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DEVELOPMENT AND OPTIMIZATION OF WATER BASED PAINT FORMULA IN ORDER TO REDUCE VOCs EMISSIONS

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Abstract

The interest in waterborne paints amelioration increased lately due to the toxicological effect of certain ingredients on human health, the restrictive environmental legislation and the depletion and escalation in price of raw materials. Research efforts in formulating waterborne paints are directed to insure low volatile organic compounds (VOCs) emission while maintaining and even improving their properties.
This paper presents a waterborne paint formulation process. The required main ingredient was an alkydic resin with 51.3 % w/w non-volatile-matter content, 51.6 mg KOH/g acidity, 8.5 pH, 80 s flow time. Aiming the highest values for paint viscosity, elasticity and hardness and the lowest VOCs emission, the optimal composition concerning the resin neutralization, type and amounts of neutralization agents, co-solvents and water were determined by Response Surface Methodology (RSM). As consequence, the resin was neutralized with a mixture of ammonia and triethylamine in 1:1.8 ratio and solubilized with butanol and butyl glycol co-solvents (2.8:1 ratio). Pigments and filling material were used in a 2.6:1 ratio reported at resin content. The final product can be described as a homogenous, viscos fluid, with 152 s flow time and 22.5% VOCs content. In the optimized drying conditions, it formed a film with a fineness of 40 μm, a semi-gloss aspect, a good adherence, an elasticity (after 7 days) of 5.5 mm and a hardness of 45, 93 and 104 s (after 24 h, 3 and 7 days respectively).

Key words: alkyd resin, enamel, mathematical optimization, primer, waterborne paint

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1. Introduction

In recent decades, conventional paints are more and more replaced by environmentally friendly formulas (Broek, 1993; Traumann et al., 2014) whose use is recommended due to ecological considerations, specifically the reduction of VOCs emissions) (Tucaliuc, 2014) and economic aspects (low volumes of organic solvents which tend to have a limited availability and are expensive). This type of paints includes powder, high-solids, polyurethanes, radiation curable, emulsion paints etc. (Barletta et al., 2006; Elhalawany et al., 2014; Klaasen and van der Leeuw, 2006; Kowalczyk et al., 2013; Salleh et al., 2013).

Owing to their reduced solvent content, the water soluble paints are characterized by low toxicity, low VOCs emission, non-inflammability (de Mariz et al., 2010). Even though they could possess a higher viscosity and require more time and heat to dry, the quality of the resulted films are comparable and sometimes superior to those obtained with

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solvent soluble paints. Based on the actual requirements for organic solvents emission (Rusu and Dumitriu, 2003) and considering the constant increase performance of existing water-based coatings, this paper was focused on the development of oxidative drying paints, primers, intermediate paints and enamels containing a water soluble resin useful for metal or wood coverage.

The first coatings with water based paints were the emulsion paints containing different resins (Athawale and Nimbalkar, 2011; Crespi et al., 2007). They showed the disadvantages of not being suitable for metal (due to the the small amounts of water remaining in film and on the support, which caused corrosion phenomena) and having a low mechanical stability. The use of additives increases the formulation complexity and affects the film water resistance (Broek, 1993). As consequence, easier to formulate paints were developed using water-soluble synthetic alkyd resins characterized by a low molecular weight and an important number of hydrophilic groups. Their dissolution in water is related to the presence of easily ionizable hydroxyl and carboxyl groups. Ammonia or amines are recommended in this case since they can ensure a good neutralization process without affecting the system rheology or the drying period. Produced by condensation reactions between polyols and polyacids, the mentioned resins contain also fatty acids which use influences in a positive way the mechanical properties of the resulting final film (Hofland, 2012).

The water used in formulation process leads to a longer drying period and support adherence issues. These drawbacks are caused by the water high dipole moment, by its tendency to form hydrogen bonds and by the fact that it reduces the resistance duration of oxygen in the excited stage and the possibility of hydroperoxide stage formation (Dyer and Cummings, 2006). The use of co-solvents such as alcohols or glycol ethers influences the water surface tension (Lisa et al., 2010) ameliorating the support adherence (Khossravi and Connors, 1993). Siccatives and pigments are added in the final step of paint formulations. Additives such as modifiers (Nor et al., 2008), wetting agents, antifoaming agents etc. ameliorate the ingredients dispersion and the film quality but their use remains optional. These paints do not show precipitation phenomena in freeze-thaw cycles or in mechanical shear that can occur during the production process.

This paper was directed to the development of resin water soluble oxidative drying paint, primers, intermediate paint and enamels formulas. An optimization process was leaded by RSM. Parameters such as the resin neutralization percentage, type and amounts of neutralization agents, co-solvents and water were used in order to find the best values able to insure the lowest VOCs content, the highest hardness and the best elasticity values. Various siccatives, pigments and additives were added and the obtained final paint formulas were submitted to different quality tests.

2. Materials and methods

2.1. Materials and reagents

Water soluble alkyd resin was produced by the Romanian Institute of Advanced Coatings. Luwipal LR 8334, Melarom 31 and Urezit 80 amino resins were supplied by BASF Romania and Rasin Romania respectively.

All reagents and solvents used for the experimental program were of analytical purity. Ethanol, butanol (BuOH), ethylene glycol, ammonia (NH_3), diethanolamine, triethanolamine, triethylamine (Et_3N), cobalt naphthenate, barium hydroxide, titanium oxide, lead (II) chromate, calcium carbonate, phthalocyanine green, phthalocyanine blue, black carbon and talc were purchased from Sigma Aldrich (Romania). Manganese naphthenate and lead naphthenate were bought from TCI Europe (Belgium). Baochemicals (Spain) supplied the butyl glycol (BG). Lithopone, iron oxide yellow, zinc potassium chromate and red iron oxide were provided by Chemos GmbH (Germany). The solutions and dilutions were carried out by using deionized water.

2.2. Paints, primers, intermediate paints and enamels formulations

The products recipes were formulated by using the ingredients listed in Table 1.

Table 1. Ingredients employed for waterborne paint formulations

Ingredients	***Required amounts, %***
Water thinnable resin (neutralized)	5-60
Water soluble solvents	15-35
Pigments	0-40
Siccatives	0.05-1.5
Slip additive	0.02-5
Wetting agent	0-4
Anti-settling agent	0-4
Rust inhibitor	0-20
Flattening agent	0-20
Water	15-40

The amount of the neutralization agent (amine) was established in order to insure the neutralization of at least 60% of the carboxylic groups existing in the resin. It was calculated from resin acid value by using Eq. (1), where: M_a is the molecular weight of the amine; A is the acid value of the solid resin (defined as milligrams of KOH per gram of solid resin required to give a phenolphthalein titration end point (Howard, 1980)); R is the quantity of the solid resin used and *56100* is 1000 times the molecular weight of KOH.

$$Amine\ amount = \frac{M_a \cdot A \cdot R}{56100} \quad (1)$$

The required quantities of siccatives (Eq. 2) were determined knowing that they were purchased as naphthenate salts solutions containing 12% of a given metal (Christhilf et al., 1986).

$$Siccative\ (solution)\ (wt.\%) = \frac{\%\ metal\ on\ vehicle\ solids\ desired \times vehicle\ solids}{\%\ concentration\ of\ metal\ in\ siccative\ solution} \quad (2)$$

The established amounts of ingredients were milled for 24 h in a hammer mill. When the mixing process was finalized, certain amounts of resins, neutralizing agents and water were added and mixed with the anterior obtained formulas in order to complete the paint systems.

2.3. Experimental design

The design and analysis of variables were evaluated using NemrodW® v.2000 and XLSTAT-Pro 7.5 version software. Preliminary experiments indicated six main factors affecting the quality of waterborne paints: the alkyd resin neutralization percentage, the type and amount of neutralization agents and co-solvents and the amount of water. In order to establish the appropriate values of these factors two optimization processes were conducted. For each process, the effect of three independent variables on the most important products quality indicators was investigated by RSM. 27 different experiments were carried out each time with three replicates in domain central point.

The independent variables selected in the first case were: the alkyd resin neutralization percentage, the amount of co-solvent (BuOH) and the amount of water. For the second optimization process, the independent variables were: neutralization agents' ratio (NH_3 - Et_3N), co-solvents ratio (BG - BuOH) and the water percentage.

The variation levels of the chosen variables are presented in Tables 2 and 3. Three response functions were followed for each optimization process: product viscosity, film hardness at 7 days and VOCs percentage emission and respectively product elasticity, hardness and VOCs emission.They were fitted in the form of a quadratic polynomial model (Eq. 3), where the values of n are between 1 and 3, ${}_nY$ is the response function (${}_1Y$ viscosity, ${}_2Y$ Persoz hardness, ${}_3Y$ VOCs percentage for the 1st RSM set of experiments and ${}_4Y$ elasticity, ${}_5Y$ Persoz hardness, ${}_5Y$ VOCs percentage for the 2nd set), ${}_nA_0$, ${}_nA_i$, ${}_nA_{ii}$, and ${}_nA_{ij}$ are the regression coefficients of variables for the intercept, linear, quadratic and interaction terms respectively and X_i and X_j are the independent variables (i≠j).

$${}_nY = A_0 + \sum_{i=1}^{3} A_i \cdot {}_nX_i + {}_n\sum_{i=1}^{3} A_{ii} \cdot {}_nX_i^2 + {}_n\sum_{i=1}^{2}\sum_{j=i+1}^{3} A_{ij} \cdot {}_nX_i \cdot {}_nX_j \quad (3)$$

2.4. Paints, primers, intermediate paints and enamels testing procedure

The obtained products were applied on supports and submitted to different quality analyses (Table 4). All tests were carried out in triplicate at room temperature.

3. Results and discussion

3.1. Water soluble resin choice

The developed waterborne paints were formulated by using a series of ingredients namely water-soluble resins, neutralization agents, co-solvents, deionized water, siccatives, pigments and additives. Their choice and amounts were based on their effects on paint properties (aspect, viscosity, hardness, elasticity, drying time, VOCs emission etc.).

The formulation process consisted in two main phases: pigment dispersion and completion each one divided in several sub-phases.

Table 2. Code and level of independent variables chosen for the 1st RSM optimization

Variables	*Symbol*		*Levels*			ΔX_i
	Coded	*Uncoded*	*-1*	*0*	*1*	
			Actual values			
Percentage of alkyd resin neutralization, %	x_1	X_1	60	70	80	10
Co-solvent, % w/w	x_2	X_2	15	20	25	5
Deionized water (including water from NH_3 solution 25% w/w), % w/w	x_3	X_3	20	25	30	5

Table 3. Code and level of independent variable chosen for the 2nd RSM optimization

Variables	*Symbol*		*Levels*			ΔX_i
	Coded	*Uncoded*	*-1*	*0*	*1*	
			Actual values			
Neutralization agents (NH_3 (25% in water) - Et_3N) ratio	x_1	X_1	1/1.5 (0.33)	1/2 (0.50)	1/3 (0.66)	0.16
Co-solvents (BG - BuOH) ratio	x_2	X_2	1/3.3 (0.3)	1/2.6 (0.4)	1/2 (0.5)	0.1
Deionized water (including water from NH_3 solution 25% w/w), % w/w	x_3	X_3	25	27	29	2

Table 4. Tests applied for developed paints, primers, intermediate paints and enamels

Test	*Reference method*	*Apparatus used*
Determination of flow time by use of flow cups	ISO 2431 (2012)	Viscosity cups (ISO 2431; ϕ = 4 mm and 5 mm) (Multilab, Romania)
Determination of fineness of grind	ISO 1524 (2013)	Grindometer ZGR 2024 (Rom Tech, Romania)
Determination of water content	ISO 760 (1994)	-
Determination of non-volatile-matter content	ISO 3251 (2008)	Air oven POL-EKO STD (Nitech, Romania)
Determination of VOCs content	ISO 11890-1 (2007a)	-
Determination of hardness	ISO 1522 (2007b)	Pendulum hardness tester type 707KP (Inspiratech 2000 Ltd., England)
Drying test	ISO 9117-3 (2010a)	Ballotini glass pearls (CDS Consultants, England)
Environmental testing	ISO 60068-2-11 (2001)	-
Determination of resistance to liquids	ISO 2812-1 (2007c) ISO 2812-2 (2007d)	-
Determination of film thickness	ISO 2808 (2007e)	Digital Coating Thickness Gauge (Elcometer Instruments GmbH, Germany)
Cross-cut test	ISO 2409 (2010b)	Cross Hatch Cutter (Paint Test Equipment, England)

For pigment dispersion the most important step was represented by the binder choice. Two types of resins were used to this purpose: an alkydic one for obtaining a classic waterborne paint and a mixture of alkydic resin and different amino resins for the hybrid paint system production.

Preliminary tests were realized in order to establish if alkyd resin alone or its combination with different amino resins represent the best choice for paint formulation. The results (Table 5) revealed no differences between the resins in terms of appearance and drying time. Moreover, the Persoz test indicated higher hardness values in the case of alkyd resin. As respects the resistance to water immersion, a color going from slightly matted for the alkyd resin and its combination with Luwipal resin to matted for combinations of alkyd resin and Melarom or Urezit was observed. As consequence, the alkyd resin was chosen for further experiments.

3.2. Paints, primers, intermediate paints and enamels formulations optimization

Water-soluble alkydic resins are stabilized by anions generated by carboxylic groups which are neutralized by amines or ammonia. If these groups are only week bases, the pH-values of the neutralized solutions are about 7.5 to 8.2. This fact leads to the saponification of resin ester groups and has as consequence a limited storage time of the resulting paint systems. In order to avoid this inconvenient, the carboxylic groups must be neutralized (Müller and Poth, 2006).

The choice of the agent used to this purpose was based on its ability to insure a good neutralization of carboxylic groups and on its influence on film aspect and drying time. Several preliminary tests were conducted with ammonia solution (25%), triethylamine, triethanolamine and diethanolamine (50%).

The results showed that the neutralization process was satisfactorily realized by all the employed agents. In regard of product appearance, the last two agents leaded to a sticky film even after 24 h from application. Ammonia conducted to the most reduced drying time but its use affected the paint color a yellowing process being detected.

An opposite effect was observed when triethylamine was used for neutralization. In terms of paint characteristics, the use of ammonia solution leaded to a higher hardness value (112 s) and to a lower elasticity (3.2 mm) compared to triethylamine which conducted to a hardness of 53 s and an elasticity of 5.3 mm. In order to insure a good solubility of the neutralized alkydic resin and an appropriate final products viscosity various amounts of water and of different solvents such as alcohols and glycol ethers were added. The use of co-solvents, besides of the cited benefits, may also help to the saponification stability.

BG for example, due to its molecular structure, forms solvates of alkyd resins in water phase, which consist of more solvent in the colloidal particles and less water. Other solvents such as ethanol, butanol, ethylene glycol or their mixtures can be employed too. On the other hand, this study was aimed to obtained paints systems with low VOCs emission. Therefore, we have tried to limit as more as possible the amounts of the employed co-solvents. Considering the above related aspects, we have decided to use the RSM in order to establish the ingredients optimal amounts. The values of the independent variables (alkyd resin neutralization percentage, co-solvent amount and water amount) and of the studied response functions (viscosity; hardness at 7 days; VOCs percentage) are reported in Table 6.

The mathematical models generated for the response functions are expressed by Eqs. (4), (5) and (6).

Table 5. Alkyd and amino resins mix characteristics

Characteristics	***Alkyd resin***	***Amino resin***		
		Luwipal LR 8334	Melarom 31	Urezit 80
		Alkyd resin and amino resin ratio		
		9/1	10/1	9/1
Appearance	viscous homogenous liquid			
Drying time at 20 °C - at dust, min - type C, h	 60 24	 60 24	 60 24	 60 24
Persoz hardness[1], s - after 24 h - after 3 days - after 7 days	 43 68 75	 34 58 65	 30 54 60	 27 45 50
Resistance to water immersion[2], 24 h	slightly matted	slightly matted	matted	

[1]determined on films applied with hand-drawn scraper, on glass plates, of 120 µm wet thicknesses; [2]films sprayed on samples covered with primer based on the same binder as the applied paint

Table 6. 1st RSM test for paint formulation and the observed and predicted values for viscosity, hardness and VOCs

Run	***Neutr. agent (NH_3)[1]***		***Co-solvent (BuOH)***		***Water[2]***		***Viscosity, s***		***Persoz hardness, s***		***VOCs, %***	
	% w. n.r.[3]	***g***	***% w. mix[4]***	***g***	***% w. mix***	***g***	***Obs.[5] ±% (w/w)***	***Pred.[6]***	***Obs. ±% (w/w)***	***Pred.***	***Obs. ±2%***	***Pred.***
1	60	0.94	15	23.29	20	31.06	147±6.1	148	107±5.5	107	17.21	17.13
2	60	0.94	15	25.23	25	42.06	144±5.2	141	105±3.7	105	17.10	17.05
3	60	0.94	15	27.53	30	55.06	138±3.2	141	101±7.1	101	17.07	17.13
4	60	0.94	20	33.65	20	33.65	139±5.5	140	109±1.6	109	22.63	22.61
5	60	0.94	20	36.71	25	45.88	133±4.9	133	108±2.1	108	22.58	22.61
6	60	0.94	20	40.38	30	60.56	134±3.3	132	106±2.4	105	22.50	22.76
7	60	0.94	25	45.88	20	36.71	121±3.2	119	107±4.3	107	28.10	28.17
8	60	0.94	25	50.47	25	50.47	109±1.7	112	106±3.3	106	28.00	28.25
9	60	0.94	25	56.08	30	67.29	111±4.8	111	104±4.8	104	28.99	28.48
10	70	1.10	15	23.33	20	31.11	145±5.3	147	112±1.0	112	17.26	17.31
11	70	1.10	15	25.27	25	42.12	144±8.1	140	110±3.8	110	17.22	17.14
12	70	1.10	15	27.57	30	55.14	137±5.5	140	106±3.1	106	17.17	17.12
13	70	1.10	20	33.70	20	33.70	136±5.5	139	113±5.0	114	22.76	22.68
14	70	1.10	20	36.76	25	45.95	133±6.8	133	112±0.9	112	22.66	22.59
15	70	1.10	20	40.44	30	60.66	135±4.6	132	109±4.4	110	22.59	22.65
16	70	1.10	25	45.95	20	36.76	121±8.4	119	112±2.5	111	28.20	28.13
17	70	1.10	25	50.55	25	50.55	110±5.7	112	111±2.7	111	28.13	28.12
18	70	1.10	25	56.16	30	67.40	110±9.2	111	109±2.6	109	28.00	28.25
19	80	1.25	15	23.37	20	31.15	146±4.1	146	112±4.1	112	17.40	17.62
20	80	1.25	15	25.31	25	42.19	144±7.0	140	110±3.2	110	17.38	17.36
21	80	1.25	15	27.61	30	55.23	137±3.2	140	106±0.8	106	17.29	17.24
22	80	1.25	20	33.75	20	33.75	138±6.8	139	114±2.4	114	22.99	22.88
23	80	1.25	20	36.82	25	46.02	131±4.7	133	113±3.0	113	22.72	22.69
24	80	1.25	20	40.50	30	60.75	133±5.6	132	111±6.6	110	22.70	22.66
25	80	1.25	25	46.02	20	36.82	122±5.4	119	112±6.8	112	28.22	28.22
26	80	1.25	25	50.63	25	50.63	108±2.9	112	111±2.1	111	28.12	28.11
27	80	1.25	25	56.25	30	67.50	113±1.1	111	109±3.6	109	28.11	28.15

[1]25% aqueous NH_3 solution; [2]total amount of water (incorporating water from the NH_3 solution); [3]% w. n.r. - percentage of neutralized resin; [4]mix. - total amount of tested paint; [5]Obs. - observed value; [6]Pred. - predicted value

$$ {}_1y = 132.556 - 0.222\cdot{}_1x_1 - 14.278\cdot{}_1x_2 - 3.722\cdot{}_1x_3 + \\ + 0.333\cdot{}_1x_1\cdot{}_1x_2 + 0.083\cdot{}_1x_1\cdot{}_1x_3 - 0.333\cdot{}_1x_2\cdot{}_1x_3 + \\ + 0.333\cdot{}_1x_1^2 - 6.500\cdot{}_1x_2^2 + 2.833\cdot{}_1x_3^2 \quad (4) $$

$$ {}_2y = 112.407 + 2.500\cdot{}_2x_1 + 0.667\cdot{}_2x_2 - 2.056\cdot{}_2x_3 + \\ + 0.750\cdot{}_2x_2\cdot{}_2x_3 - 2.056\cdot{}_2x_1^2 - 2.222\cdot{}_2x_2^2 - 0.722\cdot{}_2x_3^2 \quad (5) $$

$$ {}_3y = 22.589 + 0.042\cdot{}_3x_1 + 5.487\cdot{}_3x_2 - 0.019\cdot{}_3x_3 - \\ - 0.111\cdot{}_3x_1\cdot{}_3x_2 - 0.094\cdot{}_3x_1\cdot{}_3x_3 + 0.077\cdot{}_3x_2\cdot{}_3x_3 + \\ + 0.063\cdot{}_3x_1^2 + 0.039\cdot{}_3x_2^2 + 0.076\cdot{}_3x_3^2 \quad (6) $$

The quality of the obtained polynomial model was established by several statistical data: the standard error which estimates the standard deviation of a certain value based on all values mean (Press et al., 1992); the coefficient of determination (R^2) which considers all effects; the adjusted coefficient of determination (adj. R^2) which considers only square effects and interaction effects between two input variables; the predicted coefficient of determination (pred. R^2) which considers all effects for values generated by the employed software; the

predicted residual sum of squares (PRESS) which is a form of cross-validation used in regression analysis to provide a summary measure of the fit of a model to a sample of observations that were not themselves used to estimate the model and the precision adequacy (Adeq. Precision), which measure the ratio of signal to noise. The specific values of these statistical parameters for the studied functions are presented in Table 7. Their values indicate that the mathematical models describe with high accuracy the behavior of the obtained experimental data.

The analysis of variance (ANOVA) served to calculate the significance of the response surface quadratic models coefficients. From data shown in Table 8, it can be observed that the percentage of neutralized resin influences the paint hardness ($p < 0.01$) but does not affect in a significant way the viscosity ($p = 74.7$) and the VOCs emission ($p = 35.1$). This fact can be explained by the small amount of the neutralization agent required (0.94-1.25 g/100 g resin). On the contrary, the co-solvent amount seems to be a very important factor ($p > 0.01$) since it has a great impact on all three studied response functions. In terms of water amount, one can note that it influences only the paint viscosity and hardness ($p < 0.01$). The obtained p values reveal no effect of independent variables interactions on the mentioned functions.

In order to gain a better understanding of the results, the predicted models were presented as 3D surfaces plots (Fig. 1) based on the effects of two factors. Specifically, these plots showed how alkyd resin neutralization, co-solvent and water amounts related to paint viscosity, hardness and VOCs emission. The real values of the independent variables for the optimum results were calculated targeting the highest paint hardness, an appropriate viscosity (aiming values around 127 s) and the lowest VOCs emission values. From the obtained data (Table 9), it can be noted that for a resin neutralization of 67-72%, 21% co-solvent and 27-28% water (values reported at paint resin content) the product was characterized by a viscosity of ≈ 128 s, a hardness at 7 days of ≈ 110 s and an emission of VOCs of ≈ 23%.

The differences in desirability, meaning in finding the best simultaneous conditions of waterborne paint formulation and in the imposed conditions, for all three propose mathematical model are minimal.

In order to validate the mathematical model adequacy and to find the correct paint formulations, 5 replicates of each generated recipe were carried out. After analyzing the recorded values and taking in consideration the averages and values frequency for each characteristic, a compromise formulation composition was adopted: resin neutralization degree 70% (1.10 g NH_3/100 g resin), 21% co-solvent and 27% water (values reported at paint resin content). By testing the obtained paint systems (3 replicates) the following characteristics were measured: 127.1% ± 1.9% for viscosity, 112.0 s ± 0.6% for hardness and 23.79 g/L ± 0.3% for VOCs.

Taking into account these data, we have considered as indicate to ameliorate the obtained characteristics by using a mixture of NH_3 (25% in water) and Et_3N as neutralization agent and a mixture of BG - BuOH as co-solvent.

Thus, another optimization program was established. This time, the three independent variables were represented by the neutralization agent and co-solvent constitutive elements ratios and the percentage of added water. The used values along with the experimental and predicted results obtained for paint elasticity (mm), its hardness at 7 days (s) and VOCs emission (%) are presented in Table 10.

Table 7. Estimates and statistics of the coefficients

Statistical parameters	*Equation 4*	*Equation 5*	*Equation 6*	*Equation 7*	*Equation 8*	*Equation 9*
Standard error	2.903	0.511	0.184	0.11	1.6	0.106
R^2	0.967	0.983	0.999	0.951	0.964	0.741
Adj. R^2	0.950	0.974	0.998	0.925	0.945	0.604
R^2 *pred.*	0.916	0.960	0.996	0.854	0.901	0.348
PRESS	368.042	10.593	1.928	0.573	124.969	0.485
Adeq. Precision	20.93	41.00	102.02	18.52	26.29	4.31

Table 8. Significance of coefficients in the response equations

Coefficient	*Significance, p %*					
	Equation 4	*Equation 5*	*Equation 6*	*Equation 7*	*Equation 8*	*Equation 9*
A_0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
A_1	74.7	< 0.01	35.1	< 0.01	< 0.01	0.193
A_2	< 0.01	< 0.01	< 0.01	0.262	< 0.01	68.1
A_3	< 0.01	< 0.01	66.2	0.166	< 0.01	0.0105
A_{11}	77.8	< 0.01	41.8	0.0389	< 0.01	62.1
A_{22}	< 0.01	< 0.01	61.1	2.00	4.28	3.72
A_{33}	2.74	0.300	32.6	38.9	42.1	40.8
A_{12}	69.7	100.0	4.96	100.0	0.779	21.7
A_{13}	91.9	100.0	9.0	60.2	3.30	31.8
A_{23}	69.7	0.0112	16.3	60.2	0.540	74.7

Table 9. Optimized process variables and related response functions values

Maximum coordinates							
Variable	***Coded value***			***Factor***	***Real value***		
	1st	***2nd***	***3rd***		***1st***	***2nd***	***3rd***
X_1	-0.323209	-0.244171	0.214147	Percentage of neutralized alkyd resin	67	68	72
X_2	0.214187	0.222248	0.210315	Co-solvent	21	21	21
X_3	0.389336	0.436502	0.627537	Water	27	27	28
Maximum characteristics							
Response function				***Value***			
				1st	***2nd***	***3rd***	
$_1Y$	Viscosity, s			128.22	127.99	128.00	
$_2Y$	Hardness at 7 days, s			110.58	110.75	111.42	
$_3Y$	VOCs, %			23.79	23.83	23.77	
Desirability, %				98.64	95.39	95.82	

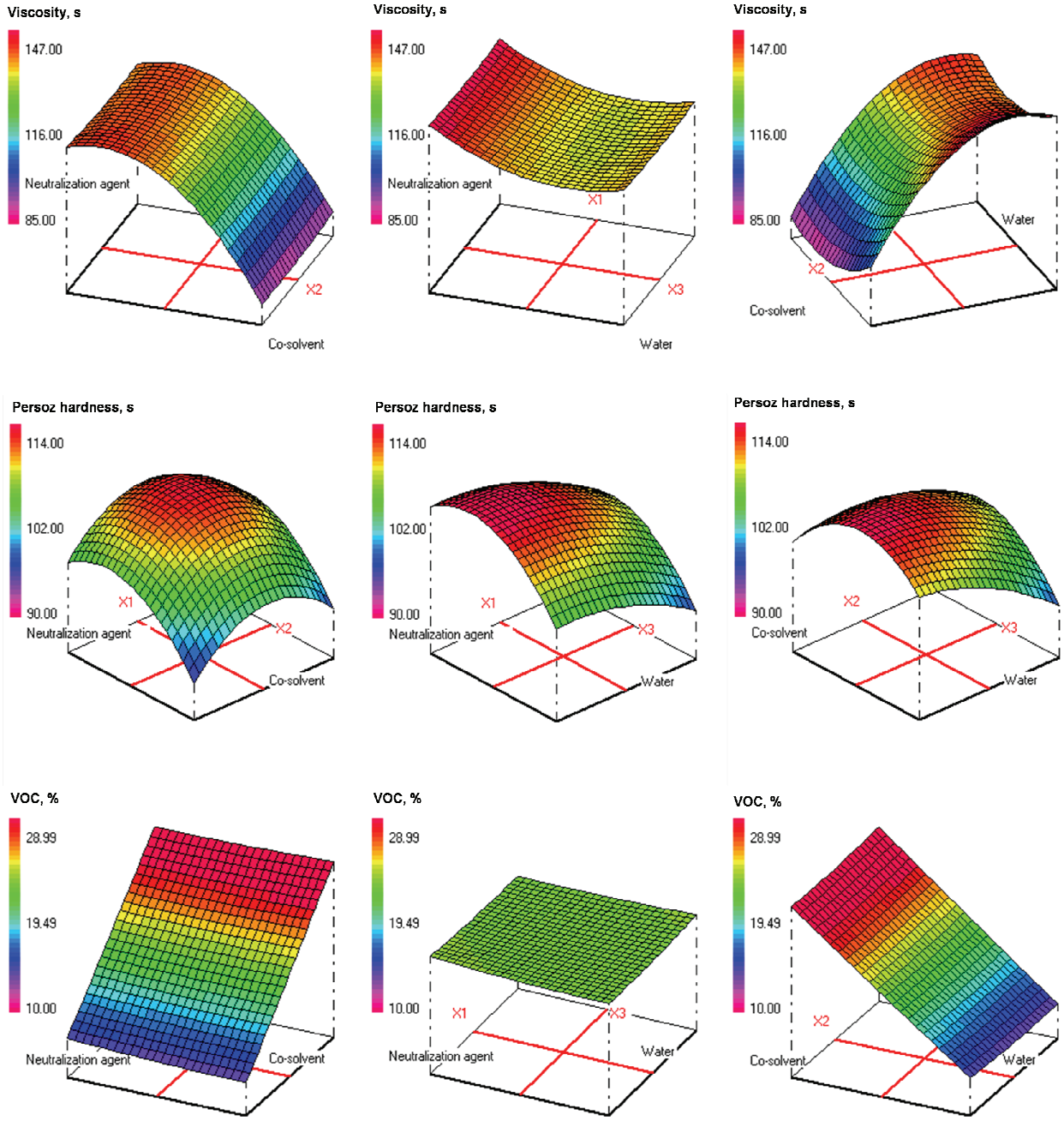

Fig. 1. 3D response surface plots for the 1st process of paint formulation optimization

The Eqs. (7-9) describe the mathematical models obtained for the response functions.

$$_4y = 5.27 + 0.42\,_4x_1 + 0.09\cdot_4x_2 + 0.09\,_4x_3 + 0.02\cdot_4x_1\cdot_4x_3 - \\ - 0.02\cdot_4x_2\cdot_4x_3 - 0.19\cdot_4x_1^2 - 0.11\cdot_4x_2^2 + 0.44\cdot_4x_3^2 \quad (7)$$

$$_5y = 88.9 - 6.1\cdot_5x_1 - 3.3\cdot_5x_2 - 2.9\cdot_5x_3 + 1.4\cdot_5x_1\cdot_5x_2 - \\ - 1.1\cdot_5x_1\cdot_5x_3 + 1.5\cdot_5x_2\cdot_5x_3 + 4.6\cdot_5x_1^2 + 1.4\cdot_5x_2^2 - 0.6\cdot_5x_3^2 \quad (8)$$

$$_6y = 23.861 + 0.092\cdot_6x_1 + 0.011\cdot_6x_2 - 0.128\cdot_6x_3 + \\ + 0.039\cdot_6x_1\cdot_3x_2 - 0.032\cdot_6x_1\cdot_6x_3 + 0.010\cdot_6x_2\cdot_6x_3 + \\ + 0.022\cdot_6x_1^2 + 0.097\cdot_6x_2^2 + 0.037\cdot_6x_3^2 \quad (9)$$

For these equations, the registered R^2 and adj. R^2 (Table 7) were between 0.741 and 0.951 and between 0.604 and 0.925 respectively. The predicted R^2 and adjusted R^2 in this study indicate that only 7.5, 5.5 and 39.6% respectively of total variations could not be explained by the models. Their values and "Adeq. Precision" reveal an acceptable degree of accuracy for the behavior of the obtained experimental data. The low values recorded for VOCs emission are due to the fact that the relative difference between minimum (23.7%) and maximum (24.3%) values is of only 2.5% indicating that the variations are influenced only by the neutralization agent (added in small amounts) and that the determined amounts are in the method precision limits.

According to the equations coefficients significance reported by ANOVA test (Table 8), the NH_3 - Et_3N ratio affects ($p > 0.01$) the elasticity and hardness of the resulted paint. In terms of employed co-solvents ratio and water, the statistical analysis shows that they have an influence only on the paint hardness ($p > 0.01$).

It can also be noted that none of the variables has an important impact on the paint VOCs emission. This observation can be explained by the fact that the amount of co-solvents, the main responsible for VOCs emission augmentation, remains constant at 21%, the neutralization agents are in reduced amounts and the water percentage ranges only 2%. Moreover, the interactions between the studied parameters do not affect the followed response functions.

Table 10. RSM test for intermediary paint formulation and the observed and predicted values for elasticity, hardness and VOCs

Run	Neutralization agent 25%NH_3/Et_3N		Co-solvent BG/BuOH		Water[1]		Elasticity, mm		Persoz hardness, s		VOCs, %	
	ratio	g	ratio	g	% w. mix[2]	g	Obs.[3] ±% (w/w)	Pred.[4]	Obs. ±% (w/w)	Pred.	Obs. ±2%	Pred.
1	1/5	5.74	1/3.3	41.12	25	48.95	4.5±2.0	4.4	111±3.8	111	24.10	24.06
2	1/5	5.74	1/3.3	42.70	27	54.90	4.5±0.6	4.5	107±3.7	106	23.88	23.92
3	1/5	5.74	1/3.3	44.41	29	61.33	4.7±1.1	4.6	98±2.9	100	23.80	23.85
4	1/5	5.74	1/2.6	41.12	25	48.95	4.6±1.1	4.6	101±1.9	103	24.00	23.93
5	1/5	5.74	1/2.6	42.70	27	54.90	4.6±0.3	4.7	98±2.2	100	23.81	23.79
6	1/5	5.74	1/2.6	44.41	29	61.33	4.7±2.4	4.8	95±1.5	95	23.75	23.73
7	1/5	5.74	1/2.0	41.12	25	48.95	4.5±1.2	4.6	99±3.7	98	23.89	23.98
8	1/5	5.74	1/2.0	42.70	27	54.90	4.7±0.7	4.6	97±1.1	96	23.90	23.86
9	1/5	5.74	1/2.0	44.41	29	61.33	4.7±0.6	4.7	95±5.1	93	23.80	23.81
10	1/2	5.91	1/3.3	41.19	25	49.03	4.9±0.9	5.0	99±2.5	98	24.10	24.12
11	1/2	5.91	1/3.3	42.77	27	54.99	4.9±0.1	5.1	95±0.8	94	24.00	23.95
12	1/2	5.91	1/3.3	44.48	29	61.43	5.1±0.4	5.2	90±2.1	89	23.88	23.85
13	1/2	5.91	1/2.6	41.19	25	49.03	5.1±0.2	5.2	91±1.6	91	23.92	24.03
14	1/2	5.91	1/2.6	42.77	27	54.99	5.3±0.6	5.3	89±1.1	89	23.70	23.86
15	1/2	5.91	1/2.6	44.48	29	61.43	5.4±0.2	5.4	84±2.7	85	23.88	23.77
16	1/2	5.91	1/2.0	41.19	25	49.03	5.3±1.4	5.2	87±3.3	88	24.30	24.13
17	1/2	5.91	1/2.0	42.77	27	54.99	5.3±0.7	5.3	86±3.3	87	23.87	23.97
18	1/2	5.91	1/2.0	44.48	29	61.43	5.5±0.6	5.4	84±2.6	85	23.91	23.89
19	1/3	6.10	1/3.3	41.26	25	49.12	5.2±0.6	5.2	91±3.3	94	24.20	24.23
20	1/3	6.10	1/3.3	42.85	27	55.09	5.3±0.6	5.3	89±3.8	91	24.10	24.02
21	1/3	6.10	1/3.3	44.56	29	61.54	5.6±0.2	5.5	87±0.6	87	23.83	23.89
22	1/3	6.10	1/2.6	41.26	25	49.12	5.5±0.1	5.4	91±2.7	89	24.25	24.17
23	1/3	6.10	1/2.6	42.85	27	55.09	5.5±0.6	5.5	89±6.2	87	23.91	23.98
24	1/3	6.10	1/2.6	44.56	29	61.54	5.6±0.9	5.6	86±3.3	85	23.89	23.85
25	1/3	6.10	1/2.0	41.26	25	49.12	5.3±0.3	5.4	87±1.5	87	24.20	24.31
26	1/3	6.10	1/2.0	42.85	27	55.09	5.5±0.3	5.5	86±2.1	87	24.30	24.12
27	1/3	6.10	1/2.0	44.56	29	61.54	5.5±1.4	5.6	86±1.1	86	23.91	24.01

[1]*total amount of water (water from NH_3 solution included);* [2]*mix. - total amount of tested paint;* [3]*Obs. - observed value;* [4]*Pred. - predicted value*

Fig. 2 depicts the 3D surfaces plots generated for the resulted mathematical models. The figure illustrates how neutralization agents ratio, co-solvents ratio and water percentage related to paint elasticity, hardness and VOCs emission.

The real values of the independent variables for the optimum results were calculated targeting the highest paint hardness and elasticity and the lowest VOCs emission values. The resulted data (Table 11) show that when the ratio between NH_3 (25 % in water) and Et_3N from neutralization agent is comprised between 1/1.45 and 1/2.32; the ratio between BG and BuOH is between 1/1.33 and 1/2.5 and the water percentage is between 26 and 28, the obtained product has an elasticity of ≈ 5.1 mm, a hardness at 7 days of ≈ 91 s and an emission of VOCs of ≈ 23%. Once the resin neutralization degree, water, neutralization agent and co-solvents type and amounts were established, the pigments dispersion phase was finalized by the addition of siccatives, pigments and extenders. In regard of utilized pigments, it must be noted that they have to be stable at the *p*H of paint formula. From the wide variety of the used substances able to insure a specific coloration we cite the following ones: titanium oxide, lithopone for white paints; black carbon for black paints; iron oxide yellow, lead (II) chromate, zinc potassium chromate for yellow paints; red iron oxide for red paints; phthalocyanine green for green paints and phthalocyanine blue for blue paints. Certain amounts of resins, neutralizing agents and water were mixed with these resulted paint formulas in the completion phase in order to rich the adequate systems composition.

After analyzing the obtained values (averages and frequency) from five replicates of each RSM optimized recipe, a new formulation was adopted: 70% of the neutralized resin with NH_3 (25% in water) and Et_3N in 1/1.8 ratio (1.10 g neutralized agent/100 g resin), 21% BG and BuOH mix in 1/2.8 ratio and 27% water (reported at paint resin content).

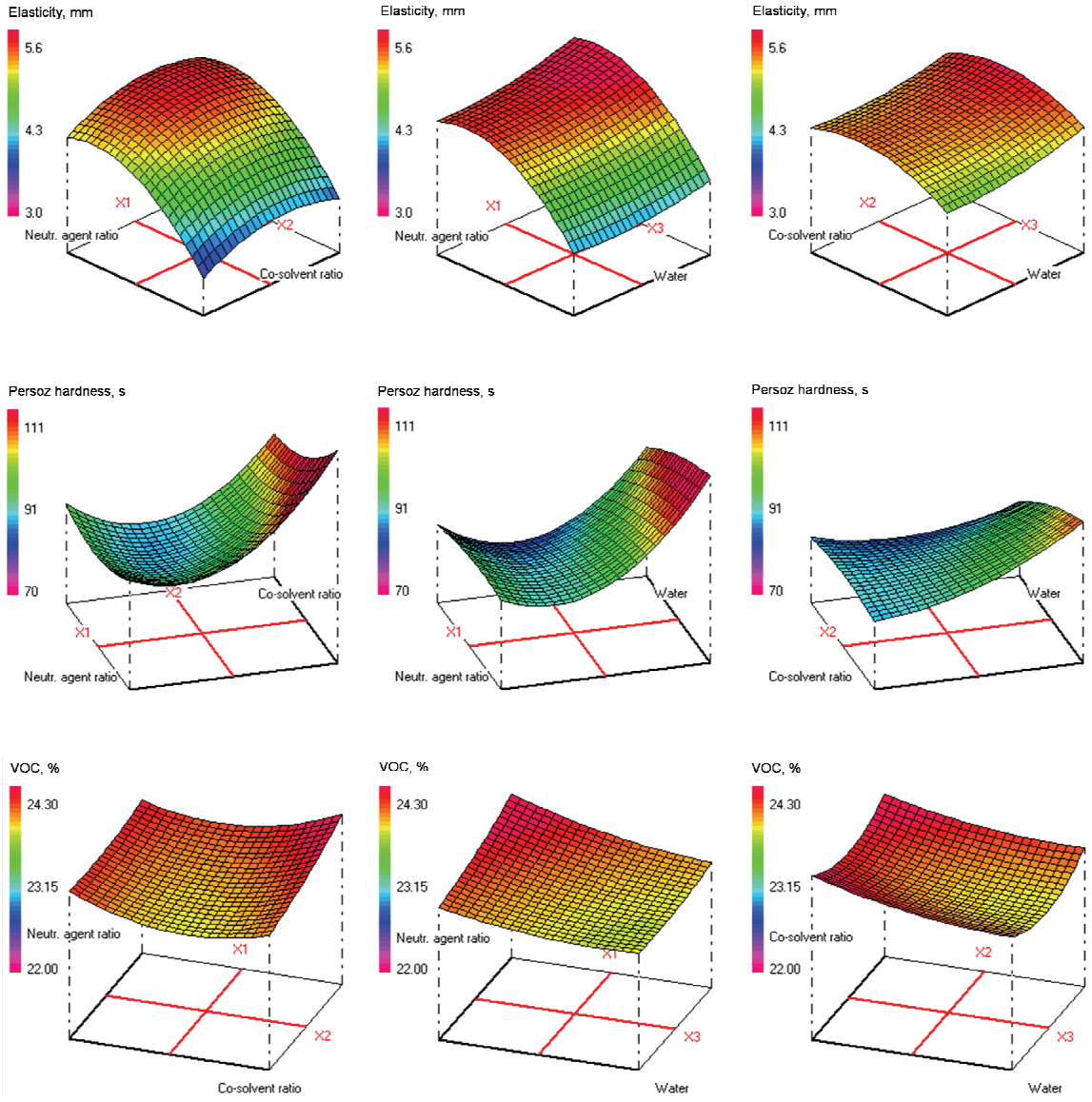

Fig. 2. 3D response surface plots for the 2nd process of paint formulation optimization

The tests of three replicates formulated with the new developed recipe confirmed the model adequacy. The response functions values were: 5.0 ± 0.1% mm for paint elasticity, 91 s for its hardness and 23.8% for VOCs emission. Considering all the presented results and after different other experimental studies (data not shown) we report bellow, as example, a possible final composition of a white (Table 12) and a colored (Table 13) waterborne paints. All the products developed in this research were submitted to different analyses (Table 14). The obtained data for both recipes and products characteristics are consistent with those mentioned in literature (Müller and Poth, 2006).

Along to the paint formulations presented above, this study included also the development of different primers, intermediate paints and enamels. They were based on the use of the same water soluble alkydic resin as for paint systems. The resin neutralization was attained with the same neutralization agent (mixture of NH_3 25% in water and Et_3N in 1/1.8 ratio).

For primers, the ratio between binder and pigment with filling materials varied between 1/2 and 1/2.6. They were characterized by a matted aspect, a viscosity of 152 - 187 s (ISO 2431 - cup 5/20 °C) and a fineness of 40 μm. In terms of drying time, the primers required a period of 50 min when the method called "at dust" was used and of 21 h when type C drying method was employed.

The elasticity registered at 7 days from the application on support was of ≈ 5.3 mm. The recorded hardness after 24 h, 3 and 7 days was of ≈ 45 s, ≈ 91 s and ≈ 105 s respectively. The primers content of VOCs was between 8 and 10%.

In the case of intermediate paints, the resin neutralization process was conducted until the products dispersion fineness attained 30 - 35 μm. The realized analyses revealed a semi glossy aspect; a viscosity (ISO 2431 - cup 4/20 °C) between 172 and 223 s; a drying time of 60 min "at dust" and of 24 h type C; an elasticity between 5.5 and 6.5 mm; and a hardness between 39 and 49 s after 24 h and between 70 and 80 s at 7 days. The resistance to water immersion test showed a matted aspect. The intermediate paints VOCs were between 11.9 and 13%. For enamels the desired dispersion fineness was of 20 to 25 μm. When they were submitted to quality analysis the following results were obtained: glossy aspect; viscosity (ISO 2431 - cup 4/20 °C): 135 - 176 s; drying time: 60 min "at dust" and 24 h type C; elasticity: 6.4 - 6.7 mm; hardness: 80 - 85 s (at 7 days); matted aspect after 24 h of water immersion and unchanged after 24 h of mineral oil immersion.

Table 11. Optimized process variables and related response functions values

Maximum coordinates							
Variable	***Coded value***			***Factor***	***Real value***		
	1st	***2nd***	***3rd***		***1st***	***2nd***	***3rd***
X_1	1.202349	-0.514089	-0.407585	Neutralization agent ratio	0.69	0.42	0.43
X_2	-0.785468	0.316674	0.505326	Co-solvent ratio	0.3	0.4	0.5
X_3	-0.256345	0.316809	-0.295560	Water	26	28	26
Maximum characteristics							
Response function				***Value***			
				1st	***2nd***	***3rd***	
$_1Y$	Elasticity, mm			5.3	5.1	5.1	
$_2Y$	Hardness at 7 days, s			91	91	91	
$_3Y$	VOC, %			24.07	23.76	23.85	
Desirability, %				100.00	100.00	100.00	

Table 12. White waterborne paint

Ingredients	***Required amounts for 100 g of final product***
Pigment dispersion phase	
Water thinnable alkyd resin	19.88
Neutralization agent, NH_3 (25% in water)/Et_3N = 1/1.8	0.22
Butanol	5.95
Butyl glycol	2.13
Titanium dioxide, rutile type	24.80
Cobalt dryer (Co 6% in solvent system)	0.13
Zinc dryer (Zn 10% in solvent system)	0.13
Talc	1.20
Deionized water	7.56
Completion phase	
Water thinnable alkyd resin	18.35
Neutralization agent, NH_3 (25% in water)/Et_3N = 1/1.8	0.20
Deionized water	19.44
64.50% solids, 27% water , 155.14 g/L VOC, density 1848 ± 20 kg/m^3	

Table 13. Red waterborne paint

Ingredients	***Required amounts for 100 g of final product***
Pigment dispersion phase	
Water thinnable alkyd resin	19.87
Neutralization agent, NH_3 (25% in water)/Et_3N = 1/1.8	0.22
Butanol	5.95
Butyl glycol	2.13
Red iron oxide	10.00
Molybdenum orange	7.50
Manganese dryer (Mn 5% in solvent system)	0.13
Zinc dryer (Zn 10% in solvent system)	0.13
Extender, $CaCO_3$	5.50
Talc	3.04
Deionized water	7.55
Completion phase	
Water thinnable alkyd resin	18.34
Neutralization agent, NH_3 (25% in water)/Et_3N = 1/1.8	0.20
Deionized water	19.41
64.50% solids, 27% water, 164.52 g/L VOC, density 1960 ± 20 kg/m^3	

Table 14. Water-borne white and red paints characteristics

Characteristics	***White topcoat***	***Red topcoat***
Liquid product		
Appearance	viscous homogenous liquid	
Viscosity, s	190	197
Fineness of dispersion, μm	30-35	
Film product		
Appearance	semi-glossy	
Drying time at 20 °C - at dust, min. - type C, h	 60 24	 60 24
Elasticity at 7 days	6	6
Adhesion at 7 days (1 mm grid)	good	
Persoz hardness, s - after 24 h - after 7 days	 35 69	 45 72
Resistance to water immersion, 24 h	slightly matted	
Resistance to mineral oil immersion, 24 h	no modification	

The VOCs of enamels was of 14.9 - 18.25%. All the experiments carried out in this study permitted us to conclude that the followed experimental program was able to establish the adequate ingredients proportions in order to obtain products characterized by an appropriate quality which can be successfully employed for metal or wood coverage.

4. Conclusions

Waterborne paints represents an attractive alternative to those based on organic solvents especially due to the fact that the last ones require expensive ingredients and are responsible for realizing important amounts of VOCs known as affecting the environment and the human health. Even though at the beginning the waterborne paints were classified as not being suitable for all types of supports because of the possible corrosion phenomena, the research conducted to improved formulas able to insure low VOCs emission while maintaining and even improving their properties (general aspect, rheological characteristics, drying time, resistance at physical, chemical and microbiological actions etc.).

In this paper we successfully developed a waterborne paint formulation process. A water soluble alkydic resin was used to this purpose. Its neutralization percentage, the type and amount of the neutralization agents, co-solvents and water known as parameters affecting some of the main paint characteristics such as viscosity, elasticity, hardness, VOCs emission etc. were chosen as independent variables and optimized in two different steps by RSM. According to the obtained results, it is recommended to neutralize 70 to 80% of the carboxylic groups existing in the employed resin.

A mixture of NH_3 (aqueous solution 25% w/w) and Et_3N in 1/1.8 ratio (1.10 g neutralized agent/100 g resin) can be used to accomplish this objective. Once neutralized, the resin must be solubilized in co-solvents (21% BG and BuOH mix in a ratio of 1 to 2.8) and water (27% reported at the alkyd resin amount) and mixed with siccatives, pigments and other necessary additives (extenders,

wetting agents, anti-settling agents, rust inhibitors, flattening agents etc.). The statistical analysis of the mathematical models obtained for the followed response functions revealed a high similarity between the data acquired experimentally and those predicted by the registered equations. In the established conditions, paint elasticity was of 5.0 mm and its hardness reached 91 s. In terms of VOCs emission, a value of 23.8% was recorded.

Several different paint formulations white or colored along to various primers, intermediate paints and enamels were also developed in the present research work. The analysis of their specific characteristics indicated that the studied parameters and the established experimental program were able to determine the appropriate ingredients types and amounts required for obtaining high quality products useful for metal or wood coverage.

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