# Oxidovanadium(V) dithiocarbamates as driers for alkyd binders

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**Keywords:** alkyd; vanadium; autoxidation; air-drying paints; primary drier

**Abstract**

A series of oxidovanadium(V) dithiocarbamates was synthesized by conventional synthetic procedure and
characterized by analytical methods. Structures of two representatives were determined by X-ray diffraction
analysis on single crystals. The initial screening of catalytic alkyd drying, performed on a commercial solvent-
borne alkyd resin of medium oil-length, revealed a promising activity of oxidovanadium(V) dithiocarbamates,
which was further proved on several alkyd formulations including slow drying high-solid binders. The kinetic
behavior of the catalyzed autoxidation process, investigated by time-resolved infrared spectroscopy on a thin
alkyd layer, was found to be very different from commercial cobalt carboxylates. Appearance of
oxidovanadium(IV) species the upon curing process was evidenced by EPR spectroscopy.

**Graphical Abstract**
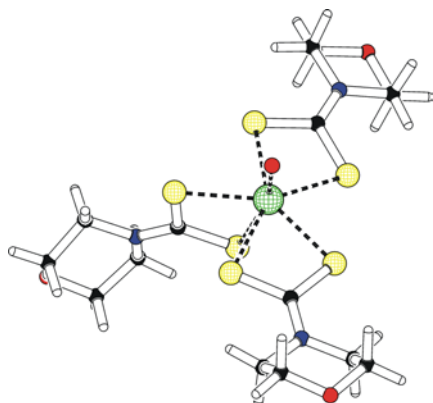
Oxidovanadium(V) dithiocarbamates were established as primary driers for solvent-borne and high-solid alkyd formulations. The kinetic behavior of the catalyzed autoxidation process, investigated by time-resolved infrared spectroscopy on a thin alkyd layer, was found to be different from commercial cobalt carboxylates. Appearance of oxidovanadium(IV) species upon the curing process was evidenced by EPR spectroscopy.

## Introduction

Air-drying paints, including alkyd binders, are widely used for protective and decorative coatings as they fulfil current ecological requirements due to high content of raw material accessible from renewable sources.[1] At ambient temperature, they exhibit a very slow film-formation process when not treated by additives. After fast solvent evaporation, the chemical drying proceeds sluggishly as it is based on autoxidation on polyunsaturated fatty acids originating from plant oil modifying the alkyd resin.[2] In practice, the drying is accelerated by additives known as primary or surface driers. In case of baking enamels, the curing of alkyd binder is accelerated by elevated temperature.[2, 3] Cobalt(II) carboxylates are currently the most common driers used for industrial use and hobby market. It is due to not only a low price and a high catalytic power but also because it works as "universal primary drier". Hence, they perform well in a large variety of commercial paint formulations and their combination with secondary and tertiary driers are well established. Although some solvents, pigments or additives could reduce its drying power, these effects are usually well described and can be avoided. The main drawback of cobalt-based driers is toxicity, which led to evaluation by European Chemical Agency.[4] 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. The cobalt replacement is currently 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).[2] It should be noted that all currently known alternatives exhibit very different drying characteristics from cobalt(II) compounds, which limits their large-scale use.[5,6]

In last decade, our research group has been focused on investigation of air-drying process and search for new alternatives of cobalt-based driers. We have described several ferrocene-derivatives with improved activity in solvent-borne formulation [7,8] and iron bispidine compounds with improved solubility in non-polar solvents.[9,10] 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,[11–13] 2-ethylhexanoate [14] and species bearing Geodken's macrocycle.[15]

This study is focused on vanadium compounds bearing dithiocarbamate ligands. Such type of compounds was chosen mainly due to a simple modification of the ligand periphery, which is beneficial for a tuning of physical-chemical properties. Furthermore, a variety of ligand precursors is readily accessible from secondary amines and carbon disulfide.[16]

## Experimental section

### Materials and chemicals

The starting materials were delivered by Acros Organics (oxidovanadium sulfate – $VOSO_4 \cdot x H_2O$, $x \approx 5$; carbon disulfide), Fisher (sodium diethyldithiocarbamate trihydrate), Penta (sodium hydroxide) and Merck (hydrogen peroxide; dibutylamine; dihexylamine; morpholine). All compounds were used as obtained without further purification. Solvents (dichloromethane, water, hexane, methanol, diethyl ether) were purified and deoxygenated before use by standard methods.[17] The synthetic procedures were performed under inert atmosphere of nitrogen using conventional Schlenk-line techniques.

Alkyd resins CHS-ALKYD S 471 X 60 (**S471**; OL = 47%, AV = 6 mg KOH/g, non-volatile content = 59.6%), CHS-ALKYD S 622 N 60 (**S622**; OL = 62%, AV = 7 mg KOH/g, non-volatile content = 58.4%), CHS-ALKYD TI 870 (**TI870**; OL = 87%, AV = 8 mg KOH/g, non-volatile content = 98.6%) and CHS-ALKYD TRI 841 (**TRI841**; OL = 84%, AV = 10 mg KOH/g, non-volatile content = 97.6%) were supplied by Spolchemie. Cobalt(II) 2-ethylhexanoate (**Co**; 65 wt.% in mineral spirits, Sigma- Aldrich) used as a standard drier.

We note that all metal concentrations are given in wt.% based on dry matter of alkyd binder.

### Synthesis of [VO(S₂CNEt₂)₃] (VO-dtc-1)

The compound was synthesized according to procedure described elsewhere.[18] A solution of oxidovanadium sulfate (100.0 g, 0.395 mol) in deoxygenated water (350 mL) was treated by hydrogen peroxide (30 wt.% solution, 80 mL) while the color changed from blue through green and red to brown. This solution was added dropwise to sodium diethyldithiocarbamate trihydrate (267.1 g, 1.185 mol) dissolved in deoxygenated water (350 mL). Fine brown powder started to precipitate during the addition and the reaction mixture was stirred until all amount of oxidized oxidovanadium sulfate was added. The appeared precipitate was separated by decantation, washed with deoxygenated water (3 × 100 mL) and vacuum drier. The crude product was recrystallized from a mixture dichloromethane/hexane to provide the final product as a red powder. Yield: 90.59 g (0.177 mol, 44.8%). Anal. Calcd. for ($C_{12}H_{30}N_3OS_6V$): C, 30.30; H, 6.36; N, 8.83; S, 40.44. Found: C, 30.62; H, 6.25; N, 8.49; S, 40.03. IR(ATR-C, cm$^{-1}$): 2978w, 2932w, 2870w, 1512s, 1484s, 1454s, 1427s, 1376w, 1354s, 1298w, 1268s, 1209s, 1142s, 1093m, 1071s, 1002m, 985s, 947s, 914m, 846m, 778m, 573w, 491w. Single crystals of **VO-dtc-1** suitable for X-ray diffraction analysis were prepared by a careful overlayering of dichloromethane solution with hexane.

### Synthesis of [VO(S₂CNBu₂)₃] (VO-dtc-2)

A mixture of sodium hydroxide (47.4 g, 1.185 mol) and dibutylamine (201.5 mL, 1.185 mol) in methanol (200 mL) was cooled to 0 °C and stirred for 20 min. The mixture was treated dropwise with carbon disulfide (71.6 mL, 1.185 mol) stirred for 10 min at 0 °C and then for 16 h at ambient temperature. Resulting light yellow-orange dispersion of [Na(S₂CNBu₂)] was cooled to 0 °C and treated with oxidized solution of oxidovanadium sulfate (100.0 g, 0.395 mol), which was prepared as described for **VO-dtc-1**. Yellow powder slowly precipitated

and turned to brown. The precipitate was separated by decantation, washed with deoxygenated water (3 × 100 mL) and vacuum drier. The crude product was recrystallized from mixtures dichloromethane/hexane and diethyl ether/hexane to provide the final product as an orange powder. Yield: 103.4 g (0.152 mol, 38.5%). Anal. Calcd. for ($C_{24}H_{54}N_3OS_6V$): C, 44.76; H, 8.45; N, 6.52; S, 29.87. Found: C, 44.24; H, 8.58; N, 6.82; S, 29.55. IR(ATR-C, cm$^{-1}$): 2956m, 2929w, 2870w, 1495s, 1464w, 1453m, 1423m, 1368m, 1307m,1289m, 1260w, 1251w, 1222m, 1189w, 1155m, 1111w, 1096w, 1014w, 984m, 949s, 911w, 798w, 782w, 732m, 603w, 528w, 442w, 426w.

## Synthesis of [VO(S$_2$CNHex$_2$)$_3$] (VO-dtc-3)

The reaction was carried out as described for **VO-dtc-2** but with dihexylamine (276.3 mL, 1.185 mol). The crude product was washed with methanol (3 × 100 mL), recrystallized from a mixture diethylether/hexane and vacuum dried to give the final product as a yellow powder. Yield: 102.2 g (0.174 mol, 44.0%). Anal. Calcd. for ($C_{36}H_{78}N_3OS_6V$): C, 53.23; H, 9.68; N, 5.17; S, 23.68. Found: C, 53.48; H, 9.75; N, 5.42; S, 23.24. IR(ATR-C, cm$^{-1}$): 2957w, 2927m, 2870w, 2855w, 1500s, 1488s, 1459w, 1448w, 1430m, 1422m, 1368w, 1296w, 1256m, 1236w, 1220w, 1194m, 1175w, 1148w, 1119w, 1102w, 1026w, 987m, 950s, 883w, 793w, 759w, 744w, 726w, 620w, 544w, 465w.

## Synthesis of [VO{S$_2$CN(CH$_2$CH$_2$)$_2$O}$_3$] (VO-dtc-4)

The reaction was carried out as described for **VO-dtc-2** but with morpholine (103.7 mL, 1.185 mol). The crude product was washed with methanol (3 × 100 mL), recrystallized from a mixture dichloromethane/hexane and vacuum dried to give the final product as a red-orange powder. Yield: 105.0 g (0.190 mol, 48.0%). Anal. Calcd. for ($C_{12}H_{24}N_3O_4S_6V$): C, 27.84; H, 4.67; N, 8.12; S, 37.17. Found: C, 27.66; H, 4.78; N, 8.30; S, 36.99. IR(ATR-C, cm$^{-1}$): 2981w, 2972w, 3921w, 2901w, 2890w, 2857w, 2848w, 1504m, 1477m, 1457w, 1442m, 1435m, 1420m, 1387w, 1355w, 1325w, 1296w, 1262m, 1238s, 1225s, 1188w, 1171w, 1104s, 1063w, 1023s, 1009m, 999m, 983m, 951s, 880w, 872w, 827w, 627w, 549m, 444w, 419w, 412w. Single crystals of **VO-dtc-4**·0.5CH$_2$Cl$_2$ suitable for X-ray diffraction analysis were prepared by a careful overlayering of dichloromethane solution with hexane.

### Preparation of test coatings

The performance of driers was tested as follows. Given oxidovanadium compound was dissolved in a mixture of DMSO (70 µl) and 3-methoxybuthanol (30 µl). The solution was treated with alkyd resin (5 g), homogenized for 2 min and sonicated by ultrasound for 3 min. In case of high-solid binders (**TI870** and **TRI8741**), the formulation was diluted with dearomatized white spirit to 90 wt.% of solid content in order to reduce viscosity.

### Drying time measurements

The freshly prepared formulations were cast on glass strips (305 × 25 × 2 mm) using a frame applicator of 76-µm gap and drying times were estimated using B. K. Drying Time Recorder BK3 (TQC, Germany) according to

ASTM D5895.[19] All tests were performed under standard laboratory conditions (T = 23°C, relative humidity = 50 %). Hemispherical-ended needle (D = 1 mm) was placed at the beginning of the wet film in horizontal position to straight-line recorder. The needles, fixed in adjustable mechanism, were equipped by 5 g weight each and pulled over the paint layer within 24 h. Resulting path formed during drying of the alkyd layer was used for the determination of set-to-touch time ($\tau_1$), tack-free time ($\tau_2$), dry-hard time ($\tau_3$) and dry-through time ($\tau_4$).[19]

### Relative hardness measurements

The appearance and relative hardness were evaluated on glass plates (200 × 100 × 4 mm). The formulations were cast using frame applicators of 150-μm gap (**S471** and **S622**) or 90-μm gap (**TI870** and **TRI8741**) and stored for 48 h in horizontal position and then in vertical position. The appearance was evaluated 5 days after application. Film hardness was measured using a Persoz-Pendulum Hardness Tester (Elcometer, UK) in conformity with ISO 1522 within 100 days.[20] The measurements of the film hardness were performed under standard laboratory conditions (T = 23 °C, rel. humidity = 50%).

### Infrared spectroscopy

Infrared spectra were collected on FTIR spectrometer Nicolet iS50 (No. of scans: 32, data spacing: 0.5 cm$^{-1}$) in the range of 4000–500 cm$^{-1}$ using built-in all-reflective diamond ATR. Samples of formulations were spread over the ATR crystal using a film applicator with 25-μm gap. Wet thickness of the coating is 5 μm as the ATR crystal is embedded 20 μm above a plate, on which film applicator abuts. The spectra were registered every 5 min. Collected series of the spectra were integrated using fixed two-point baseline in the bounds 3025–2990 cm$^{-1}$ [$v_s$(*cis-CH*=CH), isolated double bond]. Rate coefficient ($-k_{CH,max}$) was obtained from logarithmic plot of integrated area of the band as the steepest slope.

### EPR spectroscopy

EPR spectra were measured on Miniscope MS 300 spectrometer in microwave X-band (~9.5 GHz). The measurements were performed on tested films prepared by aforementioned standard procedure and cured for 100 days at room temperature. Samples were scratched of glass plates and measurements were done in quartz tubes (ID = 5 mm) at 293 K. The obtained EPR spectra were computer simulated using EPR simulation software SimFonia v.1.2 (Bruker). A second-order perturbation theory was used for description of the interaction between electronic spin and nuclear spin of vanadium. Anisotropic line-widths and mixed Lorentzian/Gaussian lines shapes were used for the simulations.

### X-ray crystallography

Crystallographic data were collected either on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoKα radiation (λ = 0.71073 Å) (**VO-dtc-1**) or on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube MoKα radiation (λ = 0.71073 Å) (**VO-dtc-4**).

The structures were solved by direct methods (XP) [21] and refined by full matrix least squares based on $F^2$ (SHELXL2018).[22] The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2 \, U_{eq}$(pivot atom), or $H_{iso}(H) = 1.5 \, U_{eq}$(pivot atom) for methyl moiety. The crystal of **VO-dtc-1** was refined as pseudo-merohedral twin, with twin matrix: −1 0 0; 0 −1 0; 0 0 1 and ratio of two components 0.709 : 0.291. Crystal of **VO-dtc-4** exhibits influence of real structure since residual peaks on final difference maps are suggesting the disorder of one of morpholine cycle. Since only few second positions of atoms could be discerned, the disorder was leaved unresolved. CCDC 1941569–1941570 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Results and Discussion

### Synthesis and characterization

Our initial attempt to extend the family of primary driers was focused on oxidovanadium(IV) dithiocarbamates [$V^{IV}O(S_2CNR_2)_2$]. Several species of this type were successfully synthesized by reaction of oxidovanadium(IV) sulfate with sodium dithiocarbamates [23] but their application in real paint formulations is questionable owing to their low air-stability even though our preliminary tests on alkyd coatings revealed promising activity.
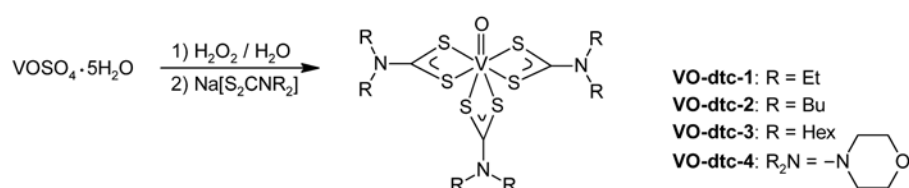


**Scheme 1.** Synthesis of oxidovanadium(V) dithiocarbamates.

Therefore, our attention was moved to oxidovanadium(V) analogues bearing three dithiocarbamate ligands. The species of the general formula [$V^VO(S_2CNR_2)_3$] were synthesized according to literature procedure (Scheme 1).[18] The protocol starts from aqueous solution of oxidovanadium(IV) sulfate, which is oxidized *in situ* by hydrogen peroxide. Subsequent reaction with sodium dithiocarbamates gives desired products. All compounds under the study were purified by recrystallization and characterized by elemental analysis and infrared spectroscopy. Structure of the two derivatives, **VO-dtc-1** and **VO-dtc-4**, were determined by single-crystal X-ray diffraction analysis. Their molecular structures are given in Figure 1 and parameters describing the coordination sphere of vanadium atom are listed in Table 1.

In both complexes, coordination sphere of vanadium atom forms a distorted pentagonal bipyramid with oxygen atom O1 and sulfur atom S6 in axial positions. The equatorial plane is occupied with sulfur atoms S1–S5. The largest distortion from ideal pentagonal bipyramid is caused by deflection of sulfur atom S6 from axial position, which results in a low value of the bond angle O1–V1–S6 [**VO-dtc-1**: 166.22(15)°; **VO-dtc-4**: 164.67(6)/ 164.80(7)°]. The bond distances between vanadium atom and equatorial sulfur atoms (S1–S5) vary in narrow range 2.4582(7)–2.5034(15) Å. The bond length V1–S6 is considerably longer [**VO-dtc-1**: 2.6187(15) Å; **VO-dtc-**

**4**: 2.6543(7)/2.6232(7) Å] due to *trans*-effect of the oxygen atom. We note that all dithiocarbamate ligands are κ²-bonded as the difference between V–S distances of each ligand does not exceed 0.1670(7) Å.
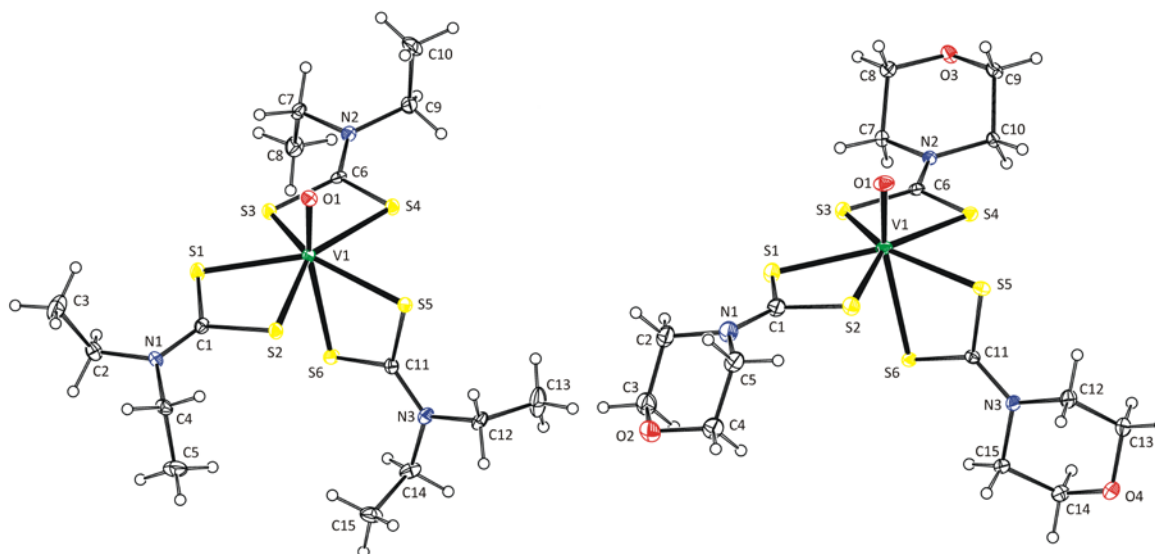


**Figure 1.** ORTEP drawing and atom numbering of **VO-dtc-1** (left) and **VO-dtc-4** (right). Thermal ellipsoids are drawn at the 30% probability level.

**Table 1.** Selected bond lengths (Å) and bond angles (°) by determined by X-ray analysis.

|  | VO-dtc-1 | VO-dtc-4 (A) [a] | VO-dtc-4 (B) [b] |
|---|---|---|---|
| V1–O1 | 1.600(3) | 1.5946(16) | 1.6000(19) |
| V1–S1 | 2.4639(16) | 2.4839(6) | 2.4729(8) |
| V1–S2 | 2.5031(18) | 2.4683(7) | 2.4870(7) |
| V1–S3 | 2.4652(16) | 2.4742(6) | 2.4711(7) |
| V1–S4 | 2.4865(17) | 2.4582(7) | 2.4829(7) |
| V1–S5 | 2.5034(15) | 2.4873(6) | 2.4858(7) |
| V1–S6 | 2.6187(15) | 2.6543(7) | 2.6232(7) |
| O1–V–S1 | 97.95(15) | 97.64(6) | 101.77(7) |
| O1–V–S2 | 94.49(13) | 93.19(6) | 91.39(7) |
| O1–V–S3 | 103.35(14) | 102.09(6) | 99.32(7) |
| O1–V–S4 | 89.76(13) | 93.12(6) | 92.92(7) |
| O1–V–S5 | 97.34(14) | 95.70(6) | 95.79(7) |
| O1–V–S6 | 166.22(15) | 164.67(6) | 164.80(7) |

[a] Crystallographically independent molecule A in the unit cell of **VO-dtc-4**·0.5CH₂Cl₂. [b] Crystallographically independent molecule B in the unit cell of **VO-dtc-4**·0.5CH₂Cl₂.

### Drying performance

Catalytic activity of the synthesized compounds was tested on two solvent borne-alkyd alkyd resins (**S471** and **S622**) and two high-solid binders (**TI870** and **TRI841**) in the range of metal concentration 0.06–0.005 wt.% in dry matter content. Initial screening was performed on the resin of medium oil-length modified with soybean oil (**S471**), which was chosen due to excellent performance in system cured by cobalt(II) 2-ethylhanoate (**Co**) and a low tendency to form surface defects.

The examined oxidovanadium(V) compounds exhibit satisfactory activity in **S471** at concentration range 0.06–0.01 wt.% (Table 2). Shortest dry-hard time ($\tau_4$) was observed for derivative **VO-dtc-4** 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 better through drying and it was further observed for the other vanadium-based driers under the study. For comparison 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-4** at 0.01 wt.% is comparable to **Co** at optimal concentration (0.03 wt.%). The films **S471** cured with vanadium-based driers show high relative hardness, estimated according to Persoz protocol, already ten days after application (17.5–37.6%). Final relative hardness, measured after 100 days of curing, varies between 40.4 and 62.4%. We note that deterioration of drying activity was observed at concentration 0.005 wt.%.

**Table 2.** 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) | $H_{rel,10d}^d$ (%) | $H_{rel,100d}^e$ (%) |
|---|---|---|---|---|---|---|
| **VO-dtc-1** | 0.06 | 5.0 | 7.5 | 8.5 | 25.9 | 50.1 |
| | 0.03 | 4.6 | 7.4 | 8.7 | 25.2 | 48.1 |
| | 0.01 | 6.9 | 7.7 | >24 | 24.1 | 43.3 |
| **VO-dtc-2** | 0.06 | 3.2 | 5.4 | 16.7 | 24.3 | 51.4 |
| | 0.03 | 3.9 | 4.4 | 7.9 | 28.5 | 53.8 |
| | 0.01 | 4.6 | 7.4 | 10.2 | 25.7 | 42.9 |
| **VO-dtc-3** | 0.06 | 3.0 | 5.4 | 10.8 | 17.5 | 47.1 |
| | 0.03 | 2.8 | 4.6 | 7.2 | 27.2 | 53.2 |
| | 0.01 | 4.7 | 6.2 | 9.5 | 19.8 | 40.4 |
| **VO-dtc-4** | 0.06 | 1.2 | 1.7 | 3.7 | 29.3 | 51.2 |
| | 0.03 | 1.4 | 2.2 | 4.6 | 33.4 | 58.6 |
| | 0.01 | 3.2 | 4.9 | 7.4 | 37.6 | 62.4 |
| **Co** [f] | 0.06 | 0.5 | 9.4 | 20.4 | 25.8 | 40.4 |
| | 0.03 | 1.6 | 4.3 | 17.4 | 31.4 | 40.2 |
| | 0.01 | 14.1 | 18.4 | 20.9 | 30.8 | 38.6 |

[a] Tack-free time. [b] Dry-hard time. [c] Dry-through (total-dry) time. [d] Relative hardness measured after 10 days of drying. [e] Final relative hardness. [f] Data reported elsewhere.[13]

**Table 3.** Drying performance **VO-dtc-2** in test coatings of various alkyd binders and its comparison with **Co**.

| Drier | Binder | Metal content (wt.%) | $\tau_1^a$ (h) | $\tau_2^b$ (h) | $\tau_3^b$ (h) | $\tau_4^b$ (h) | $H_{rel,10d}^b$ (%) | $H_{rel,100d}^b$ (%) |
|---|---|---|---|---|---|---|---|---|
| **VO-dtc-2** | **S622** | 0.06 | – | 4.0 | 5.9 | 8.2 | 22.0 | 48.4 |
| | | 0.03 | – | 2.8 | 6.9 | 14.3 | 15.8 | 39.6 |
| **Co** | **S622** | 0.06 | – | 3.1 | 16.2 | 20.5 | 24.7 | 29.7 |
| | | 0.03 | – | 1.1 | 7.5 | 9.7 | 21.1 | 26.4 |
| **VO-dtc-2** | **TI870** | 0.06 | 6.2 | 8.9 | 11.5 | 17.1 | 4.4 | 23.3 |
| | | 0.03 | 8.3 | 12.8 | 17.9 | > 24 | 4.8 | 21.4 |
| **Co** [c] | **TI870** | 0.06 | 1.0 | 6.6[d] | >24 | > 24 | 14.4 | 26.9 |
| | | 0.03 | 1.7 | 5.4[d] | 12.9 | > 24 | 12.7 | 23.3 |
| **VO-dtc-2** | **TRI841** | 0.06 | 6.9 | 9.2 | 19.6 | 20.6 | 4.4 | 17.7 |
| | | 0.03 | 7.6 | 11.3 | >24 | >24 | 5.4 | 19.7 |
| **Co** | **TRI841** | 0.06 | 0.9 | 4.9[d] | 14.0 | > 24 | 11.7 | 24.9 |
| | | 0.03 | 1.6 | 5.4[d] | 10.9 | > 24 | 9.7 | 21.1 |

[a] Set-to-touch time. [b] For definition see footnote of Table 2. [c] Data reported elsewhere.[5] [d] Needle tears the polymeric skin instead of leaving the groove and revealing the glass substrate with straight edges.

The optimal performance of the driers **VO-dtc-1**–**VO-dtc-4** is observed at concentration 0.03 wt.% as total-dry time ($\tau_4$) does not exceed 9 h. The substitution on dithiocarbamate ligand has a minor effect on the activity. Therefore, only one derivative was selected for mechanical tests on slower-drying alkyds and in-depth investigation of autoxidation kinetics. Due to high solubility in organic solvents, butyl derivative **VO-dtc-2** was chosen for these tests even through derivative **VO-dtc-4** shows better overall performance in formulations of **S471**. We note that hexyl derivative **VO-dtc-3** exhibits even higher solubility than **VO-dtc-2** but it was excluded from further examination mainly due to tedious purification process, which embarrasses a future larger-scale synthesis.

The tests on alkyd resin of a long oil-length **S622** and high-solid binders **TI870** and **TRI841** revealed good performance of the compound **VO-dtc-2**. At concentration 0.06 wt.%, the dry-hard times ($\tau_3$) nears the values obtained for **Co** at optimal concentration (0.03 wt.%). Although the dosage is higher than in case of **Co**, the 76-µm coatings are faster through-dried as evident from shorter total-dry times ($\tau_4$). Such property is of particular importance for high-solid binders since $\tau_4$ of coatings treated with **Co** usually exceeds 24 h.

## Kinetics of the autoxidation

Chemical curing of alkyd formulations **VO-dtc-2/S471** and **Co/S471** in concentration range 0.1–0.005 wt.% was followed by time-resolved infrared spectroscopy using ATR sampling technique. The measurements were performed on 5-µm coatings of the freshly prepared formulations. Rate of the autoxidation process was followed through development of C–H stretching band at 3008 cm$^{-1}$ attributed to isolated *cis*-double bonds, $v_a$(*cis*-C=*C*–*H*), which reflects consumption of the reactive substrate (Figure 2). The obtained data were processed according to protocol described in detail elsewhere.[5] Briefly, the autoxidation in liquid model system saturated with air-oxygen is considered as a reaction of pseudo-first order and our previous experiments revealed a very similar behavior in paint formulations but only in thin layers and until about 50% conversion. The use of thin layer of alkyd formulation is crucial for kinetic measurements as it enables sufficient supply of air-oxygen. The deceleration of the process at higher conversions is caused by solidification of the paint system.

**Table 4.** Kinetic parameters of the autoxidation process for formulations of **VO-dtc-2/S471** and **Co/S471**.

| Drier | Metal content (wt.%) | $k_{max}$ [a] (h$^{-1}$) | $t_{ind}$ [b] (h) | $t_{1/2}$ [c] (h) |
|---|---|---|---|---|
| | 0.1 | 0.61 | 9.2 | 10.2 |
| | 0.06 | 0.48 | 7.0 | 8.3 |
| **VO-dtc-2** | 0.03 | 0.39 | 5.5 | 7.4 |
| | 0.01 | 0.26 | 4.2 | 7.1 |
| | 0.005 | 0.16 | 4.9 | 9.8 |
| | 0.1 | 2.18 | 0.2 | 0.5 |
| | 0.06 | 1.55 | 0.5 | 0.9 |
| **Co** | 0.03 | 0.81 | 2.0 | 2.9 |
| | 0.01 | 0.45 | 6.9 | 8.4 |
| | 0.005 | 0.38 | 12.6 | 14.5 |

[a] $k_{max}$ is maximal autoxidation rate constant estimated from linear part of the logarithmic plots in Figure 2. [b] $t_{ind}$ is induction time of the autoxidation. [c] $t_{1/2}$ is half-life of the autoxidation.

Rate coefficients ($k_{max}$) and induction times ($t_{ind}$), obtained from linear parts of logarithmic plots shown in Figure 2, are listed in Table 4 together with half-lives of the autoxidation reaction ($t_{1/2}$). In the case **VO-dtc-2/S471**, the value of $k_{max}$ rises with rising metal concentration up to 0.61 $h^{-1}$ at 0.1 wt.%. Induction time ($t_{ind}$) is also concentration dependent. In concentration range 0.1–0.01 wt.%, it drops with lowering metal concentration up to 4.2 h at 0.01 wt.%. Such "inverse concentration dependence" is rather unusual and it is probably responsible for the overdose effect evidenced for formulations with high metal concentrations by mechanical tests (c.f., $\tau_3$ and $\tau_4$ in Table 2 for **VO-dtc-2/S471** at 0.06 and 0.03 wt.%).

The cobalt-based drier (**Co**) gives considerably higher values of $k_{max}$ than **VO-dtc-2/S471** at the same concentration, which clarifies the pure through drying of the coatings treated with **Co** documented by mechanical tests (see $\tau_4$ in Table 2). The surface drying of the coatings treated with **Co** is strongly influenced by induction times. At high metal concentrations, the coatings show very short tack-free times (see $\tau_2$ in Table 2). Deterioration of the drying activity, observed at low metal concentrations, is due to a very long $t_{ind}$ even through the rate coefficient remains satisfactory high even at 0.005 wt.%.
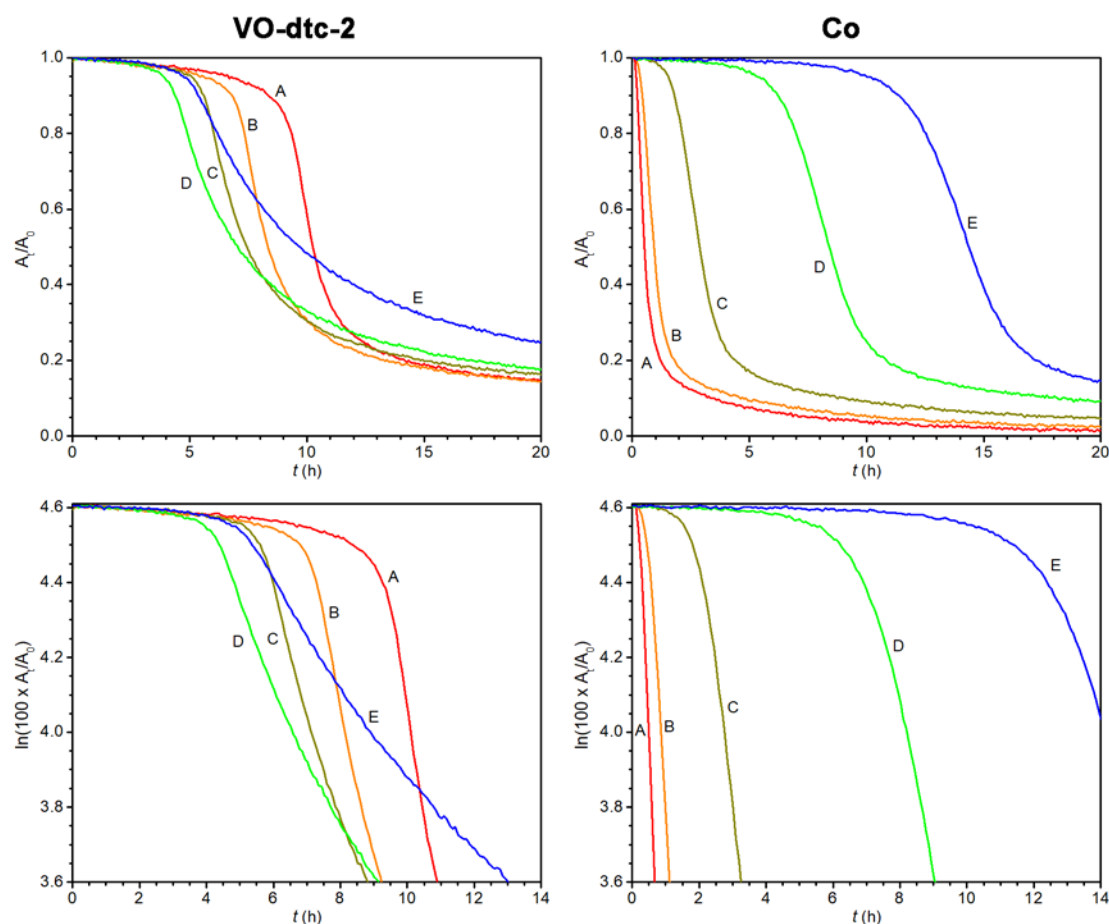


**Figure 2.** Development of $\nu_a$(cis-C=C–H) in time for **VO-dtc/S471** (left plots) and **Co/S471** (right plots) in linear (upper plots) and logarithmic scale (down plots). Metal concentrations: 0.1 wt.% (A; red line), 0.06 wt.% (B; orange line), 0.03 wt.% (C; dark yellow line), 0.01 wt.% (D; green line), 0.005 wt.% (E; blue line).

## Mechanism of the catalytic action

Autoxidation of alkyd resins is a complex chemical process involving three important steps: "peroxidation", "peroxide decomposition" and "crosslinking reactions". The main role of primary driers is decomposition of kinetically stable hydroperoxides appearing upon oxidation of unsaturated lipid chains. Three-dimensional polymeric network is then formed through addition of radicals on double bonds and through radical recombination reactions.[2] The catalytic properties of vanadium-based driers can by clarified by Haber–Weiss mechanism involving $V^{IV}/V^{V}$ redox system (Scheme 2).

$$2\ ROOH \xrightarrow{\ [V^{IV}]/[\ V^{V}]\ } ROO^{\bullet} + RO^{\bullet} + H_2O$$
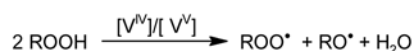
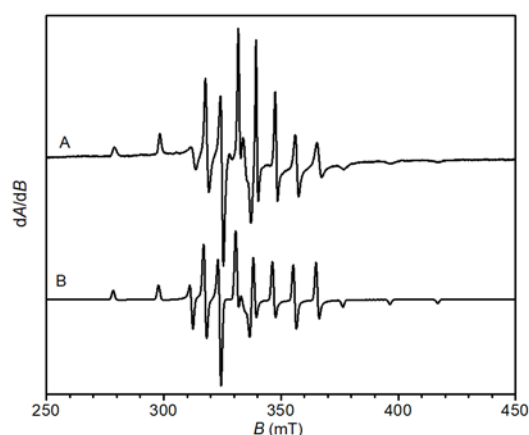**Scheme 2.** Vanadium-catalyzed decomposition of hydroperoxides.



**Figure 3.** EPR spectrum of alkyd film cured with **VO-dtc-2** (A) and its computer simulation (B).

Postulated vanadium(IV) species, involved in the catalytic cycle, has uncompensated electron spin and therefore should be followed by EPR spectroscopy. Our experiment revealed its appearance in alkyd films cured with compounds **VO-dtc-1**–**VO-dtc-4**. The EPR spectra of cured films are rhombic symmetric with parameters independent on used drier/alkyd combination ($A_{\parallel}$ = 197.8 × 10$^{-4}$ T, $A_{\perp}$ =76.2 × 10$^{-4}$ T, $g_{\parallel}$ =1.934, $g_{\perp}$ =1.980). One representative spectrum is given in Figure 3. High value of calculated $A_{iso}$ value (116.7 × 10$^{-4}$ T) suggests a dissociation of dithiocarbamate ligands and appearance of putative active species with five oxygen donor atoms and $C_{4v}$ molecular symmetry. The vanadium compounds under the study probably serve as precursors of the catalytically active species that is generated upon reaction with the alkyd binder. Although the active species seems to be the same as previously reported for oxidovanadium(IV) acetylacetonates [13] and 2-ethylhexanoate, [14] the catalytic activity of each precatalyst differs considerably due to variations of their physical-chemical properties such as long-term stability in the air-atmosphere, solubility and miscibility with alkyd resin formulations.

## Conclusions

In summary, this study reports the first example of primary driers based on oxidovanadium(V) compounds. Four complexes bearing dithiocarbamate ligands were synthesized by protocol that enables a simple extension

to the multi-gram scale. Furthermore, the prepared species are more stable than oxovanadium(IV) analogues bearing two dithiocarbamate ligands. The identity of prepared compounds was confirmed by spectroscopic methods and by X-ray diffraction analysis. Their high catalytic activity in solvent-borne formulations of alkyd resins was evidenced by standard mechanical tests. Butyl derivative **VO-dtc-2** shows a good solubility in organic solvents, which is an important feature for application in paint industry. Such derivative was found to be active in slow-drying high solid binders.

Kinetic experiments, performed on **VO-dtc-2**, revealed inverse effect of metal concentration on induction time of the autoxidation process, which could be related to a slow generation of catalytically active species and rather retardant properties the precatalysts before the catalytic cycle involving $V^{IV}/V^{V}$ redox system is established. The assumption that here reported oxidovanadium(V) dithiocarbamates perform as precatalysts is supported by EPR spectroscopic measurements. They revealed appearance of the vanadium(IV) species without dithiocarbamate ligands in their coordination sphere in the cured alkyd films. We note that tested species may also serve as antifungal agents due to presence of biologically active dithiocarbamate ligands. This feature is beyond the scope of this study and will be subject of our future investigation.

## Acknowledgements

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