Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 12, December-2016

Optimization of Pigment Dispersion Preparation for Lithographic Printing Ink

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***Abstract*—In this study optimization of parameters of the pigment dispersion for lithographic inks was carried out. The aim is to minimize the size of dispersed pigment particles. A factorial design was used to evaluate the effects and interactions of three factors, that is, varnish concentration, pigment concentration, and enhanced degree of roller pressure in each stage of the milling process, on the pigment dispersion quality. The optimal conditions obtained from the desirable response are varnish concentration of 62.27 % by weight, pigment concentration of 15.33 % by weight and pressure enhancement of 20 N/mm^2. The validity of the statistical experimental strategies was verified by the pigment dispersion samples prepared under the optimized conditions**.

***Keywords*— Lithographic Ink; Printing Ink Production; Pigment Dispersion; Experimental Design**

I. INTRODUCTION

The manufacture of printing ink is a technologically advanced, highly specialized and complex process. The basic formulation of ink involves the grinding of pigment in a vehicle to form the pigment dispersion, then letting down the pigment dispersion with suitable additives to meet rheological and functional properties.

The dispersion of pigments in printing inks is very important. The flow behavior of the ink is controlled to some extent by the dispersion properties of the material. To achieve the optimum benefits of a pigment, it is necessary to obtain as full a reduction as possible to the primary particle size [1]. The color strength of a pigment depends on its exposed surface area, and the smaller the particle the higher the surface area and thus stronger the color [2]. Increasing demands on quality printing inks regarding the optical characteristics such as gloss, transparency or color strength requires the use of more effective dispersing techniques [3].

The pigment dispersion process involves the breakdown of associated particles into smaller particles and their distribution in a fluid, leading to a colloidal suspension. The steps involved in the pigment dispersion process as follows: Wetting of the pigment particles, breakdown of the pigment particles and stabilization of the dispersion [3].

The quality of the final dispersion is dependent on the optimization of many influencing factors such as pigment volume concentration, pigment to vehicle ratio, grinding media, grinding time and pressure, temperature,…[1,3,4].

In order to optimize the parameters of pigment dispersion for lithographic inks, in this study the 2^k experimental design [5] was applied for evaluation of the individual contribution of selected variables to the final size of dispersed pigment particles. The investigated factors were varnish (vehicle resin) concentration, pigment concentration, and grinding pressure.

II. EXPERIMENTAL

A. Materials

Pigment red 146 (Naphtol Carmine FBB) was used for dispersion supplied by DIC Corporation, Japan. The physical form is a red powder with the average particle size of 0.5 µm.

High density varnish (Phenolic resin/solvent) from DIC was used as adispersing agent for pigment dispersion preparation. Solvent DIC was added to adjust the rheological properties of the system.

B. Three-roll mill Bühler

Bühler three-roll mill was used in the grinding state. Through mechanical energy (impact and shear forces), the pigment agglomerates are broken up and disrupted into smaller units and dispersed (uniformly distributed).

The schematic diagram of this machine is given in Fig. 1. The speed ratio of three rolls is 1:3:9. The pressure between the rollers can be set up in a wide range from almost 0 N/mm^2 to 20 N/mm^2. The machine has high roll speeds and excellent cooling properties.

C. Pigment dispersion preparation

The pigment powder was mixed in the varnish and the solvent under low shear for 20 min. This suspension was then added to the mill. The constant pressures between rollers ($P_{1\text{-}2}$ = 9 N/mm^2 and $P_{2\text{-}3}$ = 8 N/mm^2) were applied and the roller speedset to 200 rpm. The temperature was kept at 25 ± 1^{0}C.

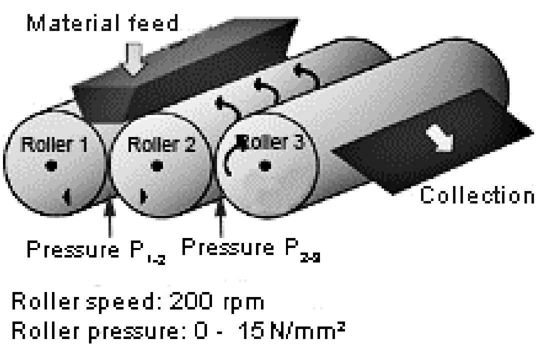

Fig. 1. Schematic diagram of three-roll mill

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 12, December-2016

The milling process lasted in 15 minutes. Again the same milling process was performed 3 more times, but the roller pressures were increased an adequate amount for each time.

After 4 passes a pigment suspension samples were taken to observe the particle size reduction.

D. Particle size determination

The degree of dispersion was measured using PD-1510 Grindometer 25. This is a stainless steel block containing a shallow groove which is graduated in depth from zero to 25 microns. A sample of ink was placed at the deep end, draw down with a steel blade towards shallower part, the degree of dispersion was taken as the point at which the continuous ink film breaks down across the groove.

E. Experimental design và data analysis

In this work, a factorial design in which the influences of three experimental factors, e.g. varnish concentration, pigment concentration, and enhanced degree of roller pressure in each stage of the milling process, on the response, i.e. the dispersed particle size, was investigated. Two different levels were assigned to each factor. The factorial design is shown in Table 1. The levels of the factors are given by – (minus) for low level and + (plus) for high level. A zero-level is also included, a centre, in which all variables are set at their mid value.

A sign table, or design matrix, used to calculate the main effects and the interaction effects from the factorial design is constructed in Table 2.

TABLE I. FACTORIAL DESIGN

Exp. No	Variable			Response
	x_1	x_2	x_3	
1	-	-	-	y_1
2	+	-	-	y_2
3	-	+	-	y_3
4	+	+	-	y_4
5	-	-	+	y_5
6	+	-	+	y_6
7	-	+	+	y_7
8	+	+	+	y_8

TABLE II. MATRIX OF FACTORIAL DESIGN

Exp.No	I	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Response
1	+1	-1	-1	-1	+1	+1	+1	-1	y1
2	+1	+1	-1	-1	-1	-1	+1	+1	y2
3	+1	-1	+1	-1	-1	+1	-1	+1	y3
4	+1	+1	+1	-1	+1	-1	-1	-1	y4
5	+1	-1	-1	+1	+1	-1	-1	+1	y5
6	+1	+1	-1	+1	-1	+1	-1	-1	y6
7	+1	-1	+1	+1	-1	-1	+1	-1	y7
8	+1	+1	+1	+1	+1	+1	+1	+1	y8

The experiments were evaluated in order to fit a regression model

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (1)$$

Where, y_j $(j = 1 \div N, N = 8)$ is the response variable to be modeled; x_j $(i = 1 \div 3)$ is the independent variable which influence y; b_0, b_i $(i = 1 \div 3)$, b_{iu} $(i = 1 \div 3, u = 1 \div 3)$ are model terms, that are estimated by

$$b_i = \frac{1}{N}\sum_{j=1}^{N} x_{ij}\, y_j \quad (2)$$

$$b_i = \frac{1}{N}\sum_{j=1}^{N} x_{ij}\, x_{uj} y_j \quad (3)$$

Analysis of variances (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The quality of the fitted model was expressed with the coefficient of determination, R^2, and its statistical significance was checked by the F-test. Model terms were selected or rejected based on the p value (probability) with 95% confidence level.

The regression model for real variables (z) describing the relationship between the investigated factors was determined from (1) by replacing variables x with z:

$$x_i = \frac{2(z_i^+ - z_i^0)}{\Delta z_i} \quad (4)$$

Where $\Delta z_i = z_i^+ - z_i^-$; z_i^+, z_i^0, z_i^- are values of the ith variable at high, low and mid level, respectively.

The optimum values of selected variables were obtained by using MATLAB 7.0. The interactive effects of the independent variables on the dependent ones were illustrated by three dimensional plots. Finally, two additional experiments were conducted to verify the validity of the statistical experimental strategies.

III. RESULTS AND DISCUSSION

Two different levels were assigned to each factor. These levels were experimentally determined to assure that the system has viscosity and tack value in the range of lithographic printing technology. The investigated results are reported in Table 3 – 5.

TABLE III. EFFECT OF VARNISH CONCENTRATION ON RHEOLOGICAL PROPERTIES OF THE PIGMENT DISPERSION

Pigment (g)	Varnish (g)	Solvent (g)	Varnish concentra-tion (% wt.)	Viscosity, 30^{0}C (Pa.s)	Tack value, 25^{0}C, 100 m/s (T.U)
100	370	30	74	80	230
100	360	40	72	74	218
100	350	50	70	72	210
100	340	60	68	65	192
100	330	70	66	56	179
100	320	80	64	48	169
100	310	90	62	42	150
100	300	100	60	39	145

International Journal of Engineering Research & Technology (IJERT)
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TABLE IV. EFFECT OF PIGMENT CONCENTRATION ON RHEOLOGICAL PROPERTIES OF THE PIGMENT DISPERSION

Pigment (g)	Varnish (g)	Solvent (g)	Pigment concentration (% wt.)	Viscosity, 30^{0}C (Pa.s)	Tack value, 25^{0}C, 100 m/s (T.U)
70	350	80	14	70	150
77	350	73	15	65	180
79	350	71	16	62	189
100	350	50	20	60	210
119	350	31	24	58	215
123	350	27	25	55	217
137	350	13	27	49	220

TABLE V. EFFECT OF ENHANCED DGREE OF ROLLER PRESSURE ON RHEOLOGICAL PROPERTIES OF THE PIGMENT DISPERSION

Enhance-ment of roller pressure (N/mm^2)	Roller pressure, P_{1-2}/P_{2-3} (N/mm^2)	Dispersed particle size (µm)	Viscosity, 30^{0}C (Pa.s)	Tack value, 25^{0}C, 100 m/s (T.U)
0.6	9.0/8.0 9.6/8.6 11.2/10.2 11.8/10.8	10	50	220
1.0	9.0/8.0 10/9.0 11/10 12/11	6	57	200
1.5	9.0/8.0 10.5/9.5 11.5/10.5 13/12	4	60	195
2.0	9.0/8.0 11/10 12/11 14/13	4	70	187
2.5	9.0/8.0 11.5/10.5 14/13 16.5/15.5 *	4	80	170

[a.] (*): Limited pressure of the machine

As required, the viscosity is from 42 to 72 Pa.s and the tack value is from 150 to 220 T.U. Corresponding to these ranges, the experimental domains of three investigated factors were determined (see Table 6).

Eight experiments in the factorial design and three experiments at the center point were simultaneously performed. All the experiment parameters are reported in Table 7 and the model matrix is given in Table 8.

Coefficient values and statistical parameters obtained for the model are given in Table 9. For assessing the statistical significance of the result, a t-test (t-Student) was carried to the 95% confidence level.

TABLE VI. INVESTIGATED FACTORS: LEVELS AND CONDITIONS

Factor	Experimental domain		
	Level (-)	*Level (0)*	*Level (+)*
z_1:Pigment concentration (% wt.)	15	20	25
z_2:Varnish concentration (% wt.)	62	66	70
z_3:Enhancement of roller pressure (N/mm^2)	0.6	1.3	2

TABLE VII. EXPERIMENT PARAMETERS

Exp No	Varnish concentration (% wt.)	Pigment concentration (% wt.)	Solvent concentration (% wt.)	Enhance-ment of roller pressure (N/mm^2)	Dispersed particle size (µm)
1	62	15	23	6	3
2	70	15	15	6	9
3	62	25	13	6	7
4	70	25	5	6	10
5	62	15	23	20	2
6	70	15	15	20	6
7	62	25	13	20	6
8	70	25	5	20	5
9	66	20	14	13	5
10	66	20	14	13	6
11	66	20	14	13	6

TABLE VIII. MODEL MATRIX AND RESPONSE

Exp. No	I	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Particle size (µm)
1	+1	-1	-1	-1	+1	+1	+1	-1	3
2	+1	+1	-1	-1	-1	-1	+1	+1	9
3	+1	-1	+1	-1	-1	+1	-1	+1	7
4	+1	+1	+1	-1	+1	-1	-1	-1	10
5	+1	-1	-1	+1	+1	-1	-1	+1	2
6	+1	+1	-1	+1	-1	+1	-1	-1	6
7	+1	-1	+1	+1	-1	-1	+1	-1	6
8	+1	+1	+1	+1	+1	+1	+1	+1	5

TABLE IX. COEFFICIENT VALUES AND STATISTICAL PARAMETERS OBTAINED FOR THE MODEL

Coefficient	Coefficient value	Standard deviation	p-value
b_0	6	0.20	< 0.05
b_1	1.5	0.20	< 0.05
b_2	1	0.20	< 0.05
b_3	-1.25	0.20	< 0.05
b_{12}	-1	0.20	< 0.05
b_{13}	-0.75	0.20	> 0.05
b_{23}	-0.25	0.20	> 0.05
b_{123}	-0.25	0.20	> 0.05

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
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As the results shown in Table 9, with the confidence value < 95%, the coefficients b_{13}, b_{23} and b_{123} are not significant and are rejected from the model. The obtained equation is as follows.

$$y = 6 + 1.5x_1 + x_2 - 1.25x_3 - x_1x_2 \quad (5)$$

This model was then analyzed by F- statistical test for analysis of variance (ANOVA) to assess the "goodness of fit". The analysis results are presented in Table 10.

TABLE X. STATISTICAL PARAMETERS OBTAINED FROM THE ANOVA TEST PERFORMED FOR THE MODEL

Source of variation	Sum of square (SS)	Degree of freedom (ddl)	Average square	Fisher number	Signification	R^2
Regression	25.5	4	6.38	5.91	4.53	0.86
Residues	6.5	6	1.08			
Lack of fit	5.83	4	1.46	4.29	19.25	
Pure error	0.67	2	0.34			

The value of F-statistic (the ratio of mean square due to regression to mean square to real error) of 5.91 is larger than $F_{0.05,4,6}$ (4.53) so the model is significant at the chosen probability level and it is correct [6]. In addition, the lack of fit error was used to test whether the model can fit the data well. The ratio between lack of fit (SS_{lof}) and pure experimental error (SS_{po}) is much smaller the critical $F_{0.05,4,2}$ (19.25). This result confirms that the model adequately fits the data. The R^2 of 0.86 also indicates that only 14% of the total variation could not be explained by the empirical model [6]. Clearly, at that significance level, it is acceptable to use the obtained model that does not include the rejected terms.

Replacing the x variables by the z factors, the model for real variables is obtained:

$$y = 1.38z_1 + 3.5z_2 - 0.18z_3 - 0.05z_1z_2 - 86.43 \quad (6)$$

The function above is now describing how the experimental variables and their interactions influence the final particle size. The model shows that pigment concentration has the largest influence on the size. An increase of this factor with one scaled unit (e.g., from 1 to 2% by weight) results in an increase of the size by 3.5 µm. An opposite effect is observed with milling pressure, higher pressure smaller particle size is. Also following (6) the interaction of varnish and pigment concentration has an effect on the dispersed particle size, but not much meanwhile the interactions of these factors with the last one are not observed. These conclusions are clearly shown in Fig. 2 and Fig. 3. A curvature in the surface of varnish and pigment concentration indicates that these factors are interdependent (Fig. 2). The response surface (Fig.3) implies that the optimal conditions were exactly located inside the design boundary. The optimal conditions are as follows. z_1 = 62.4% by weight; z_2 = 15.5% by weight; z_3 = 2.0 N/mm^2. Under these conditions the minimized value of particle size is 1.97 µm.

In order to verify the statistical analysis, the confirmation samples were prepared. The characteristics of these samples are reported in Table 11.

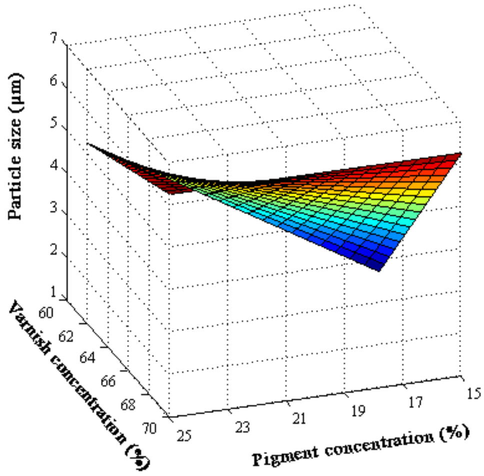

Fig. 2. Surface graph of response y (particle size) showing the effect of of varnish and pigment dosage (at enhancement of pressure = 2 N/mm^2)

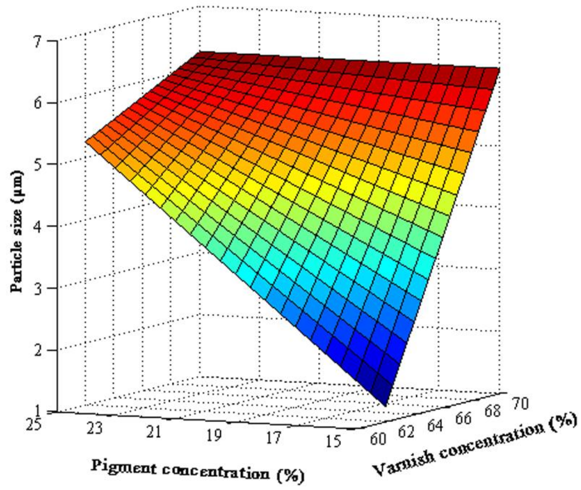

Fig. 3. Surface graph of response y (particle size) showing the optimal conditions

The result indicates that under the optimized conditions the prepared pigment dispersion has a good quality. The particle size almost reaches to the primary size and no sedimentation is observed during the storage time. In addition, the rheological properties of the dispersions are fully suitable for the preparation of lithographic printing ink [3].

TABLE XI. CHARACTERIZATION OF INK SAMPLES PREPARED UNDER THE OPTIMIZED CONDITIONS

Characteristic	Sample 1	Sample 2
Viscosity (30^{0}C), Pa.s	40	39
Tack value (25^{0}C, 100m/s), T.U	158	150
Particle size, µm	2	2
Color density (ink thickness: 5g/m^2)	1.5	1.5
Stability (25^{0}C, 1 month)	No sedimentation	No sedimentation

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
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IV. CONCLUSIONS

The results showed that the three factors considered in this study play an important role in the pigment dispersion process. The optimal conditions obtained for varnish concentration, pigment concentration, and enhancement of milling pressure are 62.4 % by weight, 15.5% by weight and 2.0 N/mm^2, respectively. Under these conditions, about 2 μm of particle size is obtained. The conducted pigment dispersions showed rheological properties and dispersion stability suitable for lithographic printing ink.

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