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Degradation of carboxylated styrene butadiene rubber based water born paints: Part 2 − Models to predict UV stability and water absorption through central composite design

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Abstract

Central composite experimental design methods have been used to examine the simultaneous effects of talc (Viaton Viatalc® 30), titanium dioxide (modified Rutile, Tioxide® TR92) and additional hindered phenolic stabiliser (Aquanox® L, a 50% w/w aqueous dispersion of Winstay® L) on the water uptake and UV stability of composite films based on a carboxylated styrene butadiene rubber (c-SBR) latex. The talc and TR92 were *in situ* treated as pre-dispersions with Solsperse® S27000 and Solplus® D540 dispersants, respectively. For water uptake related responses, quadratic models were found to provide the most accurate prediction of effects associated with interactions between talc and TR92. It was found that the addition of TR92 to formulations with high talc loading reduced the water uptake, this was attributed a packing effect that arose due to the vast difference in pigment and filler particle size. For responses related to photo-oxidation (Microscal unit/mercury lamp, carboxylic acid carbonyl growth was monitored by IR), linear models gave the best data fit, thus indicating negligible interaction between the three variables. Within the experimental space explored, the level of talc had by far the strongest influence; increasing talc level led to a proportional increase in rate of carbonyl growth. This corroborates previous single variable studies, where the iron impurities present in the talc were suspected to be associated with the pro-degradant effect observed. Interestingly, the addition of dispersants amplified the latter effect and strongly muted the UV stabilising effect of TR92. An optimised formulation based on c-SBR was determined from the response equations and subsequently evaluated; in general the actual response trends matched those predicted. The suitability of experimental design as a tool to discover effects, interactions and responses of the ingredients of a paint system, and to optimise its formulation was thus confirmed.

Keywords: Latex; Water born paints; Experimental design; UV stability; Water uptake; Titanium dioxide

1. Introduction

The application of water-based latex technology to paints has become an increasingly important research topic in the last decade. This is mainly due to the low VOC content, ease of application and good wetting and levelling characteristics [1,2]. However, their durability, both in terms of stability to UV light and water resistance when exposed to rain, is still a matter of concern for paint manufacturers, especially when formulating exterior grade paints [3,4]. The nature of the polymeric binder and the influence of fillers, pigments and stabilisers in the final formulation, including possible interactions between them, are of critical importance.

The first part of this series of two papers [5] has addressed the effect of talc and titania pigment on the UV stability of carboxylated styrene butadiene rubber (c-SBR) based water born paints. Low levels (<50 phr) of talc were found to lead to

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optimum UV stability, relative to the unfilled matrix. This was attributed partly to a UV blocking effect that was confirmed using imaging chemiluminescence analysis. However, talc levels >50 phr impaired the UV stability, but did not push UV stability below that of the unfilled matrix. This phenomena was attributed to the combination of two competing factors; i.e., the UV blocking/possible chemical stabilisation effect versus the detrimental effect of iron impurities in the talc. The modified rutile TiO_2 (Tioxide® TR92) used significantly increased the weatherability of the paint.

Moreover, our previous work had shown the c-SBR latex used in the above stability studies was also most effective in terms of reducing water absorption [6,7], this was due to the inherently low polarity of SBR and the low level of surfactant present in the latex. The effect of a variety of fillers on the water absorption characteristics of the c-SBR was explored, and the tensile properties of the composites were also evaluated. A talc filler of large particle size afforded the best combination of reduced water uptake and good tensile properties.

In real paint formulations many other components are present in addition to the binder, pigment and filler; even in a simple formulation, these are likely to be some form of UV stabiliser, dispersants (for the pigment and filler) and some form of anti-foaming additive. Investigation of the simultaneous effect of talc, TR92, and added stabiliser on the water uptake and UV stability of c-SBR based composites (in the presence of dispersants and anti-foam additive) is therefore highly worthwhile. The UV stability aspect will be the subject of this paper. Effects associated with water uptake have been explored in an earlier paper but will be summarised here as this current paper concludes with an optimisation study that brings both aspects together in an optimised formulation. A response surface experimental design approach will be used via the Stat-Ease ‘‘Design Expert’’ software. The reader is referred to Montgomery’s excellent book on this subject for further information [8,9].

2. Experimental

In Part 1 of this series the effects of talc and TR92 on UV stability were examined without added stabiliser, dispersants and anti-foaming additives. The natural progression from this is a move to commercially realistic formulations that include additional stabiliser, dispersants and anti-foaming additives. The method for production of the paints was also intended to match commercial production more closely and involved use of a Dispermat® F1 mixer (fitted with saw tooth and bead mill attachments were appropriate). Proper dispersion of the pigment and filler was therefore assured. The high shear rates encountered, however, necessitated the use of an anti-foaming additive.

2.1. Materials

The binder for the paint formulations is Synthomer 47B40, (from Synthomer, UK), a carboxylated styrene butadiene rubber latex (c-SBR); it is a random copolymer consisting of 37% w/w butadiene, 61% w/w styrene and 2% w/w of carboxylate functional monomer. The talc used was Viatalc® 30 from Viaton with a surface area of 0.3 $m^2\,g^{-1}$ and a median particle size of 10 μm. This will be referred simply as talc. The titanium dioxide used was a coated rutile variety (Tioxide® TR92 by Huntsman Pigments) with a surface area of 14 $m^2\,g^{-1}$ and a median particle size of 240 nm, and will be referred to as TR92. The proprietary coating on the TR92 featured a mixed alumina and zirconia layer followed by a shell of alumina which was finally treated with an organic treatment (most probably an alcohol such as pentaerythritol or trimethylol propane). The mixed oxide layer forms a physical barrier between the TiO_2 surface and the polymer matrix and the alumina and organic layers promote desired interfacial properties both in the wet and dry films. The anti-foam additive was Surfinol® 104e ((S104e) Air Products), and is 50% v/v 2,4,7,9-tetramethyl-5,6-decyne-4,7-diol in ethan-1,2-diol). The S104e was used at a level of 0.2% w/w (active mass) of the total formulation. The dispersants selected for the titanium predispersion and talc in the final formulation, were supplied by the Noveon Division of Lubrizol Limited. Specific selection of the dispersants and dosage determination was accomplished via dispersion rheology studies on aqueous dispersions of talc and titanium dioxide. Solplus® D540 (D540) was selected for the titanium dioxide and Solsperse® 27000 (S27000) selected for the talc. The stabiliser used for these studies was Wingstay® L (Eliokem), and was available as a 50% w/w aqueous pre-dispersion produced by Aquanox (Aquanox® L 50% w/w). Winstay® L is a hindered phenolic antioxidant that can be described as a butylated reaction product of 4-methyl phenol and dicyclopentadiene. It should be noted that the c-SBR latex contains a minimal base level of phenolic antioxidant already incorporated to reduce oxidation during storage.

2.2. Dispersion of the fillers and pigment and paint preparation

In order to properly disperse the titanium dioxide in the c-SBR latex, a pre-dispersion in water (60% w/w titanium dioxide with 4 phf Solplus® D540) was prepared as follows: The required amount of D540 was added to the water and agitated using the Dispermat® F1 fitted with the saw tooth agitator and water jacketed mixing vessel, for 5 min at 5000 rpm. The titanium dioxide was then added whilst agitation continued and after 5 min of further agitation the saw tooth mixer was changed for the bead milling attachment. Glass beads (200 phf) of 1 mm diameter were added and bead milling was carried out for 1 h at 500 rpm. The glass beads were separated from the dispersion by filtration.

This pre-dispersion was used in all the formulations. The later was produced using the following addition sequence: required amount of titanium dioxide pre-dispersion; c-SBR latex (slow addition); defoamer (S104e) [5 min agitation]; stabiliser dispersion [10 min agitation]; addition of S27000 (1.0 phf); addition of talc [60 min agitation]. The resulting paint was then kept in sealed in screw top glass jars.