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IMPROVING RESISTIVITY OF UF RESIN THROUGH SETTING OF PROCESS PARAMETERS

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Key Words

Electrostatic spraying; Refluxing; Control factor; Signal-to-noise ratio; Orthogonal array design; Analysis of variance; Confidence interval.

Introduction

In paint application, the organic substance resin is usually used as the pigment binder. For electrostatic spraying, the resin-based paint is applied in the form of atomized charged particles. The distribution of charged particles depends on the resistivity of resin. The required resistivity value of resin, to be used in paint's application, is 90–200 kΩ. Low resistivity results in the danger of electrical shorting, whereas high resistivity leads to poor deposition of paint due to insufficient charge pickup. Resin resistivity within an appropriate range is a prerequisite for such electrostatic application.

Hence, the role of resin in paints application is twofold:

1. To act as a binding agent of pigments
2. To provide required resistivity in the paint application to facilitate the uniform disposition of paints

Resins can be of different types. This study was carried out on one such resin, namely urea formaldehyde (UF) resin through the paraform route.

Problem Description

The organization at which the study was carried out was able to achieve resistivity values between 40 and 60 kΩ during its regular production of UF resin, which is far below the required minimum specified value of 90 kΩ.

The present study was taken to determine the best levels of the parameters of the UF resin manufacturing process so as to obtain resistivity values within the specification.

Brief Description of the Manufacturing Process

The manufacturing process starts with charging butanol, methanol, distilled water, and solvent distillate in a kettle. Distilled water and solvent distillate are used to facilitate the chemical reaction. Next, paraform is added to the resulting solvent and its pH value is maintained between 8.9 and 9.1 by the addition of 20% NaOH solution (anular grade).

The solution is then refluxed between 90°C and 93°C for half an hour and cooled to 45°C. *Refluxing* is the process of recycling the solvent (see Fig. 1). Urea is then added at or below 40°C, maintaining the pH value between 8.9 and 9.1. The solution is again refluxed at 93°C for 45 min. This reaction produces dimethylol urea (DMU), as shown in Figure 2. The solution is then cooled to 85°C. Phthalic anhy-

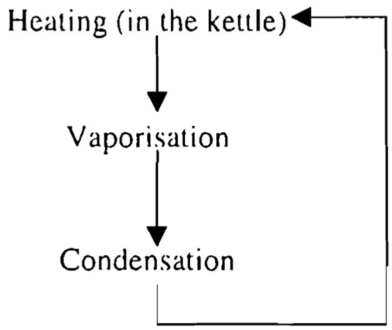

Figure 1. Schematic of the refluxing process.

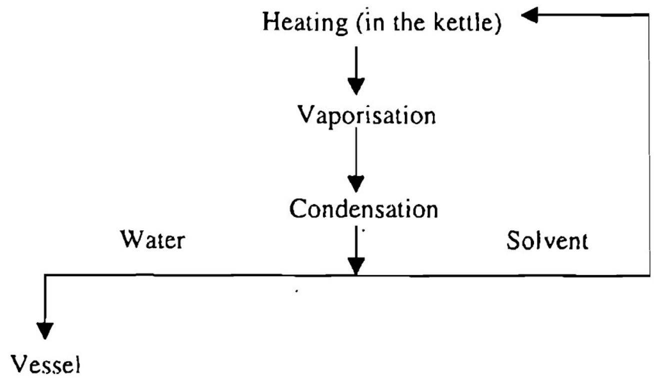

Figure 3. Schematic of the water removal process.

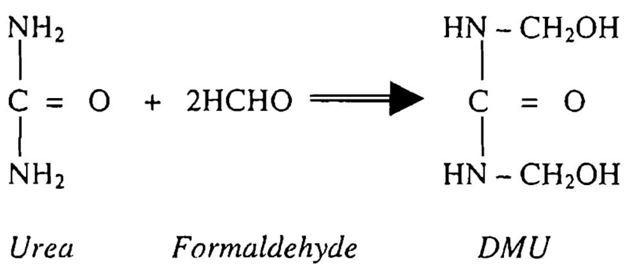

Figure 2. Reaction to produce DMU.

dride (PA) and xylene are then added and stirred for 15 min; the pH is maintained below 3.6 by adding an extra amount of PA if needed. At this stage, DMU undergoes etherification and polymerization under acidic conditions with butanol. These reactions generate water and it is removed in a phased manner over a predefined time interval (see Fig. 3). After completion of the water removal, the solvent distillate is also removed in a phased manner over a predefined time interval.

Both the etherification and the polymerization reactions take place simultaneously and depend largely on the concentration of butanol. Again, the longer the etherification and the polymerization, the greater is the possibility of the end product becoming nonpolar and, hence, less conductive. Furthermore, conductivity of the product also depends on efficient removal of water.

Selection of Factors and Levels

Based on the chemistry of reactions and previous experimental results, six process parameters (henceforth termed factors) were chosen for statistically designed experimentation. The factors chosen and the reasons behind such selections are given in the following:

1. Amount of NaOH (in mL) after addition of urea (controls DMU formation) (factor A)
2. Reflux time (in min) (controls DMU formation) (factor B)
3. Solvent distillate percentage (mainly butanol, which helps etherification) (factor C)
4. Phthalic anhydride percentage (helps etherification and polymerization) (factor D)
5. Water collection time (h) (helps in efficient water removal) (factor E)
6. Solvent distillate collection time (in min) (helps etherification) (factor F)

It was decided to study factor A at three equispaced levels and the rest of the factors at two levels. The factors and corresponding levels are given in Table 1. Aside from the above six factors, the following two, two-factor interactions, as suggested by the personnel of the organization, were considered while designing the experimental layout:

$D \times E$ and $D \times F$.

Table 1. Factors and Their Levels

	LEVEL		
FACTOR	1	2	3
A	0.20	0.35	0.50
B	40	60	
C	4.50	6.50	
D	0.60	1.00	
E	3.50	4.50	
F	30	60	

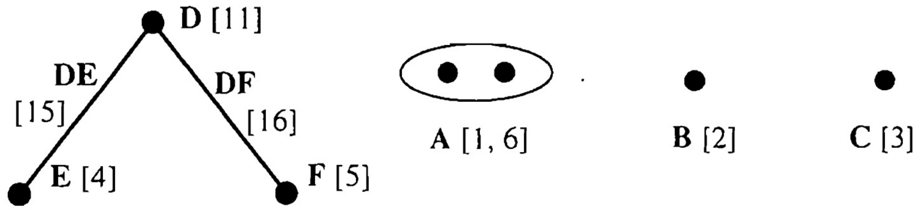

Figure 4. Linear graph and column assignment.

Designing the Experimental Layout

As the requirement was to estimate the effects of six main factors and two, two-factor interactions, a fraction of the full factorial design (of 96 trials), based on the L_{16} (2^{15}) orthogonal array (see Ref. 1), was used to design the experimental layout. Consequently, an experimental layout with 16 experimental trials was prepared based on the linear graph in Figure 4. Each experimental combination was replicated twice. Although the emphasis was to improve the resistivity of resin, the following five responses were recorded for each experimental trial:

1. Resistivity [90–200 kΩ]
2. Nonvolatile (NV) solid [51–55%]
3. Viscosity [6–14 BT at 25°C]
4. Acid value (A/V) [7–11 mg/KOH/g]
5. Petroleum ether tolerance (PET) [0.9–1.6 mL/g]

Note: Specifications are given in brackets.

Responses other than resistivity were considered with a view to finding a level of experimental factors that would not only improve the resistivity but also keep other responses within their respective specifications. The experimental layout and corresponding responses, for both the replicates, are given in Appendix 1.

Analysis and Conclusions

All five responses were analyzed using analysis of variance (ANOVA). Responses corresponding to each trial were first transformed into nominal-the-best type of signal-to-noise (S/N) ratio values using the following formula (see Ref. 2):

$$\text{S/N} = 10\log\left(\frac{SS_m - V_e}{rV_e}\right),$$

where

$$SS_m = r(\bar{y})^2, \qquad V_e = \left(\frac{\sum_{i=1}^{r} y_i^2 - r(\bar{y})^2}{r-1}\right), \qquad \bar{y} = \frac{\sum_{i=1}^{r} y_i}{r},$$

r is the number of replications and y_i is the observed response. These S/N ratio values were analyzed to find factors having adequate impact on the *noise*. Next, responses for which the ANOVA of S/N ratio values failed to indicate any contributing factors were analyzed with the original observations to find factors having a significant contribution to the *mean*.

Analysis of S/N ratio values corresponding to resistivity data revealed that factors C (solvent distillate %) and E (water collection time) had a relatively strong impact on noise (i.e., variability). However, analysis of S/N ratio values corresponding to other responses failed to identify factors affecting variability. So, it was decided to use factors C and D to control variability.

The ANOVA table on S/N ratio data of resistivity is given in Table 2. Analyses of original observations corresponding to all responses, except resistivity, revealed that factors A [amount of NaOH (in mL)] and D (phthalic anhydride %) had a large impact on the mean, whereas factors B and F had no impact on the mean response. Findings of the analyses are summarized in Table 3. Although factor C was observed to have a certain impact on the mean in the case of NV solid, its impact on the mean was ignored because it had already been decided to treat C as a *control factor* (by virtue of the analysis of the S/N ratio values of resistivity).

Second-Stage Experimentation

During analysis of the first-stage experimentation data, factors A and D were observed to affect the mean of the responses, so it was decided to carry out a *second-stage* experimentation to obtain the *best* levels of these two factors.

Because factors B and F were found to have no contribution to the mean as well as the variability, it was decided to fix their levels at their respective lower levels (i.e., 40 and 30 min, respectively) during the second stage of experimentation to reduce the processing time. Levels of C and E, the

Table 2. ANOVA Table on S/N Ratio Data of Resistivity

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	ρ %
A[a]	2	3.635	1.818	—
B[a]	1	13.195	13.195	—
C	1	460.183	460.183	37.15
D[a]	1	4.720	4.720	—
E	1	269.001	269.001	20.54
F[a]	1	27.728	27.728	—
DE[a]	1	38.630	38.630	—
DF[a]	1	28.140	28.140	—
Error	6	306.152	51.025	—
Pooled error	13	422.200	32.477	42.31
Total	15	1151.395		100.00

[a]Pooled with error to get the pooled error.

Table 3. Summary of Data Analysis

RESPONSE	DATA ANALYZED	% CONTRIBUTION		MEAN SQUARE ERROR
		FACTOR	CONTRIBUTION	
Resistivity	S/N ratio	C	37.15	32.48
		E	20.54	
		Total	57.69	
Acid value	Original	D	61.17	1.56
		A	5.12	
		Total	66.29	
NV solid	Original	C	10.35	2.91
PET	Original	Nil		0.08
Viscosity	Original	Nil		44.15

Table 4. Average Response Table for Resistivity (S/N Ratio)

LEVEL	A	B	C	D	E	F
1	8.86	9.84	3.57	9.47	13.03[a]	7.61
2	9.73	8.02	14.29[a]	8.39	4.83	10.25
3	8.57					
Δ	1.16	1.82	10.72	1.08	8.20	2.64

Note: Δ represents the levelwise absolute difference of average responses of a factor.

[a]Average response nearest the corresponding target value (i.e., specification mid-value).

Table 5. Average Responses of Factors Affecting Mean

RESPONSE	SPECIFICATION	FACTOR A_1	A_2	A_3	D_1	D_2
Acid value	9 ± 2 mg/KOH/g	9.40[a]	10.88	9.68	8.24[a]	11.58
NV solid	53 ± 2%	56.35	56.28[a]	56.97	57.01	56.27[a]
PET	1.25 ± 0.35 mL/g	2.17[a]	2.28	2.32	2.28[a]	2.26
Viscosity	10 ± 4 BT at 25°C	11.25[a]	13.31	13.25	12.03[a]	13.50

[a]Average responses nearest the corresponding target value (i.e., specification mid-value).

control factors, were fixed considering the levelwise average responses of S/N ratio values for resistivity. (see Table 4.)

Levelwise average response corresponding to resistivity for factors C and E revealed that levels 2 and 1, respectively, lead to the highest S/N ratio values. Consequently, factors C and E were fixed at 6.5% and 3.5 h, respectively. Finally, taking into account the specification for different responses, levels at which the average responses are nearest to the corresponding target values and the apparent trend in the responses (see Table 5), the experimental levels of factors A and D in Table 6 were selected for second-stage experimentation. In this stage, a full factorial experiment, with two replications, was run. Experimental layout and responses of the second-stage experimentation are given in Appendix 2.

Data obtained during second-stage experimentation was analyzed using ANOVA again. This analysis revealed that factor A contributes 48.65% and 41.27% to the variation in resistivity and PET, respectively, whereas factor D contributes 20.19% and 38.35% to the variation in resistivity and acid value, respectively. A summary of the analysis is given in Table 7.

The levelwise average values for different responses are given in Table 8. Thus, the levels of factors A and D were selected, meeting corresponding response specifications, as follows: amount of NaOH (factor A): 0.25 mL; phthalic anhydride% (factor D): 0.8%.

Table 6. Levels of Factors A and D (Second-Stage Experimentation)

FACTOR	CODE	LEVELS		
Amount of NaOH	A	0.15	0.20	0.25
Phthalic anhydride %	D	0.70	0.80	—

Table 7. Responsewise Percentage Contribution of the Experimental Factors

FACTORS	RESPONSE RESISTIVITY	PET	ACID VALUE	VISCOSITY	NV SOLID
A	48.65	41.27	4.64	3.07	
D	20.19	0.43	38.35		2.55

Table 8. Average Response Table for Second-Stage Experimentation

RESPONSE	FACTOR A1	A2	A3	D1	D3
Resistivity	177.500	112.500	**168.750**[a]	171.667	**134.167**
Acid value	7.258	7.198	8.165	6.805	**8.293**
NV solid	58.125	58.098	58.355	57.640	58.745
PET	2.555	3.220	**2.462**	2.858	2.633
Viscosity	8.000	7.125	8.750	8.083	7.833

[a]Bold-faced figures represent the average responses nearest the corresponding target (i.e., specification mid-value).

Table 9. Expected Responses and Corresponding 95% Confidence Limits

RESPONSE	UNIT	EXPECTED VALUE	95% CONFIDENCE LIMIT
Resistivity	kΩ	150.0	±30.3
NV solid	%	58.71	±3.10
Viscosity	BT at 250°C	8.62	±2.88
Acid value	mg/KOH/g	8.91	±1.74
PET	mL/g	2.34	±0.72

Note: The 95% confidence limit is calculated using $[F_{0.05,1,df(MSE)} \times (MSE)(1/n_e)]^{1/2}$, where n_e is the total number of experiments divided by the sum of the df of the sources considered for calculating $\hat{\mu}$) (see Ref. 1).

Optimal Factor Level Combination

The optimal manufacturing process parameters were, then, selected as follows:

Amount of NaOH	0.25 mL
Reflux time	40 min
Solvent distillate %	6.5%
Phthalic anhydride %	0.8%
Water collection time	3.5 h
Solvent distillate collection time	30 min

The expected responses at the above optimal factor level combination with respective 95% confidence limits were estimated as provided in Table 9.

Suggestion and Implementation

Because it was not possible to achieve the specifications for NV solid and PET, it was decided, in consultation with the technical personnel of the organization, to modify the corresponding specifications in light of the actual performance and, accordingly, the following specification was suggested:

NV solid: 55–62%
PET: 1.6–3.1 mL/g

Two batches of resin were produced at the optimum process parameter combination and all five responses were observed to lie within the corresponding specification (existing/revised, as the case may be) in both the cases.

Technologically, it was felt that these changes in the specification of resin quality characteristics should not affect the resulting paint quality characteristics. Still, a decision was taken to manufacture a few batches of paint using the resin obtained earlier to verify such belief. Consequently, two batches of paint were manufactured using the resin manufactured at the optimum factor level combination. All the quality characteristics of the resulting paints were observed to be satisfactory and to fall within corresponding specifications. The suggested specifications were then accepted by the company management.

Appendix 1: Experimental Layout and Responses for First-Stage Experimentation

Experimental Layout

TRIAL NO.	FACTOR						RUN ORDER	
	A	B	C	D	E	F	1	2
1	1	1	1	1	1	1	9	7
2	1	1	1	2	1	1	16	16
3	2	1	1	1	2	2	5	1
4	2	1	1	2	2	2	15	8
5	2	2	2	2	1	1	4	2
6	2	2	2	1	1	1	1	5
7	1	2	2	2	2	2	3	11
8	1	2	2	1	2	2	14	12
9	3	1	2	2	1	2	6	14
10	3	1	2	1	1	2	2	9
11	3	1	2	2	2	1	12	10
12	3	1	2	1	2	1	8	3
13	3	2	1	1	1	2	13	4
14	3	2	1	2	1	2	10	15
15	3	2	1	1	2	1	7	6
16	3	2	1	2	2	1	11	13

Appendix 1 (Continued)

Responses

TRIAL NO.	NV SOLID 1	NV SOLID 2	VISCOSITY 1	VISCOSITY 2	ACID VALUE 1	ACID VALUE 2	PET 1	PET 2	RESISTIVITY 1	RESISTIVITY 2
1	53.77	53.89	5.5	7.5	7.41	8.72	1.90	2.10	60	135
2	56.30	55.00	9.0	9.5	10.55	12.05	2.14	2.31	220	160
3	57.60	56.90	7.5	13.0	9.87	7.06	2.21	2.44	85	180
4	57.50	53.30	17.0	12.5	11.86	11.76	2.63	2.60	330	110
5	55.30	54.67	5.0	21.5	14.08	13.78	2.57	1.81	95	130
6	58.40	56.60	12.0	18.0	9.42	9.20	2.12	1.83	190	175
7	56.20	57.00	11.0	14.5	11.12	10.82	2.29	2.06	145	200
8	59.65	59.00	21.5	11.5	7.01	7.48	2.21	2.33	300	210
9	57.60	54.50	9.5	13.0	11.60	12.77	2.30	1.80	110	100
10	59.60	57.00	36.0	7.0	6.94	6.41	2.24	2.66	125	130
11	56.00	58.20	15.0	12.0	9.55	9.75	2.71	2.06	300	170
12	58.46	58.40	7.0	12.5	10.90	6.54	2.30	2.21	65	160
13	56.90	53.50	7.0	8.5	7.49	10.56	2.50	2.01	170	90
14	56.50	59.00	14.0	25.0	12.44	11.01	2.49	2.10	70	250
15	57.50	55.00	11.0	7.0	8.31	8.50	2.65	2.83	380	80
16	57.79	55.50	6.5	21.0	11.23	10.92	2.35	1.94	105	200

Appendix 2: Experimental Layout and Responses for Second-Stage Experimentation

EXPT. NO.	FACTOR A	B	C	D	E	F	RESPONSES % NV	VIS-COSITY	ACID VALUE	PET	RESIS-TIVITY
1	0.15	40	6.5	0.7	3.5	0.5	59.0	11.0	6.65	3.11	235
							57.8	7.0	7.32	2.58	185
2	0.20	40	6.5	0.7	3.5	0.5	56.5	6.0	6.91	3.45	110
							57.7	8.0	6.52	3.03	140
3	0.25	40	6.5	0.7	3.5	0.5	58.3	8.0	7.25	2.91	165
							56.5	8.5	6.18	2.07	195
4	0.15	40	6.5	0.8	3.5	0.5	55.5	6.0	8.50	1.92	150
							60.2	8.0	6.67	2.61	140
5	0.20	40	6.5	0.8	3.5	0.5	58.1	6.5	8.26	3.00	90
							60.1	8.0	7.10	3.40	110
6	0.25	40	6.5	0.8	3.5	0.5	58.0	9.0	9.78	2.55	140
							60.0	9.5	9.45	2.32	175

Note: For a given treatment combination, row 1 and row 2 represent replication 1 and replication 2, respectively.

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