

# Influence of Bath Acidity on Phosphating of Steel From Additive-Containing Baths— A Study by Potential-Time Measurements

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**A study of the effect of pH on coating weight of a phosphating bath determined that pH is vital in the determination of the rate and amount of coating formed. Additives undergo changes in activity that greatly influence the phosphating process as pH is varied.**

Surface pretreatment by phosphating has become popular because of its ability to improve adhesion of the organic topcoat and prevention of underfilm corrosion. The mechanism of phosphating reveals clearly that the equilibrium existing between the soluble primary phosphate and the insoluble tertiary phosphate is strongly influenced by the operating temperature and pH of the bath.<sup>1,2</sup> Accordingly, it is customary that adequate care be taken regarding these two parameters when developing a phosphating formulation. When subjected to operation on an industrial scale, however, the phosphating baths are highly susceptible to variations in bath parameters and, from the point of view of the conversion of the primary to tertiary phosphate, bath acidity is quite critical, because a change in acidity will alter the kinetics of the phosphating process. Moreover, such an effect is ex-

pected to be more pronounced in formulations incorporated with special additives, following the change in activity of the additives with the change in acidity of the bath.

To make evident this view and to elaborate its criticality in the development of phosphating baths, nine different formulations were selected. To obtain a clear picture of the influence of the variation in bath acidity and the change in activity of the special additives during the phosphating process, they were subsequently examined by potential-time measurements.

## Experimental Procedure

Mild steel specimens (hot rolled, composition conforming to IS 1079 specifications), measuring 8 x 6 x 0.2 cm, were used for this study. The chemical composition of the standard bath (Bath 1) and its operating conditions are as follows:

ZnO : 5 g/L  
H<sub>3</sub>PO<sub>4</sub> : 11.3 mL/L  
NaNO<sub>2</sub> : 2 g/L  
Temp : 27 °C  
Time : 30 min

This composition is modified by incorporating optimum concentrations of detergent-type amines and dithiocarbamates to yield Baths 2–9, respectively (Table 1):

**Table 1**  
**Chemical Composition of Phosphating Baths**

Bath	Composition
1	ZnO, 5 g/L; H <sub>3</sub> PO <sub>4</sub> , 11.3 mL/L; NaNO <sub>2</sub> , 2 g/L
2	Bath 1 + 75 mg/L DDA
3	Bath 1 + 75 mg/L TDA
4	Bath 1 + 50 mg/L HDA
5	Bath 1 + 25 mg/L ODA
6	Bath 1 + 75 mg/L DDDTC
7	Bath 1 + 50 mg/L TDDTC
8	Bath 1 + 50 mg/L HDDTC
9	Bath 1 + 50 mg/L ODDTC

Dodecylamine (DDA), 75, mg/L  
Tetradecylamine (TDA), 75 mg/L  
Hexadecylamine (HDA), 50 mg/L  
Octadecylamine (ODA), 25 mg/L  
Dodecylthiocarbamate (DDTC), 75 mg/L  
Tetradecylthiocarbamate (TDDTC), 75 mg/L  
Hexadecylthiocarbamate (HDDTC), 50 mg/L  
Octadecylthiocarbamate (ODDTC), 50 mg/L

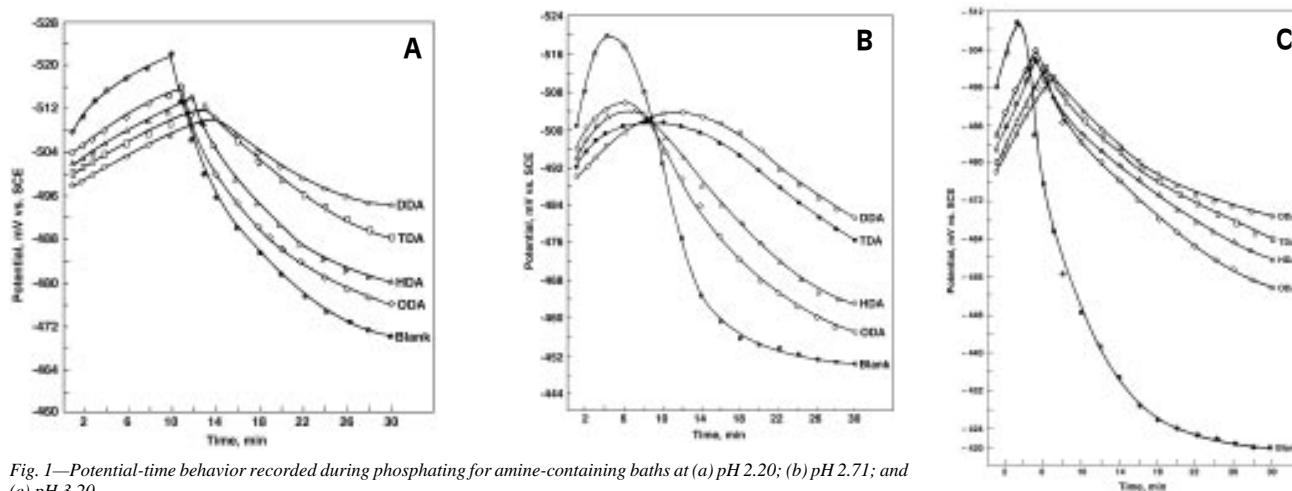


Fig. 1—Potential-time behavior recorded during phosphating for amine-containing baths at (a) pH 2.20; (b) pH 2.71; and (c) pH 3.20.

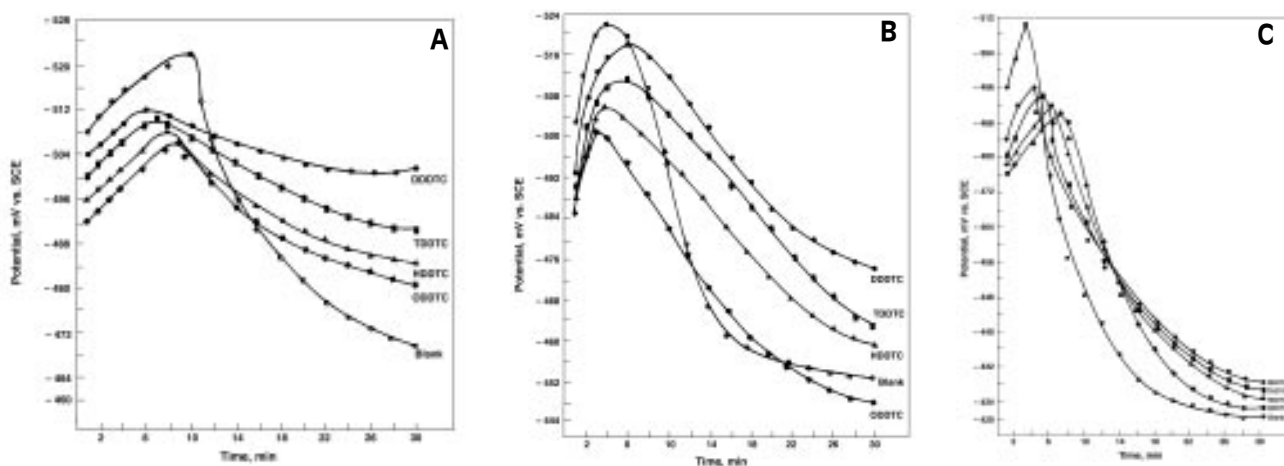


Fig. 2—Potential-time behavior recorded during phosphating for dithiocarbamate-containing baths at (a) pH 2.20; (b) pH 2.71; and (c) pH 3.20.

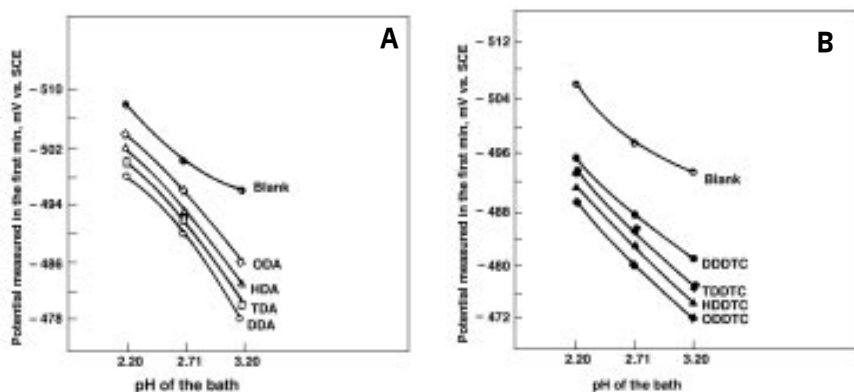


Fig. 3—Variation of the potential measured in the first minute with the pH of the bath for (a) amine-containing baths; and (b) dithiocarbamate-containing baths.

The criteria for selection of the optimum concentration of these additives are discussed elsewhere.<sup>3-6</sup> Phosphating was done by immersion process at room temperature (27 °C) for 30 min. The effect of pH on phosphating was studied by varying the pH of the standard bath (Bath 1, pH 2.71) to 2.20 and 3.20. The adjustments were made using small amounts of concentrated nitric acid and sodium hydroxide. The potential of the steel sample was monitored with time, using a calomel electrode with a Luggin probe connected to a high-impedance volt meter. The panels were placed inside the bath solution for pre-determined times and, when removed, were carefully rinsed and dried. Visual observations of the bath were made during processing and of the coated panels after completion of the coating process (30 min). In addition, coating weight measurements were also made for an effective comparison.

## Results and Discussion

### Visual Observations

During processing at pH 2.20, the phosphating solution appeared dark brown in color in all the baths. It has been reported that nitrite-accelerated baths will lead to the evolution of oxides of nitrogen if operated with acidic pH. Accordingly, dark brown coloration of these baths during operation is believed to result from evolution of oxides of nitrogen consequent to the decomposition of sodium nitrite, thereby preventing its complete utilization. Also, the coated panels were found to be dark gray, implying high acidity of the bath. In contrast, panels processed at pH 2.71 and 3.20 were gray

and grayish white, indicating the less acidic nature of these baths.

### Potential Time Measurements

The potential-time behavior, recorded as a function of the pH of the bath for the amine- and dithiocarbamate-containing baths, along with the standard baths, are shown respectively in Figs. 1a to 1c and Figs. 2a to 2c. Although the nature of the curves appears different, the following points are of great significance in each:

1. Potential measured in the first minute
2. Time at which saturation of metal (dissolution) occurs
3. Potential measured in the 30th minute
4. Extent of change in potential between the time of saturation of metal (dissolution) and the 30th minute.

Accordingly, it was decided to analyze the potential-time curves obtained, based on the above four points, as such an analysis will be of great help in revealing the nature of changes, especially when the phosphating baths experience variations in pH.

### Potential measured in the first minute

The potential measured in the first minute during coating formation in a phosphating bath having considerable processing time (30 min in this case) is indicative of the nature of the metal surface undergoing corrosive attack by the free phosphoric acid present in the bath.<sup>7</sup> Because the present study concerns the variation in bath acidity, this value is vital. It was found that addition of optimum concentrations of long-chain amines and dithiocarbamates shift the measured potential in the first minute to a less negative value as compared to the standard bath, regardless of either an increase or decrease in the pH of the standard bath (Figs. 3a and 3b).

It has already been established from our previous studies that the added amines and dithiocarbamates that exist as cations in the phosphating bath have a tendency to get adsorbed onto the cathodic sites of the panel being coated.<sup>3-6</sup> Their adsorption decreases the metal dissolution by increas-

ing the hydrogen overvoltage and results in a shift in potential as compared to the blank (without the additive).<sup>8,9</sup>

In the carbon chain series ( $C_{12}$ – $C_{18}$ ), an expected shift in measured initial potential to a less negative value occurs with the increase in chain length in the case of dithiocarbamates, which implies increased surface coverage by longer-chain compounds. A trend reversal was observed in the case of amines, however. This can be ascribed to the better solubility of DDA (in about 5 mL of acetone or ethanol) in the phosphating medium, aiding adsorption to a greater extent.<sup>10</sup> Although the observed shift in potential invariably occurs with the variation in the pH of the bath, it is evident from Figs. 3a and 3b that, at pH 3.20, the shift in the initial potential is considerably higher for both the amine and dithiocarbamate series. Figures 4a and 4b show the extent of change in potential with respect to the variation in pH of the bath, which is maximum for DDA and ODDTC in both series, indicating that the extent of their adsorption is greater at pH 3.20.

#### Time at which saturation of metal dissolution occurs

During phosphating, dissolution of iron occurs at the anodic sites of the panel being coated, the corresponding cathodic reaction being the hydrogen discharge and the deposition of tertiary phosphates. The time at which saturation of metal dissolution occurs (the point of ennobling of potential) is a significant parameter in indicating the rate and extent of coating formation in a phosphating bath.<sup>7</sup> In amine-containing baths, because some of the cathodic sites are covered by the adsorbed amine molecules, the number of available cathodic sites for hydrogen discharge is low. This leads to a decrease

in the rate of metal dissolution, resulting in lengthening of the induction period and delay in reaching the point of incipient precipitation (PIP), compared to the standard bath. This prolongation of time occurred with both an increase and decrease in the pH of the bath (the standard bath has a pH of 2.71). The time at which the PIP was attained, however, decreased with increase of pH (Figs. 5a and 5b).

In the amine series studied, the time of attainment of PIP decreased with increase in carbon chain length (Fig. 5a). This is largely a consequence of the number of adsorbable units that affects the metal dissolution and lengthens the induction period, which decreases with the increase in chain length of these amines. At pH 3.20, the time of attainment of PIP differs little from that of HDA and ODA. This is because the inhibiting effect of these amines is partly compensated by the rapid conversion of primary to tertiary phosphate at this pH.

With dithiocarbamate additives, increase in the pH of the bath from 2.20 to 2.71 causes a decrease in the time of attainment of PIP, whereas at pH 3.20, the trend was reversed (Fig. 5b). This may be due to the increased adsorption of the protonated species at this pH.<sup>11</sup> Compared to the blank, this time is increased or decreased in the case of dithiocarbamates, depending upon the conditions used and the chain length of the additive. The delay in the attainment of PIP is rationalized as follows:

In the case of dithiocarbamates, the dissolved iron readily forms a tris-chelate with the adsorbed dithiocarbamate molecule.<sup>12,13</sup> These in turn desorb, making room for a larger number of cathodic surface sites for hydrogen discharge than were available in the first minute. Because a time lag exists

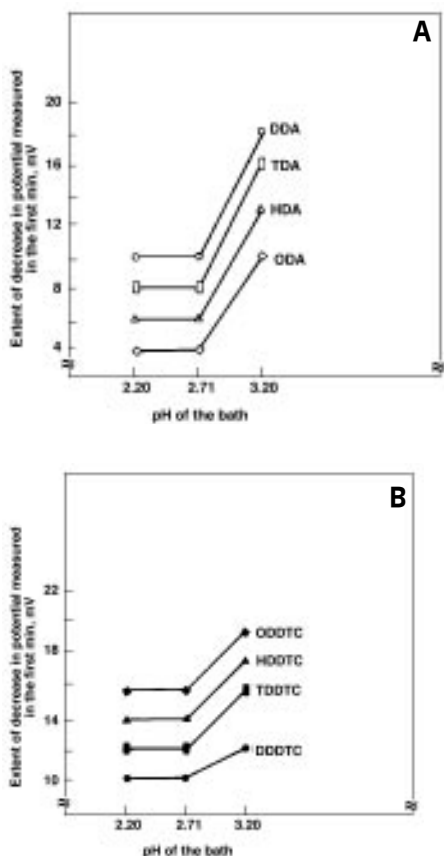


Fig. 4—Extent of decrease in the potential measured in the first minute with the pH of the bath for (a) amine-containing baths; and (b) dithiocarbamate-containing baths.

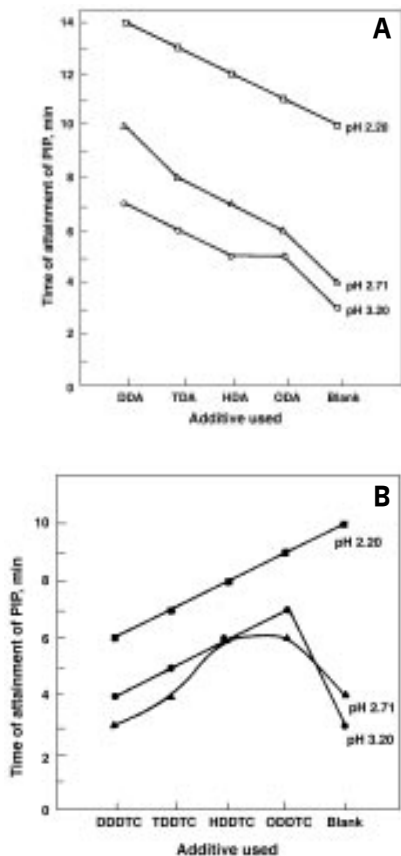


Fig. 5—Variation of the time of attainment of PIP as a function of bath pH for (a) amine-containing baths; and (b) dithiocarbamate-containing baths.

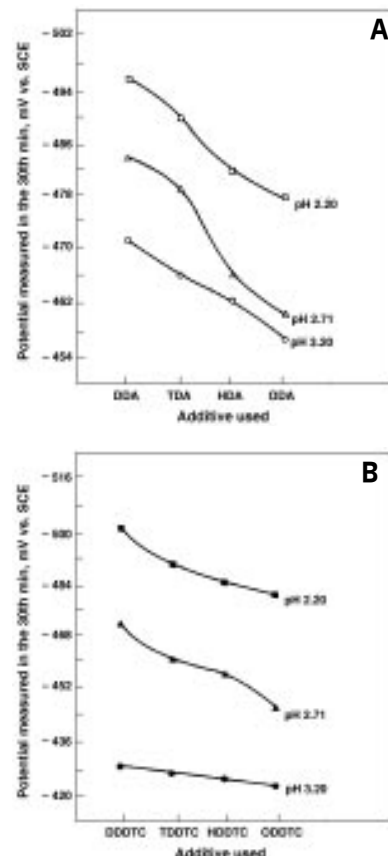


Fig. 6—Variation of the potential measured in the 30th minute as a function of bath pH for (a) amine-containing baths; and (b) dithiocarbamate-containing baths.

between the normal hydrogen discharge, as in the case of the blank, and the delayed hydrogen discharge, as in the case of dithiocarbamates, the time of attainment of PIP is greater in the latter case.

The potential measured at the point of PIP is also low (less negative) for these long-chain amines and dithiocarbamates than for the blank, regardless of the change in pH of the bath. This feature can be attributed to the presence of adsorbed amines and dithiocarbamates present at this stage. The pronounced influence of DDA and ODDTC in both the amine and dithiocarbamate series can be predicated on the greater number of adsorbing units in these cases.

### Potential measured in the 30th minute

The potential near the coating completion time (30 min) can qualitatively suggest the extent to which coating formation has occurred. When these long-chain amines are added to the phosphating bath, the potential measured at this stage is higher (more negative) than the blank, indicating less coating formation in the presence of these amines (Figs. 1a to 1c and Table 2). In the series, the potential value was found to be shifted to more noble values with increase in chain length, which implies increased coating formation (Fig. 6a). Although the observed trend has occurred regardless of the variation in the pH of the bath, the extent of decrease in final potential is greater at pH 3.20 (Fig. 6b). This can be ascribed to increased adsorption of these additives at this pH.

In the case of dithiocarbamates, as in the case of amines, the potential measured in the 30th minute was found to be shifted to more noble values with increase in chain length, which implies better coating formation for longer chain compounds. The shift in potential toward a less negative value with increase in pH signifies a greater amount of coating formation at pH 3.20 (Fig. 7a), where the extent of

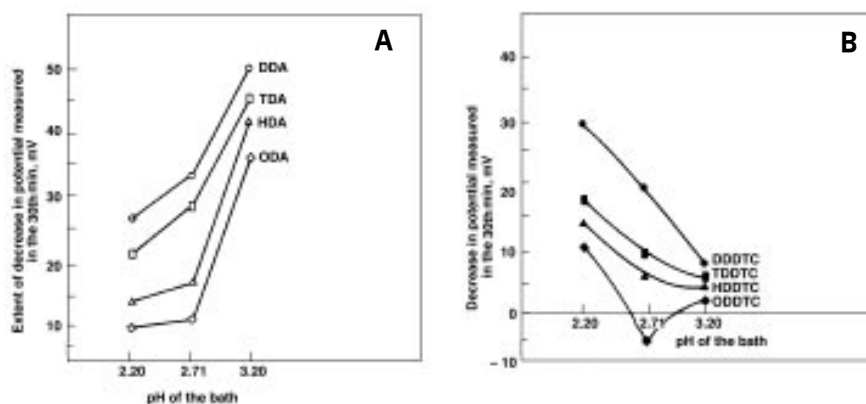


Fig. 7—Extent of decrease in the potential measured in the 30th minute with the pH of the bath for (a) amine-containing baths; and (b) dithiocarbamate-containing baths.

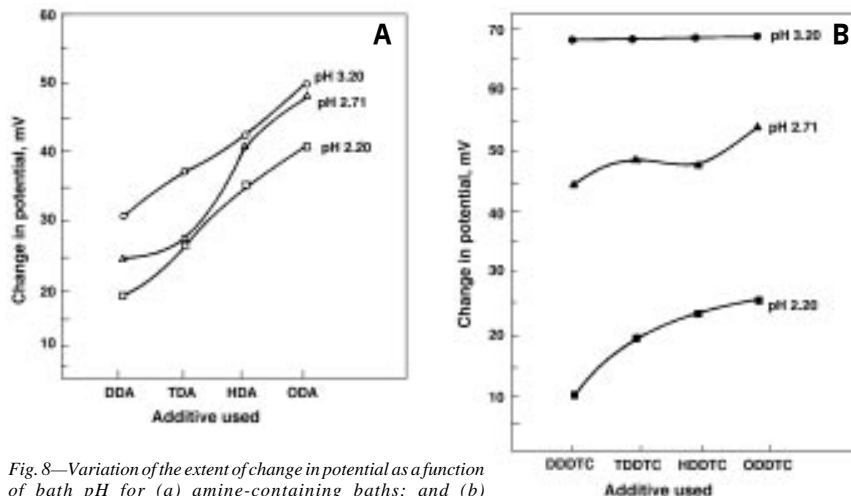


Fig. 8—Variation of the extent of change in potential as a function of bath pH for (a) amine-containing baths; and (b) dithiocarbamate-containing baths.

decrease in potential is pronounced (Fig. 7b). This can be explained on the basis of the earlier attainment of the PIP at this pH. Moreover, it should be noted that in the case of dithiocarbamate-containing baths, with the exception of ODDTC at pH 2.71, the potential measured in the 30th minute was less noble than the blank (Figs. 2a and 2b). The coating weight measurements (Table 2) have shown, however, that there is a good increase in the amount of coating formed, compared to the blank. This feature can be correlated to the fact that the expected shift in the final potential toward more noble values with deposition of the phosphate coating is partly compensated by an opposite effect—the increased metal dissolution prompted by the complexing ability of the dithiocarbamate additives.

### Extent of change in potential

The difference in potential measured at the saturation of metal dissolution and at coating completion (30 min) usually gives a measurement of the amount of coating formed. In the case of the blank, the extent of change in potential increases with increase in the pH of the bath from 2.20 to 3.20. When amines were added to the phosphating bath, this change in potential was found to be less, following the inhibiting action of these amines toward metal dissolution. In the series, the extent of change in potential was maximum in the case of ODA. The observed trend occurred regardless of the variation in the pH of the bath (Fig. 8a). Compared with the standard bath, the extent of change in potential is very small in the case of amines and the effect is more pronounced at pH

**Table 2**  
Effect of pH on Coating Weight

Bath	Coating Weight,* g/m <sup>2</sup>		
	pH 2.20	pH 2.71	pH 3.20
1	8.50	9.92	14.68
2	6.85	7.43	8.33
3	7.26	7.94	9.78
4	7.60	8.10	10.12
5	8.12	8.36	11.40
6	9.42	11.24	15.42
7	10.86	12.42	16.40
8	11.20	14.06	19.40
9	12.60	16.48	20.62

\* Average of five determinations

3.20, leading to lesser coating formation at this pH. Gravimetric measurements of coating weight obtained (Table 2) corroborate these variations.

The extent of change in potential in the case of dithiocarbamate additives was relatively larger than for amines. This was reflected in the enhanced coating weight obtained (Table 2). Among the various series, it was maximum for ODDTC. The extent of change in potential increases with increase in the pH of the bath from 2.20 to 3.20, indicating a greater amount of coating formation at pH 3.20 (Fig. 8b).

Despite the higher coating weights obtained from dithiocarbamate containing baths, the magnitude of change in potential observed at all pH values is less than that of the blank. As mentioned earlier, this is largely a consequence of the opposite effect of the increased metal dissolution caused by the dithiocarbamate additives.

## Conclusions

It is evident that the pH of the phosphating bath is vital in determining the rate and the amount of coating formed. In the case of additive-containing baths, variation of the bath pH greatly influences the phosphating process, as a result of the change in activity of the incorporated additives. Consequently, in the modern world of phosphating, which is experiencing numerous developments in phosphating formulations, a careful optimization of the bath pH and an effective process control will be the key parameters for a successful operation.

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