

# MANUFACTURE AND TESTING OF WATER-BORNE PAINTS BY USING VINYL LATEX CONTAINING VeoVa10<sup>®</sup> MONOMER

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**Abstract**— Two different water-borne dispersions (latex) containing different amounts of vinyl acetate and a commercial vinyl ester monomer (VeoVa10) were evaluated by incorporating them in paint formulations for wall protection. Three paint formulations were prepared with different PVC values. The main properties such as hiding power, washability, tension of adhesion, and elasticity were assessed. Changes in color, gloss and adhesion and the extension of chalking, checking, cracking and blistering were also evaluated in normal and accelerated weathering tests. The results indicate that both dispersions are suitable for wall protection (interior or exterior, permanent or temporary protection) and they are compatible with the most common additives used in the Argentinean and Mercosur markets. The presence of VeoVa10 in the binder composition improves the water and UV resistances of the paint. A styrenic-acrylic latex, commonly used in the local market, was used as comparative product.

**Keywords** — water-borne paints, vinyl binders VeoVa10<sup>®</sup> latex, wall protection

## I. INTRODUCTION

Latex dispersions for water-based coating formulations with low amount (or zero) of volatile organic compounds (VOCs) are obtained typically from emulsion polymerization. To produce decorative and long lasting films adequate pigments, fillers and additives are added.

With the purpose of obtaining the best coating performance with a good balance of price, it is necessary to add the smallest quantity of binder. Considering that the binder is both the promoter in the adhesion of the film coating to the substrate and the pigment packing and the fillers, a large quantity of binder reduces the hiding power of the coating.

Latex paints are most commonly applied on in- and outdoor masonry substrates. In the first case, the decorative feature is intended to be highlighted (color, gloss, film uniformity), and in the second one the resistance to aggressive agents of the environment against the film coating (UV-radiation, humidity, rain, pollution, high temperature).

Other properties such as hardness, elasticity and adhesion should be suitable enough to last ageing. Polymeric vinyl dispersions have been used for the formulation of water-based coating to be applied on masonry (Flick, 1975). However the slight resistance to water and to UV radiation of the films has limited their use and they have been substituted by acrylic dispersions that posse better resistance properties, but with a higher cost. The introduction of new vinyl compounds has contributed to the development of vinyl dispersions with better properties. In particular a Vinyl ester of Versatic acid known as VeoVa<sup>®</sup> (Shell Chemicals, 1988), which contains a polymerizable double bond, has been successfully used.

The general chemical formula of the VeoVa is shown in Fig. 1, where R1 and R2 are (branched) alkyl groups.

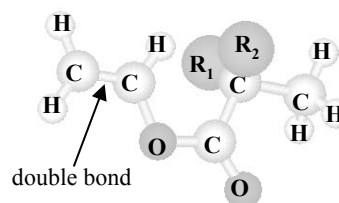


Figure 1: Chemical structure of VeoVa.

According to the total number of carbon atoms three derivatives VeoVa9, VeoVa10 and VeoVa11 are known. In this work dispersions which contain 10 carbon atoms isomers VeoVa10, for which  $R_1+R_2 = C_7H_{16}$  were tested.

The (co)polymerization in emulsion of VeoVa10 with vinyl acetate (VAc) originates vinyl latex that produces films with better water resistance, UV-resistance and alkali resistance which lead to superior durability higher than those produced by pure vinyl latexes (Aten and Vegter, 1970). VeoVa and VAc have similar reactivity in radical polymerization (Resolution Performance Products, 2001) and the random (co)polymerization protects the ester group of VAc from hydrolysis through the so-called "umbrella effect", improving the hydrolytic stability of the polymer (Decocq *et al.*, 1999). This enables such polymers to be successfully used as paint binders on alkaline substrates, such as exterior concrete. The highly branched hydrophobic struc-

ture of VeoVa also enhances the latex and final coating properties. Additionally, VeoVa10 based polymers exhibit the required hardness/flexibility for the formulation of a range of high-performance interior and exterior latex paints (Decocq *et al.*, 1999).

Copolymerization with non-vinyl monomers is also possible. For example a solvent-free binder of low MFFT has been recently developed using 2-HEA as (co)monomer (Hendrick and Nootens, 2001).

VAc/VeoVa10 based latex can be stabilized by surfactants and a functional monomer as a colloid-free system, or by a combination of surfactants and protective colloid giving in this way a colloid-stabilized system.

On the other hand, depending on the total number of carbon atoms, the polymer exhibits different glass transition temperature ( $T_g$ ) values. VeoVa content modifies also the final  $T_g$  of the polymer and therefore the water and UV resistances. These are essential facts to obtain a high performance coating.

A good review about properties and applications of dispersion containing VAc and VeoVa copolymers has been recently published (Vandenzande *et al.*, 1997).

In Europe, architectural paints represent over 90% of the market for VeoVa10 dispersion. Nearly, one-half of these latexes are used for interior applications and the other half is divided between exterior and general markets (Vandenzande *et al.* 1997). Substrates in Europe are quite different from those typically used in the United State of America (USA) due to the construction methods. In the USA the use of paper-faced drywall is common but in Europe the majority of substrates are inorganic, including brick and concrete. Thus, additional alkaline resistance is expected in this case. The different substrate properties then modify the type and relative amounts of vinyl acetate containing resins. In both regions, Europe and USA, the vinyl-based resins dominate, but the binder composition is different between the two regions. Vratsanos (2001) has reported that the VAc resins in the European Union are mainly VAc/VeoVa resins, about 34% of the overall market. Vinyl/acrylics dominate the US market with 61% of the overall water-based architectural market. Significantly, more styrene acrylic resin is used in the EU, while the amounts of acrylic are roughly comparable (Anonymous, 1998). In Argentina, the use of vinyl resins is also important and the substrates used are similar to those used in Europe, so VAc/VeoVa10 resins could be good performance binders. However, as far as the authors' knowledge no studies or lab tests using (co)polymers of VeoVa monomers in a typical local paint formulation are available, so the aim of this work was to test two types of water-borne dispersions containing 20% and 30% w/w of VeoVa10. As stated above the dispersions used were colloids stabilized, which show a rather different behavior compared to the common surfactant stabilized dispersions (Bondy and Coleman, 1970). Having in mind only comparative purposes and taking into account the possible differences arising from the stabilizing sys-

tems, a typical styrenic-acrylic dispersion of common use in the local market was included in this study.

## II. METHODS

### A. Latex dispersions

The latex dispersions used in this work were kindly supplied by Shell Chemicals (Netherlands). The solid content of VAc/VeoVa10 dispersions was  $54 \pm 1\%$ . MFFT and particle sizes were  $17 \pm 1$  °C and  $460 \pm 20$  nm respectively for the 80/20 dispersion; and  $15 \pm 1$  °C and  $420 \pm 20$  nm respectively for the 70/30 dispersion (data from the supplier). The solid content of styrenic/acrylic dispersion was 50 %, MFFT ca. 18 °C and the particle size about 100 nm (data from the supplier).

### B. Coating preparation

A typical high-speed disperser (working range from 1,200 to 2,600 rpm) having a container of double bottom water-cooled so as to work at less than 30° C, was used in order to obtain the paint dispersions. The container was filled with the whole amount of water of the formulation where the thickener/antissettling agent had been previously added. Agitation started with the selective addition of the remaining additives and pigments. After that, speed increased up to the highest level until a 20/30 grade of dispersion, according to ASTM D 1210 (2001). Finally, the milling system speed decreased and the latex dispersion was added agitating it in order to obtain a full homogenization.

### C. Composition and formulation of coatings

The amount and types of pigments together with the used fillers are considered in the composition of coatings. They contribute to the hiding power and to the pigment volume concentration (PVC) of the coating film. The following additives were selected for the preparation of the latex paints:

- Dispersing agent naphthenate-formaldehyde sodium salt obtained by condensation (25% in water).
- Thickener and colloid protector hidroxypropylmethylcellulose 4000 cp enough to obtain a final paint of 66 KU Stormer viscosity.
- Surfactant, non-ionic nonyl phenoxy polyethanol
- Antifoaming agent, low viscosity silicone.
- Coalescing agent, TEXANOL<sup>®</sup> (2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate ester).

Titanium dioxide, rutile,  $\rho = 4.20$  g/cm<sup>3</sup> (Paul, 1977) was used in the preparation as white hiding pigment and precipitated calcium carbonate,  $\rho = 2.75$  g/cm<sup>3</sup> (Paul, 1977) as filler.

Three types of paints were prepared with different content of binders.

The composition, properties and identification of tested paints for each binder content value are shown in Table 1. The painted panels were identified as in Table 2.

Table 1. Composition and properties of tested paints.

Paint component (g) / Identification	#10	#15	#20
Titanium dioxide (rutile)	10.0	10.0	10.0
Calcium carbonate	40.0	40.0	40.0
Latex dispersion (50 % w/w)	10.0	15.0	20.0
Additives and water to get	100.0	100.0	100.0
Properties			
Solid content (% w/w)	55.0	57.5	60.0
Solid content (% v/v)	22.8	25.7	27.8

Table 2: Identification of painted panels

	VAc/VeoVa10 70/30	VAc/VeoVa10 80/20	Styrenic- acrylic
#10	05-S-10	06-S-10	A-10
#15	05-S-15	06-S-15	A-15
#20	05-S-20	06-S-20	A-20

**D. Tests on coatings**

*Hiding power*

In order to obtain the total hiding power of a contrast surface (white and black.), the necessary thickness of the coating film was determined (IRAM 1109-A25, 2003). Successive coats of wet paint films were performed by using a Bird type draw-down blade at constant thickness (50 or 75 μm) on transparent glass. A drying time of 24 h was allowed between coats.

*Washability test*

Coating was applied on frosted glass (roughness R<sub>M</sub> 20 micrometers) with a 150 micrometers Bird type draw-down blade. After allowing a drying time of 7 days at room temperature, the test was carried out according to IRAM 1109-B15 (1984), by wetting the coating film with distilled water and scrubbing it with an equipment from Gardner (ASTM 4828, 1999).

The results are expressed in double oscillations, which are necessary to eliminate the coating film in the scrubbing central area, the wetting of the surface and the abrasion that results from the scrub brush are mainly obtained.

*Adhesion test*

Adhesion measurements were carried out using an Elcometer Model 106 according to ASTM D 4541 (1998) Standard Specification on a fibrocement panel. Two coats of paint under test were applied by brush, with a drying time of 24 hours between coats. It was allowed to cure at room temperature and then the metallic elements were adhered to the painted surface with liquid epoxy resin without solvents. The tensile test was carried out with the dynamometer.

*Mandrel Bend Test*

Elongation. The ¼ inch (6.4 mm) diameter mandrel was chosen to perform this test (ASTM D 522, 1998). The elongation of paint is in this case 14%. Two coats of paint were applied on substrate of sheet metal, allowing

a drying time between coats and kept in laboratory atmosphere (RH 65 ± 5% and 20 ± 2°C) for 7 days.

Tests were carried out at - 5 °C and at 20 °C and then panels were aged at 80 °C for 24 hours, the determinations were performed again at - 5°C and at 20 °C. Rating of visual defects (cracking) was designated according to Table 1 of ISO 4628 (2003) international standard.

*Weathering test*

150 x 300 mm fibrocement panels were painted (two coats) with a drying time of 24 hours between coats. They were placed on a rack at CIDEPINT terrace 45° to the North. The following observations and determinations took place every 3 months: change of color (Table 3, ISO 4628, 2003), Pfund chalking (ASTM D 4214, 2001), checking (ASTM D 660, 2001), blistering (ASTM D 714, 2001), and crackling (ASTM D 661, 2001). Adhesion test was also performed after the weathering testing.

*Accelerated ageing test*

It was carried out in a Weather-Ometer Sunshine ARC XW. This equipment produces four functions that accelerate coating film ageing. Water rain on the panels every 3 minutes with distilled water at room temperature; temperature at 60°C; high humidity (almost to a saturation level) and light action carbon-arc (UV, visible and IR radiation). This test is correlated with that of exterior exposure, assuming that 350 hours exposure equals 12 months exterior exposure (Aznar y Rascio, 2006). Fibrocement panels with two coats of paint were exposed.

**III. RESULTS AND DISCUSSION**

Tables 3-8 show the results obtained from the tested panels. Table 3 also includes the hiding power of the three paints.

According to Table 3 and bearing in mind the method used, the hiding power observed for all paints is from a practical point of view almost the same. This is because the hiding power is mainly related to the pigment content.

Table 4 shows the wet abrasion resistance results. For low and intermediate binder content the abrasion resistance for similar composition is comparable.

Table 3. Hiding power tests results

Panel ID	Thickness of wet coat to get total hiding (μm)			
	Draw-down bar thickness			Total thickness (μm)
05-S-10	75	75	---	150
05-S-15	75	75	50	200
05-S-20	75	75	75	225
06-S-10	75	50	---	125
06-S-15	75	75	---	150
06-S-20	75	75	75	225
A-10	75	75	---	150
A-15	75	75	50	200
A-20	75	75	75	225

Table 4. Wet abrasion resistance.

Panel ID	Number of double oscillations for peeling off
05-S-10	1.000
05-S-15	4.000
05-S-20	15.000
06-S-10	1.500
06-S-15	3.800
06-S-20	15.000
A-10	1.800
A-15	4.000
A-20	> 15.000

Table 5. Adhesion test results.

Panel ID	Adhesion tension (kg.cm <sup>-2</sup> )
05-S-10	2
05-S-15	5
05-S-20	10
06-S-10	2
06-S-15	6
06-S-20	11
A-10	3
A-15	6
A-20	12

Table 6. Elasticity (6 mm mandrel test)

Aging	7 days at room temperature		7 days at room temperature + 24 h at 80 °C	
	20 °C	-5 °C	20 °C	-5 °C
Temperature				
05-S-10	Nil	4	Nil	Nil
05-S-15	Nil	2	Nil	Nil
05-S-20	Nil	Nil	Nil	Nil
06-S-10	Nil	4	Nil	2
06-S-15	Nil	2	Nil	Nil
06-S-20	Nil	Nil	Nil	Nil
A-10	Nil	4	Nil	Nil
A-15	Nil	2	Nil	Nil
A-20	Nil	Nil	Nil	Nil

As expected for high binder content (20%) the abrasion resistance increased considerably.

Results from adhesion test (Table 5) are similar for all coatings, increasing with the binder content as expected.

In the mandrel bend test (Table 6), similar behavior for all coatings at 20 °C was observed. At low temperature (-5 °C) and low and intermediate binder content the elasticity is not suitable and 20 % of binder is needed for a good performance of the coating. Samples aged at 80 °C show better performance, probably due to a better coalescence of the film as a consequence of the thermal treatment. A small degree of cracking was observed in the 06-S-10 panel, due probably to the slightly

higher  $T_g$  of 06-S series compared to the 05-S one (lower content of the "flexibilising" low  $T_g$  VeoVa10 monomer).

Tables 7a, b and c show the results corresponding to 5 years tests of natural aging. The color and gloss do not change after natural exposition, but a considerable loss of coating is observed for low binder content. The general behavior is similar for all coatings, but a some degree of darkening was observed for A and 06-S series, while a negligible darkening was observed for 05-S series due to a higher content of VeoVa10 monomer. This should be due to the improved stability of the polymeric ester group when increasing monomer content (Decocq *et al.*, 1999). The adhesion tension after the natural aging test, increased in all cases, due to a complete coalescence of films.

Table 7a. Natural exposition (5 years) for A-panels

Panel identification	A-10	A-15	A-20
Color	White	White	White
Color change (visual)	Nil	Nil	Nil
Chalking (Pfund)	6	8	Nil
Cracking (obs. 10X)	6	8	Nil
Checking (obs. 10X)	Nil	Nil	Nil
Blistering	Nil	Nil	Nil
<b>Adhesion (kg.cm<sup>-2</sup>)</b>			
Initial value	3	6	12
Final value	4	6	15

Table 7b. Natural exposition (5 years) for 05-S-panels

Panel identification	05-S-10	05-S-15	05-S-20
Color	White	White	White
Color change (visual)	Nil	Nil	Nil
Chalking (Pfund)	8	Nil	Nil
Cracking (obs. 10X)	8	Nil	Nil
Checking (obs. 10X)	Nil	Nil	Nil
Blistering	Nil	Nil	Nil
<b>Adhesion (kg.cm<sup>-2</sup>)</b>			
Initial value	2	5	10
Final value	4	8	16

Table 7c. Natural exposition (5 years) for 06-S-panels

Panel identification	06-S-10	06-S-15	06-S-20
Color	White	White	White
Color change (visual)	Nil	Nil	Nil
Chalking (Pfund)	6	8	Nil
Cracking (obs. 10X)	6	8	Nil
Checking (obs. 10X)	Nil	Nil	Nil
Blistering	Nil	Nil	Nil
<b>Adhesion (kg.cm<sup>-2</sup>)</b>			
Initial value	2	6	11
Final value	5	10	15

Figure 2 shows the test panels after 5 years of natural exposition. At low binder concentration (high PVC) none of the paints are suitable for exterior protection. Coatings with 15 % of binder, behaved better and as expected those prepared with 05-S (higher amount of VeoVa10) gave a better performance. Anyway, from a practical point of view and bearing in mind the normal repainting work in 5 years, the three formulations with 15 % of binder are adequate for exterior wall protection. Increasing the binder content to 20% the durability increased but at higher cost.

Tables 8a, b and c show the results of accelerated aging.

All panels retain their initial white color and gloss after the accelerated test and the general behavior is similar for all coatings, only a small degree of yellowing, due to titanium dioxide pigment degradation, was observed for A and 05-S, series only at low and intermediate binder content, while no yellowing was observed in all cases for the 06-S series.

As in the natural aging test, the adhesion tension after the accelerated aging test, increased in all cases, due to a complete coalescence of films.

Increasing the VeoVa10 concentration in general resulted in higher durability, related to the improved flexibility of the polymer (Decocq *et al.*, 1999).

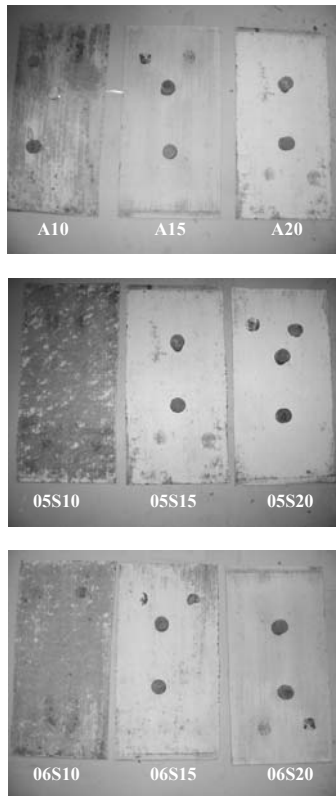


Figure 2. Test panels after 5 years of natural exposition.

#### IV. CONCLUSIONS

1. Paint samples by using the three dispersions gave good results in lab tests, as appropriated for masonry interior and exterior. Depending on the

binder content three types of coatings can be formulated;

- a) ceiling or temporary coating (easy-removing paint) (10 % of latex dispersion),
  - b) interior coating (15 % of latex dispersion),
  - c) exterior coating (20 % of latex dispersion).
2. VeoVa10 addition into the polymer chain improves water and UV-resistance properties, making vinyl latex paints suitable as exterior protecting coatings.
  3. Coatings containing binders with 30 % w/w VeoVa10 monomer showed the best performance in exterior tests.
  4. Initial adhesion and elasticity properties for VeoVa10 containing binders were lower than the styrenic-acrylic dispersion (no VeoVa10). After ageing, however, properties were similar for all paints.

Table 8a. Accelerated aging test results for A-panels

Panel identification	A-10	A-15	A-20
Color	White	White	White
Color change (visual)	1	1	Nil
Chalking (Pfund)	6	6	8
Cracking (obs. 10X)	6	6	Nil
Checking (obs. 10X)	Nil	Nil	Nil
Blistering	F3 No. 6	Nil	Nil
<b>Adhesion (kg.cm<sup>-2</sup>)</b>			
Initial value	3	6	12
Final value	3	7	15

Table 8b. Accelerated aging test results for 05-S-panels

Panel identification	05-S-10	05-S-15	05-S-20
Color	White	White	White
Color change (visual)	2	2	Nil
Chalking (Pfund)	6	6	8
Cracking (obs. 10X)	6	Nil	Nil
Checking (obs. 10X)	Nil	Nil	Nil
Blistering	Nil	Nil	Nil
<b>Adhesion (kg.cm<sup>-2</sup>)</b>			
Initial value	2	5	10
Final value	5	8	16

Table 8c. Accelerated aging test results for 06-S-panels

Panel identification	06-S-10	06-S-15	06-S-20
Color	White	White	White
Color change (visual)	Nil	Nil	Nil
Chalking (Pfund)	6	8	8
Cracking (obs. 10X)	6	Nil	Nil
Checking (obs. 10X)	Nil	Nil	Nil
Blistering	Nil	Nil	Nil
<b>Adhesion (kg.cm<sup>-2</sup>)</b>			
Initial value	2	6	11
Final value	8	9	16

5. VeoVa10-containing binders tolerated water-based additives incorporation and pigments of common use in the local market and high PVC paint formulations were easily prepared.

As a general conclusion, coatings prepared using VeoVa10-containing binders are useful for interior or exterior wall protection, and display similar properties to those of coatings prepared by using styrenic-acrylic dispersion, with lower price.

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