Iranian Polymer Journal
**14** (11), 2005, 1000-1007

# Estimation of Critical Pigment Volume Concentration in Latex Paint Systems Using Gas Permeation

Manouchehr Khorassani[*1], Saeed Pourmahdian[**1]
Faramarz Afshar-Taromi[1], and Amir Nourhani[1,2]

(1) Department of Polymer Engineering; (2) Department of Physics and Nuclear Science,
Amir Kabir University of Technology, P.O. Box: 15875/4413, Tehran, I.R. Iran

Received 19 April 2005; accepted: 10 October 2005

## ABSTRACT

Critical pigment volume concentration (CPVC) is a fundamental transition characteristics at which properties of a coating changes significantly. At this point voids begin to introduce through the film. Many methods have been proposed to determine the CPVC of indoor latex paints based on the change of a film property. These methods are mostly time consuming. In this research, a new method has been proposed based on permeability of coating and it is compared with wet scrub resistance method which is a mechanical one. Wet scrub test is based on the void contents and the strength of the interfaces of latex particles existing in the film. In contrast, permeation test is only based on the void contents through the film and therefore it is more consistent with the definition of CPVC. It was observed that this new method is several times faster and less sensitive to aging or annealing.

Key Words:
critical pigment volume concentration;
latex paint;
permeability;
wet scrub test;
pigment binding capacity (PBC)

(∗) To whom correspondence should be addressed.
E-mail: mrkhorassani@yahoo.com
pourmahdian@aut.ac.ir

## INTRODUCTION

Critical pigment volume concentration (CPVC) is a major concern in formulating highly pigmented paints. Following the early work of Calbeck [1] on the importance of volume concentration of pigment particles in paint systems, in early 1940s, Asbeck and Van Loo [2] put forth the concept of critical pigment volume concentration as a fundamental physical transition point in a pigment-binder system at which properties of an organic paint film change considerably [3]. Although the definition of CPVC is assigned to Asbeck and Van Loo, Wolff et al. have reported the existence of such a point. A historical review is prepared by Stieg [4].

Many methods have been proposed to determine CPVC based on change of coating's properties such as density [5], porosity [6], optical properties [7, 8], mechanical properties [9], scrub resistance [10], transport properties [11], gas permeability [12, 13], magnetic moment [9] and thickness of absorbed polymeric layer on the pigment surface using thermally stimulated current depolarization [14]. Stieg [4] and Bierwagen and Rich [15] have made a good review on these methods. Despite the fact that CPVC is very important for paint formulators, but due to cost and/or time-related problems in measurement in conventional laboratories, its determination is restricted. Since flat latex coatings are formulated around CPVC, the importance of CPVC determination is unarguable [15, 16]. Therefore it is required to provide a low cost and faster procedure to find it. In solvent-based paints the measurement and interpretation of the CPVC is easy and straightforward [4, 17]. On the other hand, CPVC values of a certain latex paint system measured by other methods do not match with each other. In such systems due to complexity of dispersion binder and its heterogeneity in nature, discrete polymer particles coalesce to form a more or less continuous body. Therefore, at CPVC, voids affect the physical and mechanical properties, moreover, packing and interfacial strength play an important role as well. The extent of interdiffusion of polymer chains at interface has a significant effect on mechanical properties of latex paints.

Packing characteristics of the coating formulation have an effect on CPVC. The effect of the presence of aggregates and agglomerates on the degree of system dispersion implies that CPVC is not a unique characteristics of pigmentation. The global theory of void formation does not consider the fluctuation of volume fraction of pigment particles and density throughout the film. Therefore it is expected that when pigment volume concentration exceeds CPVC value we can see an abrupt change. In contrast, experiments demonstrate a gradual transformation in coating properties starting below CPVC.

An ideal approach to CPVC assumes that at this point, pigment particles are arranged in a close-packed lattice and the amount of binder is enough to fill all the interstitial regions between them. But in practice, the value of real (actual) CPVC is always less than that of ideal, because: (1) the actual spatial arrangement of pigment particles is randomly-packed and therefore the volume fraction of the interstitial regions between particles is more than that of a close-packed lattice and (2) the absorbed layer of polymeric material (binder and/or dispersant) prevents direct contact between particles and always there is a gap between them depending on the thickness of absorbed layer. Therefore a real CPVC is a point at which all available absorption sites on the surface of pigment are occupied by the adsorbate [14]. These reasons imply that CPVC depends on the characteristics of pigment particles and some other parameters as well, such as binder characteristics, pigment-binder interactions, and film formation conditions [18]. Based on the pigment binder system, the thickness of immobilized polymer molecules may change from approximately 0.5 micron to 1.5 microns [19, 20]. It is expected that the chain mobility reduction in the vicinity of the surface is due to the crowding of chains, local ordering of chains, loss of configurational entropy of the polymer segments near the solid surface [21].

Particle packing and spatial configuration of pigment-binder particles, depends on the deformability of latex particles and their capability of spreading over pigment surface during the film formation process [22]. Pigment particles having active surfaces at the time of interaction with polymer chains lose their mobility and produce rigid layers around them. The quantity of these pigment particles in a paint system determines the mobility of the binder molecules. It is observed that increase in the concentration of active surface pigments in paint systems may lead to high $T_g$ together with the peak for the $T_g$ of bulk polymer. Increase in the quantity of mobilized chains adjacent to pigment surface is a case of this phenomenon [21, 23]. Therefore in paint systems with relatively high interactions between polymer and pigment surface, an increase in pigment volume concentration leads to decrease in the mobility of polymer chains especially at high PVCs where the binder can just act as small droplets that stick individual pigment particles together. At these levels of pigment loading, binder molecules are strongly affected by pigment surface characteristics.

Generally, estimating CPVC end-point is affected by pigment packing, PVC and polymer binder interac-

**Table 1.** All ingredients used in this study.

| Name | Supplier | Comments |
|---|---|---|
| Simacryl R790 | Simabresin Co. Ltd. | Styrene-acrylic latex |
| $TiO_2$ - 100 | Cristal Co. Ltd. | White pigment |
| Simacryl D135 | Simabresin Co. Ltd. | Acrylic dispersant |
| AW-402 | Iran Petrochemical Co. | Leveling agent |
| Tylose 4000K | Clariant | Thickener |
| EFKA-2527 | EFKA | Antifoam |
| Formalin | Sina Co. Ltd. | Preservative |

tion (first order CPVC effects) while pigment flocculation and aggregation, incomplete coalescence of latex particle and film formation (second order effects) are useful for correcting the first order effects and enhancing the accuracy of end-point CPVC determination [15].

At CPVC, permeation mechanism through the film changes from solution-diffusion mechanism to diffusive convective transport. This is due to increase in porosity of the film. Thus, increasing in PVC and formation of voids and channels throughout the film causes a change of the structure of composite layer from a dense layer to a porous one. The mechanism of the permeation of gas through coating layer may obey solution diffusion, molecular sieving (surface diffusion), Knudsen diffusion and/or convective flow . In a porous layer, the permeation mechanism mainly consists of Knudsen diffusion and Poiseuille flow with portions based on the ratio of pore radius to the mean free path of the gas molecules [24]. This mechanism transition is the foundation of our new method. In this study, gas permeability of coating is considered as the main characteristic property by which CPVC can be determined and a new method based on this approach is presented. Pigment-binding capacity determined by wet scrub test is the main application property for highly pigmented indoor paints [16]. Therefore for this study, wet scrub resistance test is considered as an appropriate method to determine CPVC. The obtained data from this method was compared with data of our new method.

## EXPERIMENTAL

### Materials

A model paint was prepared using styrene-acrylic latex binder and commercial $TiO_2$. Poly(acrylic acid) was used as a dispersing agent. No filler was used for the simplicity of the system. To prepare a white base, pigment slowly was dispersed. Dispersion was carried out using Shinmyung Servo stirrer, 7-cm-blade-diameter rotation at 1700 rpm. The materials and white-base formulation are given in Tables 1 and 2, respectively. Dispersion was done for duration of 45 min. The fineness of the grinding was measured using BYK Gardner grindometer. The size of dispersed phase was observed to be less than 10 μm in diameter.

Firstly, two basic formulas, (i) and (ii) with PVCs 20.3 and 68.7 respectively, were made by mixing different proportions of latex binder with white base. Both these basic formulations have the same quantity of pigment per unit volume of liquid paint. Thus, for all PVCs, the quantity of pigment per unit area of the final dried film are identical. Five levels of pigmentation (PVCs 39, 45, 52, 57 and 65) were prepared by mixing proportions of the above mentioned two basic paint formulations [8] using:

$$X_i = \frac{PVC_{expected} - PVC_{ii}}{PVC_i - PVC_{ii}}$$

**Table 2.** White base.

| Name | Amount wt% |
|---|---|
| $TiO_2$ - 100 | 58.66 |
| Deionized water | 38.13 |
| Simacryl D135 | 1.26 |
| AW-402 | 1.1 |
| Tylose 4000K | 0.42 |
| EFKA-2527 | 0.22 |
| Formalin | 0.22 |

where $X_i$ is the volume fraction of paint (i), $PVC_{expected}$ is the desired PVC and $PVC_i$ and $PVC_{ii}$ are the PVCs of the basic paint formula (i) and (ii) respectively.

Reproducibility of this method depends largely on the quality of mixing. Since mixture is relatively a high viscous and also the existence of voids and foam in the paint affects the permeability of dried coating layer, it is very important to have a gentle mixing to reduce the foaming.

**Permeation Test**

Figure 1 shows a schematic representation of our permeation apparatus; A transparent 56x18x18 $cm^3$ box which is divided into eight equal compartments. A stainless steel sheet is located in the top of the compartments. It has eight holes of 2 cm in diameter. The deionized water was poured in the box up to 3 cm height. Then 2 $cm^3$ of 1% wt phenolphthalein was added as an indicator and 1.5 $cm^3$ of 29 wt% hydrochloric acid to adjust (by retarding) the time of changing liquid colour to purple. Films having 700 μm wet thicknesses were made on normal paper (porous substrate) using BYK-Gardner Multi-Applicator. Dried films were cut to 5-cm-diameter-coins. These coins were attached on top of the hole of each compartment and their surroundings were sealed using silicon adhesive. The experiment was performed at ambient temperature. Ammonia gas was entered into the upper part of the box from an ammonia reservoir containing 12.5% ammonia solution to saturate its environment, then diffused through the film and changed the colour of the liquid into purple. The time at which a detectable purple layer on the surface of the liquid in each compartment observed, was recorded as the permeation time.

**Wet Scrub Test**

Since one of the most important properties of latex binders for indoor paints is the pigment binding capacity (PBC), often referred to as scrub resistance, scrubability or washability [25], determination of CPVC by means of wet scrub test is of great practical importance. Wet scrub test done using the basic idea of DIN 53778 with some changes in the testing conditions and film preparation. The same humidity and temperature conditions of permeation test for film formation of coatings with different PVCs were considered. Wet scrub resistance was evaluated quantitatively as the number of cycles required to scrub off a paint film with a brush. During the test, a soap solution was poured dropwise on the coating.

The experiments were carried out in typical relative humidity of a laboratory (55 to 65%). To reduce the effect of variation of humidity on film formation and consequently experimental data, both tests, i.e., permeability and wet scrub resistance were carried out concurrently in winter hoping to have a minimum of humidity variation. There are always stray currents of air in any room, therefore, achieving perfectly the same conditions for all experiments was hard, but for our purpose, it is enough and has minimum undesired effects on results. The samples were dried and aged for 24, 42 and 65 h at ambient temperature (23°C). Three

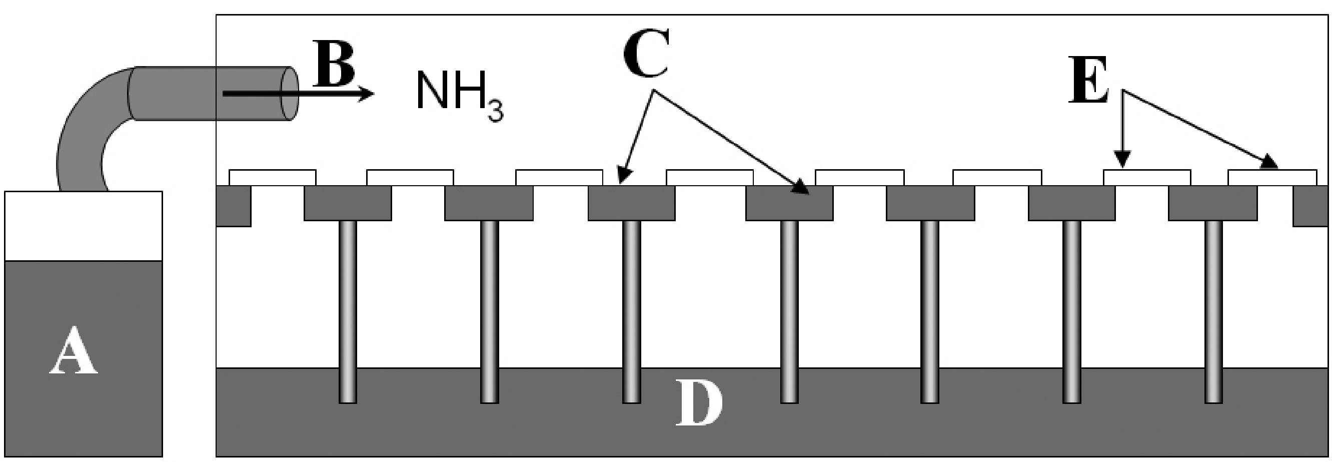


**Figure 1.** A schematic representation of permeation apparatus: (A) ammonia reservoir, (B) ammonia inlet, (C) interface plates, (D) acidic solution, (E) coated papers.

paint specimens were tested for each PVC and the average is reported for each set.

## RESULTS AND DISCUSSION

The variation of CPVC during the aging time is given in Figure 2, a plott of permeation time versus PVC. It can be seen that in spite of 6 h drying, the results showing a change for different periods of aging in the PVC range of 51 to 56. The change in diffusion time is not very significant for CPVC range after 6 h. Therefore, CPVC range may not be measured clearly, till the 24 h of experiments. Especially after 42 and 65 h the change is abrupt and CPVC range approaches a point, almost PVC=54. Increasing aging leads to increase in permeation. The change in region before CPVC is much more than that of the region beyond CPVC. Before CPVC, aging decreases the rate of permeation. This may be due to deformation and spreading of binder particles and consequent decrease in the void density of paint film. However, since CPVC deformation of binder particles has no significant effect of the void density, therefore, in different aging times, the permeation time remains almost constant.

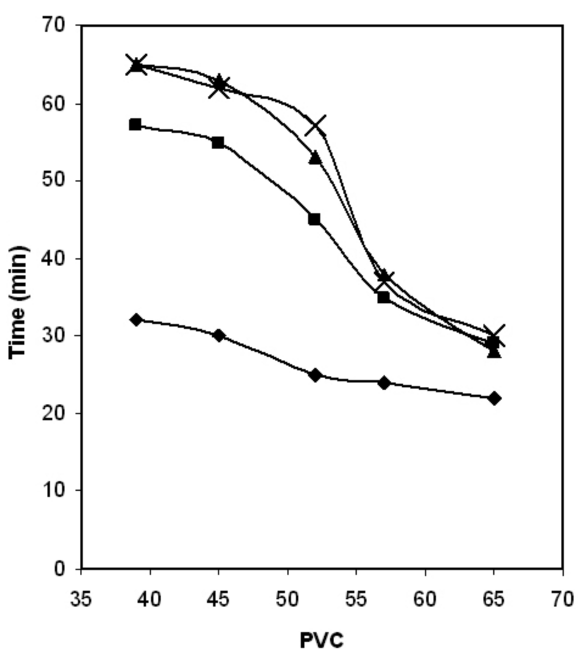


**Figure 2.** The results of permeation test at PVCs 39, 45, 52, 57 and 65 after: (◆) 6, (■) 24, (▲) 42 and (x) 65 h of aging time.

The results of wet scrub test, given in Figure 3, show a change in the PVC range of 52 to 56. With increase in time, at low PVCs, an increase in the number of cycles was observed while at high PVCs especially after the CPVC range, wet scrub resistance did not change considerably. After 6 and 24 h, wet scrub test showed an abrupt change in CPVC range while after 42 and 65 h, the change is more gradual.

In both test methods, aging affects measuring CPVC. It can be seen that wet scrub results are more sensitive to aging than permeation. At PVC = 39, a change of about 40% was observed in data between 24 and 42 h of aging while this change for permeation test was about 13%. Increase in aging causes the change in wet scrub test at different PVCs to become less abrupt while in the permeation test it becomes sharper in the CPVC region. Therefore, it would be more convenient to measure CPVC by means of permeation.

Another important issue in this research is that the time required for permeation test was seven times faster than that in wet scrub test.

Three main parameters affecting wet scrub test are interface strength of latex particles, porosity and pigment-binder interactions (adhesion) while for permeation test porosity is the main parameter. Aging causes polymer chains to diffuse across latex interfaces. This leads to reinforcement of interface and even interface healing and forming continuous polymeric matrix. But its effect on permeation does not follow the same order of mechanical properties.

Since the properties of film is affected by voids

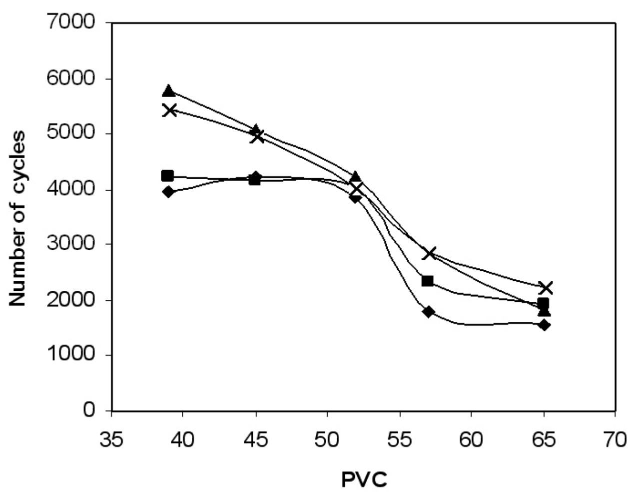


**Figure 3.** The results of Wet scrub test at PVCs 39, 45, 52, 57 and 65 after: (◆) 6, (■) 24, (▲) 42 and (x) 65 h aging time.

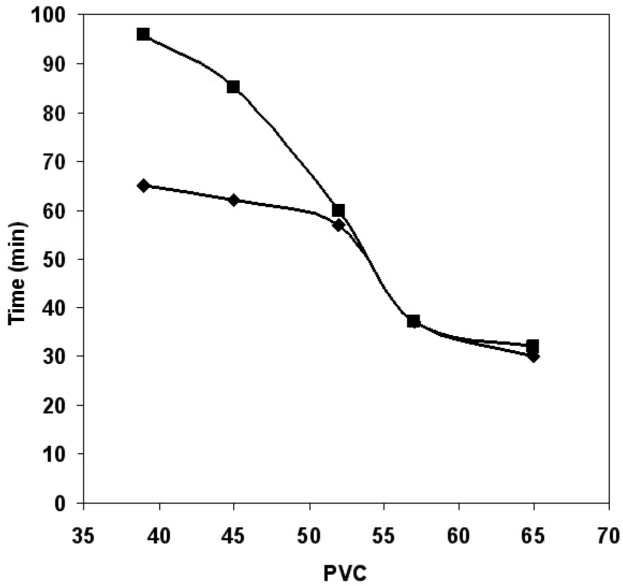


**Figure 4.** The results of permeation test at PVCs 39, 45, 52, 57 and 65 after: (◆) 65 h of aging time and (■) 65 h of annealing.

within the film introduced by insufficient binder, incomplete latex coalescence/film formation and pigment clustering and aggregation, annealing contributes to interface healing and reflow of binder throughout the film and may change the void fraction of latex coating. To investigate the effect of interdiffusion of polymer chains across the interfaces of latex particles and also the effect of spreading of binder particles over pigment surfaces on determination of CPVC, another series of samples with different PVCs were annealed at 60°C ($T_g$ + 38°C ) after the initial drying of the film at ambient temperature for 65 h . The experimental data of permeation test for both samples series (aged and annealed) are shown in Figure 4. It can be seen that after CPVC, almost both curves coincide with each other. This may be because of entrance of voids throughout the film.

In latex paints surfactants appear as binder emulsifier, pigment dispersant, improving wetting on low energy substrates, to control foaming during the application and processing, to prevent film defects caused by surface tension gradients, (as associative thickeners) to optimize the rheological properties of the formulation[31]. Since barrier properties of a pure latex system are affected by mode of film formation, the surfactant layer around the latex particles and polymer interdiffusion [26], It is reasonable to have a change in permeability of coating layer before CPVC.

According to the definition of CPVC by Asbeck and Van Loo [2] as the PVC at which the binder just fills the voids between the densest packed pigment particles , porosity arise in the coating layer. Therefore, although the determination of CPVC by wet scrub test is of practical importance, the value of CPVC obtained from test methods based on the porosity of paint film are more consistent with the definition of CPVC. In addition, beside porosity, many other parameters such as drying time and film formation conditions [27, 28], adhesion, cohesion, the spreading and the adhesion of latex particles on pigment surface within the coating [22] affect the mechanical properties of indoor latex paints. Hence, these parameters have significant effect in determination of CPVC by means of wet scrub test. Film formation of latex particles and interdiffusion of polymer chains are strongly affected by the amount of inorganic [29] and organic [30] pigments present in coating; because pigments retard the rate of polymer interdiffusion. The extent of interdiffusion of polymer chains across the interface, as an index of latex particles coalescence and binder cohesion, determines the strength of interface between latex particles. Two important parameters determine the magnitude of polymer diffusion at interface: (1) the surface-to-volume ratio of pigment particles and (2) the surface characteristic of pigment particles (which affects the mobility of polymer chains). Therefore the amount of pigment particles and consequently PVC in a paint system determines the mobility of the binder molecules. An increase in pigment volume concentration causes the interface area between the particles to decrease and leads to decrease in the influence of interdiffusion on wet scrub test especially at high PVCs (after CPVC range) where the binder can just act as small droplets that glue individual pigment particles together.

It is observed by Joanicot et al. [22] that at high PVCs the latex polymer particles never form continuous films unless they are annealed at very high temperature. Also at high PVCs, the fixation of pigments by isolated pigment particles at many discrete points supports the importance of pigment-binder adhesion. In fact, with increase in PVC starting below CPVC and ending above CPVC, the number of latex particles with respect to pigment particles decrease and hence the influence of pigment-binder interactions become more significant than latex particles interaction and cohesion.

## CONCLUSION

The so called permeation test is introduced in this article for a fast measurement of CPVC. In comparison to wet scrub method, this test measures the CPVC several times faster. Wet scrub test depends almost on the void contents and the interface strength of latex particles existing in the film. But permeation test only depends on the void contents. As a conclusion of the experimental work, one can see that permeation test method is simple, faster and less costly. The art of this test method is to separate the effect of voids and effect of interfacial strength on determination of CPVC of indoor latex paints.

## ACKNOWLEDGEMENTS

The author tends to thank Mr.Alipourian, The director of Simab Resin Co. for his cooperation and supporting during the synthesis of the emulsion resin samples, And also appreciate the help of all my friends at Taak Resin Co. in making paint samples and testing the provided films.

## REFERENCES

1. Calbeck J.H., Application of the statistical method in testing paints for durability, *Ind. Eng. Chem.*, **18**, 1220-1222 (1926).
2. Asbeck W.K., Van Loo, M., Critical pigment volume relationship, *Ind. Eng. Chem.*, **41**, 1470-1475 (1949).
3. Bierwagen G.P., CPVC Calculations, *J. Paint. Technol.*, **44**, 45-55 (1972).
4. Stieg, F.B., The influence of PVC on paint properties, *Prog. Org. Coat.*, **1**, 351-373 (1973).
5. Stieg F.B., Density method for determining the CPVC of flat latex paints, *J. Coat. Tech.*, **55**, 111-114 (1983).
6. Rasenberg C.J.F.M., Huisman H.F., Measurement of the critical pigment volume concentration by means of mercury porosimetry, *Prog. Org. Coat.*, **13**, 223-235 (1985).
7. Hesler K.K., Practical technique for the CPVC determination of titanium dioxide-containing latex paint systems, *J. Coat. Tech.*, **50**, 57-61 (1978).
8. del Rio G., Rudin A., Latex particle size and CPVC, *Prog., Org. Coat.*, **28**, 259-270 (1996).
9. Schaake R.C.F., Heijkant J.A.M. v.d., Huisman H.F., CPVC Relationships III. The real CPVC and its relationship to young s modulus, magnetic moment, abrasive wear and gloss, *Prog. Org. Coat.*, **16**, 265-276 (1988).
10. Culhane W.J., Smith D.T., Chiang C.P., Characterization of pigment volume concentration effects in latex paints, *J. Coat. Tech.*, **55**, 53-58 (1983).
11. Schaller E.J., Critical pigment volume concentration of emulsion based paints, *J. Paint. Tech.*, **40**, 433-438 (1968).
12. Khorassani M., Pourmahdian S., Afshar-Taromi F., Nourhani A., A new method to determine CPVC of indoor latex Paints, *MACRO 2004,* Paris, France 4-9, July 2004.
13. Khorassani M., Pourmahdian S., Afshar-Taromi F., A new method for measuring latex critical pigment volume concentration (LCPVC) by diffusion mechanism, *6th Iran. Sem. Polym. Sci. Technol. (ISPST 2003),* 12-15 May 2003, Tehran, Iran.
14. Kumins C.A., Knauss C.J., Ruch R.J., Determination of restricted segmental mobility dimensions of adsorbed polymers, *Prog. Org. Coat.*, **28**, 17-20 (1996).
15. Bierwagen G.P., Rich D.C., The critical pigment volume concentration in latex coatings, *Prog. Org. Coat.*, **11**, 339-352 (1983).
16. Kirsch S., Pfau A., Frechen T., Schrof W., Pfohler P., Francke D., Scrub resistance of highly pigmented paints: A study on abrasion mechanics of different scrub techniques, *Prog. Org. Coat.*, **43**, 99-110 (2001).
17. Patton T.C., Paint flow and pigment dispersion, Wiley, New York, 2nd ed., Ch. 5-8 (1979).
18. Fishman R.S., Kurtze D.A., Bierwagen G.P., Pigment inhomogeneity and void formation in organic coatings, *Prog. Org. Coat.*, **21**, 387-403 (1993).
19. Kumins C.A., Roteman J., Effect of solid polymer interaction on transition temperature and diffusion coefficients, *J. Polym. Sci., Part A*, **1**, 527-540 (1963).
20. Kwei T.K., Kumins C.A., Polymer-filler interaction: Vapor sorption studies, *J. Appl. Polym. Sci.*, **8**, 1483-1490 (1964).
21. Tsagaropoulos G., Eisenberg A., Direct observation of two glass transitions in silica-filled polymers. Implications for morphology of random ionomers, *Macromolecules*, **28**, 396-398 (1995).
22. Joanicot M., Granier V., Wong K., Structure of polymer within the coating: An atomic force microscopy and small angle neutrons scattering study, *Prog. Org. Coat.*, **32**, 109-118 (1997).

23. Tsagaropoulos, G., Eisenberg, A., Dynamic mechanical study of the factors affecting the two glass transition behavior of filled polymers, similarities and differences with random ionomers, *Macromolecules*, **28**, 6067-6077 (1995).
24. Pandey P., Chauhan R.S., Membranes for gas separation, *Prog. Polym. Sci.*, **26**, 853-893 (2001).
25. Heldmann C., Cabrera R.I., Momper B., Kuropka R., Zimmerschied K., Influence of nonionic emulsifiers on the properties of vinyl acetate/VeoVa10 and vinyl acetate/ethylene emulsion and paints, *Prog. Org. Coat.*, **35,** 69-77 (1999).
26. Vanderhoff J. W., Bradford E.B. and Carrington W.K, The transport of water through latex films, *J. Polym. Sci. Symp.*, **41**, 155-174 (1973).
27. Hoy K.L., Coalescence and film formation from latexes, *J. Coat. Tech.*, **68**, 33-39 (1996).
28. Löfflath F., Gebhard M., Rheological changes during the drying of a waterborne latex coating, *J. Coat. Technol.*, **69**, 55-74 (1997).
29. Kobayashi M., Rhabi Y., Winnik M.A., Effect of inorganic pigments on polymer interdiffusion in a low-$T_g$ latex film, *Macromolecules*, **34**, 1855-1863 (2001).
30. Feng J., Odrobina E., Winnik M.A., Effect of hard polymer filler particles on polymer diffusion in a low-$T_g$ latex film, *Macromolecules*, **31**, 5290-5299 (1998).
31. Hellgren A.-C., Weissenborn P., Holmberg K., Surfactants in water-borne paints, *Prog. Org. Coat.*, **35**, 79-87 (1999).