STUDIES ON INDIAN BENTONITE AS THE CARRYING MEDIUM IN CORROSION INHIBITIVE COMPOSITIONS FOR FERRUS METALS

by

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ABSTRACT

A new type of preservative based on chemical inhibitors incorporated in a suspension of bentonite in water was developed by Sanyal & Preston [1,2] which proved as efficacious as petroleum base compositions for protection of steel against corrosion during storage and promised to be useful in some fields where use of petroleum base compositions was not feasible. In the present investigation, the performance of Indian bentonite as the carrying medium for a wide range of chemical inhibitors and their mixtures, has been studied.

Experimental Procedure

Test panels—$2'' \times 1''$ test panels of mild steel (C—0·07%, Mn—0·40% Si—0·09%, S—0·03% and P—0·07%) were used for all tests. The panels were prepared as in the experiments reported in the earlier paper [2]. Bentonite of the composition given in Table I, (from a Madhya Pradesh firm) costing Rs. 20 per ton was used.

TABLE 1

Physico-Chemical Properties of Indian Bentonite

1. Loss on ignition at about	1000°C	24·3%
2. Silica	as SiO_2	45·2%
3. Iron	as $Fe_2 O_3$	6·7%
4. Magnesium as	MgO	1·3%
5. Aluminium as	$Al_2 O_3$	18·8%
6. Total Chloride as	NaCl	2·5% (av.)
7. Carbonate		Nil
8. Sodium		Traces
9. pH of dispersion in water (1 %)		6·8
10. Total exchangeable bases		48·70 m.e.

11. Exchangeable Cations

    (a) Ca   15·40 m.e.

    (b) Mg   11·75 m.e.

    (c) Na   18·07 m.e.

    (d) K   0·98 m.e.

12. Base Saturation Capacity   58·03 m.e.

Preparation of bentonite dispersion, inhibition and coating of metal panel were carried out as reported in previous paper ([2]).

The coated panels were exposed for corrosion test in a tropic chamber maintained at $88 \pm 4°F$ and $96 \pm 4\%$ RH respectively.

Protective efficiency of a composition was assessed on the basis of the following (a) total period during which the coated panels did not show any signs of rusting and (b) the loss of weight after cathodic derusting of another sets of panels at the end of fixed exposure period.

Effect of Different Concentrations of Inhibitors

Sodium nitrite—Studies were made with 0 to 12% sodium nitrite incorporated in 10% bentonite dispersion. Results are shown graphically in Figs. 1 and 1a. It will be seen that at about 3% concentration nitrite gives almost complete protection and only slightly better results are obtained at higher concentrations. The coating weight and nitrite content in the coating increase with the increase in the nitrite content of the bentonite paste.

Sodium benzoate—Bentonite dispersion (10%) containing 5% and 12% sodium benzoate failed to give any protection to mild steel.

Potassium chromate—Bentonite paste (10%) incorporating potassium chromate up to 10·5% was examined and results are given in Table 2.

TABLE 2

Effect of Potassium Chromate concentration on inhibition

Inhibitor Concentration					Coating weight	Loss of weight after 3 m 10 days
(percent)					(mgms)	(mgms)
0·50	..	..	..	..	..	84·7	248·0
1·00	..	..	..	..	..	120·5	15·0
1·25	..	..	..	..	..	138·1	7·4
1·50	..	..	..	..	..	152·1	6·7
2·50	..	..	..	..	..	180·0	7·2
4·50	..	..	..	..	..	133·7	6·0
7·00	..	..	..	..	..	121·8	5·2
9·00	..	..	..	..	..	125·8	3·8
10·50	..	..	..	..	..	120·1	3·8

It will be seen that below 1% rusting is uniform and heavy; at about 1·25% concentration of inhibitor, almost complete protection is obtained. Increasing the amount of inhibitor beyond 1·25% does not appreciably increase protection.

Performance of mixed Inhibitors. Sodium nitrite and Sodium benzoate—Varying proportions of these two inhibitors total 5% were incorporated in 10% bentonite suspension and their performance was evaluated. The results are shown graphically in Fig. 2. It will be seen from a comparison of Figs. 1 and 2, that at lower nitrite concentrations, benzoate has a marked beneficial effect, but when the concentration of the nitrite is above 3% no special advantage accrues by mixing benzoate with it.

Sodium nitrite and Potassium chromate—Results are given in Fig. 3. It will be seen that at 1% $NaNO_2$ and above rusting is completely inhibited, when a mixed inhibitor is used.

Sodium nitrite and Sodium Phosphate—The results are given in Fig. 4. It will be seen, as in the case of nitrite-benzoate mixture, that no improvement in the performance is provided by phosphate above 3% Na NO_2 level.

Influence of pH—Normally bentonite-nitrite dispersions have a pH of about 6·9. Effect of pH was studied by lowering or raising the pH by the addition of sulphuric acid or caustic soda respectively. Results are given in Table 3.

TABLE 3

Influence of pH on the protective effect of bentonite, containing sodium nitrite

Inhibitor % in dispersion				Coating weight	pH	Days Protected		Derusted after		Loss in weight
				(mgms)		M*.	D.	M.	D.	(mgms)
NaNO₂ (5·0%) ..	..	..		178	3·6	4	11	5	26	95·6
,, (5·0%) ..	..	..		177	4·6	5	17	5	26	1·0
,, (5·0%) ..	..	..		177	6·8	5	26	5	26	0
NaNO₂ (1·25%)	..	..		91	7·3	1	19	8	15	113
,, ,, ..	..	..		138	11·1	8	4	8	15	0
,, ,, ..	..	..		205	11·8	8	4	8	15	0

* M stands for months and D for days.

It will be seen that at a pH 11·1, even 1·25%, $NaNO_2$ gives complete protection for 8 months while 5% $NaNO_2$ fails in 4 months at pH 3·6. This shows that higher pH enhances the protective action of the bentonite coating.

Influence of chloride in bentonite—Natural bentonite contains about 3% chloride calculated as NaCl. Dispersions were made after washing the bentonite to bring down the chloride content ranging from 0·6 to 2·7%. Effect of chloride was investigated.

TABLE 4

Influence of chloride on inhibition of corrosion of mild steel by sodium nitrite (0·25—2%) in bentonite paste

Derusted after 3 months 10 days.

Percentage sodium nitrite in dispersion.	Chloride as NaCl in bentonite (dry powder)									
	2·7%		2·6%		2·1%		1·1%		0·6%	
	Protection period	Loss in weight (mgms)	Protection period	Loss in weight (mgms)	Protection period	Loss in weight (mgms)	Protection period	Loss in weight (mgms)	Protection period	Loss in weight (mgms)
0·25	1 day	390	1 day	480	1 day	514	1 day	350	1 day	89
0·50	,,	402	,,	370	,,	324	,,	116	,,	75
1·00	,,	168	,,	293	,,	174	4 months 10 days	0	>11 months 10 days	0
1·25	4 days	151	4 days	170	4 months 2 days	0	7 months	0	,,	0
1·50	4 months	0	5 months	0	7 months	0	>11 months, 10 days	0	,,	0
2·00	7—11 months	0	7—11 months	0	7—11 months	0	,,	0.	,,	0

It will be seen that chloride has inimical action on the protection afforded by sodium nitrite. Progressively larger quantities of nitrite are required to give complete protection with increasing content of chloride in bentonite.

Leaching of inhibitors from bentonite coating during exposure

Protective action of inhibited bentonite paste is due to the presence of water soluble inhibitors like $NaNO_2$ and K_2CrO_4, in the coating which are liable to be leached out by moisture during exposure. Continued protection, therefore, requires retention in the coating of an optimum amount of inhibitor, which might be different for different inhibitors. The rate of leaching of $NaNO_2$ (Table 5) from bentonite coating was determined by coating mild steel panels with bentonite dispersion inhibited with 5% and 10% nitrite and then exposing them in a selected environment (humidity cabinet maintaining a temperature cycle of 42—48°C and 100% R.H.).

Other properties of inhibited bentonite dispersion

Bentonite dispersion stored for one year did not exhibit any separation and change in pH, inhibitor content and protective efficiency. Metal components can be coated by spraying, brushing or immersion and coated panels can be depreserved by wiping with damp cloth or immersion in water. Slightly damaged areas in the coating is protected due to creeping of inhibitor. The thixotropic nature of paste prevents drainage of preservative from metal surface.

Conclusion

Indian bentonite proved suitable as a carrying medium for inhibitors in the preparation of inhibited bentonite dispersions. Physical properties of such dispersions are quite suitable for application by dipping, brushing or spraying. The keeping qualities of these dispersions have been found to be excellent.

Of the various corrosion inhibitors investigated sodium nitrite proved to be the best, the next being sodium chromate. The combination of sodium nitrite and chromate proved even better than either of the inhibitors alone. At higher sodium nitrite concentrations (at or above 3%), no such 'synergistic' effects are observed.

The presence of soluble chlorides in bentonite dispersion has been shown to be detrimental to the inhibitive action of sodium nitrite and larger quantities of inhibitor are required with increasing chloride content of bentonite. Leaching of sodium nitrite occurs in a state of continued condensation and it has been shown that under such a condition the period of protection is prolonged even beyond the optimum nitrite content required initially due to simultaneous leaching out of chloride.
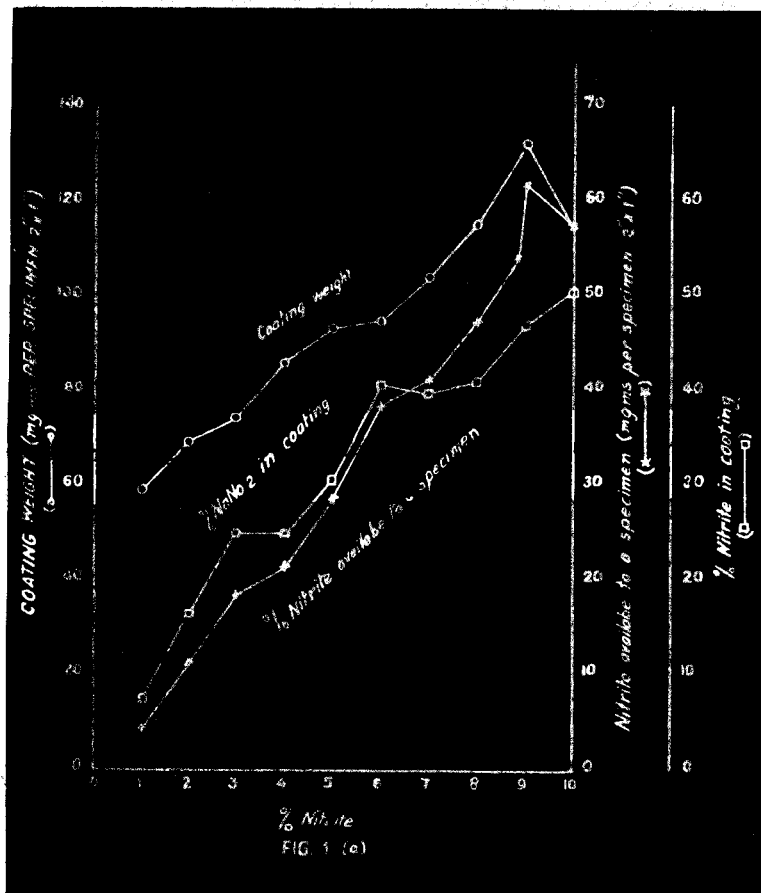
Due to the thixotropic nature of bentonite disperation uniform coating thickness could be obtained. Inhibited bentonite coating was also shown to give protection to small 'holidays' in the coating.

Acknowledgement

References

1. Preston, R.H.J. & Sanyal, B., *B.P. Application.* 15919/52.

2. Sanyal. B. and Preston, R.H., *J. Appl. Chen* . **3,** **366** 1953.

Influence of nitrite concentration in dispersion on uptake of inhibitor by bentonite coating.

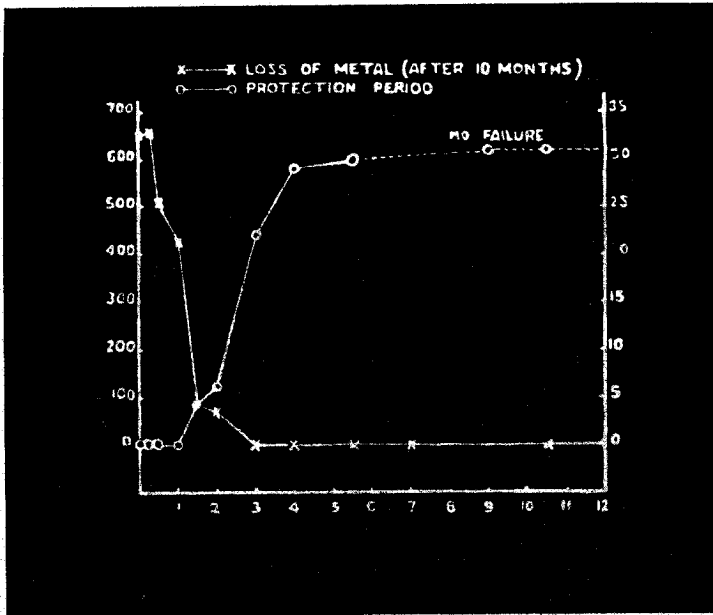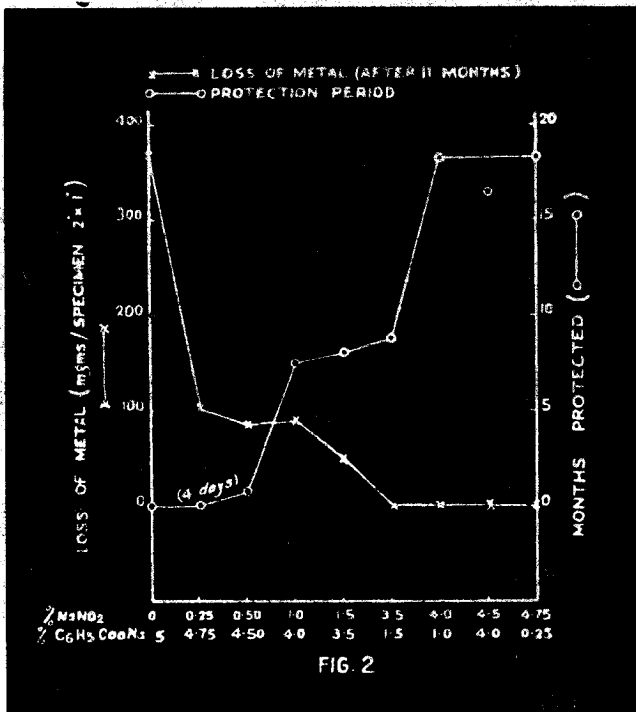FIG. 1. Protection of steel by bentonite coating containing sodium nitrite only.

FIG. 2. Protection of steel by bentonite coating containing nitrite and benzoate.