

VOLATILE CORROSION INHIBITORS

PART III—AMMONIUM STEARATE AND M-DINITROBENZENE

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ABSTRACT

In earlier studies while screening various chemical compound for their vapour phase inhibiting properties. Some ammonium salts and nitro-compounds had shown promising results. Of these, ammonium stearate and m-dinitrobenzene gave the best results in accelerated short term test as well as in long term tests. In the present paper a more detailed investigation on the corrosion protection given by them has been made.

Ammonium stearate and m-dinitrobenzene, both, have been found to perform satisfactorily under all test conditions except in SO_2 test where m-dinitrobenzene failed. Their indigenous availability, low cost and good corrosion inhibiting properties demands favourable consideration for their adoption as VCIs for general use.

Introduction

It was pointed out in Part I¹ of this series¹ that the object of the present study has been the development of inhibitors which can be produced from indigenous resources. In Part I of this series, the results obtained with organic compounds having different structural groups was presented. It showed that vapour phase protection was mainly given by amines, nitrocompounds and ammonium salts. In view of the known disadvantages in the use of amines in the free state, the scope for use of the promising amines either as adsorbed in cation exchangers or as simple salts of stearic acid and benzoic acid was next investigated (see part II). The protection given by similar salts of nitrous acid² and carbonic acid³ which had been earlier patented was also studied in this context. This study showed that amines adsorbed cation exchangers compare favourably in their performance as vapour phase inhibitors with the nitrites and carbonates in both short term and long term tests. The stearates and benzoates were found to give excellent protection under milder test conditions but they were less effective in tests involving copious condensation of moisture on test specimen.

As mentioned above, some ammonium salts and nitro-compounds were also found to give vapour phase protection in the preliminary study. Of these, ammonium stearate and m-dinitrobenzene gave the best results in the continuous condensation test in air-tight container lasting 7 days as well as in the nine months flask test in which slow diffusion of the inhibitor outwards took place. Both of these chemicals are very easily produced from indigenous chemicals like stearic acid, ammonia, benzene, and nitric acid and the current paper deals

with a more detailed investigation of the protection given by these two chemicals to steel in the vapour phase. As far as the authors are aware, there is no reference in literature to the corrosion inhibiting property of ammonium stearate or of any other stearate. Nitrophenols and aliphatic nitrocompounds stabilised with alkaline materials have been patented ^{4,5}.

Experimental

(a) *Metals, their preparation and derusting after test*

Same as in Part II.

(b) *Test Methods*

In addition to the 4 test methods employed in the previous two parts, the two chemicals were also assessed by the following methods:—

(i) *Temperature Cycle test* ⁶

3" × ½" mild steel specimen is wrapped with kraft paper coated with 2 gm. per sq. ft. of inhibitor and suspended inside a test tube containing 1 ml. of distilled water and the test tube closed with a bark cork. The test tube is then subjected to 24 temperature cycles, each comprising 45 minutes at 45°C and 15 minutes at 0°C.

(ii) *Elevated Temperature Test* ⁶

3" × 1" mild steel specimen is suspended inside a litre bottle containing 25 ccs. of distilled water and 0.5 gms. of the inhibitor in a porcelain boat. The bottle is closed with bakelite screw cap and kept inside and incubator maintained at 45°C for 6 months.

(iii) *Baker's test* ⁷

3" × ½" mild steel specimen is suspended from a rubber stopper inside test tube containing 5 drops of distilled water at the bottom. The test tube is lined with kraft paper coated with inhibitor at the rate of 3 gms. per sq. ft., closed, and stored inside an oven maintained at 150°F for one week.

(iv) *Prevention of further corrosion test* ⁶

3" × 1" mild steel specimen, with 3 rust spots on one side produced artificially by distilled water, is wrapped with kraft paper containing 3 mgms. per sq. ft. of inhibitor and over-wrapped with plain kraft. The wrapped specimen is next suspended inside 500 ccs. bottle containing 20 ccs. of distilled water and closed with a rubber cork and left inside an oven at 45°C for 500 hours.

(v) *Humidity cabinet test*

2" × ½" mild steel specimen is suspended inside a glass tube (6" × ¾") lined with kraft paper coated with inhibitor at the rate of 3 gms. per sq. feet. Top end is completely closed with a bark cork and another bark cork with a ¼" hole is fixed at the lower end. The set up is suspended inside humidity cabinet maintained at 100 percent R.H. and 35°C for 7 to 21 days.

(vi) *Package test*

3" × 1" mild steel specimen is wrapped with 1 gm. per sq. ft. of inhibitor coated paper, over wrapped with bitumen kraft paper and

the package sealed with molten paraffin wax. The package is then suspended in tropic chamber for 6 months, at the end of which it is opened and steel specimen examined.

(vii) *Total Immersion test*

2" × ½" mild steel specimen is immersed in 15 cc of ammonium stearate solution in a 6" × ¾" dia test tube. The test tube is closed with a cork and kept at 40°C for 500 hours.

(c) *Chemicals*

B. D. H. ammonium stearate and m-dinitrobenzene were used in the tests. The ammonium stearate had a stearic acid content of 96 percent and 4 percent ammonia. The m-dinitrobenzene melted at 90°C with a sharp melting point.

Results and Discussion

(a) *Corrosion inhibition tests*

The results obtained with the two chemicals are given in Tables 1 to 3 and discussed below each table.

TABLE 1

Protection given in accelerated tests involving no loss of inhibitor by diffusion outwards

Method of test	Control (no inhibitor)		Ammonium stearate		m-dinitrobenzene	
	Visual	wt. loss (mgms)	Visual	wt. loss (mgms)	Visual	wt. loss (mgms)
1. Accelerated vapour phase corrosion test	covered with rust	60.0	a few rust spots on both sides	2.7	2 to 3 black rust spots on both sides.	11.3
2. SO ₂ Test	Do.	48.0	Do.	1.1	Considerable rusting on both sides.	35.0
3. Baker's Test	Heavy rusting at bottom and moderate rusting all over	13.0	a few rust spots near edges	0.7	Clean and bright	0.2
4. Temperature cycle test	Heavily rusted all over	22.0	Very slight rusting at top & bottom	4.0	Clean and bright except for fine black spots.	1.7
5. Elevated temperature test.	General rusting on both sides	2.1	Clean & bright except for slight rusting at edges	2.0	Clean & bright except one patch of rust near hole	2.3

It is seen from the above table that ammonium stearate gives more than very high protection in the first three tests. Continuous condensation of moisture on the metal is stimulated in the first test, the additional effect of sulphur dioxide pollution in the second and the combined effect of high temperature and high humidity in the third and fifth tests. The inhibitor performs satisfactorily in all these tests. Presumably, wet packing paper comes into contact with the metal surface in the temperature cycle test and the inhibitor is less effective under these conditions. m-dinitrobenzene hardly gives any protection in the

second test and is very much inferior to ammonium stearate in the first test. It is, however, quite effective at higher temperatures and under contact conditions.

Table 2 gives results obtained with the two inhibitors in long term tests at $84 \pm 5^\circ\text{F}$ and 95 ± 5 per cent R.H. allowing restricted diffusion of the inhibitor vapours into the external atmosphere.

TABLE 2

Long term tests allowing loss of inhibitor from container by diffusion outwards

Method of test	Control		Ammonium stearate		m-dinitrobenzene	
	Visual	Wt. Loss mgms	Visual	Wt. Loss mgms	Visual	Wt. Loss mgms
long term vapour phase test.	considerable rusting on both sides	5.6	very slight rusting at places	0.6	clean and bright except for 2 or 3 light rust patches.	3.1
long-term coated paper test.	dark brown rusting on both sides all over	6.2	rusting at top and bottom	1.8	clean and bright	0.6
package test	surface covered with dark brown rust	4.0	clean & bright except for 1 or 2 rust spots on both sides.	2.6	clean & bright except for one rust spot in one corner	1.2

It is seen from the above table that a very high degree of protection, comparable with the amine salts, is afforded by both the inhibitors under the conditions of these tests.

(b) It has been claimed in the case of dicyclohexylamine nitrite⁶ and cyclohexylammonium carbonate⁸ that further rusting of rusted steel is prevented if the inhibitor is present in the surrounding atmosphere. Table 3 shows that both ammonium stearate and m-dinitrobenzene are equally effective in this respect.

TABLE 3

Prevention of further corrosion of rusted steel by ammonium stearate and m-dinitrobenzene in "prevention of further corrosion test"

No.	Inhibitor	Visual observations
1	without inhibitor	dark brown rust patches all over and around rust spots.
2	ammonium stearate	no further rusting around rust spots and very little rusting elsewhere.
3	m-dinitrobenzene	no change in the specimen.
4	dicyclohexylamine nitrite	2-3 rust points present.

(c) *Optimum concentration of inhibitor on wrapping paper and in water for protection*—Experiments carried out in liquid phase with aqueous solutions of the inhibitor and in vapour phase with kraft paper coated with different concentrations of the inhibitor show that as much as 4 per cent concentration of ammonium stearate is required in aqueous medium for giving complete protection and that paper coated with 3 gms. per sq. ft. of inhibitor gives satisfactory protection in the vapour phase up to the maximum period for which the test was carried

out. (see Table 4). 6 gms. of amm. stearate per sq. ft. give complete protection in vapour phase (in 21 days exposure).

TABLE 4

Optimum concentration of ammonium stearate on wrapping paper and in water required for satisfactory inhibition of corrosion in vapour phase and in water

Method of test	Period of test	Concentration of inhibitor in solution or on paper	Observations			
			Blank (no inhibitor)		Ammonium stearate	
			Visual	Wt. loss mgms	Visual	Wt. loss mgms
1. Total immersion test	500 hrs.	0.1%	both sides rusted heavily.	22.5	considerable rusting on both sides.	16.0
		1.0%	several rust spots on both sides.	15.4
		2.0%	one rust spot near one edge, otherwise clean and bright.	0.3
		4.0%	both sides rusted all over.	Nil
2. Humidity cabinet test	4 days	0.3 gms/sq. ft.	both sides rusted.	2.5	both sides rusted all over.	3.2
		1.5 gms/sq. ft.	a few faint rust spots.	0.2
		3.0 gms/sq. ft.	very slight rusting near edge and hole.	0.5
	8 days	0.3 gms/sq. ft.	both sides rusted	7.0	both sides rusted	4.0
		1.5 gms/sq. ft.	light rusting on both sides.	2.1
		3.0 gms/sq. ft.	rust spots near hole and edge.	0.4
	14 days	0.3 gms/sq. ft.	both sides rusted	8.7	both sides rusted	3.5
		1.5 gms/sq. ft.	2.7
		3.0 gms/sq. ft.	clean and bright except for a few rust spots.	Nil
	21 days	0.3 gms/sq. ft.	both sides rusted	7.5	both sides rusted	4.0
		1.5 gms/sq. ft.	4.0
		3.0 gms/sq. ft.	a few rust spots	2.0
6.0 gms/sq. ft.		clean and bright	Nil.	
		15.0 gms/sq. ft.	Nil

Tests with *m*-dinitrobenzene in aqueous solution were not carried out on account of its insolubility.

(d) *Action of the two inhibitors on non-ferrous metals*—The action of the two inhibitors on several non-ferrous metals has been studied by the continuous condensation test as was done in Part II, as the conditions encountered in this test are most severe. The results are given in Table 5.

TABLE 5

Action of ammonium stearate and m-dinitrobenzene on common non-ferrous metals

Metal	Control		Ammonium stearate		<i>m</i> -dinitrobenzene	
	Visual	Wt. loss mgms.	Visual	Wt. loss mgms.	Visual	Wt. loss mgms.
1. Copper ..	blackened	5.0	blackened	10.3	blackened	4.0
2. Brass ..	a number of black specks on both sides.	0.8	completely blackened.	8.0	a few black spots, otherwise clean and bright	0.5
3. Aluminium	darkened on both sides.	2.5	greyish deposit on both sides.	3.0	brownish corrosion on both sides.	5.0
4. Zinc ..	buff-coloured deposit on both sides.	9.0	white buff coloured powdery deposit all over.	3.8	thin brownish deposit on both sides.	5.0
5. Solder ..	slightly tarnished.	7.1	slightly tarnished.	8.3	no change	3.4
6. Lead ..	Thick loose white deposit.	29.1	Thin deposit on both sides.	25.1	Thick brown deposit on both sides.	42.2

It is seen from the above table that ammonium stearate is detrimental to copper and brass but it does not accelerate the attack of zinc, aluminium, lead or solder in moist atmosphere. *m*-dinitrobenzene has no detrimental effect on any of the non-ferrous metal studied. It would, therefore, appear that *m*-dinitrobenzene can be used more freely with composite equipment consisting of both ferrous and non-ferrous parts while ammonium stearate has particular applicability to ferrous equipment exposed to conditions under which moisture condensation on the metal can frequently take place.

Physico-chemical properties

(a) *Ammonium stearate*^{9, 10}

Ammonium stearate is a white powder soapy to touch. It is highly dissociable in water and is soluble in absolute alcohol to the extent of 5.5 gms. per 100 ccs of solvent at 50°C and to the same extent in 75 per cent alcohol at 40°C. It is practically insoluble in hydrocarbons. Its melting point is 81–83°C. It is fairly stable at room temperature though it has a tendency to slowly dissociate into ammonia and ammonium acid stearate. Near about its melting point it decomposes to the acid stearate and ammonia. Its chemical nature would indicate that it is harmless to handle although no studies on its toxicity have yet been carried out.

(b) *m*-dinitrobenzene¹¹

m-dinitrobenzene is a yellow solid at room temperature. It is soluble in chloroform, toluene, and ethyl acetate and has a solubility of 0.047, 2.6 and 34.7 parts in water, alcohol and benzene respectively per 100 parts of solvent. It is stable at room temperature and higher temperatures, and melts at 90°C.

Comparative performance of different vapour phase inhibitors.

Data obtained on the vapour phase protection given by ammonium stearate and *m*-dinitrobenzene is compared with earlier data on cyclohexylamine complexes and salts and dicyclohexylamine nitrite in Table 6.

TABLE 6

Comparative performance of different types of vapour phase inhibitors investigated

	Accelerated vapour-phase test		Long Term vapour phase test		SO ₂ test		Coated paper test	
	Visual	Wt. loss	Visual	Wt. loss	Visual	Wt. loss	Visual	Wt. loss
1. <i>dicyclohexylamine nitrite</i>	slight rusting	0.3	clean and bright	1.1	slightly rusted	2.2	clean and bright	0.2
2. <i>cyclohexylamine carbonate</i>	a number of dark brown spots on both sides	3.3	rusting at top and bottom	15.5	a few rust points on both sides	1.0	rusted	42.5
3. <i>cyclohexylamine benzoate</i>	considerable rusting on half the surface.	55.3	clean and bright	0.2	completely rusted on both sides	15.4	clean and bright	1.0
4. <i>cyclohexylamine stearate</i>	completely rusted.	75.3	slight rusting on one side.	0.2	dark rust on both sides	6.2	one spot of rust near hole on one side, otherwise clean and bright	3.0
5. <i>cyclohexylamine bentonite</i>	slight rusting on both sides	2.7	slight rusting at top; otherwise clean & bright	1.2	very few rust points, otherwise, clean & bright	0.9	rusting on edge and top on both sides	14.2
6. <i>cyclohexylamine Carbion</i>	very slight rusting on both sides	0.6	slight rusting on both sides	2.1	considerable rusting on both sides	19.2
7. <i>ammonium stearate</i>	slight rusting.	2.7	slight rusting on each side	0.6	3-4 tiny rust points, otherwise clean and bright	1.1	very slight rusting at top and bottom	1.8
8. <i>m</i> -dinitrobenzene	black rust patches on both sides	11.3	2-3 small rust patches	3.1	considerable rusting on both sides	35.0	clean and bright	0.6

It is seen from the table that while dicyclohexylamine nitrite gives complete protection in all the other tests, both long-term and short-term, it is little less

effective in the test using sulphur dioxide which is, presumably, due to its instability in acid environment. Cyclohexylamine carbonate performs satisfactorily in air-tight containers but is ineffective in tests allowing slow diffusion of the inhibitor out of the container. The ineffectiveness is explained by the disappearance of the inhibitor from the container after the first few weeks which was not observed in any of the other solid chemicals except ammonium carbonate. The poor performance of ammonium carbonate in similar tests reported in Part I is also explained in the same manner, cyclohexylamine benzoate and stearate perform very satisfactorily in both tests at high humidities and at high temperatures but is less effective when copious condensation of moisture on the metal specimen takes place. The bentonite complex is effective under all conditions though precise information on its life as compared to the amine itself or the salts has not yet been collected. The Carbion complex is inferior in performance to the bentonite. Probably it is less easily liberated from the pores of the exchanger-cum-adsorbent. Ammonium stearate performs very satisfactorily under all conditions though it does not give complete protection as in the case of the nitrite or benzoate salts. Unlike the other chemicals, excluding m-dinitrobenzene, for the manufacture of which the alicyclic amines have to be imported at present, ammonium stearate can be easily prepared from chemicals which are available in this country as mentioned in the introduction. The performance of m-dinitrobenzene is similar to cyclohexylamine benzoate. It is also capable of indigenous production at cheap cost.

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