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ESTIMATION OF PHENOLPHTHALEIN-ALKALINITY TITRATION IN DEGREASING PROCESS WITH STATISTIC AND PARTIAL LEAST SQUARES REGRESSION METHOD

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***Abstract*—In color coating processes, a pre-treatment process is a one of most of essential operations to clean all dusts and grease out from product parts. A degreasing step in the pre-treatment process becomes more important recently. Even though monitoring cleanser concentration in a degreasing bath can be indicated by Phenolphthalein-alkalinity (P-alkalinity) titration, this procedure carried out by human leads to unsatisfactory error. Moreover, the control of concentration of the solution is very difficult. This research focuses on estimation of P-alkalinity value represented the concentration of the cleaner solution in the degreasing bath using parameters which are measurable with standard tools such as pH, Electro conductivity, Density and Temperature. The degreasing bath of a factory in an air conditioner industry is used as a case study. The estimation approach is based on using statistic and Partial Least Squares regression (PLS). It was found that the approach can be able to provide the estimation of the cleanser concentration with the accuracy of 8.62%.**

***Index Terms*— Alkalinity, Degreasing, Partial Least Squares, Pre-treatment, Estimation, Monitoring**

I. INTRODUCTION

Degreasing process is used for eliminating contaminations (grease, dust and rust) from surfaces of metal product and it is an important step in preparing metal's surfaces to be suitable for color coating process. The capability of grease cleaning directly affects to corrosion resistance's ability of coated metal. Therefore, controlling the solution concentration in bath as an appropriate level is very crucial.

Recently, the case study factory has used the chemical degreasers which are called "*UniPrep®SP1*" and "*UniPrep® Bio Activator*". The advantages are;

- Be able to operate well without outsource heat input
- Cleaning efficiency is better than traditional chemical Equations

However the cost of latest chemical is expensive. This commercial cleaner is composed of many type of alkaline. The factory has controlled concentration by observing the value of P-alkalinity which demonstrates alkaline compound's value in liquid solution with restricted range between 1250-1450 mg/L as $CaCO_3$. Base on a study of other researches, many techniques were used to predict the amount of surfactant. In 2010, Wang et al used surface tension measurement and nuclear magnetic resonance [1]. In 2010 Veronoveski et al. and In 2009 Paillet et al., they used capillary electrophoresis and static or dynamic light scattering [2-3]. In 2009, Socomor used alkaline titration in aqueous media and electro conductivity measurement [4]. In 2005, Eva Aguilera-Herrador used Attenuated Total Reflection-Fourier Transform-Infrared (ATR-FT-IR) spectroscopy [5]. In 1987 Cutler and Kissa, they used high-performance liquid chromatography [6]. Nevertheless these methods are complicated and high cost. Furthermore they have not been used in case of complex solution.

This research emphasized on estimation of P-alkalinity of complex solution in degreasing bath. P-Alkalinity titration is a technique that recommended by detergent provider to monitor the degreasing bath. The high precise tools were used thus data from measuring should have even more accuracy and the human mistake would be suspended. These tools are:

1) Electro conductivity measurement: Conductivity has been employed because the components of commercial cleanser (alkaline surfactant) contain ions. Conductivity measuring was performed with the same simulations of degreasing bath as alkaline titration [7].

2) pH measurement: pH of pure UniPrep®SP1 is 13 that more than solute (about 7)so concentration of solution will influence to pH [8].

3) Density calculation: Density of pure UniPrep®SP1 is 1.075 g/cm^3 so density of solution is influenced by concentration of solution [8].

4) Temperature measurement: Every reaction has a reaction's heat. Solution in degreasing bath has many kinds of alkaline cleansers and oil. The assumptions are that the reactions in degreasing bath are more than one reaction and the sum of heat of reactions is not equal to zero.

Accordingly, the value of P-alkalinity measured with titration is a dependent or response variable and the values from 4 tools are used as independent or predictor variables.

Every sample was recorded by measuring properties in degreasing bath from the case study factory and all of them were analyzed following statistical procedures including PLS regression. Partial Least Squares has been very popular in areas like chemical engineering, where predictive variables often consist of many different measurements in an experiment [9-10]. Thus they will be supposed to present the relations of response variable against predictor variables in mathematic equation form. Although the experiment has controlled so well, the concluding equation still has limitation when using.

II. METHODOLOGY

A. Observing data from real sample

The data interested were P-Alkalinity, Electro Conductivity, Density, Temperature and pH.

1) Alkaline titration: Titrate 10 ml of sample with 0.1 N H_2SO_4. 5 drops of pheonptalien is an indicator. The ml of H_2SO_4 has been taken to be P-Alkalinity by Equation 1.

$$\text{P-Alkalinity (mg/L as } CaCO_3) = \frac{(\text{mL of } H_2SO_4)\times(\text{Normality of } H_2SO_4)\times 50,000}{\text{mL of Sample}} \quad (1)$$

2) pH measurement: pH pen meter from Lutron®, Taiwan was tool for measurement pH value of sample under hypothesis that pH is depend upon concentration of solution.

Specification of pH pen meter:

Manufacturer	Lutron®
Model	pH-222
Range	0-14 pH
Accuracy	±0.02 pH
Resolution	0.01 pH

3) Density calculation: 10 ml of pycnometer and 3 point decimal weighting were tools for calculating density.

4) Electro Conductivity and Temperature measurements: Electro Conductivity and Temperature are suddenly measured together by TetraCon® 325 prob.

Specification of Conductivity and Temperature meter:

Manufacturer	inoLab®
Model	TetraCon® 325
Range (Conductivity)	1µS/cm – 2S/cm
Resolution (Conductivity)	0.1 µS/cm
Range (Temperature)	0°C - 100°C
Resolution (Temperature)	0.1 °C

B. Probability distribution test:

Probability distribution is very important because samples were a part of population but they used as agent of all populations for predicting the situation in the future. To make sure that the collected-data have normal distribution, histogram graph of residual was employed to consider this condition. Since it looks like a bell shaped curve (normal curve), it will have normal distribution.

C. Finding suitable model

A linear regression was used as a tool to find the suitable model giving the best R-square and the highest degree is 3.

D. Level of correlation test

Pearson's correlation was used as a tool to determine the level of correlation and to cut some parameters out when it has no relationship with response.

E. Regression

Partial Least Squares in miniTab® program was a tool to estimate P-Alkalinity with measuring variables from degreasing bath.

III. Results and Discussions

A. Data

The data from sample have been collected for 1 month, 5 days a week. 131 of samples were measured by measuring tools and P-Alkalinity titration. The table below shows some properties of all variables in Table 1.

B. Probability distribution

Probability of data is the 1st condition before doing regression method. Histogram graph of residual was employed to consider.

Shape of histogram graph from Fig 3.1 looks like a bell shape and residuals distribution around zero-line seems to be symmetry in Versus Fits graph. All reasons supported that the collected data has normal distribution.

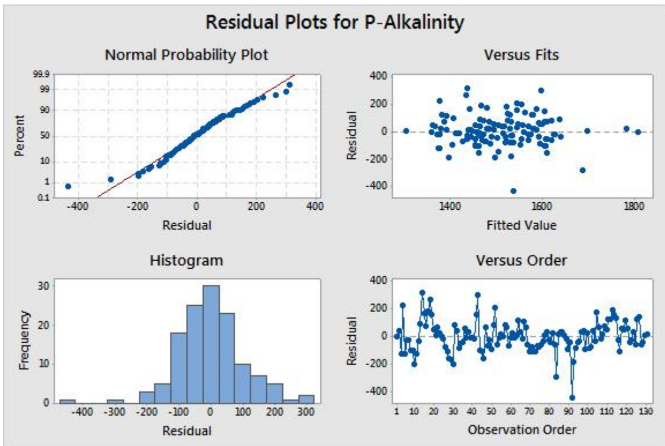

Fig. 1. Residual plots for P-Alkalinity

TABLE I. Statistical Properties of Data

Variables(unit)	Statistic properties			
	Maximum	*Minimum*	*Mean*	*Standard Deviation*
EC [a] (mS/cm)	17.370	13.720	14.936	0.627
D [b] (g/cm^3)	1.0380	1.0248	1.0284	0.0011
T [c] (°C)	31.0	29.5	30.076	0.274
pH	9.69	9.59	9.629	0.0226
P-Alkalinity [d] (mg/L as $CaCO_3$)	1900	1100	1508.9	138.6

a. Electro Conductivity, b. Density, c. Temperature of solution, d. P-Alkalinity

TABLE II. R-square of Relationship among each Independent versus Dependent Variables

Model	Value of R-square			
	EC	*D*	*T*	*pH*
Linear	54.2%	47.2%	3.0%	0.2%
Quadratic	54.6%	53.1%	3.9%	6%
Cubic	55.1%	56.1%	4.1%	6%

TABLE III. Pearson's Coefficient for each Relationship

Variables	Pearson's Coefficient			
	P-Alkalinity	*EC^3*	*D^3*	*T^3*
EC^3	0.739			
D^3	0.687	0.471		
T^3	0.172	0.127	-0.132	
pH^2	-0.039	0.198	-0.070	-0.042

From the Table 2, cubic model relation of Electro Conductivity, Density and Temperature with P-Alkalinity gave the highest R-square values, 55.1%, 56.1% and 4.1% respectively. For pH and P-Alkalinity relation, quadratic and cubic models showed same R-square that is 6%.

C. Finding suitable model

Finding suitable model from the relationship among dependence variable (P-Alkalinity) and independence variables (Electro Conductivity, Density, Temperature and pH) was a guideline when using PLS regression. R-square was used as a basis for decision suitable model: linear, quadratic or cubic model.

D. Level of correlation test

The finding suitable model step shows the best model for Electro Conductivity, Density and Temperature is cubic and pH is quadratic model. This step, Pearson's correlation was a technique to test level of correlation following the Table 3**.**

In Table 3, Pearson's coefficient (r) showed the level of relation between cubic of Electro Conductivity with P-Alkalinity is 0.739 meaning Electro Conductivity and P-Alkalinity have high positive correlation and r coefficient between cubic of Density and P-Alkalinity is 0.687 meaning Density and P-Alkalinity have moderate positive correlation. In the other hand r coefficient of cubic of Temperature and quadratic of pH are 0.172 and -0.039 respectively that showing the 2 independent variables have a little correlation according to Hinkle D.E.,2003 [11]. If consider only on pH, r coefficient was negative (-0.039) meaning pH inversely relates to P-Alkalinity. -0.039 was nearly to zero and it was 4 times less than r coefficient of cubic of Temperature. Therefore pH variable must be omitted from correlation test.

E. Regression

Partial Least Square regression is a linear regression but user can use PLS to regress nonlinear by making new variable. In this case, P-Alkalinity was estimated from 3 independent variables which were Electro Conductivity, Density and Temperature and the models of relation were not only linear. Therefore cubic of Electro Conductivity, Density and Temperature were made as new independence variables etc.

Figure 2, PLS Model Selection Plot showed four components giving optimal both R-square value. The optimal R-squares are 0.725195 (R-sq) and 0.706176 (R-sq (pred)). So the number of components selected for PLS is 4 from 13 components evaluated.

Table 4 shows coefficients of each variable which estimate P-Alkalinity form PLS regression. The Equation 2 has 14 terms including the constant value. It becomes difficult to use. If finding suitable model step is considered again. Form Table 2, R-square of each model has less difference, the simple model will be a linear formation and it have to take into regression process step by step.

$$\text{P-Alkalinity} = [B]^T [X] \quad (2)$$

Where;

$$[B] = \begin{bmatrix} -35936.5 \\ 87.6 \\ 0.7 \\ -0.1 \\ 12332.5 \\ 6249.3 \\ 4216.6 \\ 270.0 \\ 1.1 \\ -0.1 \\ 89.3 \\ -0.1 \\ 289.9 \\ -0.7 \end{bmatrix}, \quad [X] = \begin{bmatrix} 1 \\ EC \\ EC^2 \\ EC^3 \\ D \\ D^2 \\ D^3 \\ T \\ T^2 \\ T^3 \\ EC \times D \\ EC \times T \\ D \times T \\ EC \times D \times T \end{bmatrix}$$

With R-square = 72.52% and accuracy = 8.82%.

TABLE IV. Coefficient of Each Variable which Estimate P-Alkalinity from PLS Regression

Variables	Coefficients
Constant	-35936.5
EC^2	0.7
D^2	6249.3
T^2	-1.1
E	87.6
D	12332.5
T	270.0
EC *D	89.3
EC*T	-1.0
D*T	282.9
EC^3	-0.1
D^3	4216.6
T^3	-0.1
EC*D*T	-0.7

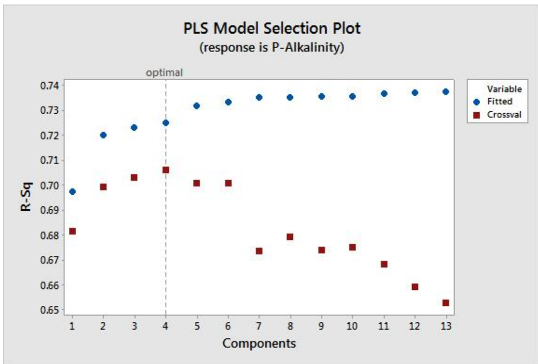

Fig. 2. PLS Model Selection Plot for cubic of variable

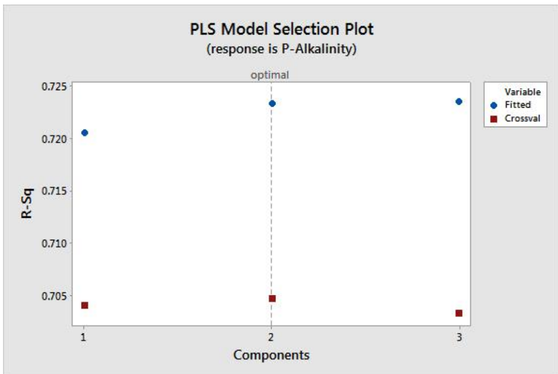

Fig. 3. PLS Model Selection Plot for linear of variable

From Fig.3, the optimal R-squares of a linear model are 0.72338 (R-sq) and 0.704669 (R-sq (pred)). So the number of components selected for PLS is 2 from 3 components evaluated. The linear equation show relationship between P-Alkalinity and Electro Conductivity, Density, Temperature is Equation 3:

$$\text{P-Alkalinity}=\begin{bmatrix}-49149.9 & 82.7 & 42614.5 & 62.2\end{bmatrix}\begin{bmatrix}1\\ EC\\ D\\ T\end{bmatrix} \quad (3)$$

With R-square = 72.34% and accuracy = 8.62%.

IV. Conclusions

A degreasing step in the pre-treatment process becomes more important recently. The monitoring of cleanser concentration in a degreasing bath is needed to control the quality of the product. Presently, the value of the concentration is obtained by P-alkalinity titration with corresponding to human error. This research presents the estimation of P-alkalinity value using statistic and Partial Least Squares regression (PLS) based on measurable states and parameters such as pH, Electro conductivity, Density and Temperature. It was found that the approach with a linear model equation and with a cubic model equation give the accuracy of 8.62% and 8.82% respectively. Therefore, the developed PLS models are applicable to be used with the consideration of specific cleansers: in this work, *UniPrep® SP1* alkaline degreaser and *UniPrep® Bio Activator*.

VI. Acknowledgment

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VII. References

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