1-Dodecyl Xanthate as a Phosphating Additive: Aspects of Chemistry and Corrosion Protection

By Usha B. Nair and M. Subbaiyan

An investigation of phosphate coatings obtained on mild steel was made, using a calcium-modified zinc phosphating bath containing 1-dodecyl xanthate (1-DDX). The coatings obtained from this cold phosphating composition were subjected to simulated aggressive environments and their performance was compared to that of coatings obtained using the reference bath. Assessments were made against the relevant standard specifications. The study revealed that the adsorption and chelation properties of the additive play vital roles in the formation of a hydrophobic film on the steel substrates, which in turn supplements the protection provided by the phosphate coatings obtained in the formulated bath.

hosphate coatings constitute the standard conversion pretreatment for a variety of sheet steel fabrications. In addition to being used as paint bases, their antiseizure properties make them a useful pretreatment prior to a variety of drawing operations.' Although they improve corrosion resistance of the base metal, the protection offered by them is temporary unless suitably complemented by further finishing. This is because these coatings are inherently porous.²The pores in phosphate coatings enable easy access to corrosives, such as oxygen and water, thereby acting as centers where corrosion begins.

Although post-rinses have found wide application in reducing the porosity (by as much as 50 percent), a significant percentage of base metal remains exposed even after this treatment. It was felt, therefore, that an alternate method of minimizing moisture ingress on phosphated surfaces was to modify the phosphating composition such that the surface of the coatings produced become hydrophobic. To do this, the obvious choice, from a range of additives considered, was those surface-active agents possessing long hydrocarbon chains in their structure. These compounds behave as corrosion inhibitors by forming surface films, which act not only as physical barriers, but prevent the approach of water to the metal as well, because of their inherent hydrophobic nature.

From a variety of surface-active agents considered, a thioltype surfactant, xanthate, was chosen for the present study. These types of compounds have been widely used in the frothflotation process for the analogous purpose of inducing hydrophobicity on the surface of metallic minerals.³The present investigation focuses on the evaluation of 1-dodecyl xanthate (1-DDX), a twelve-carbon, long-chain, aliphatic sulphur-containing compound, in an optimized calcium-zinc, coldphosphating formulation.

Experimental Procedure

Hot rolled, mild steel panels (composition conforming to IS^* 1079 specifications), 8 x 6 x 0.2 cm, were solvent-degreased, pickled in 10-percent sulfuric acid and rinsed in distilled water.

The panels were phosphate by immersion at room temperature (27 $^{\circ}$ C, 80.6 $^{\circ}$ F) for 30 min. The composition of the optimized phosphating bath used was

Zinc oxide	9 g/L
Ortho-phosphoric acid (85%)	20 mL/L
Calcium carbonate	1 g/L
Sodium nitrite	2 g/L
1-dodecyl xanthate (1-DDX)	10-2000 mg/L
рН	2.33

1-DDX used in this study was prepared as its sodium salt by the reaction of stoichiometric proportions of the parent alcohol, 1-dodecanol, and carbon disulfide in the presence of sodium hydroxide, at room temperature.⁴



The crude product so obtained was washed with ether and dissolved in acetone. The xanthate was reprecipitated with benzene after filtering any solid residues present. The cycles of washing, dissolution and reprecipitation were repeated to further purify the 1-DDX.



Fig. 1—Variation of coating weight and weight of iron dissolved during phosphating h concentration of 1-DDX.

^{*} Indian Standard

Table 1Variation of Potential*As a Function of Concentration of 1-DDX					
Conc. of 1-DDX, mg/L	Initial potent. (IP) (mV)	Max. potent. (MP) (mV)	Final potent. (FP) (mV	E₁ (MP-IP)) (mV)	<u>E</u> 2 (MP-FP) (mV)
0	-465	-490	-463	25	27
10	-457	-479	-456	22	23
50	-442	-457	-441	15	16
100	-438	-449	-436	11	13
200	-428	-452	-433	24	19
500	-419	-449	-434	30	15
1000	-414	-442	-440	28	2
2000	-411	-440	-437	29	3

*Potentials measured with respect to SCE at 27° C (80.6° F).





Following the phosphating step, a chromic acid post-rinse (using 0.0125-percent CrO_3 solution, maintained at 70 to 80 °C 158 to 176 °F), was done on panels coated in the reference bath (without 1-DDX). This step was omitted for panels processed in baths containing 1-DDX, in order to evaluate the efficiency of this filming additive as a suitable substitute for the chrome-rinse.

Coating Evaluation Studies

Coating parameters, such as coating weight and weight of iron dissolved during phosphating, were determined gravimetritally,¹at various concentrations of 1-DDX in the bath. A solution of 20 g/L of antimony trioxide in concentrated hydrochloric acid was used to strip the coatings in these measurements.⁵

Using coating weight and uniformity as the guiding parameters, an optimum concentration was chosen, at which the effect of other variables, such as variation of accelerator content (from O to 4 g/L) and pH (from pH 2 to 2.66) was investigated.

The coatings obtained at the optimum concentration were assessed visually for appearance and uniformity. Other parameters, such as absorption value and hygroscopicity of the coatings were also measured.⁶The gain in weight of coated steel panels after immersion in diacetone alcohol for two rein, followed by draining for three rein, was recorded as the absorption value. Hygroscopicity was determined as the gain in weight of coated steel panels placed two in. above water for six hr in a closed chamber, and was expressed as a percentage of the coating weight.

Potential-time measurements were carried out at various concentrations of 1-DDX in the bath as also at various accelerator concentrations and PH. These measurements were made with a high impedance millivoltmeter, ^aagainst a saturated calomel electrode (SCE), using a Luggin capillary.

The corrosion performance of panels coated in the reference bath and the additive-containing baths were compared, using the standard evaluation methods, such as observation of panels after 12 hr immersion in a solution of three-percent NaCl (IS 361 8) and the weight loss after 24 hr immersion, a salt spray test (ASTM B 117-87) and a humidity test (IS 101).

Results and Discussion

The phosphating solutions prepared in the presence of the additive were turbid, unlike those of the reference bath. The turbidity increased with increase in additive concentration and solid white precipitates began to format higher concentrations

^aModel 435, Systronics, India

	Table 2 Effect of Variation of Accelerator (Concentration	
Conc. of of NaNO ₂ g/L	Reference bath Coating wt., Weight* of iron dissolved a/m ² during phosphating, a/m ²	Ade () Coating wt., a/m²	ditive-containing bath 200 mg/L of 1-DDX) Weight* of iron dissolved during phosphating, g/m ²
0	0.89±0.21 1.56±0.18	0.81 ± .17	1.49 ± 0.21
	$6.85 \pm 0.45 \\ 10.91 \pm 0.49$	5.88 ± 0.31	7.19 ± 0.51
2	9.26 ± 0.26 7.35 ± 0.31	7.33 ± 0.47	6.13 ± 0.39
4	10.72 ± 0.39 13.49 ± 0.46 9.36 ± 0.10	12.47 ± 0.38	8.50 ± 0.42
*Average of five	determinations.		8 5 59 x X 3

of 1-DDX. It was observed that addition of NaNO₂ (accelerator) to the phosphating bath, just prior to immersion of the steel panels, considerably reduced the turbidity of the solutions. It was also noticed that a brownish-black precipitate was formed at higher concentrations of the additive, as processing of the steel panels proceeded in baths containing 1-DDX.

Effect of Variation of Additive Concentration on Coating Weight The values of coating weight and the weight of iron dissolved during phosphating were determined at various concentrations of 1-DDX (range of 10 to 2000 mg/L). The data obtained are graphically represented in Fig. 1. It is evident from the figure that

- at all concentrations of the additive, the coating weights were lower than that of the reference bath without the additive;
- in the concentration range of 10 to 150 mg/L of the additive, coating weight progressively decreased, as did the weight of iron dissolved during phosphating:
- around a concentration of 200 mg/L, coating weight increased sharply, attaining a value close to that obtained at a concentration of 10 mg/L:
- at a range of concentrations between 200 and 2000 mg/L, there appeared to be no significant change in the coating weight or weight of iron dissolved during phosphating.

The above pattern of changes may be attributed to the interplay of a variety of unique properties of the xanthate additive, stemming from its heteropolar structure comprising a hydrocarbon chain attached to a polar group, together with its ability to act as an inhibitor, as well as a complexing accelerator, depending upon its concentration in the phosphating bath.

The fact that coating weight decreased at ail concentrations of the additive, compared to the reference bath, indicates that 1-DDX hinders coating formation. It is also evident from the

values of coating weight and weight of iron dissolved during phosphating, that within the concentration range of 10 to 150 mg/L, coating formation was hindered to greater extent as the additive concentration was increased.

These phenomena may be rationalized as the result of adsorption of the additive onto the panel being coated. The adsorption process hampers coating formation by obstructing the primary initiating reaction of the phosphating process, viz., the iron dissolution process, besides decreasing the effective surface area available for coating deposition to occur. The extent of adsorption of the additive increases with additive concentration, resulting in progressive decrease in coating weight and the weight of iron dissolved during phosphating, observed up to a concentration of 150 mg/L of the additive.

Coating weight showed a marked increase between concentrations of 150 to 200 mg/L of the additive. Obvious formation of a stable brownish-black precipitate [identified, using infrared

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Table 3 Variation of Potential* As a Function of Accelerator Content

Conc. of NaNO ₂ , g/L	Initial potent. (IP) (mV)	Max. potent. (MP) (mV)	Final potent. (FP) (mV)	∴ E, (MP-IP) (mV)	∴ E₂ (MP-FP) (mV)
0	-534	-585	-585	51	0
t i t a se	-472	-502	-502	30	0
2	-428	-452	-433	24	19
3	-417	-426	-404	9	22
4	-410	-413	-385	3	28

*Potentials measured with respect to SCE at 27° C (80.6° F).



Fig. 3-Variation of potential with time as a function of accelerator content 7 $^{\circ}$ C (80.6 $^{\circ}$ F)].

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Table 4 Effect of Variation of Bath pH

Reference bath

	-		(2	200 mg/L of 1-DDX)
pH of the bath	Coating wt., g/m²	Weight* of iron dissolved during phosphating, g/m ²	Coating wt., g/m²	Weight* of iron dissolved during phosphating, g/m ²
2.00 2.33 2.66	$\begin{array}{c} 7.52 \pm 0.39 \\ 9.26 \pm 0.26 \\ 7.99 \pm 0.31 \end{array}$	$\begin{array}{c} 10.50 \pm 0.61 \\ 7.35 \pm 0.31 \\ 5.07 \pm 0.54 \end{array}$	6.67 ± 0.10 7.33 ± 0.32 7.20 ± 0.39	8.78 ± 0.43 6.13 ± 0.39 3.72 ± 0.71

*Average of five determinations.

spectroscopy, as Fe (III)-dodecyl xanthate complex] was also observed in this range of concentration during the phosphating process. This led to the conclusion that besides adsorption, the well-recognized completing ability of xanthates⁷ assumes prominence at these concentrations.

Formation of the Fe-xanthate complex occurs according to the overall equation $^{\rm 8}$

$$Fe^{3+} + 3 S = C \xrightarrow{OC_{12}H_{25}} 3H^{+} + Fe \begin{bmatrix} -S - C - OC_{12}H_{25} \\ SH \end{bmatrix} (1)$$

The process of complexation enhances the dissolution of iron and enables quicker consumption of free phosphoric acid in the bath, with consequent increase in coating weight.

No significant changes occurred in the coating weight or weight of iron dissolved during phosphating, in the concentration range of 250 to 2000 mg/L. It was observed, however, that there was a consistent increase in the amount of Fe-xanthate chelate formed during processing. This suggests that increase in concentration caused increased adsorption of the additive, concurrent with increased complexation, therefore keeping the coating weight and weight of iron dissolved constant over this range of concentrations.

Potential-Time Measurements

To obtain more information about the mechanistic aspects of the reactions occurring in phosphating baths containing 1-DDX, potential-time measurements were made. Figure 2 depicts the changes in the potential-time curves as a function of additive concentration. As suggested by the work of Ghali and Potvin,[®]the nature and extent of changes in the initial potential (IP), the maximum potential (MP), and the final potential (FP), were chosen as the key parameters for comparison of potential changes occurring at various additive concentrations. While the initial potential represents the state of the steel specimen at

Table 5 Variation of Potential*

As a Function of Bath pH

	pH of the bath	Initial potent. (IP) (mV)	Max. potent. (MP) (mV)	Final potent. (FP) (mV)	∴ E, (MP-IP) (mV)	∴ E₂ (MP-FP) (mV)	2 02 12 02 12 12 12 12 12 12 12 12 12 12 12 12 12
16 1	2.00	-477	-506	-506	29	0	
	2.33	-428	-452	-433	24	19	
Le.	2.66	-417	-425	-400	8	25	

*Potentials measured with respect to SCE at 27° C (80.6° F).

the initial stage of phosphating, the extent of shift in potential toward less noble values, up to the maximum potential (ΔE_1), can be related to the extent of metal attack by free phosphoric acid present in the bath. Because the attack on the metal modifies the equilibrium state of the phosphating bath at the metal/solution interface, thereby inducing the precipitation of phosphates, the extent of shift in potential towards more noble values beyond the maximum, up to the final potential (ΔE_2), signifies the extent of coating deposition.

Additive-containing bath

Table 1 shows the variations of the above potentials, with changes in concentration of 1-DDX in the bath. It is evident that the initial potentials at all concentrations of 1-DDX are less negative (more noble) than that of the reference bath. This may be a result of adsorption of the additive on the panel being coated. Also, this potential is shifted to more noble values with increase in additive concentration, supporting the conclusion that adsorption increases with increase in additive concentration. Consequent to increased adsorption, it could be expected that the extent of metal attack (ΔE_1) would decrease with increasing additive concentration. The expected trend, however, is followed only up to a concentration of 100 mg/L of the additive, beyond which the value increased despite the initial increase in inhibition. This observation supports the view that near a concentration of 200 mg/L, the complexation phenomenon assumes prominence and enhances the extent of metal attack by reacting with iron available at the metal/solution interface through formation of a stable chelate with it [Eq. (1)]. Values of ΔE_{a} at 200 mg/L also indicate that the extent of coating



Fig. 5—Extent of rust-creep after exposure to salt spray for panels phosphated in (a) reference bath; (b) 1-DDX-containing bath.

Table 6 Physical Properties

Property evaluated					
Bath used	Avg. coating wt., g/m ²	App	pearance	Absorption value, g/m ²	Hygroscopicity (as % of coating wt.)
Reference bath with rinse	9.26	Unif	orm, adherent, eyish-white	11.77	0.11
Bath containing 1-DDX (200 mg/	7.35 ′L)	Unif gr	orm, adherent, eyish-white	10.50	0.09

formation is enhanced at this concentration. The competitive effects of inhibition and complexation reactions occurring in the bath are manifested as the rather insignificant change in potential (toward more noble values) beyond the maximum potential at a concentration range of 1000 mg/L; although gravimetric determination of coating weight indicates significant coating formation at this concentration of the additive.

From the above studies, the proposed mechanism of the action of 1-DDX in the phosphating bath maybe consolidated as follows: The sodium salt of 1-DDX added to the phosphating medium ionizes to form sodium and xanthate ions. The xanthate anion, being an acknowledged chelating agent, particularly for a variety of heavy metals, undergoes complexation with the zinc present in the phosphating solution.



The bis-chelate of zinc, so formed, remains as a stable white precipitate in the phosphating medium. Upon addition of NaNO₂ accelerator to the phosphating bath, however, just prior to immersion of the steel panel to be coated, nitrous acid is generated in situ, as a result of the strongly acidic nature of the phosphating solution (pH 2.33). The nitrous acid formed causes dissociation of the Zn-xanthate complex, thereby liberating free xanthate ion. This ion, being surface-active and amphiphilic, undergoes adsorption onto the steel immersed for phosphating, through a process of surface chelation. The adsorption process inhibits iron dissolution and thereby hinders coating formation. The result is a decrease in coating weight (as compared to the blank).

With increase in concentration of the additive in the bath, increased adsorption occurs, causing a consistent decrease in coating weight and weight of iron dissolved during phosphating, up to 150 mg/L. Around 200 mg/L of the additive, however, its concentration becomes sufficient to enable it to participate in a concurrent chelation reaction with iron dissolved from the unabsorbed areas of the panel being coated [reaction (1)]. This

process ensures the sustained removal of ferric iron from the metal/solution interface through the formation of its stable trischelate with xanthate ions. This chelation reaction enhances metal dissolution, resulting in increased coating deposition. The opposing effects of the competing reactions of adsorption and complexation result in the insignificant variations in coating weight and weight of iron dissolved during phosphating at high concentrations. Because coating weight obtained at a concentration of 200 mg/L was maximum and the coatings were of uniform, adherent nature, this concentration was chosen as the optimum at which further studies were carried out.

Effect of Variation of Accelerator Content

At the optimum concentration of the additive in the phosphating bath and in the reference bath, the accelerator concentration was varied in the range of 0-4 g/L. The coating weight and weight of iron dissolved during phosphating obtained at each concentration of the accelerator was recorded. These data are given in Table 2.

It is evident from the data that an increase in accelerator concentration caused an increase in both the weight of iron dissolved during phosphating, and the coating weight, in both baths. At all concentrations of the accelerator, however, the additive-containing bath showed lower values for both the parameters monitored, which is the result of the inhibitive nature of the additive. It must be noted, though, that without NaNO₂, the coating weight and the weight of iron dissolved during phosphating are similar in both baths. This indicates that no marked inhibition occurred in the additive-containing baths, in the absence of NaNO₂. This observation further supports the view that the presence of NaNO₂ in the bath is an essential prerequisite for initiating liberation of the xanthate ions from the Zn-xanthate complex, so as to make them available for further adsorption onto the specimen being coated.

Significantly high values of the weight of iron dissolved during phosphating are obtained at a concentration of one g/L of NaNO₂ in the reference bath and in the additive-containing bath. This is attributed to the fact that at a concentration of accelerator below the optimum, incomplete utilization of the already insufficient NaNO₂occurs, because of its predominant

	Table 7	
Corrosion	Performance	Studies

		Study performed	
Bath used	Wt. loss in 3% NaCl after 24 hrs, g/m²	Observation made after 7 days in the humidity test	Observation made after 96 hrs of salt spray test
Reference bath with rinse	8.13	No signs of onset of corrosion	Minimal lateral rust creep from scribe. No blisters seen.
Bath containing 1-DDX (200 mg/L)	7.59	No signs of onset of corrosion	Minimal lateral rust creep from scribe. No blisters seen.

decomposition to form nitrous acid. This in turn increases the acidity of the phosphating bath, prompting further metal dissolution without significantly enhancing coating deposition. This also results in the observed formation of dark brown coloration of the phosphating solution during processing of steel panels at this accelerator concentration, besides yielding coatings of poor quality.

Figure 3 and Table 3 indicate that in baths containing 1-DDX, an increase in the concentration of NaNO₂shifted the initial potential toward more noble values and caused a decrease in the extent of metal attack (ΔE_1). The values of ΔE_2 suggest that at concentrations of O and 1 g/L of NaNO2, the coating deposition process was incomplete, because no shift in potential (toward noble values) occurred beyond the maximum, unlike at other concentrations of the accelerator. Greater values of ΔE_{2} at 2, 3 and 4 g/L NaNO₂ indicate more rapid and complete coating deposition with increase in concentration of NaNO₂.

Effect of Variation of pH

The pH of the reference bath and the additive-containing baths were adjusted to 2.00 and 2.66, using HNO₃ and NaOH, respectively. The coating weights and weights of iron dissolved during phosphating for these baths are presented in Table 4.

The data reveal that 1-DDX inhibited coating formation at all values of pH, compared to the reference bath. At higher pH (2.66), early attainment of the point of incipient precipitation, and rapid deposition of insoluble phosphates in the bath, compensated for effects resulting from reduced iron dissolution and thereby yielded coating weights of magnitude comparable to those at pH 2.33.

Prolonged metal attack and incomplete coating deposition at pH 2 are evident from the potential-time curves (Fig. 4 and Table 5). It is also seen that the extent of coating formation (ΔE_{2}) increased with increase in pH. despite consistent decrease in the values of the initial potential and ΔE_1 , with increase in pH of the bath.

Physical Properties and Corrosion Performance

The coatings obtained at the optimum concentration of the additive were uniform, adherent and gravish-white in color (Table 6). The absorption value for panels processed using baths containing 1-DDX were lower than that obtained for the reference bath (which was subjected to a chromic acid postrinse) despite the reduction in coating weight. This feature may be ascribed to the established filming nature of the xanthate additive which effectively clogs the pores of the phosphate coatings and thereby reduces its porosity.

The presence of a film of the adsorbed long-chain additive on the phosphate coating results from interaction of its polar moiety with the substrate metal. Such an interaction implies that the aliphatic chains of these compounds should point away from the metal surface, rendering it hydrophobic. The moisture permeability of the coating, measured as its hygroscopicity, is accordingly reduced in the additive-containing bath.

Table 7 shows the results of studies carried out to assess the corrosion performance of coatings obtained in presence of 1-DDX. After 12 hr of immersion in 3-percent NaCl solution, no discoloration of the solution was observed in the case of panels coated in the reference bath as well as in the presence of 1-DDX, satisfying the criterion specified by IS 3618. The weight loss resulting from corrosion of panels processed in the presence of optimum concentration of the additive after 24 hr of immersion in 3-percent NaCl was of similar magnitude as the reference. despite reduced coating weights obtained in their presence.

Panels coated with and without 1-DDX showed no onset of corrosion on exposure to 100 percent relative humidity in a humidity test chamber for seven days. Also, the extent of lateral spread of corrosion from the scribe after 96 hr of salt sprav was minimal for panels coated in the presence of 1-DDX (Fig. 5a and b). The improved corrosion performance, in spite of decreased coating weight in baths containing 1-DDX, is the result of integration of the hydrophobic filming additive into the phosphate coating formed on the metal substrate, thereby enhancing its ability to withstand aggressive environments.

Conclusions

Addition of 1-DDX to the formulated calcium-zinc phosphating bath decreased the coating weight. The additive incorporates itself as an integral part of the coating through adsorption and complexation onto the steel surface being coated. The xanthate film, formed by surface chemical reaction with the base metal, reduces the porosity and moisture permeability of the coating, which resulted in its satisfactory corrosion performance compared to the reference bath.

The optimum concentration for good coating performance in the presence of this additive was largely dependent on the solution chemistry of the xanthate under the complex conditions existing in the phosphating bath, as well as to the formation of sparingly soluble and stable heavy metal-xanthate complexes and the hydrophobic nature of the adsorbed film.

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About the Authors

Usha B. Nair is a researcher in metal finishing in the Dept. of Analytical Chemistry, University of Madras Guindy Campus, Guindy Madras 600 025. India. She holds an MSc in analytical chemistry from the University of Madras.

Prof. M. Subbaiyan is head of the Dept. of Analytical Chemistry at the University of Madras, from which he holds a doctorate in analytical chemistrv.