Autoxidation of oils according to their composition: Applications to the drying of alkyd paints

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UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

CISCO2 TEAM

Objective : improve the drying of alkyd resin

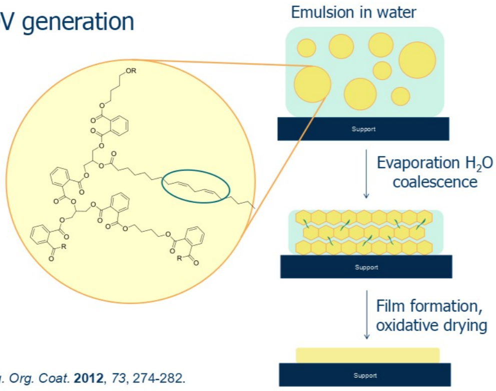
Alkyd resin : polyester backbone with copolymerized unsaturated lipids

Advantages of alkyd paints :

- can be water-born ➡ low COV generation
- large application fields
- biosourced components

The autoxidation of the lipids produces hydroperoxides.

Their decomposition into radicals will reticulate the polymer through the creation of C-O bonds.



Alkyd resins: From down and out to alive and kicking. A. Hofland *Prog. Org. Coat.* **2012**, *73*, 274-282.

Parameters influencing the drying kinetics and the physico-chemical properties of the paint film :

- Nature of the resin : molecular weight, viscosity, hydrophily, glass transition temperature…
- Oil length : amount of unsaturated oil in the resin
- **Intrinsic oxidability of the lipidic part (autoxidation)**
- **Additives : driers (siccatives)**

Alkyd resins. In *Kirk-othmer encyclopedia of chemical technology*, John Wiley & Sons, Inc., 2000 Z. W. Wicks.

The oxidative drying of alkyd paint catalysed by metal complexes. R. van Gorkum; E. Bouwman *Coord. Chem. Rev.* **2005**, *249*, 1709-1728.

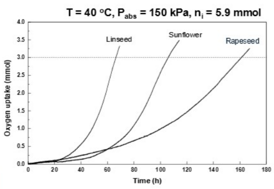
Autoxidation of FAMEs mixtures :

mixtures from oils :

kinetics by oxygen uptake (pressure drop):

Constant volume, home-made reactor:

- Stirring
- Transparency
- No limit of conversion
- High precision of the pressure probe
- Temperature < r.t. possible
- Corrosive substrates compatibility
- Study of emulsions
- Maximum of P_{abs} = 200 kPa

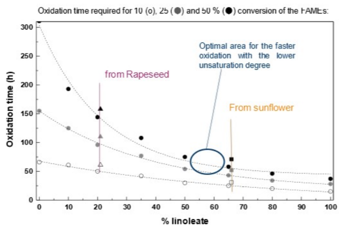


FAMEs composition % m.

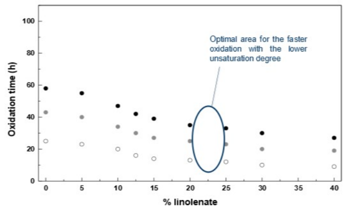
Oil	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
rapeseed	3	1	**72**	17	7
sunflower	7	6	30	**57**	-
Linseed	7	6	29	14	**44**

mixtures from pure FAMEs :

❖(C18:1) / (C18:2) binary mixture



❖(C18:1) / (C18:2) composition at 35/65 (≈ sunflower one) + (C18:3) as third component



➡ A composition of methyl oleate/linoleate/linolenate of ≈30:50:20 looks the best one to get the highest oxidation rate for a lower unsaturation degree.
It corresponds to a sunflower and linseed oils mixture of ≈ 60:40

Optimization of the vegetable oil composition in alkyd resins: A kinetic approach based on FAMEs autoxidation. L. Dubrulle; R. Lebeuf; M. Fressancourt-Collinet; V. Nardello-Rataj *Prog.Org. Coat.* **2017**, *112*, 288–294.

Effects of driers additives :

kinetics by oxygen uptake:

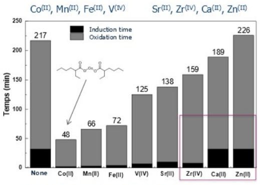
Rapidoxy® Antoon-Paar

Commercial driers :

- **Octa-Soligen Cobalt 10** (10 wt.% of cobalt(II) bis(2-ethylhexanoate)
- **BorchiOxycoat 1101** (0.09 wt.% Fe(II))
- **Octa-Soligen Manganese6** (6 wt.% manganese(II) bis(2-ethylhexanoate)
- **Octa-SoligenVP9950** (6.65 wt.% vanadium(IV) oxalate)
- **Octa-Soligen Zirconium12** (12 wt.% zirconium(IV) bis(2-ethylhexanoate)
- **Octa-SoligenStrontium 10** (10 wt.% strontium(II) bis(2-ethylhexanoate)
- **Octa-Soligen Calcium 10** (10 wt.% calcium(II) isononanoate)
- **Valirex Zn 8** (8 wt.% zinc(II) octoate)

Siccatives I — $Co^{(II)}$, $Mn^{(II)}$, $Fe^{(II)}$, $V^{(IV)}$

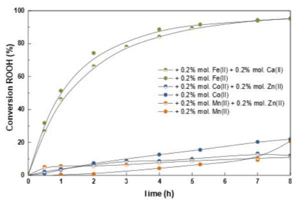
Siccatives II — $Sr^{(II)}$, $Zr^{(IV)}$, $Ca^{(II)}$, $Zn^{(II)}$



Induction and oxidation time to get 50% of dioxygen drop pressure with Sunflower FAMEs (2 mL, n = 5,9 mmol) in presence of 25 µmol of driers

Effects of driers on ROOH decomposition :

Monitoring of the hydroperoxides of sunflower FAMEs with several driers combinations, at 0.087 M in BuOAc at room temperature :

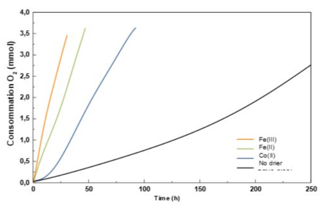


➡ Cobalt(II) gives the shorter oxidation time, but Fe(II) decomposes much faster the hydroperoxides.

➡ No effects of the secondary driers.

Alkyd resin oxidation in emulsion :

Comparison of commercial $Co^{(II)}$, $Fe^{(II)}$ and a synthesized $Fe^{(III)}$ drier at 25 µmol for 11 mL of URADIL emulsion (15% oil). T = 40 ° C, $P_{abs}(O_2)$ = 150 kPa



➡ Same reactivity order in presence of water

Catalytic activity of primary and secondary driers towards the oxidation and hydroperoxide decomposition steps for the chemical drying of alkyd resin. L. Dubrulle; R. Lebeuf; L. Thomas; M. Fressancourt-Collinet; V. Nardello-Rataj *Prog.Org. Coat.* . **2017**, *104*, 141-151.

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