.		
6 REPORT DATE October 7, 1966	7a TOTAL NO. OF PAGES 12	7b NO OF REFS 4
8a CONTRACT OR GRANT NO. NRL Problem C03-06	9a ORIGINATOR'S REPORT NUMBER(S) NRL Report 6445	
8b PROJECT NO. Y-F015-01-001	9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10 AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited		
11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Facilities Engineering Command), Washington, D.C. 20360	
13 ABSTRACT Ethylene glycol monomethyl ether (methyl cellosolve), a good solvent for organic polymers, has been evaluated by the Navy as a jet fuel anti-icing additive. The effect(s) which such an additive might have on organic coatings applied to the interior of large underground fuel storage tanks could influence any decision on its adoption. Steel and concrete panels coated with lining materials currently used by the Navy were exposed to aqueous solutions of the anti-icing additive in the presence of JP-5 for up to two years. Results indicate that 20 to 60% additive concentrations in the water phase inhibited blister size and/or density by comparison with water immersion alone. Although the presence of additive in the test media resulted in a slight softening of the Type 53 lining for concrete tanks, there is no significant difference in adhesion of this film to concrete when immersed in water alone or with additive concentrations up to 60%. No adverse effect of the additive on linings applied to steel or concrete is anticipated in the normally encountered concentrations of 20 to 40%. It is concluded that the presence of this anti-icing additive in concentrations normally to be encountered could extend the service life of the coatings.		

DD FORM 1473
1 JAN 64

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
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