

**UNIVERSITY OF PARDUBICE**

**FACULTY OF CHEMICAL TECHNOLOGY**

Institute of Chemistry and Technology of Macromolecular Materials

**Iva Charamzová**

**Investigation of Vanadium Complexes Suitable as Driers  
for Alkyd-based Paints**

*Theses of the Doctoral Dissertation*

Pardubice 2020

Study program: **Chemistry and Technology of Materials**

Study field: **Surface Engineering**

Author: **Iva Charamzová**

Supervisor: **prof. Ing. Jaromír Vinklársek, Dr.**

Year of the defence: 2020

## References

CHARAMZOVÁ, Iva. *Investigation of Vanadium Complexes Suitable as Driers for Alkyd-based Paints*. Pardubice, 2020. 190 pages. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Institute of Chemistry and Technology of Macromolecular Materials. Supervisor Prof. Ing. Jaromír Vinklárek, Dr.

## Abstract

This doctoral thesis is focused on synthesis of new oxidovanadium complexes and their catalytic activity during autoxidation process. New transition metal complexes were characterized by requisite experimental methods (infrared spectroscopy, electron paramagnetic resonance, single X-ray analysis and mass spectrometry). Catalytic activity of prepared vanadium(IV) and vanadium(V) complexes was tested on different types of alkyd resins. Dried and cured films were described by mechanical methods – determination of drying times by BK method and relative film hardness by pendulum hardness tester Persoz). Kinetics of autoxidation process were followed by Fourier transform infrared spectroscopy.

## Abstrakt

Tato disertační práce je věnována přípravě nových vanadylových komplexů a studiu jejich katalytického efektu v průběhu autooxidačního procesu alkydových pryskyřic. Pro charakterizaci syntetizovaných komplexních sloučenin byly využity odpovídající experimentální metody, jako je infračervená spektroskopie, elektronová paramagnetická resonance, monokrystalová rentgenová strukturní analýza a hmotnostní spektrometrie. Sikativační aktivita připravených komplexních sloučenin byla testována v různých typech alkydových pryskyřic. Vytvrzené nátěrové filmy byly charakterizovány mechanickými metodami – zasycháním pomocí hrotu a měřením relativní tvrdosti kyvadlovým přístrojem typu Persoz. Infračervená spektroskopie s Fourierovou transformací byla aplikována pro sledování kinetiky autooxidačního procesu v průběhu katalyzovaného vytvrzování.

## Keywords

Drier, vanadium, alkyd resin, autoxidation process, infrared spectroscopy.

## Klíčová slova

Sikativ, vanad, alkydová pryskyřice, autooxidační proces, infračervená spektroskopie.

# Table of Contents

<b>Introduction</b> .....	5
<b>1. Experimental methods</b> .....	6
<b>1.1 Preparation of test coatings</b> .....	6
<b>1.2 Determination of drying times</b> .....	6
<b>1.3 Determination of film hardness</b> .....	7
<b>1.4 Time-resolved infrared spectroscopy</b> .....	7
<b>2. Results and discussion</b> .....	7
<b>2.1 Oxidovanadium(V) dithiocarbamates</b> .....	7
<b>2.2 Benzyl substituted oxidovanadium(IV) pentane-2,4-dionates</b> .....	10
<b>2.3 Oxidovanadium(IV) complexes compensated by sulfonate anions</b> .....	13
<b>3. Conclusion</b> .....	21
<b>References</b> .....	22

## Introduction

Air-drying paints, including alkyd binders, are widely used for protective and decorative coatings as they fulfil current ecological requirements due to a high content of raw materials accessible from renewable sources.<sup>[1]</sup> Alkyd resins, as saturated polyesters modified with vegetable oils, have been established as significant group of air-drying paint binders used in protective and decorative coatings.<sup>[2]</sup> 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).<sup>[3]</sup> 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.<sup>[4]</sup> 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. At ambient temperature, they exhibit a very slow film-formation when not treated by additives. Generally, drying of alkyd coating includes physical and chemical processes. Physical drying corresponds to solvent evaporation, which is for high-solids alkyds negligible (stays liquid). The chemical drying proceeds sluggishly, both sol-gel transition and hardening 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 catalysed by transition metal compounds, so-called driers.<sup>[5,6]</sup> These catalysts considerably reduce drying time and improve physical properties of final polymeric film through redox reactions. 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) are powerful alkyd driers well established in paint producing industry. It is due to not only a low price and a high catalytic power but also because they work as “universal primary driers”. The main drawback of cobalt-based driers is toxicity, which led to evaluation by European Chemical Agency.<sup>[7]</sup> Cobalt(II) carboxylates are classified as “CMR2-Reprotoxic” and ongoing toxicological scrutiny may result in reclassification to carcinogenic, which would restrict their commercial use considerably. Many alternatives of cobalt-based driers have been reported in literature but only few of them are commercially successful. Various driers based on vanadium,<sup>[8-11]</sup> manganese<sup>[12-14]</sup> and iron<sup>[15,16]</sup> 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 and currently available replacements are limited on manganese(II) carboxylates (*e.g.* 2-ethylhexanoate and neodecanoate), their mixtures with nitrogen-containing chelating proligands and iron(II) bispidine complex (known under the trademark Oxy-Coat).<sup>[17]</sup> It should be noted that all currently known alternatives exhibit very different drying characteristics from cobalt(II) compounds, which limits their large-scale use.<sup>[18,19]</sup>

In last decade, our research group has been focused on investigation of the air-drying process and a search for new alternatives of cobalt-based driers. We have described several ferrocene-derivatives with improved activity in solvent-borne formulation<sup>[20,21]</sup> and iron bispidine compounds with improved solubility in non-polar solvents.<sup>[22,23]</sup> Nevertheless, our main aim involves the application of vanadium compounds. We have

scrutinized a large number of oxidovanadium(IV) compounds but only few of them exhibit satisfactory drying activity, usually due to a low solubility in paint formulations. So far, the promising activity has been observed only for oxidovanadium(IV) acetylacetonates,<sup>[8,10,24]</sup> 2-ethylhexanoate<sup>[9]</sup> and species bearing Geodken's macrocycle.<sup>[11]</sup>

This study is focused on drying activity of vanadium compounds bearing three types of ligands. First two groups are formed by chelating dithiocarbamate and acetylacetonate moieties. In the third case, the vanadium atom is occupied by water molecules as neutral ligands and charge produced by vanadium core is compensated by sulfonic acid anions. Catalytic performance of new driers was studied on twelve different alkyd resins (solvent-borne with different oil length, high-solid resins and alkyds modified by other monomers). The drying activity of tested formulations was primarily described by mechanical methods (determination of drying times by BK method according to ASTM D5895, relative film hardness by pendulum hardness tester according to ISO 1522). Time-resolved infrared spectroscopy (IR) as a method suitable for investigation of the thickness effect occurring upon the air-drying process was used for determination of kinetic parameters of autoxidation process for nine alkyd resins.

## 1. Experimental methods

Due to limited range of this thesis, the most important methods will be described in short versions.

### 1.1 Preparation of test coatings

All tested driers were dissolved in solvent (100  $\mu$ l) specific for their application. Oxidovanadium(V) dithiocarbamates and oxidovanadium(IV) pentane-2,4-dionate were treated with mixture of dimethyl sulfoxide and 3-methoxybutanol (7 : 3), while new benzyl substituted oxidovanadium(IV) pentane-2,4-dionates and oxidovanadium(IV) sulfonates were dissolved in dimethyl sulfoxide. Commercial cobalt(II) 2-ethylhexanoate was treated with toluene. Immediately after dissolution, mixture was treated with alkyd resin (5.00 g) and vigorously stirred for 2 min to get a homogenous mixture. Viscosity of the high-solid 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 with different gaps.

### 1.2 Determination of drying times

The drying performance has been determined by BK (Beck Koller) method on a Drying Time Recorder (BYK) according to ASTM D5895<sup>[25]</sup> and under standard laboratory conditions ( $T = 23$  °C, relative humidity = 50 %). The instrument is a straight-line recorder equipped with hemispherical-ended needle ( $D = 1$  mm). The films were casted on clean glass strips ( $305 \times 25 \times 2$  mm) using frame applicators of 38 and 76  $\mu$ m 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 ( $\tau_1$ )

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 ( $\tau_2$ ). 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-hard” ( $\tau_3$ ). After  $\tau_3$ , only very thin mark could be observed on the film. “Dry-through” time ( $\tau_4$ ) denotes total drying time.

### 1.3 Determination of film hardness

Film hardness development was monitored using a Pendulum Hardness Tester (Elcometer) with Persoz type pendulum in conformity with ISO 1522 [26] under standard laboratory conditions ( $T = 23\text{ }^\circ\text{C}$ , relative 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  $150\text{ }\mu\text{m}$  for solvent-borne alkyds and  $90\text{-}\mu\text{m}$  gap for high-solids. 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. The error in determination of surface hardness was estimated to be 0.5 %.

### 1.4 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  $0.5\text{ cm}^{-1}$  (64 scans per spectrum) under standard laboratory conditions ( $T = 23\text{ }^\circ\text{C}$ , relative humidity = 50 %). Infrared spectra obtained by attenuated total reflectance (ATR) technique (built-in all-reflective diamond crystal) were registered every 5 min for 20 h. Formulations were casted by frame applicator on plate, where the sample has intimate contact to the ATR crystal. As the top surface of ATR crystal lays  $20\text{ }\mu\text{m}$  above the sampling plate, the wet coating on the crystal was always  $20\text{ }\mu\text{m}$  thicker than the gap of the frame applicator used. Collected series of the spectra were integrated in area  $3025\text{--}2990\text{ cm}^{-1}$  using fixed two-point baseline at  $3025$  and  $2990\text{ cm}^{-1}$  [ $\nu_a(\text{cis-C}=\text{C-H})$ ]. Rate coefficients ( $-k_{\text{CH,max}}$ ) were obtained from logarithmic plots of integrated area vs. time as the steepest slope. The error in determination of ( $-k_{\text{CH,max}}$ ) was less than 10 % (three independent measurements for each run). Induction time (IT) was estimated from the logarithmic plots graphically as intersection of horizontal line at 4.605 and tangential line extending the curve after knee point. Half-life of autoxidation process ( $t_{50\%}$ ) was obtained from the integral plot, when the when the curve decreases to 50 % of initial intensity.

## 2. Results and discussion

### 2.1 Oxidovanadium(V) dithiocarbamates

Our initial attempt to extend the family of primary driers was focused on oxidovanadium(V) analogues bearing three dithiocarbamate ligands. The species of the general formula  $[\text{V}^{\text{V}}\text{O}(\text{S}_2\text{CNR}_2)_3]$  were synthesized according to literature procedure (Scheme 1).<sup>[27]</sup> The protocol starts from aqueous solution





the dry-hard time does not exceeds 11 h. However, these two complexes are less suitable to for paint industry, due to demanding synthesis of **VO-dtc-EH** resulting to gel product and worse solubility of **VO-dtc-P**.

**Table 1** Drying times and relative hardness for test coatings of alkyd binder **S471**.

Drier	Metal content (wt. %)	$\tau_2^a$ (h)	$\tau_3^b$ (h)	$\tau_4^c$ (h)	$H_{rel,10d}^d$ (%)	$H_{rel,100d}^e$ (%)
<b>VO-dtc-H</b>	0.1	2.9	7.0	19.8	24.1	55.4
	0.06	3.0	5.4	10.8	17.5	47.1
	<b>0.03</b>	<b>2.8</b>	<b>4.6</b>	<b>7.2</b>	<b>27.2</b>	<b>53.2</b>
	0.01	4.7	6.2	9.5	19.8	40.4
	0.005	8.3	17.3	20.1	28.0	43.3
<b>VO-dtc-EH</b>	0.1	6.3	9.5	10.6	18.3	45.1
	<b>0.06</b>	<b>6.8</b>	<b>10.1</b>	<b>11.9</b>	<b>17.9</b>	<b>46.8</b>
	0.03	7.8	10.2	12.7	16.5	45.0
	0.01	8.6	13.2	16.8	16.2	40.1
	0.005	13.6	>24	>24	– <sup>f</sup>	– <sup>f</sup>
<b>VO-dtc-M</b>	0.1	0.7	1.4	3.6	37.0	60.1
	<b>0.06</b>	<b>1.2</b>	<b>1.7</b>	<b>3.7</b>	<b>34.6</b>	<b>61.2</b>
	0.03	1.4	2.2	4.6	33.4	58.6
	0.01	3.2	4.9	7.4	29.3	62.4
	0.005	11.8	>24	>24	20.3	39.1
<b>VO-dtc-P</b>	<b>0.1</b>	<b>2.2</b>	<b>4.6</b>	<b>4.6</b>	<b>27.5</b>	<b>47.0</b>
	0.06	4.6	7.5	10.0	25.8	42.0
	0.03	6.9	11.4	13.9	23.2	38.6
	0.01	9.7	15.5	>24	20.0	37.5
	0.005	9.6	15.7	>24	18.9	37.0
<b>Co</b>	0.1	1.0	7.7	>24	22.5	39.6
	0.06	0.5	9.4	20.4	25.8	40.4
	<b>0.03</b>	<b>1.6</b>	<b>4.3</b>	<b>17.4</b>	<b>31.4</b>	<b>40.2</b>
	0.01	14.1	18.4	20.9	30.8	38.6
	0.005	>24	>24	>24	– <sup>f</sup>	– <sup>f</sup>

<sup>a</sup> Tack-free time. <sup>b</sup> Dry-hard time. <sup>c</sup> Dry-through (total-dry) time. <sup>d</sup> Relative hardness measured after 10 days of drying. <sup>e</sup> Final relative hardness. <sup>f</sup> Not measured.

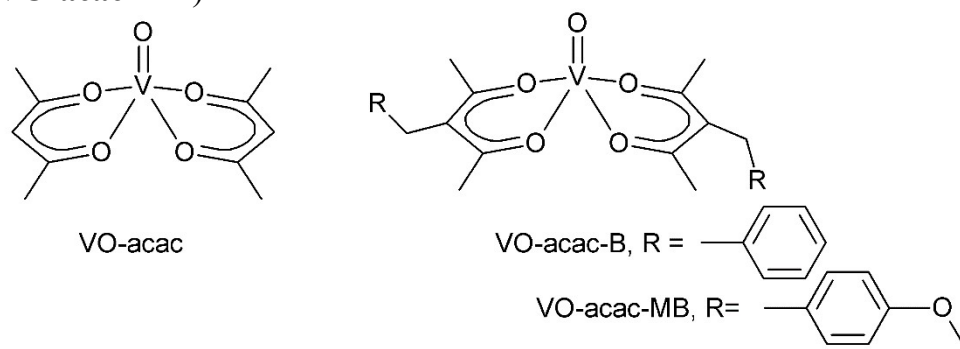
Shortest dry-hard time ( $\tau_4$ ) was observed for derivative **VO-dtc-M** at concentration 0.06 wt. % (3.7 h) but even at 0.01 wt. % the value of  $\tau_4$  is considerably lower than in case of the formulations treated with commercial **Co**. Such phenomenon is due to a better through drying and it was further observed for the other vanadium-based driers under the study. For evaluation of drier performance on surface, the dry-hard time ( $\tau_3$ ) seems to be more valuable. Based on this parameter, surface drying of **VO-dtc-M** at 0.01 wt. % is comparable to **Co** at optimal concentration (0.03 wt. %). The films of **S471** cured by vanadium-based driers show a high relative hardness, estimated according to Persoz protocol, already ten days after application (16.2–37.0 %). Final

relative hardness, measured after 100 days of curing, varies between 37.0 and 62.4 %. We note that deterioration of drying activity was observed at concentration 0.005 wt. %.

## 2.2 Benzyl substituted oxidovanadium(IV) pentane-2,4-dionates

In previous studies, oxidovanadium(IV) pentane-2,4-dionate,  $[\text{VO}(\text{acac})_2]$ , has been investigated extensively due to its physical-chemical properties and effects on biological species.<sup>[29]</sup> High affinity of chelating ligands bearing oxygen donors provides stabilized complex enabling changes in vanadium oxidation state. This catalyst is widely used in the field of oxygen-transfer reactions like oxidation of hydrocarbons (*e.g.* cyclohexane),<sup>[30]</sup> alcohols<sup>[31]</sup> and sulfur-containing compounds (*e.g.* disulfides).<sup>[32]</sup> In field of macromolecular chemistry, the catalytic system  $[\text{VO}(\text{acac})_2]/\textit{tert}$ -butyl hydroperoxide] was used for epoxidation of polybutadiene-based polymers (*e.g.* hydroxylated polybutadiene, polyisoprene, styrene-butadiene copolymer).<sup>[33]</sup> Our research group has revealed that  $[\text{VO}(\text{acac})_2]$  and its derivatives ( $[\text{VO}(\textit{O},\textit{O}\text{-MeCOCHCOPh})_2]$ ,  $[\text{VO}(\textit{O},\textit{O}\text{-PhCOCHCOPh})_2]$ ,  $[\text{VO}(\text{3-Bu-acac})_2]$ ,  $[\text{VO}(\text{3-Hex-acac})_2]$ ,  $[\text{VO}(\text{3-Oct-acac})_2]$ ) accelerates curing of air-drying paints through catalysis of autoxidation process.<sup>[8,10]</sup>

Therefore, our attention was moved to new catalysts based on oxidovanadium(IV) pentane-2,4-dionates with benzyl and 4-methoxybenzyl substituents (see Figure 2, **VO-acac-B**, **VO-acac-MB**).



**Figure 2** Structure of substituted pentane-2,4-diones.

However, the effect of the oxidovanadium(IV) pentane-2,4-dionate (**VO-acac**) on air-drying process was previously investigated, the catalyst was pre-dissolved in toluene. In this study, more ecologically friendly solvent was found to help improving drying of alkyd resins by new oxidovanadium(IV) catalysts. We note that DMSO was recently recognized as very suitable for ecologically friendly paint formulations as it is classified as a non-toxic solvent with no risk for the human health. It improves processability of paint mixtures due to good miscibility with all common solvents and wide range of polymers. It also helps to prevent appearance of surface defects due to slow evaporation at ambient temperature.<sup>[34,35]</sup> The oxidovanadium(IV) pentane-2,4-dionate showed even better catalytic activity dissolved in mixture of dimethyl sulfoxide and 3-methoxybutanol (7 : 3).

The catalytic performance of oxidovanadium(IV) pentane-2,4-dionate complexes bearing benzyl substituents were studied on four solvent-borne alkyd resins modified with semi-drying soybean oil. For clarification, in order to test versatility of our catalysts mentioned alkyd resins have medium (**S471**, **SP262**) and long (**S622**, **SP262**) oil length and these resins are produced by two different companies (Spolchemie, a.s. – S-brand;

Safic-Alcan Česko, s.r.o. – SP-brand). The complexes **VO-acac-B**, **VO-acac-MB** were pre-dissolved in dimethyl sulfoxide (DMSO) before use. Catalytic activity of these two complexes was determined by common mechanic assays on test coatings including measurements of drying time and relative hardness. Obtained results revealed high acceleration of autoxidation process resulting in short total dry times, which were compared with **VO-acac** and commercial cobalt-based drier (**Co**). The measurements were performed in range of metal concentrations 0.06–0.005 wt. %. Formulations containing 0.005 wt. % **Co** does not reach demanded catalytic activity, for all resins  $\tau_1$  is longer than 24 hours. Drying times and relative hardness obtained for the formulations under the study are summarized in Tables 2–4.

**Table 2** Drying times ( $\tau$ )<sup>a</sup> obtained for formulations of alkyd resins **S471** and **SP262**.

Alkyd resin		<b>S471</b>			<b>SP262</b>			
Drier	Metal content (wt. %)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)	$\tau_1$ (h)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)
<b>VO-acac</b>	<b>0.06</b>	– <sup>b</sup>	<b>1.5</b>	<b>3.6</b>	<b>0.2</b>	<b>0.8</b>	<b>0.9</b>	<b>1.6</b>
	0.03	0.5	2.9	2.9	0.3	0.7	1.6	2.4
	0.01	0.5	4.0	6.5	0.9	1.6	1.9	3.0
	0.005	1.5	7.6	16.9	1.8	2.4	13.9	18.9
<b>VO-acac-B</b>	0.06	0.8	2.2	3.1	0.4	1.0	6.9	6.9
	<b>0.03</b>	<b>0.9</b>	<b>3.3</b>	<b>3.3</b>	<b>0.1</b>	<b>0.7</b>	<b>1.0</b>	<b>1.9</b>
	0.01	2.1	5.9	10.4	0.2	1.4	7.5	7.5
	0.005	3.9	9.0	17.1	1.1	1.7	12.7	19.6
<b>VO-acac-MB</b>	0.06	0.6	2.2	4.5	0.3	0.5	0.9	1.9
	<b>0.03</b>	<b>1.6</b>	<b>3.0</b>	<b>5.2</b>	<b>0.4</b>	<b>0.6</b>	<b>1.0</b>	<b>2.4</b>
	0.01	3.4	9.2	17.6	1.2	1.7	10.3	17.5
	0.005	6.9	19.4	>24	3.1	4.9	14.9	14.9
<b>Co</b>	<b>0.06</b>	<b>0.5</b>	<b>9.4</b>	<b>20.4</b>	<b>2.2</b>	<b>8.6</b>	<b>15.2</b>	<b>&gt;24</b>
	0.03	1.6	4.3	17.4	2.7	12.8	>24	>24
	0.01	14.1	18.4	20.9	5.2	>24	>24	>24

<sup>a</sup>  $\tau_1$  is set-to-touch time.  $\tau_2$  is tack-free time;  $\tau_3$  is dry-hard time;  $\tau_4$  is dry-through time (total dry time); <sup>b</sup>  $\tau_1$  was not observed.

For estimation of catalytic activity, the times when surface become hard ( $\tau_3$ ) and film become through dry ( $\tau_4$ ) are the most representative. The later constant is, in case of here used resins, taken as total time of drying process.

Complexes **VO-acac-B** and **VO-acac-MB** show an excellent drying activity in all tested alkyd resins. The optimal drying performance, estimated when  $\tau_4$  is minimal, was observed at concentrations 0.06 or 0.03 wt. %. Nevertheless, in all cases, the concentration 0.03 wt. % is preferred for practical use as the value of  $\tau_4$  is not prolonged considerably and does not exceed 6 h. Optimal concentration of **VO-acac** and **Co** driers was determined to 0.06 wt. %. In all studied alkyd resins, the complex **VO-acac-B** exhibits significantly higher activity than **VO-acac-MB**. It is evident not only from shorter drying times estimated at concentration range 0.03–0.005 wt. % but also

from strong overdose effect observed for formulations **VO-acac-B/SP262** and **VO-acac-B/S622** at 0.06 wt. %.

**Table 3** Drying times ( $\tau$ )<sup>a</sup> obtained for formulations of alkyd resins **S622** and **SP252**.

Alkyd resin		<b>S622</b>			<b>SP252</b>			
Drier	Metal content (wt. %)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)	$\tau_1$ (h)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)
<b>VO-acac</b>	<b>0.06</b>	<b>0.4</b>	<b>3.5</b>	<b>3.5</b>	<b>0.9</b>	<b>1.3</b>	<b>3.9</b>	<b>3.9</b>
	0.03	0.5	6.4	17.8	1.4	2.3	4.9	7.6
	0.01	1.3	8.8	22.2	3.0	5.3	7.6	12.5
	0.005	2.9	16.3	>24	7.7	12.3	>24	>24
<b>VO-acac-B</b>	0.06	0.3	2.4	4.8	0.8	1.4	4.3	4.3
	<b>0.03</b>	<b>0.6</b>	<b>1.4</b>	<b>3.5</b>	<b>0.9</b>	<b>1.3</b>	<b>2.6</b>	<b>5.7</b>
	0.01	1.0	7.2	15.5	2.5	3.9	7.8	7.8
	0.005	2.1	19.6	19.6	7.2	11.3	18.7	18.7
<b>VO-acac-MB</b>	0.06	0.6	1.5	3.1	0.8	1.4	1.5	3.9
	<b>0.03</b>	<b>0.8</b>	<b>2.5</b>	<b>5.4</b>	<b>0.9</b>	<b>1.8</b>	<b>2.5</b>	<b>4.2</b>
	0.01	1.8	10.9	13.7	4.6	7.3	10.8	>24
	0.005	3.1	16.2	20.5	9.2	14.6	>24	>24
<b>Co</b>	<b>0.06</b>	<b>1.1</b>	<b>7.5</b>	<b>9.7</b>	<b>3.2</b>	<b>3.5</b>	<b>8.3</b>	<b>12.2</b>
	0.03	2.2	6.0	7.4	8.2	8.6	11.2	12.8
	0.01	10.8	14.5	16.6	>24	>24	>24	>24

<sup>a</sup>  $\tau_1$  is set-to-touch time.  $\tau_2$  is tack-free time;  $\tau_3$  is dry-hard time;  $\tau_4$  is dry-through time (total dry time).

Complex **VO-acac** also showed satisfying drying activity, but short values obtained for ( $\tau_4$ ) were caused by higher used concentration. Superior performance of vanadium complexes is well seen when data are compared with commercial cobalt-based drier (**Co**). At concentration recommended by supplier (0.06 wt. %), the dry-hard times ( $\tau_3$ ) and dry-through times ( $\tau_4$ ) are considerably longer than in case of the vanadium compounds at 0.03 wt. %. Moreover, at formulation **Co/SP262** through drying ( $\tau_4$ ) exceeds 24 h in the whole concentration range. The results obtained from measurements of drying time showed, that the catalytic activity of vanadyl acetylacetonate complexes rises in the series **VO-acac** < **VO-acac-MB** < **VO-acac-B**.

Although the films are considered as dry, the crosslinking reactions continue for tens of days, which is evident from increase of relative hardness. The field of application is usually indicated by final hardness of the coating estimated hundred days of drying ( $H_{rel,100d}$ ). Final hardness of the cured films ( $H_{rel,100d}$ ) well correlates with the drier performance estimated by drying time measurements. At metal concentration 0.06 wt. %.  $H_{rel,100d}$  increases in the series **Co** < **VO-acac-MB** < **VO-acac** ~ **VO-acac-B** and the excellent performance of the compound **VO-acac-B** maintains high even at preferred concentration estimated by drying time measurements (0.03 wt. %). It could be noted that final hardness of cured alkyd films strongly depends on alkyd composition.

It decreases in the series **SP262** > **S471** > **S622** > **SP252** and well correlates with declared oil length and acid values.

**Table 4** Relative hardness ( $H_{rel}$ )<sup>a</sup> obtained for formulations of alkyd resins **S471**, **SP262**, **S622** and **SP252**.

Drier <sup>b</sup>	<b>S471</b>		<b>SP262</b>		<b>S622</b>		<b>SP252</b>	
	$H_{rel,10d}$ (%)	$H_{rel,100d}$ (%)	$H_{rel,10d}$ (%)	$H_{rel,100d}$ (%)	$H_{rel,10d}$ (%)	$H_{rel,100d}$ (%)	$H_{rel,10d}$ (%)	$H_{rel,100d}$ (%)
<b>VO-acac</b>								
<b>0.06</b>	<b>34.1</b>	<b>51.3</b>	<b>18.6</b>	<b>49.3</b>	<b>20.1</b>	<b>42.1</b>	<b>12.5</b>	<b>34.6</b>
0.03	33.2	48.1	17.9	44.2	16.5	36.7	10.8	32.0
0.01	30.0	47.1	17.4	40.5	11.7	27.8	7.7	23.4
0.005	26.9	42.5	17.1	37.1	10.2	25.3	6.0	19.8
<b>VO-acac-B</b>								
0.06	31.9	47.6	23.7	49.1	20.5	39.7	16.1	34.2
<b>0.03</b>	<b>28.7</b>	<b>46.4</b>	<b>22.6</b>	<b>44.1</b>	<b>19.3</b>	<b>38.4</b>	<b>14.7</b>	<b>32.0</b>
0.01	28.3	45.7	21.2	40.7	16.7	31.7	12.3	24.5
0.005	27.6	39.1	20.9	36.7	16.4	26.9	11.4	20.4
<b>VO-acac-MB</b>								
0.06	28.5	42.8	22.2	43.0	19.9	35.2	15.4	30.5
<b>0.03</b>	<b>28.0</b>	<b>41.1</b>	<b>21.4</b>	<b>38.8</b>	<b>19.0</b>	<b>31.3</b>	<b>12.6</b>	<b>27.9</b>
0.01	27.9	38.8	21.1	32.1	16.1	25.5	12.0	20.3
0.005	25.0	35.9	20.9	31.0	16.6	22.2	12.2	19.2
<b>Co</b>								
<b>0.06</b>	<b>25.8</b>	<b>40.4</b>	<b>25.1</b>	<b>41.2</b>	<b>27.9</b>	<b>32.2</b>	<b>18.8</b>	<b>28.8</b>
0.03	31.4	40.2	25.0	39.4	24.7	29.7	18.5	25.9
0.01	30.8	38.6	24.0	36.2	21.1	26.4	16.6	23.2
0.005	26.3	35.3	23.4	34.2	20.0	24.6	13.5	19.7

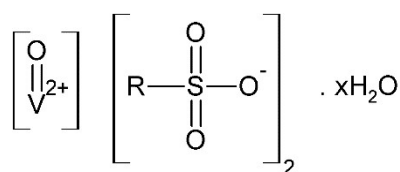
<sup>a</sup>  $H_{rel,10d}$  is relative hardness after 10 days;  $H_{rel,100d}$  is final relative hardness reached after 100 days. <sup>b</sup> Number in parentheses denotes metal concentration in wt. %.

Hence, high  $H_{rel,100d}$  value for alkyds of medium oil-length (**SP262**, **S471**) is due to higher content of phthalic acid and lower content of plasticizing fatty acid tails. Considerably lower hardness of the resin **SP252**, when compared with **S622**, reflects lower degree of polymerization, which is evident from higher acid value. We note that alkyd resins **SP262** and **SP252** show different drying behavior from **S471** and **S622**. Formulations of **SP262** and **SP252** are not set-to-touch dry immediately after application ( $\tau_1 > 0$ ) and exhibit lower surface tension, which results in better following and lower tendency to form surface defects.

### 2.3 Oxidovanadium(IV) complexes compensated by sulfonate anions

New catalysts, based on oxidovanadium(IV) sulfonates, improving drying of alkyd resins were synthesized and characterized by standard analytical methods. The infrared

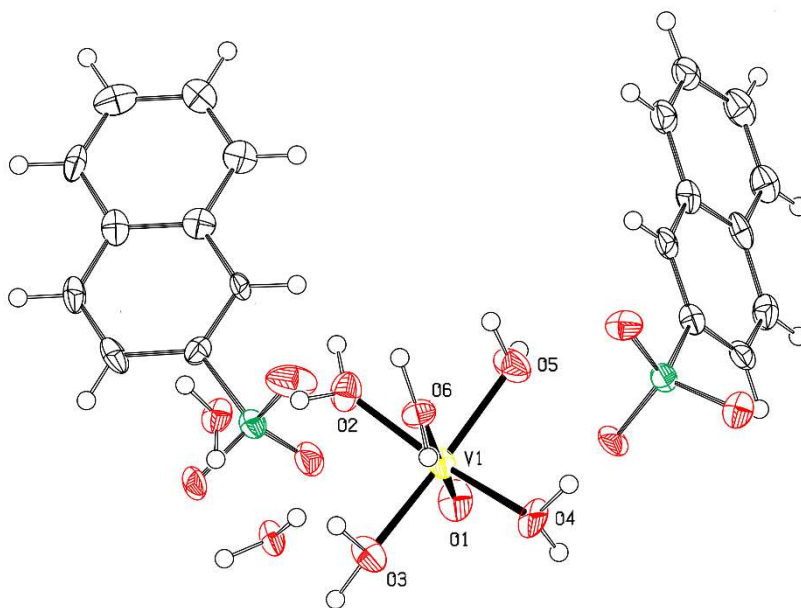
spectra of seven oxidovanadium(IV) derivatives (**VOMsO**, **VOEsO**, **VOBsO**, **VOTsO**, **VO-OH-BsO**, **VONsO**, **VOSsO**), measured by attenuated total reflectance (ATR) sampling technique, show a strong V=O stretching band at 988–1002  $\text{cm}^{-1}$ . These values fit in the range typical for oxidovanadium(IV) compounds.<sup>[36]</sup>



**Figure 3** Structure of oxidovanadium(IV) complexes compensated by sulfonate anions. R is hydrocarbon part of starting sulfonic acid.

Paramagnetic nature of these new complexes and their  $d^1$  configuration enables the use of EPR spectroscopy for characterization. Predominantly occurring vanadium is a stable isotope  $^{51}\text{V}$  ( $I = 7/2$ ) with natural abundance 99.75%.<sup>[37]</sup> It usually produces strong hyperfine coupling, which is sensitive to changes in the coordination sphere of vanadium. Solutions of these complexes in water give typical isotropic eight-line spectra. The observed values of isotropic hyperfine coupling constant (**VOTsO**:  $|A_{\text{iso}}| = 116.4 \times 10^{-4} \text{ T}$ ) suggest different donor–acceptor properties of the coordinated ligands to previously reported oxidovanadium(IV) pentane-2,4-dionate complexes bearing benzyl substituents (**VO-acac-B**:  $|A_{\text{iso}}| = 103.3 \times 10^{-4} \text{ T}$ , **VO-acac-MB**:  $|A_{\text{iso}}| = 103.1 \times 10^{-4} \text{ T}$ ).<sup>[24]</sup> The  $|A_{\text{iso}}|$  value is higher, even than the value obtained for unsubstituted analogue  $\text{VO}(\text{acac})_2$  ( $|A_{\text{iso}}| = 108.7 \times 10^{-4} \text{ T}$ ).<sup>[8]</sup> It is attributed to negligible effect of sulfonate anions on coordination sphere of vanadyl group.

Structure of three complexes (**VOBsO**, **VOTsO** and **VONsO**) was determined by single crystal X-ray structure analysis (see Figure 4). The coordination sphere of vanadium(IV) atom (V1) have deformed square bipyramidal structure for all three measured complexes with oxygen atom (O1 and O6) in apical positions.



**Figure 4** Molecular structure of the **VONsO** as representative derivative showed by ORTEP program.

The V1–O1 bonds are short, in the range of 1.5736(19)–1.605(8) Å, which documents the expected double bond character.<sup>[10]</sup> Equatorial plane is occupied by oxygen donor atoms of coordinated water molecules (O2–O5). The V1 atoms exceed the equatorial plane for 0.259(2)–0.308(1) Å. We note that bond lengths V1–O(2–5) in equatorial plane are in narrow range 2.0133(16)–2.043(9) Å. On the other hand, bond length between central vanadium atom V1 and the oxygen atom O6 in the axial position is substantially longer [2.150(8)–2.2294(15) Å]. The literature describes similar structural parameters for oxidovanadium(IV) sulfate pentahydrate.<sup>[38]</sup>

Drying activity of seven new driers (**VOMsO**, **VOEsO**, **VOBsO**, **VO-OH-BsO**, **VOTsO**, **VONsO**, **VOSsO**) was evaluated in solvent-borne alkyd resin of medium oil-length modified with soybean oil (**S471**). Unfortunately, two of new catalysts (**VO-OH-BsO**, **VOSsO**) showed negligible catalytic performance and were excluded from further testing. The results obtained from film drying time determined by BK (Beck Koller) method are summarized in Table 5. Due to high catalytic activity of oxidovanadium(IV) complexes, their drying performance was tested in wide concentration range (0.06–0.01 wt. %). The measurements of formulations containing **Co** drier remains with the same metal concentrations 0.06–0.005 wt. %. However, thanks to limited range of this paper, only optimal and lower active ( $\tau_4$  does not exceed 24 h) concentration of appropriate drier are showed in Table 5.

All oxidovanadium(IV) driers, under the study, exhibit high catalytic activity in alkyd resin **S471** at concentration range 0.06–0.006(3) wt. %. These complexes are able to reliably cure **S471** resin within 14 hours, even at ten times lower (0.006 wt. %) concentration, than the optimal concentration is reported for cobalt driers **Co** (0.06 wt. %).

**Table 5** Drying times and relative hardness for test coatings of alkyd binder **S471**.

Drier	Metal content (wt. %)	$\tau_2^a$ (h)	$\tau_3^b$ (h)	$\tau_4^c$ (h)	$H_{rel,10d}^d$ (%)	$H_{rel,100d}^e$ (%)
<b>VOMsO</b>	<b>0.03</b>	<b>0.4</b>	<b>3.4</b>	<b>4.4</b>	<b>28.0</b>	<b>46.3</b>
	0.006	1.6	9.7	13.9	26.5	43.8
<b>VOEsO</b>	<b>0.03</b>	<b>0.1</b>	<b>1.7</b>	<b>3.1</b>	<b>27.6</b>	<b>50.2</b>
	0.003	2.5	8.1	11.9	25.0	43.5
<b>VOBsO</b>	<b>0.03</b>	<b>0.1</b>	<b>1.5</b>	<b>2.5</b>	<b>31.1</b>	<b>49.3</b>
	0.006	0.5	6.0	7.2	29.7	44.9
<b>VOTsO</b>	<b>0.03</b>	<b>0.2</b>	<b>1.2</b>	<b>2.4</b>	<b>30.1</b>	<b>51.9</b>
	0.003	1.6	8.3	14.1	29.1	45.1
<b>VONsO</b>	<b>0.03</b>	<b>0.2</b>	<b>1.5</b>	<b>1.7</b>	<b>27.5</b>	<b>50.6</b>
	0.003	1.4	4.6	10.9	25.3	43.3
<b>Co</b>	<b>0.06</b>	<b>2.1</b>	<b>4.5</b>	<b>19.6</b>	<b>29.7</b>	<b>48.9</b>
	0.03	8.6	11.5	21.7	24.5	45.0

<sup>a</sup> Tack-free time. <sup>b</sup> Dry-hard time. <sup>c</sup> Dry-through (total-dry) time. <sup>d</sup> Relative hardness measured after 10 days of drying. <sup>e</sup> Final relative hardness.

So, addition of oxidovanadium(IV) driers decreases the total amount of transition metal content required for curing alkyd resins and leads to more ecologically paints with

reduced impact on environment. Commercially used cobalt(II) drier **Co** showed only negligible catalytic activity at the two lowest concentrations 0.01 and 0.005 wt. % and the total drying time was longer than 24 hours.

In case of vanadyl driers, complexes with aromatic sulfonic anions (**VOBsO**, **VOTsO**, **VONsO**) appears to be more efficient catalysts, than oxidovanadium(IV) aliphatic derivatives. The catalytic performance of all tested driers measured by film drying time increases in the series of **Co** < **VOMsO** < **VOEsO** < **VOBsO** < **VOTsO** < **VONsO**.

The alkyd resin **S471** is spontaneously cured without additives and reaches total relative hardness after 100 days only 35.3 %. The addition of oxidovanadium complexes in the optimal concentration (0.03 wt. %) improves curing and hardening of **S471** to total relative hardness of 46–52 %. The softest polymer films were provided by complex **VOMsO** (46.3 %), while the drying of the hardest alkyd films was accelerated by **VOTsO** (51.9 %). The formulation **Co/S471** containing the optimal concentration of drier recommended by the supplier (0.06 wt. %) achieves total relative hardness 48.9 %.

As the most effective oxidovanadium(IV) drier, based on simplicity of preparation, availability of starting materials, results from drying time measurements and relative hardness, was chosen **VOTsO** complex in the optimal concentration of 0.03 wt. %. Catalytic activity was further investigated in three solvent-borne alkyd resins modified with semi-drying soybean oil (**S622**, **SP262**, **SP252**) previously used for determination the catalytic activity of oxidovanadium(IV) pentane-2,4-dionates bearing benzyl substituents. Film drying times and relative hardness for all tested alkyd resins cured by **VOTsO** (0.03 wt. %) and cobalt-based drier **Co** (0.06 wt. %) are summarized in Tables 6–8.

**Table 6** Drying times ( $\tau$ )<sup>a</sup> and relative hardness ( $H_{rel}$ )<sup>b</sup> obtained for formulations of solvent-borne alkyd resins treated driers at optimal concentrations.

Drier/alkyd resin	Metal content (wt. %)	$\tau_1$ (h)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)	$H_{rel,10d}$ (%)	$H_{rel,100d}$ (%)
<b>VOTsO/S622</b>	0.03	– <sup>c</sup>	0.2	1.5	6.7	17.2	38.0
<b>Co/S622</b>	0.06	– <sup>c</sup>	0.7	6.5	8.0	19.3	39.0
<b>VOTsO/SP262</b>	0.03	– <sup>c</sup>	1.9	4.5	4.5	18.5	42.3
<b>Co/SP262</b>	0.06	1.9	8.4	14.1	>24	23.1	46.7
<b>VOTsO/SP252</b>	0.03	0.3	1.0	3.4	3.4	11.7	31.6
<b>Co/SP252</b>	0.06	3.1	3.4	7.9	12.0	13.7	32.1

<sup>a</sup>  $\tau_1$  is set-to-touch time;  $\tau_2$  is tack-free time;  $\tau_3$  is dry-hard time;  $\tau_4$  is dry-through time (total dry time); <sup>b</sup>  $H_{rel,10d}$  is relative hardness after 10 days;  $H_{rel,100d}$  is final relative hardness reached after 100 days, <sup>c</sup>  $\tau_1$  was not observed.

The highest drying activity showed complex **VOTsO** in alkyd resin **S471**, nevertheless its high catalytic performance was followed also in combination with other solvent-borne alkyd resins. For example, formulation **Co/SP262** (0.06 wt. %) does not reach dry-through time ( $\tau_4$ ) within 24 h, whereas alkyd resin **SP262** treated with **VOTsO** (0.03 wt. %) is cured up to 5 h. Better results showed **Co** drier in combination with long



oil alkyd resins (**S622**, **SP252**), which were cured till 12 h. Nevertheless, these resins achieved total drying time ( $\tau_4$ ) up to 7 h in formulation with **VOTsO** drier.

Solvent-borne alkyd resins can spontaneously reach state, when their thin polymeric film can be considered as cured. These polymers are formed very slowly, and their relative hardness is very low, for example alkyd **SP252** achieves  $H_{rel,100d} = 10.8$  %. It is caused by high content of oils, mainly for alkyd resins with long oil length. The addition of tested driers effectively increases their relative hardness (see Table 6).

Hereafter, drying activity of **VOTsO** and **Co** driers was evaluated in combination with six high-solid alkyd resins delivered by Spolchemie a.s. (**TI870**, **TRI841**, **S830**, **LM920**) and Safic-Alcan Česko, s.r.o. (**FP07**, **SP00**), and alkyd resins modified by another monomers (urethane-modified – **SPU15**, silicone-modified – **SPS15**). The samples of appropriate metal concentration were diluted with dearomatized white spirit to adjust viscosity of the formulation. The use of other additives (e.g. secondary driers and antiskinning agents) was avoided in order to estimate solely the effect of given driers. The activity of cobalt 2-ethylhexanoate (**Co**) was studied at concentrations 0.06–0.01 wt. % of the metal on solid content and for vanadium-based drier, the concentration range was adjusted to 0.1–0.01 wt. %. The results of film drying time and relative hardness obtained for two representative alkyd binders, modified with tall oil fatty acids **TI870** and dehydrated castor oil **TRI841**, cured by **VOTsO** and **Co** in their optimal concentrations (0.06 wt. %) are summarized in Table 7. The film drying times ( $\tau_1$ – $\tau_4$ ) of the alkyd formulations were estimated on coatings of 76  $\mu\text{m}$ -wet thickness. The measurements on thinner coatings (38  $\mu\text{m}$ -wet thickness) were performed in order to avoid entering in a regime where oxygen transport is the limiting factor.

**Table 7** Drying times ( $\tau$ )<sup>a</sup> and relative hardness ( $H_{rel}$ )<sup>b</sup> obtained for formulations of high-solid alkyd resins treated with **VOTsO** and **Co** driers.

Film thickness		38 $\mu\text{m}$				76 $\mu\text{m}$				90 $\mu\text{m}$	
Drier	Metal content (wt. %)	$\tau_1$ (h)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)	$\tau_1$ (h)	$\tau_2$ (h)	$\tau_3$ (h)	$\tau_4$ (h)	$H_{rel,10d}$ (%)	$H_{rel,100d}$ (%)
<b>TI870</b>											
<b>VOTsO</b>	<b>0.06</b>	<b>1.5</b>	<b>2.3</b>	<b>3.4</b>	<b>3.4</b>	<b>1.9</b>	<b>2.5</b>	<b>3.4</b>	<b>3.4</b>	<b>8.7</b>	<b>21.3</b>
	0.01	4.5	7.5	12.0	12.0	4.9	6.9	9.4	9.4	5.8	17.1
<b>Co</b>	<b>0.06</b>	<b>1.0</b>	<b>1.9</b>	<b>2.6</b>	<b>&gt;24</b>	<b>1.0</b>	<b>6.6<sup>c</sup></b>	<b>&gt;24</b>	<b>&gt;24</b>	<b>8.8</b>	<b>27.4</b>
	0.01	3.8	6.6	6.8	>24	4.1	8.0	9.6	>24	6.3	18.1
<b>TRI841</b>											
<b>VOTsO</b>	<b>0.06</b>	<b>1.9</b>	<b>2.9</b>	<b>4.0</b>	<b>7.3</b>	<b>2.2</b>	<b>2.9<sup>c</sup></b>	<b>3.5</b>	<b>4.5</b>	<b>5.2</b>	<b>20.4</b>
	0.01	5.2	7.8	>24	>24	5.2	6.5 <sup>c</sup>	11.5	11.5	5.0	15.5
<b>Co</b>	<b>0.06</b>	<b>0.9</b>	<b>3.9<sup>c</sup></b>	<b>6.9</b>	<b>&gt;24</b>	<b>0.9</b>	<b>4.9<sup>c</sup></b>	<b>14.0</b>	<b>&gt;24</b>	<b>6.9</b>	<b>23.5</b>
	0.01	4.1	4.7	6.0	>24	4.1	5.6	10.4	>24	5.6	14.6

<sup>a</sup>  $\tau_1$  is set-to-touch time;  $\tau_2$  is tack-free time;  $\tau_3$  is dry-hard time;  $\tau_4$  is dry-through time (total dry time); <sup>b</sup>  $H_{rel,10d}$  is relative hardness after 10 days; <sup>b</sup>  $H_{rel,100d}$  is final relative hardness reached after 100 days; <sup>c</sup> In time period  $\tau_1$ – $\tau_2$ , the needle tears off a skin from the coating instead of giving a bold uninterrupted path.

Generally, set-to-touch time ( $\tau_1$ ) rises with lowering of metal concentration but it is not significantly influenced by film thickness (Table 7). Such observations imply fast solvent evaporation and almost homogenous cross-linking at the beginning of the autoxidation process. It is due to saturation of the formulation by air-oxygen before spreading sample over glass panel used for tests. Strong dependence on film thickness was observed only in the next phases of the oxidative drying for formulations treated by **Co** drier. The tack-free times ( $\tau_2$ ) are considerably longer for thicker coatings (76  $\mu\text{m}$ ) due to formation of polymeric skin on the top surface decelerating the oxygen diffusion to down surface. As expected, the effect is much stronger at higher metal concentration as the skin formation is faster. Similar effects are responsible for differences in values of the dry-hard times ( $\tau_3$ ). Very fast skin formation on 76  $\mu\text{m}$ -coatings with high metal concentration is responsible for longer  $\tau_3$  than in case of coatings with lower metal content. This *inverse concentration dependence* was not observed at 38  $\mu\text{m}$ -layers because oxygen becomes available. Such phenomenon was not revealed for formulations treated with **VOTsO** drier. This situation confirms different effect of vanadium-based drier on autoxidation process and implies its function as *through-drier*. The formation of thick skin was observed on 76  $\mu\text{m}$ -coatings with high concentration of cobalt (0.06 wt. %) and for both driers in combination with alkyd **TRI841** at the same thickness. During the second phase of drying, needle of the drying time recorder has teared off a skin layer that has been forming (not giving a bold uninterrupted path as usual).

Development of relative hardness in time was measured on coatings of 90  $\mu\text{m}$ -wet thickness resulting in  $\sim 35$   $\mu\text{m}$  dry film that is common in paint application. The values of final hardness ( $H_{\text{rel},100\text{d}}$ ) depends on both the drier and the alkyd resin. Generally, harder polymeric films are formed by cobalt-based drier **Co** (see Table 7).

Flexibility of new drier **VOTsO** was confirmed by measuring film-drying time of urethane- and silicone-modified alkyd resins (**SPU15** and **SPS15**). Optimal concentration of **VOTsO** was determined to 0.03 wt. %. Addition of this amount to **SPU15** resin accelerated the curing process on 3.7 h ( $\tau_4$ ). At the same time, the formulation **Co/SPU15** also reach the total drying time but with twice higher concentration of transition metal (0.06 wt. %). High catalytic performance showed complex **VOTsO** (0.03 wt. %) in combination with silicone-modified alkyd resin, which was cured after 4.1 h. Less drying activity showed **Co** drier, formulation **Co/SPS15** reached total drying time after 17.0 h. Obtained results for relative hardness well correlates with conclusions resulting from film drying time measurements.

Chemical drying of alkyd resins was followed by a time-resolved infrared spectroscopy. The measurements revealed developments typical for autoxidation of unsaturated fatty acids.<sup>[18]</sup> Briefly, disappearance of antisymmetric *cis*-C=C-H stretching band [ $\nu_a(\text{cis-C=C-H})$ ], observed at 3008  $\text{cm}^{-1}$ , follows consumption of isolated *cis* double bonds on the fatty acid tails. Development of this vibration mode is commonly used for kinetic studies of autoxidation process those were performed on the liquid models of the air-drying paints (*e.g.* fatty acid esters).<sup>[13]</sup> So, in our case, time-resolved infrared spectroscopy was used for determination of kinetic parameters of the autoxidation process for nine different alkyd resins (**S471**, **S622**, **SP262**, **SP252**, **TI870**, **TRI841**, **FP07**, **SPU15**, **SPS15**). The results obtained for fundamental alkyd **S471** are summarized in table 8.

Our aim to follow oxidative drying of alkyd formulation with strong thickness effect led us to utilize attenuated total reflectance (ATR) sampling technique in conjunction with infrared spectroscopy. This method enables to reach infrared spectra from a thin layer of the coating on the interface sample/ATR crystal (down surface), in which the evanescent wave penetrates. In our experimental setup, depth of penetration varies around  $0.67 \mu\text{m}$  (at  $3000 \text{ cm}^{-1}$ ) depending on refractive index of the sample.<sup>[39]</sup> The coatings of  $5 \mu\text{m}$ -wet thickness were considered enough thin to be dried homogeneously as a bulk with negligible effect of oxygen diffusion. It enables to utilize these measurements as an approach to oxidative drying on the top surface. We note that saturation of the coating with air-oxygen is a necessary condition for determination of kinetic parameters as the autoxidation process is treated as a reaction of pseudo-first order, when the oxygen concentration remains effectively constant.<sup>[22]</sup>

**Table 8** Kinetic parameters ( $-k_{\text{CH,max}}$ ,  $t_{\text{max}}$ , IT)<sup>a</sup> for the coating saturated with air-oxygen ( $5 \mu\text{m}$ -wet thickness) and half-lives of the process ( $t_{50\%}$ )<sup>b</sup>.

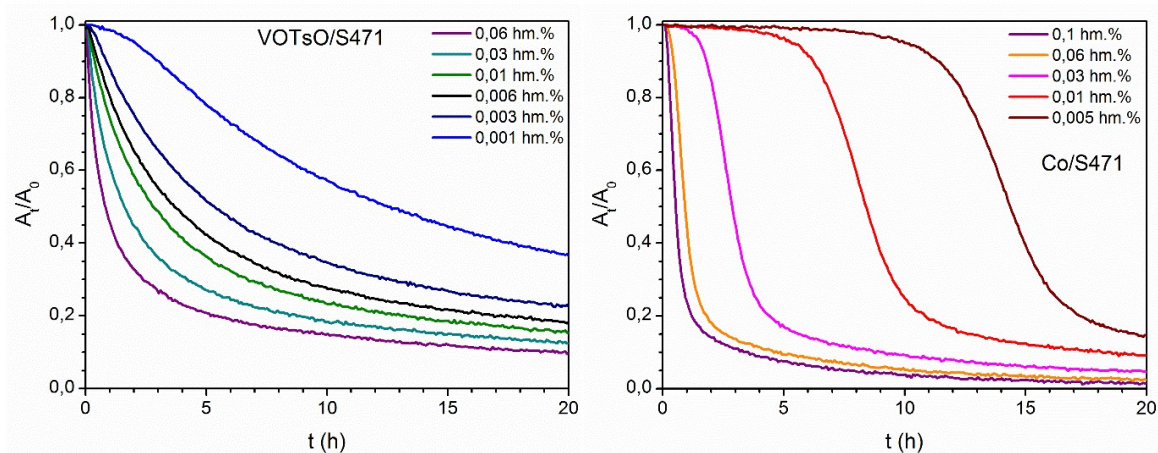
Drier	Metal content (wt. %)	$-k_{\text{CH,max}}^{\text{a}}$ ( $\text{h}^{-1}$ )	$t_{\text{max}}^{\text{a}}$ (h)	IT <sup>a</sup> (h)	$t_{50\%}^{\text{b}}$ (h)
<b>VOTsO</b>	0.06	1.36	0.1	— <sup>d</sup>	0.8
	<b>0.03</b>	<b>0.83</b>	<b>0.2</b>	— <sup>d</sup>	<b>1.6</b>
	0.01	0.43	0.2	— <sup>d</sup>	2.8
	0.006	0.26	0.2	— <sup>d</sup>	3.7
	0.003	0.19	0.6	— <sup>d</sup>	5.3
	0.001	0.11	3.2	0.3	12.6
<b>Co</b>	0.1	2.26	0.5	0.2	0.6
	<b>0.06</b>	<b>1.61</b>	<b>1.0</b>	<b>0.4</b>	<b>0.9</b>
	0.03	0.84	3.0	2.0	2.9
	0.01	0.54	8.9	6.9	8.4
	0.005	0.41	15.0	12.7	14.4

<sup>a</sup>  $-k_{\text{CH,max}}$  is maximum autoxidation rate constant observed at time  $t_{\text{max}}$ ; IT is induction time of the autoxidation. <sup>b</sup>  $t_{50\%}$  is half-life of the autoxidation. <sup>c</sup> IT was not observed.

Figure 5 shows development of the *cis*-C=C-H stretching bands for  $5 \mu\text{m}$ -layers of formulations with different concentration of **VOTsO** and **Co**. Decrease of  $\nu_{\text{a}}(\textit{cis}\text{-C=C-H})$  in intensity clearly implies that all driers, under the study, are active in used concentration ranges. In the  $5 \mu\text{m}$ -layers, the autoxidation is faster at higher metal concentration as evident from high rate constants and shorter half-life of the autoxidation reaction (see  $-k_{\text{CH,max}}$ ;  $t_{50\%}$  in Table 8).

At optimal metal concentration, 0.06 wt. %, cobalt-based drier (**Co**) exhibits very high rate coefficient ( $-k_{\text{CH,max}} = 1.61 \text{ h}^{-1}$ ) and quite long induction time (IT = 1.0 h). Lowering of the metal concentration led to lower rate coefficient and longer induction time. However, at concentration 0.005 wt. %, the autoxidation process in the  $5 \mu\text{m}$ -layer is fast ( $-k_{\text{CH,max}} = 0.41 \text{ h}^{-1}$ ), long induction time ensures deterioration of drying activity, that well correlates with longer drying times obtained from mechanical tests. In case

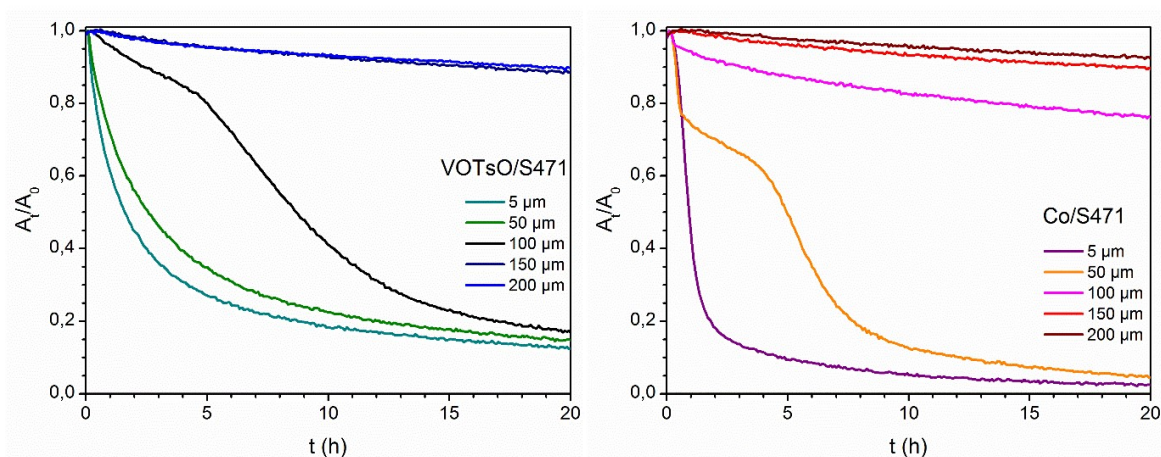
of **VOTsO**, sufficient values of  $-k_{CH,max}$  were observed in wide range of concentrations 0.06–0.006 wt. %. At optimal concentration of **VOTsO**, 0.03 wt. %, autoxidation process exhibits high rate coefficient ( $-k_{CH,max} = 0.83 \text{ h}^{-1}$ ) and none induction time.



**Figure 5** Effect of metal concentration on development of  $[\nu_a(cis-C=C-H)]$  band in alkyd coating **S471** of 5  $\mu\text{m}$ -wet thickness.

Although ATR technique cannot be used for direct profiling of the coating, the monitoring of a thin layer at the interface coating/ATR crystal enables to follow thickness effects on series of samples with the same composition but different film thickness. In our case, series of four independent experiments were used for each formulation under study. The wet thickness of the samples was set by frame applicator of given gap (50, 100, 150 and 200  $\mu\text{m}$ ). The obtained data were used as an approach to drying profile of paint film of 200  $\mu\text{m}$ -wet thickness (see Figure 6).

The comparison of time-resolved infrared spectra obtained for samples of different thickness proves that formulations of **Co** are cured homogeneously only up to 50  $\mu\text{m}$ .



**Figure 6** Effect of wet thickness on development of  $[\nu_a(cis-C=C-H)]$  band in alkyd **S471** formulations treated with **VOTsO** and **Co** driers.

In coatings thicker than 100  $\mu\text{m}$ , large part of reactive double bonds stays intact at the interface coating/ATR-crystal. Such observation implies formation of densely crosslinked skin in the top surface that blocks oxygen diffusion into substrate side of the coating, which is evident from development of *cis*-C=C-H stretch (Figure 6).

The observed consumption of the isolated *cis*-double bonds is only due to reaction with oxygen dissolved during preparation of the formulation. On the other hand, formulation treated with **VOTsO** is homogeneously cured up to 100  $\mu\text{m}$ -wet thickness. This phenomenon is probably caused by lower values obtained for rate coefficient, which inflects on formation of crosslinked skin. Slower formation of 3-dimensional crosslinked network allows continual diffusion of air oxygen to substrate and improves the curing of layers with higher thickness.

### 3. Conclusion

Cobalt(II) carboxylates are classified as “CMR2-Reprotoxic” and ongoing toxicological scrutiny may result in reclassification to carcinogenic, many alternatives of cobalt-based driers have been reported in literature but only few of them are commercially successful. The vanadyl complexes has a promising potential in paint-producing industry as a replacement of currently used toxic cobalt compounds. During testing of the drying activity, it was found that both vanadium(V) and vanadium(IV) compounds showed the ability to accelerate autoxidation reactions.

In the experimental part, 11 new vanadium compounds were synthesized and characterized by standard analytical methods. The exact structure of the four prepared single crystals was described by X-ray structural analysis. The drying activity was studied for 14 selected vanadyl complexes, which contained three different types of ligands in their structure.

The first tested group were oxidovanadium(V) complexes bearing three dithiocarbamate moieties. Their high catalytic activity in solvent-borne formulations of alkyd resins was evidenced by standard mechanical tests. Derivative with morpholine substituent showed a good solubility in organic solvents, which is an important feature for application in paint industry. However, the synthesis of these compounds is a two-step process and the starting materials are relatively high expensive ( $\text{VO}\text{SO}_4$ ,  $\text{CS}_2$ , *etc.*). In addition, working with carbon disulfide requires increased safety limits. The undeniable advantage of these compounds is their yellow or orange color, which does not significantly affect the color of the alkyd resin. Use of vanadium dithiocarbamate complexes is protected by a national patent owned by the University of Pardubice.

In next phase, catalytic performance of two oxidovanadium(IV) pentane-2,4-dionate complexes bearing benzyl substituents were studied on four different alkyd resins modified with soybean oil. Results obtained from standard mechanical tests revealed high acceleration of autoxidation process resulting in short total dry times. However, the synthesis of these compounds is also two-step process and starting substance is, as with dithiocarbamate complexes, financially demanding  $\text{VO}\text{SO}_4$ . In addition, new vanadyl acetylacetonate complexes showed lower oxidation stability, the storage requires an inert atmosphere. Moreover, these complexes have green color, so high concentrations can affect the color of cured polymer films.

The third chapter is focused on catalytic performance of seven new driers. These complexes contain the vanadium atom occupied by water molecules as neutral ligands and charge produced by vanadium core is compensated by sulfonic acid anions. Catalytic performance of new driers was studied on twelve different alkyd resins

(solvent-borne alkyds with different oil length, high-solid resins and alkyds modified by other monomers). The drying activity of tested formulations was primarily described by mechanical methods, as film drying time and relative hardness.

Our in-depth ATR-IR study, supported with classical mechanical studies, enabled to compare vanadium- and cobalt-based drier and to resolve two well-distinguished modes of film-formation in our systems drier/binder. This model reveals that each drier under study shows very specific curing properties. The cobalt-based drier (**Co**) is very powerful in studied concentration range as documented by high rate coefficient ( $-k_{CH,max}$ ). On the other hand, induction time was followed at each measurement, and drier forms very fast a densely crosslinked skin on the top of the coating, which is not permeable for air-oxygen. Only thin layers of tested coatings are cured homogeneously. The homogenous drying was observed in all formulations of vanadium-based drier (**VOTsO**). The drying process become homogenous because the consumption of oxygen is slower than its diffusion from air.

## References

- [1] A. Hofland, *Prog. Org. Coat.*, 2012, **73**, 4, 274–282.
- [2] F. N. Jones, *Ullmann's Encyclopedia of Industrial Chemistry*, 2003, pp. 429–446.
- [3] J. Lindeboom, *Prog. Org. Coat.*, 1998, **34**, 147–151.
- [4] M. Manea, *High Solid Binders*, Vincentz, Hannover, 2008, pp. 239.
- [5] R. van Gorkum, E. Bouwman, *Coord. Chem. Rev.*, 2005, **249**, 1709–1728.
- [6] M. D. Soucek, T. Khattab, J. Wu, *Prog. Org. Coat.*, 2012, **73**, 435–454.
- [7] L. Leyssens, B. Vinck, C. Van Der Straeten, F. Wuyts, L. Maes, *Toxicology*, 2017, **387**, 43–56.
- [8] O. Preininger, J. Vinklársek, J. Honzicek, T. Mikysek, M. Erben, *Prog. Org. Coat.*, 2015, **88**, 191–198.
- [9] O. Preininger, J. Honzicek, P. Kalenda, J. Vinklársek, *J. Coat. Technol. Res.*, 2016, **13**, 479–487.
- [10] O. Preininger, I. Charamzová, J. Vinklársek, I. Císařová, J. Honzicek, *Inorg. Chim. Acta*, 2017, **462**, 16–22.
- [11] I. Charamzová, J. Vinklársek, P. Kalenda, J. Honzicek, *Coatings*, 2018, **8**, 204.
- [12] E. Bouwman, R. van Gorkum, *J. Coat. Technol. Res.*, 2007, **4**, 491–503.
- [13] S. T. Warzeska, M. Zonneveld, R. van Gorkum, W. J. Muizebelt, E. Bouwman, J. Reedijk, *Prog. Org. Coat.*, 2002, **44**, 243–248.
- [14] Z. O. Oyman, W. Ming, R. van der Linde, J. ter Borg, A. Schut, J. H. Bieleman, *Surf. Coat. Int. B Coat. Trans.*, 2005, **88**, 269–275.
- [15] J. W. de Boer, P. V. Wesenhagen, E. C. M. Wenker, K. Maaijen, F. Gol, H. Gibbs, R. Hage, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3581–3591.
- [16] B. Pirš, B. Znoj, S. Skale, J. Zabret, J. Godnjavec, P. Venturini, *J. Coat. Technol. Res.*, 2015, **12**, 965–974.
- [17] Honzicek, *J. Ind. Eng. Chem. Res.*, 2019, **58**, 28, 12485–12505.
- [18] I. Charamzová, J. Vinklársek, J. Honzicek, *Prog. Org. Coat.*, 2018, **125**, 177–185.

- [19] Ö. Gezici-Koc, C. A. A. M. Thomas, M. E. B. Michel, S. J. F. Erich, H. P. Huinink, J. Flapper, F. L. Duivenvoorde, L. G. J. van der Ven, O. C. G. Adan, *Mater. Today Commun.*, 2016, **7**, 22–31.
- [20] M. Erben, D. Veselý, J. Vinklárek, J. Honzíček, *J. Mol. Catal. A Chem.*, 2012, **353–354**, 13–21.
- [21] J. Honzíček, J. Vinklárek, *J. Appl. Polym. Sci.*, 2018, **135**, 46184.
- [22] M. Křížan, J. Vinklárek, M. Erben, I. Císařová, J. Honzíček, *Prog. Org. Coat.*, 2017, **111**, 361–370.
- [23] M. Křížan, J. Vinklárek, M. Erben, Z. Růžicková, J. Honzíček, *Inorg. Chim. Acta*, 2019, **486**, 636–641.
- [24] I. Charamzová, A. Machálková, J. Vinklárek, I. Císařová, J. Honzíček, *Inorg. Chim. Acta*, 2019, **492**, 243–248.
- [25] ASTM D5895-03, Standard Test Methods for Evaluating Drying or Curing During Film Formation of Organic Coatings Using Mechanical Recorders, ASTM International, West Conshohocken, PA, 2003.
- [26] ISO 1522:2006, Paints and Varnishes - Pendulum Damping Test, International Organization for Standardization, 2006.
- [27] A. T. Casey, D. J. Mackey, R. L. Martin, A. H. White, *Aust. J. Chem.*, 1972, **25**, 3, 477–492.
- [28] H. L. Klöpping, G. J. M. van der Kerk, *Rec. Trav. Chim. Pays-Bas*, 1951, **70**, 10, 917–939.
- [29] M. W. Makinen, M. J. Brady, *J. Biol. Chem.*, 2002, **277**, 12215–12220.
- [30] A. Pokutsa, Y. Kubaj, A. Zaborovskyi, D. Maksym, J. Muzart, A. Sobkowiak, *Appl. Catal., A general*, 2010, **390**, 190–194.
- [31] Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, T. Kawamura, S. Uemura, *J. Org. Chem.*, 2002, **67**, 6718–6724.
- [32] D. A. Cogan, G. Liu, K. Kim, B. J. Backes, J. A. Ellman, *J. Am. Chem. Soc.*, 1998, **120**, 8011–8019.
- [33] A. E. Gerbase, J. R. Gregório, M. Martinelli, M. L. A. von Holleben, M. A. M. Jacobi, L. de L. Freitas, C. I. W. Calcagno, A. N. F. Mendes, M. L. Pires, *Catal. Today*, 2000, **57**, 241–245.
- [34] M. Martí, L. Molina, C. Alemán, E. Armelin, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1609–1618.
- [35] I. I. Ponomarev, I. V. Blagodatskikh, A. V. Muranov, Y. A. Volkova, D. Y. Razorenov, I. I. Ponomarev, K. M. Skupov, *Mendeleev Commun.*, 2016, **26**, 362–364.
- [36] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd ed., John Wiley & Sons, Chichester, 2004, pp. 323.
- [37] T. S. Smith II, R. LoBrutto, V. L. Pecoraro, *Coord. Chem. Rev.*, 2002, **228**, 1–18.
- [38] C. J. Ballhausen, B. F. Djurinskij, K. J. Watson., *J. Am. Chem. Soc.*, 1968, **90**, 13, 3305–3309.
- [39] B. C. Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy, second edition*, CRC Press, 2011, pp. 129–146.

## List of Publications

Iva Charamzová, Jaromír Vinklárek, Jan Honzíček

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

*Progress in Organic Coatings*, 2018, **125**, 177–185

Iva Charamzová, Aneta Machálková, Jaromír Vinklárek, Ivana Císařová, Jan Honzíček  
Benzyl substituted oxidovanadium(IV) pentane-2,4-dionates: Synthesis, structure and drying properties

*Inorganica Chimica Acta*, 2019, **492**, 243–248

Iva Charamzová, Jaromír Vinklárek, Petr Kalenda, Ivana Císařová, Jan Honzíček

Oxidovanadium(V) dithiocarbamates as driers for alkyd binders

*Journal of Coatings Technology and Research*, ISSN 1547-0091

## Patent

Jan Honzíček, Petr Kalenda, David Veselý, Jaromír Vinklárek, Iva Charamzová

Nátěrové hmoty obsahující sikativy na bázi sloučenin vanadu, a použití těchto sloučenin jako sikativů v nátěrových hmotách.

UNIVERZITA PARDUBICE. 2019. Česká Republika. 307 597. Uděleno 21.11.2018.

Zapsáno 02.01.2019.

## List of Conference Contributions

### Oral presentation

Iva Charamzová, Jan Honzíček, Jaromír Vinklárek

Curing of high-solid alkyd binders by cobalt-based drier

X. KONFERENCE PIGMENTY A POJIVA, Seč 6.–7. 11. 2017, 73–79,

ISBN 978-80-906269-2-8

Iva Charamzová, Jan Honzíček, Jaromír Vinklárek

Curing of alkyd resins by non-toxic vanadium-based driers

XI. KONFERENCE PIGMENTY A POJIVA, Seč 5.–6. 11. 2018, 82,

ISBN 978-80-906269-3-5

Iva Charamzová, Jan Honzíček, Jaromír Vinklárek

Oxo-vanadium Complexes of Dithiocarbamates as an Alternative Driers for Alkyd Resins

7th International Conference on Chemical Technology, Mikulov 15.–17. 4. 2019,

ISBN 978-80-88307-01-3

### Poster presentation

Iva Charamzová, Jan Honzíček, Jaromír Vinklárek

Transition Metal Complexes as Driers for High-solid Alkyd Binders

International Symposium on Metal Complexes, Florencie 3.–7. 6. 2018, 117–118,

ISSN: 2239-2459