

INVESTIGATION OF THE OXIDATIVE CROSS-LINKING OF MODIFIED OILS WITH COMPLEXED IRON SALTS FOR WOOD COATINGS

Winfried Barth (winfried.barth@mailbox.tu-dresden.de)

Motivation

Natural plant oils as a sustainable resource for paints and wood coatings have a long tradition but still high capability. Although drying oils are used as binders all over, the curing process during the oxidation especially in combination with additives to force drying is not understood completely, yet. In technical applications catalysts are used to accelerate the reaction and to shorten the curing time. Moreover, surface properties can be improved and the drying process is easier to control. Those catalysts are called siccatives or dryers. The most common dryers contain cobalt salts which are considered as unhealthy and suspected to be carcinogenic [1]. The current aim is to substitute the cobalt with newly complexed iron salts.



Figure 1: *Linum usitatissimum* L.

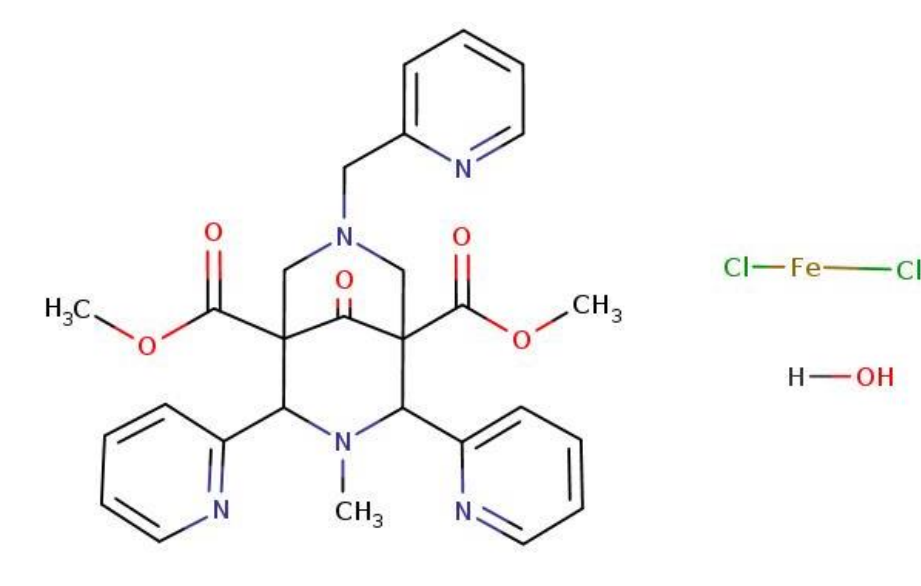


Figure 2: structure of complexed iron salt



Figure 3: oiled wood

raw material for plant oil

siccative for accelerated curing

varnish for wood protection

Methods

For technically sensible application influencing factors were figured out. The studies included the observation of relevant properties of oil binders like iodine value, peroxide value and acid value. The drying behavior of several oil siccative mixtures was investigated with instrumental analysis to gain insight in the reaction mechanism and to compare conservative cobalt systems with newly iron systems. Therefore, FTIR-ATR measurements over a long period of time were appropriate to observe the chemical decompositions of functional groups of the triglycerides. The high amount of natural antioxidant substances was detected with GCMS and in regard to chemiluminescence measurements conclusions about chemical activity in dependence of atmosphere and temperature could be drawn. The testing of the surface properties of the specimens was realized with Pendulum hardness (DIN EN ISO 1522) and visual evaluation after surface resistance test (DIN 68861).



Figure 5: wood specimens with test fluids

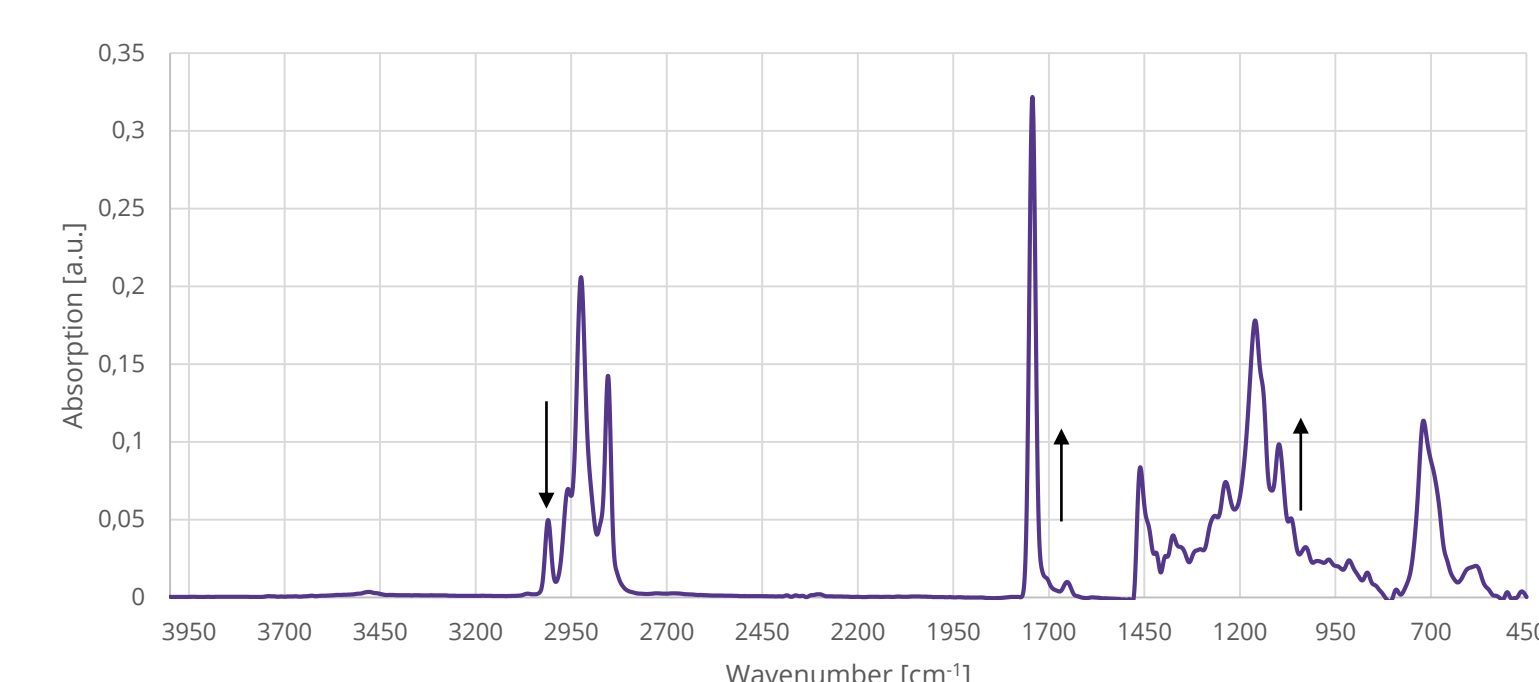


Figure 6: FTIR-ATR spectrum of linseed oil

Results

Glass and wood were used as substrates and were found to have diverse impact on the drying process. Thus, synergies were discovered because of metallic wood extractives which affect the drying time and curing positively. Hence the dryer must be suitable for the type of wood because the activity of some siccatives are inhibited strongly by low pH values [2]. Siccatives catalyse the absorption of oxygen and the decomposition of hydroperoxides [3]. The difference between cobalt and iron salts lies in the reaction mechanism.

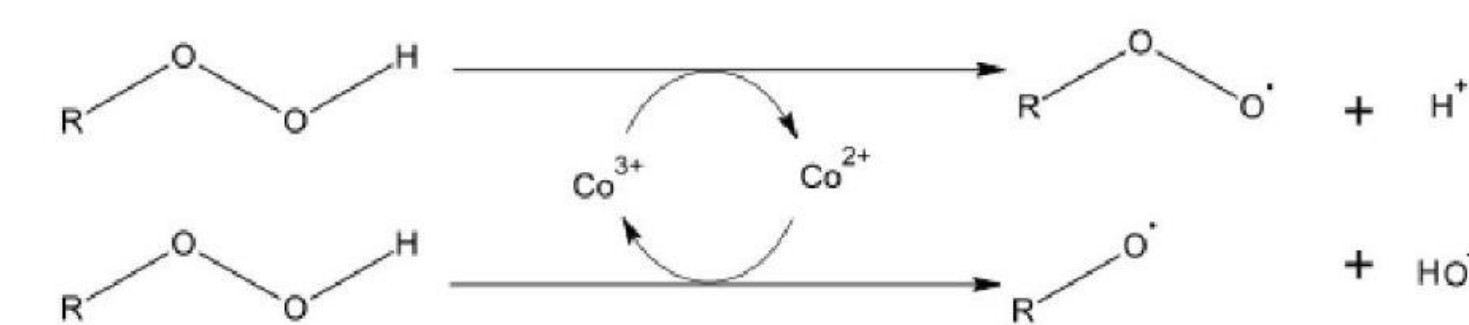


Figure 4: reaction mechanism of catalyst with hydroperoxide

The iron dryer also works good in atmospheres with low oxygen level because it reacts more with bound oxygen in hydroperoxides of oils whereas cobalt accelerates more the absorption of oxygen. Further interesting results of the studies showed that some oils contain a high proportion of antioxidant substances like Tocopherol.

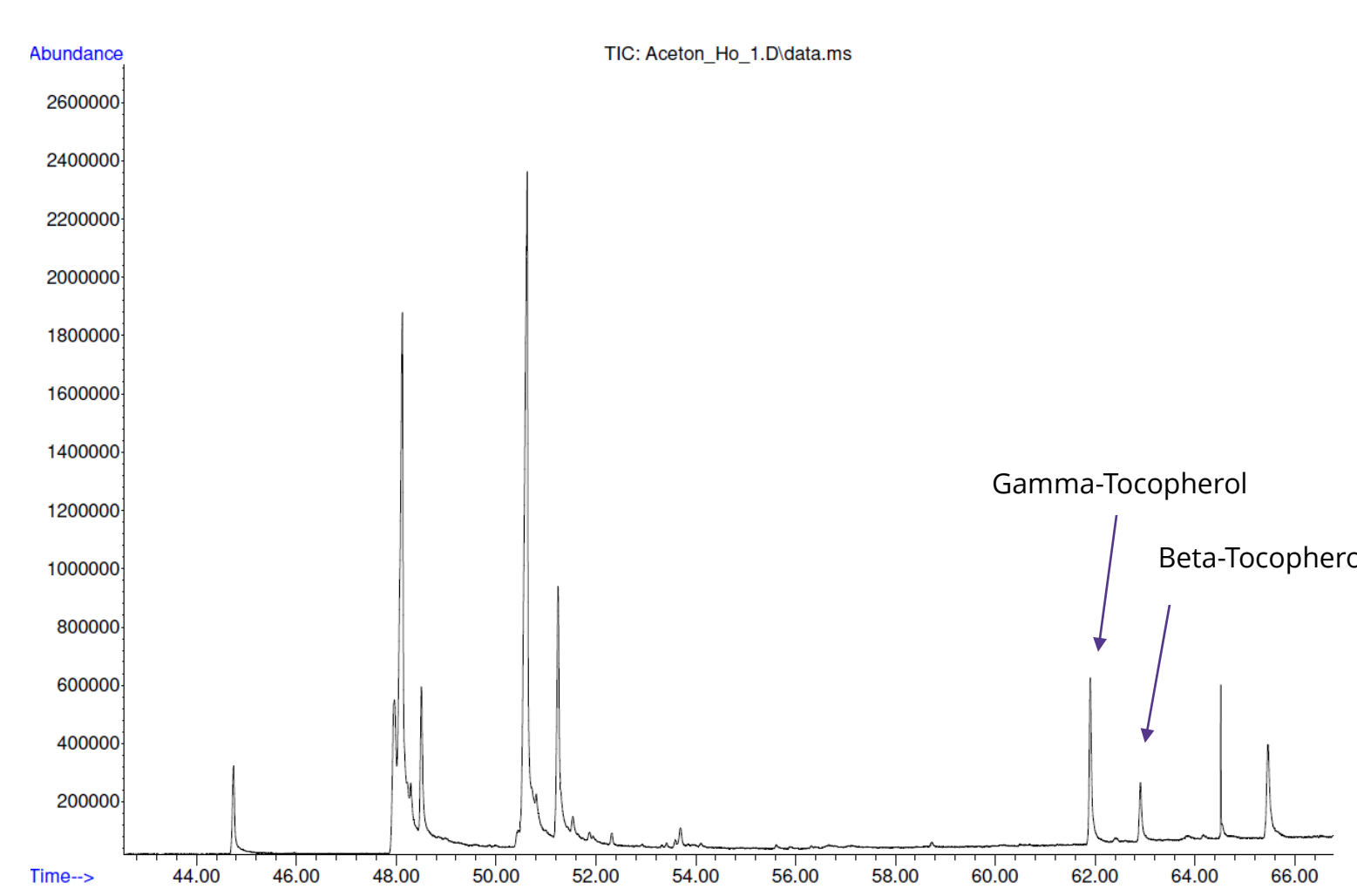


Figure 7: GCMS spectrum of Tung oil

Conclusion

Newly complexed iron salts are an appropriate substitution of toxic cobalt salts to improve the curing of oils.

Usually it is necessary to add anti skinning agent like 2-Butanonoxim to the oil to prevent prematurely drying. Because of the lower activity rate of the iron dryer and the natural antioxidants in raw materials, paints and lacquers could be produced without harmful anti skinning agents, which is another big advantage.

This polymerisation of oil as a result of oxidation is called autoxidation. To understand this chemical mechanism and the influencing factors, especially the role of metal salts, completely it should be observed more detailed. Instrumental analysis exposed as a suitable tool for this purpose.

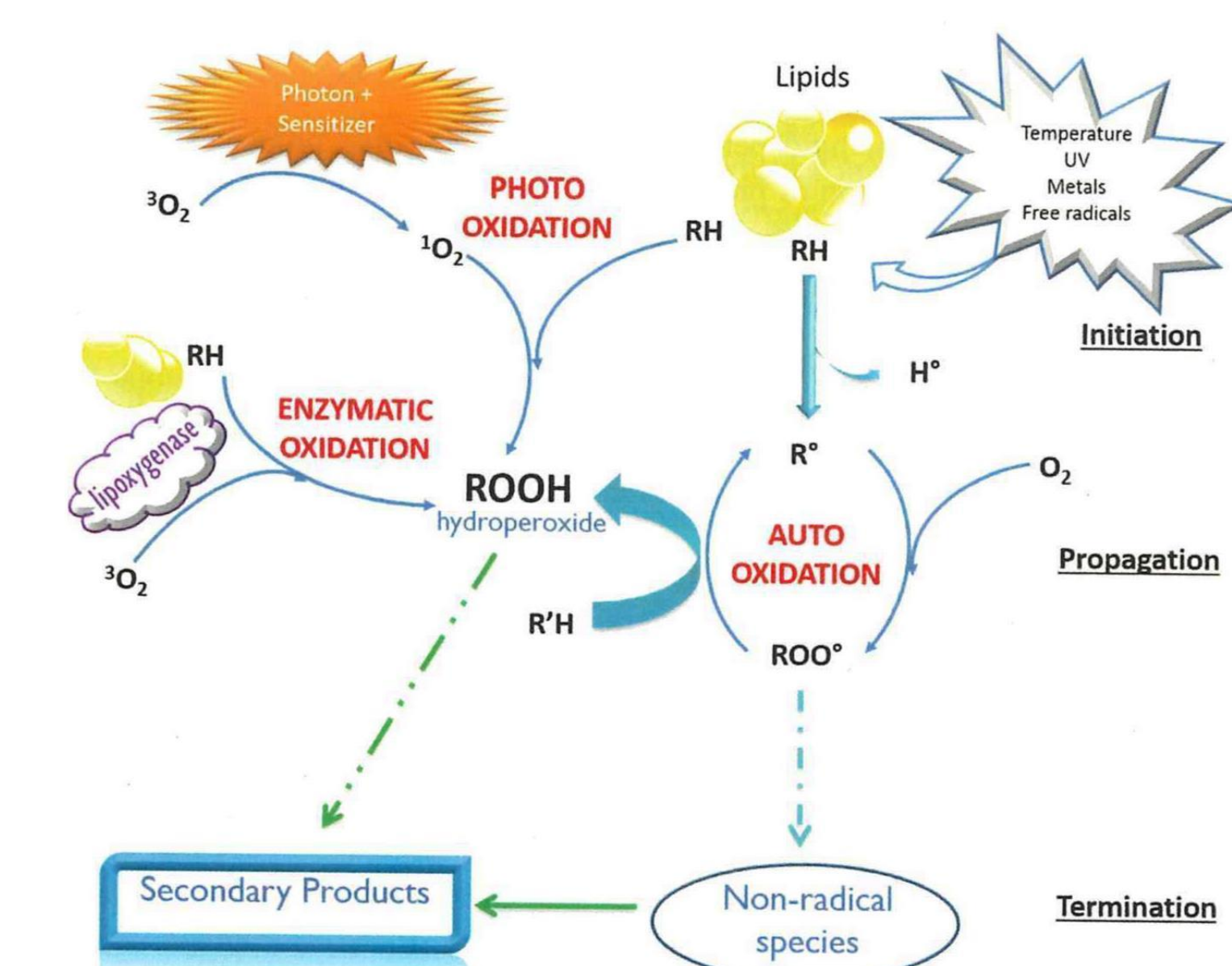


Figure 8: oxidation of lipids/oils

Figures:

- <https://de.wikipedia.org/w/index.php?oldid=196257245>
- <https://chem.nlm.nih.gov/chemview/image/478945-46-9?size=3>
- <https://www.wohnet.at/sanierung/innensanierung/holz-oelen-19434>
- <https://de.wikipedia.org/wiki/Sikkativ>
- Barth, W.: Investigation of the oxidative cross-linking of differently modified oils with complexed iron salts with the aim of shortening the curing times and the substitution of toxic cobalt salts, 2020
- Li, Y., Fabiano-Tixier, A.-S. u. Chemat, F.: Essential Oils as Reagents in Green Chemistry. SpringerBriefs in Molecular Science 2014

Literature:

- Egorova, K. S. u. Ananikov, V. P.: Toxicity of Metal Compounds: Knowledge and Myths. *Organometallics* 36 (2017) 21, S. 4071–4090
- Prieto, J. M., Prieto, J. u. Kiene, J.: Holzbeschichtung. *Chemie und Praxis. Coatings Compendien*. Hannover: Vincentz Network 2007
- Wenker, E.: Comparing the autoxidative mechanism of Co-EH and FeONIX