The Role of Auxiliary Monomers and Emulsifiers on Wet Scrub Resistance of Various Latex Paints at Different Pigment Volume Concentrations

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ABSTRACT: This work is an attempt to study the effect of different latex types containing various auxiliary monomers and emulsifiers on their pigmentation and their corresponding behavior on scrub resistance. The auxiliary monomers investigated were acrylic acid (AA), methacrylic acid (MAA), and itaconic acid and the emulsifiers contained sodium lauryl sulfate (SLS) and sodium dodecylbenzene sulfonate (SDBS). It was shown that a semi-batch polymerization technique which led to smaller particles and sharper size distributions is preferable. The best wet scrub results were obtained by using MAA and SLS. It was also shown that the proper selection of an auxiliary monomer generally depended on the range of incorporated pigment volume concentration (PVC). At high PVCs, AA gave better performances compared with MMA. The reverse effect was shown to occur at low PVCs. J Appl Polym Sci 113: 3264–3268, 2009

Key words: wet scrub resistance; pigment binding capacity; washability; auxiliary monomer; emulsifier; pigment volume concentration

INTRODUCTION

Pigment binding capacity (PBC), as determined by a standard wet scrub test, characterizes dispersion binders in highly pigmented indoor latex paints. Latex binders in outdoor paints must guarantee excellent film formation at room temperature as well as demonstrating a good level of washability and low water uptake.[1] A binder having high PBC can be formulated at a higher pigment volume concentration (PVC), without sacrificing other properties, leading to a reduction in cost of the final paint. Such a binder would possess low degrees of water sensitivity, chalking, and dirt pickup.[2]

Appropriate selection of type and amount of auxiliary monomers is crucial in adjusting latex and pigment compatibility.[3] Acrylic carboxylic acid monomers are an important family of functional monomers as a basic ingredient of almost all emulsion polymerization systems, enabling latex stability and facilitating the wetting of highly pigmented systems.[4] These monomers also control the morphology of latexes as well as giving uniform functionality distribution leading to increased pigment binding capacities and wet adhesion properties.[5]

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Type and concentration of emulsifiers have also a profound effect on particle size,[6,7] morphology,[8] and water sensitivity[9] of latexes. Anionic emulsifiers provide shear stability to a latex during the polymerization reaction, whereas nonionic emulsifiers provide electrolytic stability and contribute to enhanced mechanical properties and freeze–thaw stability.[10]

Emulsion paints could be classified according to the maximum number of scrub cycles they withstand. There are three main methods for evaluating such washability of coatings. Wet scrub resistance according to the DIN 53778 standard has two main disadvantages of prolonged test duration and relatively poor reproducibility. Additionally the results are only comparable within a set of samples, and hence, an internal standard should always be used. Wet scrub test according to the ISO 11998 standard, developed to substitute the DIN test method, has the advantages of higher reproducibility and shorter measuring times. Finally, the tribology method is comparably as fast and reliable as the ISO test with the added advantages of simple sample preparation together with quick and simple data evaluations.[11] For this reason, the standard ISO 11998 test was used in our study for its good reproducibility and more importantly because of its availability in our laboratory.

The dependency of organic coating properties on PVC, first claimed in 1926[12] and later well established by 1949,[13] also holds good for the washability

TABLE I
Specification of the Polymerization Ingredients

Material	Supplier	Inhibitor	Country
n-BA	BASF	EMHQ-50	Germany
MMA	Lucite	MEHQ-50	UK
S	Enoc	Catechol-50	UAF
AA	Atofina	EMHQ-200	France
MAA	Atofina	EMHQ-200	France
IA	Mitsui	–	Japan
SLS	P.T.KAO	–	Indonesia
SDBS	Pakvash	–	Iran
Ammonia	Loporte	–	Germany

TABLE III
Latexes Made by MMA Auxiliary Monomer at Two Levels Containing Two Kinds and Amounts of Emulsifiers

Latex number	MMA percent	Emulsifier type	Emulsifier percent
L1	4	SLS	8
L7	4	SDBS	8
L8	4	SLS	16
L9	4	SDBS	16
L4	8	SLS	8
L10	8	SDBS	8

of coating too. Washability depends not only on the nature of latex but also on the shape, size, size distribution, and surface properties of the latex as well as the pigment.

In this work, we aimed at studying the effect of carboxylic functional monomers and anionic emulsifiers on PBC of a latex paint at different levels of PVC.

EXPERIMENTAL

The latexes were prepared by a standard, seeded emulsion polymerization utilizing two techniques of batch and semibatch processes. The specifications of raw materials are shown in Table I. The fixed part of the formulation contained 261 g styrene (S), 505 g *n*-butyl acrylate (BA), 143 g methyl methacrylate (MMA), and 3.2 g potassium persulfate. The formulation also had a variable part of various ingredients: sodium lauryl sulfate (SLS) and sodium dodecylbenzene sulfonate (SDBS) were used as emulsifiers and acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) were used as auxiliary monomers. The combinations for each formulation are shown in Tables II and III. Percentage amounts of auxiliary monomers are based on the total weight of monomers. All polymerization reactions were carried out at 85°C. The pH of the products adjusted to about 9 by ammonia solution. Viscosity of the final product at around 40% solid content varied for each formulation.

A pigment slurry with the composition given in Table IV was prepared. Two primary paint formulations at PVCs of 20.3 and 68.7 were made by mixing the pigment slurry separately with the variously prepared latex binders and water in appropriate proportions [i.e., (100 : 9 : 31) and (100 : 36 : 4), respectively]. Because both formulations contained the same amount of pigment per unit volume of liquid, it could almost be claimed that their mixtures at different proportions had the same amount of pigment per unit area of the final dried film. Because the thickness of liquid paint films were also approximately the same, Four levels of pigmentations (i.e., PVCs of 31, 42, 54, and 62) were prepared by mixing various proportions of the primary paint formulations by using the Bierwagen formula [eq. (1)][14]:

$$X_i = \frac{\mathrm{PVC_{des}} - \mathrm{PVC_{ii}}}{\mathrm{PVC_i} - \mathrm{PVC_{ii}}} \quad (1)$$

where X_i is the volume fraction of paint (i), $\mathrm{PVC_{des}}$ is the desired PVC, and $\mathrm{PVC_i}$ and $\mathrm{PVC_{ii}}$ are the PVCs of the basic two primary paint formulation at PVC 20.3 (i) and PVC 68.7 (ii), respectively.

To investigate the role of auxiliary monomers, emulsifiers, and the technique of polymerization with a PVC of 40 was also prepared for comparison purposes. Films were applied at a wet thickness of

TABLE II
Auxiliary Monomers for Each Latex Made by 8% SLS Emulsifier (Based on 10% Aqua Solution and Monomer Based on Total Weight of Acrylic Monomers)

Latex number	Auxiliary monomer type	Auxiliary monomer percent
L1	MAA	4
L2	AA	4
L3	IA	4
L4	MAA	8
L5	AA	8
L6	IA	8

TABLE IV
Pigment Slurry Specifications and Its Composition

Material	Amount (wt %)	Supplier	Comments
TiO_2-100	58.66	Cristal Co.	White pigment
Deionized water	38.13	–	–
Simacryl D135	1.26	Simab Resin Co.	Acrylic dispersant
AW-402	1.1	Iran Petrochemical Co.	Leveling agent
Tylose 4000K	0.42	Clariant	Thickener
EFKA-2527	0.22	EFKA	Antifoam
Kiton	0.22	Rohm & Haas	Preservative

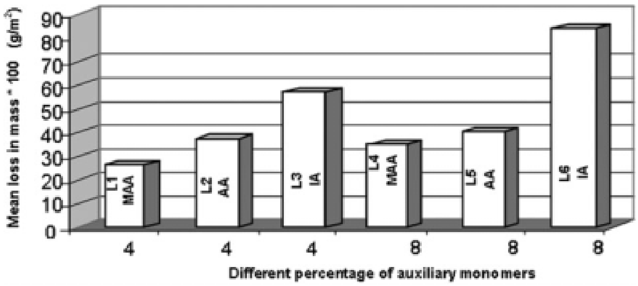

Figure 1 Effect of auxiliary monomer on loss in mass.

120 μm to polyvinyl chloride substrates by using a BYK film applicator, which was subsequently dried for 4 h at 60°C. The wet scrub test was performed according to the ISO 11998 standard with a slight modification by using a BYK Elcometer 1720 instrument having two working lines. The data obtained are an average of four experiments for each sample.

RESULTS AND DISCUSSION

The influence of auxiliary monomers on wet scrub resistance is shown in Figure 1.The results indicate that generally the MAA monomer gave better wet scrub resistances compared to the other auxiliary monomers. It can be seen that lower MAA monomer contents (i.e., 4%) provides a higher scrub resistance than the higher level (i.e., 8%). The higher loss in mass for the IA monomer may be explained in terms of existence of two polar carboxylic groups. In another words, although these two polar groups give rise to improved wetting properties, they also impart more water sensitivity to the resultant films.

All monomers used in this study contained carboxylic functionalities and hence proper wetting properties were expected for the investigated samples. AA with the least steric hindrance among the auxiliary monomers contributed to better wetting properties than MAA. However, its higher polarity leads to increased water permeability of the dried film, and hence, diminished the PBC. The existence of carboxylic groups increases the wetting and adhesion properties of the pigment–latex system, leading to higher PBC, while it reduces the resistance of the dried film against water diffusion and permeation, which has a contradictory influence on washability of the film. These counter effects are optimized by choosing an appropriate amount of auxiliary monomer to tune a desired wet scrub result. As expected, the interfacial surface tension of the resulting copolymer is greatly affected, leading to variability in wetting properties. Generally, various monomer compositions of latex binders affect the interfacial surface tension and consequently the wetting properties of the polymeric particles. This effect is strengthened by existence of auxiliary and functional monomers in the latex composition. The effects of these monomers may be due to the following: (1) number of carboxylic groups; (2) variation of density of these pendant groups in the polymer chain arising from different reactivity ratios of the various monomers; and (3) the effect of auxiliary monomers on the glass transition temperature and, therefore, on polymer chain mobility.

Considering the results in Figure 1, MAA improved the wet scrub resistance more than the other auxiliary monomers utilized. Therefore, it was used to evaluate the loss in mass for latexes with the mentioned emulsifiers. The results are shown in Figure 2. In each pair of A (L1, L7), B (L8, L9), and C (L4, L10) shown in Table III, the latexes containing SLS indicate superior wet scrub resistance in comparison with those based on SDBS. Pairs A and B have the same amount of auxiliary monomer and different amounts of emulsifiers. It is observed that lower amounts of emulsifiers for both SLS and SDBS lead to better wet scrub resistance. Pairs of A and C have the same amount of emulsifiers and different amounts of MAA. The pair with higher amounts of auxiliary monomer (C) has a higher loss in mass. SLS and SDBS have critical micelle concentration of 8.3 and 1.2 m*M*, respectively.[15] Therefore, at the same concentration during the emulsion polymerization process, they may form different micellar structures leading to different morphologies.[8] The use of these two different anionic emulsifiers leads to different particle shapes, sizes, and concentrations. Hence it has a profound effect on film formation quality of the resultant latex paint and consequently on wet scrub resistance of the dried film. The rate of radical capture by micelles, polymerization kinetics, and molecular weight distribution depends on the

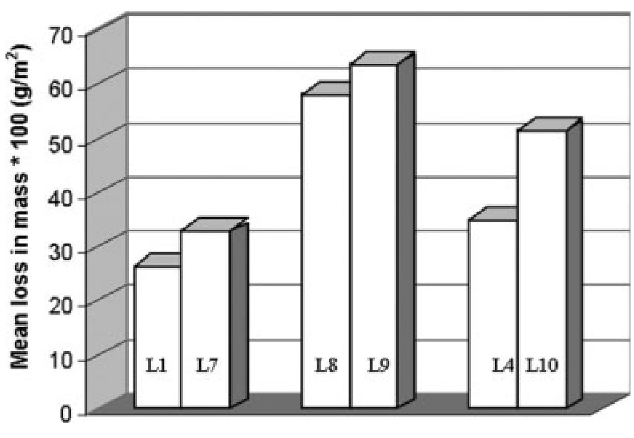

Figure 2 Effect of type and amount of auxiliary monomers and emulsifiers on loss in mass according to the data in Table III.

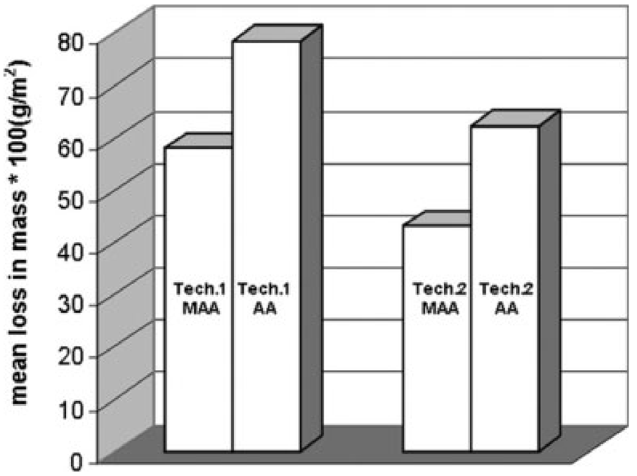

Figure 3 Effect of technique of polymerization on loss in mass (Tech1 = batch, Tech2 = semibatch) by two kinds of auxiliary monomers based on L1 formulation.

chemical nature of the emulsifier.[16,17] Considering the dependency of strength of polymer films on molecular weight, it is clear as to how emulsifier type will affect wet scrub resistances of latex coatings.

Figure 3 demonstrates how the polymerization technique significantly influenced the wet scrub properties. This may be due to the fact that polymerization technique affects the morphology and size of the resulting latex particles.[18,19] The particle sizes of two latexes with L1 composition prepared via batch and semibatch polymerization were measured by using laser light scattering method and an average mean center of 0.8 and 50 μm was observed, respectively. The semibatch technique gave a much smaller particle size, whereas the "batch" technique led to a higher particle size. The higher adsorption of emulsifier from the continuous phase results in a smaller particle size, which is accompanied by a less surplus (free emulsifiers) in the continuous media. Because the emulsifiers used in this study were hydrophilic in nature, they may increase the water sensitivity of the coating. Therefore the final solid film produced from smaller particle size latexes, prepared via the semibatch polymerization, has a higher PBC.

To investigate the effect of PVC on washability of the dried paints, it was necessary to make two other latexes with combinations L11 (MAA = 4, SLS = 16), and L12 (AA = 4, SLS = 16). The results of the wet scrub test at different levels of PVC are depicted in Figure 4. It is clear that increases in the PVC leads to lower binder content and hence lower PBC. It is worthwhile to note that the glass transition temperature (T_g) of poly(acrylic acid) is 106°C, which is lower than the T_g of poly(methacrylic acid), which is 185°C.[20] Hence, the film of MAA containing latex paints is more rigid with less elasticity to damp the forces produced by the brush. This phenomenon has led to an inferior scrub resistance of such dried films. The latexes containing MAA monomer (L1, L4, and L11) have a lower scrub resistance at higher PVCs compared with those based on AA monomer (L2, L5, and L12). Increasing PVC results in an increase in hardness of the organic coating as well as increasing the T_g of the binder in the case of surface active pigments that affect the resistance of the films against external stresses. At high PVCs AA auxiliary monomer outperforms the MAA auxiliary monomer, whereas at lower PVCs MAA gives rise to improved wet scrub resistance. The reduction of wet scrub resistance of latexes number 11 and 12 is due to consumption of a higher level of emulsifier in their formulation, leading to an increase in water sensitivity of the film. Latex critical pigment volume concentration (LCPVC) is one of the characteristics of suspension-type binders whose particle sizes are comparable to that of pigment. This also holds true for latexes in which particle sizes are influenced by monomer type, emulsifier, and polymerization technique. Therefore, it can be claimed that a latex prepared with a known monomer, emulsifier, and a polymerization technique should provide a binder enabling to bind as much as pigments it can, yet showing an improved scrub resistance in the dried film. This means that the binding capacity is as high as possible. This in turn will mean that the volume concentration of pigment (PVC) to be saturated by the binder will tend to increase values, making a pigmentation system more effective. A high loading of pigment with a great ability of the binder to bind them means that latex PVC is shifted to higher values. Therefore a greater value of LCPVC is obtained

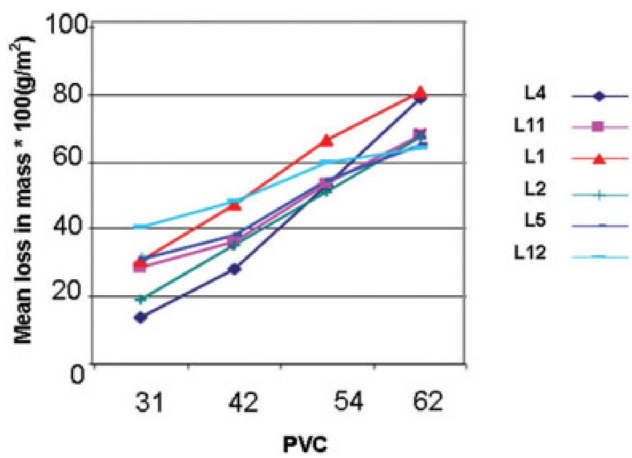

Figure 4 Effect of PVC on loss in mass for different combinations of auxiliary monomers and emulsifiers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

at the expense of higher value of PBC; these two may seem interchangeable.

CONCLUSION

In this study, the role of auxiliary monomers (AA, MAA, and IA) and emulsifiers (SLS and SDBS) for increasing the wet scrub resistance of latex paints were investigated. It was observed that MAA and SLS impart better washability to the dried film in comparison to other parameters. Also, it is observed that a semibatch polymerization technique is preferred to a batch one because a smaller particle size can be obtained. The best results were obtained for MAA auxiliary monomer/SLS emulsifier combination.

It has also been shown that due to the effect of auxiliary monomers on T_g, the proper selection of a monomer generally depends on the chosen range of PVC. At high PVCs, auxiliary monomers with low T_g (such as AA) give rise to better performance compared with high T_g, containing monomers such as MAA. The reverse effect was shown to occur at low PVCs. It may be concluded that to obtain latexes with a high wet scrub resistance, information regarding the range of required PVC is generally needed to tune the synthesis procedure.

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