



Synthesis and Surface Modification of Pigment Red 3 by Sulfonation Method for Improving Properties in Waterborne Ink

M. Rostami^{*1}, A. Khosravi², M. M. Attar²

¹ Department of Nano Materials and Coatings, Institute for Color Science Technology. P.O. Box 16765-654, Tehran-Iran

² Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, P.O. Box: 15875-4413, Tehran, Iran

ARTICLE INFO

Article history:

Received: 26 July 2016

Final Revised: 20 Dec 2016

Accepted: 2 Jan 2017

Available online: 17 Jan 2017

Keywords:

Pigment Red 3

Surface treatment

Sulfonation

Water born flexographic inks

ABSTRACT

Pigment Red 3 was synthesized and chemically treated by sulfonation. The treatment, affected the surface chemistry and the shape of pigments. The effects of reaction time, temperature, solvent/pigment ratio and acid/pigment ratio were examined on the treated pigment. The investigation of experimental design was carried out based on Taguchi method. UV-Visible spectroscopy, densitometry, turbidimetry, pH and Scanning Electron Microscopy were used to assess the treated particles. The effects of surface modification on properties of water born flexographic ink were studied using dispersion rate, gloss, chroma, hue, lightness and K/S of ink coating. Optimum samples were selected according to the results of the analyses as well as the Variance Analysis and by considering the effect of each independent parameter. Prog. Color Colorants Coat. 10 (2017), 51-65 © Institute for Color Science and Technology.

1. Introduction

Since pigment manufacturers should produce pigments which possess acceptable wettability in different media, surface treatment of organic and inorganic pigments has become one of the most important goals. The shape and surface chemistry of synthesized pigments should be modified before applying in the final product. The final properties of the pigments are not only dependant on their chemical structure but also on factors such as particle shape, particle size, type of crystal and surface chemistry of pigment particles. For example, final properties like tinting strength, opacity and transparency depend on the type of crystal [1-3]. Methods such as resination [4], treating with surfactants [5, 6], acid- base (alkali) treatment [7], solvent treatment [8], treatment with pigment derivative [9], inorganic materials [10], gases [11], silane coupling agent [12, 13], polymers [14-16] and

finally, treatment with sulfonating agents [17, 18] are applied in order to produce surface treated pigment particles. It should be noted that the final application and also the pigment structure will decide what method should be carried out. Organic pigments have low surface energy and their wettability in polar media is low. With sulfonating method, the surface energy of the pigments increases. On the other hand, the surface treated organic pigment with sulfonating agent has excellent dispersibility and long-term dispersion stability in water and organic polar solvent. In sulfonating method, reaction of a sulfonating agent with a dispersed organic pigment occurred in a solvent in which the organic pigment is insoluble or sparingly soluble, and thereby it results in the introduction of a sulfonic group to the surface of each particle of organic pigment [19].

After surface modification of pigments, this work

*Corresponding author: rostami-m@icrc.ac.ir

aims to surface modification of pigment Red 3 by different sulfonating agents. Analytical techniques including UV-Visible spectroscopy, densitometry, turbidimetry, pH value and Scanning Electron Microscope were performed. Dispersion rate, fineness, gloss, K/S, chroma, hue, lightness and tinting strength are measured to evaluate the effects of the surface modification of Pigment red-3 on properties of the ink coating.

2. Experimental

2.1. Materials

Nitro benzene and sulfuric acid were provided from Merck. In this study, surface modification of the toluidine red 3 was done by sulfonating agent in order to enhance its compatibility with water based flexographic inks. Toluidine red 3 with the chemical structure given in Figure 1 was synthesis. Water based flexographic inks were prepared using acrylic resins (R94, R95) from Neo Resin and a Dispersing agent BYK184, anti-foam BYK023 from BYK Co.

2.2. Synthesis of Pigment Red 3

At first, Pigment Red 3 was synthesized as follows. 16.5 g amine (Meta nitro para toluidine prepared from Merck Co.) and 60.25 g hydrochloric acid (5N) were mixed. Then the mixture was charged into the reactor. The temperature of the reactor was kept between -2 to

5 °C. Then the NaNO₃ olution was gradually (16 mL/min) added to the reactor. After the reaction was completed, the final product of the reaction was filtered. The diazotization yield was at 98%, and then the diazotization solution was gradually (2 mL/min) added to the β-naphthol solution (20 g β-naphthol dissolve in 643 mL distilled water with 4.43 g NaOH). After the completion of the reaction, the temperature of the reactor was 37 °C. The product was filtered and then washed using hot distilled water. The reaction yield was 94.7%. The efficiency was calculated according to Eq. 1. The structure of Pigment Red 3 is shown in Figure 1.

$$\text{Coupling efficiency} = \frac{\text{Weight of final pigment}}{\text{Theoretical weigh of pigment}} \times \text{Diazotization Output} \quad (1)$$

2.3. Treatment of Pigment Red 3

2.3.1. Method of treatment

In this process, four independent factors were selected, including temperature, time, solvent/pigment ratio and acid/pigment ratio. For each independent factor, four levels were considered. Based on Taguchi method, for 4 levels and 4 factors, 16 arrays are investigated (L 16). It should be noted that if we didn't use Taguchi method, we had to do 256 (44) experiments. The values corresponding to the independent factors and their levels are shown in Table 1.

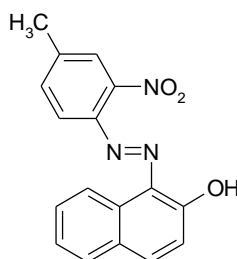


Figure 1: The chemical Structure of Pigment Red 3.

Table 1: Independent Factors.

Independent Factors		1	2	3	4
Solvent/Pigment	A	25	50	100	150
Acid / Pigment	B	0.5	1	1.5	2
Time (hr)	C	1	2	3	4
Temperature (C)	D	20	40	60	80

In Table 2, the first column corresponds to the number of treatments. The values of independent factors of each treatment reaction are selected. For example, in Treatment No 9, the parameter A corresponds to solvent/pigment ratio, which its value corresponds to the third column of Table 1 which is equal to 100. The parameter B corresponds to acid/pigment ratio, which its value corresponds to the first column of Table 1 which is equal to 0.5. The parameter C corresponds to reaction time, which corresponds to the third column of Table 1 which is equal to 3 and parameter D is the temperature of reaction which corresponds to the fourth column of Table 1 which is equal to 80 °C.

Independent parameters for each treatment are selected according to Table 2. The nitrobenzene was poured into the reactor as a solvent and then Pigment Red 3 was added to it. The homogenizer was adjusted to 13000 rpm in order to disperse the pigment, and the

temperature was adjusted to the corresponding temperature. When the homogenizer was at 16000 rpm, sulfonating agent was added to the reactor. When the reaction time was completed, the slurry was poured in water and filtered. The treated pigment was characterized, using UV-Visible spectroscope, scanning electron microscope, densitometer, and turbidimeter and pH value.

2.4. Preparation of flexographic ink

Different weight loadings (1, 2 and 3 wt.%) of modified and unmodified nanoparticles were dispersed in acrylic polyol resin using zirconia pearls (Spherical Beads). Then, isocyanate was added to the dispersions prepared at weight ratio of 1:4 (isocyanate: acrylic). The nanocomposites prepared were applied on the clean glass sheets using film applicator. Finally, coatings were cured at 70 °C for 4 h. The dry thickness of the coating was 45±5 µm.

Table 2: 16 arrays for independent Factors.

Treatment. No	D	C	B	A
1	1	1	1	1
2	2	2	2	1
3	3	3	3	1
4	4	4	4	1
5	3	2	2	2
6	4	1	2	2
7	1	4	3	2
8	2	3	4	2
9	4	3	1	2
10	3	4	2	3
11	2	1	3	3
12	1	2	4	3
13	2	4	1	4
14	1	3	2	4
15	4	2	3	4
16	3	1	4	4

2.5. Characterization

2.5.1. Characterization of sulfonating agent on the surface of Pigment Red 3

2.5.1.1. UV-Visible spectroscopy

The maximum wavelengths of all specimens were studied by UV visible spectrophotometer (ENGLAND CICECIL 9200). 0.001 g of each specimen was dissolved in chloroform and then the maximum wavelength of specimens was measured. The values of

maximum wavelength of pigments are illustrated in Figure 2.

2.5.1.2. Scanning electron microscopy (SEM)

The morphology of treated and untreated pigments was examined by SEM (LEO 14551 VP). The pigments were applied on a specific surface (Copper grid), and then the surface of particles was covered with platinum. The photos of treated and untreated pigments are represented in Figure 3.

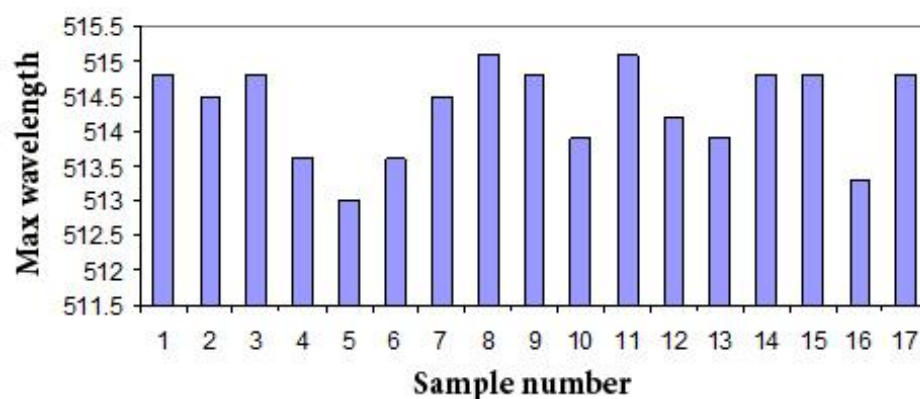


Figure 2: Maximum wavelength (nm) of particles.

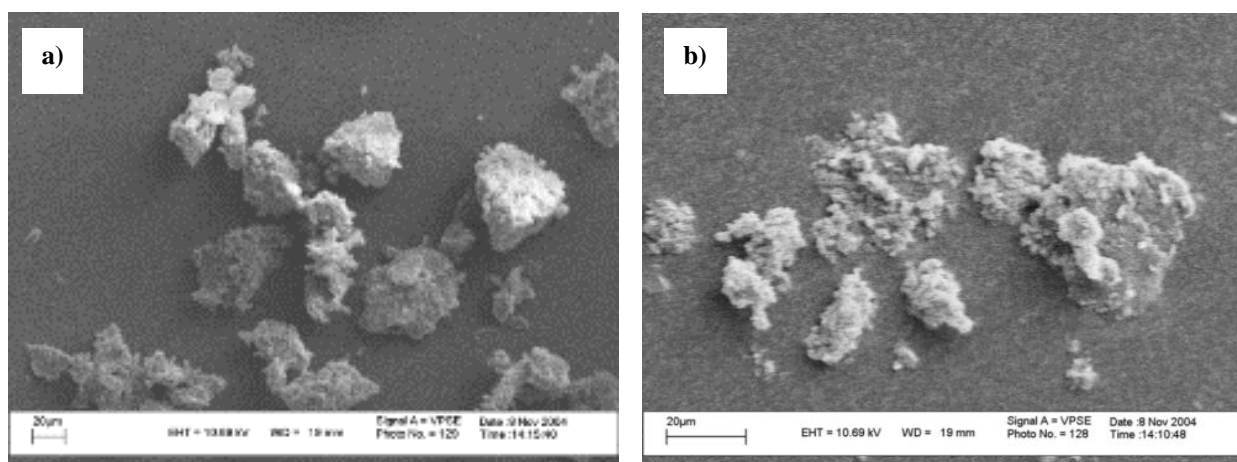


Figure 3: SEM images of the treated pigments No 1 to 16 (a-q) and r) the untreated sample.

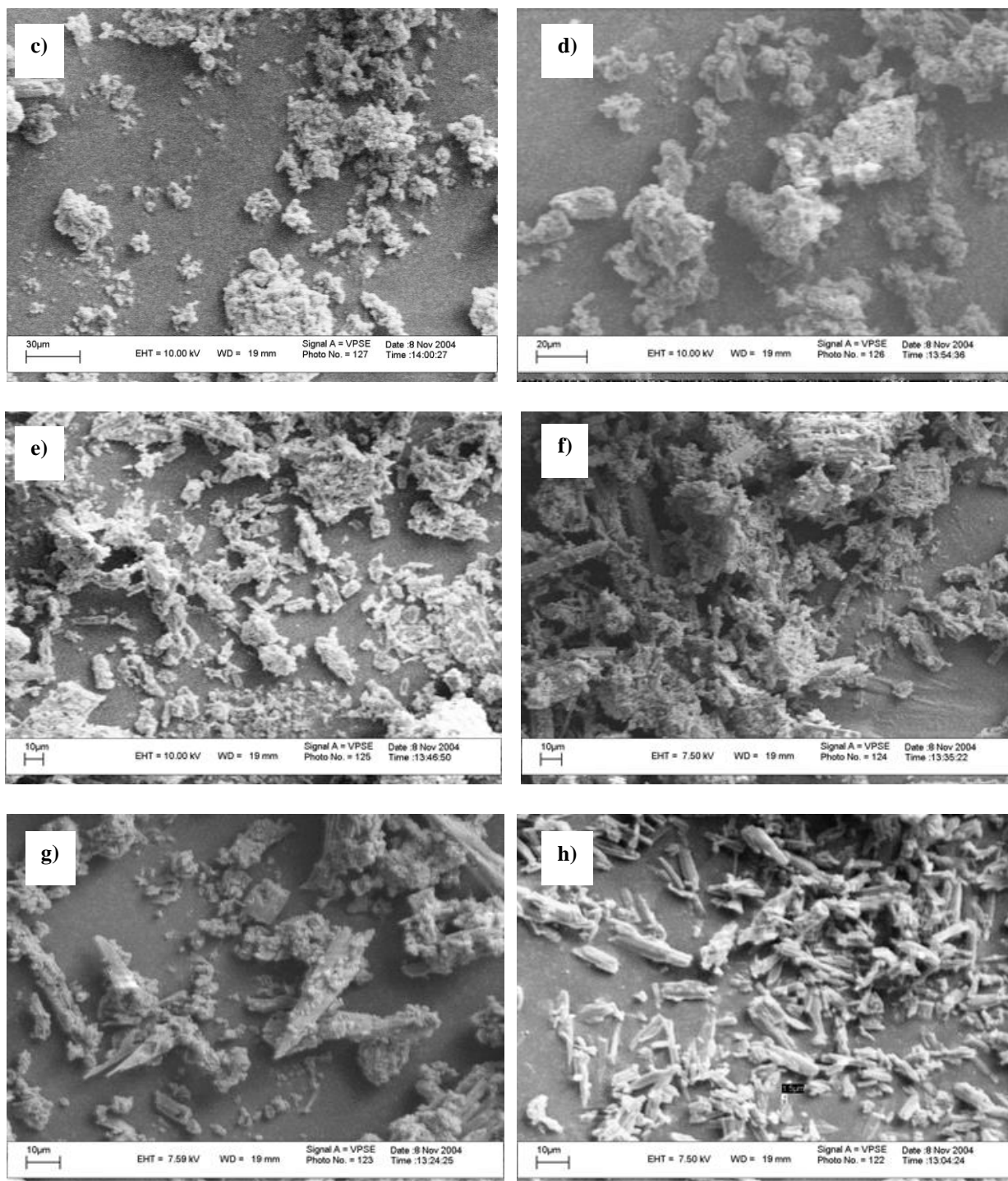


Figure 3: Continue.

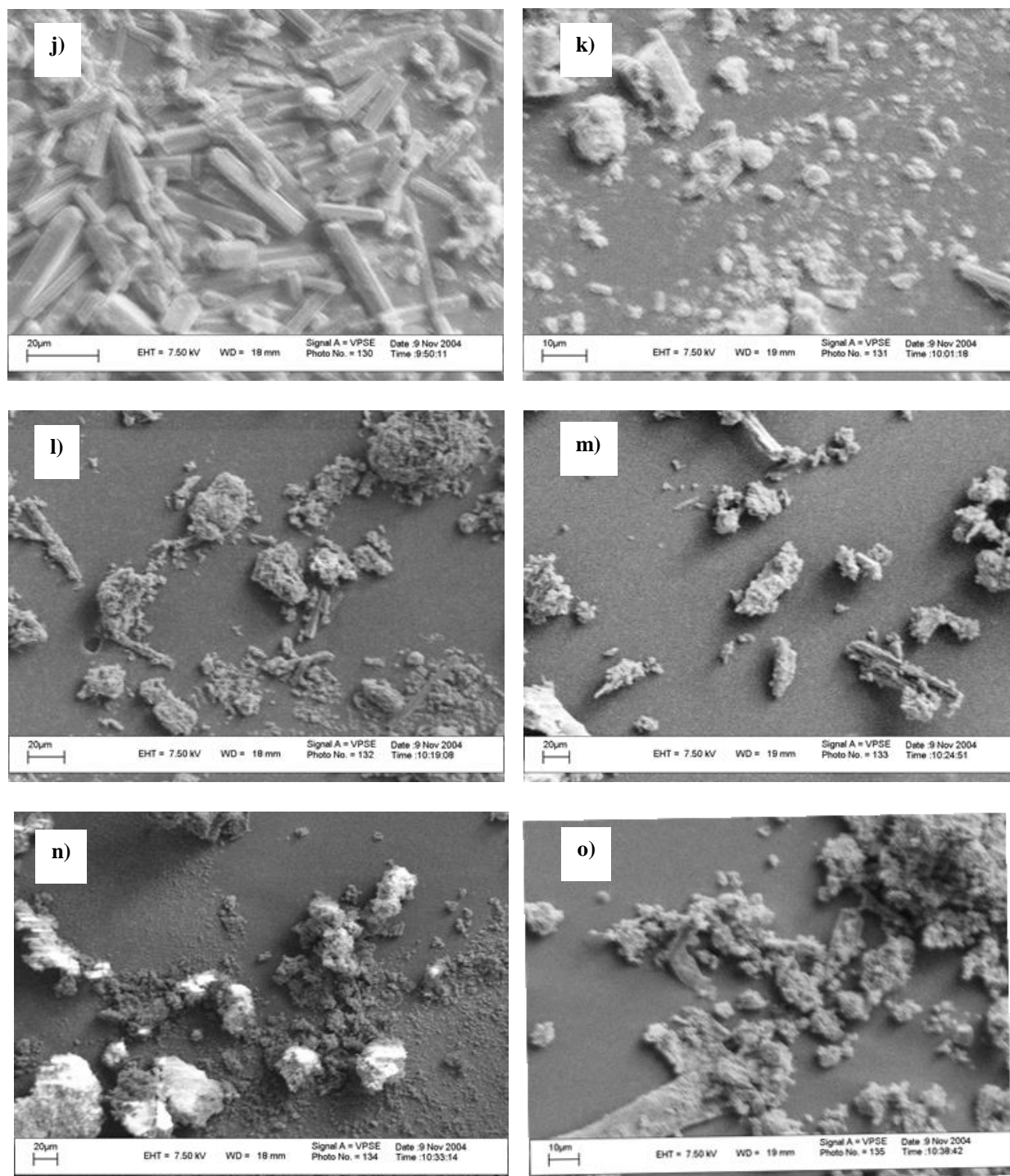


Figure 3: Continue.

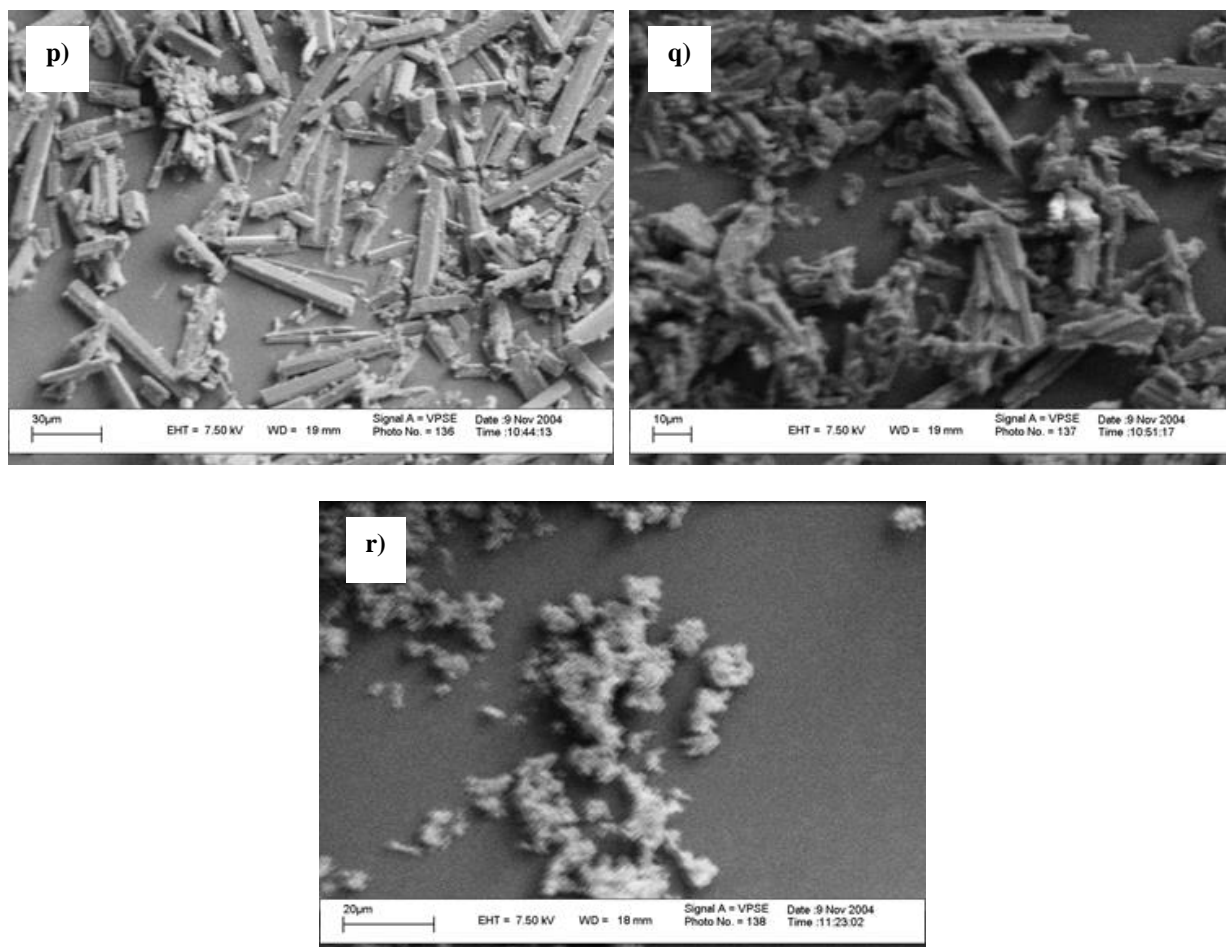


Figure 3: Continue.

2.5.1.3. Measurement of density

Densities of particles were measured using helium pycnometer (USA Micrometric Accutec 1330). The powders (0.5 g) were poured in the cylindrical vessel, and then the helium gas was injected until the porosities between particles were filled. Then the densities of particles were measured with pycnometer. Densities of pigments are presented in Figure 4.

2.5.1.4. pH measurement

The pH values of particles were evaluated by digital HACH pH meter according to ISO-787. The pH values of treated and untreated pigments are illustrated in Figure 5.

2.5.1.5. Turbidity

In order to quantify particles' dispersion in different media, turbidimeter (HACH 2100AN) was used. Turbidity of particles depends on particle size, particle shape and concentration of particles in area unit. 0.002 g of each specimen was dispersed in four solvents with various polarities. Turbidity of each particle is investigated during 2 hours. The solvents for measuring turbidity were selected according to Hansen solubility parameter [19] with components possessing different polarities. The solvents are isopropanol ($\delta_p = 6.1$), ethanol ($\delta_p = 8.1$), methanol ($\delta_p = 12.3$) and the mixture of water and ethylglycol ($\delta_p = 13.1$). The rates of turbidity decrease for 2 hours are demonstrated in Table 3.

2.5.2. Water born flexographic ink characterization

2.5.2.1. Dispersion rate

To study wettability and interaction of treated particles with water based resin, the rate of fineness of pigments were studied for ten hours. The dispersion rate is shown in Table 4. Also the effect of pH on the dispersion rate is shown in Figure 6.

2.5.2.2. Gloss

The gloss of films was measured according to ASTM D523. The coatings were applied on polyethylene sheet

with dry film thickness of 8 micron. After curing, the gloss of coatings was measured with (BYK GARDNER-MICRO-TRI-GLOOS). The gloss of films is shown in Table 5. The effect of pH on gloss is shown in Figure 7. Also, the effect of dispersion rate on gloss is shown in Figure 8.

2.5.2.3. Lightness, Chroma, Hue (H, C, L)

Spectrophotometer (Gretaymacbeth coloreye 7000A) was used to measure the Lightness (L), Chroma (C), Hue (H) and K/S of the coating. The results are shown in Figure 9 a to c and Table 6.

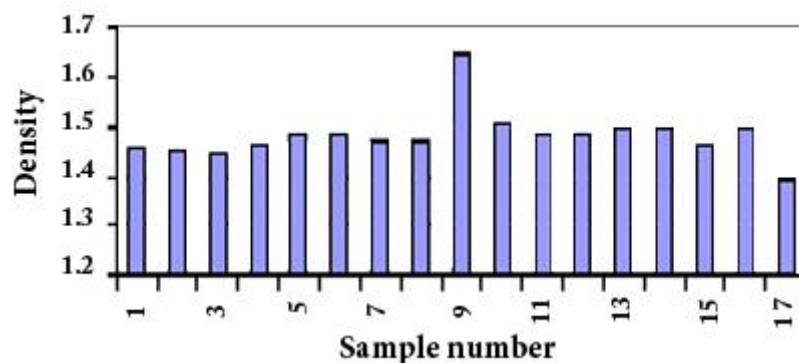


Figure 4: Density of pigments.

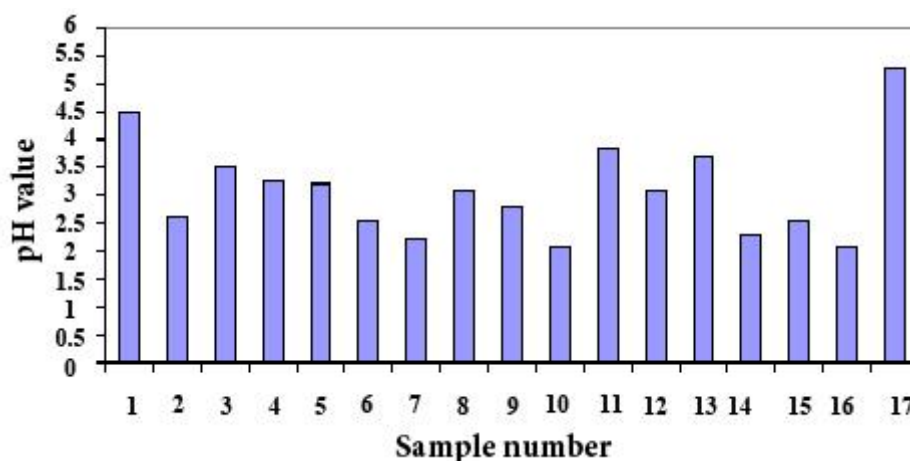


Figure 5: pH values of pigments.

Table 3: The slope of decreased turbidity in different solvents.

Sample	H ₂ O/Ethyl glycol	Ethanol	Methanol	ISO propanol
1	0/5282	0.4346	0.0619	0.4115
2	0.5595	0.1222	0.9217	0.9942
3	0.1384	0.408	0.688	0.1098
4	0.126	0.065	0.0738	0.0833
5	0.0854	0.1515	0.2254	0.3442
6	0.336	0.0758	0.2188	0.844
7	0.1326	0.1334	0.219	0.1771
8	0.0711	0.0723	0.211	0.3314
9	0.1316	0.0603	0.0788	0.6136
10	0.8319	0.0814	0.085	0.1779
11	0.3029	0.2671	0.602	0.2335
12	0.1722	0.0727	0.1315	0.1782
13	0.1561	0.0836	0.1345	0.1763
14	0.1092	0.0722	0.1176	0.147
15	0.1105	0.0587	0.0693	0.4813
16	0.3012	0.0618	0.0833	0.2049
17	0.389	0.4346	0.1841	0.4558

Table 4: Dispersion rate of inks.

Sample	Fineness (μm)	Rate of dispersion (Δμ/2hr)
1	14	0.7283
2	12	0.4822
3	6	0.8075
4	5	0.8611
5	4	0.0793
6	5	0.9971
7	6	0.2162
8	8	0.764
9	5	0.9068
10	8	0.603
11	9	0.8391
12	6	0.9248
13	5	0.8998
14	10	0.5818
15	4	0.0135
16	15	0.602
17	16	0.999

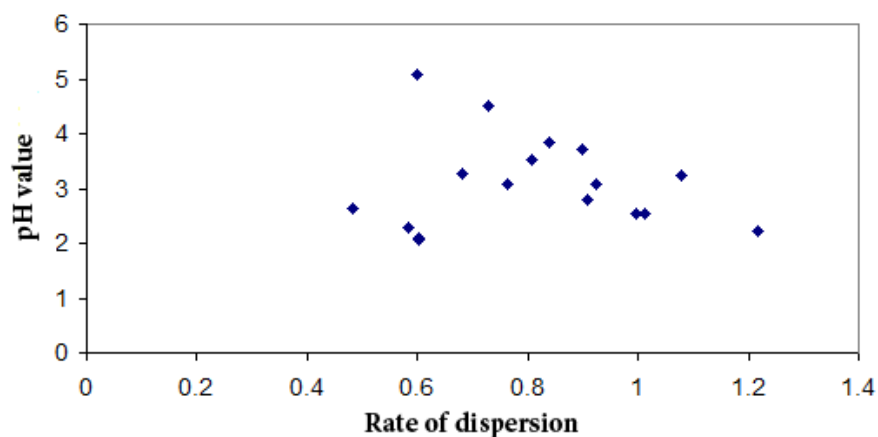


Figure 6: The effect of pH on the dispersion rate.

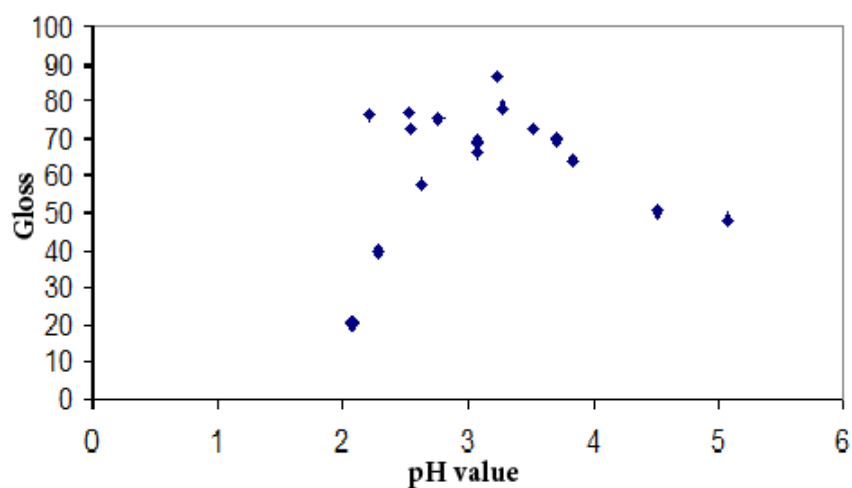


Figure 7: The effect of pH on gloss of coatings.

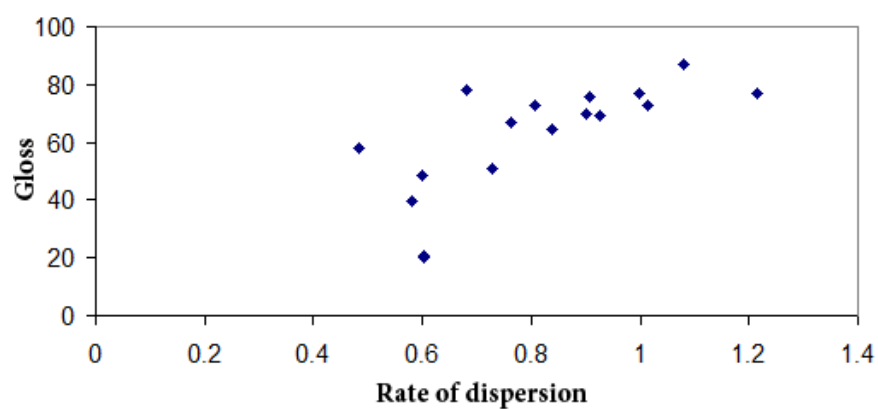


Figure 8: The effect of dispersion Rate on gloss of coatings.

Table5: The gloss films.

Sample	Gloss
1	50.8
2	58.2
3	73
4	78.2
5	86.9
6	77.2
7	76.8
8	66.7
9	75.8
10	68
11	64.3
12	69.4
13	70
14	39.8
15	73.6
16	20.2
17	48.3

Table 6: The K/S of films.

Sample	Tinting Strength (K/S)
1	0.9757
2	0.8942
3	0.9457
4	0.9977
5	1.0056
6	0.9918
7	1.0001
8	0.9861
9	0.978
10	0.9886
11	0.9699
12	1.0069
13	0.9827
14	0.9797
15	1
16	0.0034
17	-

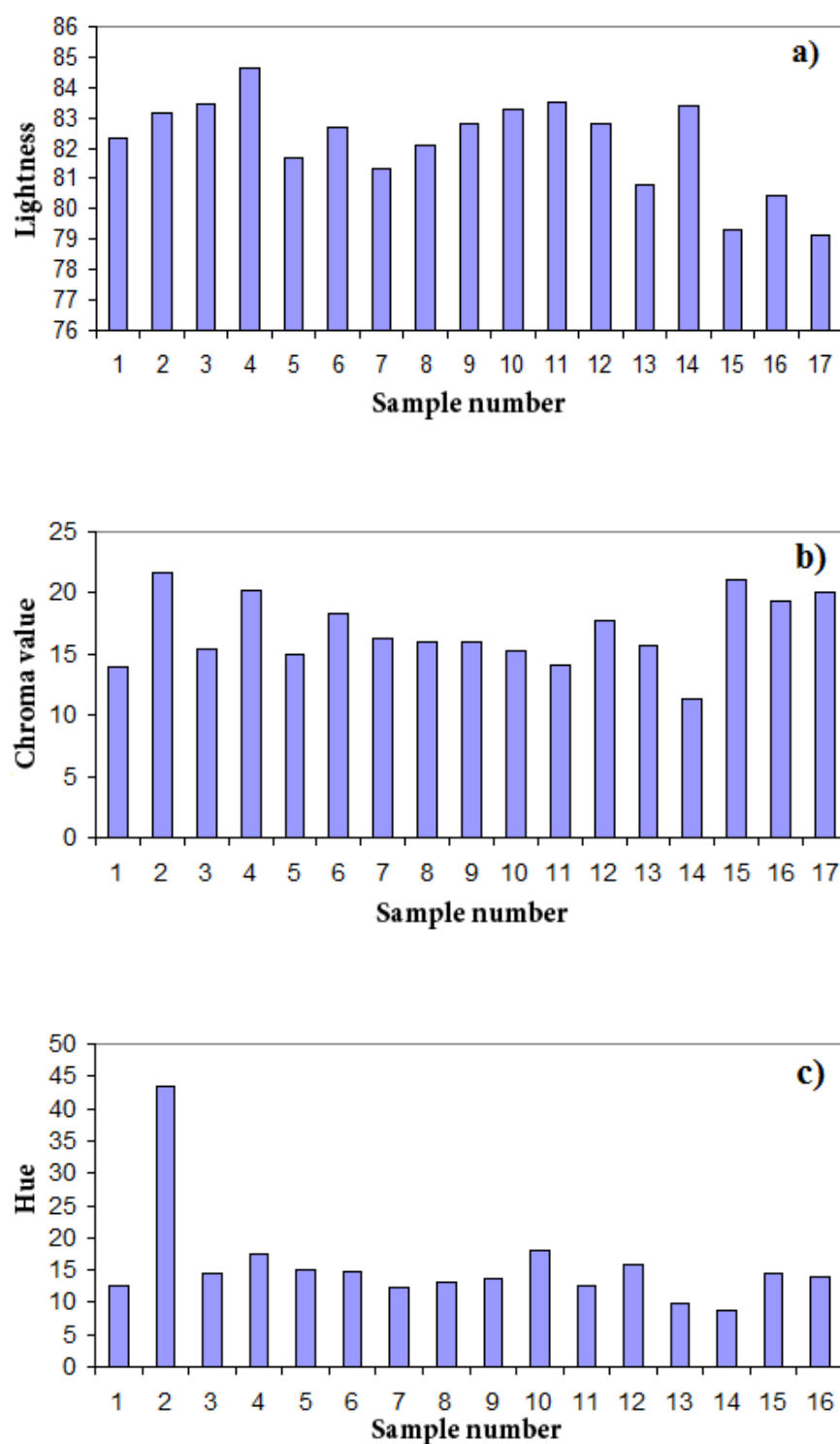


Figure 9: a) The Lightness of coatings, b) the chroma of coatings and c) the hue of coatings.

3. Results and discussion

The aim of this study was to investigate the effect of surface treatment of Pigment Red 3 with sulfonating agent on surface chemistry of particles. In order to evaluate the amount of sulfonation, maximum wavelengths of treated and untreated pigments were measured. The values of maximum wavelengths are shown in Figure 2. There is not any difference between the wavelengths of treated and untreated pigments according to Figure 2. Thus, it should be concluded that substantially there is no sulfonic acid group inside each particle but sulfonic acid groups only exist on their surface. If the particle is sulfonated molecularly, the hypsochromic shift observed in the maximum wavelength of the treated pigment. The values of maximum wavelengths are approximately between 513 to 515.2 nm which are demonstrated in Figure 2.

Scanning Electron Microscopy of the treated pigments (sample No 1 to 16) and untreated pigment (sample No 17) are shown in Figure 3. There is no significant change in the shape of samples No 1, 2, 3, 4, 10, 11, 13 and 14 in comparison to the untreated pigment. Therefore, it can be concluded that these treatment conditions have a rather small effect on the morphology and shape of the particles. The shape of samples No 8, 9 and 15 are different from other samples. The samples were in the form of rod and needle. The shape of Sample No 15 in comparison to samples No 8 and 9 is completely different. The shape of the pigment particles affects some coating properties such as yield strength, dispersion, opacity, tinting strength and film penetration. For example, in mineral pigments and fillers, particles with rod and needle shape increase the strength of coatings. Pigments and fillers with the shape of rod and needle increase roughness of the primer surface coating and hence the adhesion of the second layer on the primer layer.

The density of particles is measured with Helium pycnometer. The density and pH of samples are depicted in Figure 4 and 5. The increased density of treated pigments is related to the increase of the mass (because of introducing sulfonating agent on each particle) and decrease of particles' volume.

The pH values of treated pigments in comparison to the untreated pigment (sample No 17) were increased. It can be concluded that the acidity of treated pigments, under the effect of sulfonating agents, was increased. The acidic pigments in alkaline polar media have negative surface charges and these charges on the

particle surface can stabilize particle dispersion in polar media.

The covalent bond between carbon and sulfur was formed when sulfonating agent was introduced on the surface of each particle. Also due to the longer distance of the bonds of C-S than C-H, the size of pigment crystals was increased. On the other hand, in high acidic pH values, the numbers of C-S bonds were higher, which also resulted in an increase in the volume of pigment crystals. Both factors i.e. increase in mass which is the effect of introducing sulfonating agent on the surface of particles (direct effect), and increase in the volume of particles which is the effect of sulfonating group (indirect effect), affect the density of treated particles. For example, sample No 9 is more acidic than sample No 16 according to the curves no. 1 and 2, but the density of sample No 9 is more than No 16. Therefore, in the sample with high acidic properties, the effect of volume increasing is more than that of mass increasing. Because of the existence of sulfonating agents on the pigment surface, the densities of those samples are lower than samples with higher pH value.

In order to study the dispersibility of treated pigments in polar media and to select optimum sample, turbidity of treated and untreated pigments in solvents with different polarity was investigated. Solvents with different polarity (σ_p) are selected, and the dispersion stability of pigments in these solvents is studied with NTU (Nephelometric Turbidity Units) method. The curves of turbidity decrease versus time are nonlinear, and the slope of curves is different. For this reason, the slope of logarithmic curve of each sample was calculated. The rate of decreased turbidity or the slope of logarithmic curves of each sample in the solvents is shown in Table 3.

The surface chemistry of particles could be investigated by assessment of dispersion stability of particles in various solvents according to Hanssen recommendation [20, 21]. On the other hand, if the cohesive parameters (σ_p , σ_d , σ_H) of particles are the same as the cohesive parameters of solvent, the particles have stable dispersion in that solvent. To study the surface properties of treated particles, 0.05 g of pigments are dispersed in solvents with different σ_p , and the rate of precipitation was investigated. The rate of precipitation is quantified with the turbidimeter instrument. Turbidity of dispersions depends on particle shape, size, the number of particles per volume

unit and the amount of particles interaction with solvent. The rate at which turbidity decreases is related to the rate of settlement of powders. If the rate of NTU decreases, the powder will have good interaction with solvent and has stable dispersion in the media. Untreated pigment (sample No 17) has a lower slope in ethanol which can be seen in Table 3. Thus, it can be said that the surface chemistry of untreated pigment is compatible with a media where $\sigma_p = 8.1$. In other words, the surface energy of the untreated pigment is the same as the cohesive parameter of solvents with ($\sigma_p = 8.1$). About the rate of turbidity decrease of samples No 1 and 11, it could be said that, they have the lowest slope in ethanol. The slope of sample No 11 is lower than sample No 1. Considering the evaluation of the rate of turbidity decrease of the other samples in ethanol, it could be said that sample No 11 has the lowest rate of turbidity decrease in ethanol. Thus the surface chemistry of sample No 11 has good interaction in a media where $\sigma_p = 8.1$ and has stable dispersion in that media. The slope of samples No 5 and 8 in the mixture of H_2O and ethyl glycol was the lowest. Slope or rate of turbidity decrease of all samples in the mixture of H_2O and ethyl glycol is the lowest. Thus, the surface properties of these samples are compatible in a media where $\sigma_p = 13.1$ and have stable dispersion in that media. The dispersion stability of sample No 8 is more than sample No 5, because the slope of sample No 8 is lower than sample No 5. Samples 2, 3, 4, 6, 7, 9, 10, 11, 13, 14, 15 and 16 have the lowest rate of turbidity decrease in methanol. To assess the rate of turbidity decrease of these samples in methanol, it could be said that the samples No 4, 9 and 15 have the lowest slope. Thus the surface properties of these samples are compatible in a media where $\sigma_p = 12.3$ and they have good interaction and stable dispersion in that media.

The effect of independent parameters on pigment properties is studied using Analysis of Variance (ANOVA). The effects of independent factors on each property are as follows:

Evaluation of the independent factors which affect the turbidity in isopropanol, ethanol, methanol and the mixture of water and ethyl glycol is dependent on mean square of each independent factor, these results are obtained as follows:

a. The independent factors which affect the turbidity of samples in isopropanol were temperature, time, solvent/pigment ratio and acid/pigment ratio,

respectively.

b. The independent factors which affect the turbidity of samples in ethanol were solvent/pigment ratio, time, temperature and acid/pigment ratio, respectively.

c. The independent factors which affect the turbidity of samples in methanol were time, solvent/pigment ratio, temperature and acid/pigment ratio, respectively.

d. The independent factors which affect the turbidity of samples in the mixture of water and ethyl glycol were temperature, solvent/pigment ratio, acid/pigment ratio and time, respectively.

In relation to mean square values of independent factors, the independent factors which affect the density were solvent/pigment ratio, acid/pigment ratio, time and temperature, respectively. Corresponding to the mean square values of independent factors, the independent factors which affect the pH values were solvent/pigment ratio, acid/pigment ratio, temperature and time, respectively.

Corresponding to the obtained results for particles' shape, particles' density, pH values and particles' turbidity, it could be said that samples No 5 and 8 are suitable for a media where $\sigma_p = 13.1$, because they have good dispersion stability in that sort of media. The pH values of these samples are 3.229, 3.072, respectively, and the density of these samples are 1.486, 1.474, respectively.

Samples No 4, 9 and 15 have good dispersion stability in media where $\sigma_p = 12.3$. The pH values of these samples are 3.265, 2.779 and 2.553, respectively, and the density of these samples are 1.4654, 1.6437 and 1.4653, respectively.

The results in Figure 6 show that particles with acidic pH have better wettability and dispersion rate. Thus particles with acidic surface chemistry increased the gloss of ink. In other words, particle with pH 2.5-3.5 had better dispersion rate in polar media and provided better gloss in flexographic ink.

4. Conclusion

In this work, the effect of reaction parameters on surface treatment of pigments was studied. The results show that surface chemistry and morphology of all samples were affected by surface treatment reaction. Morphology, pH, density and surface chemistry of samples have changed after treatment. Results show that the surface chemistry of particles becomes acidic

after treatment process. Also the dispersion rate of acidic particles is better than that of other particles in water-based flexographic ink. Good dispersion of particles results in an increase of the gloss and K/S ratio of the inks. Also, the lightness of inks included treated particles is higher than untreated. The chroma and hue of flexographic inks with acidic pH 2.5-3.5 is higher than those of untreated ink. The effects of

independent parameters on each property are carried out with Analysis Of Variance. Results showed that each reaction parameter has significant effects on the final properties of the pigments. Finally, samples No 15 and 9 as optimum samples are selected, because they have hydrophilic properties and the shapes of their particles were modified successfully.

5. References

1. M. Ettlinger, T. Ladwig A. Weise, Surface modified fumed silicas for modern Coatings, *Prog. Org. Coating*, 40(2000), 31-34.
2. Y. Sun, Z. Zhang, C. Wong, Study on mono-dispersed nano-size silica by Surface modification for under fill applications, *J. Colloid Interf. Sci.*, 292(2005), 436-444.
3. M. Rostami, M. Mohseni, Z. Ranjbar, Investigating the effect of pH on the Surface chemistry of an amino silane treated nano silica, *Pigment Resin Technol.*, 40(2011), 363-373.
4. K. Kanou, J. Amano, N. Sakai, Aqueous pigment dispersion, water soluble resin, US Pat No 5913972.Jul.22, 199.
5. J. Bieleman, Additive for Coatings, Wily-VCH., 2000.
6. F. Najafi, B. Shirkavand Hadavand, F. Manouchehr, Synthesis and Characterization of Anionic Polyurethane Dispersants for Waterborne Paints, *Prog. Color Colorants Coat.* 7(2014), 147-154.
7. E. H. Sung, H. Velasquez. Poly phosphoric acid swelling of organic pigment, US PATENT NO 6537362B2, Mar 25, 2003.
8. U. Nickel, K. kund, E. Dietz, J. weber, O. Schupp, Conditioning of organic pigments, US patent No 6562121B2, May.13, 2003.
9. J. Hetzenegger, G. Henning, Pigment Preparation with Perylene Derivatives as Dispersant, US PATENT NO 5472494. Dec 5, 1995.
10. P. Bugnon, Surface Treatment of pigments. Treatment with inorganic materials, *Prog. Org. Coating.*, 29(1996), 39-43.
11. G. Chishom, B. Hag, K. D. M. Harris, Effect of Fluorination on the properties of organic pigments, *Dye. Pigment*, 42(1999), 159-172.
12. M. Alkan, M.G. Tekin, H. Namli, FTIR and zeta potential measurements of sepiolite treated with some organosilanes, *Micropor. Mesopor. Mat.*, 84(2005), 75-83.
13. S. Lee, D. Kim, J. H. sin, Y. S. Lee, J. Ind. Polyurethane/ silica Composites, Prepared Via in-situ Polymerization in the Presence of Chemically Modified Silica's, *Eng. Chem.*, 5(2007), 786-792.
14. N. Tsubokawa, M. Kobayashi, T. Ogasawara, Graft polymerization of vinyl Monomers initiated by azo group introduced on to organic pigment surface, *Prog. Org. Coating.*, 36(1999), 39-44.
15. K. S. Siow, L. Britcher, S. Kumar, H. J. Griesser, Sulfonated Surfaces by Sulfur Dioxide Plasma Surface Treatment of Plasma Polymer Films, *Plasma Process. Polym.*, 6(2009), 583-592.
16. Z. Q. Wen, Y. Q. Feng, X. G. Li, Y. Bai, X. X. Li, J. An, M. Lu, Surface modification of organic pigment particles for microencapsulated electrophoretic displays, *Dye. Pigm.*, 92(2011), 554-562.
17. K. Schröder, Surface treatment of pigments, *Prog. Org. Coating.*, 16(1988), 3-17.
18. F. Babler, Process for preparation of a pigment composition, US Pat No 5843220. Dec.1, 1998.
19. T. Uemura, T. Iguchi, S. Satake, H. Uraki, Y. Idia, Surface Treated Organic Pigment and Process for the Production Thereof, US Pat No 5928419, 1999.
20. C. M. Hansen, Hansen Solubility Parameters, CRC Press © 2007 by Taylor & Francis Group, LLC.

How to cite this article:

M. Rostami, A. Khosravi, M. M. Attar, Synthesis and Surface Modification of Pigment Red 3 by Sulfonation Method for Improving Properties in Waterborne Ink, *Prog. Color Colorants Coat.*, 10 (2017), 51-65.

