



Effect of primary driers on oxidative drying of high-solid alkyd binder: Investigation of thickness effects by mechanical tests and infrared spectroscopy



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ABSTRACT

Catalytic activity of four primary driers was investigated in high-solid alkyd binder modified with tall oil fatty acids. The drying activity was established by mechanical tests. Infrared spectroscopy was used for detailed investigation of chemical changes during the autoxidation process. Due to strong thickness effect, the infrared study was performed using attenuated total reflectance (ATR) technique, which measures spectra of a thin layer from the interface sample/ATR crystal (down surface of the sample). Coatings of 30 μm-wet thickness were found to be enough thin to be considered as a homogeneously dried bulk with negligible effect of oxygen diffusion. It makes the 30 μm-layers very suitable for determination of kinetic parameters of the autoxidation process. For the first time, ATR-IR experiments on several samples of the same composition but different film thickness were used for detailed investigation of the thickness effect.

Two well-distinguished modes of film-formation were observed in studied drier/binder systems. Front front-forming drying occurs when the autoxidation is fast and air-oxygen diffusion is slower than its consumption. In extreme case, the film-formation process is practically ceased because impermeable skin is formed and the coating is not through-dried for very long time. The second mode, homogenous drying, is observed when autoxidation is slow and oxygen consumption is not fast enough to establish oxygen gradient in the coating.

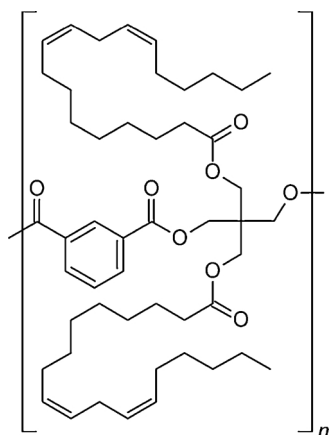
1. Introduction

Saturated polyester resins modified with vegetable oils, known as alkyd resins, have been established as significant group of air-drying paint binders used in protective and decorative coatings [1]. In last few decades, the formulations based on alkyd resins have reached great attention mainly due to high content of material available from renewable sources [2,3]. Modern alkyd paints suitable for industry and hobby market are based on high-solid (HS) and water-borne (WB) formulation fulfilling ecological concerns about low emission of volatile organic compounds (VOC) [4]. The HS formulations, with less than 30% of solvents, usually contain polymers of low molecular weight, high functionality and special architecture that ensures low viscosity and satisfactory film-forming properties [5]. In case of alkyd resins, it is usually not necessary to build particles with core-shell structure as the requirements are provided by hard polyester backbone covered by soft polyunsaturated fatty acid chains (Scheme 1). After solvent

evaporation, the HS alkyd layer stays liquid. Both sol-gel transition and hardening process are based solely on the cross-linking of the fatty acid tails, which occurs in the presence of air-oxygen. Such process, known as autoxidation, is generally very slow at ambient temperature and has to be catalyzed by transition metal compounds, so-called driers [6,7]. These catalysts considerably reduce drying time and improve physical properties of final polymeric film. In case of HS formulation, the role of drier is crucial for film-forming process owing to negligible contribution from physical drying. Cobalt carboxylates (e.g. cobalt(II) 2-ethylhexanoate, Co) are powerful alkyd driers well established in paint producing industry. Nevertheless, global demand for their replacement is constantly increasing due to ecological reasons [8,9]. Various driers based on vanadium [10–13], manganese [14–16] and iron [17–21], reported in literature, exhibit promising properties in alkyd formulation or liquid model systems (e.g. methyl linoleate). Unfortunately, recent comparative studies have revealed that cobalt compounds cannot be easily replaced. The alternatives show some differences in kinetics of

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Scheme 1. Simplified structure of pentaerythritol-based HS alkyd resin. Tails of linoleic acid are shown as a representative of fatty acids suitable for oxidative drying.

the autoxidation process that leads to cured films of different properties [22,23].

Various experimental methods, including liquid chromatography [24], mass spectrometry [25], measurements of oxygen uptake [26], measurements of viscoelastic properties on quartz crystal microbalance [27] and vibration spectroscopy [28,29], have been used for investigation of the air-drying process on alkyd resins or their liquid model systems (e.g. fatty acids esters). Nevertheless, majority of these methods are suitable only for investigations of reaction mechanisms or determination of the reaction kinetics in homogenous mixtures saturated with air-oxygen. So far, only confocal Raman microscopy [16,30] and NMR imaging [31,32] were successfully used for description of thickness effect caused by concentration gradient of molecular oxygen.

The aim of this study is to establish time-resolved infrared spectroscopy (IR) as a method suitable for investigation of the thickness effect occurring upon the air-drying process. For this purpose, HS alkyd resin with high double bond density (CHS-ALKYD TI 870, **TI870**) was chosen, for which a strong effect of the film thickness is expected. The binder was cured with common cobalt-based drier **Co**, which performance is compared with three commercial alternatives; namely manganese 2-ethylhexanoate (**Mn**), vanadium compound VP 0132 (**V**) and iron bispidine complex (**Fe**). Before the detailed infrared study, behavior of each drier/binder combination was established by standard mechanical tests commonly used for paint testing. We note that each drier/binder system under study have shown a very different performance, which will be documented by mechanical tests and IR studies.

2. Experimental section

2.1. Materials

Solventless alkyd resin based on tall oil fatty acids CHS-ALKYD TI 870 (**TI870**; oil length = 87%, acid value = 8 mg KOH/g) was supplied by Spolchemie. The commercial drier cobalt(II) 2-ethylhexanoate (65 wt.% in mineral spirits; **Co**) was supplied by Sigma-Aldrich. Borchers VP0132 (**V**), Octa-Soligen Manganese 10 (manganese 2-ethylhexanoate; **Mn**), Borchhi OXY-Coat (iron bispidine complex, 1 wt.% in 1,2-propylene glycol; **Fe**) were supplied by Borchers. Dearomatized white spirit (Thinner S 6006 Aromafree) was supplied by Severochema. All reported metal concentrations are given in wt.% based on solid of the alkyd resin.

2.2. Preparation of test coatings

Appropriate drier was treated with toluene (100 μ l). Immediately after dissolution, it was treated with **TI870** (5.00 g) and vigorously

stirred for 2 min to get a homogenous mixture. Viscosity of the formulation was reduced by dearomatized white spirit to 90 wt.% of solid content. Mixture was vigorously stirred for 2 min again and degassed in ultrasound bath (3 min in degas mode). The test films were casted on the substrate by frame applicators.

2.3. Film drying time

The drying performance has been determined by BK (Beck Koller) method on a Drying Time Recorder (BYK) according to ASTM D5895 [33] and under standard laboratory conditions ($T = 23^\circ\text{C}$, rel. humidity = 50%). The instrument is a straight-line recorder equipped with hemispherical-ended needle ($D = 1\text{ mm}$). The films were casted on clean glass strips ($305 \times 25 \times 2\text{ mm}$) using frame applicators of 38 and 76 μm gaps. The needle was placed in horizontal direction at the beginning of the wet film and equipped with 5 g weight. The mark, appeared during 24 h, was used for the estimation four drying stages of given formulation. “Set-to-touch” time (τ_1) is reached when film stops flowing behind needle and pear-shape deformed film appears. During the second period needle gives bold and uninterrupted line revealing the glass substrate. It finishes, when the film is “tack-free” dry (τ_2). After this time, the needle starts to climb over the film. The needle tears the layer and lefts groove with wrinkled and distorted edges until the film is “dry-through” (τ_3). After τ_3 , only very thin mark could be observed on the film [33].

2.4. Determination of film hardness

Film hardness development was monitored using a Pendulum Hardness Tester (Elcometer) with Persoz type pendulum in conformity with ISO 1522 [34] under standard laboratory conditions ($T = 23^\circ\text{C}$, rel. humidity = 50%). The method is based on registering the number of pendulum swings it takes before the amplitude of the pendulum is damped to a certain extent. Test films were casted on glass plates ($100 \times 200 \times 4\text{ mm}$) using frame applicator of 90- μm gap and their properties were measured within 100 days (average value from three measurements is given). The obtained values were related to the hardness of a glass standard (limit value of the pendulum test) and expressed as relative hardness [35]. The error in determination of surface hardness was estimated to be 0.5%.

2.5. Visual control and adhesion tests

Test formulations were cast on glass plates ($100 \times 200 \times 4\text{ mm}$) using frame applicators of 90 and 150 μm gaps and left horizontally for 72 h to prevent certain surface defects such as paint spillage (runs) or changes in film thickness. After that the panels were stored for 100 days in vertical position under standard laboratory conditions ($T = 23^\circ\text{C}$, rel. humidity = 50%). Appearance of cured films and visual defects were evaluated after 10 and 100 days of curing. The adhesion test was performed on the same coatings using a cross-cut tester (Zehntner) according to ISO 2409 [36]. Briefly, the tester was held vertically to test panel surface placed on a firm base. Lattice pattern was made by two successive cuts penetrating the coating down to substrate in 90° angle to each other. 75-mm long tape was centered over the grid and smoothly placed. The tape was removed 5 min after applying, steadily in 0.5–1.0 s at an angle as close as possible to 60° . Resulting grid was evaluated according to percentage of removed area as follows: 0 (0%), 1 (< 5%), 2 (5–15%), 3 (15–35%), 4 (> 65%), 5 (any degree of flaking that cannot be classified by classification 4).

2.6. Time-resolved infrared spectroscopy

The infrared spectra of alkyd coatings were measured on a FTIR spectrometer Nicolet iS50 in the range of $4000\text{--}500\text{ cm}^{-1}$ with the data spacing of 0.5 cm^{-1} (64 scans per spectrum) under standard laboratory

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