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1 Incorporation of an acrylic fatty acid derivative as comonomer for oxidative cure in  
2 acrylic latex

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## Abstract

An acrylic fatty acid derivative (AcFAD) was evaluated as comonomer for promotion of oxidative cure in waterborne latexes. AcFAD was polymerized by solvent homopolymerization and copolymerization and by emulsion copolymerization, and the final products characterized. In the two polymerization processes, NMR analyses confirmed that the reaction occurred involving both the terminal acrylic double bond and the conjugated double bonds of the aliphatic chain.

Compared with a reference acrylic latex, the results obtained after AcFAD incorporation showed time-dependent increase in gel content and in solvent resistance of dry films. These were ascribed to oxidative cure and consequent self-crosslinking of the acrylic polymer, involving the conjugated double bonds in AcFAD side-chains. Oxidative cure was also confirmed by FT-IR analyses. In addition, reduction in minimum film-forming temperature (MFT) evidenced that AcFAD has an internal plasticization effect during film formation. Incorporation of this comonomer in acrylic paint binder formulations constitutes a promising alternative to the use of volatile coalescing agents.

Keywords: Acrylic fatty acid derivative; Emulsion polymerization; Oxidative cure; Acrylic latex; Reactive coalescing agent

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### 3 1. Introduction

4 Environmental regulations are imposing increasing limitations to emission of volatile organic  
5 compounds (VOC) to atmosphere, since this ultimately leads to formation of tropospheric ozone  
6 and other harmful substances<sup>1</sup>. These regulations are pushing forward the development of low VOC  
7 emission paints. One strategy involves reduction of organic solvents in waterborne paints. This  
8 implies developing of polymeric binders for paint formulations that are capable of film formation at  
9 room temperature without the need for addition of volatile coalescing agents. This may be achieved  
10 by taking advantage of the same drying mechanism used in oil-based alkyd paints. A lipid  
11 autoxidation process takes place upon solvent evaporation and exposure to atmospheric oxygen,  
12 involving conjugated double bonds present in aliphatic side chains<sup>2</sup>; this inter-chain crosslinking  
13 process promotes effective film hardening along a relatively short time<sup>3-5</sup>. Vegetable oils, such as  
14 castor, linseed and sunflower oil, and their derivatives have been used in paints, varnishes and  
15 textiles for many years. Extensive studies have focused on the introduction of acrylic, vinylic,  
16 epoxy and styrenic groups in the vegetable oils, usually involving esterification or  
17 transesterification reactions<sup>6-8</sup>, and evaluate their applicability in homo and copolymerization and in  
18 emulsion and miniemulsion polymerizations<sup>9-12</sup>.

19 Incorporation of fatty acid derivatives as comonomers in emulsion polymers has also been  
20 suggested as a strategy for obtaining waterborne paints capable of self-crosslinking<sup>13-17</sup>. The  
21 oxidative cure mechanism inherent to the presence of conjugated double bonds allows formation of  
22 a hard, non-tacky, film surface without evaporation of a coalescing agent. Additionally, the drying  
23 rates can be accelerated by addition of catalytic driers<sup>13, 15, 18</sup>.

24 Another approach described in literature is the use of reactive coalescing agents, which remain in  
25 the film after drying instead of evaporating into the atmosphere during, therefore minimizing VOC  
26 emissions<sup>19-21</sup>.

27 In this study, an acrylic fatty acid derivative (AcFAD) is shown to be suitable for copolymerization  
28 in acrylic polymer formulations, providing oxidative cure mechanism to the dry films. Two  
29 different approaches to free radical addition polymerization were studied: in solution and in  
30 emulsion. In solution polymerization the monomer and the catalyst are dissolved in a non-reactive  
31 solvent, while in emulsion polymerization the reaction occurs in surfactant-stabilized micelles  
32 containing monomers and growing polymer chains, dispersed in a continuous water phase<sup>22, 23</sup>. The

1 resulting products from acrylic fatty acid derivatives (AcFAD) homo and copolymerization were  
2 characterized, focusing on its potential use.

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## 5 2. Experimental

### 6 2.1. Materials

7 A mixture of conjugated fatty acids (CFA) derived from sunflower oil, xylene, benzoyl peroxide  
8 (BP), methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), dodecyl  
9 benzenesulfonic acid sodium salt (DBSA), fatty alcohol ether sulfosuccinate disodium salt (FAES),  
10 ethoxylated alkyl sulphate, sodium persulfate, dibutyltin oxide were kindly supplied by Resiquímica  
11 - Resinas Químicas, S.A. (Mem Martins, Portugal). CFA contains 48 wt.% of compounds with two  
12 conjugated double bonds (conjugated linoleic acids, CLA), 27 % with one double bond (oleic acid),  
13 11 % with two non-conjugated double bonds (linoleic acid)<sup>15, 16</sup>.  
14 18:2, 48 %,) and one double bond (18:1, 27 %)

15

16 Methanol was purchased from Merck; deuterated chloroform (CDCl<sub>3</sub>, 99.8 % D) from Sigma-  
17 Aldrich. All chemicals were used as received. The drying catalyst (a combination of cobalt, barium  
18 and zirconium) was kindly dispensed by CIN – Corporação Industrial do Norte (Maia, Portugal).

19

### 20 2.2. Characterization methods

21 <sup>1</sup>H NMR spectra were acquired on a Bruker Avance III - 400 spectrometer operating at a frequency  
22 of 400 MHz, using deuterated chloroform as solvent. Chemical shifts were reported in part per  
23 million (ppm,  $\delta$ ) and referenced to CDCl<sub>3</sub>. Polymer latexes were freeze-dried prior to NMR spectra  
24 collection.

25 Infrared (IR) spectra were recorded with an ABB - Bomem spectrometer, equipped with an ATR  
26 cell. Each spectrum was an average of 32 scans taken with 4 cm<sup>-1</sup> resolution in the 4000-650 cm<sup>-1</sup>  
27 range. Savitzky-Golay method was used, to obtain second derivatives by means of 17 points  
28 smoothing filter and a second order polynom<sup>24, 25</sup>.

29 Solid content of the latexes was determined by evaporating the water in pre-weighed dishes in an  
30 oven at 105 °C for 1 h. The results reported are an average for at least three determinations.

1 Filtration residue was obtained by filtering the final latex with a mesh of 160  $\mu\text{m}$ . The value  
2 presented is the ratio between the residue mass and the total latex mass.

3 Minimum film-forming temperature (MFT) was determined according to standard ISO 2115:1996.  
4 MFT was measured using a Rhopoint MFFT 60 instrument.

5 Viscosity was measured using a Brookfield LV instrument, and all the measurements were made  
6 with a Spindle number 2, at 100 rpm rotational speed and at room temperature. pH value was  
7 determined at 23  $^{\circ}\text{C}$ , by electrometric measurement, using a glass electrode.

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

10 For the gel content and solvent resistance tests, the dry films of the prepared latexes were prepared  
11 by doctor blading on a glass plate. The wet thickness of the films was 200  $\mu\text{m}$ .

12 Gel content was determined by mixing about 0.0500 g of dried films with 5 mL of toluene, during 1  
13 h at 80  $^{\circ}\text{C}$ . The solutions were filtered using 0.45  $\mu\text{m}$  nylon filters, which were dried for 5 weeks  
14 and weighed until constant weight, in order to determine the amount of insoluble crosslinked  
15 material. The values reported are an average of at least three determinations.

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

20

### 21 2.3. Solution polymerization of AcFAD

22 AcFAD was obtained from conjugated fatty acids (CFA) esterification (first step) with ethylene  
23 glycol followed by esterification with acryloyl chloride (second step). The process is described in  
24 detail in a previous work<sup>15</sup>. The overall reaction is presented in Fig. 1.

25 For homopolymerization, AcFAD (0.002 mol) was placed with 2 ml of toluene and 2 % (molar %  
26 relative to AcFAD) of BP in a 25 ml round bottom flask, equipped with magnetic stirrer,  
27 thermometer, nitrogen bubbling and a water condenser. The reaction was carried out with vigorous  
28 stirring at 85  $^{\circ}\text{C}$  for 7 h. After reaction, the polymer was precipitated in methanol and  
29 dichloromethane was added to the solid filtered to remove some unreacted monomer. Finally, the  
30 solvent was removed under vacuum using a rotary evaporator.

31 AcFAD (10 % molar) was also copolymerized with MMA (90 % molar). The monomer mixture  
32 was placed with 2 ml of toluene and 2 % (molar) of BP into a 25 ml round bottom flask, equipped

1 with magnetic stirrer, thermometer, nitrogen bubbling and a water condenser. The reaction was  
2 carried out with vigorous stirring at 85 °C for 7 h. After reaction, the polymer was precipitated in  
3 methanol and dichloromethane was added to the solid filtered to remove some unreacted monomer.  
4 Finally, the solvent was removed under vacuum using a rotary evaporator.

5

#### 6 2.4. Emulsion copolymerization of AcFAD

7 The comonomer composition used is based on a commercial acrylic latex formulation where 10  
8 wt.% of the main acrylic monomer mixture was replaced by AcFAD. Surfactant ethoxylated alkyl  
9 sulphate was initially used, while dodecyl benzenesulfonic acid sodium salt (DBSA) and fatty  
10 alcohol ether sulfosuccinate disodium salt (FAES) were used in a subsequent stage of development.

11 The latex was synthesised by aqueous free radical emulsion polymerization at 80 °C, carried out in  
12 a 250 ml jacketed flask reactor equipped with water condenser, mechanical stirrer, thermometer and  
13 nitrogen bubbling system. The reaction temperature was controlled by circulating hot water from a  
14 temperature controlled water bath in the reactor jacket. The resins compositions are shown in Table  
15 1. A pre-emulsion was prepared by mixing half of water and half of the surfactant with the  
16 monomers (MMA, BA, AA and AcFAD) under vigorous stirring. The remaining surfactant and  
17 water were initially charged into the reactor at 80 °C. Simultaneously, the pre-emulsion previously  
18 prepared and the sodium persulfate (0.3 wt. %) were fed dropwise into the reactor over a period of 2  
19 h. The pre-emulsion was added in two portions. While the first was added, the remaining portion  
20 was kept under stirring to prevent phase separation.

21 *AcFAD*: **IR** (cm<sup>-1</sup>): 3006 (CH, unsaturated stretching), 2924 and 2854 (saturated [(CH<sub>2</sub>)<sub>n</sub>]  
22 stretching), 1732 (C=O stretching), 1637 (C=C stretching), 1458 and 1408 (CH<sub>2</sub>, CH<sub>3</sub> bending),  
23 1173 (C-O, stretching), 984 and 808 ((CH=CH<sub>2</sub>, out-of-plane deformation), 723 (CH<sub>2</sub>, rocking). **<sup>1</sup>H**  
24 **NMR** (CDCl<sub>3</sub>): δ in ppm (*J* in Hz) = 0.79 (*t*, *J*= 7.2, CH<sub>3</sub>, H<sub>-18</sub>), 1.19 (*m*, 16H, aliphatic CH<sub>2</sub>, H<sub>4</sub>-H-  
25 7 and H<sub>14</sub>-H<sub>17</sub>), 1.52 (*m*, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-C(=O)-, H<sub>-3</sub>), 1.90-2.06 (*m*, 4H, CH<sub>2</sub> allylic), 2.24 (*t*, *J*=  
26 7.2, -CH<sub>2</sub>-C(=O)-, H<sub>-2</sub>), 2.68 (*t*, 2H, *J*= 6.2, CH<sub>2</sub> doubly allylic), 4.27 (*t*, 2H, COO-CH<sub>2</sub>-, *J*= 7.2, H<sub>-  
27 20</sub>) and 4.22 ppm (*t*, 2H, COO-CH<sub>2</sub>-, *J*=7.2 Hz, H<sub>-19</sub>), 5.18 ppm (*dt*, *J*=11.0 and 7.0, H<sub>-9</sub>), 5.3-5.1  
28 ppm (4H from C18:2 CH=CH-CH<sub>2</sub>-CH=CH and 2H from C18:1 double bond of the CFA mixture),  
29 5.51 (*dt*, *J*=15.0 and 7.0, H<sub>-12</sub>), 5.76 (*dd*, 1H, *J*=10.4 and 1.2, CH<sub>2</sub>=CH-, H<sub>-23a</sub>), 5.80 (*t*, *J*=11.0, H<sub>-  
30 11</sub>), 6.04 (*dd*, 1H, *J*= 17.4 and 10.4, CH<sub>2</sub>=CH-, H<sub>-22</sub>), 6.24 (*dd*, *J*=15.0 and 11.0, H<sub>-10</sub>), and 6.33 (*dd*,  
31 1H, *J*=17.4 and 1.2, CH<sub>2</sub>=CH-, H<sub>-23b</sub>)<sup>15</sup>.

32 *Reference Acrylic latex*: **IR** (cm<sup>-1</sup>): 2957 and 2874 (CH<sub>3</sub> stretching, asymmetric and symmetric  
33 respectively), 1729 (C=O stretching), 1449 and 1386 (CH<sub>2</sub>, CH<sub>3</sub> bending), 1160 and 1147 (C-O,

1 stretching). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ in ppm = 0.89 (6H, CH<sub>3</sub> from BA and α-CH<sub>3</sub> syndiotactic from  
2 MMA), 1.04 (3H, α-CH<sub>3</sub> isotactic from MMA), 1.39 (2H, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> from BA),  
3 1.61 (2H, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> from BA), 1.75-2.51 (2H, CH<sub>2</sub> of the α-methanediyl protons),  
4 3.61 (3H, -O-CH<sub>3</sub> from MMA *racemic* configuration), 3.66 (3H, -O-CH<sub>3</sub> from MMA *meso*  
5 configuration), 4.02 (2H, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> from BA).

6 *Latex B*: IR (cm<sup>-1</sup>): 3006 (CH, unsaturated stretching), 2924 and 2854 (saturated [(CH<sub>2</sub>)<sub>n</sub>]  
7 stretching), 1732 (C=O stretching), 1637 (C=C stretching), 1458 and 1408 (CH<sub>2</sub>, CH<sub>3</sub> bending),  
8 1173 (C-O, stretching), 984 and 808 (CH=CH<sub>2</sub>, out-of-plane deformation), 723 (CH<sub>2</sub>, rocking). <sup>1</sup>H  
9 NMR (CDCl<sub>3</sub>): δ in ppm = 0.88 (CH<sub>3</sub>, H<sub>18</sub> from AcFAD), 0.96 (CH<sub>3</sub> from BA and α-CH<sub>3</sub>  
10 syndiotactic from MMA), 1.1-1.4 (α-CH<sub>3</sub> isotactic from MMA, 2 CH<sub>2</sub> from BA, aliphatic CH<sub>2</sub>, H<sub>4</sub>-  
11 H<sub>7</sub> and H<sub>14</sub>-H<sub>17</sub>, from AcFAD), 1.62 (CH<sub>2</sub>, H<sub>3</sub>, from AcFAD and CH<sub>2</sub> from BA), 2.04 (CH<sub>2</sub>  
12 allylic from AcFAD), 2.36 (CH<sub>2</sub>, H<sub>2</sub> from AcFAD), 2.65 (CH of the α-methanetriyl protons), 2.88  
13 (CH<sub>2</sub> doubly allylic from AcFAD), 3.61 (CH<sub>3</sub> from MMA *racemic* configuration), 3.67 (CH<sub>3</sub> from  
14 MMA *meso* configuration), 4.02 (CH<sub>2</sub> from BA), 5.36 (4H from C18:2 CH=CH-CH<sub>2</sub>-CH=CH and  
15 2H from C18:1 double bond of the CFAs mixture).

16

### 17 3. Results and discussion

#### 18 3.1. Solvent polymerization

19 To assess the ability of AcFAD to copolymerize, preliminary studies were focused on solution  
20 polymerization. Homopolymerization of AcFAD and copolymerization with MMA were  
21 investigated by NMR analyses. Since radical propagation can involve both the aliphatic double  
22 bonds and the acrylic group, the spectra of AcFAD and of the homopolymerization or  
23 copolymerization products were compared in terms of the ratio of the integrals assigned to the  
24 aliphatic conjugated double bonds at δ 6.24, 5.80, 5.51 and 5.18 ppm (H<sub>9</sub> to H<sub>12</sub>)<sup>15</sup> and the acrylic  
25 double bonds at δ 5.76, 6.04 and 6.33 ppm (H<sub>23a</sub>, H<sub>22</sub> and H<sub>23b</sub> respectively).

26 In homopolymerization, reductions of 43 % in the area of the signals corresponding to acrylic  
27 double bonds and of 88 % in the area of the signals of aliphatic conjugated double bonds were  
28 observed. The unsaturated polymer obtained had 12 % of conjugated double bonds. Previous works  
29 on homopolymerization of long chain vinyl and allyl esters derived from fatty acids have shown  
30 that polymerization occurs between the aliphatic double bonds of one molecule and the vinyl or  
31 allyl group of another<sup>26-28</sup>. In addition, according to Harrison and Wheeler<sup>26</sup>, polymerization  
32 through conjugated unsaturation is slightly higher than through unconjugated unsaturation.

1 In copolymerization of AcFAD with MMA, the results indicated that 99 % of the acrylic double  
2 bonds were consumed, indicating that both monomers have been almost completely consumed in  
3 the radical copolymerization reaction. Concerning AcFAD's conjugated aliphatic double bonds, one  
4 of them was 99 % consumed, while the other was preserved. This higher conversion of AcFAD in  
5 presence of MMA is explained in terms of minimization of steric effects involved in  
6 homopolymerization of large AcFAD molecules<sup>29</sup>.

7

### 8 3.2. Emulsion polymerization

9 AcFAD was incorporated as a comonomer in a reference acrylic latex (described in section 2.4),  
10 replacing 10 wt.% of the monomer mixture (latex A). Except for the monomer composition, the two  
11 formulations were identical, namely in terms of the surfactant system used. The properties of both  
12 latexes are very similar, as shown in Table 1, except for the MFT, which decreased by about 9 °C  
13 with addition of AcFAD, indicating a plasticization effect.

14 However, complete incorporation of AcFAD in the acrylic latex was not achieved in this  
15 formulation, as demonstrated by the presence of a yellow supernatant liquid in the final product.  
16 The surfactant used in the reference acrylic latex formulation (ethoxylated alkyl sulphate) was  
17 inefficient to emulsify highly hydrophobic AcFAD in the liquid medium. As a consequence, too  
18 large monomer drops were formed, and oil/water interfacial area was not high enough for  
19 establishing an adequate diffusional flow into micelles, and AcFAD addition to the growing  
20 polymer chain. AcFAD is still acting as a plasticizer in the dry film, as shown by the decrease in  
21 MFT, but is not effectively incorporated in the acrylic latex.

22 Following existing information on emulsion polymerization involving a linolenic acid derivative<sup>30</sup>,  
23 the surfactant was replaced by a combination of dodecyl benzenesulfonic acid sodium salt – DBSA  
24 - and fatty alcohol ether sulfosuccinate disodium salt - FAES. Combination of surfactants with  
25 different hydrophilic-lipophilic balance (HLB) values is often used in emulsion polymerization<sup>22</sup>,  
26 <sup>31-34</sup>. The polymerization product remained stable along several weeks and no evidence of yellow  
27 supernatant was observed. As seen in Table 1, the MFT for this formulation (latex B) is  
28 significantly lower than for the previous cases (18 °C lower than the reference), indicating a more  
29 effective intrinsic plasticization effect, associated with the presence of long aliphatic side chains  
30 from AcFAD in the polymer. This originates higher segment mobility through increased  
31 intermolecular distance<sup>31</sup>, eliminating the need for coalescing agent additives.

32 Latex B and the reference acrylic latex were stable, showing zeta potential values lower than -30  
33 mV, specifically, -95 mV and -83 mV, respectively. Latexes with zeta potential values between -30



1 mV and + 30 mV are most often unstable and prone to coagulation, unless a steric stabilization  
2 mechanism is present<sup>35</sup>.

3 AcFAD copolymerization with MMA and BA in latex B was confirmed by NMR (Fig. 2) and the  
4 chemical shift values were attributed according to the poly(methyl acrylate) (PMA) and  
5 poly(methyl methacrylate) (PMMA) values given in the literature<sup>36-39</sup>. Comparing the spectra of the  
6 latex copolymerized with AcFAD (Fig. 2b) and the reference acrylic latex (Fig. 2c) the following  
7 differences were observed: presence of the signals at  $\delta$  2.36 (-CH<sub>2</sub>-C(=O)-, H<sub>-2</sub>) and  $\delta$  0.88 ppm  
8 (CH<sub>3</sub>, H<sub>-18</sub>), from the non-acrylated region of the AcFAD, and the signal at  $\delta$  2.65 ppm, attributed to  
9 the CH of the  $\alpha$ -methanetriyl protons formed during the acrylated copolymerization reaction. On the  
10 other hand, a signal around  $\delta$  1.20 ppm, assigned to aliphatic CH<sub>2</sub> (H<sub>-4</sub>-H<sub>-7</sub> and H<sub>-14</sub>-H<sub>-17</sub>) of AcFAD  
11 (which is not present in the reference emulsion) was observed and the acrylic double bond signals  
12 (at  $\delta$  5.76, 6.04 and 6.33 ppm, H<sub>-23a</sub>, H<sub>-22</sub> and H<sub>-23b</sub> respectively) disappeared, indicating complete  
13 polymerization of AcFAD<sup>38</sup>. Due to the relatively low amount of AcFAD present (only 10 wt. % of  
14 AcFAD was added and the fraction of CFA in the commercial CFA mixture used is 50 %<sup>15</sup>), the  
15 intensity of the signals assigned to the conjugated (CH=CH-CH=CH, C18:2) and non-conjugated  
16 (CH=CH-CH<sub>2</sub>-CH=CH, C18:2) double bonds were difficult to detect. However, by comparing the  
17 ratio of the integrals assigned to the doubly allylic CH<sub>2</sub> (at 2.88 ppm) in AcFAD and the latex  
18 copolymerized with AcFAD, was verified that 95 % of one double bond from the non-conjugated  
19 double bonds was consumed. Nevertheless, there are at least 22 % of conjugated double bonds and  
20 portions of polymerized chains with one double bond available for oxidative cure.

21 To evaluate the oxidative cure behaviour (since NMR confirmed the presence of double bonds) of  
22 latex B, the gel content of films dried for up to five weeks was determined and compared with the  
23 reference acrylic latex (Fig. 3). The films obtained were homogeneous, non-tacky and clear.  
24 Although some crosslinking may have occurred during the polymerization reaction, no gel content  
25 was observed in latex B at the beginning of the drying period. The results indicate a final gel  
26 content of 6 wt.% for the reference, and of 60 wt.% in latex B. This demonstrates occurrence of  
27 auto-crosslinking in latex B. This phenomenon is represented in Fig. 4, showing the formation of  
28 peroxide bonds by reaction between the conjugated double bonds in AcFAD's aliphatic chains and  
29 atmospheric oxygen. This is just an example of the type of bonds that can be formed in oxidative  
30 cure<sup>15, 41</sup>.

31 FT-IR analyses of films dried in air for five weeks also confirmed occurrence of oxidative cure.  
32 Since the acrylic latex formulated with AcFAD displays a complex spectrum, causing overlapping  
33 and suppression of bands, the analysis was based on the second derivative spectra (Fig. 5). Some  
34 differences were observed between the spectra obtained after one day and after five weeks of

1 drying: i) slight reduction in the intensity of the bands at 2924 and 2854  $\text{cm}^{-1}$  (symmetric and  
2 asymmetric  $(\text{CH}_2)_n$ ), due to hydrogen abstraction on a methylene group on the allylic position<sup>3, 15</sup>,  
3 and ii) slight decrease in the intensity of the band at 3006  $\text{cm}^{-1}$ , assigned to the double bonds of the  
4 aliphatic chain (CH, unsaturated stretching), due to the high reactivity towards radical addition of  
5 the conjugated double bonds<sup>42, 43</sup>. The decrease in the intensity of the band at 723  $\text{cm}^{-1}$ , assigned to  
6 the out-of-plane deformation of CH=CH, was not so evident, since it is overlapped by the  $[(\text{CH}_2)_n]$   
7 rocking vibration of the aliphatic chain<sup>15</sup>. It was also noticed that, in films containing catalytic  
8 driers, reaction with atmospheric oxygen was very fast, making it impossible to detect the bands  
9 related to the formation of hydroperoxide bonds at 3400  $\text{cm}^{-1}$  <sup>44</sup>.

10 The solvent resistance of latex B was evaluated and compared to the reference acrylic latex, for  
11 films dried up to 5 weeks (Fig. 6). Solvents of different polarities, xylene and propanone, were used  
12 on the tests. Latex B showed a much higher resistance towards rubbing with both solvents than the  
13 reference acrylic latex. In addition, solvent resistance increased significantly during the drying time,  
14 which again confirms that oxidative cure occurs progressively, due to the presence of the AcFAD as  
15 comonomer in the latex formulation.

16

#### 17 4. Conclusions

18 An acrylic fatty acid derivative (AcFAD) was tested in solvent homopolymerization and  
19 copolymerization and the final products were characterized by NMR. The results showed that the  
20 reactions involved the acrylic double bond and the conjugated double bonds. In  
21 homopolymerization around 43 % of the acrylic double bonds and about 88 % of the conjugated  
22 double bonds were consumed. In copolymerization 99 % of the both type of double bonds were  
23 consumed.

24 Experiments using AcFAD as comonomer in acrylic emulsion polymerization were performed.  
25 NMR analyses confirmed that copolymerization occurred, involving the acrylic double bonds, and  
26 maintaining a significant number of unsaturations. Resistance to solvents (xylene and propanone)  
27 and gel content were significantly higher for the latex containing AcFAD than for the reference  
28 acrylic latex. These results, together with FT-IR analyses with application of mathematical spectra  
29 treatment (second derivative), showed that oxidative cure took place upon film drying.  
30 Additionally, the MFT was considerably lower for the latex with AcFAD, indicating an intrinsic  
31 plasticization effect.

32 AcFAD has potential interest as comonomer in acrylic binders for waterborne paints, since it acts as  
33 intrinsic coalescing agent and as a promoter of autoxidative cure. This may provide an alternative to

1 the use of co-solvents, such as coalescing agents, in this type of paints, therefore reducing VOC  
2 emissions in the final product.

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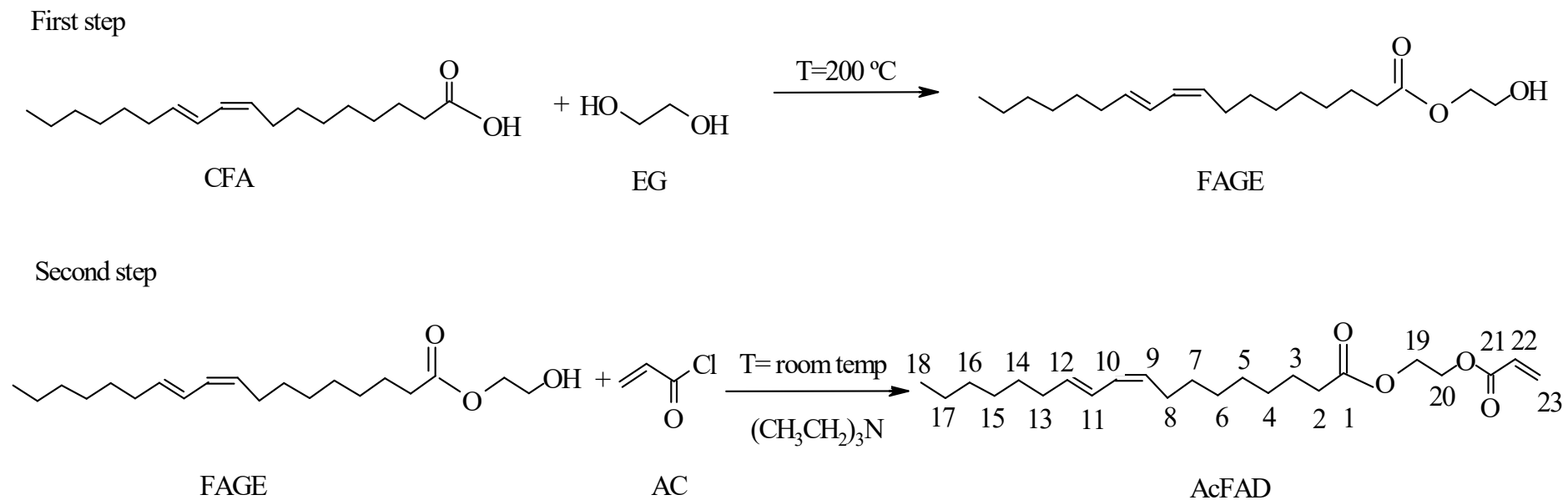
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**Fig. 1** – Scheme of the reactions involved on AcFAD synthesis process (AcFAD structure represents the main component of the conjugated fatty acid).



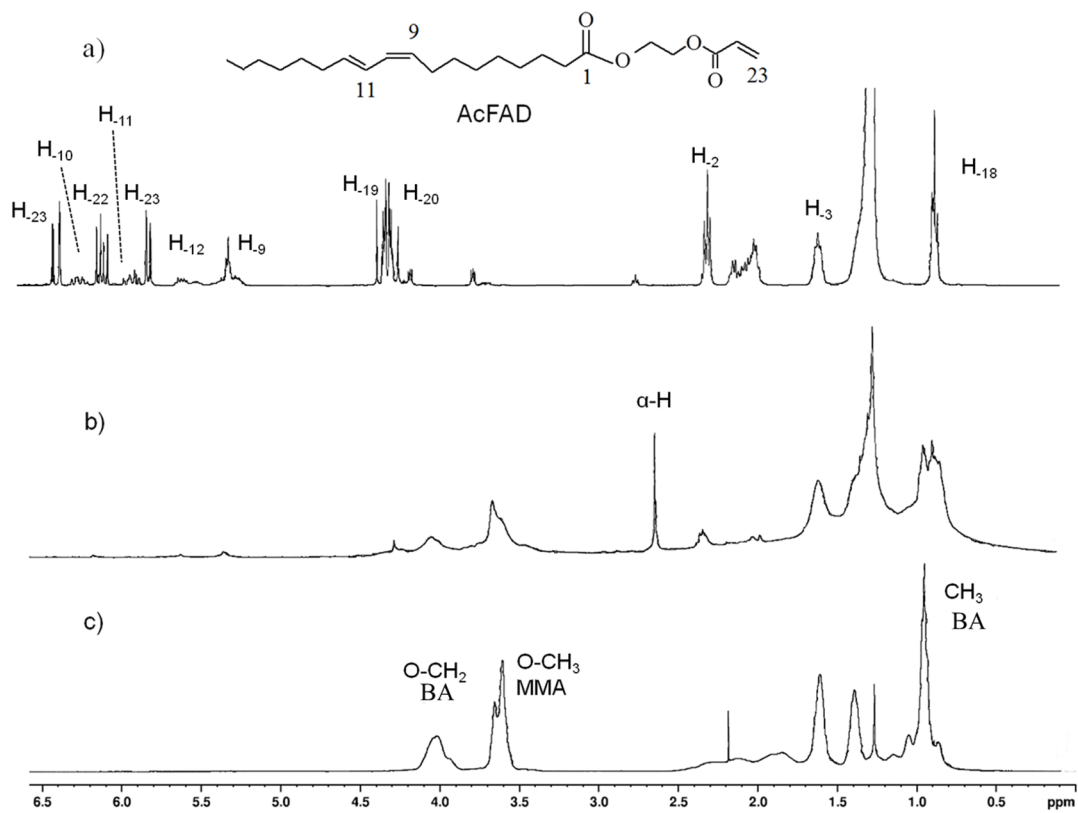


Fig. 2 - <sup>1</sup>H-NMR spectrum of a) AcFAD, b) latex B and c) reference acrylic latex.

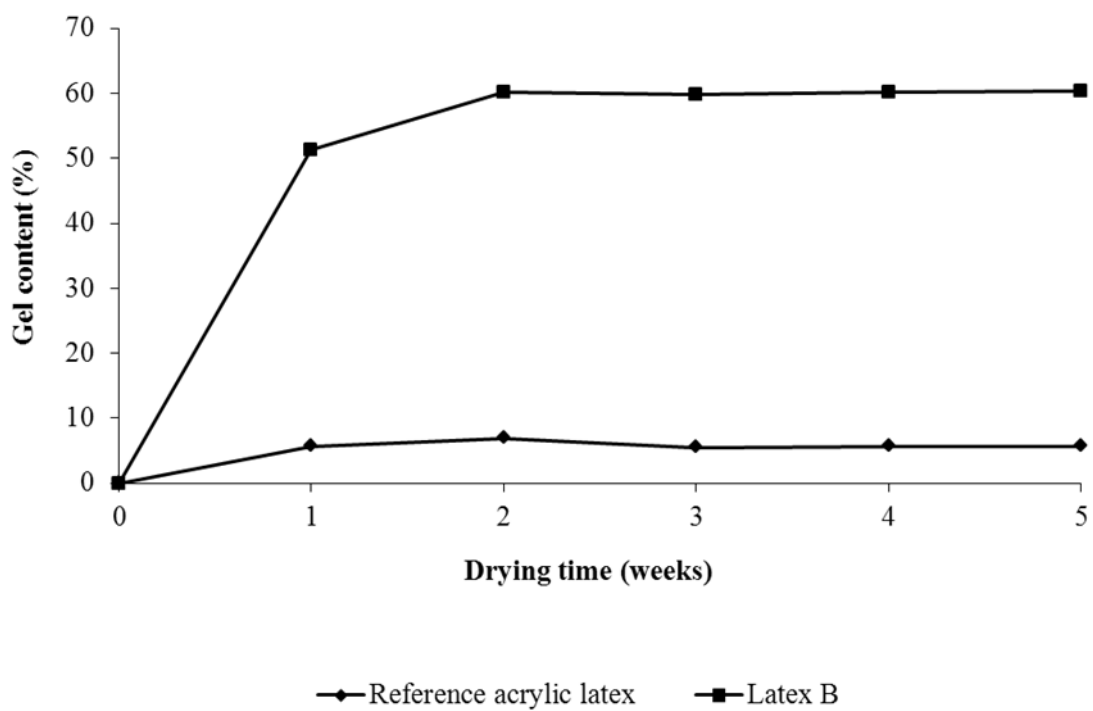
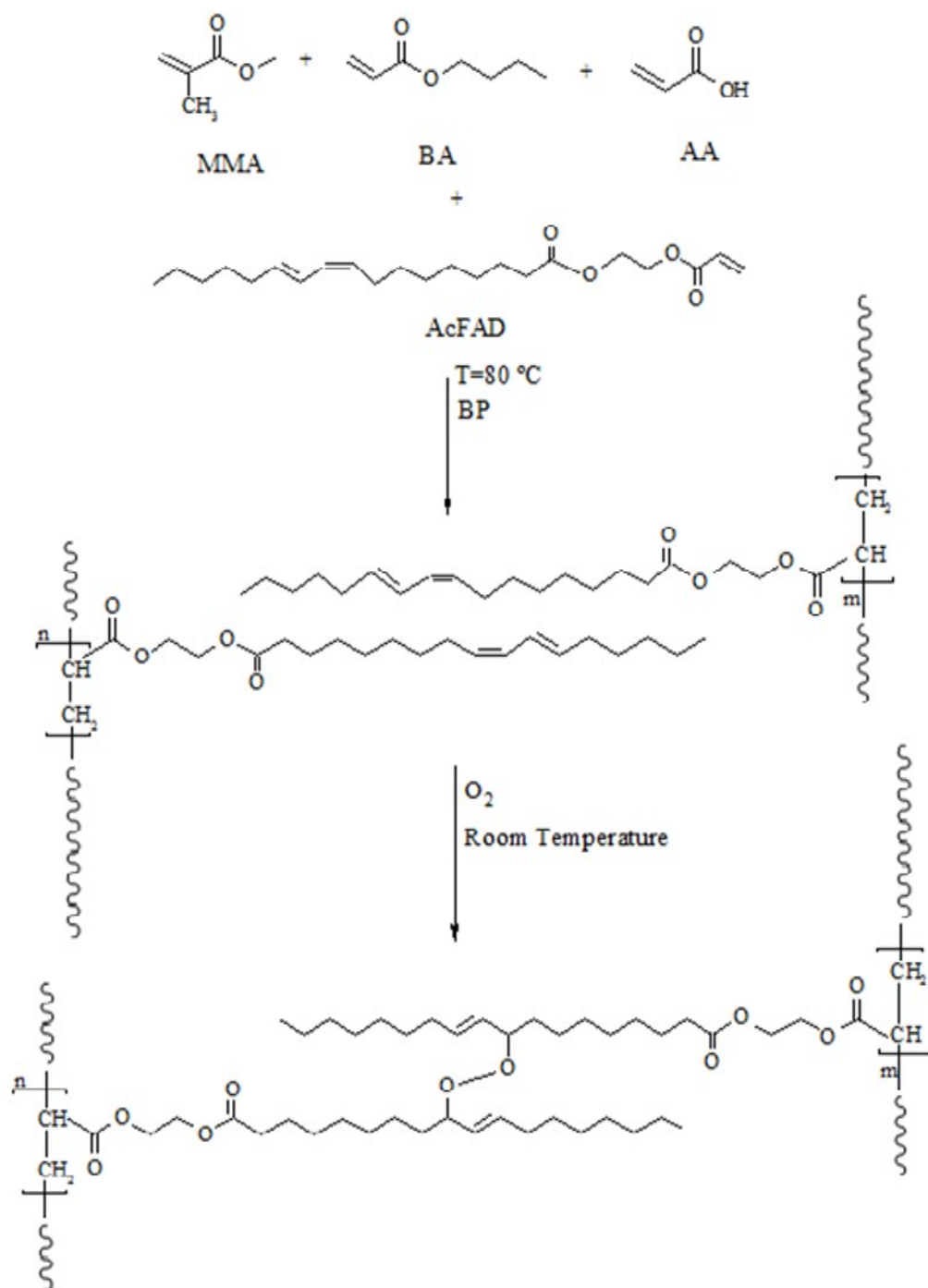
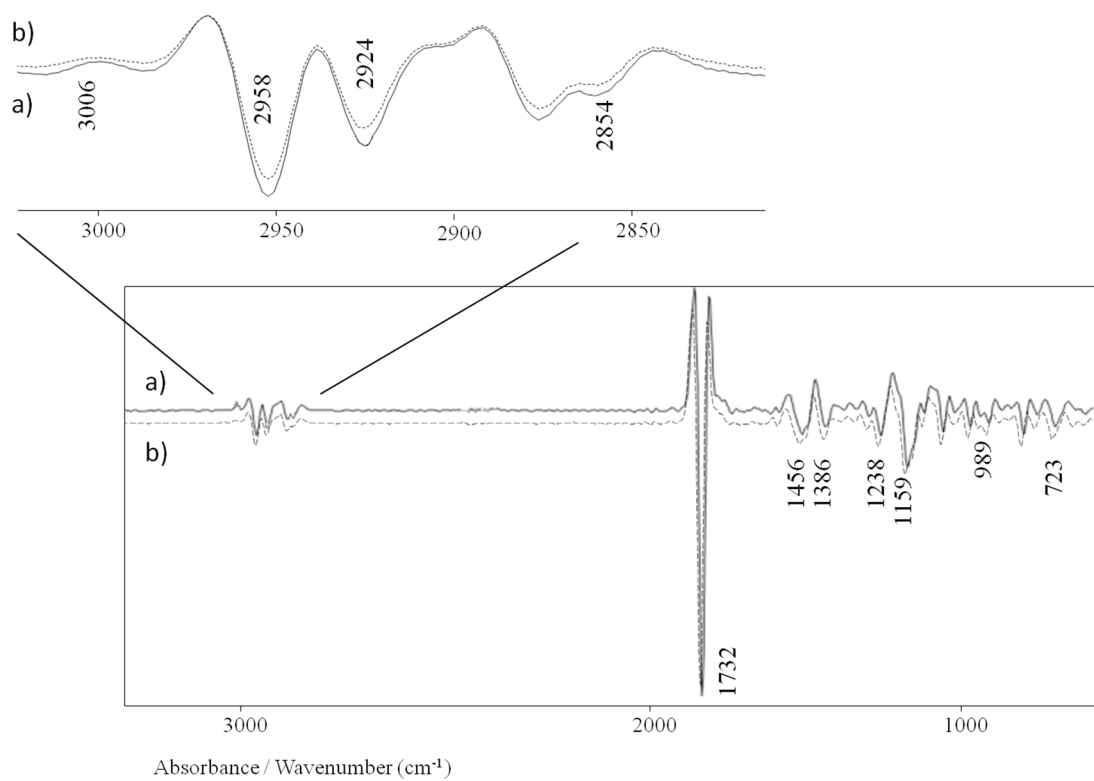


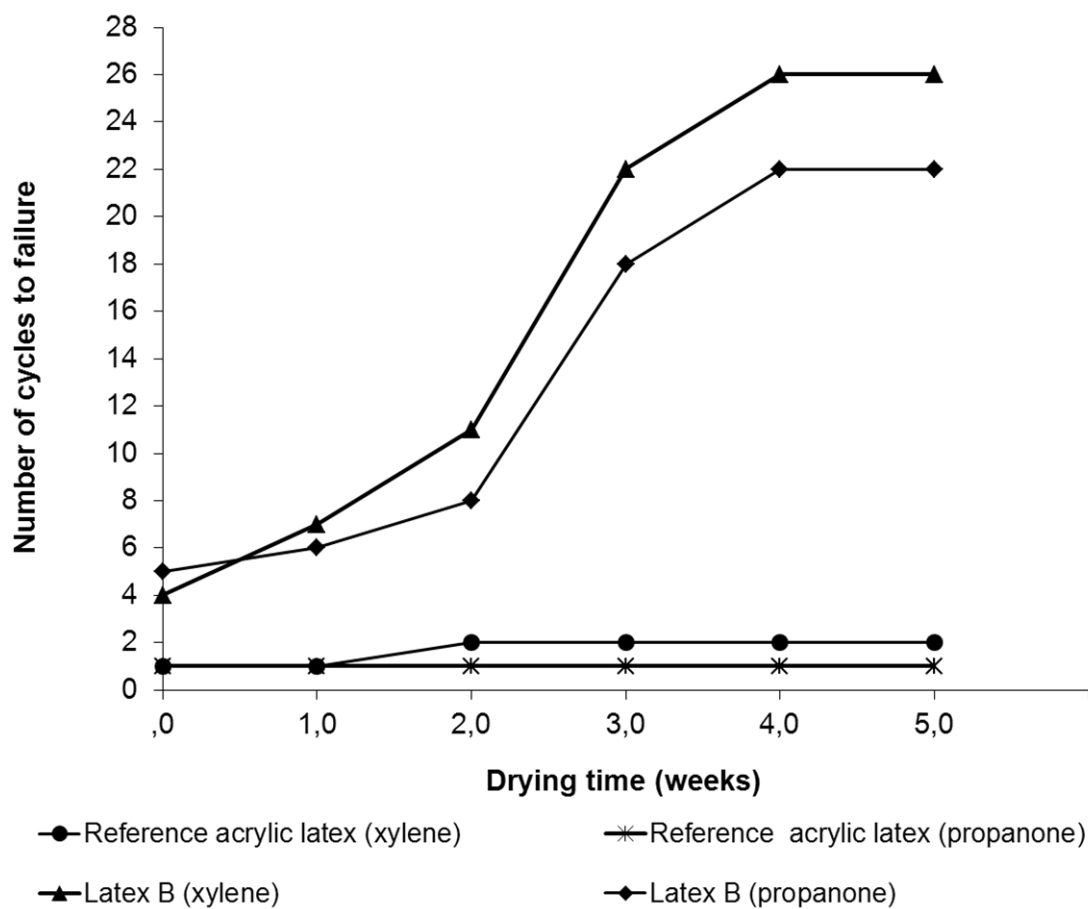
Fig. 3 – Gel content of latex B (copolymerized with AcFAD) and reference acrylic latex along drying time (AcFAD structure represents one of the possible CFAs derivatives).



**Fig. 4** – Polymeric chain formation and crosslinking by peroxide bond.



**Fig. 5** – Second derivative FT-IR spectra and of: a) acrylic latex formulated with AcFAD after one day of drying and b) acrylic latex formulated with AcFAD after five weeks of drying.



**Fig. 6** – Solvent resistance of latex B (copolymerized with AcFAD) and reference acrylic latex, using a) xylene and b) propanone solvents.

**Table 1** –Characterization of acrylic emulsion formulations

	<b>Reference emulsion</b>	<b>Emulsion A</b>	<b>Emulsion B</b>
<b>Monomers</b>			
Methyl methacrylate (wt.%)	19.1	14.1	14.1
Butyl acrylate (wt.%)	19.1	14.1	14.1
Acrylic acid (wt.%)	2.3	2.3	2.3
AcFAD (wt.%)	0.0	10	10
<b>Surfactants</b>			
Ethoxylated alkyl sulphate (wt.%)	2.0	2.0	0.0
Dodecyl benzenesulfonic acid sodium salt (wt.%)	0.0	0.0	1.0
Fatty alcohol ether sulfosuccinate disodium salt (FAES) (wt.%)	0.0	0.0	1.0
<b>Others</b>			
Sodium persulfate, additives (biocides, anti-foaming, pH control agent) (wt.%)	1.5	1.5	1.5
<b>Water (wt.%)</b>	56.0	56.0	56.0
<b>Theoretical solid content (%)</b>	44.0	44.0	44.0
Viscosity (mPa·s)	32.5	26.4	59.1
Solids contents (%)	42.6	37.3	42.4
Filtration residue (%)	1.1	2.6	1.3
MFT (°C)	15.0	6.5	-3.3