

Boron Phosphate/*Poly(p-phenylenediamine)* as a Corrosion Inhibitive System for Steel Protection

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CORROSION never sleeps, therefore, industries rather than governments do their best to resist the different types of corrosion by all possible methods and techniques particularly in high-risk areas. Nevertheless, organic coatings are considered the most widely applied route for protection of metallic surfaces from corrosion and they are of a special importance in transportation and infrastructure. Accordingly, the main goal of this study is to provide a detailed overview of a protective pigment/inhibitor system based on low-cost boron phosphate and *poly(p-phenylenediamine)* as a new type of corrosion inhibitive coating that works holistically to obtain long-term performance for steel protection. However, characterization and investigation of boron phosphate and/or *in-situ* polymerized *p-phenylenediamine* were achieved *via* XRD, XRF, FT-IR, SEM and thermal analysis. Besides, different concentrations of boron phosphate/*poly(p-phenylenediamine)* were applied within controlled paint formulations based on epoxy resin, subsequently, they showed good physico-mechanical properties and high protection level against corrosion.

Keywords: Boron phosphate, *Poly(p-phenylenediamine)*, Pigments, Inhibitors, Coatings, Surface treatment, Corrosion protection.

Introduction

Boron phosphate is widely used in many industrial applications due to low cost, low toxicity and its outstanding properties. Boron phosphate has a chemical formula (BPO_4). It is a white solid which belongs to the class of orthophosphates. It can be prepared by solid state reaction using several reactants such as phosphoric acid with boric acid, phosphoric acid with triethyl borate, triethyl phosphate and boron trichloride [1, 2]. Furthermore, synthesis of BPO_4 was achieved *via* microwave irradiation routes [3, 4]. However, our concern is the preparation of boron phosphate by mixing boric acid (H_3BO_3) and phosphoric acid (H_3PO_4) at elevated temperature.

Boron phosphate can exist in two forms, one is amorphous and soluble in water which is prepared at low temperatures and another crystalline insoluble form which is prepared at elevated temperatures. It has been proved that the crystallinity of these compounds increased

with increasing temperature and heating time. In addition, the solubility of the BPO_4 compounds decreased with increasing the temperature of reaction and with decreasing pH [1, 5].

Boron phosphate has found applications in agriculture and fertilizers when applied to soil [5] and also in manufacturing of synthetic herbicides [6]. It has been widely used as a catalyst [7, 8]. Besides, boron phosphate was used as a good smoke reducer and economic flame retardant with different resins applied as composites [9-12]. It is used as a phosphating agent for various metals [13, 14]. In addition, as an additive in glass and ceramic manufacture [4, 15, 16], in electrical insulation [17] and electronic packaging [18]. Recently, boron phosphate has found application in fuel cell membranes [7,19]. According to authors' knowledge and survey, there is no doubt that literature is scanty concerning the application of boron phosphate as inhibitive pigment in corrosion protection of metals.

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Inhibitors can be considered as the first line of defense against corrosion. By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to a medium, effectively decreases the corrosion rate. In general, the efficiency of an inhibitor increases with limited increase in inhibitor concentration. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. From the economical and environmental points of view, only very few inhibitors are actually used in practice [20,21]. However, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Their effectiveness depends on the chemical composition, molecular structure, and their affinities for the metal surface [22, 23].

In continuation to research work of corrosion protection of steel *via* conducting polymers, there are several reported results concerning with the application of some polyanilines, and polyaniline derivatives as corrosion inhibitors or *in-situ* polymerized aniline moieties with phosphate pigments or other fillers during polymerization process [24-27].

However, it is clear that there is no single protective mechanism is operative in organic coatings and that their long-term performance is predicated on a number of collaborative processes working holistically. The properties of individual components in a coating may be well-known, when combined within a formulated product the overall outcome is not predictable and extended empirical testing is required to validate performance [28].

According to the best of our knowledge, there are no recent studies concerning application of modified boron phosphate (boron phosphate/*poly(p-phenylenediamine)* hybrid system) as a corrosion inhibitive coat for steel. This system was performed *via in-situ* polymerization of *p-phenylenediamine* in presence of boron phosphate. Hence, the main goal of this study is to prepare, characterize and evaluate unmodified and modified boron phosphate as an eco-friendly corrosion inhibitive pigment for high performance anti-corrosive paint applications for steel protection.

Experimental

Materials

Boric acid and hydrochloric acid are products of Nasr Co., ortho phosphoric acid (85%) is a

product of Panreac Quimca SA. Ammonium peroxydisulphate initiator and *p-phenylenediamine* are products of Merck Co. *Pigments and extenders*: titanium dioxide pigment is a product of Crystal Co. and zinc phosphate pigment is a product of Wayne-USA. Barite and talc are products of Faltas and Green Egypt Companies. *Binders*: epoxy resin and its hardener are products of Bayer and Huntsman Companies. *Solvents*: xylene, toluene, ethyl acetate and ethyl alcohol are products of Merck Co., Nasr Co. and BHD Laboratory Supplies, GPR.

Preparation of boron phosphate pigment

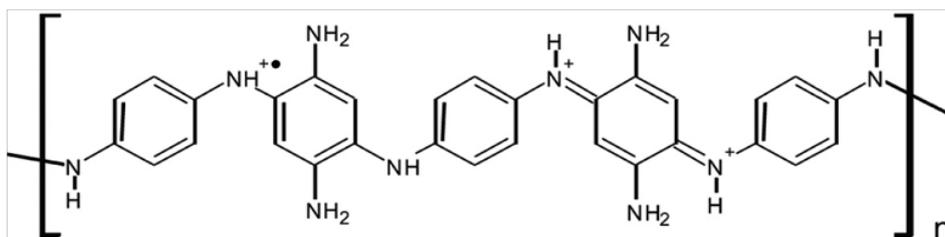
Boric acid (0.2 mol) and o-phosphoric acid (85%) (0.2 mol) were mixed together into 100 mL porcelain crucible with complete stirring. Then the wet mixture was heated to ~ 200 °C for a few minutes to get rid of water and have solidified mixture. Pyrolysis of the prepared sample mixture was adjusted at the required time 2h and temperature 1000°C under normal atmosphere.

In-situ polymerization of p-phenylenediamine in presence of boron phosphate pigment

This method was carried out according to our reported studies by *in-situ* polymerization techniques [26]. (0.005, 0.01 & 0.02 mol) *p-phenylenediamine* (pPDA), each was dissolved in 50 mL ethanol and stirred with 30 g of prepared boron phosphate. (0.005, 0.01 & 0.02 mol) ammonium peroxydisulphate initiator, each was dissolved in distilled water and was added drop wisely to corresponding prepared (0.005, 0.01 & 0.02 mol) *p-phenylenediamine* respectively. Then, addition of 1, 2, 4 mL of 1M hydrochloric acid to each prepared mixture respectively. Each mixture was left with continuous stirring for 14 hours. The products were filtered off and the resultant precipitates were washed several times with distilled water and were subjected for drying. (Scheme 1).

Characterization methods

The characterization methods included the following techniques: X-ray diffraction analysis (XRD) was carried out by using Bruker AXS D8 advance, with Ni filtered Cu-K α radiation. Images of scanning electron microscope (SEM) were performed using (Joel Jx-840, Japan) and the FT-IR analysis for the prepared samples (using KBr media) was performed by Fourier Transform Infrared spectrometer (Jasco FT/IR-6100, Japan). Thermal analysis was obtained by differential scanning calorimetry DSC131 EVO (SETARAM Inc., France) which was used to



Kohl M. and Kalendova A., *Adv. Sci. Tech. Res. J.*, 9 (28), 47-50 (2015).

Scheme 1. Proposed chemical structure of *poly(p-phenylenediamine)*

perform the differential scanning calorimetric analysis. X-ray fluorescence analysis was carried out by wave dispersive X-ray fluorescence WD XRF PANalytical Axios advanced.

Methods for evaluation of boron phosphate as a pigment

The international standard test methods were applied for evaluation of the boron phosphate as a pigment (illustrated in table 3) including: specific gravity [29], bulking value [30], oil absorption [31], bleeding test [32], chemical resistance [33] and hydrogen ion concentration (pH value) [34].

Preparation of paint formulations

Paint formulations based on boron phosphate /epoxy resin (as illustrated in Table 4) were prepared as follows:

1. Dissolving the epoxy resin in a solvent mixture of suitable solvents such as ethyl acetate and n-butanol.
2. The mixture of pigments (titanium dioxide, zinc phosphate, barite, talc, boron phosphate) was first mixed with the half portion of the epoxy resin to produce a semi-paste sample.
3. A ball mill was used to grind and disperse the pigments mixture in the vehicle solution. The grinding process continued for 2-4 hours.
4. After the paint has been grinded in a semi-paste form, it was incorporated with the reminder half portion of the vehicle to produce the ready mixed paint and followed by filtration and filling.
5. Consequently, the prepared paint formulation (after adding of hardener portion) was ready for application of one layer of wet film thickness (about 200 micron) by wire-wound drawdown bar onto the glass or steel panels and left for drying to give layer of dry film thickness of about 100 - 140 micron.

Physical and mechanical properties of paint films

Evaluation of physical and mechanical properties of dry paint films was carried out *via* international standard methods including: preparation of steel panels [35], preparation of

paint films of uniform thickness on test panels [36, 37], measuring the drying time [38], film thickness [39], pendulum hardness on glass panels [40], adhesion by cross-cut tester [41], degree of gloss [42] and resistance of organic coatings to the effects of rapid deformation [43] as well as testing the ductility by cupping test machine [44]. However, Ductility can be defined as it is a measure of a material's ability to undergo significant plastic deformation (under tensile or compression stresses) before rupture, which may be expressed as percent elongation or percent area reduction from a tensile test.

Corrosion tests

The coated steel panels (edged by epoxy resin) were immersed in artificial seawater (35 g NaCl/L) for 28 days taking into consideration the gradual change of salt solution and washing of panels with distilled water periodically. At the end of this period, the panels were washed with distilled water and left to dry. Hence, the degree of blistering [45], filiform corrosion [46] and the degree of rusting [47] on the surface of the steel panels were evaluated. In addition, photographic inspection of painted plates after the period of immersion was recorded.

Results and Discussion

Characterization of boron phosphate pigment

X-ray diffraction analysis

The characteristic d-values of XRD (Fig. 1 & Table 1) appeared clear and sharp, particularly the most remarkable intense line of BPO₄ phase (d = 3.617: 100% at 2-theta = 24.61) followed by other characteristic peaks with lower intensities. This pattern confirms high purity of the characterized BPO₄ phase in comparison with the standard XRD card of reference code no. 96-101-0300.

The importance of the XRD is contributed to considering this analysis as a fingerprint for the
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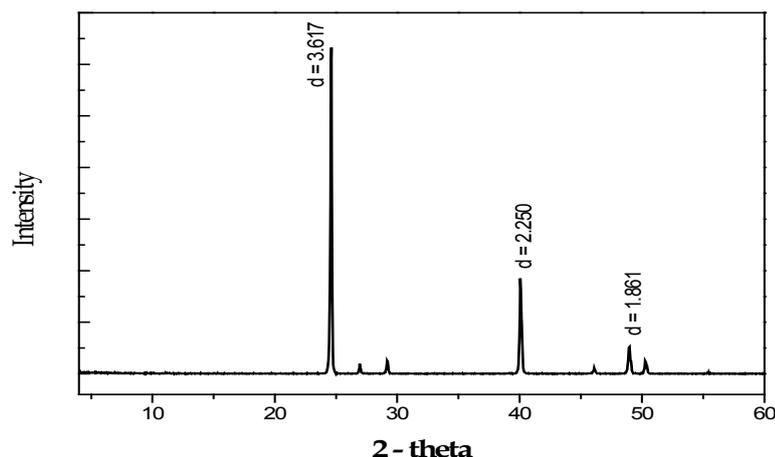


Fig. 1. XRD pattern of prepared boron phosphate

TABLE 1. “d” Values and relative intensities of X-ray diffraction pattern for prepared boron phosphate compared with standard reference card number 96-101-0300.

Pos. [$^{\circ}$ Th.]	d-spacing [\AA]	Height [Counts]	FWHM Left [$^{\circ}$ Th.]	Rel. Int. [%]
24.6104	3.61740	3237.87	0.1181	100.00
26.9422	3.30939	94.97	0.1574	2.93
29.2024	3.05819	123.29	0.1574	3.81
40.0737	2.25009	937.33	0.2362	28.95
46.0836	1.96968	48.33	0.1968	1.49
48.9400	1.86119	250.36	0.2755	7.73
50.2678	1.81510	123.45	0.2362	3.81

Standard XRD card of highly pure boron phosphate

Ref. Code	Mineral Name	Chemical Formula	Semi-Quant [%]
96-101-0300	-----	$\text{P}_{2.00}\text{B}_{2.00}\text{O}_{8.00}$	100

studied compound depending on characteristic values of d-spacing between its atoms. However, it has the ability to give a quick answer for formation of phase under study or not even in presence of other overlapped phases. In addition, it provides a clear view of the purity (crystallinity) of the compound by means of the degree of sharpness of the observed peaks.

X-ray fluorescence analysis

It is clear from Table 2 that the P_2O_5 content equal to approx. 99.5 % indicating the presence of boron phosphate as high pure grade. Taking in our consideration, the XRF instrument cannot detect the elements of very low atomic weight (e.g. H, ... Be, B, ...C and N).

FT-IR studies of uncoated boron phosphate

The IR spectrum of boron phosphate is shown in Fig. 2., the peaks at 560 cm^{-1} and 626 cm^{-1} are

TABLE 2. XRF analysis of prepared boron phosphate.

Main Constituents	Sample (wt %)
SiO_2	0.08
TiO_2	0.098
Al_2O_3	0.14
Fe_2O_3	0.02
CaO	0.02
P_2O_5	99.45
SO_3	0.04
NiO	0.012
CuO	0.012
ZnO	0.085
BaO	0.048

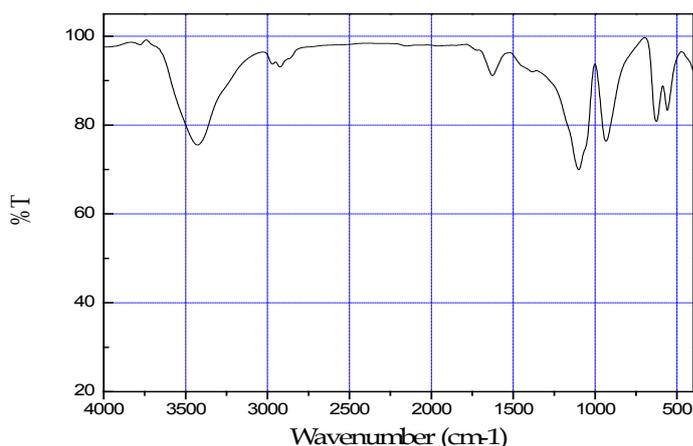


Fig. 2. IR spectrum of prepared boron phosphate.

due to bending vibrations of PO_4^{3-} and the broad band at 1100 cm^{-1} is assigned to the asymmetric stretching vibrations of PO_4^{3-} , while the peak at 933 cm^{-1} is attributed to B-O stretching. The spectrum of prepared BPO_4 is in good agreement with literature [4, 9, 48].

It clear that partially hydrolyzed species are also released and the corresponding broad band can only be seen in the spectrum. Kmecl *et al.* showed that broad shoulder-like absorption band in the area of $3700\text{--}2500\text{ cm}^{-1}$ can be attributed to stretching modes of O-H group bound geminally to P or B atom with hydrogen atom bound with hydrogen bond to oxygen atom of geminal or neighboring O-H group. In addition, absorption bands at 3210 and 1640 cm^{-1} may be attributed to stretching and deformation modes of adsorbed water [1, 9].

There are no bands at 1470 and 790 cm^{-1} which would belong to the stretching and bending modes of boric acid which indicates that there is no free acid in the prepared sample [1], these results are in a good agreement with our results obtained by XRD pattern.

Scanning electron microscope

It is clearly seen from the SEM image (Fig. 3a,b) performed at magnifications $\times 15000$ that the particles have semi-regular shape and appear in groups of accumulated particles collected together giving a reinforcing effect that impart good protecting properties to the paint films. There is no characteristic difference can be illustrated from the two images 3a&3b of SEM uncoated and *poly(p-phenylenediamine)* coated samples

of boron phosphate respectively. However, the observations by Mulla *et al.* indicated that surface area of BPO_4 decreases with increase in calcination temperature [49].

Characterization of boron phosphate coated with inhibitor PpPDA

One of the most important challenges with inhibitors is that although effective behavior at inhibition and/or preventing corrosion when incorporated into paints but they can be toxic. From the earliest days of the development of industry of paints, scientists and technologists have tried to minimize if not eliminate this problem. In addition, they design and concern with continuous release of inhibitor during and after coating process to improve corrosion protection of coated metal surface [22, 28, 50]. Thus, the inhibitor of our interest is *poly(p-phenylenediamine)* PpPDA. It is safe and eco-friendly with respect to the corresponding applied monomer [51] or other applied organic inhibitors [52, 53]. Besides, the studied inhibitor was prepared and polymerized at the surface of boron phosphate pigment before its incorporation within the paint formulations, i.e., it acts as homogeneous and regular leachable species within the coating system providing long term performance against corrosion process.

FT-IR studies of coated boron phosphate

The IR spectrum of boron phosphate coated with PpPDA contains four strong bands at 560 , 628 , 935 , and 1103 cm^{-1} , which can be seen clearly in Fig. 4. Rather broad band at 3438 cm^{-1} that was decreased with respect to the corresponding one shown in Fig. 2. In addition, absorption bands at 3210 and 1640 cm^{-1} were also decreased or diminished.

Thermal analysis

As shown in the DSC thermograph of uncoated BPO_4 (Fig. 5), there is an observed peak appears slightly before 120°C . This peak may be attributed to loss of partially hydrolyzed species at this stage of heating, that is confirmed and discussed by IR results of Fig. 2 [1].

On the other hand, the DSC thermograph of BPO_4 coated with *PpPDA* (Fig. 6) showed disappearance of the last detected peak that appears slightly before 120°C in Fig. 5. This indicates the behavior of applied inhibitor to stabilize the surface of boron phosphate pigments and its ability to replace the sites of hydrolyzed species [9]. Accordingly, this can also emphasise and explain the disappearance and/or decreasing the IR bands discussed in Fig. 4.

In addition, Fig. 6 shows that there is no observed thermal decomposition in the sample all over the range of temperature curve. In other words, no degradation of polymeric inhibitor was observed. This may due to very low concentrations of inhibitor and because it makes just a thin film covering the surface of studied boron phosphate pigment. However, if we considered the very slight changes within the thermal curve of Fig. 6 (i.e. at $240\text{--}300^\circ\text{C}$ & $400\text{--}450^\circ\text{C}$), it can match easily with literature of thermal degradation of *PpPDA* [54].

Evaluation of boron phosphate as a pigment

Boron phosphate was evaluated as a pigment (Table 3) for coating applications according to standard testing methods [29-34].

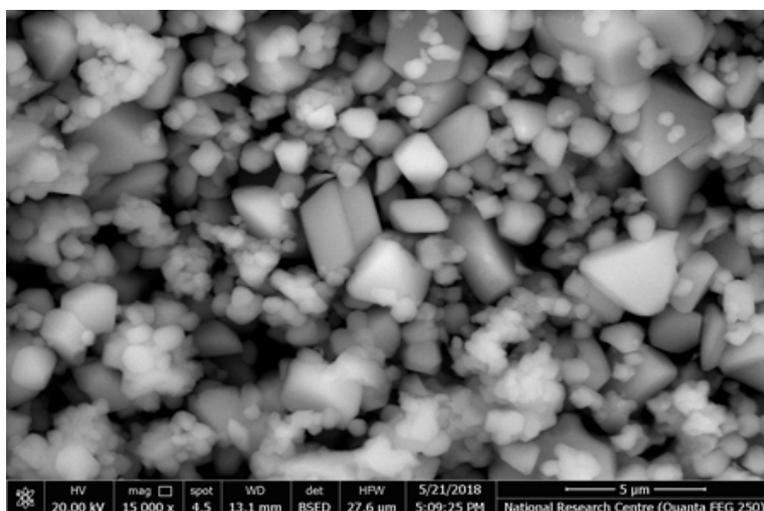


Fig. 3a. SEM image of the prepared uncoated boron phosphate at magnification of x15000.

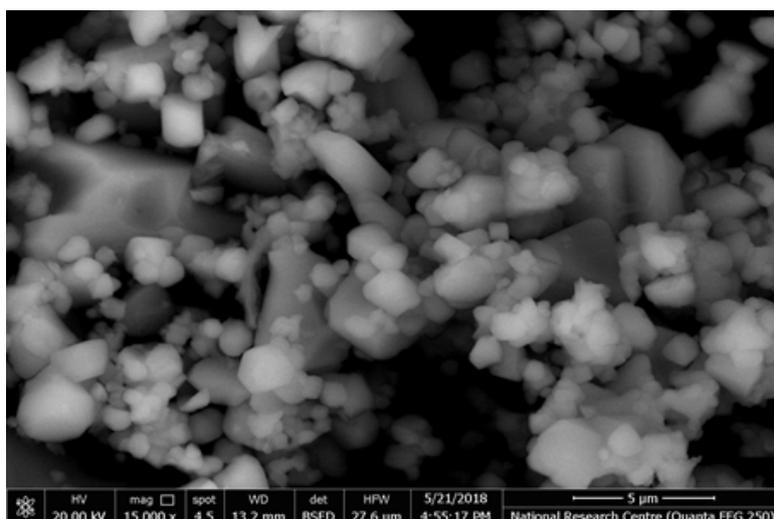


Fig. 3b. SEM image of the coated boron phosphate at magnification of x15000.

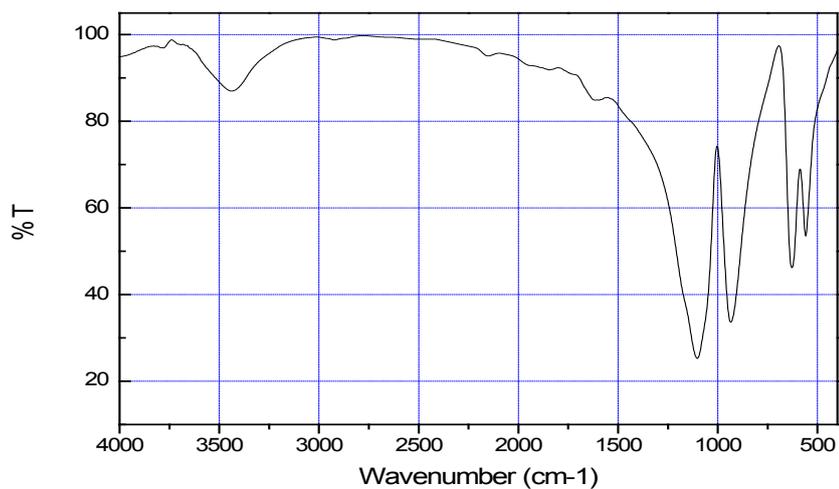


Fig. 4. IR spectrum of boron phosphate coated with *PpPPD*.

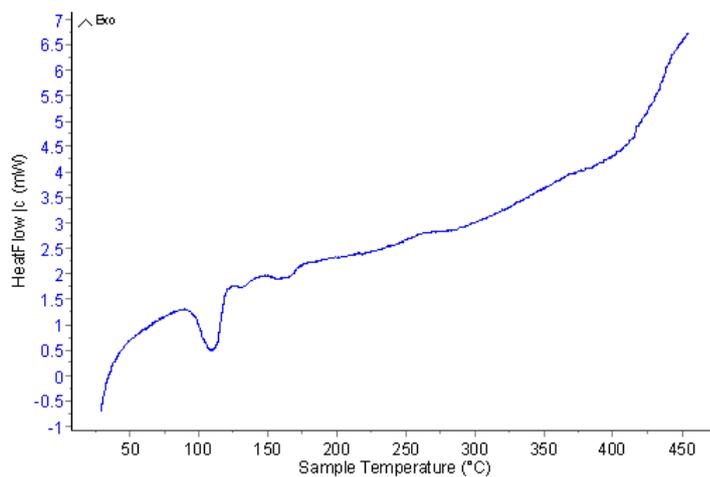


Fig. 5. DSC Thermograph of uncoated boron phosphate.

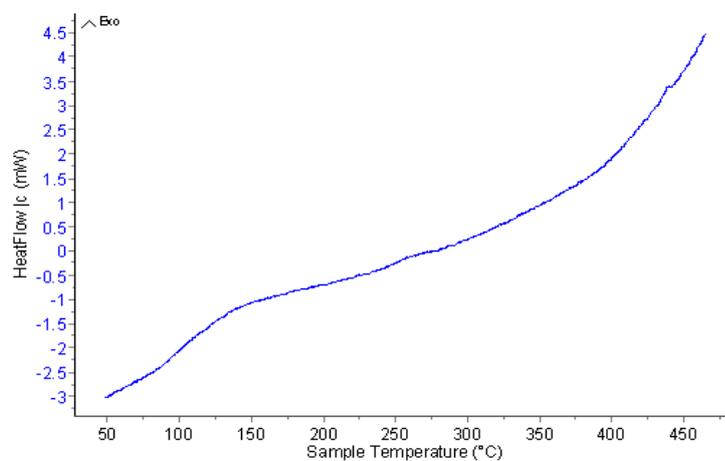


Fig. 6. DSC Thermograph of boron phosphate coated with *PpPPD*.

From Table 3, the following findings can be documented:

1. Boron phosphate shows moderate value of specific gravity and bulking value. 2. The oil absorption value is relatively low for boron phosphate. It is useful and important to reduce the required resin content used for paint formulation and consequently to reduce the paint cost. 3. The results of bleeding tests carried out in various solvents (such as toluene and xylene) indicate a high degree of stability. 4. Chemical resistance tests in alkaline and acidic media showed high resistance of the boron phosphate samples against the effect of alkalis (such as NaOH and CaCO₃) and effect of acids (such as H₂SO₄). 5. The measured pH value referred slightly acidic properties of boron phosphate which is acceptable criterion.

Surface coating applications based on boron phosphate

Table 4 shows the solvent paint formulations based on boron phosphate with epoxy resin and its hardener in comparison with blank formulations free of boron phosphate. However, epoxy resin was used as a good binder giving high degree of adhesion and good physical properties against corrosion. In addition, because the coated metal surface is proportional to the inhibitor concentrates, so, the concentration of the inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration. Thus, we concern with studying the different doses of the prepared inhibitor (*PpPPD*) with the boron phosphate pigment applied within the prepared paint formulations.

TABLE 3. Characteristics of prepared boron phosphate.

Evaluation Test	Results
Specific Gravity	2.83
Bulking Value (gal/100lb)	4.26
Oil Absorption (g oil / 100g pigment)	26
Degree of Bleeding	None
Acid Resistance	Excellent
Alkali Resistance	Excellent
pH Range	Slightly acidic

TABLE 4. Paint formulations based on boron phosphate and epoxy resin

Constituents (g)	Formulation No.						
	B1 (blank)	B2 (blank)	B3	B4	B5	B6	B7
TiO ₂ (Rutile)	20	--	--	5	5	5	5
Zinc phosphate	--	20	--	15	10	10	10
Boron phosphate	--	--	20	5	5	5	5
BaSO ₄	18	18	18	15.5	15.5	15.5	15.5
Talc	16	16	16	13.5	13.5	13.5	13.5
BPO ₄ - <i>PpPPD</i> 0.005	--	--	--	--	5	--	--
BPO ₄ - <i>PpPPD</i> 0.01	--	--	--	--	--	5	--
BPO ₄ - <i>PpPPD</i> 0.02	--	--	--	--	--	--	5
Total pigment	54	54	54	54	54	54	54
Epoxy resin & Hardener (2:1) (Total binder)	27	27	27	27	27	27	27
Solvents Blend of solvents	19	19	19	19	19	19	19
Total	100	100	100	100	100	100	100
P/B ratio Pigments/Binder ratio	2/1	2/1	2/1	2/1	2/1	2/1	2/1

It is worthy to mention that during the mixing of paint formulation B3 in the containers of ball mill, its color was changed to black. However, after search for the reason of this change of color, literature reported that some boron compounds can be converted into black powder at relatively high temperature [55]. Thus, this change in color may be due to the produced heat during the milling process particularly, the formulation B3 is the only one that has the predominant ratio of boron phosphate.

Physical and mechanical properties of boron phosphate paint formulations

The data of the physico-mechanical properties of dry paint films of different paint formulations (while adjusting the viscosity of the paint formulations in a range of 4 poise) and dry films based on boron phosphate and epoxy resin are shown in Table 5.

From Table 5 the following results can be addressed:

1. The paint films show suitable touch drying time (30-45 min) and 4-5 hr for hard dry. The coated films of all paint formulations show good adhesion values of 5B indicating that the edges of cuts are completely smooth (without paint film detachment). 2. Dry paint films of various formulations show good hardness value. 3. The cupping test for the various paint films shows good ductility values, indicating the good adhesion and

good elasticity of dry paint films. 4. Coated steel panels for all paint formulations pass the impact resistance test. 5. Gloss values of coated films for all paint formulations at angle 60° indicate that the paints are of low gloss. In general, all coated steel panels show good and acceptable physico-mechanical properties of the dry paint films.

Evaluation of corrosion protective properties of the prepared paint formulations

It is clear from the data of the corrosion tests of the dry paint films based on boron phosphate (summarized in Table 6 and illustrated in Fig. 7) that:

Formulations B3, B4, B5, B6 and B7 show an improvement in the disappearance of blisters with respect to blank formulations B1 and B2.

Degree of rusting under the paint films has also a good improvement by increasing the dose of boron phosphate and/or inhibitor in the investigated formulations. However, the paint formulation of high inhibitor concentration B7 gives slightly difference. On the other hand, the blank formulations B1 and B2 gave a remarkable defect in blistering as well as rusting. In addition, the filiform corrosion test showed a significant enhancement for formulations B3, B4, B5, B6 and B7 compared with the blank formulations B1 and B2. In general, based on the corrosion resistance studies, we can observe that formulations B6 and B7 show better improvement than other corresponding formulations.

TABLE 5. Physico-mechanical properties of dry paint films of different paint formulations based on boron phosphate and epoxy resin.

Test	Formulation No.						
	B1	B2	B3	B4	B5	B6	B7
Wet film characteristics							
Drying time	----- 30-45 min -----						
- Touch dry	----- 4-5 hr -----						
- Hard dry							
Dry film characteristics							
Dry film thickness (m)	~ 120	~ 120	~ 120	~ 120	~ 120	~ 120	~ 120
Adhesion (cross-cut method)	5B	5B	5B	5B	5B	5B	5B
Hardness (sec)	57	55	44	49	51	70	67
Ductility (mm)	~ 4	~ 4	~ 4	~ 4	~ 4	~ 4	~ 4
Impact resistance (at 40 cm height)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Gloss (angle 60°)	25	18.5	20	21.5	18.5	13.5	16

TABLE 6. Corrosion test data of dry paint films based on BPO₄ / epoxy resin after immersion in artificial seawater for 28 days

Test	Formulation No.						
	B1	B2	B3	B4	B5	B6	B7
Degree of Blistering*	2MD	2M	6F	6F	8F	8F	8F
Degree of Rusting**	5-G 3% rusted	5-G 3% rusted	9-G 0.03% rusted	8-G 0.1% rusted	9-G 0.03% rusted	9-G 0.03% rusted	9-G 0.03% rusted
Filiform Corrosion***	Fig.3 Med dense A	Fig.3 Med dense A	Fig.1 Few A	Fig.2 Med A	Fig.1 Few A	Fig.1 Few A	Fig.2 Med A

* Degree of blistering is evaluated by two characteristics: size and frequency. Size is determined by a numerical scale from 10 to zero, in which 10 represents no blistering and blistering standards of 6, 4, and 2 represent progressively larger sizes. Frequency at each step in size is designated as Dense = D, Medium dense = MD, Medium = M and Few = F.

** Degree of rusting is evaluated using a scale from 10 to 0 based on the percentage of visible surface rust (scale 10 = no rust or rust < 0.01 % and scale 0 = rust > 50 %). The distribution of the rust is classified as spot rust (S), general rust (G), pinpoint rust or hybrid rust (P).

*** Filiform corrosion is a special type of corrosion that occurs under coatings on metal substrates that is characterized by a definite thread-like structure and directional growth according to standard figures in the ASTM D 2803-93.

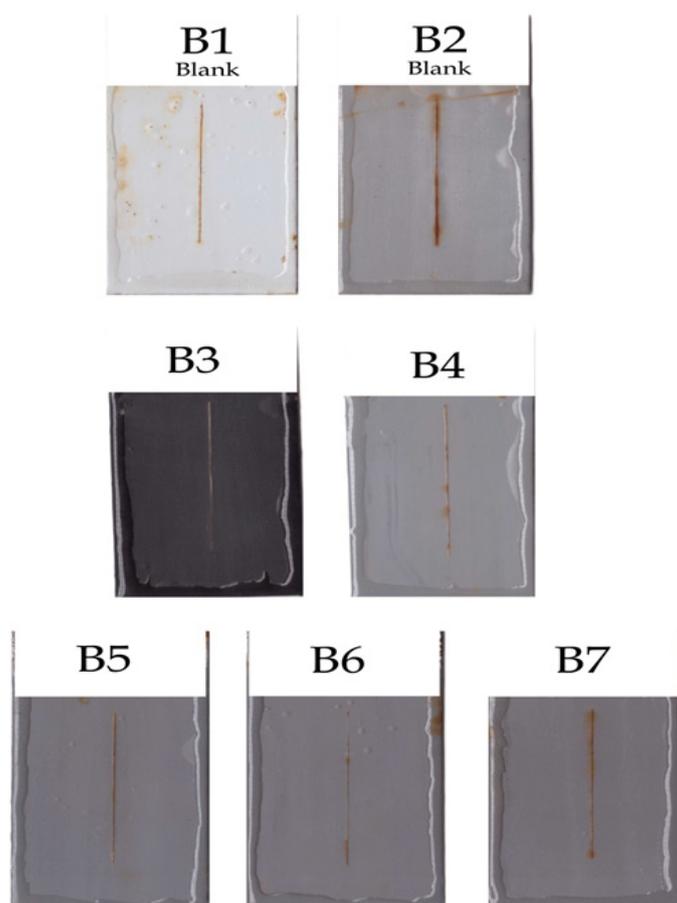


Fig. 7. Photographs of paint films based on BPO₄ / epoxy resin showing the degree of blistering and filiform corrosion after immersion in artificial seawater for 28 days.

Conclusions

Long-term performance requires utilization of excellent inhibitive pigment(s) and presence of inhibitive leachable species within the applying coating system which is designed to limit the corrosion processes that might arise underneath the coating surface. Thus, our work devoted to providing a protective pigment/inhibitor system based on boron phosphate and *in-situ* polymerized PpPPD as a corrosion inhibitive system.

Low-cost and safe boron phosphate pigment was prepared and investigated individually and in association with *in-situ* prepared polymeric inhibitor PpPPD. Besides, they were applied and incorporated within controlled paint formulations to measure their physico-mechanical and corrosion protective properties. They are of good physico-mechanical properties and record high protection against corrosion of steel.

References

1. Kmecl P. and Bukovec P., Boron phosphate: its synthesis, gradual crystallisation and characterisation of bulk properties. *Acta Chim. Slov.* **46**, 161–171 (1999).
2. Keary C. and Moffat J. B., Boron phosphates: their preparation and characterization and the existence of a high surface area, mesoporous, excess boron solid. *J. Colloid Interface Sci.* **154** (1), 8-16 (1992).
3. Wang R., Jiang H., Gong H. and Zhang J., Synthesis of nanosize BPO₄ under microwave irradiation. *Mater. Res. Bull.* **47**, 2108 – 2111(2012).
4. Baykal A., Kizilyalli M., Toprak M. and Kniep R., Hydrothermal and microwave synthesis of boron phosphate, BPO₄. *Turk. J. Chem.* **25**, 425–432 (2001).
5. Abat M., Degryse F., Baird R. and McLaughlin M. J., Formulation, synthesis and characterization of boron phosphate (BPO₄) compounds as raw materials to develop slow-release boron fertilizers. *J. Plant Nutr. Soil Sci.* **177**, 860–868 (2014).
6. Power P. P. and Woods W. G., The chemistry of boron and its speciation in plants. *Plant and Soil* **193**, 1–13 (1997).
7. Hutchings G. J., Hudson I. D. and Timms D. G., Deactivation and reactivation of boron phosphate catalysts. *Studies in Surface Science and Catalysis* **88**, 663-668 (1994).
8. Hutchings G. J., Hudson I. D., Bethell D. and Timms D. G., Dehydration of 2-methylbutanal and methyl isopropyl ketone to isoprene using boron and aluminium phosphate catalysts. *Journal of Catalysis* **188** (2), 291-299 (1999).
9. Çakmakçı E. and Güngör A., Preparation and characterization of flame retardant and proton conducting boron phosphate/polyimide composites. *Polym. Degrad. Stab.* **98**, 927-933 (2013).
10. Zhou Y., Feng J., Peng H., Qu H. and Hao J., Catalytic pyrolysis and flame retardancy of epoxy resins with solid acid boron phosphate. *Polym. Degrad. Stab.* **110**, 395-404 (2014).
11. Zhao K., Xu W., Song L., Wang B., Feng H. and Hu Y., Synergistic effects between boron phosphate and microencapsulated ammonium polyphosphate in flame-retardant thermoplastic polyurethane composites. *Polym. Adv. Technol.* **23**, 894–900 (2012).
12. Dogan M., Yılmaz A. and Bayramlı E., Flame retardant polymer compositions with coated boron phosphate. *Polym. Degrad. Stab.* **95**, 2584-2588 (2010).
13. Vasovic D. D. and Stojakovic D. R., Use of boron phosphate in the solid-state preparation of crystalline iron(III) phosphate and manganese(II) diphosphate. *J. Am. Cer. Soc.* **77** (5), 1372-1374, (1994).
14. Vasovic D. D. and Stojakovic D. R., Metal phosphate preparation using boron phosphate. *Mater. Res. Bull.* **32**, 779–784 (1997).
15. Shiryaev K.V., Quartz ceramics containing boron phosphate additive. *Tekhnologiya* **48**, 26-28 (1991). (trans.)
16. Hsu R., Kim J. Y., Kumta P. N. and Feist T.P., Modified oxide sol-precipitation (MOSP) approach for synthesizing borophosphosilicate glasses and glass-ceramics. *Chem. Mater.* **8**, 107-113 (1996)
17. Croop E. J. and Vondracek C. H., Insulation utilizing boron phosphate. USP 3383275 (1968).
18. Hu Y., Shannon R. D. and Tomic E. A., Boron aluminum phosphates and boron aluminum phosphosilicates for electronic packaging. EP0538397 B1 (1995).
19. Mamlouk M. and Scott K., A boron phosphate-phosphoric acid composite membrane for medium temperature proton exchange membrane fuel cells. *Journal of Power Sources* **286**, 290-298 (2015).
20. Roberge P. R., *Handbook of Corrosion Engineering*. Ch. 10, 833-862, New York (2000).

21. Revie R. W., *Uhlig's Corrosion Handbook*, 3rd Edition, Ch. 71, 1021-1032, John Wiley & Sons, Inc. (2011).
22. Saji V. S., A review on recent patents in corrosion inhibitors. *Recent Patents on Corrosion Science* **2**, 6-12(2010).
23. Soeda K. and Ichimura T., Present state of corrosion inhibitors in Japan. *Cement & Concrete Composites* **25**, 117-122(2003).
24. Abd El-Ghaffar M. A., Shaffei K.A., Zikry A.A. F., Mohamed M. B. and Marzouq K. A.G., Novel conductive nano-composite ink based on *poly* aniline, silver nanoparticles and nitrocellulose, *Egypt. J. Chem.* **59** (4), 429 - 443 (2016).
25. Abd El-Ghaffar M. A., Abdelwahab N. A., Sanad M. A., and Sabaa M. W., High performance anti-corrosive powder coatings based on phosphate pigments containing *poly*(o-aminophenol). *Prog. Org. Coat.* **78**, 42-48 (2015).
26. Abd El-Ghaffar M. A., Abdelwahab N. A. and Youssef E. A., Polyaniline and poly (m-toluidine) prepared by inverse emulsion pathway as corrosion inhibitors in surface coatings. *Pigm. & Resin Tech.* **33**(4), 228-236 (2010).
27. Abd El-Ghaffar M. A., Youssef E.A.M., Darwish, W.M. and Helaly, F.M., A novel series of corrosion inhibitive polymers for steel protection. *J. Elastomers Plast.* **30** (1), 68-94 (1998).
28. Lyona S.B., Bingham R. and Mills D.J., Advances in corrosion protection by organic coatings: What we know and what we would like to know. *Prog. Org. Coat.* **102**, 2-7 (2017).
29. ASTM D 5965-96, Standard test methods for specific gravity of coating powders (2001).
30. ASTM D16-00, Standard terminology for paint, related coatings, materials, and applications (2001).
31. ASTM D281-95, Standard test method for oil absorption of pigments by spatula rub-out (2001).
32. ASTM D279-87 (Reapproved 1997), Standard test methods for bleeding of pigments, (2001).
33. H. Payne, *Organic Coating Technology*, Vol. 2, John Wiley & Sons, Inc., London, p. 870 (1961).
34. ASTM D1208-96, Standard test methods for common properties of certain pigments (2001).
35. ASTM D 609-00, Standard practice for preparation of cold-rolled steel panels for testing paint, varnish, conversion coatings, and related coating products (2001).
36. ASTM D 4147-99, Standard practice for applying coil coatings using the wire-wound drawdown bar (2001).
37. ASTM D 823-95 (Reapproved 2001), Standard practices for producing films of uniform thickness of paint, varnish, and related products on test panels (2001).
38. ASTM D 1640-95 (Reapproved 1999), Standard test methods for drying, curing, or film formation of organic coatings at room temperature (2001).
39. ASTM D 1005-95 (Reapproved 2001), Standard test method for measurement of dry-film thickness of organic coatings using micrometer (2001).
40. ASTM D 4366-95, Standard test methods for hardness of organic coatings by pendulum damping tests (2001).
41. ASTM D 3359-97, Standard test methods for measuring adhesion by tape test (2001).
42. DIN 67530, Reflectometers as a means for gloss assessment of plane surfaces of paint coatings and plastics (1982).
43. ASTM D 2794-93 (Reapproved 1999), Standard test method for resistance of organic coatings to the effects of rapid deformation (Impact) (2001).
44. DIN 53156 - EN ISO 1520, Testing the ductility (deformability) by cupping test machine (1995).
45. ASTM D 714-87 (Reapproved 2000), Standard test method for evaluating degree of blistering of paint (2001).
46. A) ASTM D 2803-93, Standard guide for testing filiform corrosion resistance of organic coatings on metal (2001). B) "Pictorial Standards of Coatings Defects" Federation of Societies for Coatings Technology.
47. ASTM D 610-01, Standard test method for evaluating degree of rusting on painted steel surface (2001).
48. Chen S., Ye M., Chen H., Yang X. and Zhao J., Synthesis and characterization of nanostructure BPO₄. *J Inorg Organomet Polym* **19**, 139-142 (2009).

49. Mulla I. S., Chaudhary V.A. and Vijayamohan K., Humidity sensing properties of boron phosphate. *Sensors and Actuators A* **69**, 72-76 (1998).
50. Kendiga M., and Mills D. J., An historical perspective on the corrosion protection by paints, *Prog. Org. Coatings* **102**, 53-59 (2017).
51. Hegazy M.A., Hefny M.M., Badawi A.M. and Ahmed M.Y., Nanosilicon dioxide/o-phenylenediamine hybrid composite as a modifier for steel paints. *Prog. Org. Coat.* **76**, 827- 834 (2013).
52. Ismail M.N., Megahed H.E., Ali A. I. and El-Etre M. A., Application of theophylline anhydrous as inhibitor for acid corrosion of aluminum. *Egypt. J. Chem.* **60**(1), 95 -107 (2017).
53. Mohamed S. G., N-aminophthalimide as a synthon for heterocyclic Schiff bases: Efficient utilization as corrosion inhibitors of mild steel in 0.5 mol.L⁻¹ H₂SO₄ solution. *Egypt. J. Chem.* **61**(3), 300-310 (2018).
54. Archana S. and Jaya Shanthi R., Synthesis and characterization of poly (p-phenylenediamine) in the presence of sodium dodecyl sulfate. *Res. J. Chem. Sci.* **4**(2), 60-67 (2014).
55. Hristov H., Nedyalkova M., Madurga S. and Simeonov V., Boron oxide glasses and nanocomposites: synthetic, structural and statistical approach. *Journal of Materials Science & Technology* **33**(6), 535-540 (2017).

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فوسفات البورون/بولي(فينيلين داى أمين) كمنظومة مثبطة للتآكل لحماية الأسطح المعدنية

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التآكل لا يفتقر أبداً، من أجل ذلك، فإن الصناعات فضلاً عن الحكومات تبذل قصارى جهدها لمقاومة التآكل بمختلف أنواعه بكل السبل والوسائل والتقنيات الممكنة ولا سيما في الأماكن الأكثر تضرراً بهذا الخطر. ومع هذا، تُعتبر الطلاءات العضوية هي الوسيلة الأكثر تطبيقاً لحماية الأسطح المعدنية من التآكل، وهي من الأهمية بمكان خاصة في حماية وسائل النقل والبنية التحتية.

وبناء على ما سبق ذكره، فإن الهدف الرئيسي من هذه الدراسة هو تقديم لمحة تفصيلية عن منظومة دهان (مُخضب/ مثبّط) تعتمد في تركيبها على مُخضب فوسفات البورون و مثبّط البولي(فينيلين داى أمين)، وذلك كنوع جديد من الطلاءات المثبّطة للتآكل و التي تعمل بشكل أكثر شمولية للحصول على أداء عالي طويل المدى لحماية الأسطح المعدنية.

لذلك، تم توصيف و دراسة مُخضب فوسفات البورون و/أو مثبّط البولي(فينيلين داى أمين)، الذي تم بلمرته أنياً مع المخضب، عبر استخدام تقنيات حيود الأشعة السينية، الأشعة تحت الحمراء، التصوير الميكروسكوبى الماسح و التحليل الحراري. بالإضافة إلى ذلك، تم تطبيق تراكيزات مختلفة من مُخضب فوسفات البورون/ مثبّط البولي(فينيلين داى أمين) داخل تركيبات طلاءات حاكمة تعتمد فى أساسها على راتنج الايبوكسي، وتبعاً لهذا، فقد أظهرت تلك التركيبات خواصاً فيزيكو-ميكانيكية جيدة ومستوى عالي من الحماية ضد التآكل.