VOLATILE CORROSION INHIBITORS

PART II—AMINE SALTS AND AMINE ADSORBED CATION-EXCHANGERS

by

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ABSTRACT

Amine salts and amine adsorbed cation-exchangers have been examined to ascertain their vapour phase inhibition property for protection of metals against corrosion.

The investigation has shown that amine adsorbed cation-exchangers are efficient inhibitors. They can be conveniently handled unlike free amines, are less harmful to non-ferrous metals and possess a longer life. Amine nitrites and carbonates which are well known volatile corrosion inhibitors, have shown good results. Amine benzoates and stearates have been found to provide good inhibition under milder test conditions but failed in severe exposure conditions.

Introduction

In part I of this series[1], a number of amines were shown to exhibit excellent vapour phase inhibiting properties and it was shown that, among all types of organic compounds, the amines formed the most promising group. The use of amines in corrosion preventive packaging is, however, circumscribed by a number of other factors such as their very pronounced basic character, probability of non-ferrous metal parts being attacked by them, their high volatility and very pungent odour. Salts of amines have been shown to be free from the above mentioned defects to a greater or lesser extent and several of them have also been found to be efficient vapour phase inhibitors for ferrous equipment, e.g., amine nitrites[2], amine carbonates[3] and amine benzoates[4]. It is, however, not known whether the amines themselves could be used effectively and with less action on non-ferrous metals by absorbing them on some of the commonly known absorbents which also have base exchange properties e.g., bentonite. It is also not known whether complexes of the amines with the acid-forms of cation exchangers *e.g.*, sulfonated coal, cation-exchange resins would make the amines more effective over longer periods. The use of the amines in such forms may be considered under conditions where large stocks of mainly ferrous equipment stored in big godowns have to be protected and high volatility combined with efficient use of the inhibitor is required. A comparative study between the vapour phase protection given by amines in these forms and their known salts was, therefore, undertaken. In this study, stearates of the amines were also included in view of the promising results obtained with ammonium stearate in earlier part.

Results with dicyclohexylamine nitrite and cyclohexylamine carbonate are given for each test for comparison. These chemicals are known to be the base materials of VPI 260[9] and CHC[3] respectively.

Experimental

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

The following metals were used—(*i*) mild steel having the composition described in earlier part, (*ii*) copper free from arsenic, (*iii*) 60:40 brass, (*iv*) commercially pure zinc and (*v*) commercially pure aluminium.

Mild steel, copper, brass and zinc panels were abraded with No 1 emery cloth and No. 0 emery cloth till a bright, smooth finish was obtained. Aluminium was used as buffed or after removal of scratches with No. 1 glass paper.

The degreasing procedure was the same as followed in the earlier paper.

After tests, the corroded metal specimens were derusted as follows:—

Steel—Cathodically cleaned at 20 amps per sq dm in 5 per cent H_2SO_4 solution inhibited with 0·1 per cent purified glue at 74°C.

Copper and brass—Chemically cleaned by dipping in 7 per cent H_2SO_4 solution for 3 minutes at room temperature.

Aluminium—5 minutes treatment in a solution containing 35 gms of 85 per cent phosphoric acid and 20 gms of chromium trioxide per litre at 85°C. This is followed by a dip in Conc. HNO_3.

Zinc—1 minute immersion in 20 per cent chromic acid solution at 80°C.

Solder and lead—1 minute immersion in boiling 1 per cent acetic acid.

(*b*) *Test Methods.*

(*i*) *Accelerated vapour phase corrosion test*—as described in Part I.

(*ii*) *Sulphur dioxide test*

$1'' \times 1''$ mild steel specimen is suspended in a boiling tube ($8'' \times 1\frac{1}{2}''$ dia) from its rubber stopper. The boiling tube contains 50 cc of 0·007 per cent SO_2 water and 0·5 gm of inhibitor (1·0 gm in case of amine-carriers) added to it. Two-third of the tube is immersed in a copper water bath kept at 40 ± 2°C and the upper one-third is exposed to room temperature. The test is conducted in batches of nine boiling tubes for the duration of 24 hours. 15 control tests (without inhibitor) carried out gave an average loss in wt of 52 mgms and were found severely rusted.

(*iii*) *Long-term vapour phase test*—as described in Part I.

(*iv*) *Long-term coated paper test*

Glass tube 8″ long and 3/4″ dia and open at both ends is lined with 3 gms inhibitor per sq. ft. coated paper. $2'' \times \frac{1}{2}''$ mild steel specimen is suspended inside from cork closing top end and the bottom-end is closed with a cork having a $\frac{1}{4}''$ dia hole so as to allow free diffusion of external atmosphere into the tube from the bottom-end. The tube is then suspended inside tropic chamber maintained at 95-100 per cent R.H. and 84°F for 12 months. The control (wrapped in untreated kraft paper) was found rusted all over and gave 6 mg loss in weight after derusting.

(*c*) *Preparation of inhibitor*

(*i*) *amine nitrites*

Ethylenediamine, benzylamine, cyclohexylamine and morpholine nitrites were prepared by the method described by Temple and Wolfe[6].

Dicyclohexylamine nitrite was prepared by crystallising from a solution of 'V.P.I. 260' (Shell product containing mostly dicyclohexylamine nitrite[7]) in methanol.

(*ii*) *amine carbonates*

The method of preparation of amine carbonates was as described by Stroud and Vernon[8]. Only cyclohexylamine, benzylamine and morpholine carbonates could be prepared by this method.

(*iii*) *amine benzoates and stearates*

The acid is dissolved in hot ethanol, stoichiometric amount of amine added and the acid salt crystallised out. Ethylenediamine and morpholine benzoates were not prepared as they did not easily crystallise out.

(*iv*) *amine bentonite*

Bentonite from Rajasthan was suspended in slightly alkaline water for 24 hours to separate the coarser fractions from the suspension containing the fine fraction (2 micron). The suspension is taken out by suction and filtered through Buchner funnel. The residue on the Buchner funnel was dried at 105°C and kept in contact with excess amine for 24 hours and amine in excess filtered off under vacuum.

(*v*) *amine-sulfonated charcoal*

Cation exchanger 'Carbion' based on sulphonated charcoal is prepared from Indian coal by Fuel Research Institute Jealgora.

The 'amine Carbion' was prepared by leaching Carbion repeatedly with N/100 HCl, followed by washing with water and drying at 105°C. The dry material was kept in contact with excess amine for 24 hours and amine in excess filtered off under vacuum. Dicyclohexylamine Carbion was not prepared for want of amine.

(*vi*) *amine-resin*

Two resins, one based on carboxylic acid (Amberlite IRC-50) and the other based on sulphonic acid (Amberlite IRC-120) and marketed by Amberlite Co. U.S.A.were used. As both were present in acid form, no acid treatment was given and the amine-resin was prepared as in the case of carbion. Only amine-resins of ethylenediamine with the Amberlites were prepared for want of more samples of the two resins.

Results and Discussion

(*a*) *Ethylenediamine and benzylamine salts and complexes*

The degree of protection given to steel by several salts and complexes prepared from ethylenediamine and benzylamine in accelerated tests simulating highly humid industrial and non-industrial atmospheric conditions is given in Table 1.

TABLE 1

Protection given by ethylenediamine and benzylamine salts and complexes

Serial No.	Inhibitor-material	Observations	
		Test I loss in wt. mgms/ 1″×1″ specimen	Test II loss in wt. mgms/ 1″×1″ specimen
1	Ethylenediamine	0·7	3·4
2	Benzylamine	0·2	0·8
3	Ethylenediamine bentonite	2·2	4·7
4	Benzylamine bentonite	5·3	1·1
5	Ethylenediamine Carbion	1·6	6·2
6	Benzylamine Carbion	9·9	1·1
7	Ethylenediamine Amberlite IRC-50	1·8	9·1
8	Ethylenediamine Amberlite IRC-120	3·6	..
9	Ethylenediamine nitrite	1·6	..
10	Benzylamine nitrite	30·1	..
11	Ethylenediamine stearate	77·4	3·3
12	Benzylamine stearate	55·0	3·4
13	Benzylamine benzoate	75·1	13·6
14	Benzylamine carbonate	1·5	..

It is seen from the above that the complexes of the amines with bentonite, Carbion and Amberlites are nearly as effective as the amines though complete protection is not given by them under the conditions of test. Benzoate and stearate salts of benzylamine give hardly any protection under the conditions of the accelerated test, but the same chemicals give more protection under the conditions of the sulphur dioxide test. This is possibly the result of chemical reaction between sulphur dioxide and the amine salt leading to the depletion of sulphur dioxide in the system. Benzylamine carbonate, which easily dissociates into the amine and carbon dioxide, is as effective as the complexes. Ethylenediamine nitrite is more effective than benzylamine nitrite.

(*b*) *Cyclohexylamine and dicyclohexylamine salts and complexes*

Results obtained with salts and complexes prepared from cyclohexylamine and dicyclohexylamine are given in Table 2.

TABLE 2

Protection given by cyclohexylamine and dicyclohexylamine salts and complexes

Serial No.	Inhibitor-material	Observations	
		Test I loss in wt. mgms/ 1″×1″ specimen	Test II loss in wt. mgms/ 1″×1″ specimen
1	Cyclohexylamine	0·4	0·6
2	Dicyclohexylamine	1·4	1·0
3	Cyclohexylamine bentonite	2·7	0·9
4	Dicyclohexylamine bentonite	2·8	2·3
5	Cyclohexylamine Carbion	0·6	19·2
6	Cyclohexylamine stearate	75·3	6·2
7	Dicyclohexylamine stearate	49·0	4·6
8	Cyclohexylamine nitrite	0·3	5·0
9	*Dicyclohexylamine nitrite*	0·2	2·2
10	*Cyclohexylamine carbonate*	3·3	1·0
11	Cyclohexylamine benzoate	55·3	15·4
12	Dicyclohexylamine benzoate	74·2	12·4

The conclusion drawn earlier that complexes formed with bentonite and Carbion are nearly as effective as the amines themselves in preventing vapour phase corrosion is confirmed by the results obtained in Table 2. As observed earlier the stearates and benzoates of the two amines do not prevent corrosion under the conditions of the accelerated test but have an appreciable corrosion-inhibiting effect in the sulphur dioxide test. Cyclohexylamine and dicyclohexylamine nitrites which are completely inhibiting under the conditions of the accelerated test are not equally effective in the sulphur dioxide test although conferring better protection than stearates and benzoates. Wachter's work [7] has shown that amine nitrites are likley to behave in this manner. Vernon's [8] observation that cyclohexylamine carbonate would be particularly effective under industrial atmospheric conditions where a high concentration of sulphur dioxide is present, is confirmed by the above tests.

(c) *Morpholine salts and complexes*

Results obtained with salts and complexes of morpholine are given in Table 3.

TABLE 3

Protection given by morpholine salts and complexes thereof

Serial No.	Inhibitor-material	Observations	
		Test I loss in wt. mgms/ 1″×1″ specimen	Test II loss in wt. mgms/ 1″×1″ specimen
1	Morpholine	0·2	..
2	Morpholine bentonite	35·8	..
3	Morpholine Carbion	2·4	1·4
4	Morpholine nitrite	20·3	7·1
5	Morpholine carbonate	4·4	8·5
6	Morpholine stearate	35·8	3·1

It is seen from the above table that morpholine bentonite, morpholine nitrite and morpholine stearate inhibit rusting under the conditions of the accelerated test only to a slight extent but morpholine Carbion and morpholine carbonate give a very high degree of protection. As in the other tests, the stearate is more effective under the conditions of the sulphur dioxide test.

(d) *Further tests with promising materials*

The protection given by the complexes and salts in two long term tests lasting upto 6 months and 9 months is given in Table 4. The Carbion and Amberlite complexes were not subjected to the coated paper test as they could not be applied on kraft paper.

TABLE 4

Serial No.	Inhibitor-material	Observations	
		Test III loss in wt. mgms/ 3″×½″ specimen	Test IV loss in wt. mgms/ 2″×½″ specimen
1	Ethylenediamine	12·6	34·4
2	Benzylamine	0·3	0·6
3	Cyclohexylamine	1·2	1·6
4	Dicyclohexylamine	0·2	1·1
5	Morpholine	65·8	..
6	Ethylenediamine bentonite	18·7	7·5
7	Benzylamine bentonite	0·3	0·6
8	Cyclohexylamine bentonite	1·2	14·2
9	Dicyclohexylamine bentonite	0·5	1·0
10	Morpholine bentonite	36·5	..
11	Ethylenediamine Carbion	11·4	..
12	Benzylamine Carbion	0·4	..
13	Cyclohexylamine Carbion	2·1	..
14	Morpholine Carbion	290·3	..
15	Ethylenediamine Amberlite IRC-50	6·4	..
16	Ethylenediamine Amberlite IRC-120	2·8	..
17	Ethylenediamine nitrite	0·1	0·5
18	Benzylamine nitrite	0·6	54·4
19	Cyclohexylamine nitrite	0·4	0·8
20	Dicyclohexylamine nitrite	1·0	0·2
21	Morpholine nitrite	1·0	..
22	Benzylamine carbonate	0·4	..
23	Cyclohexylamine carbonate	15·5	42·5
24	Morpholine carbonate	176·2	..
25	Benzylamine benzoate	0·1	0·4
26	Cyclohexylamine benzoate	0·2	1·2
27	Dicyclohexylamine benzoate	0·4	1·1
28	Ethylenediamine stearate	4·0	..
29	Benzylamine stearate	0·3	1·0
30	Cyclohexylamine stearate	0·2	3·0
31	Dicyclohexylamine stearate	0·3	..
32	Morpholine stearate	9·3	..

It is seen from Table 4 that the bentonite complexes follows the amines closely in respect of the degree of protection given over long periods. Ethylenediamine and morpholine as well as their bentonite complexes are ineffective in long-term tests. Among amine-Carbions benzylamine Carbion gives protection in the long term tests. Ethylenediamine Amberlite complexes give more protection than ethylenediamine itself. The amine nitrites are as effective in the long term tests as in the accelerated test. The benzoates and stearates are very effective in the milder long term tests as compared to the degree of protection given by them in the accelerated test. Morpholine carbonate behaves similarly to the amine in the long term test in not giving protection.

(*e*) *Effect of promising inhibitors on non-ferrous metals*

The action of the inhibitor materials considered in earlier sections on several commonly used non-ferrous metals was assessed under the severe atmospheric conditions simulated in accelerated vapour corrosion test. (Test I). The results obtained with the free amines are given in Table 5. Morpholine was left out from these studies as it did not give promising results in the long term tests.

Action of amines on copper, brass, aluminium, zinc and lead

No.	Inhibitor-material	Observations (loss in wt—mgms/1″×1″ specimen)									
		Copper		Brass		Aluminium		Lead		Zinc	
		visual	loss in wt.	visual	loss in wt.	visual	loss in wt.	visual	loss in wt.	visual	loss in wt.
1	Control (without inhibitor)	blackened ..	5·5	a number of black spots on both sides	1·0	both sides darkened	2·5	silky deposits at places	44·0	buff coloured deposit on both sides	9·0
2	Ethylenediamine ..	completely blacked with violet tint	14·0	completely blackened	33·2	white corrosion product on specimen	8·2	thick white deposits	154·4	blackened on both sides	25·6
3	Benzylamine	one side completely blackened, black spots on the other sides	7·5	green and bluish stains	1·5	black stains at middle and bottom on both sides	1·0	white deposits at hole and bottom	5·3	whitish deposit at places	0·5
4	Cyclohexylamine ..	completely blackened	14·0	slight blackening on both sides	1·5	darkened on both sides	15·2	whitish coat on one side	16·0	very thin deposit on one side	1·5
5	Dicyclohexylamine ..	very slight bluish stains on both sides	0·5	both sides blackened	2·0	darkened ..	1·5	thin white coat at places	21·0	white deposits at bottom	5·0

It is seen from Table 5 that ethylenediamine accelerates corrosion of all the metals by several times. Benzylamine inhibits corrosion of lead and zinc appreciably and, to a slight extent, of aluminium. Cyclohexylamine accelerates corrosion of copper and aluminium but inhibits corrosion of zinc and lead. Dicyclohexylamine inhibits corrosion of copper.

Table 6 gives results obtained with the amine complexes and salts.

TABLE 6

No.	Inhibitor	Observations (loss in wt—mgms/1″× 1″ specimen)											
		Copper		Brass		Aluminium		Lead		Zinc		Galvanized Iron	
		visual	loss in wt.	visual	loss in wt.	visual	loss in wt.	visual	loss in wt.	visual	loss in wt.	visual	loss in wt.
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Ethylenediamine bentonite	completely blackened	6·5	..	..	..	..	white powdery deposit all over the specimen	117·0	thick dirty coloured deposit on both sides	18·0	..	..
2	Benzylamine bentonite	darkened ..	0·5	..	..	..	..	very thin slaty deposit on each side	5·0	very thin whitish deposit on both sides	2·0	..	..
3	Cyclohexylamine bentonite	black rust patch in middle on one side	1·5	..	..	..	..	slaty deposit	40·0	white deposit	36·0	..	..
4	Dicyclohexylamine bentonite	blackened both sides at places	2·7	..	..	..	..	thin white deposit on both sides	22·0	thin white powdery deposit	9·0	..	..
5	Ethylenediamine Amberlite IRC-50	most of panel blackened	3·5	completely blackened	5·0	coloured slaty	4·5	white deposit at top and middle	21·4	Buff coloured deposit at places	8·5	white deposit on both sides, edges rusted	21·0
6	Benzylamine Carbion ..	blackened ..	4·0	clean and bright	1·0	darkened grey	3·5	white powdery deposit all over	115·0	white powdery film	27·0	2·3 rustpoints on each surface	1·3
7	Ethylenediamine nitrite	blackened ..	5·0	..	..	..	..	..	..	..	..	..	..

TABLE 6—*contd.*

1	2	3	4	5	6	7	8	9	10	11	12	13	14
8	Cyclohexylamine nitrite	very faint blackening at 2-3 places	1·5	..	..	..	..	thick loose white deposits on both sides	180·0	white powdery deposits on both sides	4·0	thin white deposit on both sides	8·0
9	Cyclohexylamine benzoate	Slight darkening at places	0·2	slightly darkened and blackened	1·0	clean and bright	0·5	white loose deposit all over	368·5	white powdery deposit at bottom and near hole	2·0	white powdery deposit at places, edge and hole rusted	8·0
10	Benzylamine benzoate ..	clean and bright	0·1	clean and bright	0·0	grey coat on both sides	3·5	thick white silky deposit	50·4	white powdery spots	6·0	thin white deposit on both sides, edges rusted	16·0
11	Dicyclohexylamine benzoate	clean and bright	0·2	clean and bright except for 1-2 black spots	0·3	clean and bright	0·5	white spots on both sides	14·0	4-5 white powdery spots on each side	1·5	white deposit on both sides & edges rusted	19·5
12	Benzylamine stearate ..	clean and bright	0·5	clean and bright	0·5	greyish coat	3·0	..	..	greyish loose deposit all over	17·0	..	..
13	Cyclohexylamine stearate	blackened slightly	1·0	clean and bright	1·0	dark grey on both sides	2·0	loose white deposit on both sides	81·0	white powdery film on half panel	5·0	thin whitish deposit on both sides, edges rusted	25·0
14	*Dicyclohexylamine nitrite*	faint black rusting	1·2	clean	0·3	slightly dark spots	0·8	thin white spots	6·1	white powdery deposits	2·9	thin white deposit, edges rusted	23·4
15	*Cyclohexylamine carbonate*	blackened	13·6	clean	0·3	slaty spots	2·5	few patches of thin deposits	5·2	white powdery spots at places	5·6	white deposit at places	10·6

Both ethylenediamine bentonite and ethylenediamine Amberlite are less harmful to the non-ferrous metals than the free amine and, in fact, reduce attack or lead and copper. The corrosive action of benzylamine towards lead and zinc is accelerated by benzylamine Carbion but not by bentonite. The reason for this difference in behaviour is not understood. The increased corrosion of copper, aluminium and lead observed in the presence of cyclohexylamine is reduced by cyclohexylamine bentonite but corrosion of zinc is accelerated as against inhibiting action of the free amine. The benzoates inhibit corrosion of copper brass, aluminium and zinc but accelerate attack, on lead. Cyclohexylamine stearate behaves in a similar way. Benzylamine stearate is slightly corrosive towards aluminium and zinc. Cyclohexylamine carbonate accelerates corrosion of copper and cyclohexylamine nitrite accelerates corrosion of lead.

Conclusion

The above study shows that amine adsorbed cation exchangers are efficient vapour phase inhibitors and compare very favourably with some of the known vapour phase inhibitors in both short-term and long-term tests. They can be conveniently handled unlike the free amines and are less harmful to non-ferrous metals in general than the free amines, this being apparently due to their presence in reduced concentration in the system. Benzoates and stearates are found to give good vapour phase inhibition in milder test conditions but are definitely ineffective for application under severe exposure conditions. Their application to mild atmospheric conditions should, however, be seriously considered as they are very easy to prepare and consequently, likely to be more economical to use.

The long-term experiments described above do not, however, give very precise idea as to the superiority of the amine-carriers from the point of view of long-term protection, as compared to the free amines; as the free amines have also given satisfactory protection under the conditions of test considered here. Practical tests running over longer periods will give a more decisive answer on this question.

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