

# Glossy topcoat exterior paint formulations using water-based polyurethane/acrylic hybrid binders

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## Abstract

The development of glossy topcoat one-pot exterior paint formulations using water-based polyurethane/acrylates hybrid binders as well as the assessment of its properties through different conventional tests is discussed in this work. Polyurethane (PU) anionomer having 2-ethoxymethacrylate terminal groups was prepared following a prepolymer mixing process. This prepolymer was chain extended in aqueous solution and after addition of acrylic monomers radical polymerized. Paints were prepared using titanium dioxide as unique pigment. Panels coated with air-dried paints with three pigment to volume concentration (PVC) values were subjected to standardized tests including adhesion, flexibility, gloss and color determination. Accelerated weathering tests were carried out to evaluate changes in properties, especially gloss and color, of painted panels. Solvent-based acrylic and polyurethane paints were included as high gloss quality reference coatings. It was found that air-dried formulations based on hybrid polyurethane/acrylic with up to 50 wt.% of acrylic component, show a gloss as high as 70 and the relative gloss change after accelerated weathering test is lower than the pure solvent-based acrylic and polyurethane paints.

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## 1. Introduction

Polyurethane-based coating systems have a proven record in the coatings industry dominating the market in some applications because they exhibit a high level of quality. In addition, PU coatings are solvent and chemical resistant offering good weather stability. It is possible to formulate both clear coats and pigmented topcoats with a high gloss finish. The films have very good mechanical properties and provide the ideal balance of hardness and flexibility, even at low temperatures. Good scratch resistance is also a feature of polyurethane coatings. This high level of quality results from the primary and secondary structures of the polyurethane chains. The polymer chains (hard and soft segments) are protected against solvents, acids, bases and other chemicals by the urethane groups which are resistant to

chemicals and by the hydrogen bridge bonds forming a stable physical network. The hydrogen bridge bonds and the block-like structure of the polyurethane chains, which can combine and arrange themselves in microdomains, ensure the excellent mechanical properties of the paint film. PU coatings allow high variability of the property profile and can be fitted for a specific application by changing, for example, the chemical structure of the soft segments (polyether, polyester or polycarbonate), the distribution and length of the hard segments or the molecular weight and degree of branching of the chains. The hard segments are related to the hardness, strength and toughness of the paint film and the soft segments determine the flexibility and the glass transition temperature ( $T_g$ ). Polyurethane chemistry also permits the incorporation of functional groups, which can be used to change properties. Polyurethane coatings may dry in different ways, including physical drying and chemical drying, like oxidation or with the aid of a cross linking agent. Solvent-borne two components PU coatings have been used for many years in a wide variety of applications [1] where high performance is required in terms of film appearance and resistance properties. However, nowadays the main mar-

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ket requirement is products with reduced emission (low VOCs) and the coating industry and the manufacturers of coating raw materials have been forced to increase their efforts in developing suitable products and technologies. There are a number of options for producing low VOC coatings including waterborne polyurethane. These new waterborne systems must fulfill the property profile of similar solvent-borne systems. Waterborne PU technology is now a very common practice in the industry. However PU coatings (solvent or water-based) are in general more expensive than acrylics and in some applications there are cost restrictions. To take advantage of PU film-forming properties, a combination with cheaper materials is now coming a common practice in the coating market, leading to new different products. One of the most popular second component is the acrylic dispersion and the new product combines the excellent mechanical and chemical properties of the PU resin with the low price of the acrylic component. There are some papers dealing with combinations of PU with acrylic dispersions, which include PU as a co-binder of acrylic emulsions [2] dispersants [3], physical mixtures and composites [4–7]. In a new type of dispersion, a chemical coupling between the urethane and the acrylic components is established, and these dispersions are known as polyurethane-acrylates or acrylic-polyurethane hybrids [8–11]. Unsaturated polyurethane resins are reacted with acrylic monomers in the aqueous phase in a special copolymerization process to produce solvent free PU-acrylates hybrid dispersions. This type of chemical coupling was also used to prepared UV-curable polyurethane-acrylates composites [12–14] and emulsions [15]. These hybrid systems should produce binders with better technological properties in paints than those obtainable from physical mixtures of the two polymers or composites, and several studies were performed in connection with film properties. It was reported that they have improved shear resistance due to the ionic stabilization of the urethane component. Their water resistance is also good, since little or no external emulsifiers are required for stabilization. Kim and Lee [11] investigated the effect of the monomer amount and the type on the film properties of acrylic-PU hybrid and found that the film properties increased with the amount of acrylates incorporation. Hirose et al. [16] investigated the structure and properties of acrylic-polyurethane hybrid emulsions. They found that the emulsions form a core-shell structure in the aqueous media and the adhesion properties depend on the character of the shell component. Recently, Kukanja et al. [17] reported a comparison of mechanical properties of hybrid and physical blends. Hybrid emulsions have better chemical and mechanical properties than blends. Hegedus and Kloiber [6] compared the film properties and coatings made from an acrylic emulsion, a polyurethane dispersion and three acrylic-polyurethane alloy dispersions, but little information is given to allow a detailed analysis of results. However to the knowledge of the authors, no systematic studies on coating properties and performance varying the proportion of the acrylic component have been performed using hybrids like PU/acrylic as binders. Different acrylic monomers can be included in these hybrid systems, but since copolymers of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) are commonly used in paint and coating for-

mulations it seemed of interest to test the effect of the overall acrylic content in the performance of coatings prepared from them.

## 2. Experimental

### 2.1. Dispersion preparation

#### 2.1.1. Materials

Isophorone diisocyanate (IPDI), polypropylene glycol (PPG) Mw 1000 (Voranol 2110), dimethylol propionic acid (DMPA), 2-hydroxy ethylmethacrylate (HEMA), *N*-methyl-2-pyrrolidone (NMP), triethylamine (TEA), ammonium persulfate (APS), hydrazine monohydrate (H2M) and dibutyltin dilaurate (DBTDL) were of analytical grade. PPG was dried and degassed at 80 °C at 1–2 mm Hg overnight before used. DMPA was dried at 80 °C for 2 h in an oven. Acrylic monomers, *n*-butyl acrylate (*n*-BuA), methyl methacrylate (MMA), methacrylic acid (MAA), hydroxy propyl methacrylate (HPMA), ethylene glycol methacrylate (EGDMA) were cleaned before used. NMP and TEA, were dried over 4 Å molecular sieves before used. Surfactants Ethoxyl A-25 (Indioquímica), Arkopal N-230 and N-40 (Clariant Argentina) were used as received.

#### 2.1.2. Prepolymer synthesis

A 1000 ml six-neck separable flask with a mechanical stirrer, thermocouple, condenser, sampling tube, and inlet system for dry N<sub>2</sub> and pump feed inlet was used as a reactor. A tube with a drying agent (CaCl<sub>2</sub>) was fitted in the condenser to avoid atmospheric moisture coming into the reaction flask. IPDI, PPG, DMPA, NMP were charged into the dried flask. While stirring, the mixture was heated to 90 °C and homogenized for approximately 1 h, followed by addition of DBTDL catalyst. The mixture was allowed to continue at this temperature for approximately 2 h until the isocyanate (NCO) content reached the desired value. The free isocyanate content was determined using the conventional dibutylamine back-titration method [18]. The same technique was also applied to raw materials. Upon obtaining the theoretical NCO value (ca. 5%) HEMA was added slowly and allowed to react for approximately 1.5 h at 45 °C. In the last part of the HEMA feeding, the temperature was raised to 60 °C and kept constant for 1.5 h. As the NCO content reached the theoretical value (2.4%) the mixture was cooled to 55 °C and the required amount of TEA was fed in slowly over 30 min. After neutralization the temperature was lowered at room temperature.

#### 2.1.3. Emulsification and chain extension

An aqueous dispersion of PU was obtained by adding the PU prepolymer to water at 30 °C at 300 rpm in a water jacket glass reactor for temperature control. After emulsification the appropriate amount of H2M was added to perform the chain extension reaction (45 min). The resulting PU dispersion containing 30 wt.% solid content was divided into six parts and after addition of the required amount of acrylic monomers they were polymerized (see below).

#### 2.1.4. Emulsion polymerization

The emulsion polymerization of PU-acrylic mixtures was performed in batch mode using a glass reactor (500 ml) with a water jacket for temperature control and the emulsion polymerization was started by adding an aqueous solution of initiator. The resulting product was a stable dispersion of pH 8 and with solid content of approximately 30 wt.% as determined by gravimetric analysis. The composition (wt.%) of the acrylic component was *n*-BuA 19.6, MMA 78.4 and MAA 2.0.

#### 2.1.5. Pure acrylic dispersion

The pure acrylic dispersion was prepared using a semicontinuous emulsion polymerization method. A 2 l capacity glass reactor fitted with condenser, stirrer, nitrogen inlet, thermocouple and feeding of chemicals was used. Polymerization was performed at 80 °C and 200 rpm, starting the reaction with 10 wt.% of the monomer mixture and the aqueous solution of the initiator (0.15 wt.% on monomer base). After feeding the remaining monomer mixture and initiator solution the reaction was conducted during 4 h and the dispersion was fixed at pH 9 using an ammonium hydroxide aqueous solution.

#### 2.1.6. Dispersion characterization

Particle size was determined by dynamic light scattering (DLS) with a Malvern 4700 instrument. This technique gives an intensity weighted average particle size,  $d_{\text{int avg}} = \Sigma(n_i I_i d_i) / \Sigma(n_i I_i)$ , where  $I_i$  is the intensity of light scattered from  $n_i$  particles of diameter  $d_i$  and is close to the  $z$ -average particle size ( $d_z = \Sigma(n_i d_i^7) / \Sigma(n_i d_i^6)$ ). Solid content was determined by gravimetric analysis and density by using a Micromeritics AccuPyc 1330 He-pycnometer.

### 2.2. Coating manufacture

#### 2.2.1. Paint preparation

Water-based paints were prepared using the binders described previously at three PVC values namely 10, 15 and 20% using titanium dioxide (rutile). The pigment was mixed using a high-speed mixer with a double jacket vessel and a small amount of dispersant agent (Polacril D, 28 wt.%, Diransa San Luis – Argentina). Glass beads (equivalent to 1/3 of paint volume) were added during the dispersion and filtered out after getting the final degree of dispersion 0–10 according to ASTM 1210 [19]. Final viscosity of 65 U.K (20 °C, Stormer [20]) was fixed with a small amount of cellulose-based thickener (Natrosol® B hydroxyethylcellulose, Hercules – USA). Typical latex paint additives from the local market were also used (see Tables 2–4).

#### 2.2.2. Application

The formulated paints were brush applied on SAE 1010 [21] steel panels (7.5 cm × 15 cm × 0.2 cm), previously degreased with toluene, sandblasted to ASa 2½ according to SIS 05 59 00 [22] and with one coat of anticorrosive alkyd paint. Two coats of the topcoat white paints were applied and the treated panels were kept in laboratory atmosphere (RH 65 ± 5% and 20 ± 2 °C) for 7 days.

Table 1

Summary of particle size and density data for the acrylic/polyurethane hybrids dispersions studied in this work

Dispersion type	Acrylic content (wt.%)	Particle diameter (nm) <sup>a</sup>	Density (g cm <sup>-3</sup> ) <sup>b</sup>
PU dispersion	0	131	1.100
Ac/PU 10/90	10	250	1.165
Ac/PU 20/80	20	213	1.130
Ac/PU 30/70	30	256	1.128
Ac/PU 40/60	40	220	1.141
Ac/PU 50/50	50	232	1.163
Acrylic dispersion	100	127	1.187

<sup>a</sup> Determined from DLS studies.

<sup>b</sup> Measured by helium pycnometry.

Table 2

Solvent-based acrylic paint formulation

Component, PVC	wt.%		
	10	15	20
Acrylic resin (Indacryl SC1170, Indur), 60 wt.%	42.00	38.00	36.20
Titanium dioxide (rutile) (Bayertitan, Bayer)	14.00	18.00	20.00
Aerosil 380 (fumed silica)	0.87	0.86	0.84
Bentone SD-1 Rheological additive (Rheox)	0.25	0.26	0.27
Diocetyl phthalate (DOP)	3.95	3.77	3.30
Toluene	18.96	18.87	18.66
Xylene	7.12	7.12	7.12
Solvesso 100 (Esso)	12.27	12.55	13.25
Octylic alcohol	0.32	0.32	0.32
Soya lecithin	0.26	0.25	0.24

Table 3

Solvent-based polyurethane paint formulation

Component, PVC	wt.%		
	10	15	20
Part A			
Desmophen A450BA/X, hydroxyl-bearing polyacrylate, 50 wt.%, butylacetate/xylene, 1:1 (Bayer)	18.80	17.70	15.52
Indacryl SM1528 60 wt.% xylene/butyl acetate, acid index: 5 mg KOH/g	14.16	13.16	12.46
Bentone SD-1 Rheological additive (Rheox)	0.44	0.43	0.53
Octylic alcohol	0.43	0.42	0.52
Titanium dioxide (rutile) (Bayertitan, Bayer)	14.01	16.68	20.93
Toluene/MEK, 1:1	35.45	35.47	34.67
Part B			
Desmodur N75 (75 wt.%), xylene	17.30	16.67	15.37

### 2.3. Laboratory tests

#### 2.3.1. Specular gloss

Specular gloss was determined at 60° using Dr. Lange REFO 3D instrument according to ASTM E 284 [23].

#### 2.3.2. Color determination

Chromatic coordinates (*L*, *a* and *b*) were measured using a REFO 3D (Dr. Lange) instrument according to ASTM E 308 [24].

Table 4  
Water-based paints formulation

Component, PVC	wt. %		
	10	15	20
Water-based dispersion (33 wt.%)	76.51	72.01	68.41
Titanium dioxide (rutile) (Bayertitan, Bayer)	13.50	18.00	21.60
Rheolate 255	0.23	0.23	0.23
Rheolate 350	0.12	0.12	0.12
Diocetyl phthalate	0.27	0.29	0.30
Tween 80	0.44	0.45	0.46
Parmetol DF19 Forte (carbendazim, diuron) (Schülke & Mayr)	0.38	0.38	0.38
Nopco NXZ (Deofamer)	0.28	0.28	0.28
Texanol	0.25	0.23	0.22
Water	8.02	8.01	8.00

### 2.3.3. Flexibility

The 3.2 mm mandrel (equivalent to 28% of elongation) was chosen to perform this test [25]. One layer of topcoat paint was applied on steel panels (0.4 mm thick) and kept in laboratory atmosphere (RH  $65 \pm 5\%$  and  $20 \pm 2^\circ\text{C}$ ) for 7 days.

### 2.3.4. Adhesion

Adhesion measurements were carried out using the tape test method according to ASTM D 3359 standard specification [26].

### 2.3.5. Buchholz hardness

Hardness was carried out using an indentation method according to DIN 53153 [27].

### 2.3.6. Washability

Washability measurements were carried out using a standard method according to ASTM D 4828-1999 [28].

### 2.3.7. Accelerated weathering (Xenon lamp type) and water exposure apparatus

Panels were exposed for 700 h according to ASTM G 155 [29]. The aging cycle applied on panels was a continuous UV radiation lamp working at 6000 W (luminous flux 2.1 parts per million),  $500\text{ cm}^3\text{ min}^{-1}$  of water for specimen and keeping at 100% RH and  $60/65^\circ\text{C}$ . The specular gloss at  $60^\circ$ , flexibility and adhesion were measured before and after test. The color modification of panels and common surface defects, like cracking and blistering were also evaluated.

For adhesion and non-destructive tests (gloss, color and hardness) five determinations were performed for each sample according to the standard specification. For washability and flexibility tests determinations were performed in two panels for each sample.

## 3. Results and discussion

### 3.1. Dispersions properties

Table 1 shows selected properties of dispersions used in this work. The physical mixtures have, as expected, similar particle sizes to those of the pure PU and acrylic dispersions and

hybrids have, as expected, bigger particle sizes than those of the mixtures, due to the polymerization method. According to Hirose et al. [16] this particular method where both components have carboxylic functionality, gives core-shell particle structure and the PU component occupies the shell region of the particle. The final size should be the result of a balance between the relative amount of PU dispersion acting as colloidal stabilizer and the acrylic monomer. In this work a medium value of about  $230 \pm 20\text{ nm}$  is found, so a particle size effect on coating tested should be negligible.

### 3.2. General performance of coatings

The prepared paints were easy to apply either by brush and roller and depending on the PVC value the gloss varied from glossy (60) to high glossy (85). Adhesion values and the wet abrasion resistance of the tested coatings were very high. On the contrary, no suitable paints could be prepared using the physical mixtures of the acrylic and the PU dispersion. Films cast from this mixtures gave very bad quality coats with low water resistance, low adhesion, and low elasticity. This is probably due to phase segregation of both kind of polymer [30], so the following discussion will deal only with the paints prepared using the polyurethane/acrylic hybrids dispersion.

## 4. Adhesion

As expected, the adhesion obtained for panels scored the maximum value, 5B, and equivalent to 0% of the removed area, due to the binders' properties. Adhesion properties were unchanged after the accelerated weathering test.

## 5. Flexibility by mandrel bend test method

The systems behaved satisfactorily in this test and no cracks were observed within the film after bending.

## 6. Hardness by Buchholz test

The hardness values found were higher than the maximum value (125 Buchholz units) and are within expected values for the binders used.

## 7. Washability

No reemulsification was observed after 15,000 cycles indicating a good washability property of all coatings.

## 8. Gloss

Because the end application of gloss is perhaps the most important property discussed in this paper, it will be dealt with in detail. Fig. 1 shows the dependence of gloss on the acrylic content. A close linear relationship for the three PVC values is found and, as expected, it is observed that gloss decreases with increasing PVC values. A global decrease in gloss is also observed when the acrylic content increases, due to lower availability of



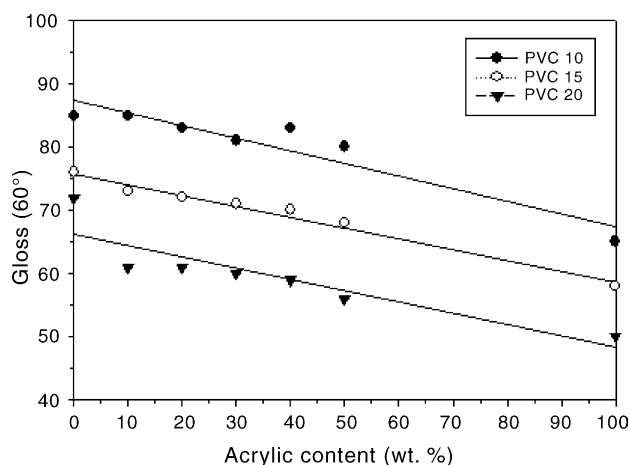


Fig. 1. Gloss dependence on acrylic content for different PVC values.

PU chains, of higher mobility, in the coalescence process. However, high gloss values (higher than 80%) are observed for all paints with PVC 10. For PVC 15 and 20 gloss values between 65 and 80% are observed. A close examination indicates a local maximum in gloss at about 40 wt.% of acrylic content. A similar behavior was found in other properties, like density [31], where a minimum value at this particular composition is observed. The film coat packing at this composition should be optimum due to the interaction between the soft PU chains, the rigid acrylic chains and the pigments.

Anyway, the gloss observed for a PVC value of 15% and 50 wt.% of acrylic content is about 70, a good value when comparing it with 85 of a pure water-based PU dispersion or 90 of pure solvent-based PU, taking into account the cost reduction by including acrylics monomers, with lower cost than the components, polyol and diisocyanate, used in the polyurethane synthesis.

Interesting enough is to compare the initial gloss with the value after the accelerated weathering test (see below).

## 9. Accelerated weathering (Xenon lamp type) and water exposure

Fig. 2 shows the changes in gloss after 700 h of exposition. The results of this test indicates that the end gloss and the relative change are almost the same for the pure PU dispersion, and the decrease in gloss follows the increasing PVC values, i.e. the greatest changes are observed for PVC 20%. However, when increasing acrylic content the formulations with PVC 10 and 15% behave different from that with PVC 20% at the beginning (10 wt.%) but then at 20 wt.% the PVC 15% differs from the other two and a minimum gloss variation at about 20–30 wt.% is observed. From 30 wt.% for PVC 10 and 20% the changes in gloss follow a similar variation and a minimum value is observed at about 40 wt.%. The gloss of typical highly glossy pure acrylic and pure PU solvent-based paints with initial gloss higher than 85, decreases to a great extent after test (not shown in Fig. 3).

The changes in the chromatic coordinate  $L$  are in all cases lower than 2%, similar to that of the pure PU, but better than that of the pure acrylic where  $-4\%$  is observed, indicating a

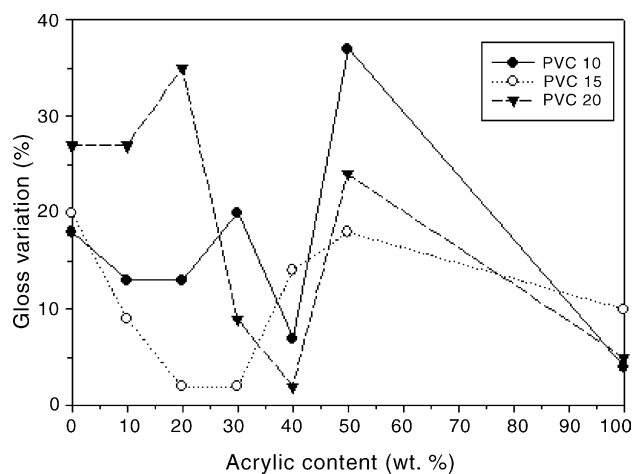


Fig. 2. Gloss variation (%) after accelerated weathering test as a function of acrylic content for different PVC values.

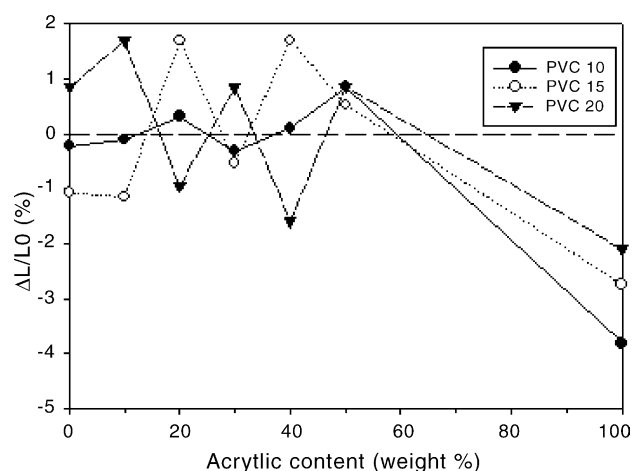


Fig. 3. Relative difference of chromatic coordinate  $L$  ( $\Delta L/L_0$  %) after accelerated weathering test as a function of acrylic content for different PVC values.

slight darkening. Similar results were found for the  $a$  parameter (Fig. 4). The change in this parameter is lower than 20%, indicating only a slight reddening compared to the pure acrylic-base paint where a 45% is observed. For  $b$  parameter (Fig. 5) the change is lower than 40%, indicating a slight yellowing compared to that of the pure acrylic-base paint where a value as high as 90% is observed. Finally the change in the modulus  $E$  (Fig. 6), is lower than 2% in most of cases, compared to the 4 to 6% found in the pure acrylic-based paint. Although this quantity gives no indication of the character of the difference, the smaller values found for the hybrids indicate a better color retention. Therefore, when using hybrids, a general trend in the loss of optical properties (gloss and color) is observed after accelerated weathering. Even with a high acrylic content such as 50 wt.%, gloss and color changes are remarkable low.

Regarding the adhesion, the values found here are relatively high and compared very well with data reported by Hegedus and Kloiber [6] and did not change after weathering test. Flexibility, hardness and washability were within expected values and unchanged after the accelerated weathering test.

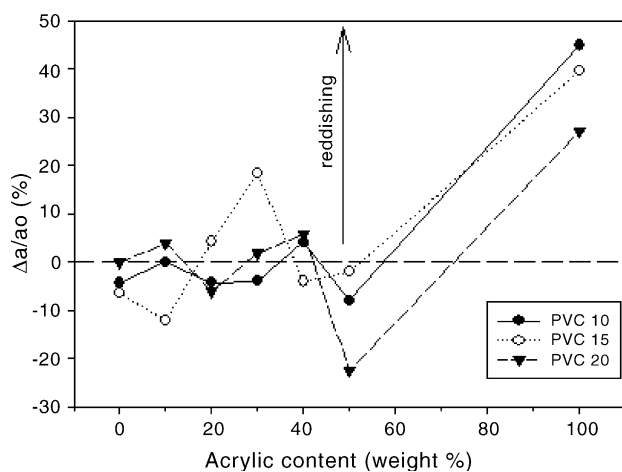


Fig. 4. Relative difference of chromatic coordinate  $a$  ( $\Delta a/a_0$ %) after accelerated weathering test as a function of acrylic content for different PVC values.

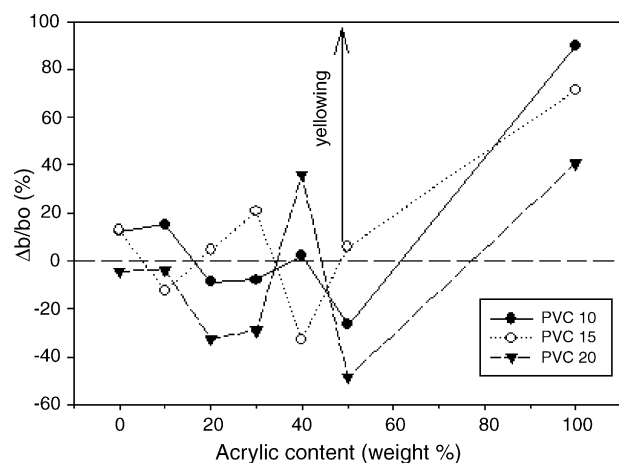


Fig. 5. Relative difference of chromatic coordinate  $b$  ( $\Delta b/b_0$ %) after accelerated weathering test as a function of acrylic content for different PVC values.

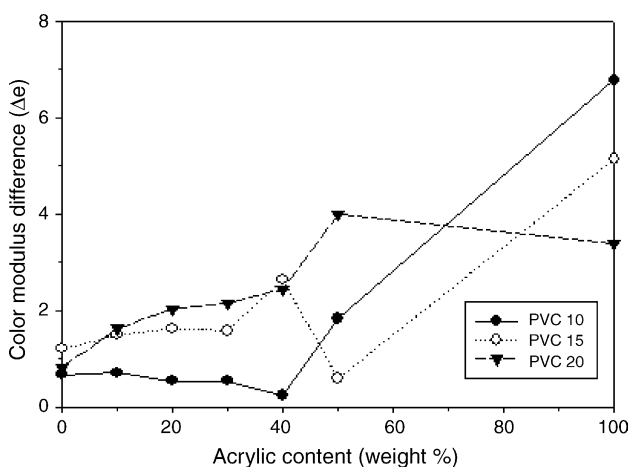


Fig. 6. Color modulus difference  $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$  after accelerated weathering test as a function of acrylic content for different PVC values.

## 10. Conclusions

The test results indicate that it is possible to prepare good quality paints using PU/acrylics hybrids dispersions.

It is possible to incorporate as much as 30 wt.% without losing initial gloss properties. On the other hand, end gloss is higher for these hybrid-based paints than for pure PU-based paints.

Optical properties after weathering are better when using hybrids than when using pure acrylic-based paints.

The results found in this work indicate that depending on the end-application of the paint it is possible to replace pure polyurethane water-based binders by hybrid polyurethane/acrylic binders, thus a more economical new product with good finishing and durability is obtained. Interesting enough is that the changes in gloss vary depending on the PVC values, so at 10 and 20, gloss does not change so much with 40 wt.% of acrylic content after accelerated weathering. For PVC 15%, 20 or 30 wt.% of acrylic content the same change in gloss is obtained after weathering, so it is possible to choose between both contents depending on the required properties of the paint (hardness, elasticity, economy). The other optical properties, flexibility and adhesion are almost unchanged compared to pure PU binders.

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