

ACIDITY ADJUSTMENT OF THE SOLUTIONS FOR COATING DEPOSITION AND FURTHER SEALING BY LOURIER BUFFERS

Stefania Portolesi, Erasmus MS-student

University of Calabria (Italy)

E-mail: stefania.portolesi@live.com

Dr. Stephan Kozhukharov, PhD, dipl. Eng.

Department of Physics

University of Chemical Technology and Metallurgy – Sofia

E-mail: s.kozhukharov@uctm.edu

Assoc. Prof. Temenuzhka Haralanova, PhD

Department of Chemistry, Food and Biotechnologies

University of Ruse “Angel Kanchev”, Razgrad Branch

E-mail: tharalanova@uni-ruse.bg

Assoc. Prof. Dr. Christian Girginov, PhD, dipl. Eng.

Department of Physical Chemistry

University of Chemical Technology and Metallurgy – Sofia

E-mail: girginov@uctm.edu

***Abstract:** The present paper provides valuable practical information on the preparation of buffer solutions in accordance with data presented in the encyclopedic handbook of Y.Y. Lourier. Among the wide variety of buffer solutions proposed by the author, only phosphate and borate are discussed here. The main reason for the interest in these types of buffers is that phosphating is a common procedure for sealing various primers for corrosion protection, while $\text{Na}_2\text{B}_4\text{O}_7$ and H_3BO_3 are usually preferred electrolyte additives for electrochemical film deposition. For the reader's convenience, pH-composition tables are presented. The data in these tables enable preparation of suitable buffers for various coatings and other technological purposes.*

***Keywords:** pH buffers, Buffer compositions, Electrochemical deposition electrolytes, Phosphating solutions*

INTRODUCTION

Painting and coating deposition are common industrial practices for effective corrosion protection of industrial aluminum alloys such as AA2024-T3. Usually, the coatings are multi-layered and each layer has its own function. Thus, advanced anti-corrosion coatings must possess a variety of properties for active and passive anti-corrosion protection. In addition, the coatings and related technologies for their deposition also need to be environmentally acceptable.

In addition, the ever-increasing requirements regarding coating characteristics in aggressive environments necessitate the development of new generations of advanced multi-layer paint systems. Figure 1 shows the main trends for the development of environmentally acceptable, advanced corrosion protection coatings. Coating primers are indispensable for all types of protective coating systems. Therefore, the formation of cerium conversion coatings (CeCC) on aluminum-based alloys is considered as an approach to develop “stainless” aluminum (Mansfeld F., Wang Y., Shih H. 1992), (Mansfeld F., Wang, Y. 1995). Successful CeCC deposition requires appropriate preliminary surface treatments of the metal substrates. In this sense, a comparative study of this preliminary stage was carried out in either acidic or alkaline conditions (Pinc W., Geng S., O’Keefe M., Fahrenholtz W. and O’Keefe T. 2009). Hence, it is the pH of the etching medium that is the main object of these authors.

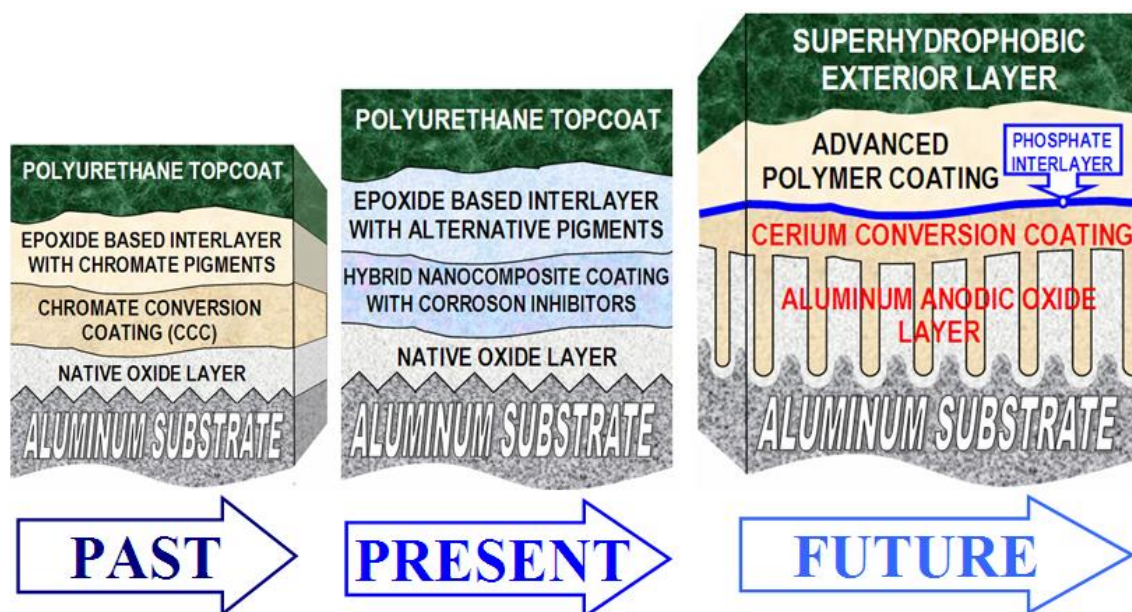


Fig. 1. Evolution of the concepts for elaboration of environmentally acceptable corrosion protective layers

Furthermore, the performance of CeCC in corrosive environments can be further improved by sealing through phosphating. This procedure was applied to CeCC layers by immersion in a 2.5 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ solution, for different durations (10, 30 and 120 s), and temperatures (55, 70 and 85°C), respectively (Heller D. K., Fahrenholtz W. G., O’Keefe M. J., 2010). Other authors (Chen D-C, LI W-F., Gong W-H., Wu G-X and Wu J-F., 2009) determined that the optimal conditions for this final sealing procedure were: pH = 4.5 and 85°C. Finally, phosphating turned out to be quite suitable for corrosion protection of zinc (Ivanova D. I., 2011), carbon steel (Tumbaleva Y., Ivanova D., Fachikov L., 2011) and copper (Ignatova K., Kozhukharov S., Alakushev M., 2018).

On the other hand, H_3BO_3 is an indispensable compound for the electrochemical deposition of Ag (Kiradzhyska D., Mantcheva R., Girginov Ch., Kozhukharov S., 2018), as well as Cu and Ni (Girginov Ch., Kozhukharov S, Tsanev A and Dishliev A., 2021) in the pores of anodized aluminum.

Therefore, the aim of this article is to propose two buffer solutions containing phosphorus and boron, based on the encyclopedic handbook of Lourier.

DISCUSSION

The pH of the medium is among the main technological parameters that must be controlled whenever an aqueous or other type of polar liquid medium is used. pH is a relative (i.e., dimensionless) measure equal to the negative decimal logarithm of the molar concentration of the hydrogen ions $[H^+]$ or of the activity of hydroxonium ions $[a_{\text{H}_3\text{O}^+}]$, at equilibrium:

$$pH = -\log[H^+] \quad ; \quad pH = -\log[a_{\text{H}_3\text{O}^+}]. \quad (1)$$

Therefore, any neutral aqueous solution with pH = 7 contains 10^{-7} mol dm^{-3} H_3O^+ ions, while an alkaline one, for instance containing 10^{-10} mol dm^{-3} of H_3O^+ ions, has pH = 10, and in an acidic one with pH = 2 there are 10^{-2} mol dm^{-3} of these ions.

pH measurements are usually performed using Ag/AgCl/3M KCl reference electrodes and a platinum counter electrode immersed in an aqueous electrolyte. In practice, pH meters are specially calibrated millivoltmeters connected to so-called “universal glass electrodes”. These electrodes are composed of silver chloride and Pt encapsulated in a glass body filled with a saturated KCl solution. Contact with external fluids (whose pH is to be measured) is provided by a semi-permeable membrane. Thus, the pH values can be determined by the following equation:

$$pH = \frac{(E^0 - E)}{2.3RT} F, \quad (2)$$

where $\Delta E = (E^0 - E)$ is the potential difference between the electrodes, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the standard temperature, (298 K) and F is the Faraday constant (96485 C mol^{-1}).

The easiest way to maintain constant pH values during any technological process is by adding pH buffers. These pH buffers are also needed to calibrate pH meters before the corresponding pH measurements. Calibration of pH meters is performed by comparative measurements of buffer solutions with known (i.e., accurately determined to at least 3 significant figures) pH values. Various possible buffer solutions exist, but in general all buffers are stable aqueous, dilute solutions of acids and salts of the same anion (acid buffers) or bases and salts of the same cation (alkaline buffers). Each buffer has its own buffer capacity (β), capable of maintaining stable pH equilibrium when alkaline or acidic solutions are added.

The buffer capacity (β) of a solution is defined as the number of moles of a strong acid or a strong base that causes 1 dm^{-3} of the buffer to undergo a unit change in pH. Mathematically, buffer capacity is given by

$$\beta = \frac{dc_b}{d(pH)} = -\frac{dc_a}{d(pH)}, \quad (3)$$

where dc_b is the number of moles per liter of strong base, and dc_a is the number of moles per 1 dm^3 of strong acid added to the buffer. Since adding strong acid to a buffer causes the pH to decrease, $dc_a/d(pH)$ is negative, and buffer capacity is always positive (Skoog D. A., West D. M., Holler F. J., Crouch St. R., 2014).

According to various authors (Babko A., and Piatnitskiy I., 1968; Koreman I. M. 1949; Vasiliev V. 1989) the values of buffering capacity (β) can be calculated by the following equation:

$$\beta = \frac{MV_{sol}}{\Delta(pH)V_{buff}} \left(\frac{1}{n} \right), \quad (4)$$

where β is the (mol pH^{-1}), (MV_{sol}) is the quantity of the added alkaline or acidic solution (mol), $\Delta(pH)$ is the pH change (dimensionless) and V_{buff} is the volume of the buffer solution. The coefficient ($1/n$) is attributed to the compound, whose solution is submitted to pH measurement. If it is alkaline, then n = number of OH^- anions from any compound molecule. If it is acidic, then n = number of H_3O^+ (i.e., H^+ cations) moieties from each molecule of the dissolved compound.

Further literature analysis showed that some phosphate and borate solutions can also be used as buffers. Two examples from the encyclopedic handbook of Y.Y. Lourier (Lourier Y. Y., 1979) are given in Tables 1 and 2. They were chosen specifically because the proposed buffer solutions are very suitable as liquid electrolyte media for chemical or electrochemical deposition of metals and phosphating of the final coating. The data in the presented tables provide valuable information for the preparation of buffers with a desired nominal pH. Furthermore, these data allow the reader to prepare different buffers in order to perform extensive comparative research on the effect of pH on the deposition of different electrochemically deposited films, formation of conversion coatings, and/or final phosphating. The buffer solutions presented in these tables cover a relatively wide pH interval, making them suitable for different types of coating primers on aluminum, steel, zinc, copper or other metal substrates.

Table 1 presents ratios for preparing phosphate-based buffers. In this case, the first solution is $S_1 = 0.067 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (11.866 g pure compound dissolved in 1 dm^3). The volumes shown in the table are to be added to the second solution to give 100 ml of buffer with the desired pH value. The composition of the second solution is $S_2 = 0.067 \text{ mol dm}^{-3} \text{ KH}_2\text{PO}_4$ (9.072 g of the pure compound dissolved in 1 dm^3).

The following example serves to explain in more detail how the data in the table are handled. So, the task is to obtain a phosphate solution with $\text{pH} = 6.78$. In this case, to 47.90 ml of S_1 the

corresponding volume of S_2 up to 100 ml must be added (for greater accuracy a volumetric flask is used).

Table 1. Necessary volumes of S_1 for preparation of phosphate-based buffer solution with desired pH, until the third digit of the value

pH	+0.00	+0.01	+0.02	+0.03	+0.04	+0.05	+0.06	+0.07	+0.08	+0.09
4.8	0.35	0.37	0.39	0.41	0.43	0.45	0.48	0.51	0.54	0.57
4.9	0.60	0.63	0.66	0.69	0.72	0.75	0.79	0.83	0.87	0.91
5.0	0.95	0.99	1.03	1.07	1.11	1.15	1.19	1.23	1.27	1.31
5.1	1.35	1.39	1.43	1.47	1.51	1.55	1.60	1.65	1.70	1.75
5.2	1.80	1.85	1.90	1.95	2.00	2.05	2.10	2.15	2.20	2.25
5.3	2.30	2.37	2.44	2.51	2.58	2.65	2.72	2.79	2.86	2.93
5.4	3.00	3.09	3.18	3.27	3.36	3.45	3.54	3.63	3.72	3.81
5.5	3.90	3.99	4.08	4.17	4.26	4.35	4.46	4.57	4.68	4.79
5.6	4.90	5.02	5.14	5.26	5.38	5.50	5.62	5.75	5.90	6.05
5.7	6.20	6.35	6.50	6.70	6.85	7.00	7.20	7.35	7.55	7.70
5.8	7.90	8.10	8.25	8.45	8.60	8.80	9.00	9.20	9.40	9.60
5.9	9.80	10.00	10.20	10.40	10.60	10.80	11.10	11.30	11.60	11.80
6.0	12.10	12.40	12.70	12.90	13.20	13.50	13.80	14.10	14.40	14.70
6.1	15.00	15.30	15.70	16.00	16.40	16.70	17.00	17.40	17.70	18.10
6.2	18.40	18.70	19.10	19.40	19.80	20.10	20.50	20.90	21.90	21.70
6.3	22.10	22.50	22.90	23.40	23.80	24.20	24.60	25.10	25.50	26.00
6.4	26.40	26.90	27.30	27.80	28.20	28.70	29.20	29.70	30.30	30.80
6.5	31.3	31.90	32.40	33.00	33.50	34.10	34.70	35.30	35.90	36.50
6.6	37.10	37.70	38.30	38.90	39.40	40.00	40.60	41.20	41.80	42.40
6.7	43.00	43.60	44.20	44.80	45.40	46.00	46.60	47.30	47.90	48.60
6.8	49.20	49.80	50.40	51.00	51.60	52.20	52.80	53.40	54.00	54.60
6.9	55.20	55.80	56.40	57.00	57.60	58.20	58.80	59.40	60.00	60.60
7.0	61.20	61.80	62.40	63.00	63.60	64.20	64.80	65.40	65.90	66.50
7.1	67.00	67.60	68.10	68.70	69.20	69.80	70.40	70.90	71.50	72.00
7.2	72.60	73.20	73.70	74.30	74.80	75.40	75.90	76.30	76.80	77.20
7.3	77.70	78.10	78.60	79.00	79.50	79.90	80.30	80.70	81.00	81.40
7.4	81.80	82.10	82.50	82.80	83.20	83.50	83.80	84.20	84.50	84.90
7.5	85.20	85.50	85.90	86.20	86.60	86.90	87.20	87.50	87.90	88.20
7.6	88.50	88.80	89.10	89.30	89.60	89.90	90.20	90.40	90.70	90.90
7.7	91.20	91.40	91.70	91.90	92.20	92.40	92.60	92.90	93.10	93.40
7.8	93.60	93.80	94.00	94.20	94.40	94.60	94.80	95.00	95.10	95.30
7.9	95.50	95.60	95.80	95.90	96.10	96.20	96.30	96.50	96.60	96.80
8.0	96.90	-	-	-	-	-	-	-	-	-

In the same manner, through Table 2, Lourier proposes preparation of $Na_2B_4O_7/HCl$ buffer solutions, suitable for a pH range of 7.71 to 9.23. Each of the tabulated volumes of Solution 3 ($S_3 = 0.067 \text{ mol dm}^{-3} Na_2B_4O_7 \cdot 10H_2O$ or 19.069 g of pure compound dissolved in 1 dm^3) should be filled up with Solution 4 ($S_4 = 0.1 \text{ mol dm}^{-3} HCl$) up to 100 ml. It should be noted here that the term “pure

compound” means that the weight of the initial precursor must be recalculated relative to its concentration.

A practical example is needed to better understand the contents of the table and how it is used to prepare a buffer. For instance, if the task is to obtain a borate solution with pH = 8.33, then row for pH 8.3 is intercepted with column +0.03. Hence, it is obvious that the desired volume of S₃ equals to 61.40 ml. After filling the volumetric flask with this volume of S₃, it should be filled up to the mark (up to 100 ml) by adding the corresponding volume of S₄.

Table 2. Necessary volumes of S₃ for preparation of borate-based buffer solution with desired pH, until the second digit of the value

pH	+0.00	+0.01	+0.02	+0.03	+0.04	+0.05	+0.06	+0.07	+0.08	+0.09
7.7	-	52.50	52.60	52.70	52.8	52.9	53.0	53.10	53.20	53.30
7.8	53.4	53.50	53.60	53.70	53.85	53.95	54.10	54.25	54.40	54.55
7.9	54.65	54.75	54.85	55.00	55.10	55.25	55.35	55.50	55.60	55.75
8.0	55.85	56.00	56.10	56.25	56.35	56.50	56.60	56.75	56.90	57.00
8.1	57.15	57.25	57.40	57.50	57.65	57.80	57.95	58.10	58.30	58.45
8.2	58.65	58.80	59.00	59.20	59.40	59.60	59.80	60.00	60.20	60.45
8.3	60.7	60.95	61.15	61.40	61.60	61.85	62.05	62.30	62.50	62.70
8.4	62.95	63.20	63.45	63.65	63.90	64.10	64.35	64.55	64.80	65.00
8.5	65.25	65.50	65.75	66.05	66.30	66.60	66.90	67.20	67.50	67.75
8.6	68.0	68.25	68.55	68.80	69.10	69.40	69.70	70.00	70.40	70.80
8.7	71.2	71.60	72.00	72.40	72.80	73.20	73.60	74.00	74.50	75.00
8.8	75.5	76.00	76.50	77.00	77.50	78.00	78.50	79.00	79.50	80.00
8.9	80.5	81.00	81.50	82.00	82.50	83.00	83.50	84.00	84.50	85.00
9.0	85.6	86.25	86.90	87.50	88.10	88.75	89.40	90.00	91.60	91.25
9.1	91.9	92.50	93.10	93.75	94.40	95.00	95.60	96.25	96.90	97.50
9.2	98.1	98.75	99.40	100.0	-	-	-	-	-	-

CONCLUSION

The efficient corrosion protection of metals requires their covering with advanced multi-layered protective coatings. Each of the layers, making up the entire coating serves its own function. In this sense, the Cerium Conversion Coatings (CeCC) appear to be the most promising coating primers for alloys, such as AA2024, AA7075, etc.

The entire technology for the formation of CeCC includes three stages: (i) preliminary surface treatment, (ii) chemical or electrochemical deposition of the CeCC and (iii) its final sealing.

The pH of the medium appears to be among the key factors for each of the stages of CeCC formation. This is the reason for the need to control the pH value during the entire process of CeCC formation.

Phosphate- and borate-based pH buffers seem to be very suitable for the final sealing of CeCC, as they provide valuable components for the phosphate/borate sealing top layer.

Summarizing all these conclusions, it should be noted that the data presented in this paper can serve as a valuable source of information for the preparation of suitable buffers for chemical and electrochemical deposition of metals or conversion coatings, as well as for their phosphate/borate sealing.

The tables presented allow the preparation of variety of buffers different buffers over a relatively wide pH range. Therefore, these data make it possible to carry out comprehensive comparative investigations dedicated to the development of advanced coating primers.

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