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The Optimization of Process Forming Of Conservative Liquids Based On Theoxidized Liquid Rubber And Amidoamines

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ABSTRACT: *In this proceeding, the compositions of the T-30 turbine oil with oxıdızed liquid rubber, the complex of polyethylene polyamine with natural petroleum acid (NPA) and nitrocompounds have been investigated in different ratio and contents as conservative liquids. The experiments have been operated with different concentrations of inhibitor on the steel plates in condensation and environment phases in the experiment chamber. On the bases of experimental data has been developed the regression mathematical model reflecting the ratio of the major factors (NPA and polyethylene polyamine, as well as their concentrations) for the indications of the process.Statistical analysis of the obtained models was held, proved the adequacy of the developed equations to the experimental data. Optimal importance of relations of components and their concentrations leading to the best protective properties from corrosion was found.*

***Keywords**: optimization, regression mathematical model, conservative liquids*

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I. INTRODUCTION

According to the opinions of the majority of the corrosion specialists, the most economically efficient method is the application of the inhibitors among the protection methods against this problem. So, the addition of a small amount of an inhibiting substance to the aggressive system is enough for protecting the metal without any changes to the current technical system.[1-3].The majority of the inhibitors those are used in order to protect the metal-based technological appliances of oil-gas extraction and refinery industries from corrosion are complex compounds which contain nitrogen. The size of the molecules of the inhibitors those are absorbed to the surface of the metals and creates a protective coating is directly related to its influence mechanism. So that, when the radical of the inhibitor increases up to a certain level, the protection effect will be higher [4;5].As a result of its chemisorption ability, inhibitor in the conservative liquid decreases the dissolution by pacifying the processes on the surface, provides a protective coating by creating a complex in the sphere of influence and prevents the corrosion of metal. In recent years, the application of the composition based reagents as corrosion inhibitors are actual[6;7].

In this paper, we present a solution for optimizing the composition of inhibitors based on the processing of experimental data by methods of mathematical statistics.

II. EXPERIMENTAL

In this proceeding, the compositions of the T-30 turbine oil with oxıdızed liquid rubber, the complex of polyethylene polyamine with natural petroleum acid and nitrocompounds which are synthesized on the basis of $C_{14}H_{28}$ α-olefins have been investigated in different ratio and contents as conservative liquids.T-30 turbine oil has been used as a solvent.The mole ratios of the NPA and DETA, TETA and PEPA are different in amidoamine synthesis (T=130 – 140°C). It should be mentioned that it is possible to synthesize amidoamines which contain a number of amine group in the molecule by changing the mole ratio of the acid and amine. For example, 1- 3, 1-4 and 1-6 mole ratios of acid are applicable when diethylene triamine, tetraethylenetetraamine and polyethylene polyamine are taken as feedstocks, respectively. The number of amide functional groups in the synthesized amidoamines increases by increasing the concentration of the acid in the process.

The oxıdızed liquid rubber which is used in the process has been synthesized on the basis of stereo regular structured 1,4 cis – polybutadiene (low molecular weight, M_r ~1800-3000), which has a wide range of industrial application microstructure: 1,4 cis-75~80% ; 1,4 trans-18~22% ; 1,2-units-2~7%, number of units~80)[8;9].Nitro compound is synthesized by using treating $C_{14}H_{28}$ which is produced by the oligomerization of ethylene with nitro compound with nitric acid in optimum condition. The amount of the active components was 1:1:1 (in grams).

Obtained composition has been tested as MWF on steel plates by dissolving T-30 oil (5%, 7% and 10%). The experiments were carried out with DC01 (CR4) carbon steel specimens. The mainly chemical composition (wt%) of the carbon steel was listed as follows: C%~0.07; Si%~0,01; Mn%~0.2-0.35; Ni%~0.06; S%~0.025; P%~0.02; Cr%~0.03; Al%~0.02-0.07; Cu%~0.06; Fe balance. The test sample size was 150x100x1mm.The carbon steel plates were prepared, degreased and cleaned with deionized water and alcohol.

The experiment has been operated according to the current standards in the chamber called «CORROSİONBOX-1000E» which is considered as a modern technological device. The process has been carried out in two phases: condensation and atmospheric phase. Electronic appliances have been used in order to adjust the standard parameters for obtaining sustainable trials in the experiment chamber. For the condensation phase, these parameters are the temperature of the chamber and the duration of the trial, for the environmental phase, these are the temperature of the moisturizing agent and the chamber and the duration of the trial. The duration of the trial was in the interval of 1 minute – 9999 hours and the temperature of the chamber was 20 – 50°C for the condensation phase, whereas the temperature of the moisturizing agent was 20 – 80°C and the remaining parameters were the same for the environmental phase.

III. RESULTSANDDISCUSSION

To establish quantitative relationships reflecting the influence of the main factors of the technological regime, the ratio of NPA: PEPA (X_1, mol / mol) and inhibitor concentration(X_2,%) to the process index (Y duration of protection against corrosion in the chamber, day) the method of active experiment planning was used with subsequent mathematical and statistical processing of the experimental data [10].

Tables 1, 2, 3 show the planning matrices and the results of the experiments for three types of samples obtained on the basis ofamidoamines. (The symbols "+", "-", "0" - encoding the values of the upper, lower and base levels).

Preliminarily, the limits of changes in the input variables were chosen: 1: $1 \leq X_1 \leq 5$: 1 mol / mol; $3\% \leq X_2 \leq 10\%$

Table 1. ***Planning matrix and experimental results for amidoamines based on NPA: PEPA***

experiment№	Inputvariables				Outputparameter, day	
	coded		natural			
	X_1	X_2	Z_1, mol / mol	Z_2%	$У_{1\ эксп}$	$У_{1\ расч}$
1.	+	+	5:1	10	297	295
2.	–	+	1:1	10	415	416
3.	+	–	5:1	3	155	152
4.	–	–	1:1	3	197	198
5.	0	0	3:1	6,5	266	265

Table 2.*Planning matrix and experimental results for amidoamine-based NPA: DETA*

experiment№	Inputvariables				Outputparameter, day	
	coded		natural			
	X_1	X_2	Z_1 mol / mol	Z_2 %	$У_{2exp}$	$У_{2Calc}$
1.	+	+	3:1	10	316	318
2.	–	+	1:1	10	337	340
3.	+	–	3:1	3	157	156
4.	–	–	1:1	3	179	176
5.	0	0	2:1	6,5	250	251

Table 3. ***Planning matrix and experimental results for amidoamines based on NPA: TETA***

experiment№	Inputvariables				Outputparameter, day	
	coded		natural			
	X_1	X_2	Z_1mol / mol	Z_2 %	$У_{3\ exp}$	$У_{3\ Calc}$
1.	+	+	4:1	10	301	303
2.	–	+	1:1	10	344	345
3.	+	–	4:1	3	159	155
4.	–	–	1:1	3	181	180
5.	0	0	2,5:1	6,5	252	253

The mathematical expression for the dependence of the optimization parameter on the input independent variables is presented in the form of a regression equation

$$Y_k = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{\substack{i=1 \\ i \neq j}}^{n} a_{ij} x_i \cdot x_j \qquad (1)$$

Where Y_k is the optimization parameter; Xi, Xj - encoding the designation of model factors: n-number of factors; - free term in the regression equation, -coefficients, respectively, linear effect and pair interaction of factors: k-number of output parameters.

To determine the coefficients of equation (1), the program S-plus 2000 Professional [11], developed by the Mathworkscompany for automated mathematical processing of the experimentally obtained data, was used. statistical analysis of calculation data for regression coefficients.

The processing of the experimental data made it possible to determine the values of the coefficients of equation (1) (Table 4.)

Table 4. ***Numerical value of the coefficients of the regression equation***

	a_0	a_1	a_2	a_{12}
$У_1$	266	-40	90	-19
$У_2$	250	-14,5	83	-3,5
$У_3$	252	-21,5	76,5	-5,5

From the values of linear coefficients, it is possible to judge the degree of influence of individual factors on the optimization criterion.
The Evaluation of the significance of the regression coefficients was determined using the Student's test [12]
t = a_{ik} / $S_k \geq t_T$
Where t_T_T is the table value of the Student's test; SK is the variance of the error of the regression coefficient, defined by the formula:

$$S_k = \sqrt{\frac{S^2_{repr}}{N}},$$

Where N is the number of experiments in the matrix; S^2_{krepr} -variance of reproducibility, defined by the formula:

$$= \frac{1}{m-1} \cdot \sum_{1}^{m} (y_j^p - y_j^э)^2 \qquad (4)$$

Where m is the number of repetitions of experiments at the center of the plan, i.e. at the basic level; $Y_j^p Y_j^э$– are the calculated and experimental values of the response function in the j-m experiment.
Knowing the average values of the output parameters at the center of the plan $У_{1aver}$=266, $У_{2aver}$ =250, $У_{3aver}$ =252 and substituting them into formula (4), we determined the variances of the reproducibility: S^2_{1repr} = 0,307; S^2_{2repr} = 0,707 ; S^2_{3repr} = 1,125 ; Substituting the numerical values of variances of reproducibility into formula (3) have defined:
S_1 = 0,278; S_2 = 0,42 S_3 = 0,532
Knowing S1, S2, S3 values and substituting them in a formula (2), we have defined calculated values of criterion of Student of "t" for each coefficient.
Calculations have shown that all coefficients significant. Taking into account this equation of regression take a form:

$У_1$ = 266 – 40 · X_1 + 90 · X_2 – 19 · X_1· X_2; (5)
$У_2$ = 250 – 14,5 · X_1 + 83 · X_2 – 3,5 · X_1· X_2; (6)
$У_3$ = 252 – 21,5 · X_1 + 76,5· X_2 – 5,5· X_1· X_2; (7)

IV. CONCLUSION

The optimization problem was solved on the basis of the mathematical model (10) ÷ (12). To determine the optimal values of the input variables it is necessary to select the optimization criterion [13]. For the process of receiving amidoamines based on (NPA to DETA, PEPA and TETA), the maximum number of days of operation in the test chamber was chosen as the criterion in which surface corrosion is not yet observed. To solve the optimization problem, the Matlab-6.5 program was used [14].
1) It follows from the solution of equations (10) ÷ (12) that at a ratio of the initial components (NPA: PEPA) of 1: 1 and their concentration of 10%, the duration of protection against corrosion in the chamber is 415 days.
2) With these values of the input variables, the duration, corrosion protection for the original components (NPA: DETA) was 352 days.
3) For initial components (NPA: TETA) of 1: 1 and an inhibitor concentration of 10%, the duration of protection against corrosion in the chamber is 355 days.

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