

# Modifications of the phosphate coatings microcrystalline structures induced by dehydration and rehydration processes

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Bare and electrogalvanized steel sheets were subjected to phosphatation in three different phosphatation baths. The aim of the work was to characterize and to compare the behaviour of pure hopeite, phosphophyllite and manganese modified hopeite crystals during dehydration and rehydration processes. Scanning electron microscopy, thermal analysis and X-ray diffraction were employed to study the obtained phosphate coatings. Thermogravimetric analysis showed that all the considered phases underwent the total loss of two water molecules above 150°C. X-ray diffraction measurements showed the formation of bihydrated phases which appear very similar independently from the use of the phosphatation bath. After exposure to a hydrating environment only the pure hopeite bihydrated crystals underwent a rehydration process which led to the tetrahydrated phase and consequently to a decreased paint-phosphate adhesiveness. On the contrary both the bihydrated phosphophyllite phase and the bihydrated manganese modified hopeite phase revealed their inability to return to the completely hydrated crystal and consequently improved paint adhesion.

## 1. Introduction

Phosphatation of steel sheet, electrogalvanized or not, is a widespread industrial process. It is well known, in fact, that such a chemical conversion treatment is able to improve the sheet corrosion resistance in terms of a better adhesiveness of the electrophoretic coatings [1-3].

Using low zinc phosphatation baths it is possible to obtain mainly phosphophyllite crystals layers whose corrosion resistance is much better than that of the usual hopeite ones [4].

The existing bibliography uniformly agree in attributing an improved behaviour to the phosphophyllite layers, and there are several reasons to justify this finding:

1. the iron presence, which improves the electrical conductivity, favouring the electrophoretic film adhesiveness;
2. the reduced phosphophyllite solubility in alkali medium, such as the one formed during electrophoretic deposition;
3. the microcrystallinity of the phosphophyllite structures;
4. the surface chemical cleaning obtained using lower pH values.

In the phosphophyllite crystals the ferrous ions come from the steel substrate, so it is impossible to obtain such a phase on the electrogalvanized steel.

In recent years the aim of research was the formulation of a phosphatation bath which would be able to produce on electrogalvanized steel, crystal structures

with chemical and physical properties similar to the ones of phosphophyllite [5].

Promising results were obtained by using low zinc conversion products, suitably modified introducing other heavy metals such as manganese or nickel.

As it has been recently observed, the rehydration of the bihydrated hopeite crystals induces residual stresses able to reduce the phosphate-paint adhesiveness [6]. Thus the irreversibility of the hydration of the phosphophyllite layers after the baking process of the cathionic electrodeposition could be another possible explanation of the improved behaviour of the phosphophyllite coatings.

The aim of this work is to ascertain the behaviour of the hopeite and phosphophyllite crystals during dehydration and rehydration processes, and particularly to characterize the behaviour of the hopeite crystals obtained on electrogalvanized steel by using nickel and manganese modified phosphatation baths.

## 2. Experimental procedure

AISI 1006 deep drawing steel sheets with a surface carbon content of 7.2 mg m<sup>-2</sup> were phosphatized as-received or after a two-sided electrogalvanizing to a thickness of about 9 µm. As a preliminary to zinc phosphating, alkaline degreasing was applied at 60°C.

Three different zinc phosphatation baths were used as described in Table I in order to obtain four different types of material, as follows: (A) hopeite (Ho) crystals on steel substrate, (B) phosphophyllite (Ph) crystals on steel substrate, (C) Ho crystals on zinc substrate, (D) manganese modified Ho crystals on zinc substrate.

TABLE I Characteristics of the phosphatation baths

Bath number	Heavy metal component	Etching agent	Application technique
1	Zn, Ni, Mn	$\text{NO}_2^-$ , $\text{NO}_3^-$	Spray
2	Zn, Ni	$\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{ClO}_3^-$	Dip
3	Zn, Ni, Mn	$\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{F}^-$	Dip

Scanning electron microscopy (SEM) observations were performed on the samples during heating in the temperature range from 20 to 180°C in order to check possible crystal deformations.

The dehydration process analysis was carried out by means of thermogravimetric analysis using a Mettler TA1 instrument with a heating rate of 1°C min<sup>-1</sup>.

X-ray diffraction technique was also used to determine the crystal phases present in the coating after thermal treatments for various times at different temperatures in the 20 to 180°C range. The same technique was used to examine some samples after heating at 160°C for 90 min and subsequent rehydration in a humidostatic chamber at different temperatures.

Finally all phosphatized materials were painted with a cataphoretic epoxy-amino type coating to a thickness of 20 to 22 µm and successively cured at 180°C for 30 min. These specimens were then subjected to the wet adhesion test in deionized water at 40°C for 240 h, evaluating the paint adhesion by the tape test.

### 3. Results

The as-received materials were characterized from a chemical, structural and morphological point of view. Table II shows the amount of the heavy metals present in the coating. These data were obtained after a chemical coating dissolution, using atomic absorption spectrophotometry. It is important to note the high manganese content (~6%) retained in the crystal structure after phosphatation in the bath number 3.

Figure 1 shows the diffraction patterns relevant to the four studied materials. Samples A and B show respectively the presence of the Ho phase and of the Ph. Both samples C and D show the presence of the Ho phase partly covered with the peaks of the zinc substrate. It is interesting to note that in spite of the high manganese content observed in sample D, no significant change was shown in the diffraction pattern of its Ho phase. Mn<sup>++</sup> ions are probably substitutional with respect to the Zn<sup>++</sup> ions, nevertheless they don't change the structure as the Fe<sup>++</sup> ions do in the Ph phase.

As far as the morphological characterization, the structures observed are typical of the Ho and Ph phases, already described in the literature [5]. An

interesting result is the reduced dimensions of the crystalline grains observed in the hopeitic structures containing manganese.

The SEM characterization during heating to 180°C showed no substantial transformation of the phosphate crystals as a consequence of the heat treatment.

The dehydration process of the tetrahydrated Ho and Ph crystals was then studied using the thermogravimetric analysis. A remarkable quality of this technique is the possibility of defining, with a very high precision, the crystals transformation temperatures. The thermogravimetric curves of Fig. 2 show, for all the considered samples, a very similar trend. In fact, all the curves present a small weight loss which starts from room temperature and may be attributed to a non-structural water loss. The curves show successively a more pronounced weight loss which finishes almost completely at about 160°C. The samples show such trend, respectively, at: A = 116°C, B = 130°C, C = 110°C, D = 122°C. If we attribute such weight loss to the release of two of the four crystallization water molecules, it follows that the water bond energy, by which crystallization water is bound, is quite different in the two phases (Ho samples A and C, and Ph sample B), and in particular we can note the manganese action (sample D) which in its turn is able to change the crystallization water loss temperature.

Yet the data obtained by thermogravimetric analysis did not allow a precise quantitative interpretation of the observed phenomena as a consequence of our particular experimental condition. In fact, as the phosphates were produced as coatings, it was very difficult to separate them completely from the zinc or iron substrates.

Thus to confirm our results, diffraction measurements were performed on samples, heat treated at temperatures suitably chosen on the basis of the data obtained by thermal analysis.

In Figure 3 the results obtained with the sample B (Ph prevailing phase) are reported; it is interesting to note how the diffraction patterns show no change with respect to that obtained at room temperature (Fig. 1b) for both heat treatments at 65 and 115°C (Fig. 3a, b). After heat treatment at 150°C (Fig. 3c), instead, it is possible to note the total disappearance of the characteristic Ph peaks at  $2\theta = 10.0$  and  $20.2$ , whereas new peaks appear, and those at  $2\theta = 11.3$  and  $22.7$  may be attributed to the bihydrated zinc phosphate, this being indicated in literature as  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

For sample A (Fig. 4a, b, c), only the treatment at 65°C induces no change, whereas already at 115°C it is possible to observe structural modifications concerning the crystal lattice highlighted by a wide

TABLE II Sample description

Sample	Substrate	Bath number	Main crystal	Coating mass (g m <sup>-2</sup> )	Crystal composition wt %			
					Zn	Fe	Ni	Mn
A	steel	1	Hopeite	2.5	38-68	2-5	0.2-0.4	0.8-1
B	steel	2	Phosphophyllite	2.8	28-32	8-13	1-1.5	
C	electrogalvanized	2	Hopeite	3.1	40-42		1-1.5	
D	electrogalvanized	3	Hopeite	3.2	35-38		1-2	4.5-6

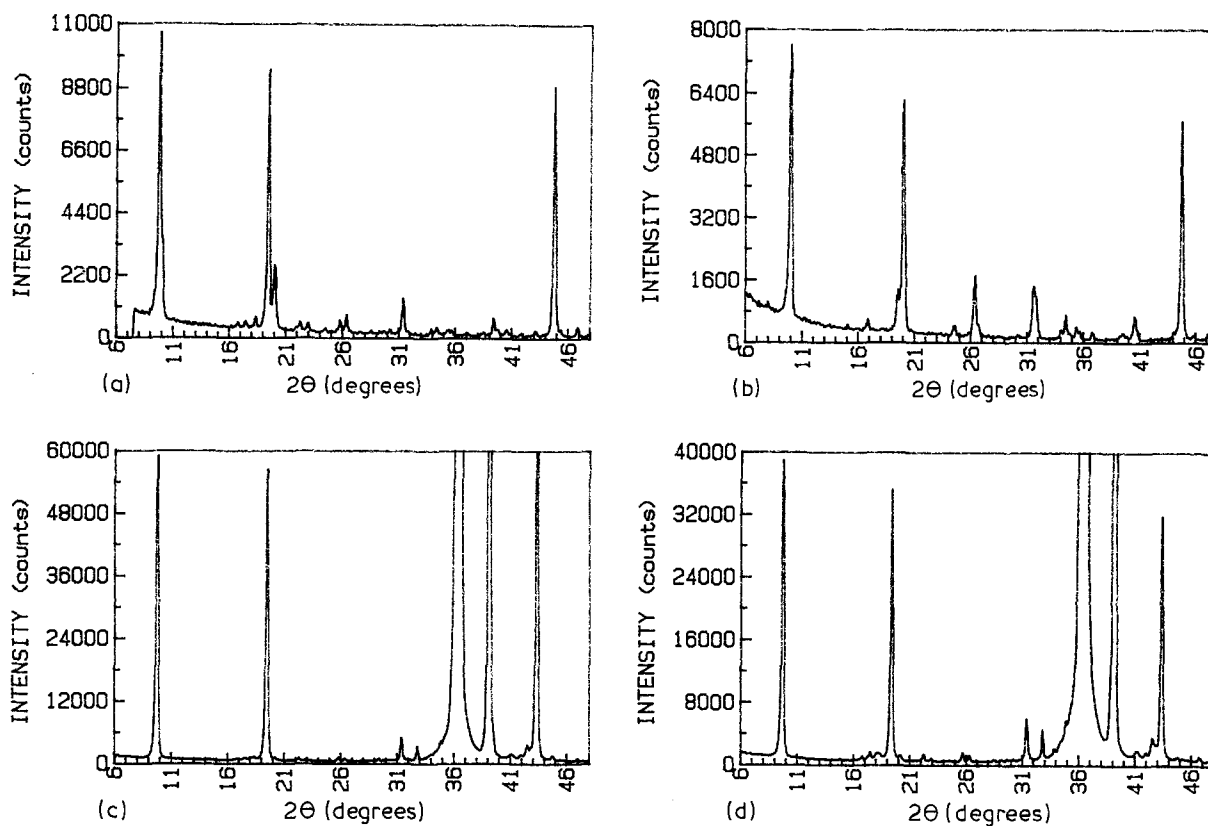


Figure 1 X-ray diffraction pattern of: (a) sample A; (b) sample B; (c) sample C; (d) sample D.

broadening of the Ho peaks at  $2\theta = 9.8$  and  $19.4$ . The subsequent heat treatment at  $150^\circ\text{C}$  leads to the disappearance of these peaks and to the rise of the same peaks related to the bihydrated phase, already observed in the sample B.

Our results agree with FTIR spectroscopy measurements [7], which show that the hopeitic structure seems to lose only one crystallization water species, which may be rapidly released during a progressive heating; on the contrary the Ph structure seems to have three different crystallization water types, each with different bond types, which cause a differential release during the progressive heating.

Figure 5a, b, shows the diffraction patterns of samples C and D after heat treatment at  $150^\circ\text{C}$ . These measurements reveal the unchanged zinc peaks and, for what concerns the phosphate coating, both the materials show the transformation already observed for samples A and B, that is the disappearance of the tetrahydrated Ho phase and the bihydrated phosphate peaks rise at  $2\theta = 11.3$  and  $22.7$ .

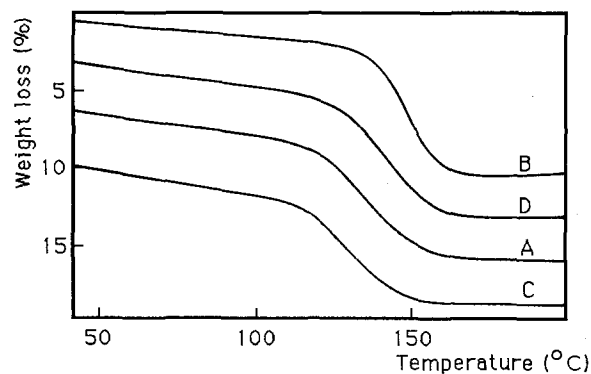


Figure 2 Thermogravimetric curves of the four samples.

So we can conclude that the progressive heat treatment up to  $150^\circ\text{C}$  leads to the dehydration of all our phosphate coatings with a loss of two water molecules; the obtained bihydrated phase appears, from a structural point of view, to be the same for all the considered materials. This affirmation appears reliable for samples A, C and D, which show the same tetrahydrated Ho phase at room temperature, but not for sample B (Ph phase at room temperature). Yet, since a specific definition of the bihydrated Ph phase is not found in the literature, the obtained experimental data induce us to identify the bihydrated Ph phase in the bihydrated Ho phase.

As the baking temperature for the cathoretic process is generally  $180^\circ\text{C}$ , it is likely that these conditions affect the hydrated crystals. Then it is particularly important, for a better protection of a steel sheet, to study the bihydrated phase behaviour when placed in a rehydration condition, as dipped in an aqueous solution or exposed to high humidity atmospheres. Recent studies [6], performed on dehydrated Ho structures dipped in water, showed that in this condition such a phosphate coating reacts leading to zinc oxide (ZnO) and to a tetrahydrated phase. Both these reactions, due to the induced volumetric changes and to the different chemical bonds obtained, are able to produce stresses and bond relaxation at the paint-phosphate interface. This fact noticeably compromises the paint adhesion so that the steel sheet protection fails.

Therefore our study continued, using X-ray diffractometry, in order to characterize the rehydration behaviour of both the manganese modified Ho phase and the Ph phase, comparing it to that, already known, of the pure Ho.

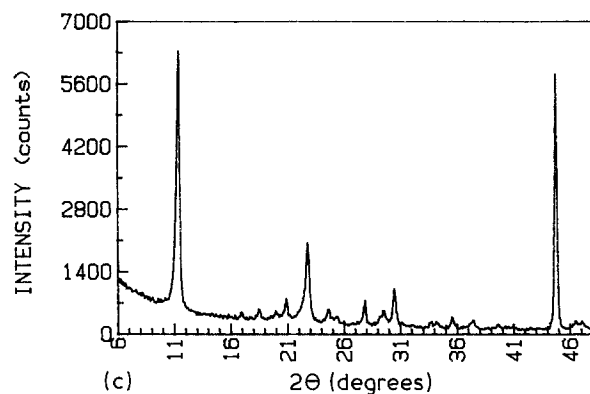
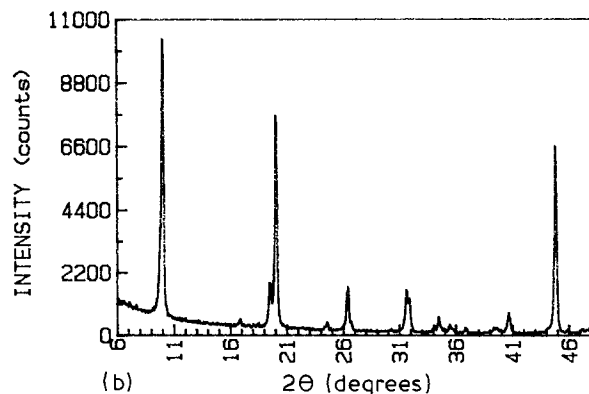
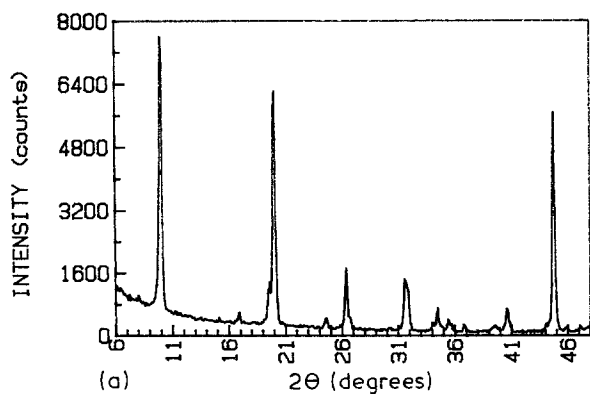


Figure 3 X-ray diffraction pattern of sample B heat treated, for 1.5 h, at different temperatures: (a) 65°C; (b) 115°C; (c) 150°C.

All the samples were heat treated at 160°C for 90 min and then exposed to a rehydration process at room temperature in a humidostatic chamber at 100% r.h. Figure 6 shows the diffraction patterns relevant to the four materials after the rehydration treatment. It is possible to note how the samples A and C show, already after a few hours of treatment (5 h), the rise of the characteristic peaks of the tetrahydrated Ho phase. This phenomenon continues with time, progressively slower, up to the almost complete disap-

pearance of the bihydrated phase. On the contrary no substantial transformations are perceptible in the samples B and D, even after very long treatment times (120 h). These materials were subjected to other rehydration tests at 100% r.h. up to 60°C temperature, but no appreciable change of the bihydrated phase was found. This result clearly points out the structural stability of the bihydrated phases either containing  $Fe^{++}$  ions or a sufficient amount of the  $Mn^{++}$  ions. In this case the phase is no longer able to accept the two water molecules lost during the 160°C heat treatment, so that no structural changes or bond relaxations can happen and the paint adhesion to the metallic substrate may remain very good.

The reversibility of the de-rehydration process in the Ho structure seems to be related to the flexibility of the  $Zn^{++}$  ion coordination state which is able to exist in octahedral or tetrahedral coordination. In the case of Ph phase, instead, the octahedral sites are occupied by  $Fe^{++}$  ions, which have a clear preference for such a coordination sphere with respect to the tetrahedral one. So during dehydration the  $Fe^{++}$  ions are in an unsaturated coordination state and could cause an irreversible structural modification [8].

At this stage of the research, the mechanism by which manganese is also able to avoid the rehydration process can not be explained. Studies are in progress to clarify this important aspect of the problem.

As an example, to emphasize the importance of the obtained results, the behaviour of samples C and D

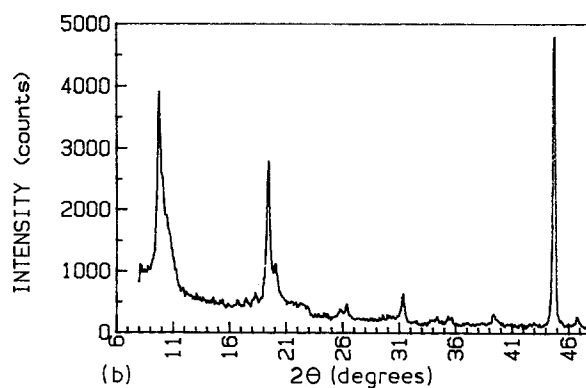
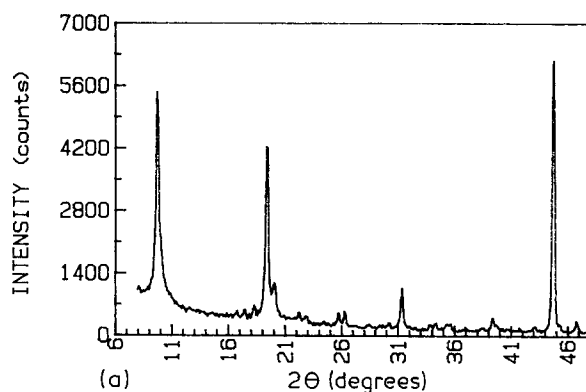
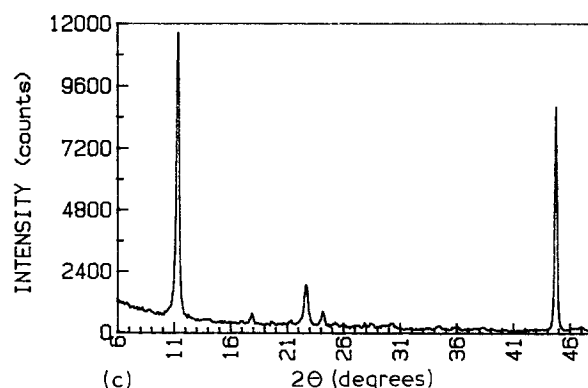


Figure 4 X-ray diffraction pattern of sample A heat treated, for 1.5 h, at different temperatures: (a) 65°C; (b) 115°C; (c) 150°C.



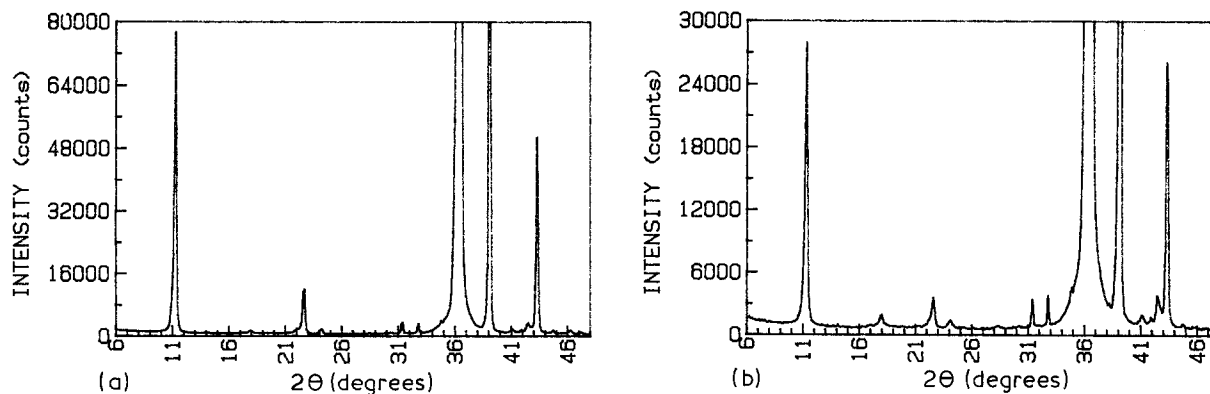


Figure 5 X-ray diffraction pattern after heat treatment for 1.5 h at 150°C: (a) sample C; (b) sample D.

Painted with a cataphoretic coating and then subjected to wet adhesion test and successively to the tape test are shown in Fig. 7. After 240 h it is clear that the paint adhesion of the sample obtained in the manganese rich phosphatation bath is markedly better with respect to that of the samples having only a pure hopeitic phosphate coating.

#### 4. Conclusion

Research was performed with the aim of characterizing the dehydration and the following rehydration behaviour of Ph and Ho crystalline phases present in the phosphate coatings. From a pure morphological point of view no noticeable crystal modifications were observed during a progressive heating to about 200°C.

Yet the thermogravimetric analysis showed that all the considered crystalline species show a dehydration

phenomenon when subjected to heating; all the phases undergo the total loss of two water molecules above 150°C.

The higher the manganese content in the Ho phase, the higher the temperature at which the transformation from tetra to bihydrated phase happens.

The diffraction pattern obtained from the samples after heat treatment at 160°C appears very similar independently from the phosphatation bath used.

Finally X-ray diffraction analysis showed that after exposure in a hydrating environment the pure Ho bihydrated crystals undergo a rehydration process which leads to the tetrahydrated phase and consequently to a decreased paint-phosphate adhesiveness. On the contrary both the bihydrated Ph phase and the bihydrated manganese modified Ho phase reveal the inability to return to the completely hydrated crystal and a consequently improved paint adhesion.

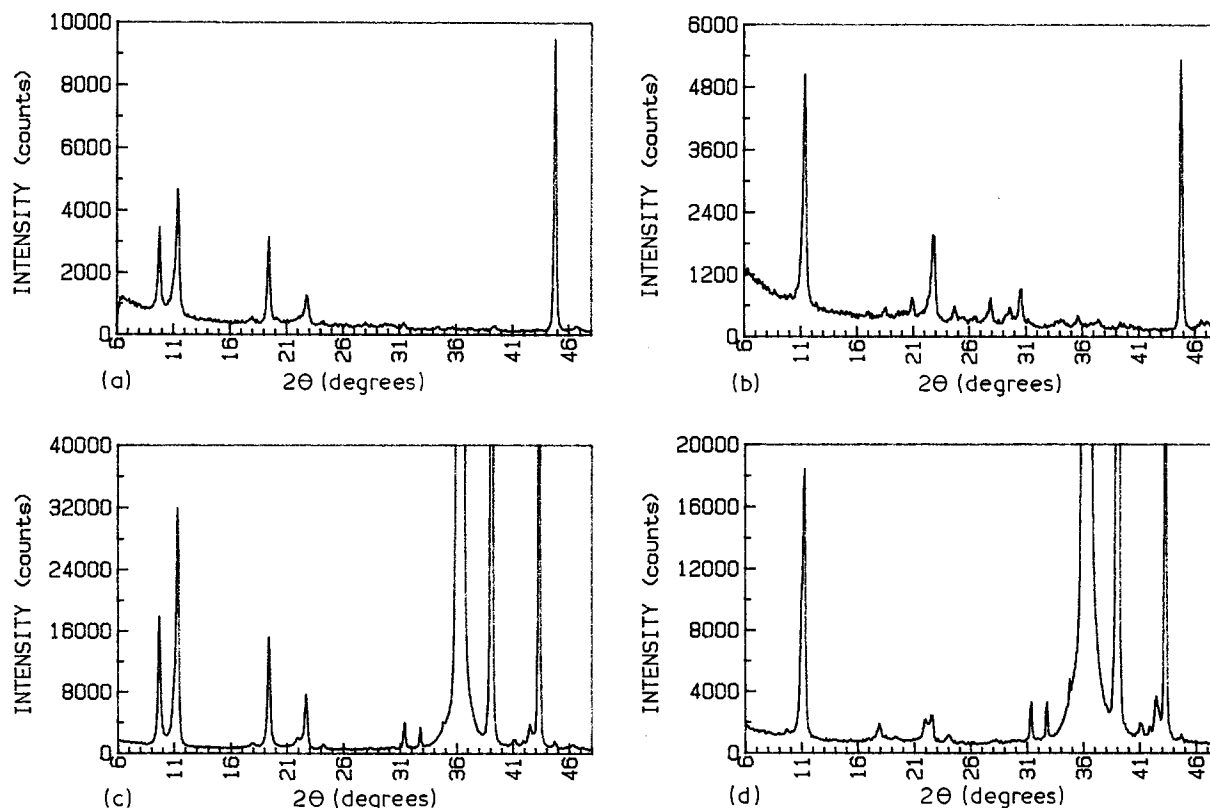


Figure 6 X-ray diffraction pattern after heat treatment at 160°C and subsequent exposure in a humidostatic chamber at 100% r.h.:

(a) sample A; (b) sample B; (c) sample C; (d) sample D.

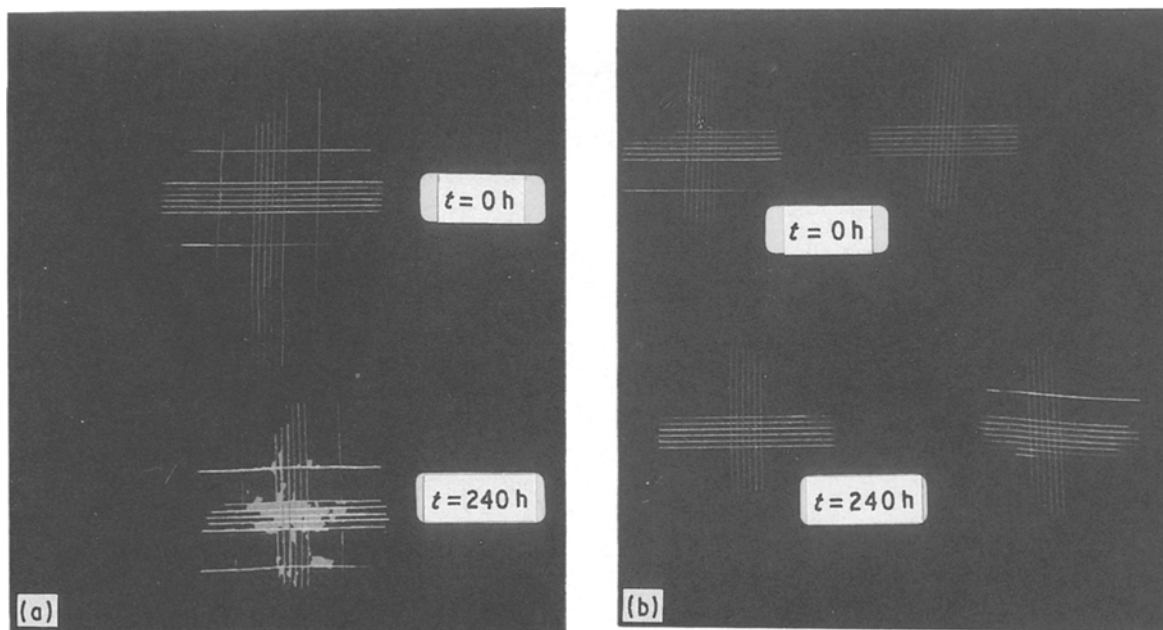


Figure 7 Wet adhesion test after 240 h exposure: (a) sample C; (b) sample D.

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