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Жуманов М.А., Щанова Б.Б.

ЖЭО жылулық энергия блоктарындағы жылуды талдау және жұмысын жетілдіру

Түйіндеме. Мақалада құрамында азот мөлшері төмен болатын негізгі жану технологияларының сипаттамалары қарастырылған. Құрамында азот мөлшері төмен болатын жануды түрлендіргеннен кейін қарапайым сыртқы апарттық жағдайға талдау жүргізіле отырып, ауаның таралуын реттеу, оттегіні бақылауды оңтайландыру және жануды дұрыс арапастыру сияқты жылулық энергия блоктарының жұмыстарын оңтайландыру үшін кейір мақсатты шешімдер ұсынылған. Олар жану тұрақтылығын азот оксидінің шығарылу концентрациясын төмендетуді тиімді түрде қамтамасыз ете алады.

Кілттік сөздер: азот мөлшері төмен жану, жануды реттеу, арапас жану, көмір мен ауаның қатынасы, жылулық блок.

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ENLARGING THE COATINGS PROTECTIVE RESOURCE BY IMPROVING THE COMPONENTS MOISTENING IN SILICONE COATING COMPOSITION

Abstract. The article is devoted to the effect of phosphorus-containing surfactants on the aluminum moistening substrates with solutions of polyphenylsiloxanes research, the change in the moistening process is calculated, and their effect on the porosity of the coatings is shown.

Keywords: Silicone surfactant, copolymer, polyether, applications, liquid crystal, microemulsion, wetting, synthesis, foam, emulsion

1. Introduction.

Silicone coating materials historically occupy a significant market share of coatings [1]. These materials are hybrid organic-inorganic composites. Combining the characteristics of organic and inorganic substances, such structures have great potential to develop new coatings with various combinations of physical, technical and operational characteristics [2]. Besides the basic requirements for pigmented coatings which is the ability to build coatings with the specified security features, they are requirements related to the decorative (color, shine), and structural and mechanical (hardness, durability) properties. Quality coatings on these parameters are largely dependent on the degree of dispersion of pigments and fillers.

Metallopigment - aluminum powder traditionally is used in the silicone coatings. For the efficient flow of pigment dispersing the great importance has the ability of the pigmented particles to be wetted with the components of the liquid dispersion medium. When using aluminum powder (hydrophilic pigment) surface properties, which are caused by a large number of polar active sites, the wetting ability of the liquid medium depends on its affinity with the contacting phase on its polarity. However, the most industrial silicone resins are inherently low-polarity substances. Despite the polar nature of the bond Si-O, silicones are close to the hydrocarbon energy of adhesion to the water and effect of the weakly adsorbed on the hydrophilic surface.

The study [6] reports chemical treatment of pigment titanium dioxide (TiO_2) with silicone to give surface functionalized TiO_2 . The surface functionalization was confirmed by Fourier Transform Infra Red Spectroscopy, Scanning Electron Microscopy, Transition Electron Microscopy and Dynamic Light Scattering analysis. Coatings were formulated by incorporation of these functionalized TiO_2 into the epoxy polymer matrix and compared for coating properties with untreated TiO_2 . To reduce the hydrophilicity of aluminum powder (and thus increasing its wettability by solutions of silicones) may be recommended for the use of additives, phosphorus-containing surfactants (hereinafter SAS) forming a "grafted layer".

The aim of this work was to study the effect of phosphorus-containing surfactants (additives) on the wetting of aluminum powder in silicone coatings.

3. Methods.

Silicone resin - polyphenylsiloxane lacquer (the SFC), the solvent - toluene (GOST 14710-78) and the additives, two types of phosphite (Table 1) were used for the research:

Tab. 1. Characteristics of additives

Name of additive	Chemical formula	Average weighted molecular mass, a.m.m	Chemical name
DEF	$(EtO)_2P(O)H$	138	Diethylphosphite
TABF	$(Et_2N)_2P(O)Bu-t$	248	Tetraethyldiamidotributyl phosphite

For an assessment of moistening activity of investigated additives concerning aluminium substrate (a content of aluminium is 99, 98 %) defined following characteristics of their solutions: a superficial tension (in system: "solution PFS –water phase" – Δll) on a method of "the greatest pressure of air bubbles" (device of Rebinder) and regional angle of wetting (on the border "solution PGS - aluminium substrate - a water phase" - Θ°) on the method of "selective wetting" in isothermal conditions, at temperature 298K [3].

The given characteristics (a superficial tension and regional angle of wetting) of individual solutions (toluene-additive; toluene PFS) and solutions of the mixed structure (toluene-PFS-additive) established, varying in them the content of additives (0÷2 g/dm³) and silicone pitches, PFS (0÷30 %, concerning weight of mixture).

4. Results.

The results of the researches of moistening activity of the individual and mixed solutions are presented in table2.

Tab.2. The influence of concentration phosphorcontaining additives and PFS on a superficial tension (mG/m²) "solution PFS –water phase" (Δll) and regional angle of wetting "solution PGS - aluminium substrate - a water phase" (Θ°)

CPFS, %	CSAS, g/dm ³	DEF		TABF	
		Δll	Θ°	Δll	Θ°

	0	35,70	116,28	35,70	116,28
0	0,25	34,51	115,54	33,92	115,20
	0,5	33,32	114,07	32,13	114,01
	1	33,92	111,81	34,51	101,24
	2	35,50	103,49	35,70	99,91
	0	33,92	123,44	33,92	123,44
10	0,25	32,13	120,95	33,92	119,83
	0,5	30,34	119,95	33,32	116,69
	1	32,13	112,97	31,54	113,51
	2	33,92	110,69	33,92	110,12
	0	32,73	125,14	32,73	125,14
20	0,25	31,54	122,20	29,15	123,22
	0,5	29,75	120,76	30,00	118,78
	1	30,94	116,45	31,73	101,24
	2	32,50	102,93	32,73	100,38
	0	30,94	126,86	30,94	126,86
30	0,25	30,34	126,15	28,56	115,98
	0,5	27,96	121,36	29,75	115,12
	1	29,75	115,12	30,34	114,34
	2	30,94	113,12	30,94	111,14

The analysis of the presented data (Tab.2) testifies to the positive influence on the decrease in specific superficial energy on interphase border “solution PFS – water phase” increases on the one hand – contents of PFS, and on the another – additives in concentration of boundary from 0 up to 0,5 g/dm³. Maximum of superficial activity investigated of phosphates marked, at their content in toluene at the level of 0,5 g/dm³, and in the mixed solutions at the level - 0,25÷0,5 g/dm³.

The further increase of additive concentration in solutions of the individual and mixed structure (from above 0,5 g/dm³) stimulated them concentration not in the superficial layer on border with air (water), and in volume of solution [4].

At carrying out of researches was established, that the layer formed by toluene on an aluminium substrate on border with water hydrophoben, regional angle is equal 116,3 (Tab.2). For comparison, according to the literary data, the drop of water on teflon has regional angle equal to 112÷130. At addition toluene PFS (CPFS = 30 %) are observed an increase of regional angle of wetting with 116,3 up to 126,86, that testifies about hydrophobization of surfaces of an aluminium substrate. On the contrary, the interphase layer which has been generated at presence of additives, had quite different superficial properties (possessed significantly smaller water repellency); so at introduction in toluene DEF (up to 2 g/dm³) regional angle of wetting by water has decreased on 13, for TABF similar variation has made about 16°. At introduction of additives, in the pitches diluted on a content solutions (CPFS=10 %) the given tendency (reduction of regional angle of wetting) is kept, $\Delta\Theta^\circ$ for DEF and TABF makes 13. In solutions of the mixed structure with the raised content polyphynilsilixan (CPFS =30 %), the moistening effect of additives increases, for DEF it is 14 °, for TABF $\Delta\Theta^\circ = 15 \div 16$ °. The moistening effect solutions of additives amplifies in process of them concentration in system.

About quantitative variation of character of interoperability of firm surface with moistening liquid as a result of adsorption of sufriants it is possible to judge by work of wetting (Wsm.). Work of wetting is defined as a difference: $\delta_{T\mathcal{K}_1} - \delta_{T\mathcal{K}_2}$ and according to the equation of Yung it maybe calculated as:

$$W_{cm.} = \delta_{\mathcal{H}_1, \mathcal{H}_2} \cdot \cos \theta \quad (1)$$

Difference between works of wetting during the contact of a drop of water with a surface covered adsorbtion layer of SAS (Wsm. SAS) and a surface, free from it (Wsm.) will be equal

$$\Delta Wsm.: \Delta Wsm. = Wsm. SAS - Wsm. \quad (2)$$

The Given variation (ΔW_{cm}) characterizes the influence on work of wetting adsorption processes of SAS. Thus, on variation of values of work of wetting is possible to judge variation of a superficial tension on border "liquid-firm". Variations of work of wetting in solutions of the individual and mixed structure, are presented in Table 3.

Tab.3. The influence of PFS and SAS containing on the change of wetting work, (ΔW_{sm} , mG/m²)

SAS	C _{PFS} , %									
	0					10				
	C _{PFS} , g/dm ³					C _{PFS} , g/dm ³				
	0	0,25	0,5	1	2	0	0,25	0,5	1	2
DEF	-	1	2,2	3,2	7,5	-	2,2	3,5	6,1	6,7
TABF	-	1,4	2,7	9,1	9,7	-	1,8	3,7	6,1	7
SAS										
	20					30				
	C _{PFS} , g/dm ³					C _{PFS} , g/dm ³				
	0	0,25	0,5	1	2	0	0,25	0,5	1	2
DEF	-	2	3,6	5	11,6	-	0,7	4	6	6,4
TABF	-	2,9	4,4	13	13	-	6	6	6,1	7,4

Summarizing the above-stated, it is possible to ascertain, that the greatest moistening activity in industrial silicon varnish (CPFS =30 %), concerning aluminium substrate, shows TABF. The given fact closely correlates with the laws of variation of disperse structure established earlier (according to optical microscopy) aluminium powder in silicon coatings [5].

For the assessment of joint influence on parameters of optimization (CSAS and CPFS) the multifactorial equation of nonlinear plural correlation which in the implicit form looks like (3) is used:

$$d = \frac{f(X_1) \cdot f(X_2) \cdots \cdot f(X_n)}{g_{cp}^{n-1}} \quad (3)$$

Where x1, x2 ... xn – factors;

n – quantity of factors;

gav – a general average.

Meaning of gav was counted with the formula:

$$g_{cp} = \frac{\sum_{i=1}^M Y_i}{M} \quad (4)$$

where Y_i - set of experimental data in matrix;

M - number of lines in matrix.

Sample of an experimental file on each level was carried out for each factor within the limits of bidimensional matrix Yx (5):

$$Y = \begin{matrix} yx11, yx12, \dots, yx1z \\ yx11, yx12, \dots, yx1z \\ \dots \end{matrix} \quad (5)$$

yxm1, yxv2, ..., ymlz

where m – number of levels;

z – number of functional expressions for each level.

After approximation of private dependences, with the usage of standard programs "Advanced Grapher" and "Microsoft Excel", the one-parametrical equations describing influence on Θ° , of each factor separately, for $\Theta^\circ=f(\text{CPFS})$ (the equation 6) are received.

$$\Theta^\circ = a \cdot (\text{CPFS})^3 - b \cdot (\text{CPFS})^2 + n \cdot \text{CPFS} + C \quad (6)$$

The factors entering into the equation 6 for additives are presented in tab. 4.

Tab. 4. Value of factors a, b, n and C for compositions with various content of PFS

SAS	a	b	n	C
DEF	0,0014	0,070	1,096	112,24
TABF	0,0030	0,133	1,798	109,33

for $\Theta^\circ=f(\text{CSAS})$ (the equation 7).

$$\Theta^\circ = a_0 \cdot (\text{CSAS})^2 - b_0 \cdot \text{CSAS} + C_0 \quad (7)$$

The factors entering into the equation 6 for additives are presented in tab. 5

Tab.5. Value of factors a, b, n and C for compositions with various content of SAS

SAS	a0	b0	C0
DEF	0,877	9,650	123,27
TABF	5,650	20,40	123,42

Multifactorial equation nonlinear multiple correlation, reflecting the contribution (CSAS and CPFS) on parameters of the contact angle:

$$\Theta^\circ = \frac{a \cdot (C_{\text{PFC}})^3 - b \cdot (C_{\text{PFC}})^2 + n \cdot C_{\text{noc}} + C}{[a_0 \cdot (C_{\text{PAB}})^2 - b_0 \cdot C_{\text{PAB}} + C_0]^{-1} \cdot 117,00} \quad (8)$$

The adequacy of the resulting model (for 95-ground level of significance) was evaluated on the basis of correlation coefficients (R) and significance (tR), which was calculated by the equations.

$$t_R = R \cdot \sqrt{\frac{n-2}{1-R^2}} \quad (10)$$

$$R = \sqrt{1 - \frac{(n-2) \cdot \sum(y_s - y_t)}{(n-1) \cdot \sum(y_s - y_{cp})}} \quad (9)$$

where n - number of experimental points;

k - number of variable parameters;

yt - the theoretical value of the response function calculated from the generalized equation;

ye - experimental values of the response function;

yav - mid-arithmetic set of experimental values;

The calculations showed satisfactory convergence of experimental and calculated response function: R>0,90, tR> 2.

4. Discussion.

1. Investigated additives in solutions of siloxans (various concentrations) reduce water repellency of aluminium substrate and shape “the imparted layer”, increasing “affinity” of a solution film-forming to aluminium substrate that causes improvement course of process dispergation of aluminium powder.

2. Correlation in character of variation of disperse structure and variation of work of wetting is revealed. Condition of achievement maximal diswedging effect (maximal dispergation) on interphase demarcation line “the solution film-forming-pigment” is maintenance of the maximal wetting with a solution film-forming surfaces of aluminium powder to that the maximum “variations of work of wetting ΔW_{cm} ” conforms. At presence of additives moistening and at the same time desaggregating activity (in an industrial varnish) decrease in a number: TABF > DEF (at C_{SAS} 0,25 g/dm³).

3. On the basis of the lead experiment the mathematical model of process of the wetting, reflecting the contribution of a content of pitch and SAS on parameters of regional angle of wetting is deduced. Calculations have shown the satisfactory convergence of experimental and rated values. The given model can find application in the industry, at a stage of reception silicon coatings.

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Гумиров Т.Ш., Тлемс А.Т., Тюканько В.Ю., Савинкин В.В., Дюрягина А.

Силиконды бояулар мен лактардағы компоненттердің сулануын жақсарту арқылы жабының қорғаныс ресурсын арттыру

Резюме. Мақала құрамында фосфор бар беттік-белсенді заттардың алюминий субстраттарының полифенилсилоксан ерітінділерімен сулануына әсерін зерттеуге арналған, суландыру жұмысының өзгерісі есептелген және олардың жабындардың кеүектілігіне әсері көрсетілген.

Түйін сөздер: Силиконды беттік белсенді заттар, сополимер, полизэфир, қосымшалар, сұйық кристалдар, микроэмulsionя, сулану, синтез, көбік, эмульсия.

Гумиров Т.Ш., Тлемс А.Т., Тюканько В.Ю., Савинкин В.В., Дюрягина А.

Увеличение защитного ресурса покрытий путем улучшения смачивания компонентов в силиконовых лакокрасочных материалах

Резюме Статья посвящена исследованию влияния фосфорсодержащих поверхностно-активных веществ на смачивание алюминиевых подложек растворами полифенилсилоксанов, рассчитано изменение работы смачивания и показано их влияние на пористость покрытий.

Ключевые слова: Силиконовые поверхностно-активные вещества, сополимер, полизэфир, аппликации, жидкие кристаллы, микроэмulsionя, смачивание, синтез, пена, эмульсия.

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INTERVAL ANALYSIS APPLICATION TO HANDLE CHEMICAL REACTOR

Abstract. The article is devoted to the use of interval analysis for controllability of a chemical reactor. The relevance of the task of determining the controllability of a chemical reactor is shown. A mathematical model of a chemical reaction is considered. This model is built by the law that the frequency coefficients and activation energies have constant values. The paper considers the problem of choosing the optimal control of a chemical reactor. A program in Pascal for numerical modeling is developed. The methods of penalty functions and the gradient method for solving the optimal control problem are proposed.

Key words: chemical reactor, interval analysis, temperature, concentration, reaction, optimal control.

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ПРИМЕНЕНИЕ ИНТЕРВАЛЬНОГО АНАЛИЗА ДЛЯ УПРАВЛЯЕМОСТИ ХИМИЧЕСКОГО РЕАКТОРА

Аннотация. Статья посвящена применению интервального анализа для управляемости химического реактора. Показана актуальность задачи определения управляемости химическим реактором. Рассматривается математическая модель химической реакции. Данная модель построена закону, что частотные коэффициенты и энергии активации имеют постоянные значения. В работе рассмотрена задача выбора оптимального управления химическим реактором. Разработана программа на языке Паскаль для численного моделирования. Предложены методы штрафных функций и градиентный метод для решения задачи оптимального управления.

Ключевые слова: химический реактор, интервальный анализ, температура, концентрация, реакция, оптимальное управление.

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