Next Generation Cobalt – free Drier

Health Goes High-Tech

Marco Bachler
Ramspec, Italy, October 2018

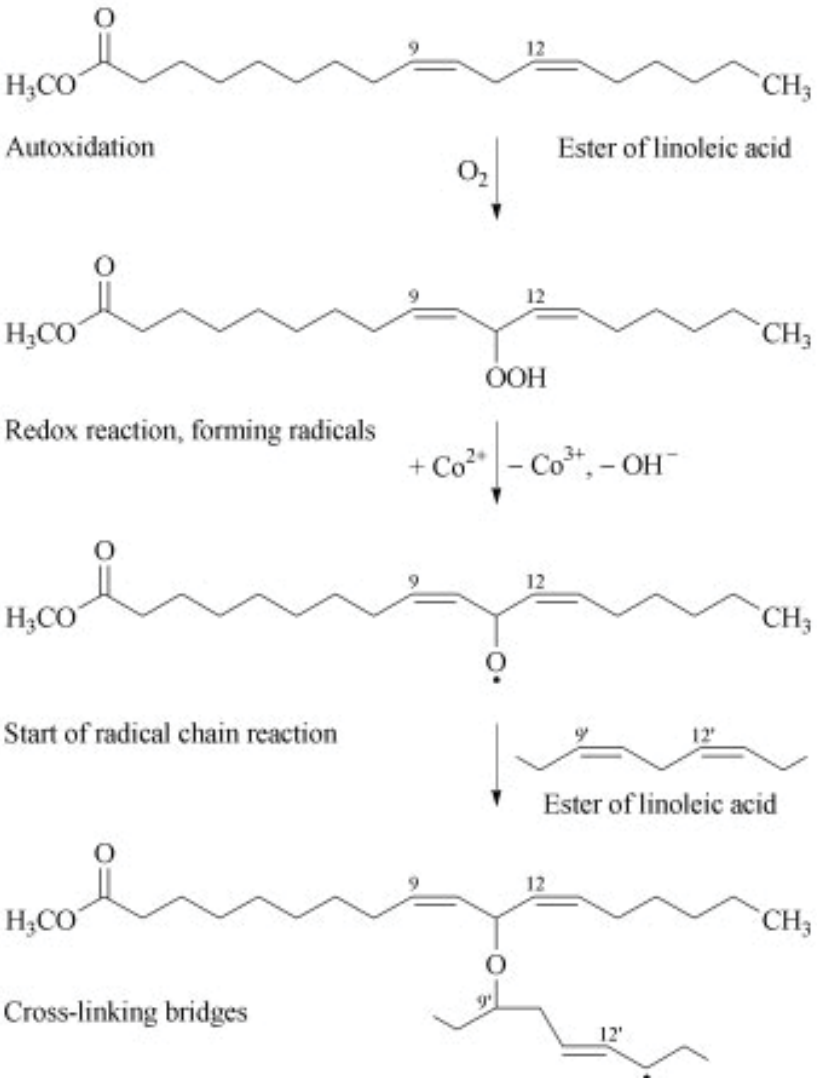
endless inspiration

allnex
The Coating Resins Company

Drying mechanism of alkyd paints

During the drying of alkyd paints several different stages can be identified. The **first process** is the **physical drying** of the paint. In this process, the solvent evaporates and a closed film forms through coalescence of the binder particles. Then **chemical drying** (also called oxidative drying) occurs, a lipid autoxidation process, which means that the paint dries by **oxidation of the binder compound with** molecular **oxygen from the air**.

Possible drying reactions



Formation of hydro-peroxide (oxygen uptake)

$Me^{3+} + O_2 \rightarrow MeOO^{3+}$ (0xygen carrier)
$MeOO^{3+} + RH \rightarrow MeOOH^{3+} + R^*$
$R^* + O_2 \rightarrow ROO^*$ (Propagation – fast reaction)
$Me^{3+} + RH \rightarrow R^* + H^+ + Me^{2+}$ (direct reaction)

Decomposition of hydro-peroxide

$ROOH + Me^{2+} \rightarrow RO^* + OH^- + Me^{3+}$ (faster)
$ROOH + Me^{3+} \rightarrow ROO^* + Me^{2+} + H^+$ (slower)

} Haber - Weiss

$Me^{2+} + O_2 \leftrightarrow [Me^{3+}(O_2)^-]^{n+}$
$[Me^{3+}(O_2)^-]^{n+} + RH \rightarrow [Me^{2+}(OOH^-)]^{n+} + R^*$

} a-polar medium Me superoxide complex

Combination with another unsaturated side chain

(start of auto polymerization)

Generation of a carbon-based radical

>>>Further polymerization

Me (transition metal)

Primary drying metals

Cobalt

- Historically most important & widely used active drier
- Strong surface drying
- Low to medium discoloration impact
- Tendency to cause surface wrinkling
- Less good through drying
- High hardness
- ✘ Reclassified „reprotox Cat.2 (CLP)“, next move to “Cat.1B (CMR)”

Manganese

- Longer induction time as Co but faster polymerization rate
- Very good through drying performance
- Low risk of surface wrinkling
- Higher risk of discoloration in white paints

Iron

- General low efficiency at room temperature
- Higher reactive in aqueous solutions but less redox potential in apolar solvents
- Negative impact on anti corrosion performance in Industrial applications
- Low risk of discoloration

allnex

endless inspiration

Auxiliary drying metals

Zirconium

- Lowest discoloration risk
- Used in combination with Cobalt, Calcium and Manganese
- Good through drying support
- Needs combination with Lithium or Barium for better room temp dry

Barium

- Longer open time allows better application and leveling
- Good support on through drying in combination with primary driers

Lithium

- Very good through drying support in both HS and WB paints
- Reduces wrinkling in high film thickness
- Very efficient at room temperature

Cobalt classification update

“Cobalt and certain cobalt compounds” are reasonably anticipated to be human carcinogens based on sufficient evidence from studies in experimental animals and supporting mechanistic data.

Referring to those cobalt compounds – including soluble and poorly water-soluble cobalt compounds and particles – that can release cobalt ions in vivo, which mechanistic data indicate are key for cobalt-induced carcinogenicity.

Cobalt legislation, toxicology & regulations

Following Cobalt substances have been reclassified as **repro toxic Cat. 2 (H361)** (CLP).
It is suspected that these substances will be **reclassified as carcinogenic, Cat. 1B** like their bioavailable homologues (e.g. Cobalt chloride, Cobalt acetate, etc.). This would mean that all mentioned substances as well as paint resin formulations containing equal or higher than **0.1%** of these substances would not be allowed for the public sale any longer. Once REACH registration as CMR Cat. 1B is completed, Cobalt and below listed Cobalt containing compounds would be subject for identification as ***"Substances of Very High Concern" (SVHC).*** Consequently, Cobalt is suspected to be phased out in the European coatings market soon.

Substance	CAS number
Cobalt, borate neodecanoate complexes	68457-13-6
neodecanoic acid, cobalt salt	27253-31-2
cobalt(2+) neodecanoate	52270-44-7
naphthenic acids, cobalt salts	61789-51-3
fatty acids, tall-oil, cobalt salts	61789-52-4

Today´s Cobalt metal alternatives

Polymeric Cobalt driers

- ✓ Meet today's regulations (CLP Cat.2) & (CMR Cat.1B)
- ✓ Performance comparable to Cobalt metal drier (higher dosage required)
- ✗ Higher formulation costs
- ✗ Formulations still containing Cobalt

Iron complex driers

- ✓ Acceptable drying performance in WB alkyd paints
- ✗ Compatibility problems in SB & HS alkyd paints
- ✗ Negative impact in WB anticorrosion formulations
- ✗ General performance loss during paint ageing (strong adsorption on particle surfaces)
- ✗ Common anti skin agents (MEKO) don't work

Manganese complex driers

- ✓ Partially acceptable discoloration levels
- ✓ Good gloss retention
- ✗ Lower set drying & hardness development in WB paints
- ✗ General longer drying time in SB paints & skinning tendency
- ✗ General performance loss during paint ageing (strong adsorption on particle surfaces)
- ✗ Common anti skin agents (MEKO) don't work

allnex

allnex' "next gen" Cobalt free technology

allnex's next generation driers are based on
"twin aromatic heterocyclic nitrogen accelerated Manganese"

ADDITOL® dry CF series

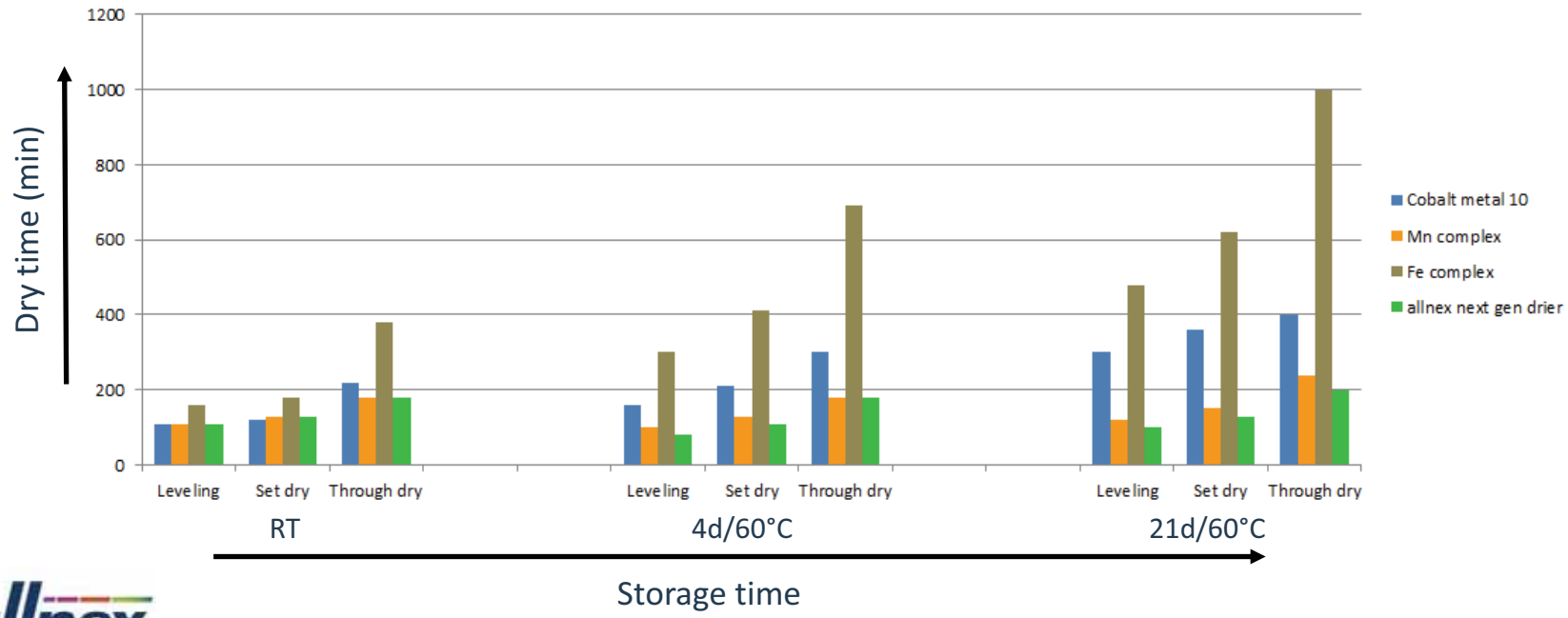
Key performance highlights

- Supports modern, eco-friendly and low VOC alkyd paint formulations.
- Universal use - compatible with WB, SB, HS and UHS paint formulations.
- Improved hydro peroxide decomposition and reaction cycle time compared to other complex driers.
- Long term performance during paint ageing through patented ligand protection technology.
- Less discoloration tendency compared to Cobalt and Manganese driers
- Strongly improved anti corrosion performance support in DTM Industrial applications compared to Iron driers
- Improved anti wrinkle effect through balanced differential catalysis during set drying phase

allnex' "next gen" drier performance 1

Drying performance and stability test in a HS long oil alkyd white paint

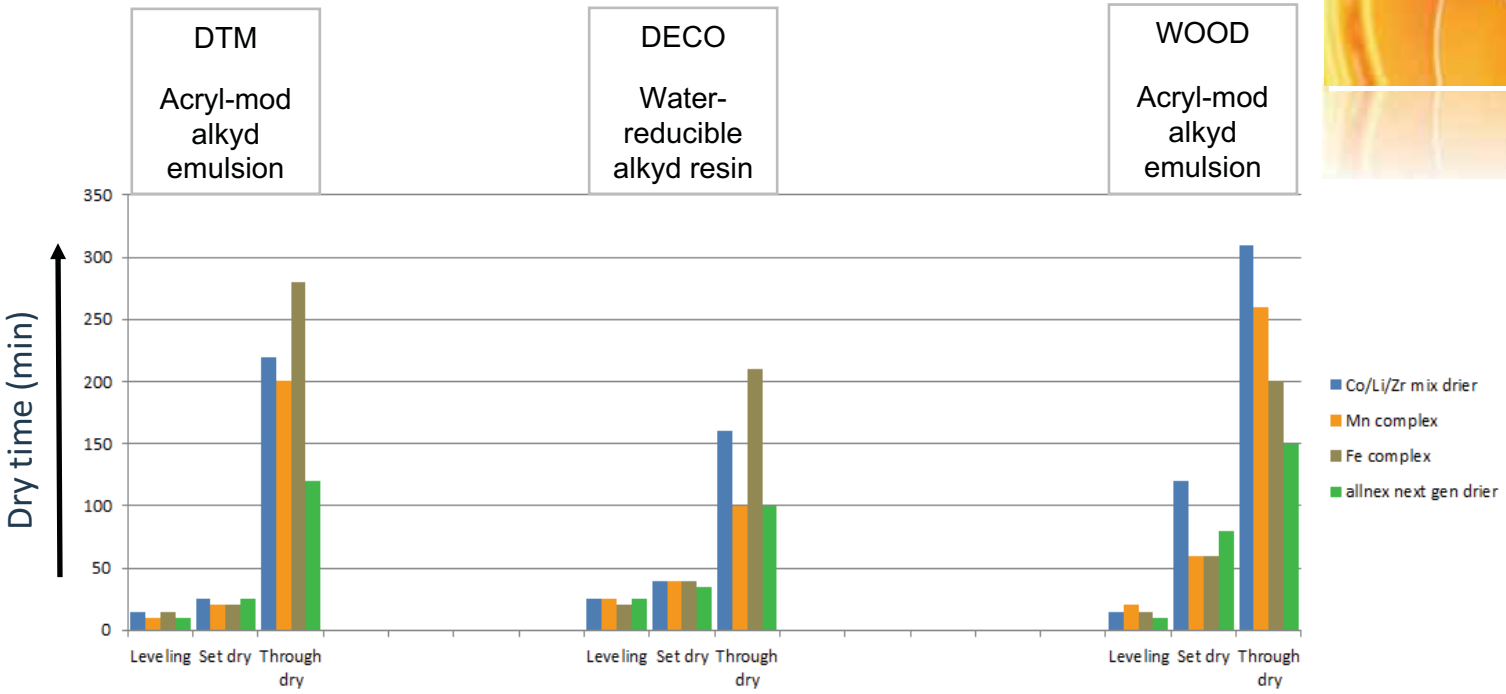
(Auxiliary driers are Ca and Zr) Accelerated ageing in hot box 60°C.



allnex' "next gen" drier performance 2

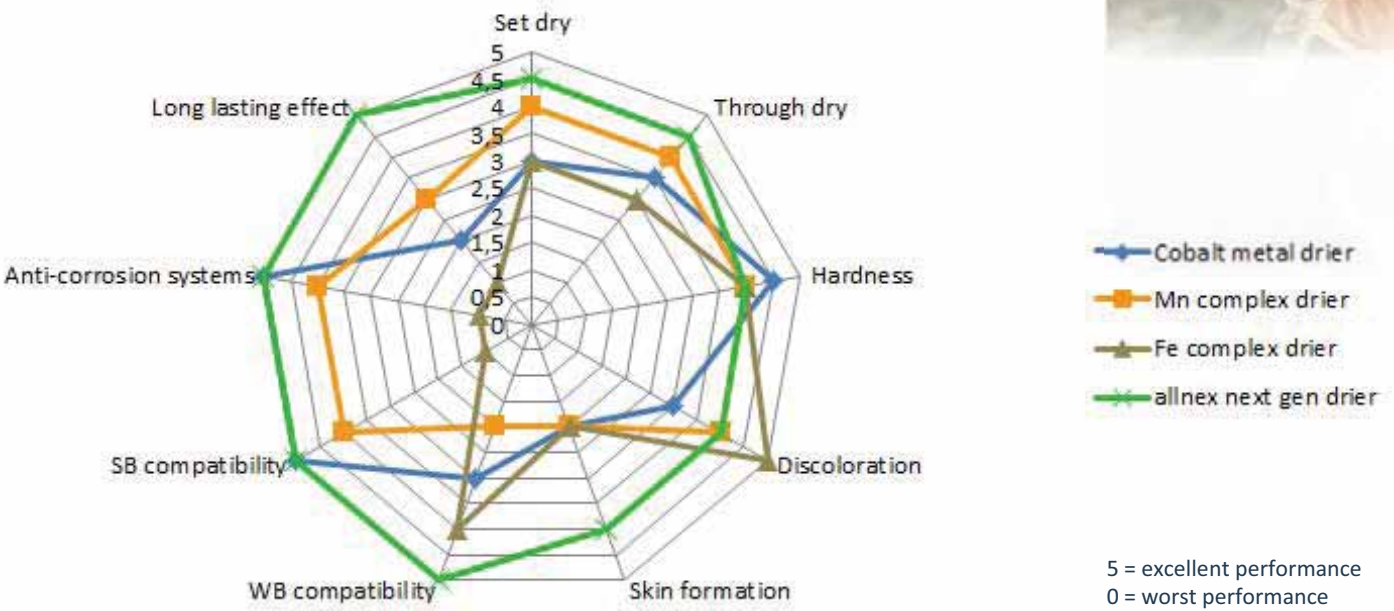
Drying performance in different WB white alkyd paint formulations

Auxiliary combination drier containing Li and Zr



allnex' "next gen" drier performance 3

Overall performance diagram
allnex's next generation drier vs competitive Cobalt and Cobalt alternative driers



5 = excellent performance
0 = worst performance

ADDITOL® dry CF Series - Product Line

ADDITOL® dry CF 100	ADDITOL® dry CF 101	ADDITOL® dry CF 200
Cobalt free Primary Driers		Cobalt free Auxiliary Drier
Universal driers – can be used with solvent-based, water-based, high solids and ultra high solids systems		Used with ADDITOL® dry CF 100/101 in water-based systems
• Best dry time and storage stability • Best solvent based performance	• Good universal application for solvent & water-based systems • No SNUR	• Multi-metal drier for simpler paint formulation • Excellent water-based incorporation
Minimal color impact, Clear and pigmented systems, Excellent hardness development, Used to formulate Low VOC coatings, Exceptional storage stability, No impact on final coating appearance		

Application of ADDITOL® dry CF100 & CF101

ADDITOL® dry CF100 & CF101

- Can be added **directly** to the paint system **at any stage of production**
- Dosages of **0.3 to 0.9 %** calculated on solid binder
  are recommended for medium solid and waterborne alkyds
- Ultra high solid alkyds requires up to **1.3%** calculated on solid binder
- When being used for direct Cobalt replacement in existing formulations:
  ADDITOL® dry CF100 & CF101 **can be used in FOD at same levels as a Cobalt 10 %**
- The new products can be combined with all common secondary and auxiliary driers e.g. Aluminum, Barium, **Calcium**, **Lithium**, Potassium, Strontium, Zinc or **Zirconium.**
- In some cases the auxiliary driers have to be adjusted when switching from Cobalt to our new products (we have seen **higher levels of Zirconium** are needed)

allnex's ADDITOL® CF series SPF's

SPF based on SETAL® 312 SM-88 Cobalt free

Brush able glossy white topcoat

Mill base:	17,00	SETAL® 312 SM-88
	3,34	Shellsol D40
	0,38	Ca 10% (auxiliary drier)
	33,04	Kronos 2190
	53,76	
Let down:	30,55	SETAL® 312 SM-88
	54,05	Millbase
	4,00	Shellsol D40
	1,66	Zr 12% (auxiliary drier)
	0,42	*ADDITOL® dry CF 100 (co free drier)*
	0,25	ADDITOL® XL 297 (anti skinning agent)
	9,07	Shellsol D40
	100,00	

SPF based on RESYDROL® AY 6150w/45WA Cobalt free

DTM anti-corrosion monolayer, glossy

Mill base:	66,10	RESYDROL® AY 6150w/45 WA
	0,30	Ammonia /25%
	0,10	AMP-90 (multipurpose additive)
	0,30	ADDITOL® dry CF 100 (co free drier)
	0,45	ADDITOL® dry CF 200 (auxiliary drier)
	0,30	ADDITOL® XL 297 (anti-skinning additive)
	0,70	ADDITOL® VXL 4930 (slip & leveling additive)
	18,20	Kronos 2190
	2,90	Nubirox 102
	1,90	Blanc fixe micro
	0,50	ADDITOL® VXW 6387 (anti-settling additive)
	0,70	ADDITOL® VXW 6208 (dispersing additive)
	0,40	ADDITOL® XW 376 (foam control additive)
Let down:	5,75	water deion.
	1,5	Acrysol RM 6000/Fod. (thickener)
	100,0	

allnex's next generation cobalt free driers are compatible in WB as well as SB, HS & UHS alkyd paint formulations.

Thank you for your attention

Q & A

endless inspiration

allnex
The Coating Resins Company

Notice: Trademarks are owned by their respective owners.

Disclaimer: Allnex Group companies ("Allnex") decline any liability with respect to the use made by anyone of the information contained herein. The information contained herein represents Allnex's best knowledge thereon without constituting any express or implied guarantee or warranty of any kind (including, but not limited to, regarding the accuracy, the completeness or relevance of the data set out herein). Nothing contained herein shall be construed as conferring any license or right under any patent or other intellectual property rights of Allnex or of any third party. The information relating to the products is given for information purposes only. No guarantee or warranty is provided that the product and/or information is adapted for any specific use, performance or result and that product and/or information do not infringe any Allnex and/or third party intellectual property rights. The user should perform its own tests to determine the suitability for a particular purpose.