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The vanadium and molybdenum complexes as additives into oxopolymerization drying paints

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Abstract

This dissertation is focused on the study of the effect of complexes of molybdenum and vanadium on the drying of air-drying paints. The theoretical part is focused on the properties of alkyd resins and the substantial part of the theory is focused on autooxidation drying. The mechanism of film formation and the catalysts used to accelerate the autooxidation process are described in detail.

The practical part describes the preparation of test compounds. These compounds were characterized by FTIR and EPR spectroscopy. The three completely new complexes were prepared. These complexes were characterized by single crystal X-ray diffraction analysis. Furthermore, the effect of these compounds on the drying of alkyd resins of various types was studied. A number of experimental techniques have been used for this purpose. The most important of these was the measurement of kinetics using FTIR spectroscopy. From these studies, it is very clear that vanadium complexes have a great potential to replace the commonly used cobalt-based driers.

Abstract

Tato disertace se zabývá studiem vlivu komplexů molybdenu a vanadu na zasychání na vzduchu schnoucích nátěrových hmot. Teoretická část je zaměřena na vlastnosti alkydových pryskyřic a podstatná část je zaměřena na autooxidační zasychání. Je podrobně popsán mechanismus tvorby filmu a používané katalyzátory pro urychlení autooxidačního procesu.

V praktické části je popsána příprava testovaných sloučenin. Tyto sloučeniny byly charakterizovány pomocí FTIR a EPR spektroskopií. V rámci disertace byly připraveny tři zcela nové komplexy, které byly charakterizovány pomocí monokrystalické rentgenové difrakční analýzy. Dále byl studován vliv těchto sloučenin na zasychání alkydových pryskyřic různých typů. Za tímto účelem byla použita celá řada experimentálních technik. Nejdůležitější z nich bylo měření kinetiky pomocí FTIR spektroskopie. Ze získaných výsledků je velmi dobře patrné, že komplexy vanadu mají velký potenciál nahradit v současné době používané sikativy na bázi kobaltu.

Key words:

Autoxidation, driers, molybdenum, vanadium, FTIR, EPR

Klíčová slova:

Autooxidace, sikativy, molybden, vanad, FTIR, EPR

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Introduction

This Thesis was focused on the study of the drying activity vanadium and molybdenum complexes for the air–drying paints. Air-drying binders have been established as a significant group of paints used in modern organic coatings. Presence of double bonds in the binder molecules enables the reaction with air oxygen to give three-dimensional polymeric structure. This radical process, called autoxidation, results in conversion of the liquid paint layer to firm coating [1, 2]. Alkyd resins modified with highly unsaturated fatty acids are able to provide polymeric film without addition of any curing agents. This process is generally slow giving the paint film with very low final hardness. Nevertheless, the use of metal catalysts, so-called driers, enables to efficiently reduce the drying time and considerably improve the final properties of polymeric film [3, 4].

Commercially used cobalt-based driers, such as cobalt(II) 2-ethylhexanoate (**Co-Nuodex**), are one of the most powerful drying agents. However, the pronounced toxicity of cobalt(II) compounds [5, 6] stimulate the legislative pressure on paint-producing industry to replace these compounds with less toxic alternatives. Although driers based on manganese (*e.g.* Mn-bipyridine or Mn-triazacyclononane complexes) [7, 8] or iron (*e.g.* acylferrocenes) [9-11] are known, the most of them still suffers from some disadvantages, such as intense color or lower activity at ambient temperature [3]. Very recently, high drying activity was reported for Fe-bispidon complex [12]. It exhibits a considerably higher activity than common cobalt-based driers and seems to be suitable not only for solvent-borne alkyd paints but also for water-borne binders but the quest for novel inexpensive and highly efficient species is still ongoing.

Our scrutiny for new drying agents leads us to organometallic molybdenum and vanadium compounds. Hence, high-valent molybdenum compounds and oxovanadium(IV) seem to be promising candidates for this purpose, because they are established as potent oxygen-transfer catalysts in various organic syntheses [13-17]. Furthermore inorganic molybdenum compounds exhibit very low overall toxicity [18, 19]. Nevertheless particular organometallic molybdenum compounds are biologically non-innocent [20]. Unfortunately the overall toxicological profile of the molybdenum compounds under the study is still missing. Also inorganic vanadium compounds exhibit only low overall toxicity [21]. To the best of my knowledge, no original research article dealing with air-drying performance of these compounds has been published when omitting a review mentioning the ability vanadium compounds to accelerate autoxidation process [4]. So far, only the patent literature has dealt with performance of vanadium compounds[22] and two vanadium-based trial driers of confidential composition are currently commercially available (OMG Borchers GmbH). All these vanadium driers are usually combined with secondary driers (soaps of Sr, Zn, Zr, Ca or Li) to improve through-drying of the coated film [4,23].

1 Methods

The several experimental methods were used to determine drying activity of studied compounds. Due to the limited space of this annotation I will describe only three of them which are the most important.

1.1 Film drying time

The drying performance of studied catalytic systems has been determined using a BYK Drying Time Recorder. The instrument is a straight-line recorder equipped with hemispherical ended needle (5 g weight used) that travels the length of the test strip under standard laboratory conditions (temperature 23°C, relative air humidity 50%). A glass test strip was prepared by casting a film upon it (thickness was 76 μm of wet film). The trace left on the film during the drying has been used to define tack free time (τ_1) and total dry time (τ_2). Three stages of the drying process were considered in accordance with literature [24]. During stage 1 ($t = 0$–τ_1), the paint flows together and starts to polymerize. It gives bold and uninterrupted line. During the stage 2 ($t = \tau_1$–τ_2), the surface is sticky and the path is ripped. After τ_2 (stage 3) the paint is through dry and needle travels on top of the surface and no trace in the film is observable. This method gives us information about drying activity of the studied driers at the beginning of the autoxidation.

1.2 Determination of film hardness

Film hardness development was monitored using a Persoz type pendulum (Elcometer Pendulum Hardness Tester, UK) in conformity with ISO 1522. 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. The more swings observed, the harder is the film. A plain glass test plate (10 × 20 cm) was coated with a 90 μm film (wet thickness) dried with the appropriate drier system and film hardness was measured within 100 days. The measured value was related to the hardness of a glass standard and expressed as relative hardness in percents. The error in determination of surface hardness was estimated to be ±0.5%. On summarizing of obtained data, dependence of film hardness versus time has been determined.

1.3 Time resolved FTIR experiments

The oxidation of alkyd resin was followed by time-resolved FTIR on Nicolet 6700 spectrophotometers (32 scans per spectrum with a resolution of 2 cm^{-1} giving series of 110 spectra per hour) in the range of 4000–500 cm^{-1} as described recently [11]. Analyzed regions of alkyd resin IR spectra are 3650–3125 cm^{-1} (OH stretch), 3014–2997 cm^{-1} (methylenic CH stretch) and 1011–947 cm^{-1} (conjugated double bonds), respectively. Autoxidation of EL catalyzed by studied driers has been followed on diamond ATR sphere (128 scans, resolution 2 cm^{-1}, 60 spectra per hour) and obtained data were analyzed as described previously [3, 25].

2 Results and discussion

This part of the annotation is divided into two parts. The first part is focused on reducing the amount of the cobalt based driers used in paints by molybdenum compounds as a secondary drier. The second part is focused on replacement cobalt based drier with vanadium compounds.

2.1 η3-C3H5)(η5-C5H5)Mo(CO)2 as a secondary driers

As I wrote at the beginning of the annotation the high-valent molybdenum compounds are established as potent oxygen-transfer catalysts in various organic syntheses and for this reason seem to be promising candidates for driers. The virtual

drawback of the high-valent molybdenum compounds is their low solubility in non-polar solvents. However, it could be easily overcame by the use of organometallic molybdenum(II) precursors, such as $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)Mo(CO)_2]$ (**Mo-1**), see figure 1[26, 27]. This compound is highly soluble in non-polar solvents and another salient feature of **Mo-1** is its light yellow color that gradually fades during the oxidation to give almost colorless alkyd films.
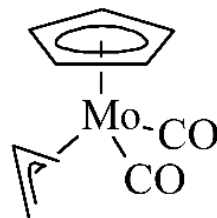

Figure 1: Chemical structure of studied drier.

Drying activity of the molybdenum(II) complex **Mo-1** and drying behavior of **Mo-1** combinations with commercial **Co-Nuodex** were studied in solvent-borne phtalic-type alkyd resin modified with soybean oil. The experiments were performed at various drier ratio combinations with overall metal concentrations 0.1 or 0.05 wt.% in dry matter content. Table **1** summarizes observed drying times and relative hardness for each system under the study. Although alkyd binder dried with 0.1 wt.% of **Mo-1** gives tack-free film within 4 hours, which is comparable to pure **Co-Nuodex** ($\tau_1 = 3.8$ h), the overall drying activity of **Mo-1** significantly lower. The total dry time (τ_2) exceeds 48 h and film remains soft even after 100 days of drying ($H_{rel,100d} = 20.2\%$). Nevertheless, further investigation on mixed catalytic systems has ascertained that the addition of **Mo-1** into composition containing **Co-Nuodex** considerably shortens drying time. At overall metal concentration 0.1 wt.%, mixed catalytic systems with drier ratios 2:1, 1:1, and 1:2 (Mo:Co), respectively, are able to dry the alkyd binder significantly faster ($\tau_1 = 1.5$–2.5 h; $\tau_2 = 3.2$–5.4 h) than single component catalysts and give polymeric films with hardness similar to **Co-Nuodex**. Further increasing of the Mo:Co ratio leads to apparent decrease of the drying activity. The effects of the combination of **Mo-1** with **Co-Nuodex** were observed also at overall metal concentration 0.05 wt.%. Although **Mo-1** itself is almost inactive at this concentration, mixed systems with drier ratios 2:1, 1:1, and 1:2 (Mo:Co) cure paint film similarly or even better than single **Co-Nuodex** at this concentration. The total drying times of mixed systems do not exceed 15 h and final hardness is higher than 40%. The main advantage of the mixed catalysts is the fast hardness development during first few days of drying and this feature is nicely seen ten days after application. At this stage, the mixed systems give the much harder coatings ($H_{rel,10d} = 27.2$–28.6%) than **Co-Nuodex** (18.8%).

Table 1: Drying times (τ) and relative hardness (H_{rel}) of the alkyd films containing molybdenum and cobalt based driers

Metal concentration		τ_1 [b]	τ_2 [c]	$H_{rel,10d}$ [d]	$H_{rel,100d}$ [e]
Mo	Co	(h)	(h)	(%)	(%)
–	–	>48	>48	2.0	6.2
0.050	–	>48	>48	2.4	8.4
0.100	–	4.0	>48	4.6	20.2
–	0.020	32.5	34.5	19.3	39.9
–	0.033	13.4	28.0	17.8	39.3
–	0.050	7.5	11.8	18.8	44.6
–	0.067	4.0	7.6	20.7	43.9
–	0.100	3.8	10.4	19.1	48.2
0.080	0.020	2.9	26.8	21.2	40.4
0.067	0.033	2.6	5.4	34.6	44.8
0.050	0.050	1.5	4.2	33.3	44.5
0.033	0.067	2.5	3.9	22.7	45.4
0.040	0.010	5.3	>48	22.0	41.3
0.033	0.017	9.2	14.5	27.1	40.5
0.025	0.025	5.8	10.8	28.6	40.2
0.017	0.033	7.0	10.3	28.3	44.6

[a] Concentrations are given in wt.%. [b] Tack free time. [c] Total dry time. [d] Relative hardness after 10 days. [e] Final relative hardness was reached after 100 days.

For better understanding of the mechanism of the autoxidation process catalyzed by **MO-1**, kinetic measurements using FTIR spectroscopy were performed. Figures **2** shows time-dependent changes of FTIR spectra of alkyd binder monitored in regions ~3008 cm^{-1}.
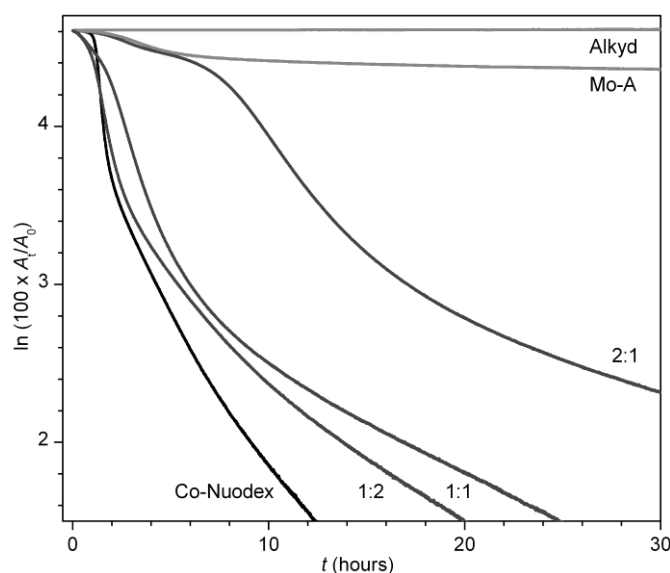

Figure 2: Time dependent integral plots of 3008 cm^{-1} band in the alkyd films. Systems with overall metal concentration 0.1 wt.% are compared with pure alkyd. Numerical legends represent Mo:Co ratio in mixed drier systems.

The analysis of peak area at 3008 cm^{-1} gives useful information about the rate of autoxidation and the slope of obtained curve is closely related to drying activity of used catalyst. The most significant parameter describing drier activity is rate constant $k_{CH,max}$ observed at the time t_{max}. The values $t_{5\%}$ and $t_{95\%}$ represent the time when the conversion of substrate with active CH bonds reach 5% and 95%, respectively. These parameters are more suitable for the characterization of the progression of higher-order reaction than simple inhibition period used in the case of model substrate such as ethyl linoleate. Single **Mo-1** is able to promote alkyd autoxidation only within the first 5 hours after exposition of binder film onto air. After this time the reaction is significantly slowed down. . Cobalt-molybdenum drier mixtures accelerate conversion of unsaturated substrate and show no inhibition period. Anomalous curve with two inflexion points was observed for 2:1 mixed drier suggesting that two independent processes are present. The kinetic data are list in the table **2**.

Table 2: Autoxidation activity of studied driers in thin layer of alkyd binder.

Metal concentration [a]		$k_{CH,max}$ [b]	t_{max} [b]	$t_{5\%}$ [c]	$t_{95\%}$ [c]
Mo	Co	(h^{-1})	(h)	(h)	(h)
0.100	–	0.07	3.2	2.8	–[d]
–	0.100	1.39	1.4	1.1	11.6
0.067	0.033	0.08/0.23[e]	2.7/10.2[e]	2.3	54.6
0.050	0.050	0.46	2.6	0.6	23.0
0.033	0.067	0.49	4.1	0.5	18.7

[a] Concentration of the metal is given in wt.%. [b] Maximum oxidation rate constant ($k_{CH,max}$) observed at drying time t_{max}. [c] The time $t_{5\%}$ and $t_{95\%}$ is determined as a point when 5% and 95% of active CH bonds are consumed. [e] Not determined [e] Two points of inflexion were observed.

2.2 Vanadium based driers

The drying activity of the vanadium is known for a quite long time but nobody interested about it at details. I decided to start my investigations with familiar and well defined diketonate compounds of the formula [VO(O,O-R$_1$COCHCOR$_2$)$_2$] (VO-1: R$_1$= R$_2$= Me; VO-2: R$_1$= Me, R$_2$= Ph; VO-3: R$_1$= R$_2$= Ph), see figure 3.
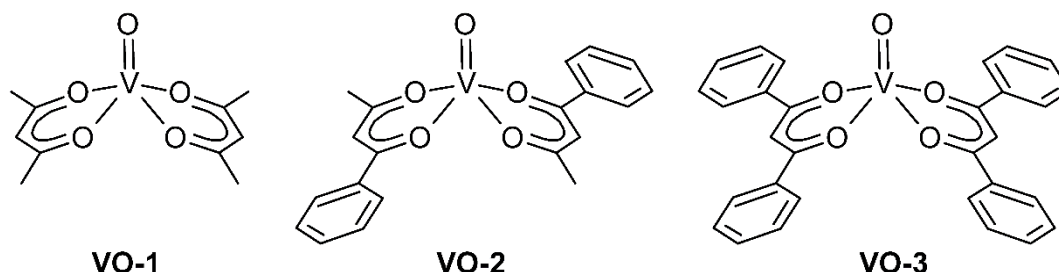

Figure 3: Chemical structures of studied driers.

Drying activity of the oxovanadium(IV) complexes (**VO-1**, **VO-2** and **VO-3**) was studied in solvent-borne phtalic-type alkyd resin modified with soybean oil. The optimization of drying process started at overall metal concentration 0.1 wt.% in dry matter content that is optimal for commercial cobalt-based drier **Co-Nuodex.** Lower

concentrations (0.03, 0.01 and 0.005 wt.%) were used in attempt to reduce metal content in the paint. Table **3** summarizes observed drying times and relative hardness for each system under the study. All results of this study were compared with performance of **Co-Nuodex** under the same conditions.

The compound **VO-1** shows an excellent drying activity. The tack free times as well as the total drying times are considerably shorter than observed for **Co-Nuodex** for all concentrations under the study (0.1, 0.03, 0.01 and 0.005 wt.%). Interestingly, the performance **VO-1** at concentration 0.01 wt.% seems to be similar to **Co-Nuodex** at ten times higher concentration (see τ_1 and τ_2 in table **1**) that implies high efficiency of this drier. At the concentration 0.005 wt.%, the total drying of **VO-1** time exceeds one day ($\tau_2 = 25.8$ h) but even here it is shorter than observed for **Co-Nuodex** at 0.03 wt.%. These data are in agreement with film hardness development. Hence, all coatings treated with **VO-1** exhibit considerably higher values of surface hardness 10 days after application than those treated with **Co-Nuodex** (table **3**). The final hardness of the coatings treated by **VO-1** is lower than observed for cobalt-based drier at the same concentration. Nevertheless, they are still in the range suitable for application. The sharp rise in relative hardness induced by studied oxo-vanadium(IV) complexes at the start of the drying process is very promising feature due to reduction of film tackiness after application of alkyd paint onto substrate (compare values τ_i and $H_{ref;10d}$). The performance of further two oxovanadium complexes under the study, **VO-2** and **VO-3**, is very similar similarly to **VO-1**. The differences in hardness developments near the error of the measurements. Nevertheless, **VO-2** as well as **VO-3** shows shorter tack free time (τ_1) and total dry time (τ_2).

These results confirm very high drying activity all three oxovanadium complexes under the study even at very low concentrations those are insufficient in case of cobalt-based drier.

Table 3: Drying times (τ) and relative hardness (H_{rel}) and coloration of alkyd films dried with various concentrations of studied driers.

| Metal content wt. %	Drier	$\tau_1{}^a$ (h)	$\tau_2{}^b$ (h)	$H_{rel;10d}{}^c$ (%)	$H_{rel;100d}{}^d$ (%)
0.10		0.4	6.2	35.1	53.1
0.03	**VO-1**	1.1	6.5	32.3	47.9
0.01		2.2	11.5	29.3	46.0
0.005		2.7	25.8	28.5	42.7
0.10		0.6	1.5	36.1	53.6
0.03	**VO-2**	0.5	4.3	34.2	48.7
0.01		1.4	9.2	33.3	47.6
0.005		1.2	15.6	32.6	41.7
0.10		0.5	2.2	38.1	55.0
0.03	**VO-3**	0.8	2.6	36.9	52.3
0.01		0.9	6.5	35.2	47.2
0.005		1.1	11.2	32.7	43.6
0.1		3.8	10.3	29.2	55.9
0.03	**Co-Nuodex**	13.4	28.0	23.8	46.4
0.01		32.5	34.7	23.3	44.2
0.005		>48h	–	21.3	41.8

[a] Tack free time; [b] Total dry time; [c] Relative hardness after 10 days; [d] Relative hardness after 100 days

I also studied the mechanism of autoxidation by direct FTIR examination of polymeric films (solvent-borne phtalic-type alkyd resin modified with soybean oil) dried with studied compounds. By monitoring band intensity area at 3006 cm^{-1} one can follow the abstraction of hydrogen atom from the activated methylenic group adjoined with double bond. Figure 4 depicts logarithmic plots of integrated area of the band at 3006 cm^{-1} vs. time for studied driers; determined kinetic data are listed in the table **4**. The commercial drier **Co-Nuodex** reached the highest value of the rate constant ($k_{CH,max}$= 1.39 h^{-1}) but there is significant inhibition period of 30 min at 0.1 wt.% metal content. With decreasing concentration of cobalt in the binder, the $k_{CH,max}$ decreases and inhibition period extends. Studied oxovanadium(IV)driers give slightly lower rate constants (0.92–1.1 h^{-1}) and for the most active vanadium compounds **VO-1** and **VO-3**, respectively, no inhibition period is present. In the case of **VO-2** at 0.1%, I have observed short inhibition period but with decreasing concentration inhibitive effect vanished. This could be caused by **VO-2**drier overdosing as has been previously reported for other powerful autoxidation catalysts, e.g. for iron-bispidon complex [11].Overdosing of **VO-2** in this formulation is also evident from slightly higher tack free time at metal dosing of 0.1%, see table **3**. All studied vanadium(IV) compounds show strong drying effect even at low concentrations. The significant difference between them and commercial Co-Nuodex drier is the absence of inhibition period. For the high drying activity of oxovanadium(IV) complexes are also witnessing low values of t_{max} representing the time is which the rate constant k_{CH} is maximal.

Table 4: Autoxidation activity of studied driers in thin layer of alkyd binder.

Metal content (wt.%)	Drier	$-k_{CH,max}{}^{a}$ (h^{-1})	$t_{max}{}^{a}$ (h)	IT^{b} (h)
0.100	**VO-1**	1.00	0.3	–
0.030		0.38	0.6	–
0.010		0.1	4.1	–
0.100	**VO-2**	0.92	1.1	0.5
0.030		0.64	0.7	–
0.010		0.20	2.1	–
0.100	**VO-3**	1.10	0.4	–
0.030		0.53	0.9	–
0.010		0.20	1.8	–
0.100	**Co-Nuodex**	1.39	1.4	0.5
0.030		0.43	13.3	10
0.010		0.22	17.9	13.4

[a]Maximum oxidation rate constant ($k_{CH,max}$) observed at drying time t_{max}. [c] Induction time (IT) has been determined graphically as intersection of tangential lines extending the curve before and after knee point.
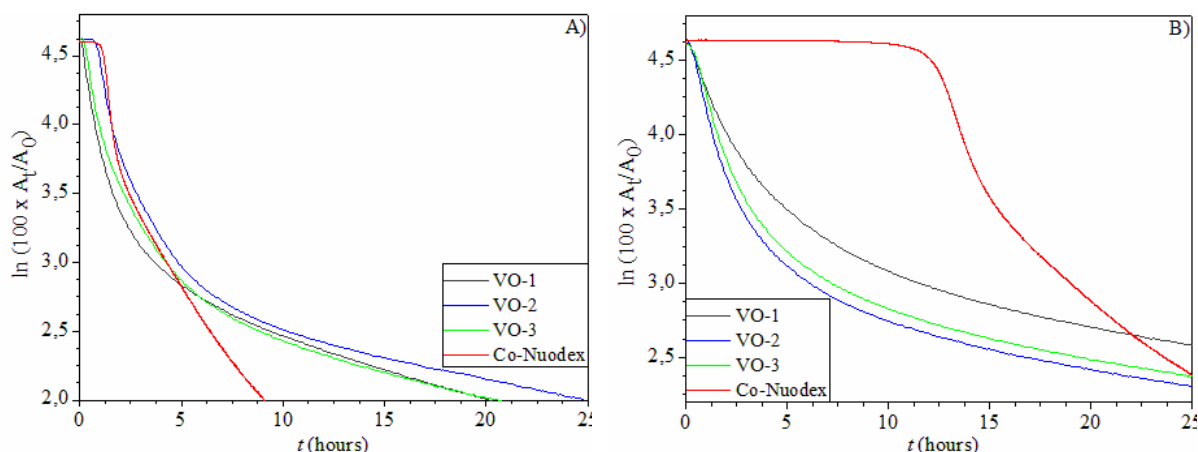
Figure 4: Time dependent integral plots of the 3008 cm^{-1} band observed in alkyd autoxidation at metal content A) 0.1 wt.%; B) 0.03 wt.%;

A virtual drawback of the simple oxovanadium complexes such as **VO-1, VO-2** and **VO-3** is their lower solubility in the non-polar solvents. So I synthesized series of new oxovanadium compounds with increased solubility in non-polar solvents. This target was achieved by attachment of linear alkyl tails on acetylacetonate ligands. It were prepared 5 oxovanadium(IV) compounds (see Figure **5**).
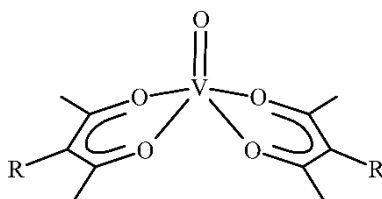
Figure 5: Chemical structures of studied driers. When VO-4 R= Me, VO-5 R= Et, VO-6 R= n-Bu, VO-7 R= n-Hex, VO-8 R= n-Oct.

Due to the limited space in this annotation I will discuss only the compounds **VO-6**, **VO-7** and **VO-8**. For the all data see the Thesis.

The compounds **VO-6-8** were prepared by the following procedure: The ligands were prepared by the mixing acetylacetonate with the relevant alkylbromide in the present of the carbonate and potassium iodide. The reaction mixture was heated under reflux under inert atmosphere for 48h. After cooling at room temperature, the suspension was filtered on glass frit and washed with acetone. The volatiles were evaporated on rotavapor and the crude product was purified by vacuum distillation. The complexes were prepared by the mixing vanadyl sulphate with the required ligand. The mixture was dropwise neutralized with aqueous solution of sodium carbonate. The reaction mixture was stirred for 3 hours at room temperature. The crude product was extracted with dichloromethane. The volatiles and unreacted ligand were removed by the vacuum distillation on Kugelrohr. The product was recrystallized from hexane at low temperature (–30°C) and vacuum dried. The compounds were characterized by the EPR and the molecular structure was determined by single-crystal X-ray diffraction (see Figure **6**).
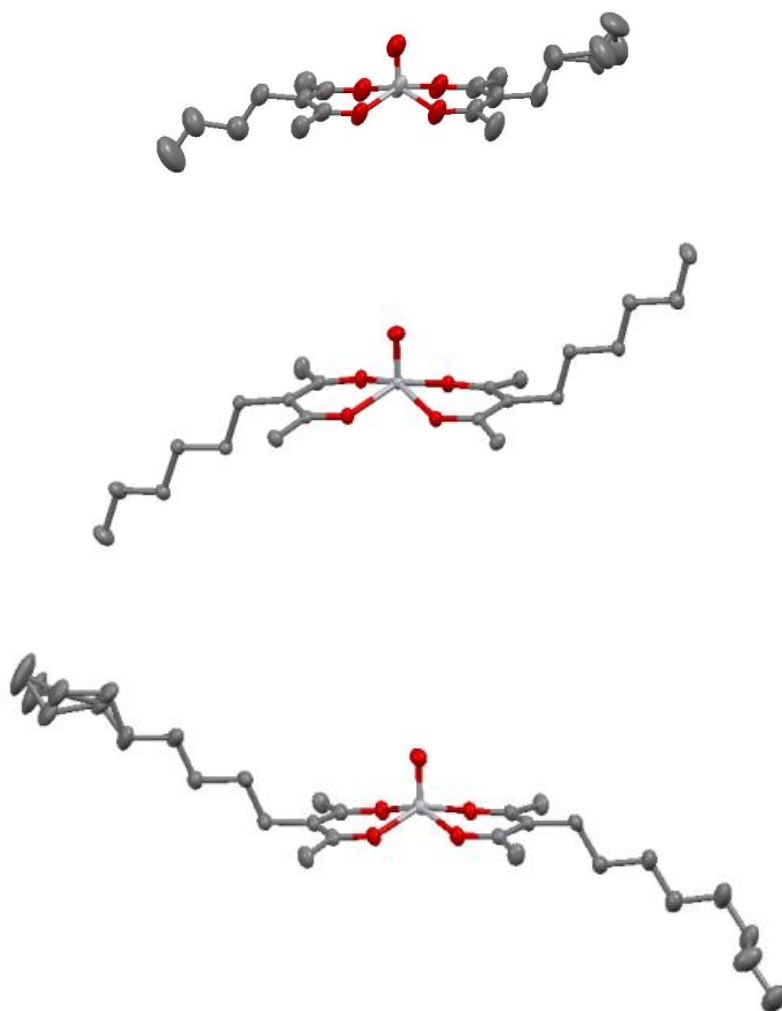

Figure 6: Molecular structure of the **VO-6**, **VO-7** and **VO-8** (from the top to the bottom).

Drying activity of the prepared compounds was studied on three solvent-borne alkyd resins. The alkyd resins were modified by soybean oil about different oil length (**S40, S50** and **S60**). In the case of the **S40** the overall metal concentrations for the drying

time and relative hardness were 0.03, 0.01 and 0.005 wt.% on dry matter content for the tested compounds. In the case of the **S50** and **S60** the overall metal concentrations were 0.1, 0.06, 0.03, 0.01 and 0.005 wt.% on dry matter content for the driers under the study. The concentrations of the commercial Co-based drier were the same for the all alkyd resins (0.1, 0.06 and 0.03 wt. % metal on dry matter content).

Drying times and relative hardness for the alkyd **S40** are summarized in Table **5**.

Table 5: Drying times (τ) and relative hardness (H_{rel}) of alkyd **S40** dried with studied driers at various concentrations.

Metal content (wt.%)	Drier	$\tau_1{}^a$ (h)	$\tau_2{}^a$ (h)	$H_{rel;10d}{}^a$ (%)	$H_{rel;100d}{}^a$ (%)
0.03		0.6	3.3	34.0	45.7
0.01	**VO-6**	1.2	6.3	37.0	45.8
0.005		2.5	10.6	38.4	43.4
0.03		0.3	3.1	27.3	46.5
0.01	**VO-7**	0.6	6.4	25.6	39.8
0.005		1.9	10.1	34.4	50.2
0.03		1.4	4.9	24.8	44.9
0.01	**VO-8**	3.2	10.3	22.8	40.6
0.005		4.6	14.4	24.5	39.6
0.1		5.5	7.6	25.9	61.2
0.06	**Co-Nuodex**	2.7	6.9	35.3	58.5
0.03		5.5	15.4	35.8	57.4
–	–	>24	>24	6.8	45.7

^{a} For definition see footnote of Table **3**

For the short oil length alkyd type the drying activity is excellent for all driers under the study. The highest activity exhibits **VO-7.** The total drying time was in the range 3.1-10.1 h when even at very low concentration (0.005 wt.%) the total drying time is slightly longer than for commercial drier **Co-Nuodex** at concentration 0.06 wt. % (6.9 h) which is recommended by supplier for this type of alkyd resin. In the case of the **VO-6,** and **VO-8** the drying times are very similarly. The concentration 0.03 and 0.01 exhibit similarly activity as the **VO-7.** The drying times are shorter or the same (3.3-10.3) as a drying time for commercial drier at the concentration recommended by supplier. These data are in agreement with film hardness development. The final hardness of the coatings treated by vanadium based driers is lower than observed for cobalt-based drier at the same concentration. Nevertheless, they are still in the range suitable for application.

Drying times and relative hardness for the alkyd **S50** are summarized in Table **6**. For the medium oil length alkyd resin the tested compounds exhibit good drying activity as well. **VO-8** exhibits the highest activity for this alkyd type. The total dry times of systems with **VO-8** are about half (for concentration range 0.1-0.03 wt.%) or practically the same (for concentration 0.01 wt.%) than the drying time for cobalt-based drier. The total drying time for concentration 0.005 wt.% exceeded 24 hours and the concentration is not effective anymore. The total drying times for the systems with **VO-6** and **VO-7** are very similarly to each other. The effective concentration range is 0.1-0.03 wt.% (2.2-

8.5 h). The drying times for the concentrations 0.01 and 0.005 wt% are much longer (more than 16 hours) and for this reason they are not suitable for drying alkyd paints. The relative hardness is very similarly for all systems. Only hardness for the films with the lowest concentration (0.005 wt.%) is lower than 40%.

Table 6: Drying times (τ) and relative hardness (H_{rel}) of alkyd **S50** dried with studied driers at various concentrations.

Metal content (wt. %)	Driers	$\tau_1{}^a$ (h)	$\tau_2{}^a$ (h)	$H_{rel;10d}{}^a$ (%)	$H_{rel;100d}{}^a$ (%)
0.1		0.6	2.2	30.3	56.2
0.06		0.6	2.5	32.1	54.3
0.03	**VO-6**	2.5	8.5	28.6	49.6
0.01		5.5	17.7	26.1	44.2
0.005		14.5	24	24.5	42.6
0.1		1	2.2	27.4	54.8
0.06		0.8	3.7	30.5	53.4
0.03	**VO-7**	2	5	26.9	50.4
0.01		4.5	16.5	25.6	48.8
0.005		8.2	24	23.1	46.6
0.1		0.7	1.8	34.1	55.1
0.06		0.7	2.4	31.2	54.8
0.03	**VO-8**	1.0	3.2	28.3	50.5
0.01		1.8	10	26	45.2
0.005		10.7	24	20.8	39.1
0.1		5.2	6.7	20.7	54.1
0.06	**Co-Nuodex**	7.7	9.5	20.6	53.7
0.03		19.2	24.0	22.4	49.8
–	–	>24	>24	2.4	33.8

^{a}For definition see footnote of Table **3**

Drying times and relative hardness for the alkyd **S60** are summarized in Table **7**. For the long oil length alkyd resin the all tested compounds exhibit excellent drying activity. The total dry times of the all three systems are about half or slightly shorter (for the concentration range 0.1-0.01 wt.%) than the drying time for cobalt-based drier. The total drying times for concentration 0.005 wt.% were quite long but for the **VO-8** and **VO-6** the drying times did not exceed 24 hours. The relative hardness is very similarly for all systems. Only hardness for the films with the lowest concentration (0.005 wt%) is lower than 40%.

Table 7: Drying times (τ) and relative hardness (H_{rel}) of alkyd S60 dried with studied driers at various concentrations

Metal content (wt. %)	Driers	$\tau_1{}^a$ (h)	$\tau_2{}^a$ (h)	$H_{rel;10d}{}^a$ (%)	$H_{rel;100d}{}^a$ (%)
0.1		0.8	2.8	22.5	37.6
0.06		0.8	3.6	19.8	34.0
0.03	**VO-6**	1	5.1	16.2	30.9
0.01		1.7	8.3	12	26.0
0.005		4.8	18.4	11.9	23.7
0.1		0.8	1.6	26.5	42.2
0.06		0.9	2.8	23.8	40.2
0.03	**VO-7**	1.0	6.2	17.6	35.3
0.01		1.9	15.7	14.8	29.6
0.005		7.8	24	14.7	27.0
0.1		1	1.5	25.1	39.7
0.06		1.1	2.7	22	35.2
0.03	**VO-8**	1.2	4.2	16.5	31.7
0.01		2.5	9.6	13.6	25.7
0.005		5.7	21.2	14.1	23.5
0.1		0.8	4.6	16.0	39.4
0.06	**Co-Nuodex**	0.9	7.1	15.6	37.2
0.03		1.7	8.5	14.9	33.5
–	–	>24	>24	2.4	18.8

^{a}For definition see footnote of Table **3**

In order to increase the solubility of the oxovanadium species, we decided to continue our study with a complex of the 2-ethylhexanoic acid (aka. octoic acid), see Figure **7**. The soaps of this acid are well established in paint-producing industry as primary(soaps of Co, Mn, Fe, and Ce), secondary (soaps of Pb, Zr, Bi, Ba, Al, or Sr), and auxiliary driers (soaps of Zn,Ca, Li, and K) due to increased solubility in organic solvents when compared with soaps of carboxylic acids with shorter or unbranched alkyl tail.
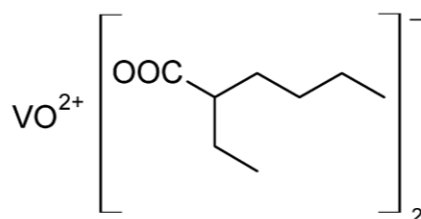

Figure 7: Chemical structures of studied drier (**VO-9**).

VO-9 was prepared by a reaction of oxovanadium(IV) sulfate ($VOSO_4 \cdot xH_2O$) with an excess of 2-ethylhexanoic acid and neutralized with sodium hydroxide. The product was isolated as a 20–35% solution in the acid. The exact concentration was estimated by atomic absorption spectroscopy. The infrared spectrum of **VO-9** shows two strong bands of C=O stretching at 1625 and 1603 cm^{-1}. It clearly confirms the coordination of 2-ethylhexanoate via carboxylic groups (*c.f.* with spectra of **VO-9** and 2-ethylhexanoic

acid in Figure **8**). The presence of oxovanadium moiety is associated with the appearance of the strong band of V=O stretching at 997 cm^{-1}.
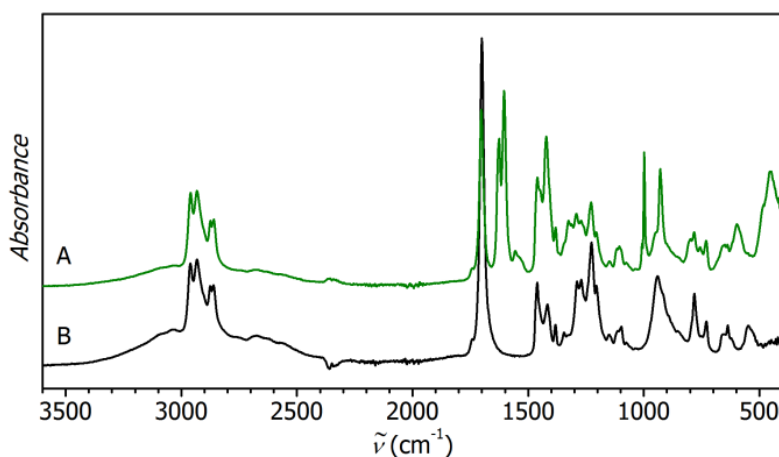

Figure 8: The infrared spectra of A)VO-octoate; B) 2-ethylhexanoic acid.

Drying activity of **VO-9** was studied on one solvent-borne alkyd resin of medium oil length modified by tall oil (**T50**) and three resins of different oil length modified by soybean oil (**S40**, **S50** and **S60**). The optimization of drying process started at overall metal concentration of 0.1 wt.% in dry matter content that is common for commercial cobalt-based drier **Co-Nuodex**. Lower concentrations of the driers were used in attempt to reduce the metal content in the paint. Drying times and relative hardness for each system under the study are summarized in Table **8**.

The initial experiments on alkyd resin **T50** revealed short drying times and high final hardness even at low concentration of **VO-9**. At metal concentration 0.03 wt.%, the performance resembles commercial **Co-Nuodex** at 0.1 wt.%. Considerably prolonged initial stage of drying process was observed only at much lower metal concentrations (0.01 and 0.005 wt.%). It is evident mainly from long total dry time (τ_2) that exceeds 20 hours and on a decrease of the final hardness below 50%. At concentration of vanadium 0.1 wt.%, no signs of overdosing were observed. Nevertheless, performance in not improved since the reduction of drying time and the increase of final hardness are insignificant. In case of resins modified by soybean oil (**S40**, **S50** and **S60**), the performance of **VO-9** at overall metal concentration 0.03 wt.% exceeds, in some terms, **Co-Nuodex** at 0.1 wt.% of metal. Hence, the total dry times (τ_2) of systems bearing **VO-9** are about half of that observed for cobalt-based drier or even shorter while the final hardness is comparable for both systems. The range of the suitable concentrations depends mainly on the oil length of the alkyd binder. In case of short oil resin **S40**, the vanadium based-drier could be used in range of concentrations 0.005–0.05 wt.%. Total dry time of these formulations does not exceed 10 h and final hardness of the coatings varies between 49.9 and 59.5%. At higher concentration (0.1 wt.%), the effect of overdosing appears as evident from much longer drying times τ_1 and τ_2. The autoxidation process is probably decelerated owing to a thin polymeric layer on the surface of the film that slows down the oxygen diffusion into the whole volume of the film. The performance of **VO-9** in medium oil resin **S50** is very similar to the formulation **VO-9/T50** with optimal concentration 0.03 wt.%. The main difference is that the system **VO-9**/**S50** shows the first signs of overdosing already at concentration 0.1 wt.%. In case of system with long oil resin **S60**, the range of concentrations suitable

for application is moved to higher values (0.03–0.1 wt.%). In this range, very short drying times were observed. The lower limit gives a coating with the final hardness 37.2% that is comparable to the performance of **Co-Nuodex** at 0.1 wt.% ($H_{rel,100d}$ = 39.4%). Higher concentration of vanadium enables to enhance the final hardness up to 45.1%. Since **VO-9** shows very good performance at 0.03 wt.% of vanadium in dry matter content in all tested alkyd resins, following investigation is restricted on this concentration.

Table 8: Drying times (τ) and relative hardness (Hrel) of alkyd films dried with studied driers at various concentrations.

Metal content (wt.%)	Formulation	τ_1 [a] (h)	τ_2 [a] (h)	$H_{rel;10d}$ [a] (%)	$H_{rel;100d}$ [a] (%)
–	**T50**	>24	>24	4.6	41.7
0.1		0.5	3.2	23.0	57.0
0.03	**VO-**	1.5	4.5	23.3	55.9
0.01	**octoate/T50**	0.3	22.9	18.9	49.1
0.005		5.2	22.6	14.9	41.1
0.1	**Co-**	3.4	4.5	23.4	60.6
0.06	**Nuodex/T50**	4.8	10.6	22.9	59.5
0.03		6.5	13.2	22.1	52.5
–	**S40**	>24	>24	6.8	45.7
0.1		2.8	10.5	34.0	60.1
0.03	**VO-**	0.9	2.2	30.6	59.5
0.01	**octoate/S40**	0.7	3.9	28.9	54.1
0.005		3.5	6.9	28.0	49.9
–	**S50**	>24	>24	2.4	33.8
0.1		1.6	5.5	28.6	56.4
0.03	**VO-**	1.5	3.3	25.0	54.1
0.01	**octoate/S50**	4.1	14.3	18.7	47.8
0.005		16.6	23.1	17.0	44.3
–	**S60**	>24	>24	2.4	18.8
0.1		0.7	1.8	17.9	45.1
0.03	**VO-**	1.2	2.1	13.4	37.2
0.01	**octoate/S60**	2.5	14.2	9.6	30.2
0.005		11.3	22.3	8.9	26.8

[a] For definition see footnote of Table **3**. For the drying time and relative hardness of the films with **Co-Nuodex** see the tables **5-7**.

To establish the behavior of **VO-octoate** in real paints, the formulations with **meko** (0.2 wt.%) as anti-skinning agent were prepared. The parameters describing the drying activity of the formulations are summarized in Table **9**. They reveal that **meko** does not influence the activity of vanadium-based drier significantly. Hence, the most of the formulations bearing **meko** show slightly shorter drying times τ_1 and τ_2 as well as the higher hardness ten days after application. The only drawback is a lower final hardness of the systems bearing alkyd resins modified by soybean oil. Nevertheless, even these formulations are very suitable for application since they are considerably higher than

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observed for drier-free alkyd resins. The observed behavior of the formulations bearing **meko** suggests that its anti-skinning properties prevent the appearance of a thin polymeric layer on the surface of the film making easier the diffusion of the air oxygen and thus acceleration the first stages of the drying process. The lower final hardness of the coating is probably caused by inhibition of the reactive radicals appearing during the drying process.

Table 9: The effect of meko on drying activity of VO-octoate.[a]

Formulation	τ_1 [b] (h)	τ_2 [b] (h)	$H_{rel;10d}$ [b] (%)	$H_{rel;100d}$ [b] (%)
VO-octoate/T50/meko	1.8	5.4	28.7	57.1
VO-octoate/S40/meko	0.5	1.8	32.0	50.7
VO-octoate/S50/meko	1.2	3.2	25.6	47.0
VO-octoate/S60/meko	0.8	4.0	16.1	33.0

[a] The experiments were done concentration of vanadium 0.03 wt.% and concentration of **meko** 0.2 wt.%. [b] For definition see footnote of Table 3

Conclusion

The main goal of the Ph.D. Thesis was the testing drying activity of the molybdenum and vanadium compounds.

At the beginning I focused on the decreasing of the amount cobalt-based drier using in the paint by molybdenum compound as a secondary drier. **Mo-1** itself has poor drying activity, the combinations of **Mo-1** with commercial **Co-Nuodex** perform better than pure **Co-Nuodex** at the same overall metal concentration. The investigation of the drying process by infrared spectroscopy has ascertained that **Mo-1** decomposes hydroperoxides but it does not induce their formation as cobalt based driers do. Therefore, **Mo-1** works in first few hours only and the drying process is suppressed when present hydroperoxides are consumed. It was further shown that **Mo-1** and **Co-Nuodex** perform in mixed systems almost independently and no synergic effect was approved. The shortening of the drying times, observed for the mixed drier systems is caused by reduction of the induction period of the drying process.

At the second stage I focused on the replacement of the cobalt-based driers by oxovanadium(IV) compounds. The first tested oxovanadium compounds (**VO-1, VO-2** and **VO-3**) exhibit drying activity. The drying activity related on weight percent of metal is higher than for commercial **Co-Nuodex.** The values of drying time and film hardness comparable with commercial **Co-Nuodex** were found at concentrations for **VO-1** 0.03 and 0.01 wt.% for **VO-2** and **VO-3** 0.03, 0.01 and 0.005 wt.%. The virtual drawback of these compounds is their worse solubility in non-polar solvents. This issue was resolved by attachment of linear alkyl tails on acetylacetonate ligands. It were prepared 5 oxovanadium(IV) compounds. The molecular structure of the **VO-6, VO-7** and **VO-9** was determined by single-crystal X-ray diffraction. The all tested compounds exhibit good drying activity for the 3 types of alkyd binders. The suitable concentration for the application depended on the type of alkyd binder but the most universal concentration is 0.03 wt. % on dry matter content. The last oxovanadium compound **VO-9** exhibits an excellent drying activity At concentration 0.03 wt.% of the metal, its performance on series of solvent-borne alkyd binders resembles commercial **Co-Nuodex** at concentration recommended by supplier (0.1 wt. %). The application of **VO-9** is not limited by solubility. Hence, it was synthesized as a solution in 2-ethylhexanoic acid and is well miscible with the alkyd resins under the study. The behavior of **VO-9** in real paint was simulated on formulations bearing commercial inhibitor of autoxidation (**meko**). The observed minor effects on tack free times and total dry times suggest no or negligible interactions with vanadium-based catalyst.

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List of Publications

1) THE EFFECT OF [(η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$)MO(CO)$_2$] ON DRYING OF SOLVENT-BORNE ALKYD PAINTS
    Ondřej Preininger, Jan Honzíček, Jaromír Vinklárek, Milan Erben, *Prog. Org. Coat,* **2014**, *77*, 292

2) A PROMISING DRYING ACTIVITY OF ENVIRONMENTALLY FRIENDLY OXOVANADIUM(IV) COMPLEXES IN AIR-DRYING PAINTS, Ondřej Preininger, Jan Honzíček, Jaromír Vinklárek, Tomáš Mikysek, Milan Erben, *Prog. Org. Coat.*, **2015**, *88,* 191

3) DRYING ACTIVITY OF OXOVANADIUM(IV) 2-ETHYLHEXANOATE IN SOLVENTBORNE ALKYD PAINTS
    Ondřej Preininger, Jan Honzíček, Petr Kalenda, Jaromír Vinklárek, *J. Coat. Technol. Res.,* **2016**, *13,* 479

4) OXOVANADIUM(IV) COMPLEXES BEARING SUBSTITUTED PENTANE-2,4-DIONATE LIGANDS: SYNTHESIS, STRUCTURE AND DRYING ACTIVITY IN SOLVENT-BORNE ALKYD PAINTS.
    Ondřej Preininger, Iva Charamazová, Jaromír Vinklárek, Ivana Císařová, Jan Honzíček, *Inorg. Ch. Act.*, **2017**, *462, 16*

List of Conference Contributions

Oral presentation

1) <u>O. Preininger</u>, J. Honzíček, J. Vinklárek, M. Erben, INFLUENCE OF (η^3-ALLYL)-(η^5-CYKLOPENTADIENYL)-DIKARBONYLMOLYBDENUM COMPLEX ON THE FILM FORMING PROPERTIES OXOPOLYMERIZATION DRYING PAINT, 65. Zjazd chemikov, Tatranske Matliare, September 9th – 13rd, **2013**, 3P05

2) <u>O. Preininger,</u> J. Honzíček, J. Vinklárek, M. Erben, (η^3-ALLYL)-(η^5-CYKLOPENTADIENYL)-DIKARBONYLMOLYBDENUM COMPLEX AND ITS DERIVATES AS ADDITIVES INTO OXOPOLYMERIZATION DRYING PAINTS, Mezinárodní konference projektu Partnerství pro chemii, Pardubice, September 19th – 20th, **2013**

3) <u>O. Preininger</u>, J. Honzíček, J. Vinklárek, M. Erben, COMPOUNDS V(IV) AS DRIERS FOR OXOPOLYMERIZATION DRYING PAINTS, VII. Conference on pigments and binders, Seč, November 10th -11st, **2014**

4) <u>O. Preininger</u>, J. Honzíček, J. Vinklárek, OXOVANADIUM(IV) 2-ETHYLHEXANOATE AND ITS EFFECT ON DRYING ALKYD RESINS ABOUT DIFFERENT OIL LENGHTS, VIII Conference on pigments and binders, Seč, November 2nd – 3rd, **2015**

5) <u>O. Preininger</u>, J. Honzíček, J. Vinklárek, P. Kalenda, OXOVANADIUM(IV) 2-ETHYLHEXANOATE AS A DRYING AGENT FOR SOLVENT-BORNE ALKYD PAINTS, 4thInternational conference on chemical technology, Mikulov, April 25th – 27th, **2016**

Poster Presentation

1) <u>O. Preininger</u>, J. Honzíček, J. Vinklárek, M. Erben, INFLUENCE OF COMPLEXES Mo ON THE FILM FORMING PROPERTIES OF THE AIR-DRYING PAINTS, 1stInternational conference on chemical technology, Mikulov, April 8th – 10th, **2013**

2) <u>O. Preininger</u>, J. Vinklárek, D. Veselý, INFLUENCE OF THE PROPOLIS ON THE FILM FORMING PROPERTIES OXOPOLYMERIZATION PAINT, 44th International Conference on Coatings Technology, Pardubice, May 20th – 22nd, **2013**