

# Synthesis and characterization of the aluminium phosphates modified with ammonium, calcium and molybdenum by hydrothermal method

Kinga Łuczka<sup>1\*</sup>, Barbara Grzmil<sup>1</sup>, Bogumił Kic<sup>1</sup>, Krzysztof Kowalczyk<sup>2</sup>

<sup>1</sup>West Pomeranian University of Technology, Szczecin, Institute of Chemical and Environment Engineering, ul. Pułaskiego 10, 70-322 Szczecin, Poland <sup>2</sup>West Pomeranian University of Technology, Szczecin, Polymer Institute, ul. Pułaskiego 10, 70-322 Szczecin, Poland \*Corresponding author: e-mail: kluczka@zut.edu.pl

Synthesis and characterization of the aluminum phosphates modified with ammonium, calcium and molybdenum were conducted. The influence of process parameters (reactive pressure and molar ratios) in the reaction mixture were studied. The contents of the individual components in the products were in the range of: 10.97-17.31 wt% Al, 2.65-13.32 wt% Ca, 0.70-3.11 wt% Mo, 4.36-8.38 wt% NH<sub>3</sub>, and 35.12-50.54 wt% P<sub>2</sub>O<sub>5</sub>. The materials obtained in the experiments were characterized by various physicochemical parameters. The absorption oil number was in the range from 67 to 89 of oil/100 g of product, the surface area was within the range of 4-76 m<sup>2</sup>/g, whereas the average particle size of products reached 282–370 nm. The Tafel tests revealed comparable anticorrosive properties of aluminum phosphates modified with ammonium, calcium, molybdenum in comparison with commercial phosphate.

Keywords: hydrothermal method, anticorrosive pigments, modified aluminum phosphates.

# INTRODUCTION

The aim of pigment mixture development is to enhance the anticorrosion efficiency of non-toxic pigments and shift their efficiency closer to the old, toxic (but very efficient) chromate and lead pigments. Such development is necessary to meet tough environmental norms that are steadily becoming stricter<sup>1, 2, 3</sup>. The latest EU legislation on organic coatings took effect in 2010 and was aimed at reducing volatile organic compounds in paint systems<sup>2</sup>.

Literature reports seem to suggest that the anticorrosion properties of pigments are affected not only by their chemical composition, but also by other factors, including their particle size, oil number, specific surface area and water solubility<sup>4, 5, 6</sup>. Changes in the structure and chemical composition of various materials can be obtained by using different process parameters in their preparation (e.g. substrate molar ratio, the pH of a reaction mixture, reaction time, pressure, temperature) or with microwave radiation<sup>7, 8, 9</sup>. Microwave is an energy source which has found its applications in many scientific research areas. Microwave radiation has shown its capability for fast preparation of size controlled metallic nanostructures on different substrates<sup>10, 11</sup>. Microwave technique attracts more interest because it can generate heat internally inside the sample so the heat can be transferred homogeneously and rapidly. The microwave technique requires far less energy than resistive heating and is less polluting than gas or oil fired heaters and is therefore more environmentally friendly<sup>12</sup>. Moreover, rapid initial heating of the microwave can enhance the kinetics of the reaction due to the formation of high temperature throughout the sample<sup>13</sup>.

The aim of the presented work was to elaborate the preparation process of aluminum phosphates modified with ammonium, calcium and molybdenum by hydrothermal method. Their steel corrosion inhibition efficiency was investigated by means of the potentiodynamic polarization technique. The influence of preparation process parameters on several physicochemical properties of the products such as chemical composition, oil absorption and specific surface area was determined. Based on the Tafel test results the corrosion potential, corrosion current density and corrosion rate for steel immersed in a phosphate extract in an aqueous NaCl solution were calculated and presented.

## EXPERIMENTAL

## Procedure

Studies on the synthesis of aluminum phosphates modified with ammonium, calcium and molybdenum were performed on the basis of the experimental planning and analysis according to a three-level  $3^{(k-p)}$  fractional factorial designs with 9 experiments using the hydrothermal method. The process independent variables were:  $x_1$  – the pressure (1.1 ± 1 MPa),  $x_2$  – the molar ratio of Ca<sup>2+</sup> to PO<sub>4</sub><sup>3-</sup> in the substrates 0.2 ± 0.13 : 1 corresponding to the molar ratios of Al<sup>3+</sup> to Ca<sup>2+</sup> to Mo<sup>6+</sup> to PO<sub>4</sub><sup>3-</sup> in the reaction mixture (0.67 : 0.2 ± 0.13 : 0.2 ± 0.13 : 1).

The aim of the study was to obtain products with the molar ratio of  $(NH_4)_3Al_2(PO_4)_3$  to  $CaMoO_4$  varying in the range of 1 :  $(0.6 \pm 0.4)$ . Therefore, to obtain a product with the molar ratio of  $(NH_4)_3Al_2(PO_4)_3$  to  $CaMoO_4$  equalling 1 : 1, the reactor had to be feed with substrates in the molar ratios corresponding to those in the following reactions:

 $\begin{array}{l} 14Al(OH)_{3} + 21(NH_{4})_{2}HPO_{4} \rightarrow 7(NH_{4})_{3}Al_{2}(PO_{4})_{3} + \\ + 21NH_{4}OH + 21H_{2}O & (1) \\ 7CaCO_{3} + (NH_{4})_{6}Mo_{7}O_{24} + 3H_{2}O \rightarrow 7CaMoO_{4} + \\ + 6NH_{4}OH + 7CO_{2} & (2) \end{array}$ 

During the experiments, it turned out that a competitive reaction involving hydroxylapatite precipitation was also proceeding:

 $3(NH_4)_2HPO_4 + 5CaCO_3 + 4NH_4OH \rightarrow Ca_5(PO_4)_3(OH) + 5(NH_4)_2CO_3 + 3H_2O$ (3)

Multiple dependent variables defining the physicochemical properties of prepared products were as follows: the content of  $Al^{3+}$  (y<sub>1</sub>),  $Ca^{2+}$  (y<sub>2</sub>),  $Mo^{6+}$  (y<sub>3</sub>),  $NH_3$  (y<sub>4</sub>), P<sub>2</sub>O<sub>5</sub> (y<sub>5</sub>), oil absorption number (y<sub>6</sub>), specific surface area S<sub>BET</sub> (y<sub>7</sub>), and average particle size (y<sub>8</sub>).

	Independent variables		Dependent variables							
Phosphate acronym	x <sub>1</sub> x <sub>2</sub>		<b>y</b> 1	<b>y</b> <sub>2</sub>	<b>у</b> 3	<b>y</b> 4	<b>y</b> 5	<b>y</b> 6	<b>y</b> 7	<b>y</b> 8
	[MPa]		[wt%]				[g/100g]	[m²/g]	[nm]	
AACMPH1	0.1	0.07	17.31	3.50	1.07	6.41	43.5	73	76	346
AACMPH2	1.1	0.07	17.31	2.98	0.70	6.51	44.2	75	54	297
AACMPH3	2.1	0.07	15.25	2.65	0.79	8.38	50.54	67	34	343
AACMPH4	0.1	0.2	14.32	8.47	1.21	5.65	40.51	74	55	320
AACMPH5	1.1	0.2	13.49	9.45	1.58	5.78	40.68	75	57	311
AACMPH6	2.1	0.2	13.65	8.95	2.28	5.74	41.16	68	52	370
AACMPH7	0.1	0.33	10.97	13.32	3.11	4.36	35.12	81	51	282
AACMPH8	1.1	0.33	11.57	13.11	3.00	4.98	40.55	89	69	305
AACMPH9	2.1	0.33	11.08	13.09	2.55	5.71	42.44	74	41	310

**Table 1.** Three-level 3<sup>(k-p)</sup> fractional factorial design and physicochemical properties of aluminum phosphates modified with ammonium, calcium and molybdenum obtained hydrothermal conditions

The aim of the performed experiments according to the established plan was to determine the fractional design at 3 levels of the important factors affecting the investigated parameters and to find the right input values enabling to obtain a product with the expected properties<sup>14</sup>. A factorial plan and the results obtained from experiments are summarized in Table 1. Basing on the beginning studies it was take that the constant conditions process were equal to: pH of the reaction was 6 and time reaction was allowed 20 minutes. The total salt concentration amounted to 40 wt%.

## Sample preparation

Reagent grade substrates: (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, CaCO<sub>3</sub>,  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ , an aqueous ammonia (25 wt%) of NH<sub>3</sub>) and amorphous Al(OH)<sub>3</sub> were used. Aluminum hydroxide was precipitated in the reaction of aluminum nitrate with potassium hydroxide at  $pH = 7.5^{15}$ . The molar ratios of Al<sup>+3</sup>: Ca<sup>2+</sup>: Mo<sup>6+</sup>: PO<sub>4</sub><sup>3-</sup> in the reaction mixture amounted to  $0.67 : (0.2 \pm 0.13) : (0.2 \pm 0.13) : 1$ . The constant process parameters were: pH of the reaction equal to 6 and the total salt concentration amounted to 40 wt%. A suspension of amorphous aluminum hydroxide and calcium carbonate was dosed into an ammonium molybdate and ammonium phosphates solution at a constant stirring velocity. The suspension of reactants with an appropriate pH was prepared in a glass reactor and the mixture was transferred into the microwave reactor and treated at a pressure of  $1.1 \pm 1$  MPa (microwave reactor type ERTEC Magnum, output 750 W at a frequency of 2.45 GHz, Ertec Poland), for 20 min. The obtained precipitate was separated from the mother liquor using a vacuous filter, followed by triple washing with distilled water (the weight ratio of the liquid to the solid phase was 3 : 1). Finally, the obtained product was dried for 3 h at 70°C.

Anticorrosive properties of the modified aluminum phosphate for cold rolled steel were investigated by means of the potentiodynamic polarization technique. For comparison purposes, two commercial anticorrosive pigments, i.e. zinc phosphate and zinc aluminum phosphate (FC-M2, FAC) were tested.

#### Sample characterization

The content of aluminum, calcium and molybdenum in the products was determined by ICP-AES analysis (Optima 5300 DV, Perkin Elmer). The phosphates and ammonium contents were determined using a spectrophotometric method<sup>15</sup> and ion selective electrode Orion 11–35 type, respectively<sup>16</sup>. The phase composition of the products was studied with X-ray diffraction analysis (CuKá radiation, X'Pert PRO Philips diffractometer). The oil absorption (grams of oil required to form a homogeneous paste with 100 g of the tested dry pigment) was determined according to PN-EN ISO 787-5 standard<sup>17</sup>. The measurements of Brunauer-Emmett-Teller surface area (S<sub>BET</sub>) of the materials were performed using Micrometrics Quadrasorb SI Quantachrome Instrument. N2 adsorption/desorption measurements were carried out at liquid N<sub>2</sub> temperature. The average particle size of the materials was determined using a laser scanning microscope (VK-9700, Keyence, USA). The phosphate morphology was examined with a scanning electron microscope SU-70 (Hitachi, Japan). The chemical composition of the phosphates was determined using a scanning electron microscope with a cold field emission (HITACHI SU8020, resolving power 1.3 nm), coupled with the energy dispersive X-ray analyzer (EDX – Thermo Scientific).

Tafel experiments in the range from -250 to 500 mV in relation to OCP (scan rate 0.25 mV  $s^{\text{--}1}$ ) for an uncoated steel substrate (SEA 1008/1010, Q-Panels, Q--Lab Europe, England) were performed using DC105 software and FAS2 femtostat (Gamry, USA). As a result, corrosion potential  $(E_{corr})$ , corrosion current density  $(i_{corr})$  and corrosion rate (P) were determined using Echem Analyst software (Gamry). Steel polarization was carried out using electrolytes prepared by shaking a phosphate filler (2.5 g) with 100 g of 3.5 wt% NaCl aqueous solution for 2 h (i.e. twice for 1 h with a 22 h interval). Then, the suspension was centrifuged (4000 rpm, 10 min) and an aqueous extract was carefully decanted. The Tafel tests were made after 20 h of a glass cell filling with an electrolyte (aqueous NaCl solution or phosphate extract). The corrosion inhibition efficiency  $(\eta, \%)$  of phosphate extracts was calculated according to the following equation:

$$\eta = \left[\frac{i_0 - i}{i_0}\right] \times 100 \tag{1}$$

where  $i_0$  and *i* are corrosion current densities registered for steel substrate immersed in a 3.5 wt% NaCl aqueous solution and the aqueous extract of phosphate filler, respectively.

## **RESULTS AND DISCUSSION**

Figure 1 and Table 2 shows the phase composition of the precipitated products, which was determined

Phosphate acronym	Independent variables		Phase c	omposition (peak i	ntensity)	Molar ratio
	<b>X</b> 1 [MPa]	<b>x</b> <sub>2</sub>	(NH <sub>4</sub> ) <sub>3</sub> Al <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	CaMoO <sub>4</sub>	Al <sup>3+</sup> :Ca <sup>2+</sup> :Mo <sup>6+</sup> :NH <sub>4</sub> <sup>+</sup> :PO <sub>4</sub> <sup>3-</sup>
AACMPH1	0.1		***	**	-	1.0 : 0.1 : 0.02 : 0.62 : 1
AACMPH2	1.1	0.07	***	**	-	1.0 : 0.1 : 0.01 : 0.62 : 1
AACMPH3	2.1		***	**	-	0.8 : 0.1 : 0.01 : 0.69 : 1
AACMPH4	0.1	0.2	**	**	**	0.9 : 0.4 : 0.02 : 0.58 : 1
AACMPH5	1.1		**	**	**	0.9 : 0.4 : 0.03 : 0.59 : 1
AACMPH6	2.1		**	**	**	0.9 : 0.4 : 0.04 : 0.58 : 1
AACMPH7	0.1	0.33	*	**	***	0.8 : 0.7 : 0.07 : 0.52 : 1
AACMPH8	1.1		*	**	***	0.8 : 0.6 : 0.05 : 0.51 : 1
AACMPH9	2.1		*	***	***	0.7 : 0.5 : 0.04 : 0.56 : 1

Table 2. The phase composition and molar ratio of the components in obtained products



Figure 1. X-ray diffraction patterns of products obtained (AACMPH3 and AACMPH9) [■] (NH<sub>4</sub>)<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>;
[●] CaMoO<sub>4</sub>; [▲] Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)

using XRD analysis.  $(NH_4)_3Al_2(PO_4)_3$ ,  $CaMoO_4$  and  $Ca_5(PO_4)_3(OH)$ , crystalline compounds, were identified. Their ratio varied depending on the composition of substrate mixture. For the lowest molar ratio of  $Al^{3+}$ :  $Ca^{2+}$  in the initial mixture equalling 2 ( $Al^{3+}$ :  $Ca^{2+}$  0.67 : 0.33), the content of  $CaMoO_4$  in the products was the highest. However, the higher was the molar ratio of reagents containing aluminum and calcium, the higher was the content of  $(NH_4)_3Al_2(PO_4)_3$  in the precipitated solid phases.

The chemical composition of the obtained materials mainly depended on the substrate molar ration which determined the phase composition. Products with a higher molar ratio between  $(NH_4)_3Al_2(PO_4)_3$  and  $CaMoO_4$  contained more aluminum and ammonia and less calcium and molybdenum. Therefore, products in each group had similar chemical and phase compositions: I – AACMPH1-3, II – AACMPH4-6, III – AACMPH7-9. Similarly, products from different groups had different chemical and phase compositions (Tables 1 and 2). The precipitated products were in the range of: 10.97–17.31 wt% Al, 2.65–13.32 wt% Ca, 0.70–3.11 wt% Mo, 4.36–8.38 wt% NH<sub>3</sub>, and 35.12–50.54 wt% P<sub>2</sub>O<sub>5</sub> (Table 1).

A statistical analysis, focused on determining process parameters that had a significant influence on the physicochemical properties of the obtained phosphates, was conducted to assess the effects of changes in input values  $y_{1-8}$  for the extremum input values  $x_{1,2}$ . Pareto charts were drawn to illustrate the trends (Fig. 2). To confirm the assessment significance of obtained effects, Anova analysis was performed (Table 3).

The molar ratio of  $Ca^{2+}$  to  $PO_4^{3-}$  in substrates  $(x_2)$  was found to have a statistically significant effect on aluminum content  $(y_1)$  in the products. Bearing in mind that (x2(L), effect-5.42) has a negative number (Table 3), it was fair to think that a lower values of  $x_2$  would result in the increase of the dependent variable  $y_1$ .

Therefore, aluminum phosphates modified with ammonium, calcium and molybdenum with a higher content of aluminum (the average content of 16.6 wt% Al) were to be precipitated from the reaction mixture with the  $Al^{3+}$ :  $Ca^{2+}$ :  $Mo^{6+}$ :  $PO_4^{3-}$  molar ratio of 0.67 : 0.07 : 0.07 : 1.

The molar ratio of reagents  $(x_2)$  was found to have the highest statistic effect on calcium content  $(y_2)$  in the products. The positive effect  $(x_2(L), effect 10.13)$  of this influence seems to indicate the increase of  $y_2$  values, starting from approximately 3 wt% Ca to about 13 wt% Ca along with the increase of  $x_2$  from 0.07 : 1 to 0.33 : 1 (Table 3). The dependent variable  $y_3$  denoting molybdenum content in the obtained phosphates, also depended on the molar ratio of Ca<sup>2+</sup> : PO<sub>4</sub><sup>3-</sup> in the reaction mixture. The statistical analysis demonstrated the positive sign of the effect ( $x_2(L)$ , effect 2.03) which translated into the increase of molybdenum content in the products (from approximately 0.8 wt% to about 3 wt%) along with the increase of the independent variable (Table 3).

The content of ammonium groups (the dependent variable  $y_4$ ) in the obtained products also depended on the Ca<sup>2+</sup> : PO<sub>4</sub><sup>3-</sup> ratio in the reaction mixture (x<sub>2</sub>(L), effect -2.08). It was found that the less calcium (and at the same time molybdenum) was introduced into the reaction mixture, the higher was the content of nitrogen in the products. It increased from approximately 5 wt% NH<sub>3</sub> to about 7 wt% NH<sub>3</sub>.

It was demonstrated that another dependent variable  $y_6$ , i.e. the content of phosphates in the products was affected only by the molar ratio of the substrates. Following the analysis of effect assessment ( $x_2(L)$  –6.71), the highest content of phosphates in the obtained products was observed for the Ca<sup>2+</sup> : PO<sub>4</sub><sup>3-</sup> molar ratio of 0.07 : 1 in the reaction mixture.

It was statistically demonstrated that the above discussed input variables correlated with the chemical composition of the products were not affected by the pressure of the process (0.1–2.1 MPa).





Standardized effect estimate (absolute value)



Standardized effect estimate (absolute value)



Standardized effect estimate (absolute value)

Figure 2. Pareto charts of standardized  $y_{1-8}$ 



Pareto charts of standardized effects for y<sub>4</sub>



Standardized effect estimate (absolute value)



Pareto charts of standardized effects for y<sub>8</sub>



Standardized effect estimate (absolute value)

Verification         Lower Bound         Upper Bound           Vir         yi           Meanloonstant         13.88333         0.236741         58.64356         0.000001         13.22603         14.54063           (1)X1(L)         -0.87333         0.579895         -1.56662         0.206528         -2.4335         0.73671           (2)X2(L)         -5.4667         0.579895         -9.34078         0.600731         -7.02671         -3.80662           X2(Q)         -0.09500         0.502203         -0.18917         0.589173         -1.48934         1.29934           Meaniconstant         8.39111         0.144279         58.15881         0.000001         7.90553         8.7166           (1)X1(L)         -0.21677         0.335411         26.66282         0.000009         9.15044         11.12289           X2(Q)         0.85803         0.306663         2.77933         0.049822         0.0017         1.70660           Weanvonstant         18.10000         0.151021         11.188967         0.000278         1.38070         2.22302           (1)X1(L)         0.076687         0.308925         0.20726         0.845386         -0.96447         0.91444           (2)X2(L)         2.033333         0.36	Independent	Effect	Std. Error	t[4]	p	95% Confidence Interval for Difference				
y         y           BeanConstant         13.8333         0.238741         58.64395         0.000011         13.22803         14.54083           (1)X1(L)         -0.87333         0.578955         -5.34078         0.000731         -7.02871         -3.36062           X2(Q)         -5.04667         0.579895         -5.34078         0.000731         -1.48934         1.28994           X2(Q)         -0.09500         0.502033         -0.18817         0.489173         -1.48934         1.28994           MeanConstant         8.39111         0.14279         58.15881         0.000011         7.99053         8.79169           (1)X1(L)         -0.21677         0.353411         -0.57663         0.598778         -1.16289         0.77986           X1(Q)         0.190383         0.306063         2.7993         0.49822         0.0107         1.70606           X2(Q)         0.85083         0.306063         2.7993         0.49822         0.0107         1.70807           X1(Q)         0.85083         0.306084         -0.23411         0.82598         -0.95441         1.103743           X1(Q)         -0.075000         0.320344         -0.23411         0.825985         -0.96447         0.814474	variables					Lower Bound	Upper Bound			
Mean/constant         13.88333         0.238741         98.84360         0.00001         13.2203         14.54063           (1)X1(L)         -0.33600         0.502203         0.71684         0.513101         -2.48338         0.73741           (2)X2(L)         -6.41667         0.579895         -9.34078         0.000731         -7.0271         -3.8062           (2)X2(L)         -0.41667         0.579895         -9.34078         0.000701         -7.0271         -3.8062           (1)X1(L)         -0.20167         0.353411         -0.57063         0.598778         -1.16289         0.077856           (1)X1(L)         -0.20167         0.353411         2.866826         0.000009         9.15044         11.11289           (2)X2(L)         10.18633         0.30663         2.77993         0.04922         0.0017         1.03663           (1)X1(L)         0.07667         0.369825         0.20725         0.845383         -0.96447         1.03443           X1(Q)         -0.076667         0.369825         5.49661         0.00026         1.9067         1.90774           X1(Q)         -0.16000         0.320344         -0.24141         0.82236         -0.94474           X1(Q)         -0.16000         0.320344				<b>y</b> 1						
(1)X1(L)         -0.67333         0.57995         -1.5062         0.208268         -2.4338         0.7371           X1(Q)         0.36000         0.562203         0.71864         0.513101         -1.0434         1.75434           X2(Q)         -0.09500         0.502203         0.71864         0.560013         -1.4934         1.29334           X2(Q)         -0.09500         0.502203         -0.18917         0.600731         -7.0267         -3.30662           X1(L)         -0.20167         0.353411         -0.57083         0.598978         -1.1829         0.77956           X1(Q)         0.16083         0.30663         0.56644         0.568386         -0.66693         1.30601           X1(Q)         0.85083         0.30663         0.50275         0.049822         0.01007         1.70060           X2(Q)         0.85083         0.30663         0.20275         0.445935         -0.96441         1.10373           X1(Q)         -0.075600         0.320364         -0.56186         0.604202         -1.06947         0.34972           X1(Q)         -0.18000         0.320364         -0.56186         0.604202         -1.06947         0.347427           X1(Q)         -0.28500         0.400666	Mean/constant	13.88333	0.236741	58.64356	0.000001	13.22603	14.54063			
X1(Ω)         0.36000         0.002203         0.71684         0.01011         I=1.0344         1.75434           (2)X2(L)         -5.41667         0.579995         -9.34078         0.000731         -7.02671         3.30662           X2(Ω)         -0.09500         0.02023         -0.18917         0.6589173         -1.48934         1.29934           Wean/constant         8.39111         0.14279         58.15811         0.00001         7.99053         8.79169           (1)X1(L)         -0.20167         0.353411         2.65628         0.00001         7.99053         8.79169           X1(Ω)         0.1803         0.306063         2.77993         0.049822         0.00107         1.10260           X1(Ω)         0.056083         0.306063         2.77993         0.049822         0.0017         1.30070         2.225020           (1)X1(L)         0.076667         0.369925         0.20275         0.448938         -0.09641         1.111203           X1(Ω)         0.076667         0.369925         5.49661         0.00228         -0.09441         1.010743           X1(Ω)         0.376667         0.482649         2.45866         0.069927         -0.14747         2.421187           X1(Ω)         0.38	(1)X1(L)	-0.87333	0.579895	-1.50602	0.206526	-2.48338	0.73671			
(2)X2(1)         -5.41667         0.75985         -9.4078         0.00971         -7.40271         -7.48934           X2(0)         -0.09500         0.502203         -0.18917         0.589173         -1.48934         1.29934           Mean'constant         6.39111         0.142279         58.15861         0.000001         7.9905         8.79169           (1)X1(1)         -0.20167         0.353411         -0.57063         0.589378         -1.18289         0.79956           X2(0)         0.180633         0.590644         0.588338         -0.68033         1.03060           (2)X2(1)         10.13167         0.353411         2.86828         0.00009         9.15444         111289           X2(0)         0.85663         0.306063         2.77993         0.048822         0.00107         1.229301           (1)X1(1)         0.076667         0.369925         0.20725         0.484938         -0.95441         1.103743           X1(0)         -0.075000         0.320364         -0.23411         0.826355         -0.96447         0.814474           (2)X2(1)         -0.26833         0.462649         2.45866         0.069302         -1.06947         0.70947           Mean'constant         5.94667         0.188876 </td <td>X1(Q)</td> <td>0.36000</td> <td>0.502203</td> <td>0.71684</td> <td>0.513101</td> <td>-1.03434</td> <td>1.75434</td>	X1(Q)	0.36000	0.502203	0.71684	0.513101	-1.03434	1.75434			
X2(Q)         -0.08500         0.62203         -0.18917         0.869173         -1.48934         1.29934           Wean(constant         8.39111         0.144279         58.15881         0.000001         7.99053         8.79169           (1)X1(1)         -0.2167         0.335411         2-0.67063         0.58978         -1.18289         0.77585           X1(Q)         0.16093         0.306063         0.56084         0.5608389         -0.66893         1.03090           (2)X2(L)         10.13167         0.353411         28.66826         0.00009         9.15044         11.11289           X2(Q)         0.86803         0.36063         2.77993         0.404822         0.0007         2.22302           (1)X1(L)         0.076667         0.369925         0.20215         0.845938         -0.96444         0.814474           (2)X2(L)         2.03333         0.369925         5.49661         0.000248         1.00627         3.6647107           X1(Q)         -0.168000         0.320344         -0.58166         0.604202         -1.06977         0.70474           X2(Q)         -0.38060         0.462649         2.45686         0.060227         -0.44785         2.42187           X1(Q)         -0.28500	(2)X2(L)	-5.41667	0.579895	-9.34078	0.000731	-7.02671	-3.80662			
yz           Mean/constant         8.39111         0.144279         58.15881         0.00001         7.9905         8.79166           (1)X1(L)         -0.20167         0.353411         -0.57063         0.590778         -1.18280         0.77356           X1(0)         0.18083         0.300063         0.590844         0.568338         -0.66893         1.10300           (2)X2 (L)         10.13167         0.353411         28.66826         0.000009         9.15644         11.11289           Mean/constant         1.810000         0.151021         11.98607         0.00278         1.39070         2.22332           (1)X1(L)         0.076667         0.369925         0.20725         0.845938         -0.96447         0.81447           X1(Q)         -0.075000         0.320384         -0.283411         0.82335         -0.96447         0.81447           X1(Q)         -0.180000         0.320384         -0.58186         0.604202         -1.06947         0.709474           Wean/constant         5.94667         0.18876         31.48453         0.00000         5.4225         6.471070           (1)X1(L)         1.13667         0.462649         2.456866         0.069927         -0.14785         2.421187 <tr< td=""><td>X2(Q)</td><td>-0.09500</td><td>0.502203</td><td>-0.18917</td><td>0.859173</td><td>-1.48934</td><td>1.29934</td></tr<>	X2(Q)	-0.09500	0.502203	-0.18917	0.859173	-1.48934	1.29934			
Mean/constant         8.39111         0.144279         58.15881         0.00001         7.99053         8.79169           (1)X1(L)         -0.20167         0.353411         -0.57083         0.598778         -1.18289         0.77956           (1)X1(L)         10.13167         0.353411         28.66826         0.00009         9.15044         11.11289           X2(Q)         0.85083         0.306063         2.77993         0.049822         0.00107         1.70960           X2(Q)         0.67667         0.36925         0.20725         0.455338         -0.35641         1.03743           X1(Q)         -0.076600         0.320344         -0.23411         0.826395         -0.98447         0.814474           (2)X2(L)         2.03333         0.39925         5.49661         0.000340         1.00624         3.06010           X2(Q)         -0.18000         0.32034         -0.5616         0.604202         -0.64768         2.421187           X1(Q)         -0.18000         0.32034         -0.64653         0.00000         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45086         0.000092         -0.44768         2.421187           X1(Q)         -0.28500	у <sub>2</sub>									
(1)X1(1)         -0.2167         0.353411         -0.57063         0.58978         -1.1828         0.77956           X1(0)         0.18083         0.306063         0.59084         0.58038         -0.66833         1.03060           X2(0)         0.13167         0.353411         28.66826         0.00009         9.15644         11.1128           X2(0)         0.85983         0.306063         2.77933         0.049822         0.00107         1.22302           (1)X1(1)         0.076667         0.369925         0.20725         0.845938         -0.95041         1.103743           X1(0)         -0.075000         0.320364         -0.23411         0.826395         -0.96447         0.814474           X2(2)         -0.18000         0.320364         -0.55186         0.604202         -1.06847         0.769474           X2(2)         -0.18000         0.320364         -0.55186         0.604202         -1.06847         0.769474           X1(1)         1.13667         0.482649         2.45866         0.609927         -0.4785         2.421167           X1(0)         -0.33500         0.400666         -0.3311         0.456132         -1.4743         0.77927           X1(0)         -0.33503         1.844886 </td <td>Mean/constant</td> <td>8.39111</td> <td>0.144279</td> <td>58.15881</td> <td>0.000001</td> <td>7.99053</td> <td>8.79169</td>	Mean/constant	8.39111	0.144279	58.15881	0.000001	7.99053	8.79169			
X1(0)         0.18083         0.306063         0.59084         0.586398        0.68833         1.03060           (2)X2 (L)         10.13167         0.353411         28.6826         0.00009         9.15044         11.11289           X2(0)         0.35063         0.306063         2.77933         0.049822         0.0017         1.70060           V         y         v         v         v         v         v         v           Mean/constant         1.810000         0.151021         11.98507         0.00278         1.39070         2.229302           (1)X1(L)         0.076667         0.389925         0.49661         0.005340         -0.95041         1.103743           X2(Q)         -0.180000         0.320364         -0.23411         0.826395         -0.96447         0.814474           X2(Q)         -0.180000         0.320364         -0.56186         0.060927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.516171         -1.39743         0.827427           X2(Q)         -0.33500         0.400666         -0.39151         0.45613         -0.2299         10.23662           X1(Q)         -0.28633         0.462649	(1)X1(L)	-0.20167	0.353411	-0.57063	0.598778	-1.18289	0.77956			
(2)X2 (L)         10.13167         0.338411         28.682/6         0.000009         9.15044         11.1128           X2(Q)         0.85083         0.306063         2.77933         0.049822         0.00107         1.70060           Mean/constant         1.810000         0.151021         11.98507         0.000278         1.39070         2.229302           (1)X1(L)         0.076667         0.369825         0.20725         0.845938         -0.95041         1.103743           X1(Q)         -0.075000         0.320364         -0.28411         0.862595         -0.96447         0.814474           (2)X2(L)         2.033333         0.369925         5.49661         0.0603202         -1.06947         0709474           X2(Q)         -0.180000         0.320364         -0.28410         0.80000         5.42226         6.471070           (1)X1(L)         1.13667         0.482649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28330         0.462649         4.450305         0.010797         -3.36785         -0.798813           X2(Q)         -0.33500         0.400666         -0.33611         0.450132         -1.44743         0.777427           Mean/constant         4	X1(Q)	0.18083	0.306063	0.59084	0.586398	-0.66893	1.03060			
X2(Q)         0.85083         0.306063         2.77993         0.049822         0.00107         1.70060           y           Wean/constant         1.810000         0.151021         11.98507         0.000278         1.39070         2.229302           (1)X1(L)         0.076667         0.369925         0.20725         0.845938         -0.96447         0.814474           (2)X2(L)         2.03333         0.369925         5.49661         0.0005340         1.00626         3.060410           X2(Q)         -0.180000         0.320364         -0.56186         0.609202         -1.06947         0709474           Wean/constant         5.94667         0.188678         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.7132         0.516171         -1.39743         0.827427           (2)X2(L)         -2.03330         0.462649         4.55305         0.010797         -3.36765         -0.798613           X2(Q)         -0.33500         0.406666         -0.83611         0.450132         -1.44743         0.777427	(2)X2 (L)	10.13167	0.353411	28.66826	0.000009	9.15044	11.11289			
ys         ys           Mean/constant         1.810000         0.151021         11.98907         0.000278         1.39070         2.229302           (1)X1(L)         0.076667         0.369925         0.20725         0.845938        0.95041         1.103743           X1(Q)         -0.075000         0.320364         -0.23411         0.826395         -0.96447         0.814474           (2)X2(L)         2.033333         0.369925         5.49661         0.005340         1.00626         3.060410           X2(Q)         -0.180000         0.320364         -0.66186         0.604202         -1.06947         0709474           X2(Q)         -0.180000         0.320364         -0.56186         0.60927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.518171         -1.37423         0.827427           (2)X2(L)         -2.08333         0.462649         4.50305         0.010797         -3.36785         -0.798613           X2(Q)         -0.33500         0.406666         -0.71132         0.565718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049	X2(Q)	0.85083	0.306063	2.77993	0.049822	0.00107	1.70060			
Mean/constant         1.810000         0.151021         11.98507         0.000278         1.39070         2.229302           (1)X1(L)         0.076667         0.369925         0.20725         0.844938         -0.95041         1.103743           X1(Q)         -0.075000         0.320364         -0.23411         0.828395         -0.96447         0.814474           X2(Q)         -0.180000         0.320364         -0.56186         0.604202         -1.06947         0709474           Wean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.33611         0.450132         -1.44743         0.827427           (2)X2(L)         -2.08333         0.462649         2.45686         0.000001         39.9413         44.21426           (1)X1(L)         -0.3500         0.400666         -0.33611         0.460132         -1.44743         0.779427           V         -0.30303         1.88486         2.65445         0.056718         -0.2299         10.23662           X1(Q)         -0.4016				<b>y</b> 3						
(1)X1(L)         0.076667         0.369925         0.20725         0.845938         -0.95041         1.103743           X1(Q)         -0.075000         0.320364         -0.23411         0.820395         -0.96647         0.814474           (2)X2(L)         2.033333         0.369925         5.49661         0.005340         1.00626         3.060410           X2(Q)         -0.160000         0.320364         -0.56186         0.604202         -1.06947         0709474           Y*           Mean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.8611         0.450132         -1.44743         0.777427           X2(Q)         -0.33500         0.400666         0.08611         0.450132         -1.44743         0.777427           Mean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.0333         1.84886         -3.55990         0.023588         -11.9433         -1.47672 <td>Mean/constant</td> <td>1.810000</td> <td>0.151021</td> <td>11.98507</td> <td>0,000278</td> <td>1.39070</td> <td>2.229302</td>	Mean/constant	1.810000	0.151021	11.98507	0,000278	1.39070	2.229302			
X1(Q)         −0.075000         0.320364         −0.23411         0.826395         −0.96447         0.814474           (2)X2(L)         2.033333         0.369925         5.49661         0.005340         1.06926         3.060410           X2(Q)         −0.180000         0.320364         −0.66186         0.604202         −1.06947         0709474           Mean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         −0.14786         2.421187           X1(Q)         −0.28500         0.400666         -0.71132         0.516171         −1.39743         0.827427           X1(Q)         −0.33500         0.400666         -0.83611         0.450132         −1.44743         0.777427           Wean/constant         42.07778         0.769502         54.66186         0.000001         39.9413         44.21426           (1)X1(L)         5.0333         1.884886         2.65445         0.056718         −0.2299         10.23662           X2(Q)         −1.94167         1.832359         −1.24607         0.817743         −4.9333         4.13049           (2)X2(L)         −6.	(1)X1(L)	0.076667	0.369925	0.20725	0,845938	-0.95041	1.103743			
(2)X2(L)         2.033333         0.369925         5.49661         0.005340         1.00626         3.060410           X2(Q)         -0.180000         0.320364         -0.66186         0.604202         -1.06947         0709474           Mean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14765         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.516171         -1.39743         0.827427           X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           X2(Q)         -0.30167         1.632359         -0.24607         0.817743         -4.9338         41.3049           (J)X2(L)         -6.71000         1.884866         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Mean/constant         75.11	X1(Q)	-0.075000	0.320364	-0.23411	0,826395	-0.96447	0.814474			
X2(Q)         -0.180000         0.320364         -0.56186         0.604202         -1.06947         0709474           Wean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (I)X1(L)         1.13667         0.482649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.516171         -1.39743         0.827427           (I)X1(L)         -0.33500         0.462649         4.50305         0.010797         -3.36785         -0.798813           X2(Q)         -0.33500         0.460666         -0.83611         0.450132         -1.44743         0.777427           Mean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21266           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (I)X1(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Wean/constant	(2)X2(L)	2.033333	0.369925	5.49661	0,005340	1.00626	3.060410			
y         y           Mean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.516171         -1.39743         0.827427           (2)X2(L)         -2.08333         0.462649         4.50305         0.010797         -3.36785         -0.798813           X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           Wean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884886         2.85445         0.056718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -0.24607         0.817743         -4.9338         1.407672	X2(Q)	-0.180000	0.320364	-0.56186	0.604202	-1.06947	0709474			
Mean/constant         5.94667         0.188876         31.48453         0.000006         5.42226         6.471070           (1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.516171         -1.39743         0.827427           (2)X2(L)         -2.08333         0.462649         4.50305         0.010797         -3.36785         -0.798813           X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           ys           Mean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.0023588         -11.9433         -1.47672           X2(Q)         -1.4167         1.632359         -0.24607         0.817743         -4.9338         4.13049     <		•	•	y4						
(1)X1(L)         1.13667         0.462649         2.45686         0.069927         -0.14785         2.421187           X1(Q)         -0.28500         0.400666         -0.71132         0.516171         -1.39743         0.827427           (2)X2(L)         -2.08333         0.462649         4.50305         0.010797         -3.36785         -0.798813           X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           Mean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884866         2.65445         0.056718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         +1.3049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Valeat         Vs         -         -         -4.9333         1.476797         -0.26879         -0.915103         2.1828         11.48382 </td <td>Mean/constant</td> <td>5.94667</td> <td>0.188876</td> <td>31.48453</td> <td>0.000006</td> <td>5.42226</td> <td>6.471070</td>	Mean/constant	5.94667	0.188876	31.48453	0.000006	5.42226	6.471070			
X1(Q)         −0.28500         0.400666         −0.71132         0.516171         −1.39743         0.827427           (2)X2(L)         −2.08333         0.462649         4.50305         0.010797         −3.36785         −0.798813           X2(Q)         −0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           Wash         Ws         Vs         Vs         Vs         Vs         Vs           Mean/constant         42.07778         0.769502         54.66186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884886         -3.55990         0.023588         −11.9433         −1.47672           X2(Q)         −1.94167         1.632359         −1.18948         0.300029         −6.4738         2.59049           Vs         Vs         Vs         Vs         Vs         Vs         Vs           Mean/constant         75.1111         0.789593         95.12639         0.000000         72.9189         77.30337           (1)X1(L)         −6.33333         1.934099         −3.27456         0.036657         −11.7033         −0.96341           X1(Q)         6.83333         1.674979         4.07965	(1)X1(L)	1.13667	0.462649	2.45686	0.069927	-0.14785	2.421187			
(2)X2(L)         -2.08333         0.462649         -4.50305         0.010797         -3.36785         -0.798813           X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           ys           Mean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884886         2.65445         0.056718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Wean/constant         75.1111         0.789593         95.16239         0.000000         72.9189         77.30337           (1)X1(L)         -6.33333         1.674979         4.07965         0.015103         2.1828         11.48382           (2)X2(L)         9.66667         1.934099         4.99802         0.007501         4.2967         15.03659 <td>X1(Q)</td> <td>-0.28500</td> <td>0.400666</td> <td>-0.71132</td> <td>0.516171</td> <td>-1.39743</td> <td>0.827427</td>	X1(Q)	-0.28500	0.400666	-0.71132	0.516171	-1.39743	0.827427			
X2(Q)         -0.33500         0.400666         -0.83611         0.450132         -1.44743         0.777427           Wean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884886         2.65445         0.056718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           y6	(2)X2(L)	-2.08333	0.462649	-4.50305	0.010797	-3.36785	-0.798813			
ys           Mean/constant         42.07778         0.769502         54.68186         0.000001         39.9413         44.21426           (1)X1(L)         5.00333         1.884886         2.65445         0.056718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.9167         1.632359         -1.18948         0.300029         -6.4738         2.59049           ////////////////////////////////////	X2(Q)	-0.33500	0.400666	-0.83611	0.450132	-1.44743	0.777427			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<b>y</b> 5									
(1)X1(L)         5.00333         1.884886         2.65445         0.056718         -0.2299         10.23662           X1(Q)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Vs           Mean/constant         75.1111         0.789593         95.12639         0.000000         72.9189         77.30337           (1)X1(L)         -6.33333         1.934099         -3.27456         0.030657         -11.7033         -0.96341           X1(Q)         6.83333         1.674979         4.07965         0.015103         2.1828         11.48382           (2)X2(L)         9.66667         1.934099         4.99802         0.007501         4.2967         15.03659           X2(Q)         -4.1667         1.674979         -2.48759         0.067659         -8.8172         0.48382           (1)X1(L)         9.66667         1.934094         12.79333         0.000215         42.5418         66.12490	Mean/constant	42.07778	0.769502	54.68186	0.000001	39.9413	44.21426			
X1(Ω)         -0.40167         1.632359         -0.24607         0.817743         -4.9338         4.13049           (2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Vs         Vs         Vs         Vs         Vs         Vs         Vs           Mean/constant         75.1111         0.789593         95.12639         0.000000         72.9189         77.30337           (1)X1(L)         -6.33333         1.934099         -3.27456         0.030657         -11.7033         -0.96341           X1(Q)         6.83333         1.674979         4.07965         0.015103         2.1828         11.48382           (2)X2(L)         9.66667         1.934099         4.99802         0.007501         4.2967         15.03659           X2(Q)         -4.1667         1.674979         -2.48759         0.067659         -8.8172         0.48382           (2)X2(L)         9.66667         1.934099         -1.76231         0.152804         -47.2167         10.55000           X1(Q)         6.43333         1.040299         -1.76	(1)X1(L)	5.00333	1.884886	2.65445	0.056718	-0.2299	10.23662			
(2)X2(L)         -6.71000         1.884886         -3.55990         0.023588         -11.9433         -1.47672           X2(Q)         -1.94167         1.632359         -1.18948         0.300029         -6.4738         2.59049           Vs         Vs         Vs         Vs         Vs         Vs         Vs           Mean/constant         75.1111         0.789593         95.12639         0.000000         72.9189         77.30337           (1)X1(L)         -6.33333         1.934099         -3.27456         0.030657         -11.7033         -0.96341           X1(Q)         6.83333         1.674979         4.07965         0.015103         2.1828         11.48382           (2)X2(L)         9.66667         1.934099         4.99802         0.007501         4.2967         15.03659           X2(Q)         -4.16667         1.674979         -2.48759         0.067659         -8.8172         0.48382           V         y         -         -         -         -         -         -         0.152804         -47.2167         10.55000           X1(Q)         8.5000         9.00925         0.94347         0.398860         -16.5137         33.51370           (2)X2(L)         -1.00	X1(Q)	-0.40167	1.632359	-0.24607	0.817743	-4.9338	4.13049			
X2(Q) $-1.94167$ $1.632359$ $-1.18948$ $0.300029$ $-6.4738$ $2.59049$ Wean/constant75.1111 $0.789593$ $95.12639$ $0.00000$ $72.9189$ $77.30337$ (1)X1(L) $-6.33333$ $1.934099$ $-3.27456$ $0.030657$ $-11.7033$ $-0.96341$ X1(Q) $6.83333$ $1.674979$ $4.07965$ $0.015103$ $2.1828$ $11.48382$ (2)X2(L) $9.66667$ $1.934099$ $4.99802$ $0.007501$ $4.2967$ $15.03659$ X2(Q) $-4.16667$ $1.674979$ $-2.48759$ $0.067659$ $-8.8172$ $0.48382$ Wean/constant $54.3333$ $4.24700$ $12.79333$ $0.000215$ $42.5418$ $66.12490$ (1)X1(L) $-18.3333$ $10.40299$ $-1.76231$ $0.152804$ $-47.2167$ $10.55000$ X1(Q) $8.5000$ $9.00925$ $0.94347$ $0.398860$ $-16.5137$ $33.51370$ (2)X2(L) $-1.0000$ $10.40299$ $-0.09613$ $0.928044$ $-29.8833$ $27.88333$ X2(Q) $0.5000$ $9.00925$ $0.05550$ $0.958403$ $-24.5137$ $25.51370$ Wean/constant $320.4444$ $7.20682$ $44.46405$ $0.000002$ $300.4351$ $340.4538$ (1)X1(L) $25.0000$ $17.65303$ $1.41619$ $0.229663$ $-24.0127$ $74.0127$ X1(Q) $-24.1667$ $15.28798$ $-1.58076$ $0.189087$ $-66.6129$ $18.2796$ (2)X2(L) $-29.6667$ $17.65303$ $-1.68076$ $0.168148$ $-78.6793$ <td>(2)X2(L)</td> <td>-6.71000</td> <td>1.884886</td> <td>-3.55990</td> <td>0.023588</td> <td>-11.9433</td> <td>-1.47672</td>	(2)X2(L)	-6.71000	1.884886	-3.55990	0.023588	-11.9433	-1.47672			
y6           Mean/constant         75.11111         0.789593         95.12639         0.000000         72.9189         77.30337           (1)X1(L)         -6.33333         1.934099         -3.27456         0.030657         -11.7033         -0.96341           X1(Q)         6.83333         1.674979         4.07965         0.015103         2.1828         11.48382           (2)X2(L)         9.66667         1.934099         4.99802         0.007501         4.2967         15.03659           X2(Q)         -4.16667         1.674979         -2.48759         0.067659         -8.8172         0.48382           Wean/constant         54.3333         4.24700         12.79333         0.000215         42.5418         66.12490           (1)X1(L)         -18.3333         10.40299         -1.76231         0.152804         -47.2167         10.55000           X1(Q)         8.5000         9.00925         0.94347         0.398860         -16.5137         33.51370           (2)X2(L)         -1.0000         10.40299         -0.09613         0.928044         -29.8833         27.88333           X2(Q)         0.5000         9.0925         0.05550         0.958403         -24.5137         25.51370 <th< td=""><td>X2(Q)</td><td>-1.94167</td><td>1.632359</td><td>-1.18948</td><td>0.300029</td><td>-6.4738</td><td>2.59049</td></th<>	X2(Q)	-1.94167	1.632359	-1.18948	0.300029	-6.4738	2.59049			
Mean/constant $75.11111$ $0.789593$ $95.12639$ $0.00000$ $72.9189$ $77.30337$ (1)X1(L) $-6.33333$ $1.934099$ $-3.27456$ $0.030657$ $-11.7033$ $-0.96341$ X1(Q) $6.83333$ $1.674979$ $4.07965$ $0.015103$ $2.1828$ $11.48382$ (2)X2(L) $9.66667$ $1.934099$ $4.99802$ $0.007501$ $4.2967$ $15.03659$ $X2(Q)$ $-4.16667$ $1.674979$ $-2.48759$ $0.007511$ $4.2967$ $15.03659$ $VT$ $VT$ $VT$ $VT$ $VT$ $VT$ $VT$ Mean/constant $54.3333$ $10.40299$ $-1.76231$ $0.152804$ $-47.2167$ $10.55000$ $X1(Q)$ $8.5000$ $9.00925$ $0.994347$ $0.398860$ $-16.5137$ $33.51370$ $(2)X2(L)$ $-1.0000$ $10.40299$ $-0.09613$ $0.928044$ $-29.8833$ $27.88333$ $X2(Q)$ $0.5000$ $9.0925$ $0.05550$ $0.958403$ $-24.5137$ $25.51370$ $VS(Q)$ $VS(Q)$ $17.65303$ $1.41619$ $0.229663$ $-24.0127$ $74.0127$ $X1$	<u> </u>									
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean/constant	75.11111	0.789593	95.12639	0.000000	72.9189	77.30337			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(1)X1(L)	-6.33333	1.934099	-3.27456	0.030657	-11.7033	-0.96341			
(2)X2(L)9.666671.9340994.998020.0075014.296715.03659X2(Q) $-4.16667$ $1.674979$ $-2.48759$ $0.067659$ $-8.8172$ $0.48382$ yrMean/constant $54.3333$ $4.24700$ $12.79333$ $0.000215$ $42.5418$ $66.12490$ (1)X1(L) $-18.3333$ $10.40299$ $-1.76231$ $0.152804$ $-47.2167$ $10.55000$ X1(Q) $8.5000$ $9.00925$ $0.94347$ $0.398860$ $-16.5137$ $33.51370$ (2)X2(L) $-1.0000$ $10.40299$ $-0.09613$ $0.928044$ $-29.8833$ $27.88333$ X2(Q) $0.5000$ $9.00925$ $0.05550$ $0.958403$ $-24.5137$ $25.51370$ ysMean/constant $320.4444$ $7.20682$ $44.46405$ $0.000002$ $300.4351$ $340.4538$ (1)X1(L) $25.0000$ $17.65303$ $1.41619$ $0.229663$ $-24.0127$ $74.0127$ X1(Q) $-24.1667$ $15.28798$ $-1.58076$ $0.189087$ $-66.6129$ $18.2796$ (2)X2(L) $-29.6667$ $17.65303$ $-1.68054$ $0.168148$ $-78.6793$ $19.3460$ X2(Q) $19.8333$ $15.28798$ $1.29732$ $0.264287$ $-22.6129$ $62.2796$	X1(Q)	6.83333	1.674979	4.07965	0.015103	2.1828	11.48382			
X2(Q) $-4.16667$ $1.674979$ $-2.48759$ $0.067659$ $-8.8172$ $0.48382$ Wean/constant $54.3333$ $4.24700$ $12.79333$ $0.000215$ $42.5418$ $66.12490$ (1)X1(L) $-18.3333$ $10.40299$ $-1.76231$ $0.152804$ $-47.2167$ $10.55000$ X1(Q) $8.5000$ $9.00925$ $0.94347$ $0.398860$ $-16.5137$ $33.51370$ (2)X2(L) $-1.0000$ $10.40299$ $-0.09613$ $0.928044$ $-29.8833$ $27.88333$ X2(Q) $0.5000$ $9.00925$ $0.05550$ $0.958403$ $-24.5137$ $25.51370$ VsMean/constant $320.4444$ $7.20682$ $44.46405$ $0.000002$ $300.4351$ $340.4538$ (1)X1(L) $25.0000$ $17.65303$ $1.41619$ $0.229663$ $-24.0127$ $74.0127$ X1(Q) $-24.1667$ $15.28798$ $-1.58076$ $0.189087$ $-66.6129$ $18.2796$ (2)X2(L) $-29.6667$ $17.65303$ $-1.68054$ $0.168148$ $-78.6793$ $19.3460$ X2(Q) $19.8333$ $15.28798$ $1.29732$ $0.264287$ $-22.6129$ $62.2796$	(2)X2(L)	9.66667	1.934099	4.99802	0.007501	4.2967	15.03659			
yrMean/constant $54.3333$ $4.24700$ $12.79333$ $0.000215$ $42.5418$ $66.12490$ $(1)X1(L)$ $-18.3333$ $10.40299$ $-1.76231$ $0.152804$ $-47.2167$ $10.55000$ X1(Q) $8.5000$ $9.00925$ $0.94347$ $0.398860$ $-16.5137$ $33.51370$ $(2)X2(L)$ $-1.0000$ $10.40299$ $-0.09613$ $0.928044$ $-29.8833$ $27.88333$ X2(Q) $0.5000$ $9.00925$ $0.05550$ $0.958403$ $-24.5137$ $25.51370$ VsMean/constant $320.4444$ $7.20682$ $44.46405$ $0.000002$ $300.4351$ $340.4538$ $(1)X1(L)$ $25.0000$ $17.65303$ $1.41619$ $0.229663$ $-24.0127$ $74.0127$ X1(Q) $-24.1667$ $15.28798$ $-1.58076$ $0.189087$ $-66.6129$ $18.2796$ $(2)X2(L)$ $-29.6667$ $17.65303$ $-1.68054$ $0.168148$ $-78.6793$ $19.3460$ X2(Q) $19.8333$ $15.28798$ $1.29732$ $0.264287$ $-22.6129$ $62.2796$	X2(Q)	-4.16667	1.674979	-2.48759	0.067659	-8.8172	0.48382			
Mean/constant $54.3333$ $4.24700$ $12.79333$ $0.000215$ $42.5418$ $66.12490$ $(1)X1(L)$ $-18.3333$ $10.40299$ $-1.76231$ $0.152804$ $-47.2167$ $10.55000$ $X1(Q)$ $8.5000$ $9.00925$ $0.94347$ $0.398860$ $-16.5137$ $33.51370$ $(2)X2(L)$ $-1.0000$ $10.40299$ $-0.09613$ $0.928044$ $-29.8833$ $27.88333$ $X2(Q)$ $0.5000$ $9.00925$ $0.05550$ $0.958403$ $-24.5137$ $25.51370$ y <sub>8</sub> Mean/constant $320.4444$ $7.20682$ $44.46405$ $0.000002$ $300.4351$ $340.4538$ $(1)X1(L)$ $25.0000$ $17.65303$ $1.41619$ $0.229663$ $-24.0127$ $74.0127$ $X1(Q)$ $-24.1667$ $15.28798$ $-1.58076$ $0.189087$ $-66.6129$ $18.2796$ $(2)X2(L)$ $-29.6667$ $17.65303$ $-1.68054$ $0.168148$ $-78.6793$ $19.3460$ $X2(Q)$ $19.8333$ $15.28798$ $1.29732$ $0.264287$ $-22.6129$ $62.2796$				V7						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mean/constant	54.3333	4.24700	12.79333	0.000215	42.5418	66.12490			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(1)X1(L)	-18.3333	10.40299	-1.76231	0.152804	-47.2167	10.55000			
V2(L)         -1.0000         10.40299         -0.09613         0.928044         -29.8833         27.88333           X2(Q)         0.5000         9.00925         0.05550         0.958403         -24.5137         25.51370           y <sub>8</sub> Mean/constant         320.4444         7.20682         44.46405         0.000002         300.4351         340.4538           (1)X1(L)         25.0000         17.65303         1.41619         0.229663         -24.0127         74.0127           X1(Q)         -24.1667         15.28798         -1.58076         0.189087         -66.6129         18.2796           (2)X2(L)         -29.6667         17.65303         -1.68054         0.168148         -78.6793         19.3460           X2(Q)         19.8333         15.28798         1.29732         0.264287         -22.6129         62.2796	X1(Q)	8.5000	9.00925	0.94347	0.398860	- 16.5137	33.51370			
X2(Q)         0.5000         9.00925         0.05550         0.958403         -24.5137         25.51370           Vs	(2)X2(L)	-1.0000	10.40299	-0.09613	0.928044	-29.8833	27.88333			
ys         ys           Mean/constant         320.4444         7.20682         44.46405         0.000002         300.4351         340.4538           (1)X1(L)         25.0000         17.65303         1.41619         0.229663         -24.0127         74.0127           X1(Q)         -24.1667         15.28798         -1.58076         0.189087         -66.6129         18.2796           (2)X2(L)         -29.6667         17.65303         -1.68054         0.168148         -78.6793         19.3460           X2(Q)         19.8333         15.28798         1.29732         0.264287         -22.6129         62.2796	X2(Q)	0.5000	9.00925	0.05550	0.958403	-24.5137	25.51370			
Mean/constant         320.4444         7.20682         44.46405         0.000002         300.4351         340.4538           (1)X1(L)         25.0000         17.65303         1.41619         0.229663         -24.0127         74.0127           X1(Q)         -24.1667         15.28798         -1.58076         0.189087         -66.6129         18.2796           (2)X2(L)         -29.6667         17.65303         -1.68054         0.168148         -78.6793         19.3460           X2(Q)         19.8333         15.28798         1.29732         0.264287         -22.6129         62.2796	Vo									
(1)X1(L)         25.0000         17.65303         1.41619         0.229663         -24.0127         74.0127           X1(Q)         -24.1667         15.28798         -1.58076         0.189087         -66.6129         18.2796           (2)X2(L)         -29.6667         17.65303         -1.68054         0.168148         -78.6793         19.3460           X2(Q)         19.8333         15.28798         1.29732         0.264287         -22.6129         62.2796	Mean/constant	320.4444	7,20682	44,46405	0.000002	300.4351	340,4538			
X1(Q)         -24.1667         15.28798         -1.58076         0.189087         -66.6129         18.2796           (2)X2(L)         -29.6667         17.65303         -1.68054         0.168148         -78.6793         19.3460           X2(Q)         19.8333         15.28798         1.29732         0.264287         -22.6129         62.2796	(1)X1(L)	25.0000	17.65303	1.41619	0.229663	-24.0127	74.0127			
(2)X2(L) $-29.6667$ 17.65303 $-1.68054$ $0.168148$ $-78.6793$ 19.3460           X2(Q)         19.8333         15.28798         1.29732         0.264287 $-22.6129$ 62.2796	X1(Q)	-24,1667	15,28798	-1.58076	0.189087	-66.6129	18,2796			
X2(Q) 19 8333 15 28798 1 29732 0 264287 -22 6120 62 2796	(2)X2(L)	-29.6667	17.65303	-1.68054	0.168148	-78.6793	19.3460			
	X2(Q)	19.8333	15.28798	1.29732	0.264287	-22.6129	62.2796			

**Table 3.** ANOVA table analysis for dependent variables  $(y_1-y_8)$ 

The statistical analysis of the effect of independent variables  $(x_1, x_2)$  on the dependent variables characterizing the morphology of materials demonstrated that the substrate molar ratio in the reaction mixture  $(x_2(L) 9.67)$  and the pressure of the process  $(x_1(L) - 6.33)$  had a statistically significant influence on their oil number  $(y_6)$ . The lower the pressure and the higher the Ca<sup>2+</sup>:

 $PO_4^{3-}$  molar ratio, the higher oil number tended to be, characterizing the sorption properties of the products. Both of the input variables had no effect on the specific surface area and on the average particle size of the precipitated phosphates. Their specific surface area (y<sub>7</sub>) and particle size (y<sub>8</sub>) were in the range of 34–76 m<sup>2</sup>/g and 280–370 nm, respectively.

The spatial graphs in Figure 2 show the effect of pressure and Ca<sup>2+</sup>: PO<sub>4</sub><sup>3-</sup> ratio in the reaction mixture on the dependent variables  $y_{1-8}$ . The depicted areas can help to assess the influence of the above process parameters on the properties of precipitated phosphates. Based on that, a conclusion was drawn that only the substrate molar ratio affected the content of aluminum, calcium and molybdenum in the products, which is consistent with the results of the statistical analysis. The specific surface area was found to be slightly affected by the pressure of the process, which in the statistical assessment of the effects was described to have a negligible effect.

The shape of the surface presented in Figure 3, depicting the effect of variables  $x_1$  and  $x_2$  on the oil number of the products, suggest the influence of both parameters with a maximum observed for the average pressure. The finding is consistent with the statistical analysis of  $(x_2(L) 9.67; x_1(L) -6.33; x_1(Q) 6.83)$  effects. However, the interpretation of the shape in terms of the effect of the independent variables on the content of nitrogen



Figure 3. Response surface for dependent variables  $x_{1-2}$  to independent variables  $y_{1-8}$ 

and phosphates and the particle size  $(y_4, y_5, and y_8)$  in the products, is anything but an easy task.

The molar ratio of the substrates had a significant effect on the first two input variables. However, the shape of the surface seems to suggest the effect of the pressure of the process. The effect of variables  $x_1$  and  $x_2$  on the particle size of the precipitated phosphates was thought to be statistically insignificant. The surface analysis suggests that products with the biggest particle size can be obtained at the Ca<sup>2+</sup>: PO<sub>4</sub><sup>3</sup> molar ratio of 0.2 : 1 and maximum pressure values.

Figure 4 presents a comparison of SEM images for the products precipitated in the reaction mixture with the Al<sup>3+</sup>: Ca<sup>2+</sup>: Mo<sup>6+</sup>: PO<sub>4</sub><sup>3-</sup> molar ratios of (a) 0.67 : 0.33 : 0.33 : 1 (a); 0.67 : 0.2 : 0.2 : 1 (b), and 0.67 : 0.07 : 0.07 : 1 and (c) at the pressure of 2.1 MPa. The shape of particles was observed to be dependent on the molar ratio of the reagents. With the decreasing content of Ca<sup>2+</sup> and Mo<sup>6+</sup> ions in the substrates, the product particle size was bigger. The observed associations correlated with the content of the  $(NH_4)_3Al_2(PO_4)_3$  crystalline phase, whose share was bigger at the lower Al<sup>3+</sup> : Ca<sup>2+</sup>: Mo<sup>6+</sup>: PO<sub>4</sub><sup>3-</sup> reagent molar ratio of 0.67 : 0.07 : 0.07 : 1. The particles of products with the highest content of the crystalline phase had the biggest size, although the statistical assessment did not show any effect of the reagent molar ratio on the property.

The relationship between the chemical composition of the prepared aluminum phosphates modified with ammonium, calcium and molybdenum and their corrosion inhibition efficiency was investigated using the presented Tafel test results.

Table 4 presents the results of corrosion inhibition efficiency tests for different extracts. The results were compared with those of FC-M2 zinc phosphate and FAC





Figure 4. SEM images of the aluminum phosphates modified ammonium, calcium and molybdenium precipitated from reaction mixture with a molar ratio  $Al^{3+}$ :  $Ca^{2+}$ :  $Mo^{6+}$ :  $PO_4^{3-}$  equal: (a) 0.67 : 0.33 : 0.33 : 1; (b) 0.67 : 0.2 : 0.2 : 1 (b) and (c) 0.67 : 0.07 : 0.07 : 1 at the pressure of 2.1 MPa

 Table 4. Potentiodynamic polarization test result for steel immersed in extract of phosphate pigments in 3.5 wt% NaCl aqueous solution

Phosphate acronym	I <sub>corr</sub> [μΑ/cm²]	E <sub>corr</sub> [mV vs. SCE]	P [mm/year]	η [%]
-	2.17	-799	0.025	_
FAC	1.1	-725	0.013	49
FC-M2	1.2	-796	0.014	45
AACMPH1	2.71	-775	0.0316	-25
AACMPH2	1.13	-779	0.0132	48
AACMPH3	1.44	-767	0.0168	34
AACMPH4	2.81	-767	0.0327	-29
AACMPH5	1.91	-771	0.0222	12
AACMPH6	2.26	-776	0.0263	-4
AACMPH7	2.16	-779	0.0251	0.5
AACMPH8	2.14	-772	0.0249	1.4
AACMPH9	1.99	-776	0.0232	8

aluminum-zinc phosphate (manufactured by Złoty Stok Antykorozja Sp. z o.o. in Złoty Stok, Poland).

Following the analysis of results, the corrosion of steel was concluded to proceed the slowest with AACMPH2 and 3 materials out of all the tested extracts of modified aluminum phosphates, precipitated in a microwave reactor. The rates of corrosion for AACMPH2 and 3 were 0.0132 mm/year and 0.0168 mm/year, respectively. While comparing the obtained results with those of steel investigated in a NaCl aqueous solution, the corrosion inhibition efficiency for phosphates obtained in the experiments was 48% and 34%, respectively. The effectiveness was close to that of commercial anti-corrosive pigments (FAC and FC-M2). The lowest corrosion inhibition efficiency was determined for phosphates used in the experiments involving AACMPH1 and 4, which amounted to -25% and -29%, respectively. Corrosion was observed to proceed with the slowest rate in the phosphate extracts with the lowest Ca to Mo molar ratio and with a higher total amount of aluminum and ammonium moles per one mole of phosphates.

Sediments precipitated in Tafel tests (Table 5) were examined using XRD and SEM-EDX analysis. Unfortunately, the identification of the crystalline phases in obtained powders was impossible due to their amorphous nature. The powders had different contents of aluminum, calcium, iron and phosphates. Molybdenum content was not determined. No correlation was found between the chemical properties of the extracted phosphates, the corrosion inhibition efficiency examined in potentiodynamic tests and the chemical composition of corrosion products. anti-corrosive pigments (FAC and FC-M2) which were used for comparison purposes.

The statistical assessment of planned examinations enables a selection of process parameters conducive to obtaining aluminum phosphates modified with ammonia, calcium and molybdenum with preset physicochemical properties.

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Phosphate acronym	Al	Ca	Мо	Fe	Р	Molar ratio of
			Content [wt%	AI : Ca : Mo : Fe : P		
AACMPH1	2.49	0.44	0	15.41	3.18	0.90 : 0.11 : 0 : 2.69 : 1
AACMPH2	1.77	0.03	0	2.43	0.10	20.30 : 0.23 : 0 : 13.47 : 1
AACMPH3	0.58	0.29	0	22.98	5.39	0.12 : 0.04 : 0 : 2.36 : 1
AACMPH4	14.32	2.90	0	31.08	2.07	7.94 : 1.08 : 0 : 8.33 : 1
AACMPH5	1.99	0.34	0	4.89	1.55	1.47 : 0.17 : 0 : 1.75 : 1
AACMPH6	4.71	1.02	0	31.30	2.29	2.36 : 0.34 : 0 : 7.58 : 1
AACMPH7	11.29	1.67	0	53.27	0.97	13.35 : 1.33 : 0 : 30.45 : 1
AACMPH8	4.38	0.91	0	7.78	1.98	2.54 : 0.36 : 0 : 2.18 : 1
AACMPH9	2.36	0.63	0	14.46	2.53	1.07 : 0.19 : 0 : 3.17 : 1

 Table 5. EDX analysis of sediments precipitated during the electrochemical studies

#### CONCLUSIONS

Crystalline materials with varied content of nitrogen, aluminum, molybdenum, calcium, phosphorus and crystalline phases depending on process parameters were obtained using the hydrothermal method.

It was statistically demonstrated that the content of Al, Ca, Mo, N and P in the products was dependent on the variable  $x_2$ , i.e. on the Al<sup>3+</sup> : Ca<sup>2+</sup> : Mo<sup>6+</sup> : PO<sub>4</sub><sup>3-</sup> reagent molar ratio. The input variable  $x_1$  (pressure) had no statistically significant effect on the dependent variables  $y_{1-5}$ . The input variables did not have any statistically significant effect on either S<sub>BET</sub> specific surface area or the particle size of the obtained products. The pressure and the reagent molar ratio were shown to have a significant effect on oil number.

The highest corrosion inhibition efficiency for the phosphates discussed above was 48% and 34%, respectively. The efficiency was close to that of commercial

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