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A Fourier transform interferometric study of phosphate coatings on iron

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A Fourier transform interferometric study of phosphate coatings on iron plates using absorption–reflexion techniques indicated the following succession of chemical events on the surface of Armco iron dependent on time of immersion into the standard zinc phosphating solution: (a) activated formation via a redox reaction of an initial layer of hydrated iron oxide/hydroxides and nitrosyl iron complexes containing isolated PO_4^{3-} (and possibly NO_2^-) ions in water solution; (b) chemical transformation of the initial layer into a first, adherent and chemically stable layer containing amorphous hydrated iron phosphate and acid iron phosphates; (c) growth of thicker layers progressively enriched of zinc ions, until only hydrated zinc phosphate crystals are deposited in the outer layer. This complex structure of the coating does not undergo significant chemical changes by heating to normal technological temperatures between 150 and 180° C. Only minor changes in water content are shown by the chemical evolution of the infra-red spectra up to such temperatures. Strong changes of the chemical structure of the coating (producing pyro- and metaphosphates) require temperatures higher than 200° C, and coincide with loss of adhesion of the coating to the iron support.

1. Introduction

The development of interferometric absorption–reflection study techniques has greatly improved the possibilities of utilization of infra-red (i.r.) spectroscopy for the study of thin coatings on metal surfaces [1–3]. Their application to research on phosphate coatings on iron seems particularly attractive because of the technological interest of these protective layers.

Recently, some preliminary results were presented [4] confirming the possibilities of the suggested experimental method for similar problems. The present paper refers to more systematic results obtained on both the structure and the mechanism of the formation of phosphate coatings on Armco iron using a standard phosphating solution in well-defined conditions of pH, temperature and time-of-immersion.

Some data are available [5], mainly from X-ray diffraction measurements, concerning the chemical composition of the phosphate layers and its possible evolution in different experimental conditions. From the work presented now some new features have been noted, particularly on the role of structural water in the process, and on the succession of chemical events on the surface during and after immersion into the phosphating solution used.

2. Experimental procedure

Absorption–reflection spectra of phosphate coatings on Armco iron were recorded in the range 400 to 3800 cm^{-1} with an FTS-14 V Digilab Fourier transform interferometer, using a Harrick reflectance attachment [6]. The angle between the sample plate and the light beam was 30°. The measurement parameters were: resolution 4 cm^{-1}; sampling interval 1; number of scans 100. The Fourier transform was calculated with double precision, using 32-bit words.

The standard phosphating solution contained zinc, with $NaNO_2$ as an accelerator in the proportions H_3PO_4, 68.7 g + H_2O, 41.7 g + ZnO, 15.0 g,

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diluted before use as follows: solution 8 cm^3, H_2O 90 cm^3, 20% $NaNO_2$ 2 cm^3. Experiments were also performed using a similar solution in D_2O. The phosphoric acid solution was prepared by dissolution of P_2O_5 in D_2O. Special effects obtained using a modified phosphating solution or particular immersion techniques will be described in the following discussion.

The normal pH (≈ 2) of the solution was increased to 3 and 4 (controlled with pH-meter), for studies on the effect of pH, by adding drops of 10 M NaOH solution.

The normal temperature used was 75° C although some experiments to determine the effect of temperature were performed at 40° C and 60° C.

During all experiments the system was thermostatically held at a fixed temperature and stirred mechanically.

The modification of the i.r. spectra by thermal decomposition of the phosphate coatings *in situ* on Armco iron in the furnace, measured at up to 350° C for 30 min, was also studied.

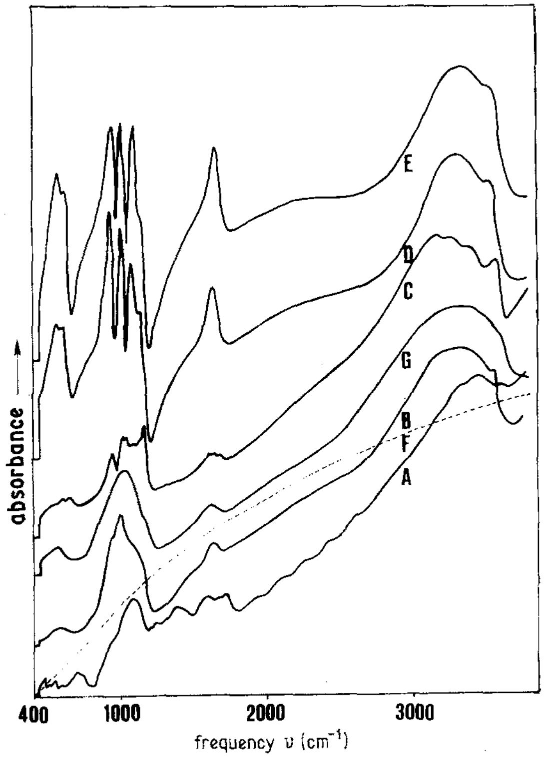

Figure 1 Phosphate coatings on Armco iron: Spectra A–E: standard solution (see text); spectrum F: same solution without $NaNO_2$; spectrum G: H_3PO_4 0.1 N solution. Temperature: 75° C. Immersion times: A, 1 sec; B, 5 sec; C, 15 sec; D, 2 min; E–G, 15 min.

3. Results and discussion

The evolution of the i.r. spectrum of the overall coating with time-of-immersion is represented in Fig. 1. The first layer formed on the iron surface upon very short immersion into the phosphating solution is very thin, as is confirmed by the presence of interferences in the absorption–reflection spectrum (A in Fig. 1) between frequencies, ν, of 2000 cm^{-1} and 3000 cm^{-1}. No defined phosphates seem to be present in this layer, as the band centered at frequency 1100 cm^{-1} and of the shoulder near frequency 960 cm^{-1} correspond to those measured [7] for the ν_3 and ν_1 vibrations of the free PO_4^{3-} tetrahedra in water solution. Water in the liquid or pseudo-liquid state is identified by its characteristic bending vibration at frequency 1590 cm^{-1}, and by the two OH stretching absorptions near 3240 cm^{-1} and 3430 cm^{-1}.

As the only well measurable band in the lower frequency region (700 cm^{-1}) indicates the presence on the surface of hydroxyl groups, the initial layer can be considered as an iron hydroxide gel phase (possibly β-FeOOH, [8]), including some solution of PO_4^{3-} ions and possibly also of NO_2^- ions, which could be responsible for the absorptions near 1240 cm^{-1} and 1380 cm^{-1} [9, 10]. The band at 1710 cm^{-1} in A in Fig. 1 could indicate the presence in the layer of NO^+ ions (formed through reduction of NO_2^- ions) co-ordinated to iron ions, their stretching frequency having been situated in this region from i.r. data on a wide range of nitrosyl complexes by Lewis *et al.* [11] and by Griffith *et al.* [12, 13].

The initial layer therefore seems to be established mainly through redox reactions between the iron surface and the accelerator $NaNO_2$, with primary formation of iron hydroxides and nitrosyl complexes. This mechanism is confirmed by the fact that even after prolonged immersion in the phosphating solution, such as described in the experimental part, with the exception of the $NaNO_2$ addition, no bands are visible in the i.r. absorption–reflection spectrum (see F in Fig. 1). However, once the initial layer has formed, the layer grows into a non-accelerated phosphating solution (without $NaNO_2$), as was confirmed by experiments performed by initial immersion of the sample into an accelerated solution for a few seconds, and then into a non-accelerated solution for longer lengths of time. On increasing the time of immersion (see B in Fig. 1), the spectrum evolves showing absorptions corresponding to those of hydrated iron phosphate such as that formed on the same surface by immersion into a pure 0.1 N H_3PO_4 solution (see G in Fig. 1). A chemical reaction is therefore realized between the primary layer and the solution, giving the first phosphate coating an amorphous structure, which is however partly crystalline, as is shown by the beginning of splitting of the ν(P–O) absorption band centred at frequency $1000\,cm^{-1}$, and by the narrow band at $3530\,cm^{-1}$ characteristic of free OH stretching vibrations, indicating the presence of acid anions $(H_2PO_4)^-$ or $(HPO_4)^{2-}$ in the coating structure.

A further strong evolution of the coating takes place as a result of increasing the time of immersion (see C–E in Fig. 1) under the conditions described. The interpretation of the rather complex spectrum is only possible by considering first the spectrum E in Fig. 1, where well crystallized hydrated zinc phosphate, possibly hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$ [14], is the main component of the coating. The proposed assignment is given in Table I.

The growth of the coating realized from a phosphating solution in partially deuterated water allows for a defined assignment of bands as a result of water in the crystal (Fig. 2). For the H_2O bending vibration at $1620\,cm^{-1}$, the corresponding vibration for D_2O appears at $1220\,cm^{-1}$, the isotopic ratio being 1.33; but two other bands undergo isotopic shift, i.e. the $1000\,cm^{-1}$ and the 600 cm^{-1} bands, which are shifted respectively to $750\,cm^{-1}$ and $490\,cm^{-1}$.

Various authors [15–17] have identified bands in the same region that are characteristic of the wagging and rocking modes of co-ordinated water in various inorganic salts. These bands therefore indicate that water molecules are situated in the first co-ordination sphere of the Zn^{2+} ions. Both bands have two components (see E in Fig. 1) in agreement with the results obtained by Trillat and Saison [18] on the existence of two types of water molecules in the hopeite structure. In some spectra, the higher frequency stretching and bending bands of the water molecule also show a complex structure.

TABLE I Assignment of the i.r. absorption–reflection bands of a zinc phosphate coating

Frequency ν (cm^{-1})	Assignment
570	ν_4(O–P–O) TO component
600	H_2O wagging
630 shoulder	ν_4(O–P–O) LO component
930 shoulder	ν_1(P–O)
1000	H_2O rocking
1080	ν_3(P–O) TO component
1150 shoulder	ν_3(P–O) LO component
1640	H_2O bending
3350	H_2O stretching
3520	free O–H stretching

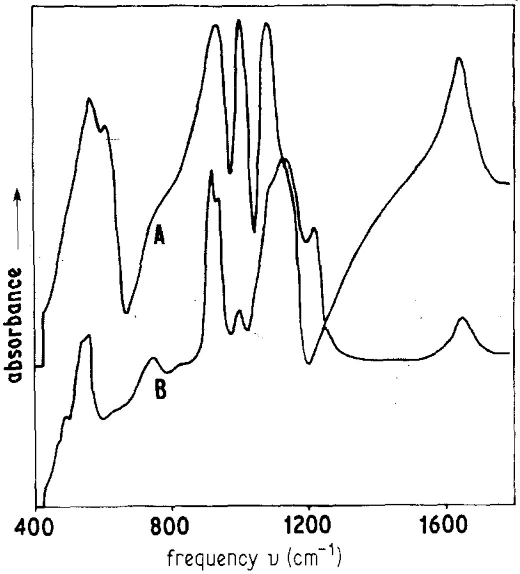

Figure 2 Partially deuterated phosphate coatings on Armco iron. Temperature: 75° C. Immersion time: 15 min. Spectrum A: standard solution (see text); Spectrum B: same solution partially deuterated.

The assignment of the remaining bands in E of Fig. 1 to ν_1, ν_3 and ν_4 vibrations of PO_4^{3-} ions is then univoque. It can be seen that TO–LO splitting can be observed in the spectra (where TO and LO are the transverse and longitudinal oscillations, respectively), the LO component being predominant in thinner layers (see C in Fig. 1).

The spectrum represented in C in Fig. 1 is characteristic of an intermediate situation where both zinc phosphate and acid iron phosphates (identified through the relatively strong band at frequency $3530\,cm^{-1}$) coexist in the coating. The complex absorptions corresponding to OH stretching (3100 to $3400\,cm^{-1}$) and H–O–H bending ($1600–1700\,cm^{-1}$) of water molecules denote the presence of different (probably three) types of water in the layer. The bands at $1030\,cm^{-1}$ and $1125\,cm^{-1}$, which disappear in spectrum D in Fig. 1, together with the marked simplification of both characteristic water absorption regions, are then associated with the crystallization water or OH

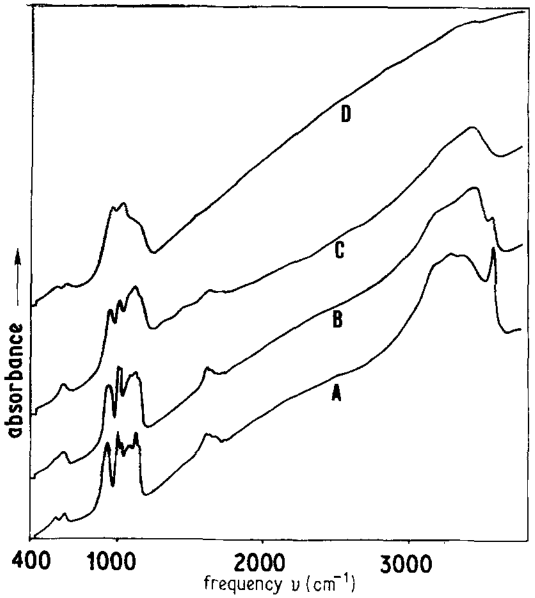

Figure 3 Thermal decomposition of phosphate coatings on Armco iron. Standard solution (see text). Temperature: 60° C. Immersion time: 10 min. Spectrum A shows reference layer; spectrum B taken after heating for 30 min at 140° C; spectrum C: taken after further heating for 30 min at 200° C; spectrum D: taken after further heating for 30 min at 350° C.

vibrations. This assignment is confirmed by the series of spectra in Fig. 3, where a coating specially prepared in order to show more clearly absorptions of three different types of water and a marked quantity of acid phosphates (strong band at 3530 cm^{-1}) has been successively heated to increasing temperatures. Corresponding to the progressive decrease in the intensity of the free OH band and of the lower frequency components at 3160 cm^{-1} and 3260 cm^{-1} of the water OH stretching band (together with the less marked decreasing of H_2O bending bands in the 1600 cm^{-1} region), there is a progressive disappearing of the two bands at 1030 cm^{-1} and 1125 cm^{-1}. The 1000 cm^{-1} band previously assigned to co-ordinated water only disappears after heating to temperatures higher than 200° C (see D in Fig. 3). After heating for 30 min at 350° C a thick zinc phosphate coating (see A in Fig. 4) still shows the existence of the same band (see B in Fig. 4) thus confirming its assignment to water strongly co-ordinated to Zn^{2+} ions. In these experimental conditions the coating undergoes partial chemical transformation into a polyphosphate structure $[Zn(PO_3)_2]_x$ characterized by the modified position of the P–O stretching vibrations and, by a completely new structure of bands in the region 600 to 700 cm^{-1} [19]. This is also confirmed by the far i.r. spectra shown in Fig. 5. Until only amorphous phases are present in the coatings (see A in Fig. 5) no absorption bands are detected in this region. The formation of crystalline phases progressively activates the ν_2 vibration of phosphate ions (375 cm^{-1}) as well as lattice vibrations (290 cm^{-1}) (see B and C in

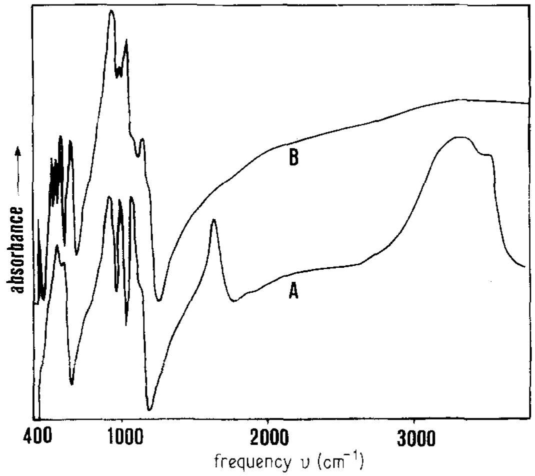

Figure 4 Thermal decomposition of thick phosphate coatings on Armco iron. Standard solution (see text). Temperature: 75° C. Immersion time: 15 min. Spectrum A: reference layer; spectrum B: after heating for 30 min at 350° C.

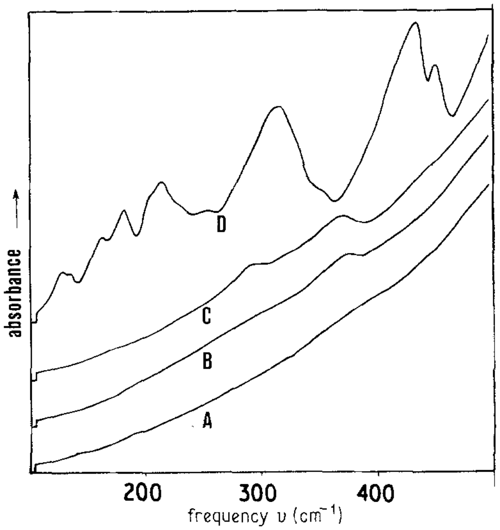

Figure 5 Phosphate coatings on Armco iron (Far infra-red spectra). Standard solution (see text). Temperature: 75° C. Immersion times: Spectrum A, 5 sec; spectrum B, 15 sec; spectrum C, 2 min; spectrum D, 2 min after heating for 30 min at 350° C.

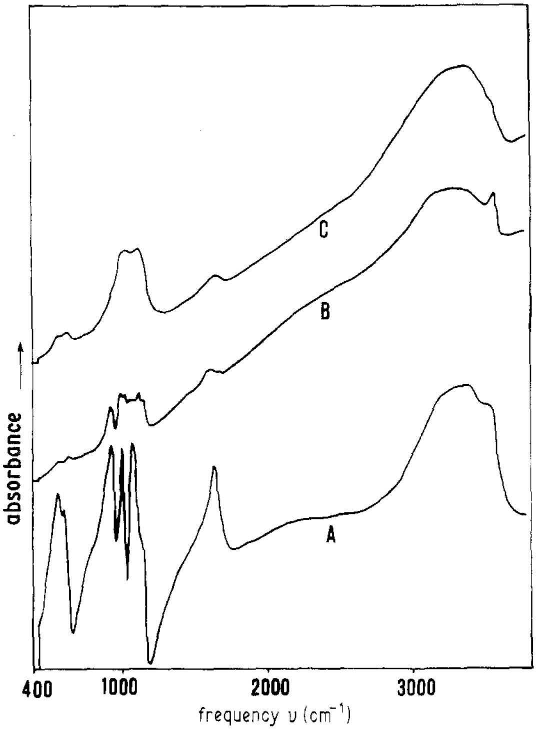

Figure 6 Effect of pH on phosphate coatings on Armco iron. Temperature: 75° C. Immersion time: 15 min. Spectrum A: standard solution (see text), pH = 2; spectrum B: standard solution + NaOH, pH = 3; spectrum C: standard solution + NaOH, pH = 4.

Fig. 5). Heating of the coating to 350° C for 30 min (see C in Fig. 5) gives a new very complex spectrum which can only correspond to a crystalline polyphosphate phase.

The influence of pH and temperature variations on the coating formation was also investigated. In Fig. 6 spectra of coatings obtained after immersion for 15 min in the original phosphating solution (see A in Fig. 6) (pH ≈ 2) are compared with those of coatings obtained in the same conditions but with pH increased to 3 (see B in Fig. 6) and 4 (see C in Fig. 6), the pH being changed by addition of a NaOH solution to the original solution. The evolution of the spectra clearly shows that the effect of increasing pH is similar to that of reducing the time of immersion. The concentration of Zn^{2+} ions in these conditions is strongly reduced by the formation of insoluble basic salts. Comparison of spectrum C in Fig. 6 with that of the coating obtained by immersion in pure 0.1 N H_3PO_4 confirms that only hydrated iron phosphate is present in the coating at higher solution pH.

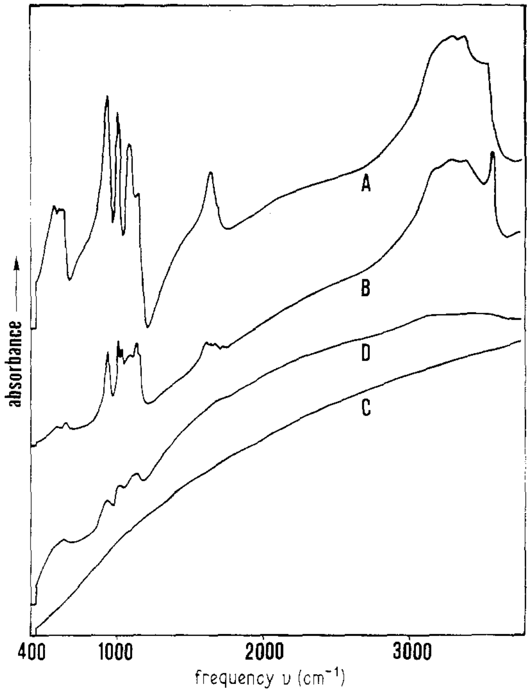

Figure 7 Effect of temperature on phosphate coatings on Armco iron. Standard solution (see text). Immersion time: Spectra A–C, 10 min; spectrum D, 30 min. Temperature: A, 75° C; B, 60° C; C–D, 40° C.

Temperature effects are shown in Fig. 7, indicating that phosphate coating formation not only needs low pH and oxidizing agents, but is strongly activated by temperature. The same time of immersion (10 min) which gives a highly crystalline zinc phosphate coating at 75° C (A in Fig. 7), only gives, at 60° C, a complex layer equivalent to the one obtained after a 15 sec immersion at 75° C (see B in Fig. 7 and compare it with C in Fig. 1). No detectable coating is formed after 10 min at 40° C (see C in Fig. 7); only after a prolonged immersion (30 min) does a very amorphous layer (see D in Fig. 7) begin to form on the iron surface at this temperature.

4. Conclusions

The i.r. spectroscopic results discussed in this paper allow us to propose the following succession of chemical events on the surface of Armco iron with time-of-immersion into the standard zinc phosphating solution used in these experiments:

(a) activated formation via a redox reaction of an initial layer of hydrated iron oxide/hydroxides and nitrosyl iron complexes containing isolated PO_4^{3-} (and possibly NO_2^-) ions in water solution;

(b) chemical transformation of the initial layer into a first, adherent and chemically stable layer containing amorphous hydrated iron phosphate and acid iron phosphates.

(c) growth of thicker layers progressively enriched of zinc ions, until only hydrated zinc phosphate crystals are deposited in the outer layer.

This complex structure of the coating does not undergo significant chemical modifications by heating to normal technological temperatures between 150 and 180° C. Only minor changes in water content are shown by the chemical evolution of the i.r. spectra up to such temperatures. Strong changes of the chemical structure of the coating (producing pyro- and metaphosphates) require temperatures higher than 200° C, and coincide with loss of adhesion of the coating to the iron support.

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