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# Low VOC self-crosslinking waterborne acrylic coatings incorporating fatty acid derivatives

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## ABSTRACT

Acrylic waterborne coatings free of volatile coalescing agents were produced and characterized. The film-formers used in the coatings were resins incorporating an allylic fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD), either as reactive (non-volatile) coalescing agents or as co-monomers. The minimum film-forming temperatures of the new coatings were lower than the reference, confirming that AFAD and AcFAD act as coalescing agents. On the other hand, the observed reductions in through drying-time and increase in scrub resistance, more evident for AcFAD, indicating that reaction between the conjugated double bonds in the fatty acid derivatives and atmospheric oxygen–oxidative cure–took place and provided an effective self-crosslinking drying mechanism.

## 1. Introduction

Acrylic waterborne coatings usually include in their formulation pigments, fillers, water, multi-purpose additives, and film forming components. The latter, commonly referred to as binders or vehicles, are aqueous polymer dispersions (or latexes) that are responsible for binding the pigments and fillers and forming a homogeneous film with good adhesion to the substrate [1]. Each coating formulation has a characteristic minimum film-forming temperature (MFT), which must be below the ambient temperature at which the coating is intended to dry. It is usually necessary to add coalescing agents to lower the MFT and obtain good film properties under all application conditions. These are low molecular weight compounds that act as plasticizers, softening the polymer particles and providing formation of a homogeneous and continuous film [2,3]. After evaporation of these additives, the film hardens and a non-tacky surface is obtained. Some examples are glycol ethers (butyl glycol or methoxy propanol), and alcohols (as the various butanols or propanols), [2]. However, current environmental regulations restrict the emissions of volatile organic compounds (VOC) into the atmosphere [4]. Thus, coatings and varnishes industries are forced to replace volatile additives with non-volatile substances [5,6]. Coalescing agents are an example of VOC in paint formulations and their removal implies developing formulations capable of not only coalescing uniformly, but also possessing a hardening mechanism not dependent on evaporation of additives. Reactive coalescing agents are a possible strategy, as these remain in the film after drying [7–9]. Some studies mention dicyclopentenyl esters, mono-functional epoxy acrylates and aliphatic epoxides containing polar groups to act as reactive coalescing agents for coatings and adhesives [10,11]. Another approach is the introduction of self-crosslinking agents, as homo-polymers or co-monomers [9,12]. Over the last years several studies have been done in this area, including the modification of unsaturated vegetable oils by the addition of acrylic, vinyl and styrene functions [13–17].

Self-crosslinking compounds have in their structure double bonds that can be easily attacked by atmospheric oxygen. Throughout the life service of the film, this auto-oxidation promotes the formation of hydroperoxides, which then decompose into radicals, through a metal-catalyzed reaction, leading to peroxy, carbon-carbon and ether crosslinking [18–20]. This self-crosslinking process leads to effective formation of hardened and non-tacky films.

Fatty acid derivatives are good examples of self-crosslinking agents [20]. In this study, acrylic resins were modified with an allyl fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD). Their performance in waterborne acrylic coatings was evaluated.

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## 2. Experimental

### 2.1. Materials

Sunflower oil-derived conjugated fatty acids (CFA), ethylene glycol, xylene, benzoyl peroxide (BP), vinyl acetate (VA), methyl methacrylate (MMA), butyl acrylated (BA), acrylic acid (AA), dodecyl benzene sulfonic acid sodium salt (DBSA), disodium laurylcitrate sulfosuccinate (DSL), sodium persulfate, dibutyltin oxide and all other raw materials (defoamer, fungicides and ammonia) used to synthesize latexes were kindly supplied by Resiquímica – Resinas Químicas, S.A. (Mem Martins, Portugal). Allylic alcohol, phosphorus trichloride and acryloyl chloride were purchased from Fluka; petroleum benzin and diethyl ether from Merck; dichloromethane, anhydrous magnesium sulphate ($MgSO_4$) and anhydrous calcium chloride ($CaCl_2$) from Panreac. Triethylamine, drying catalyst (a combination of 3% cobalt, 3% barium and 5% zirconium) and all the other raw materials used for the coatings formulations (titanium dioxide, thickeners, 2,2,4-trimethyl-1,3-pentandiol-monoisobutyrate (TPM), propylene glycol (PG), defoamer and fungicides), were kindly provided by CIN–Corporação Industrial do Norte, S. A. (Maia, Portugal). All chemicals were used as received.

### 2.2. Characterization methods

Solid content of the resins was determined by evaporating the volatiles in pre-weighed dishes in an oven at 105 °C for 1 h. It was previously confirmed that this drying time was sufficient for attaining constant weight.

Minimum film-forming temperature (MFT) was determined according to standard ISO 2115:1996.

Viscosity was measured using a Brookfield LV instrument, with a Spindle number 2, at room temperature.

pH value was determined at 23 °C, by electrometric measurement, using a glass electrode.

Zeta potential was determined using a Zetasizer Nano (Malvern). The results reported are an average for at least three determinations.

Infrared (IR) spectra were recorded with an ABB – Bomen spectrometer, equipped with an ATR cell. Each spectrum was an average of 32 scans taken with 4 $cm^{-1}$ resolution in the 4000–650 $cm^{-1}$ range.

Degree of crosslinking was determined by mixing about 0.0500 g of dried films with 5 mL of toluene, during 1 h at 80 °C. The solutions were filtered using 0.45 μm nylon filters, which were dried and weighed until constant weight, in order to determine the amount of insoluble crosslinked material [21]. The degree of crosslinking was computed as the percentage of insoluble material in the original dry film. The measurements were performed on films air dried along 5 weeks. The values reported are an average for at least three determinations.

Rubbing resistance test consisted on evaluation of the number of cycles (double rubs) until film failure. Rubbing was performed manually with a piece of white cotton embedded with solvent over a 3 cm of paint film. The solvents used were xylene and propanone. The values reported are an average result for at least two test runs.

Gloss was measured according to standard procedure ISO 2813. Coating films with 150 μm wet thickness were applied on glass plates and allowed to air dry for 24 h. Gloss was measured at 60°, using a gloss meter, and is expressed in gloss units.

Drying time was determined by applying 100 μm film thickness on 10 cm × 15 cm glass plates, at 23 °C and measuring the time until the surface was dry. Finger pressure was applied on the paint film and the presence of finger prints was also assessed.

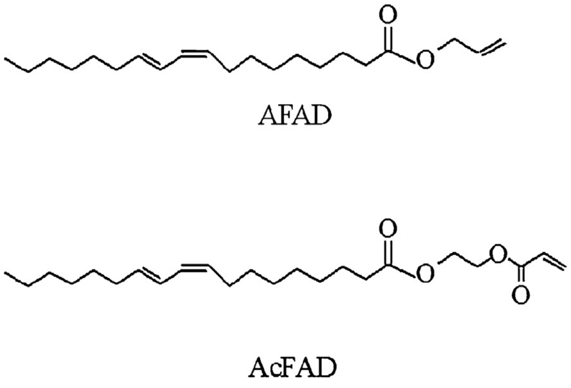

**Fig. 1.** Allyl fatty acid derivative (AFAD) and acrylic fatty acid derivative (AcFAD) structures.

For the block resistance test, 200 μm wet thickness coating films applied on 6 cm × 6 cm charts were air dried for one week. The surface of two painted squares were then put in contact and hold under a 5 kg block during 15 min in an oven at 50 °C. After that, the squares were detached and the films appearance was evaluated.

Mixtures of 5 wt. % AFAD or AcFAD with acrylic resin were prepared by mixing the resin under vigorous stirring for 30 min. Films were then obtained by doctor-blading on a glass surface and drying at room conditions.

### 2.3. Fatty acid derivatives synthesis and copolymerization

Allyl fatty acid derivative (AFAD, Fig. 1) was obtained by indirect esterification of a conjugated fatty acids mixture (CFA) with allylic alcohol. CFA was charged into a reactor with nitrogen purge, thermometer and water condenser, and heated to 60 °C. Phosphorous trichloride was added very slowly under constant stirring for 1 h. The reaction product was then cooled to 10 °C and allylic alcohol was added dropwise for 45 min. Further details can be found in our previously published work [16].

Acrylic fatty acid derivative (AcFAD, Fig. 1) was also synthesized by indirect esterification of CFA with an acrylic derivative. CFA was charged into a reactor with nitrogen purge, thermometer and water condenser, and heated at 200 °C in the presence of dibutyltin oxide. Ethylene glycol was added dropwise for 2 h. The reaction product was mixed with dichloromethane and triethylamine at room temperature. Acryloyl chloride and dichloromethane were added dropwise for 2 h. Further details can be found in our previously published work [22].

Acrylic resins used for coatings formulations were synthesized by aqueous radical emulsion polymerization. The so-called “reference resin” contains MMA, BA (50:50 ratio) and a small fraction of AA. Two other resins were produced, containing in addition one of the synthesized fatty acid derivatives as co-monomers. The resins compositions are shown in Table 1. Pre-emulsion was prepared by mixing water and surfactants under vigorous stirring, followed by the addition of the monomers (MMA, BA, AA and AFAD or AcFAD), added slowly for 1 h. The remaining surfactants and water were charged into the reactor equipped with a water condenser, a mechanical stirrer, thermometer, nitrogen bubbling and heated at 80 °C. Simultaneously, the pre-emulsion previously prepared and the sodium persulfate (previously dissolved in 10 ml of water) were fed dropwise into the reactor over a period of 2 h. The reaction was allowed to proceed for 15 min longer. A volume of 100 g of resin was prepared in each batch, in a 250 ml jacketed glass vessel.