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Phosphorus modified cardanol: a greener route to reduce volatile organic compounds and impart flame retardant properties to alkyd resin coatings.

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Abstract: Novel phosphorylated cardanol molecules based on phosphonate (PO_3CR) and phosphate (PO_4CR) functions have been synthetized. Those molecules have two main actions which are described in this article: the reduction of volatile organic compounds (VOC) and the development of flame retardant (FR) properties conferred to alkyd resin coatings. Phosphorylated cardanol compounds have been successfully grafted by covalent bonds to alkyd resins thanks to auto-oxidative reaction. The impact of the introduction of PO_3CR and PO_4CR on the film properties such as drying time and flexibility have been studied and the thermal and flame retardant properties through differential scanning calorimeter, thermogravimetric analysis and pyrolysis-combustion flow calorimeter. These studies underscored an increase of the thermal stability and FR properties of the alkyd resins. In cone calorimeter test, the lowest pHRR was obtained with 3 wt% P of phosphate-cardanol and exhibited a value of 170 $KW.m^{-2}$, which represented a decrease of almost 46 % compared to the POxCR-free alkyd resins. Moreover, a difference about the mode of action between phosphonate and phosphate compounds has been highlighted. The most effective coating which combined excellent FR properties and good coating properties has been obtained with 2 wt% P of phosphate-cardanol. Indeed, the film properties were closed to the POxCR-free alkyd resin and the pHRR decreased of 41 % compared to the reference alkyd resin.

Keywords: Alkyd resins, VOC, reactive diluent, cardanol, phosphonate, phosphate, flame retardant

1. Introduction

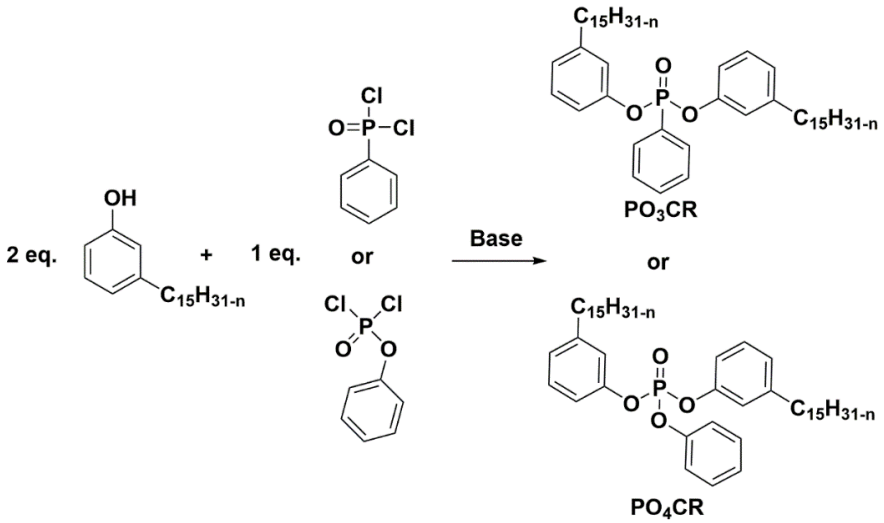
Since their first synthesis in the mid-1920s, alkyd resins have been widely used as binders in paints and varnishes for coating applications [1–4]. Alkyd resins are polyesters obtained by polycondensation reaction between fatty acids or vegetable oils, anhydrides or acids and polyols [5–7]. Alkyd resins present the major advantage to composed mainly of biobased raw materials Nevertheless, to allow the application by reducing the viscosity, traditional alkyd coating formulations are composed of 20 to 60 wt% of solvent. Those solvents are usually hydrocarbons such as xylene or white spirit, derived from fossil resources [8,9]. Those are volatile organic compounds (VOC), released in the atmosphere that may lead to environmental and human health concerns [10,11]. Hence, their use is limited by European regulations [1,7,12]. Therefore, since several decades, research have focused on the development of water-based alkyd coatings through the use of emulsifiers [13]. Despite great progress waterborne alkyd coatings suffer from poor scrub resistance, low corrosion resistance, undesirable yellowing effect and necessity the use of biocide [7,13,14]. In order to overcome these limitations, inorganic or organic fillers have to be incorporated in water-based alkyd coatings [15]. Nevertheless, these fillers

could be expensive and modify the mechanical properties. An effective approach to reduce the VOC content of alkyd coating formulations and maintain traditional alkyd performances is the use of reactive diluents to replace a part of the volatile solvent. Reactive diluents are chemical compounds that reduce the viscosity of the formulation, while reacting with the polymer during the curing and therefore reducing VOC content [16,17]. Hence, such reactive diluents need a low viscosity, a low volatility, a great compatibility to promote solubility and the capacity to form a 3D network with alkyd resins during the drying process by auto-oxidative reactions [18–21].

Nowadays, the use of industrial wastes or by-products is one of the environmental challenges faced by many industries and universities over the past few years [6]. Cashew nut shell liquid (CNSL), is a non-edible by-product of the cashew nut industry, directly extracted from the cashew nut shell [22]. With an annual production approaching one million tons, CNSL is a major and economical renewable resource [23, 24]. Cardanol is readily obtained from CNSL, composed of a phenol group which can provide corrosion resistance, and of an unsaturated fatty chain compatible with alkyd resins and able to achieve auto-oxidative reaction during the curing process. Wang *et al.* studied the advantages of cardanol (CO), cardanol methacrylate (MACO) and triethoxysilane-functionalized cardanol (TSCO) as reactive diluents for alkyd coatings [25]. They have demonstrated that the viscosity of the alkyd resins decreased with the growing amount of CO, MACO and TSCO. In a second study, the authors demonstrated that the introduction of 5 wt% MACO or TSCO can reduce the amount of xylene up to 9 wt% while maintaining the viscosity of the alkyd coating formulations [13].

Moreover, as all polymers, alkyd resins suffer from their flammability because of their high contents of hydrogen and carbon elements. The new efficient generation of friendly-environmentally flame retardants (FR) combines phosphorus-containing groups and biobased compounds [26]. The association of cardanol with phosphonate or phosphate functions could provide a double solution in terms of diluent and FR properties. One way to overcome the flammability is the addition of flame retardant (FR) in the polymer matrix. Pillai *et al.* have synthetized a flame retardant through the modification of cardanol hydroxyl group with phosphoric acid [24]. This phosphorylated cardanol exhibited high thermal stability. Ecochard *et al*. have investigated the flame retardancy of phosphoryl chloride ($POCl_3$) modified cardanol in epoxy resins [27]. These resins exhibited lower peak of heat release rate (pHRR) and total heat released (THR) in cone calorimeter analysis as well as an increase of char residue which indicated good flame retardancy properties. Phalak *et al.* have synthetized an acrylated cardanol diphenyl phosphate with flame retardant properties [28]. The UV cured coatings exhibited higher char residue and enhanced LOI value and UL-94 rating. Mestry *et al.* have demonstrated the increase of LOI value and char residue for polyurethane coatings based on cardanol modified with phenylphosphonic dichloride [29].

Furthermore, to the best of our knowledge, a cardanol-based FR reactive diluent has never been reported in the literature. Hence, this article studies the modification of cardanol with phosphorus-containing compounds (**Scheme 1**) in order to synthetize novel reactive diluents with flame retardant properties. The phosphorylated cardanol reactive (PO_xCR) diluents were introduced in alkyd resin formulations to reduce the amount of VOC. Molecular structures of PO_xCR diluents were characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) and alkyd resins by size exclusion chromatography (SEC). The viscosity of the alkyd resins was determined by rheological analysis. The flame retardancy properties were investigated by thermogravimetric analysis (TGA), pyrolysis combustion flow calorimeter analysis (PCFC) and cone calorimeter. Char formation and heat release rate were discussed in function of phosphonate and phosphate molecules. Furthermore, the film properties of alkyd resins were also studied through characterizations such as gloss, hardness, chemical resistance and drying time.



Scheme 1. General synthesis of the phosphonate- or phosphate-cardanol as reactive diluent (PO_3CR and PO_4CR).

2. Materials and methods

2.1. Materials

Tall oil fatty acid (TOFA), glycerol, phthalic anhydride, benzoic acid, mix of driers (a solution containing cobalt octoate, calcium octoate and zirconium octoate) were kindly supplied by Lixol (Groupe Berkem, Blanquefort, France). Cardanol NX-2026 was kindly provided by Cardolite. Phenylphosphonic dichloride, phenyl dichlorophosphate, triethylamine (TEA) and xylene were purchased from Sigma Aldrich. Sodium chloride (NaCl), sodium bicarbonate (NaHCO3), hydrochloric acid (HCl), magnesium sulfate (MgSO4), dichloromethane (DCM) and tetrahydrofuran (THF) were purchased from VWR International S.A.S (Fontenay-sous-Bois, France). The NMR solvent used were CDCl3 and THF-d8 from Eurisotop. All reagents were used as received.

2.2. Methods

2.2.1 Nuclear Magnetic Resonance

NMR samples were prepared with $CDCl_3$ as solvent and the analyses were performed using a Bruker Avance I 400 MHz spectrometer at 25 °C. The structure of monomers was determined by hydrogen nuclear magnetic resonance (^{1}H NMR), and phosphorus nuclear magnetic resonance (^{31}P NMR). The ^{1}H NMR spectra were recorded at 8 kHz for spectral width, 3 kHz for transmitter frequency offset, 4 seconds for acquisition time and 8 scans were performed. Quantitivity conditions were obtained with a 30° pulse (3 μs) and a relaxation delay at 1 second. The ^{31}P NMR spectra were recorded at 64 kHz for spectral width, 8000 Hz for transmitter frequency offset, 1 second for acquisition time and 4 scans were performed. Quantitivity conditions were obtained with a 30° pulse (2.7 μs) and a relaxation delay at 20 seconds. External references were trimethylsilane (TMS) for ^{1}H and phosphoric acid (H_3PO_4) for ^{31}P NMR. Shifts were given in ppm. Furthermore, to confirm the crosslinking between the alkyd resins and phosphorylated cardanol monomers high resolution magic angle spinning (HRMAS) NMR experiments have been investigated. HRMAS NMR experiments were carried out on a Varian VNMRS 600 MHz spectrometer equipped with a wide bore magnet (B0 = 14.1 T). Prior to ^{1}H HRMAS NMR experiments, cured alkyd resins were grinded thanks to a cryogenic grinder and the powders were injected in a 4 mm quartz zirconia HRMAS rotor. Then, THF-d_8 was in-

jected as solvent and experiments were performed at 20 °C, 9.6 kHz for spectral width, 1200 Hz for transmitter frequency offset, 1.7 seconds for acquisition time and 8 scans. Quantitivity conditions were obtained with a 30° pulse (3.9 µs) and a relaxation delay at 1 second.

2.2.2 Acid value (AV)

Acid values were determined according to ISO 2114:2000 standard. It corresponds to the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin mass. Approximatively, 1 g of the reaction mixture was withdrawn and solubilized in a neutralizing solution (80/20 xylene/ethanol). The solution was then titrated with a KOH solution at 0.1 mol.mL^{-1}. Thanks to the following equation (1), the acid value was calculated.

$$AV = \frac{V_{KOH} \times M_{KOH} \times C_{KOH}}{m \times N.V.C.} \quad (1)$$

AV: Acid value; V_{KOH}: volume of KOH solution introduced to neutralize the alkyd resin (mL); M_{KOH}: molecular weight of KOH (g.mol^{-1}); C_{KOH}: concentration of KOH (mol.mL^{-1}); m: mass of alkyd resin withdraw (g); N.V.C.: Non Volatile Content of the sampled resin.

2.2.3 Rheological analysis

Rheological analyses were performed on a ThermoScientific Haake Mars 60 rheometer equipped with a 35-mm-cone-plate geometry. The analyses were performed at 20 °C with a shear rate of 10 s^{-1}.

2.2.4 Size-exclusion chromatography (SEC)

Molecular weights of alkyd resins were determined by size-exclusion chromatography (SEC). SEC was recorded using a triple-detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multidetector GPC calculation. The system used two PL1113-6300 ResiPore 300 × 7.5 mm columns with THF as the eluent with a flow rate of 1 mL min^{-1}. The detector was a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35 °C. Polymethylmethacrylate (PMMA) standards were used for calibration between 540 and 2 210 000 g.mol^{-1}. The typical sample concentration was 15 mg.mL^{-1}.

2.2.5 Gel content (GC)

The resins were mixed with 5 wt% of mix of driers (cobalt octoate, calcium octoate and zirconium octoate) to crosslink them with the phosphorus reactive diluent. Then, three samples from the same alkyd resin films, of around 20 mg each, were separately immersed in THF for 24 h. The three samples were then dried in a ventilated oven at 70 °C for 24h. The gel content (GC) was calculated using equation (2), where m_2 is the mass of the dried material and m_1 is the initial mass. Reported gel content are average values of the three samples.

$$GC = \frac{m_2}{m_1} \times 100 \quad (2)$$

2.2.6 Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a Netzsch DSC200F3 calorimeter. The calibration was performed using adamantane, biphenyl, indium, tin, bismuth and zinc standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at 20 °C/min between -100 and 100 °C to observe the glass transition temperature.

2.2.7 Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) of the cured alkyd resins were carried out to determine the thermal stability and were performed on a Netzsch TG 209F1 apparatus under 40 $mL.min^{-1}$ nitrogen flow. The protective gas used was nitrogen with a 20 $mL.min^{-1}$ flow. Approximately 10-12 mg of sample were placed in an alumina crucible and heated from room temperature to 850°C with a 20°$C.min^{-1}$ heating rate.

2.2.8 Pyrolysis combustion flow calorimeter (PCFC)

Flammability of resins was analyzed using a pyrolysis combustion flow calorimeter (PCFC). About 3-4 mg were placed in the pyrolyzer, undergoing an increase of temperature from 100 °C to 750 °C at a rate of 1 °$C.s^{-1}$ under a nitrogen flow. Pyrolytic gases were sent to a combustor heated at 900 °C under air flow (N_2/O_2 = 80/20). At this temperature and with 20% of oxygen, combustion was considered to be complete. Heat release rate (HRR) was determined according to oxygen depletion (Huggett's relation) as in cone calorimeter test. PCFC analyses correspond to anaerobic pyrolysis followed by high temperature oxidation of decomposition products (complete combustion) [30]. All samples were tested in triplicate.

2.2.9 Cone calorimeter

Cone calorimeter tests were carried out to investigate the fire behavior of resins used as coating on wood specimens. The alkyd resins were applied on a pine wood sample (100*100*25 mm) to obtain a coating of 0.01 $g.cm^{-2}$. The samples were placed at 2.5 cm below a conic heater and isolated by rock wool. The samples were exposed to a 35 $kW.m^{-2}$ heat flux in well-ventilated conditions (air rate 24 $L.s^{-1}$) in the presence of a spark igniter to force the ignition. Heat release rate (HRR) was determined by oxygen depletion according to Huggett principle (1 kg of consumed oxygen corresponds to 13.1 MJ of heat released) [31]. Peak of Heat Release Rate (pHRR) is the maximal value of the heat release rate. The total heat released (THR) was obtained by integration of HRR curves. All samples were tested in triplicate.

2.2.10 Film properties

100 μm wet films were applied with a film applicator and dried at 25 °C under relative humidity of 30 %. The dry film thickness was 60 μm in all cases. Adhesion was measured using a cross-cut tester 1 mm BYK according to ISO 2409:2020 standard. The hardness (Persoz hardness) was determined according to ISO 1522:2006 standard with a TQC SP0500 pendulum hardness tester. Gloss was measured based on ISO 2813:2014 standard and the measurements were performed on substrates at 60° and 20° using a TQC Polygloss. The values for the hardness and the gloss measurements were determined at day +10 (D+10) after the application of the film. The drying time of the resins was considered as the time required to obtain a tack-free film. The chemical resistance of the alkyd resins was studied on water (H_2O), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl) [30]. Approximatively 30 ± 1 mg of the cured alkyd resins were immersed inside each solvent during six hours at room temperature and stirred at 200 rpm. Then, they were dried in an oven at 70 °C for 12 hours. The residual

mass percentage (wt% residue) was determined using equation (3). The analyses were made in triplicate for each sample and the reported residual mass percentages are average values of the three samples.

$$wt\%\ residue = \frac{m_2}{m_1} \times 100 \quad (3)$$

m_1: mass of the alkyd resin sample before being immersed in solvent; m_2: mass of the alkyd resin sample after being immersed in a solvent and dried in oven.

2.2.11 Synthesis of phosphonate cardanol diluent (PO_3RC)

A solution of 100 g cardanol NX-2026 (0.333 mol, 2 equiv.) and 37.03 g of triethylamine (0.366 mol, 2.2 equiv.) in 500 mL of dichloromethane was purged with nitrogen during 20 min and cooled down to 0 °C. Then, 32.5 g of phenylphosphonic dichloride (0.166 mol, 1 equiv.) was added dropwise over 1 h with a dropping funnel. The mixture was stirred for additional 30 minutes at 0 °C and then allowed to warm up to room temperature. The mixture was stirred overnight. When the reaction was completed, the mixture was washed three times with 300 mL of HCl 1M solution, a saturated aqueous solution of $NaHCO_3$ and then a saturated aqueous solution of NaCl. The organic layer was dried with anhydrous $MgSO_4$ and distilled under reduced pressure (10 mbar) at 30 °C to give 114.7 g of phosphonate-cardanol as a pale-yellow oil (95 % yield). The phosphonate-cardanol exhibited a phosphorus percentage of 4.3 %. The structure of phosphonate-cardanol is presented in **Figure 1a**.

^{31}P NMR (161.6 MHz, $CDCl_3$, ppm): δ: 11.5

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ: 7.99 (m, 2H, aromatic protons 5 and 9), 7.59 (dt, 1H, aromatic protons 7), 7.50 (m, 2H aromatic protons 6 and 8), 7.19 (t, 2H, aromatic protons 2), 6.99 (m, 6H, aromatic protons 1, 3, and 4), 5.80–5.90 (m, 1H, CH of C_{15} chain, proton i), 5.34–5.50 (m, CH of C_{15} chain, internal double bond protons h), 4.98–5.11 (m, 2H, CH_2 of C_{15} chain, protons of the terminal double bond g), 2.82 (m, 2H, CH_2 of C_{15} chain, protons f), 2.61 (t, 2H, CH_2 of C_{15} chain, protons e), 2.00–2.15 (m, 2H, CH_2 of C_{15} chain, protons d), 1.64 (m, 2H, CH_2 of C_{15} chain, protons c), 1.20–1.50 (m, CH_2 of C_{15} chain, protons b, b′), 0.92 (m, 3H, CH_3 of C_{15} chain, terminal –CH_3, protons a, a′).

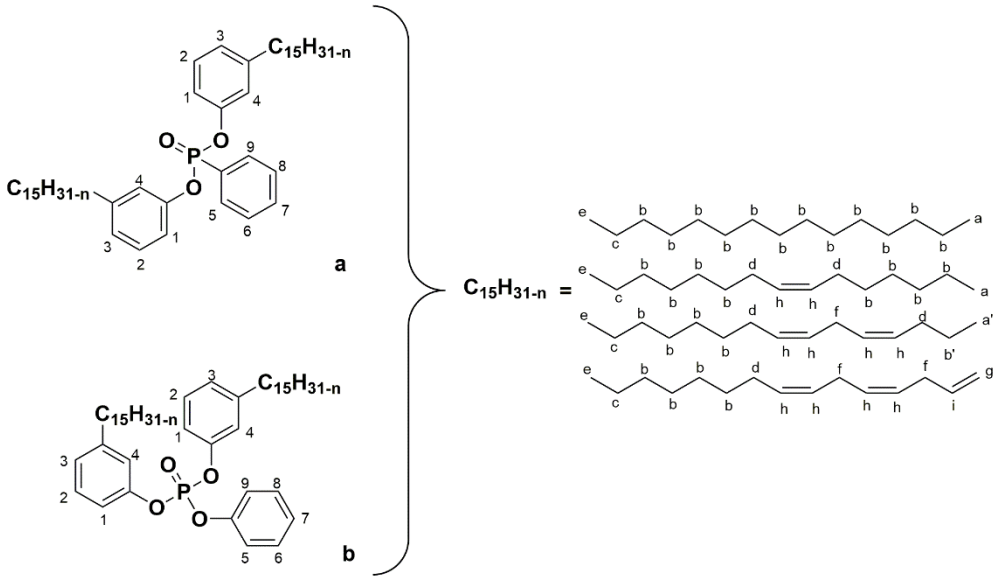


Figure 1. Structure of phosphonate- and phosphate-cardanol.

2.2.12 Synthesis of phosphate cardanol diluent (PO_4RC)

A solution of 100 g cardanol NX-2026 (0.333 mol, 2 equiv.) and 37.03 g triethylamine (0.366 mol, 2.2 equiv.) in 500 mL of dichloromethane was purged with nitrogen during 20 min and cooled down to 0 °C. Then, 35.1 g of phenyl dichlorophosphate (0.166, 1 equiv.) was added dropwise over 1 h with a dropping funnel. The mixture was stirred for additional 30 minutes at 0 °C and then allowed to warm up to room temperature. The mixture was stirred overnight. When the reaction was completed, the mixture was washed three times with 300 mL of HCl 1M solution, a saturated aqueous solution of $NaHCO_3$ and then a saturated aqueous solution of NaCl. The organic layer was dried with anhydrous $MgSO_4$ and distilled under reduced pressure (10 mbar) at 30 °C to give 115.9 g of phosphonate cardanol as a pale-yellow oil (94 % yield). The phosphate-cardanol exhibited a phosphorus percentage of 4.2 %. The structure of phosphate-cardanol ispresented in **Figure 1b**.

^{31}P NMR (161.6 MHz, $CDCl_3$, ppm): δ: -17.7

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ: 7.37 (m, 2H, aromatic protons 5 and 9), 7.24-7.28 (m, 3H, aromatic protons 6, 7 and 8), 7.19-7.24 (m, 2H, aromatic proton 2), 7.05 (m, 6H, aromatic protons 1, 3, and 4), 5.80–5.90 (m, 1H, CH of C_{15} chain, proton i), 5.34–5.50 (m, CH of C_{15} chain, internal double bond protons h), 4.98–5.11 (m, 2H, CH_2 of C_{15} chain, protons of the terminal double bond g), 2.82 (m, 2H, CH_2 of C_{15} chain, protons f), 2.61 (t, 2H, CH_2 of C_{15} chain, protons e), 2.00–2.15 (m, 2H, CH_2 of C_{15} chain, protons d), 1.64 (m, 2H, CH_2 of C_{15} chain, protons c), 1.20–1.50 (m, CH_2 of C_{15} chain, protons b, b′), 0.92 (m, 3H, CH_3 of C_{15} chain, terminal –CH_3, protons a, a′).

2.2.13 Synthesis of tall oil fatty acids (TOFA) alkyd resin

A short oil TOFA alkyd resin was prepared by solvent process using TOFA, glycerol, phthalic anhydride and benzoic acid. TOFA and glycerol were firstly added in a five-necked reactor flask equipped with a mechanical stirrer, a Dean Stark, a thermometer and a nitrogen inlet. Then, when the mixture reached 200 °C, phthalic anhydride and benzoic acid were added. Reaction mixture was heated to 220 °C using xylene as azeotropic solvent to remove water. The reaction was continued until an acid value of 14 mg of KOH/g of resin was reached.

2.2.14 Preparation of the mixture alkyd resin – reactive diluent

Different ratios of PO_xCR diluents (with x=3 or 4) were added to obtain alkyd resins with 0 wt%, 1 wt%, 2 wt% and 3 wt% of phosphorus. The different formulations of alkyd resins with phosphorylated cardanol reactive diluents are presented in **Table 1**. The structure of short oil TOFA alkyd resin is presented in **Scheme 3**.

Table 1. Composition of phosphorylated cardanol reactive diluent alkyd resins at the same viscosity (5.3 Pa.s)

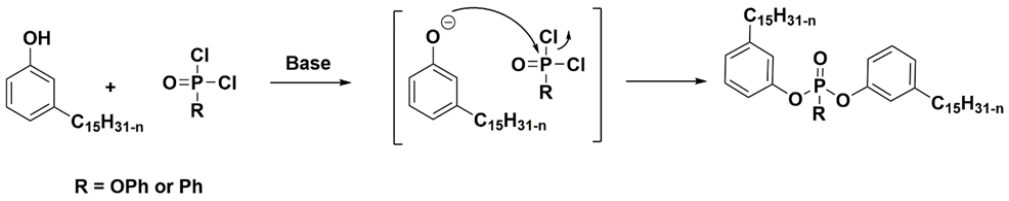
	Reference	**Phosphonate**			**Phosphate**		
Wt %P	0	1	2	3	1	2	3
Xylene content (wt%)	40	31	20	9	29	20	9
Reactive diluent content (wt%)	0	16	37	63	17	38	64
Alkyd resin content (wt%)	60	54	43	27	53	42	26

N.V.C. (wt%)	60	70	80	90	70	80	90

3. Results and discussion

3.1 Synthesis of phosphorus cardanol reactive (POxCR) diluent containing TOFA alkyd resin

The synthesis of POxCR diluents (with x=3 or 4) is represented in **Scheme 2**. The derivative Williamson reaction with phosphorus-containing compounds has been widely investigated in several articles [27, 33–35]. Phosphorus chloride and cardanol were added in ratio 1:2 and stirred overnight at room temperature. This Williamson reaction allowed the formation of P-O bond through a SN_2 mechanism.



Scheme 2. Mechanism of Williamson reaction with phosphorus dichloride compounds.

Phosphorus-containing cardanol molecules were characterized by ^{31}P and ^{1}H NMR (**SI Figures 1 and 2**) spectroscopy. The ^{31}P NMR spectra in $CDCl_3$ are presented in Figure 2. The disappearance of signal at 34.4 ppm for phenylphosphonic dichloride in the ^{31}P NMR spectra and the appearance of the chemical shift at 11.5 ppm confirmed the formation of phosphonate-cardanol (**Figure 2 a) and b**)). Likewise, in the ^{31}P spectrum, the disappearance of the chemical shift at 3.2 ppm for phenyl dichlorophosphate and the appearance of the chemical shift at -17.7 ppm demonstrated the formation of phosphate cardanol molecule through P-O bonds (Figure 2 c and d).

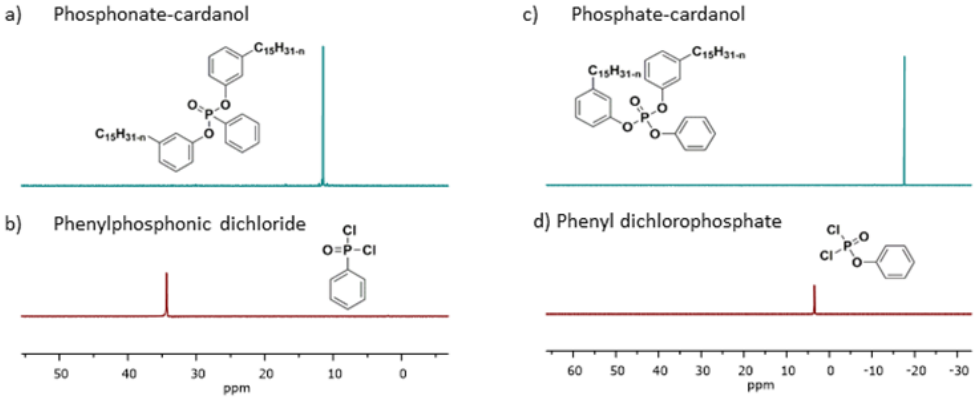
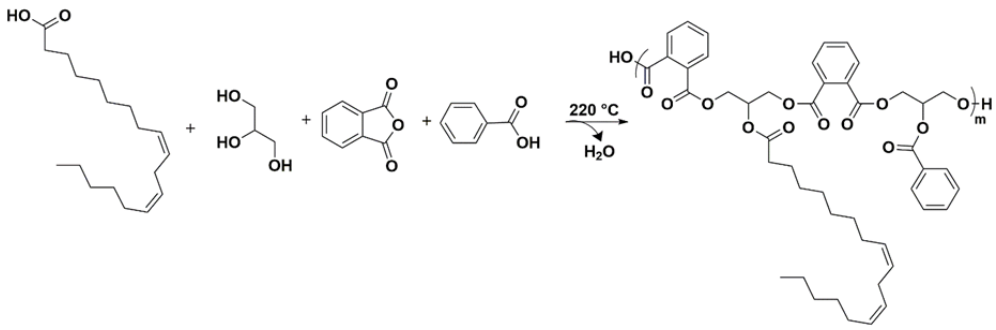


Figure 2. ^{31}P NMR spectra of phosphonate- and phosphate-cardanol compounds and their initial phosphorylated reagents.

The alkyd resins have been synthetized through a fatty acid process with the presence of xylene as an azeotropic solvent. The presence of a low amount of xylene (9 wt%) is necessary to allow the progress of the esterification reaction. The synthesis of tall oil fatty acid (TOFA) alkyd resin is presented in **Scheme 3**. The resins have been designed to present a same weight percentage of oil in their composition (also named oil length) of 38 wt%, that is why they can be classified as short oil length resins.



Scheme 3. Synthesis of TOFA alkyd resin.

Size exclusion chromatography (SEC) allowed to determine the weight average molecular weight Mw of the resins. The results (PMMA equivalent) exhibited Mw values at 200 000 $g.mol^{-1}$. High molecular weight is characteristic of short oil alkyd resins since the molecules are more compact, rigid and has less fatty acid side chain in the polymer linkages [36].

A minimal amount of 9 wt% of xylene was required to obtain a homogenous solution. Nevertheless, this study focused on the maximal reduction of solvent content to reduce the VOC of the final alkyd resins. Thereby, the PO_xCR diluents were introduced with different phosphorus percentages in the resins.

The amount of xylene was adjusted in order to reach a viscosity of 5.3 ± 0.2 Pa.s for all the resins, which is the viscosity of the reference alkyd resin without reactive diluent (**Table 1**).

Then, the non-volatile content (NVC) was determined thanks to a desiccant balance. As expected, the growing amount of PO_xCR diluent introduced in alkyd resins allowed to reduce the amount of solvent to reach the same viscosity at ± 0.2 Pa.s for all the alkyd resins. The increased amount of PO_xCR diluent introduced, decreased the quantity of alkyd resin, which also impact the viscosity diminution. The introduction of 3 wt% of phosphorus (3 wt% P) with PO_3CR and PO_4CR diluent allowed the reduction of the amount of solvent by 30 wt% compared to the reference alkyd resin. Thereby the introduction of reactive diluent allowed a sharp reduction of the volatile compounds.

Then, in order to have comparable results with the alkyd resin without reactive diluent for the following analyses, the viscosities of all the resins were also compared with the same non-volatile content of 60 wt%, as presented in Table 2. First, the introduction of 1 wt% P, which represents 16 wt% and 17 wt% of PO_3CR and PO_4CR diluents, reduced the viscosity by 68 % compared to the reference alkyd resin. With a phosphorus percentage increased from 2 wt% P to 3 wt% P, the viscosity decreased from 0.17 to 0.03 Pa.s, as presented by the asymptote curve (**SI Figure 11**). As alkyd resins are used for a wide range of paints applications, each application requires a specific viscosity. Hence, these reactive diluents offer the possibility to modify the viscosity and to reduce the VOC content.

Due to the fixed value of the volatile content, the dry films obtained exhibited the same final thickness of 60 µm which allows the comparison of the film characteristics.

During the curing of the resins, the PO_xCR diluents were crosslinked to the alkyd resins thanks to the introduction of 5 wt% of mix of driers (cobalt octoate, calcium octoate and zirconium octoate), a catalyst of autoxidation process. Indeed, cardanol and alkyd resins are both composed of unsaturated fatty acids which allow oxygen-curing in air [37]. The curing process occurs in three steps: peroxidation, peroxide decomposition and

cross-linking reaction that occurs by a free-radical mechanism. Firstly, the oxygen penetrates in the film allowing the oxidation of fatty acids and promoting the formation of hydroperoxides. As soon as they are formed, the hydroperoxides dissociate into free radicals (ROO• and RO•) which react through radical-radical combinations to form covalent carbon-carbon, ether, and peroxide bonds. To confirm the presence of a crosslinked network, different analyses were performed such as the determination of the gel content (GC) and the investigation of the disappearance of the chemical shift of unsaturations (C=C) by ^{1}H HRMAS NMR. The GC was defined as the mass of insoluble material after being exposed for 24 h in THF solvent. Indeed, an insoluble 3D network is formed when the alkyd resin is cured. For all the alkyd resins, the GC were higher than 91 % confirming the crosslinking (**Table 2**). The GC of the reference alkyd resin exhibited the highest value with 95 %. Nevertheless, the GC slightly decreased with the amount of phosphorylated cardanol. This may be attributed to the percentage of saturated chains of cardanol which accounted for 5-8 % of the alkyl chains [22]. Indeed, depending on the amount of phosphorylated cardanol introduced, the percentage of saturated chains oscillated between 1 and 5 wt% of the total mass of the alkyd resins. Those values were in accordance with the GC results. Moreover, all the resins exhibited a very close GC, allowing to conclude that phosphorylated cardanol created covalent bonds with the polymer matrix and did not deteriorate the crosslinking density. ^{1}H HRMAS experiments were also performed to confirm the crosslinking between alkyd resin and phosphorylated cardanol. In all the HRMAS NMR spectra (**SI Figure 8, 9, 10**) of the phosphorylated cardanol-modified alkyd resins, the peaks of the protons of terminal double bond (i and g Figure 1) disappeared. This result was expected because the protons of the terminal double bonds are more reactive than the protons of internal double bonds in the alkyl chains. Moreover, it showed that the phosphorylated cardanol has been crosslinked with the alkyd resin. ^{1}H NMR spectra of the alkyd resins before curing have been performed and are presented in **SI Figure 3, 4, 5 and 6**. Then, ^{1}H HRMAS NMR spectra of all the alkyd resins have been achieved and are showed in **SI Figure 7, 8, 9 and 10**. Nevertheless, only the reference alkyd resin and phosphate cardanol alkyd resins exhibited HRMAS NMR spectra with good resolutions. That is why, analyses have been performed only on those resins. The peak at 5.4-5.7 ppm corresponded to the protons of the internal double bonds. The decreased of the signal of these protons by 50 % for the reference alkyd resin and completely for the phosphorylated cardanol modified alkyd resins are consistent with the results obtained for the GC and confirmed the crosslinking between phosphorylated cardanol and alkyd resins.. These results allowed us to consider similar results with phosphonate-cardanol alkyd resins since the change of oxidation degree of the phosphorus function had no influence on the grafting of double bonds during the alkyd resin drying.

Differential scanning calorimetry (DSC) analyses were carried out to determine the glass transition temperature (Tg) of curing films and are summarized in **Table 2**. The curves are presented in **SI Figure 12**. Indeed, the flexible alkyl chain and bulky phenyl groups of PO_xCR diluents may impact the physical properties of the resins compared to the use of xylene that is theoretically removed during the drying step. The PO_xCR-free resin exhibited a Tg value of 40 °C while the introduction of PO_xCR diluent (causing the diminution of the alkyd resin content) reduced the Tg values of modified alkyd resins. Indeed, for alkyd resins containing phosphonate-cardanol, Tg values ranged from 27 °C for the alkyd resin with 1 wt% P to -11 °C for the alkyd resin with 3 wt% P. This evolution was mainly due to the introduction of alkyl chains provided by PO_xCR diluent which exhibited a low molecular weight and improved the flexibility thanks to the alkyl chain of cardanol. Moreover, the decrease of polymer content with the increased amount of PO_xCR diluent also reduced the Tg. These results showed that the oxidation state of phosphorus did not have an influence on Tg values. The Tg of 2 wt% P alkyd resins were respectively -3 °C for both PO_3CR and PO_4CR. Depending on the Tg values, the applica-

tion of alkyd resins could be different. Indeed, alkyd resins with negative Tg would rather be used for surfaces that required flexible coatings such as wood. However, high Tg would instead be used for surface that required hard coating such as metal.

Table 2. Viscosity, Tg and gel content of phosphorylated cardanol reactive diluent alkyd resins with a fixed NVC at 60 wt%.

	Reference	**Phosphonate**			**Phosphate**		
Wt %P	0	1	2	3	1	2	3
η (Pa.s) (xylene: 40 wt%)	5.3	1.67	0.17	0.03	1.65	0.16	0.03
Tg(°C)	40	27	-3	-11	26	-3	-12
Gel content (%)	95	94	93	91	94	92	91

3.2 Thermal and flame retardant properties

Thermal and flame retardancy properties were investigated in this part to highlight the influence of the PO_xCR diluents in alkyd resins. Firstly, the thermal decomposition of PO_3CR and PO_4CR was studied and compared to the thermal decomposition of cardanol, as presented in **Figure 3**. Phosphonate and phosphate functions improved the thermal stability of cardanol. Indeed, the temperature at 50 % weight loss ($T_{d,50wt\%}$) increased by 131 and 139 °C for phosphonate-cardanol (448 °C) and phosphate-cardanol (462 °C) compared to the neat cardanol (350 °C). Moreover, the char yield at 850 °C was also increased for the cardanol grafted with phosphorus compounds. Indeed, the residual yield were 2.6 %, 5.4 % and 16.5 % respectively for cardanol, phosphonate-cardanol and phosphate-cardanol. Those results were expected as phosphonate and phosphate compounds act in condensed phase by promoting char formation. Indeed, rearrangement and Diels-Alder reactions led to the formation of a carbon layer [38]. However, phosphonate compounds are much less efficient than phosphate compounds to promote char.

The thermal properties of all alkyd resin films were investigated by thermogravimetric analyses (TGA) under nitrogen flow. **Figure 4** shows the thermograms of the alkyd resins, and with respectively 1 wt%, 2 wt%, and 3 wt% of phosphorus brought by PO_xCR diluent. Thermal properties such as the decomposition temperature at 5 % weight loss, temperature at 50 % weight loss, and the residue yield at 850 °C, are summarized in **Table 3**. Thermal stability increased with the addition of PO_3CR or PO_4CR. Firstly, temperature at 5 % weight ($T_{d,5wt\%}$) increased from 140 °C for the alkyd resin without PO_xCR diluent to 180 °C and 204 °C for the resins with respectively 1 wt% P of PO_3CR and 1 wt% P of PO_4CR. Moreover, the growing amount of PO_xCR introduced in alkyd resins also increased the $T_{d,5wt\%}$. For example, the $T_{d,5wt\%}$ increased by 41 °C as the amount of phosphonate-cardanol increased from 1 wt% P to 3 wt% P. Considering the temperature at 50 % weight loss ($T_{d,50wt\%}$) the thermal stability was higher with the increasing the amount of PO_xCR . Indeed, $T_{d,50wt\%}$ varied from 350 °C for the reference resin to 390 °C and 416 °C for the resins with 3 wt% P of phosphonate-cardanol and 3 wt% P of phosphate-cardanol respectively. As expected, the thermal stability of both PO_3CR and PO_4CR alkyd resins is similar, but slightly higher for phosphate in good agreement with the stability of PO_4CR. During combustion, PO_3CR and PO_4CR may generate free radicals such as PO•, HPO•, PO_2•. Those radicals can quench the active radicals generated by the flame (H• and OH•) and then, reduce the combustion in gaseous phase, as presented in **Scheme 4** [39,40]. Nevertheless, no evidence of such mode-of-action can be provided in the present paper. Indeed, flame inhibition may be assessed by calculating the combustion efficiency in cone calorimeter (from

the comparison between the heat of complete combustion and the effective heat of combustion). Unfortunately, while the alkyd resins are used as a thin coating on woods, effective heat of combustion is mainly driven by wood combustion. Therefore, flame inhibition may be only suggested. The residue yield was impacted by the oxidation degree of the phosphorus as well as the amount of phosphorus introduced in alkyd resins. The reference alkyd resin exhibited a char yield of 5 % at 850 °C. The char yield at 850 °C increased by 7.5 % and 13.1 % for the resins with respectively 3 wt% P brought by PO_3CR and PO_4CR respectively, compared to the reference resin. Those results were also in good agreement with the better char promotion effect of phosphate observed previously. Moreover, in the literature, most reports indicated that the char residue increases as the oxidation state of phosphorus increases [40-43]. In **Scheme 4**, a mechanism of the char formation in condensed phase has been proposed. Char layer could be provided through cyclization, cross-linking and aromatization by dehydration of the polymeric structure, induced by phosphorus-cardanol. Moreover, each phosphorus-cardanol molecule contain three aromatic rings, which could bring high char content during combustion.

The residue increase may entail an insulating effect during combustion with cone calorimeter. Indeed, during combustion, phosphonate and phosphate functions provide a continuous protective carbon layer. This carbon layer could insulate the polymer and prevent heat and gas transfer between gas and condensed phases [44, 45]. Those results demonstrated that the replacement of harmful volatile compounds by environmentally friendly phosphorus reactive diluents provided excellent thermal stability.

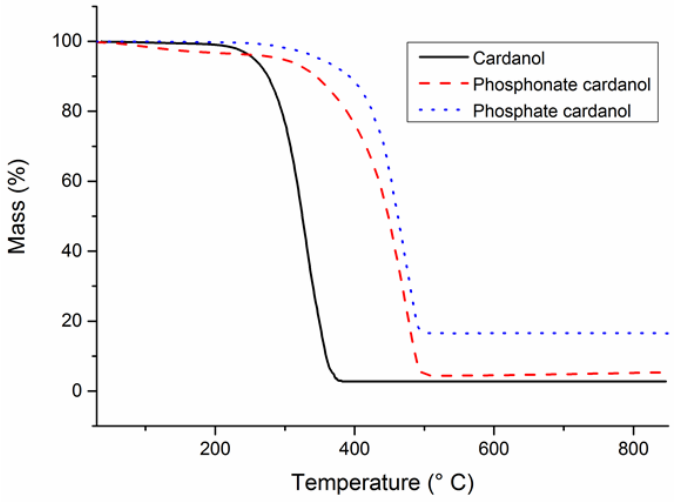


Figure 3. TGA thermograms of cardanol, phosphonate-cardanol and phosphate-cardanol.

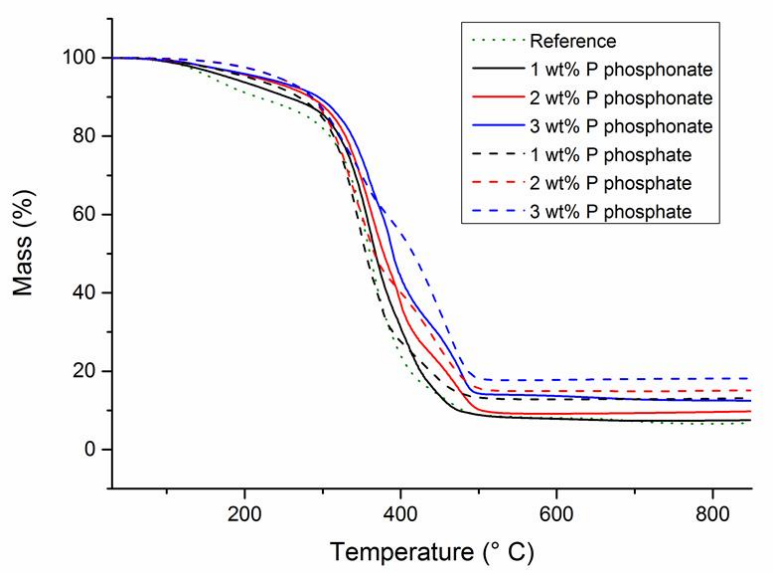
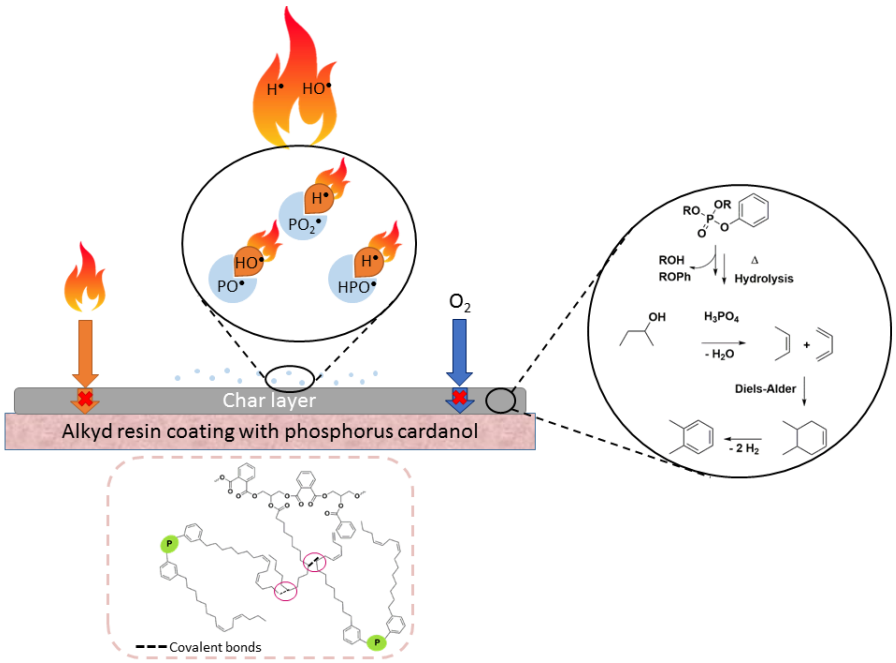


Figure 4. TGA thermograms of reference alkyd resin and phosphorylated cardanol modified alkyd resins.

Table 3. Results of TGA analyses of PO_xCR diluent alkyd resins.

	Wt %P	$T_{d,5wt\%}$ (°C)	$T_{d,50wt\%}$ (°C)	Residue at 850°C (%)
Reference	0	140	350	5.0
Phosphonate-cardanol	Monomer	294	448	6.4
	1	180	368	7.5
	2	214	378	9.8
	3	221	390	12.5
Phosphate-cardanol	Monomer	350	462	16.5
	1	204	357	14.1
	2	242	367	15.2
	3	242	416	18.7



Scheme 4. Schematic illustration of possible flame retardant mechanism

Table 4 summarizes the data obtained from PCFC analyses. In standard conditions, combustion is complete in PCFC test due to the high combustor chamber (900 °C) in presence of an excess of oxygen. The total heat release (THR) and peak of heat release rate (pHRR) are important characteristics to evaluate the flame retardant (FR) properties of a material. **Figure 5** exhibits the PCFC curves of the phosphorylated cardanol modified alkyd resins. It can be noticed that all the alkyd resins exhibited two pHRR peaks. The increased amount of phosphorylated cardanol provided a reduction of pHRR and THR values which demonstrated the FR properties of PO_3CR and PO_4CR diluents. The pHRR of the PO_xCR-free alkyd resin exhibited values of 246 and 137 $W.g^{-1}$ whereas the pHRR were 176 and 110 $W.g^{-1}$ for the alkyd resins with 1 wt% P of PO_3CR and 178 and 71 $W.g^{-1}$ for the alkyd resins with 1 wt% P of PO_4CR. Moreover, the introduction of 3 wt% P of phosphorus-cardanol, decreased the pHRR to 115 $W.g^{-1}$ and 114 or 108 $W.g^{-1}$ for PO_3CR and PO_4CR, respectively.

The temperature of the pHRR decreased with the introduction of phosphorylated cardanol. Nevertheless, all the phosphorylated cardanol modified alkyd resins exhibited a temperature of the pHRR around 350 °C. The growing amount of FR did not have an influence on this temperature.

THR values slightly decreased with increasing amounts of PO_xCR diluent in alkyd resins. Indeed, the THR value was decreased from 25.7 $KJ.g^{-1}$ for the PO_xCR-free alkyd resin to 17.3 $KJ.g^{-1}$ and 17.1 $KJ.g^{-1}$ for the alkyd resins with 3 wt% P phosphonate-cardanol and phosphate-cardanol, respectively. Moreover, the energy of complete combustion (Δh) slightly decreased with the amount of phosphorylated cardanol.

Furthermore, the residual content increased from 0.5 % to 12.0 % and 15.5 % for the reference resin and the resins with respectively 3 wt% P of PO_3CR and PO_4CR. These increases were consistent with the TGA results and demonstrated that phosphonate and phosphate compounds promoted char formation. Moreover, the residual content was slightly higher for the phosphate-cardanol, as already observed in TGA, which mainly acts in condensed phase.

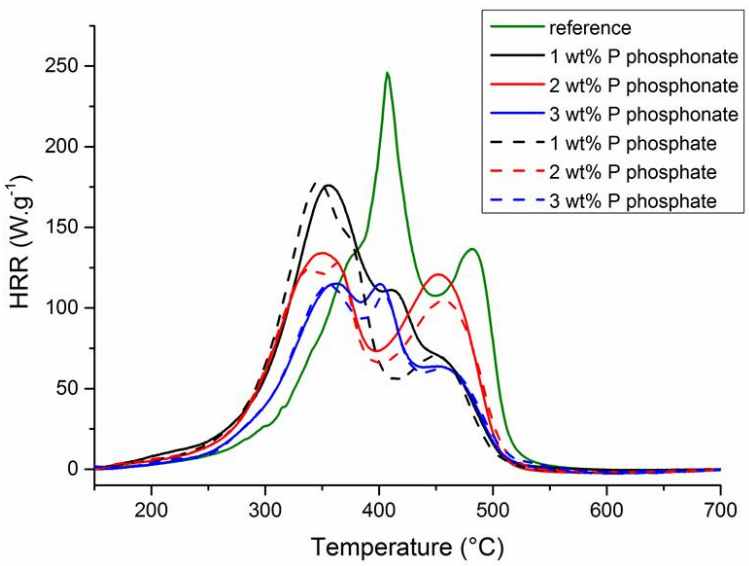


Figure 5. PCFC curves of reference alkyd resin and phosphorylated cardanol modified alkyd resins

Table 4. Results of PCFC analyses of POxCR diluent alkyd resins

	Reference	Phosphonate			Phosphate		
Wt %P	0	1	2	3	1	2	3
pHRR (W.g^{-1})	246	176	134	115	178	125	115
	137	110	120	114	71	105	108
T at pHRR (°C)	406	353	350	356	347	341	358
	482	417	453	399	450	454	402
THR (KJ.g^{-1})	25.7	23.2	21.7	17.3	21.1	20.9	17.1
Residue content (%)	0.5	5.3	8.1	12.0	10.4	12.3	15.5
Δh (KJ.g^{-1})	25.8	24.5	23.6	19.7	23.5	23.8	20.2

The cone calorimeter analyses provide important information on the fire behavior of a material [46]. Cone calorimeter tests were performed with a heat flux of 35 kW.m^{-2} under ventilated conditions. The results are summarized in **Table 5**, and **Figure 6** exhibits the cone calorimeter curves. Tests were performed on wood samples with around 1 g of dry resin as coating. The rate of heat release (HRR) as well as the total heat release (THR) are important parameters to characterize the fire performance of materials. The curves present two pHRR which is very common with wood samples. The first peak represents the heat release rate (pHRR$_1$) reached just after the ignition. After this first peak corresponding to the decomposition of the top surface of wood including the coating, the heat release rate decreases until reaching a plateau which corresponds to the steady-state decomposition rate until reaching the bottom of the sample. The lower is the plateau, the slower the pyrolysis front progresses through the thickness of the wood. When heat reaches the unexposed surface (insulated by rockwool), the heat cannot be evacuated, leading to a second peak of heat release rate (pHRR$_2$). This second peak of heat release rate is an artefact due to the geometry of cone calorimeter test and is independent of the coating. All the samples have a wood thickness around 25 mm ± 0.2 mm.

Wood without coating presented a moderate pHRR$_1$ at 190 KW.m^{-2} and the FR-free alkyd resin led to a strong enhancement of the pHRR$_1$ (up to 316 kW.m^{-2}). Indeed, coat-

518 ings usually negatively affect the flame retardancy. The use of a coating layer usually
519 negatively affects the flame retardancy of wood, but provides protection from external
520 aggressions such as UV, weather, insects. Note that the typical effective heat of combus-
521 tion of wood was close 12 $kJ.g^{-1}$ while heat of combustion measured in PCFC was 25.8
522 $kJ.g^{-1}$ for the FR-free alkyd resin. The objective was to provide a coating with better flame
523 retardancy than a standard coating. The introduction of PO_3CR and PO_4CR diluents had
524 a strong influence on the $pHRR_1$ due to their ability to act in condensed phase. Indeed,
525 alkyd coatings with PO_xCR released less quickly the energy due to the modification of the
526 degradation mechanism due to the promoted char formation. Thereby, pHRR1 decreased
527 with the amount of phosphorylated cardanol. The introduction of up to 3 wt% P
528 phosphonate-cardanol has improved flame retardancy by decreasing the pHRR from 316
529 $KW.m^{-2}$ to 174 $KW.m^{-2}$. The lower pHRR for PO_4CR was obtained with 3 wt% P and ex-
530 hibited a value of 170 $KW.m^{-2}$. Indeed, $pHRR_1$ decreased of almost 46 % compared to the
531 PO_xCR-free alkyd resins. Furthermore, the difference between PO_3CR and PO_4CR was
532 not significant with the cone calorimeter results. The increased amounts of phosphorus
533 content up to 2 wt% allowed to significantly improve the flame retardant properties.
534 However, the change from 2 wt% P to 3 wt% P did not show a further improvement of
535 flame retardancy. Moreover, the pHRR values for 2 and 3 wt% P were equivalent to the
536 pHRR of the raw wood sample.

537 Time to ignition (TTI) measures the time to achieve sustained flaming combustion at
538 a particular external heat flux. TTI was not impacted by the introduction of phosphory-
539 lated cardanol as all the alkyd resins provided a TTI around 30 s. Nevertheless, TTI for all
540 the woods with alkyd resins were at least two times lower than TTI for the uncoated
541 wood. Indeed, the addition of alkyd coatings on the wood substrate considerably re-
542 duced the TTI.

543 The effective heat of combustion (EHC), the total heat release (THR) and the resid-
544 ual mass were not discussed because the coating only influenced $pHRR_1$. All those results
545 confirmed the benefits of phosphorus cardanol reactive diluent on flame retardant
546 properties and the reduction of VOC amounts.

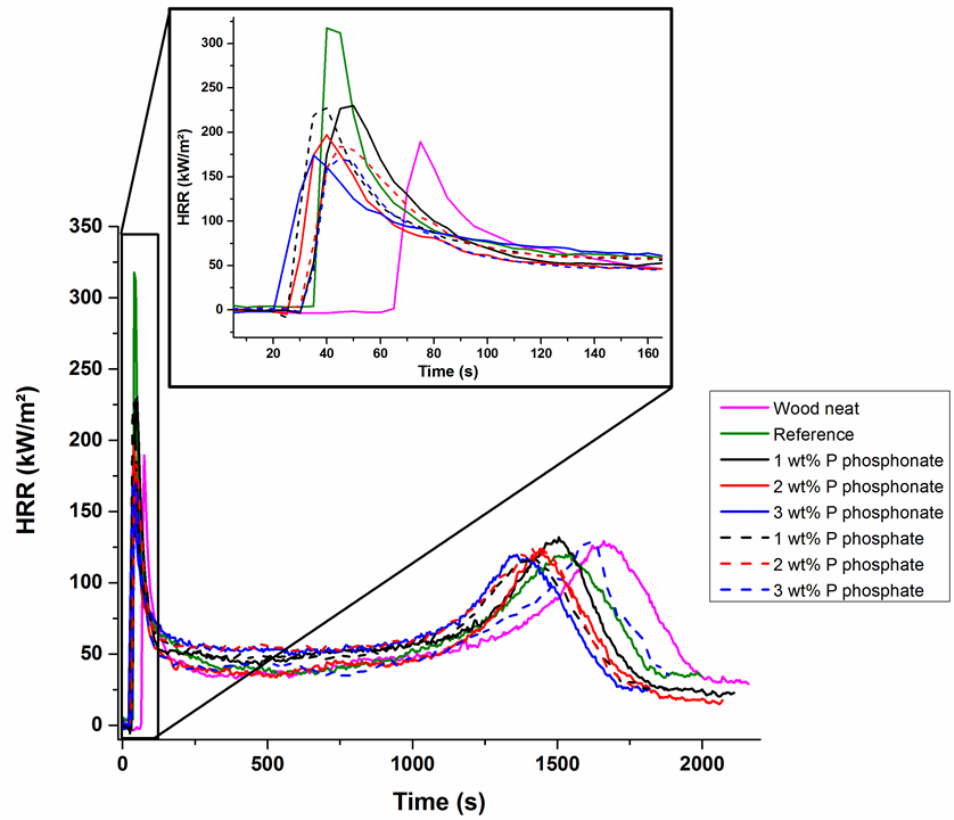


Figure 6. Curves of cone calorimeter tests for wood, reference alkyd resin and phosphorylated cardanol modified alkyd resins

Table 5. Cone calorimeter analyses of phosphorylated cardanol reactive diluent alkyd resins.

	Wood neat	Reference	Phosphonate			Phosphate		
Wt %P	0	0	1	2	3	1	2	3
TTI (s)	65	35	30	26	22	26	32	31
pHRR$_1$ (KW.m^{-2})	190 ± 10	316 ± 11	229 ± 9	197 ± 10	174 ± 13	227 ± 11	186 ± 8	170 ± 7
THR (KJ.g^{-1})	9.4	10.0	10.0	8.7	8.9	8.6	8.8	8.4

3.2 Film properties

Films of the different resins have been applied with a film applicator to provide dry films with a final thickness of around 60 µm for all the alkyd resins. Adhesion, flexibility, gloss, drying time and chemical resistance have been determined and the results are presented in the following section in **Table 6** and **Table 7**.

Table 6. Adhesion, hardness, gloss and drying time of phosphorylated cardanol reactive diluent alkyd resins.

	Reference	Phosphonate			Phosphate		
Wt %P	0	1	2	3	1	2	3
Adhesion	0	0	0	0	0	0	1
Hardness (s)	67	58	48	48	67	58	48
Gloss 20°/60°	81/96	82/98	79/97	83/98	84/98	80/97	80/95
Drying time (min)	90	180	340	420	180	340	420

All the samples exhibited excellent adhesion properties. Indeed, the edges of the cuts were completely smooth and none of the squares of the grid were torn off. The results allow an an evaluation as class 0 according to ISO2409:2020, except for the resin with 3 wt% P phosphate-cardanol which was rated at class 1. Indeed, Small flakes of the coating were detached at intersections but less than 5 % of the area was affected, which was not significant. The introduction of phosphorylated cardanol in alkyd resins did not impact the adhesion properties of the resins.

The hardness of the coating was impacted by the amount of phosphorylated cardanol introduced. The more flexible is the film, the faster the pendulum is damped and therefore the less oscillations are required (One second corresponds to one oscillation of the pendulum). Indeed, the more flexible is the film, the more it is able to absorb the energy of the pendulum. The number of oscillations decreased from 67 for the PO_xCR-free-alkyd resin to 48 for the resins with 3 wt%P phosphorylated cardanol. The introduction of phosphorylated cardanol in alkyd resins provided more flexible films. Moreover, the flexibility increased with the amount of phosphorylated cardanol. These results agree with the DSC results which showed lower Tg values with the increase of phosphorylated cardanol amount in alkyd resins. Nevertheless, even if the films were more flexibles with phosphorylated cardanol, the values were closed to that of the reference resin which means that the films remained hard enough allowing the resin to maintain its film-forming properties for wood substrates.

The gloss of the coatings was firstly measured at 60 ° to determine the gloss level. All the alkyd resins exhibited a high gloss level with values superior to 70 (between 95 and 98). The measurements were then study at 20 °. The reference resin showed a value of 81 and all the alkyd resins containing phosphorylated cardanol exhibited values between 79 and 84. The introduction of phosphorylated cardanol in alkyd resins did not impact the gloss of the resins.

The introduction of phosphorylated cardanol as a reactive diluent in alkyd resins increased the drying time. The drying time was increased by 1h30 min for the 1 wt% P modified alkyd resins compared to the drying time of PO_xCR-free-alkyd resin. Moreover, the alkyd resins with 3 wt% P showed the longest drying time, which was 7 hours. Those results are expected because the proportion of alkyd resins is lower in the formulations and as the phosphorylated cardanol exhibited a low molecular weight and acted as a plasticizer by spacing the polymer chains. Thereby more covalent bonds had to be formed to create a crosslinking network. Moreover, the incorporation of phosphorylated cardanol increased the content of fatty chains, allowing to classify PO_xCR-alkyd resins as medium oil length alkyd resins. The more an alkyd resin contains the same fatty chains, the longer is the drying time [36]. Thereby, the drying time exhibited for the 1 wt% P and 2 wt% P modified alkyd resins remained competitive with drying time of some commercial alkyd resins with medium/long oil length.

Table 7 presents results of the determination of chemical resistance of the resins. The higher is the weight loss, the lower is the residual mass percentage and the less resistant is the resin to the solvent. The chemical resistance of the alkyd resins in water was slightly better for PO_xCR modified alkyd resins. Indeed, all the PO_xCR alkyd resins exhibited a residual mass percentage superior to 95 % compared to the phosphorylated cardanol free alkyd resin at 86 %. The chemical resistance to HCl exposure presented a residual mass percentage above 90 % for all alkyd resins containing PO_xCR diluent versus 80 % for the reference alkyd resin. In the case of NaOH solution, the alkyd resins resistance was low compared to the other solutions. Indeed, all the alkyd resins exhibited a residual mass percentage around 70 %. Alkyd resins were highly resistant to NaCl solution with a residual mass superior to 95 %. The introduction of phosphorylated cardanol showed higher chemical resistance for all the alkyd resins. Nevertheless, the lower resistance to alkali solution can be due to hydrolysable ester groups in the alkyd resins [32, 47]. Indeed, saponification reactions could occur under those conditions.

Table 7. Evaluation of chemical resistance of PO_xCR-alkyd resins.

	Reference	**Phosphonate**			**Phosphate**		
Wt %P	0	1	2	3	1	2	3
Water	86 ± 2	96 ± 2	95± 3	95 ± 1	99 ± 1	98 ± 1	96 ± 2
HCl (0.1 M)	80 ± 4	91 ± 2	91 ± 1	92 ± 3	92 ± 1	91 ± 1	91 ± 1
NaOH (0.1 M)	69 ± 1	74 ± 2	75 ± 2	73 ± 3	74 ± 3	74 ± 2	73 ± 2
NaCl (5 %)	95 ± 3	97 ± 1	96 ± 1	96 ± 1	95 ± 2	95 ± 4	97 ± 1

4. Conclusion

New phosphorylated cardanol flame-retardants have been successfully synthesized and used as reactive diluent in alkyd resins in order to reduce the VOC content. Indeed, the viscosity of the alkyd resins has been strongly reduced. Phosphorylated cardanol compounds were grafted into alkyd resins after drying, highlighted by GC content and HRMAS NMR analysis. The introduction of phosphorylated cardanol reactive diluent slightly improved the chemical resistance of the alkyd resins. Nevertheless, as expected, the drying time has been increased and the T_g has been decreased with the amount of phosphorylated cardanol introduced but remained competitive. The fire behavior of those resins has been investigated by TGA, PCFC and cone calorimeter. All the alkyd resins exhibited better thermal behavior with phosphorylated cardanol. It has been demonstrated that PO_3CR and PO_4CR provided very similar results, excepted for a better char yield with PO_4CR. These results were expected as phosphate compounds mainly act in condensed phase and promote char formation. The best result was obtained with an alkyd resin modified with 2 wt% P phosphate-cardanol. Indeed, this resin exhibited strong solvent reduction and high flame retardancy properties while maintaining adequate film properties for wood application

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1. Figure 1: ^{1}H NMR spectra of phosphonate-cardanol compound. Figure 2: ^{1}H NMR spectra of phosphate-cardanol compound. Figure 3: ^{1}H NMR spectrum of reference alkyd resin before curing. Figure 4: ^{1}H NMR spectrum of phosphate cardanol modified alkyd resin (1 wt% P) before curing. Figure 5: ^{1}H NMR spectrum of phosphate cardanol modified alkyd resin (2 wt% P) before curing. Figure 6: ^{1}H NMR spectrum of phosphate cardanol modified alkyd resin (3 wt% P) before curing. Figure 7: ^{1}H HRMAS NMR spectrum of reference alkyd resin after curing. Figure 8: ^{1}H HRMAS NMR spectrum of phosphate cardanol modified alkyd resin (1 wt% P) after curing. Figure 9: ^{1}H HRMAS NMR spectrum of phosphate cardanol modified alkyd resin (2 wt% P) after curing. Figure 10: ^{1}H HRMAS NMR spectrum of phosphate cardanol modified alkyd resin (3 wt% P) after curing. Figure 11: Viscosity of the alkyd resins at different amounts of phospho-

rus-cardanol reactive diluents. Figure 12: DSC curves of alkyl resins. Table 1: Cutting tool blades depending on the coating thickness. Table 2: Damages depending on the ISO 2409 class.

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