OPTIMIZATION OF THE PROCESSES OF DISAGGREGATION OF PIGMENTS AND FILLERS USING THE METHODS OF PROBABILISTIC DETERMINISTIC MODELING

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An important technological characteristic of paintwork materials, which determine the coverage and protective properties of their coatings, is the degree of disaggregation of pigments and fillers [1,2]. In freshly prepared suspensions of paintwork materials the development of aggregation and disaggregation processes depends both on the surface properties of the solid-phase components themselves and on the qualitative and quantitative composition of cover-formers, solvents and surfactants. To optimize the composition of coatings, it is necessary to know how the set of all these components will affect the dispersion processes, which involves the construction of a generalized mathematical model of the system under study [3,4].

We attempted withdrawal of multifactor models of the dispersion process of the pigment of titanium dioxide (R-02), and filler, calcite (M-20), in the coating system on the basis of the varnish PF-060, white spirit, surface-active substances (surfactants) AS (an amine derivative with the number of carbon atoms in the chain 6-8, TU 655-RK 056006434-002-2000) on the basis of the principles of probabilistic and deterministic simulation.

During the experiments, a modified plan-matrix of the four-factor experiment was used at three levels, which was achieved by taking the factor C_{TiO2} (pigment concentration) beyond its limits. As the main factors affecting the indicators of pigment and filler disaggregation, the quantitative content of the added solvent in suspensions (CP,%, 10÷50 volume relative to PF-060,%), surfactant ($C_{surfactant}$, in terms of the total mass of solid-phase components, — 0÷16%), the relative content of titanium dioxide with a constant mass content of pigment and filler in suspensions — 16% (C_{TiO2}, 0÷100% RH) was determined.).

The method of preparation of suspensions of paintwork materials with different content of cover-forming substance was the preliminary dilution of white spirit varnish PF-060 in the following volume ratios: 1:9, 3:7, 1:1. The resulting solutions (hereinafter-A) were directed to the preparation of suspensions, which was carried out at 20 °C in a hermetic reactor (volume 0.2 dm^3), equipped with a mixing device (impeller agitator, frequency — 700 rpm). The duration of the operation, in which the stabilization of the equilibrium characteristics of suspensions and the fractional composition of the pigment and filler was fixed, was 1 hour.The relative pigment contents varied due to changes in its mass concentration in the solid phase. To estimate the disaggregating effect of surfactants, the calculated index — its concentration (in mass, %) by mass of pigment. For this purpose, a series of solutions with different surfactant content (from 0 to 16%) was pre-prepared by dissolving the surfactant in a fixed volume of solution A. The resulting solution (hereinafter — B) was sent to the preparation of suspensions. The method of preparation of modified suspensions using solution B is similar to the above.

The studied samples of paint suspensions were placed on a slide, fixed with a cover glass and maintained for a certain time under load with the help of a microdispenser (the volume of the drop was 0.02 ml). As it is known, as the solvent evaporates (in time), due to the tightening effect (in height and in plane), the development of deformation processes that affect the characteristics (geometric, structural) of the films themselves, as well as the width of the gap between the object and cover glasses, increases. The results of preliminary tests carried out on samples of different compositions showed that the load regime should be $p \geq 10$ g/cm^2. At the same time, the period of holding the samples under load was optimized, which was set according to the time required to stabilize the deformation processes in the films. For the system under study, the static load period was 5 minutes.

The response function was the total number of solid phase particles (N) falling on a fixed area of the substrate:

$$S : N = N_{relative} \cdot S,$$

The values of N in the samples were determined at a given magnification ratio (X350) using a computer-optical control system [4-6], which calculates the number of particles at S = 0.38 mm^2.

After the implementation of the active experiment the experimental array was sampled for each level of each factor within the two-dimensional matrix Yx :

$$Y = \begin{vmatrix} yx_{11}, yx_{12}, \ldots, yx_{1z} \\ yx_{11}, yx_{12}, \ldots, yx_{1z} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ yx_{m1}, yx_{v2}, \ldots, ym_{1z} \end{vmatrix},$$

m – number of levels; z - number of functional expressions for each level.

Particular dependences N = f (Ci)

$$N = f(Ci)$$

for each individual factor are shown in Fig

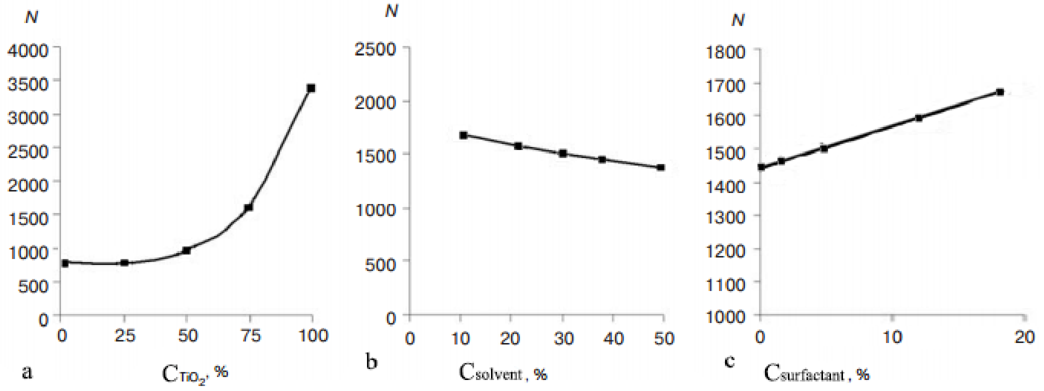

Fig. 1. Effect on pigment disaggregation rates of concentration: a - TiO_2; b - added solvent, c - AC surfactant

From the analysis of particular dependences follows a natural increase in the number of particles as the total concentration of solid-phase components in the paintwork system increases (Fig. 1, a); at the same time, the positive contribution of the as surfactant concentration to the change in N is consistent with its disaggregating effect previously established for other pigments [5,8]. Reducing the degree of disaggregation of the pigment and filler as dilution of the cover-former by solvent indicates a positive (surface-active) role of functional groups (hydroxy-, carboxy-) in the pentaphthalic resin [9,10].

After approximation of partial dependences using standard programs "Advanced Grapher" and "Microsoft Excel", one-parameter equations characterizing the effect on the response function of each factor separately (equations 1-3) are obtained.

$$N = -7{,}9 \cdot C_{solvent} + 1755{,}7 \quad (1)$$

$$N = 0{,}48 \cdot C^2_{TiO_2} - 23 \cdot C_{TiO_2} + 880 \quad (2)$$

$$N = 14{,}95 \cdot C_{surfactant} + 1436{,}6 \quad (3)$$

To build a generalized model, we used a multivariate equation of nonlinear multiple correlation, which in an implicit form has the look [2]:

$$Y_{general} = \frac{f(x_1) \cdot f(x_2) \cdot \ldots \cdot f(x_n)}{g_{average}^{\,n-1}},$$

x_1, x_2,..., x_n — factors; n — number of factors; $g_{average}$ — general average. Values of $g_{average}$ were calculated by the formula:

$$g_{average} = \frac{\sum_{i=1}^{M} Y_{exp.}}{M}$$

$Y_{exp.}$ - the set of experimental data in the matrix; M - the number of rows in the matrix. After substituting the approximated expressions (1-3) into equation (4), we obtain a generalized equation that takes into account the joint contribution of all factors:

$$N = ((-7{,}9 \cdot C_S + 1756)\,(0{,}48 \cdot C^2_{TiO_2} - 23 \cdot C_{TiO_2} + 880)\,(14{,}95 \cdot C_{surf.} + 1436{,}6))/1519^2. \quad (6)$$

The adequacy of the obtained model (for the 95th significance level) was estimated on the basis of the correlation coefficients (R) and significance (t R), which were calculated by the equations:

$$R = \sqrt{1 - \frac{(n-2) \cdot \Sigma\,(y_{experimental} - y_{theor.})^2}{(n-1) \cdot \Sigma\,(y_{experimental} - y_{average})^2}}$$

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

The calculations showed a satisfactory convergence of the experimental and calculated (according to equation 6) values of the response function:

$$R = 0{,}94,\ t_R > 2.$$

Based on the solution of the generalized equation, the optimal expenditure of the surfactant, solvent and pigment in the suspension of paintwork materials were determined, providing the required degree of disaggregation of titanium dioxide. The joint contribution of the two factors to N is represented by nomograms (Fig. 2) obtained by equation 6.

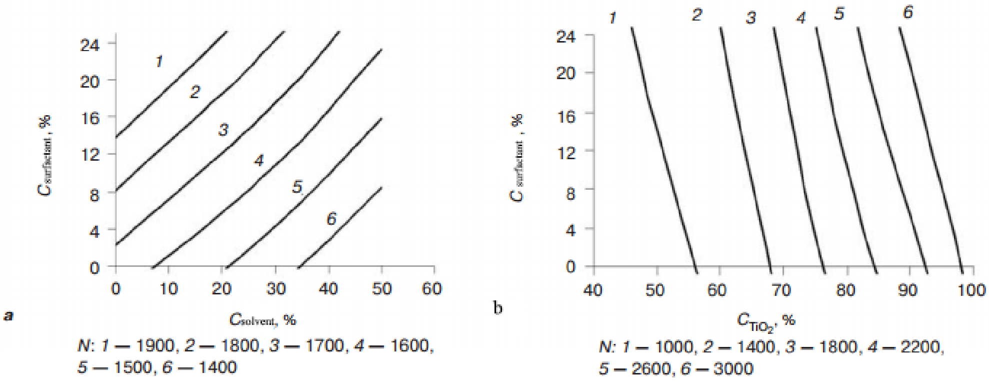

Fig. 2. Two-factor monograms: a - N = f ($C_{surfactant}$, $C_{solvent}$, C_{TiO_2} = 67,8%);
b - N = f ($C_{surfactant}$, C_{TiO_2}, $C_{solvent}$ = 30 %)

The analysis of the obtained dependences shows that in order to stabilize the indices of pigment disaggregation at a fixed level, providing, for example, N = 1800, required to increase the surfactant consumption or reduce the relative pigment content as the paintwork composition is diluted with a solvent. Calculations according to equation (6) showed that if Cp = 10%, then the given N = 1800 in paintwork materials is achieved at $C_{surfactant}$ = 6,95% and C_{TiO2} = 70% (relatively); a similar indicator of the degree of dispersion can be achieved by reducing the relative pigment content to 68.2%, but this will require an increase in surfactant expenditure to 12%. According to the results of balance experiments performed with paintwork compositions of these two compositions, a satisfactory convergence in the predicted and practical values of N was established; the mean-square deviation for the two examples considered does not exceed 1.2%.

Thus, the use of probabilistic-deterministic methods of modeling with an extended plan-matrix provides an adequate multifactorial mathematical model of the processes of disaggregation of pigments and fillers and, as a consequence, the solution of applied problems in the optimization of the composition of paintwork materials.

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