borchers

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Value through expertise

Cobalt and MEKO classification issues:

The new Generation of Co-free and MEKO-free solution for solvent-borne, high-solid and waterborne alkyds

29 November 2016 Laurent Barnils *Hungarocoat 2016*

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Hungarocoat

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Introduction

Air-drying alkyd resins have many advantages:

- outstanding application properties:
  gloss, leveling, pigment wetting and drying at adverse conditions
- high content of naturally based raw materials
- alternatives to fossil sources
- inexpensive and extremely stable
- allow to formulate coatings with long open times
- yield relatively hard surfaces
- good stain blocking abilities and protective properties for a 1K system

Motivation

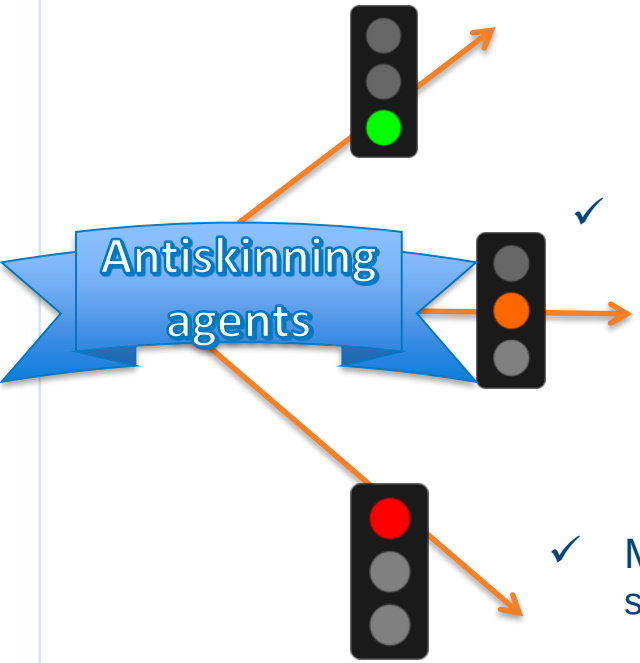
Threat of labeling of two key ingredients of alkyd paints

- **MEKO** (Methyl Ethyl Ketoxime)
- **Cobalt**

MEKO-Replacement

- Major anti-skin agent during manufacture and storage of air-drying alkyd paints
- Pressure in Europe to reduce workplace exposure to levels difficult to meet!
  (i.e Germany limit now to <0.3 ppm in the working place)
- Proposal of reclassification in carcinogen 1B, H350 already submitted – now a question of time and administration
- Classification as carcinogen 1B, H350 will affect sales to the general public and the substance would fulfil the criteria for identification as SVHC
- Alternatives antiskinning agents slow the drying after application, by reducing the activity of the metal driers and by insufficient evaporation.

MEKO replacement



✓ **Ascinin® Antiskin range: oxime** oxime-free and phenol-free

Toy Safety Norm compliance EN 71-3

Swiss Ordinance 817.023.21 Food Contact Materials (all components listed in Annex 6) for Ascinin 0444 & 0445

✓ Other oximes (REACH 31/05/2018)

2-pentanone-oxime?? **31/05/18 →start discussions**

acetone-oxime?? **31/05/18 →start discussions**

cyclohexanone-oxime?? **31/05/18 →start discussions**

✓ MEKO (Methyl Ethyl KetOxime) CLP: Carc. 2, H351
suspected of damaging the unborn child

Pending discussion ….. + Carciogenic 1b!!!!!

already banned in Offset inks,
limited in Germany for professionals (<0.3 ppm in the air at working place!!!)

Our MEKO-Replacement options

Borchers can supply:

Borchi® Nox M2 (100% MEKO) as long you would or could buy!

Borchi® Nox C3 (100% cyclohexanone-oxime- pellet form but easy to disperse)

Borchi® Nox 1640 (cyclohexanone-oxime- 30% solution in DPM)

<u>oxime-free/phenol-free:</u>

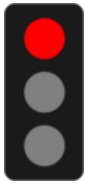
Ascinin® Antiskin 0444	for solventborne and high solid systems
Ascinin® Antiskin 0445	for solventborne and waterborne systems
Ascinin® Antiskin 1240	for solventborne, specifically tinting systems (more headspace protection)

Extension of storage stability

Better smell

Excess lead to extension of drying time
→ Dosage need to be more finely tuned

Cobalt driers: reclassification? When?



✓ Cobalt carbox CLP: already Repr. 2, H361d suspected of damaging the unborn child

✓ Pending discussion ….. → Carciogenic 1b ? The cascade effect ☹

✓ When? That's a difficult topic…

Not easy to be predictive on dates there is a read-across process for the cobalt carboxylates that should take place.
But there is 1st a cascade effect that should take place:
-the **cobalt metal** in powder was classified carcinogen in the USA: this lead to a proposal of same classification from the cobalt metal consortium (where we stay before as OMG, but we sold this business few years ago);
The issue is it have been slower than expected; The Public Consultation has not yet started further to the CLH proposal submitted in April 2016 by Dutch Authorities to ECHA:

Consortium self-classification	CLH proposal
Carc 1B (H350i) – inhalation GCL 0,1% (Generic Concentration Limit)	Carc 1B (H350) – all routes SCL 0,01% (Specific Concentration Limit) Repr. 1B (H360f) Muta 2 (H341)

-then this decision will influence the classification of 5 Cobalt salts (dichloride, carbonate, sulfate, dinitrate and diacetate) but also the cobalt carboxylates (produced from the metal or from these salts)
About the cobalt salts themselves (dichloride, carbonate, sulfate, dinitrate and diacetate):
There was a potential request from Dutch Authorities for the de-classification (remove Muta 2) of the current harmonised classification applied by Consortium:

Consortium harmonised classification	Potential de-classification
Carc 1B (H350i) – inhalation Repr. 1B (H360f) Muta 2 (H341)	Carc 1B (H350i) – inhalation Repr. 1B (H360f)

Under evaluation / discussion - The de-classification effort is now uncertain and may be reconsidered. There is inconsistency with the CLH proposal for Cobalt metal (as Muta 2). So not sure at all it will be accepted to coming back on the Muta 2 classification.

Cobalt driers: reclassification? When?

About the cobalt carboxylates:
Currently, all Cobalt compounds (eg. carboxylates: 2ethylhexanoate, propionate, naphthenate, neodecanaote, tallate,…) have been self-classified – Repr. 2 (H361f) – as precautionary measure and adopted on provisional basis. These substances do not appear to be genetoxic in vivo, for this reason there is no mutagenicity self-classification applied by consortium.
Under evaluation / discussion - Long Term Human Studies is on-going and will be subjected to ECHA's approval of the testing. The endpoint Carcinogenicity is a bit more challenging.

Once approval, Consortium will review the classification accordingly based on read-across and grouping approach for oral route of exposure. Therefore, the approach is not considered final and no decision has been taken so far.

…to be continued….

Motivation

Cobalt-Replacement

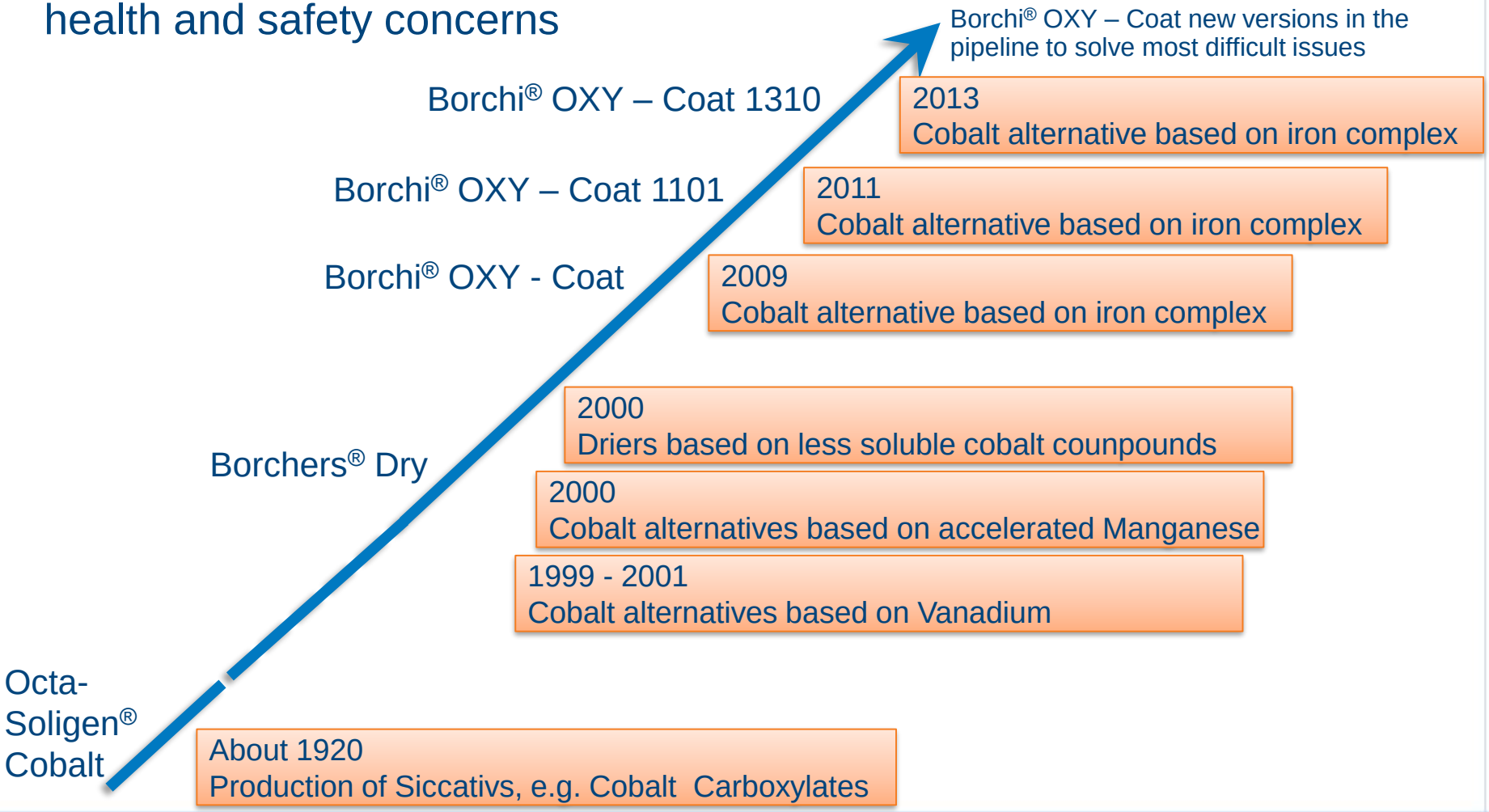
- So depending if you are **optimistic** (and don't need to be cobalt-free for your markets) and would wait the last limit or if you are **realistic** and would be prepared ASAP because not so easy to replace and/or **need for your markets**, need to consider that the reclassification could occur from soon to end 2018??
- possible classification changes are the driver to replace Cobalt as standard surface drier
- Probable classification of several cobalt driers as carcinogenic
- Carcinogenic classification is not acceptable in DIY paint formulations
- Great interest in possible alternatives for Co with no technical drawbacks
- Only Mn- and Fe-based driers prove to be viable alternatives

FeLT – drier (Borchi OXY Coat technology)

Cobalt-drier

History of Co-Replacement Development

Strong desire in the European marketplace to replace Cobalt due to health and safety concerns

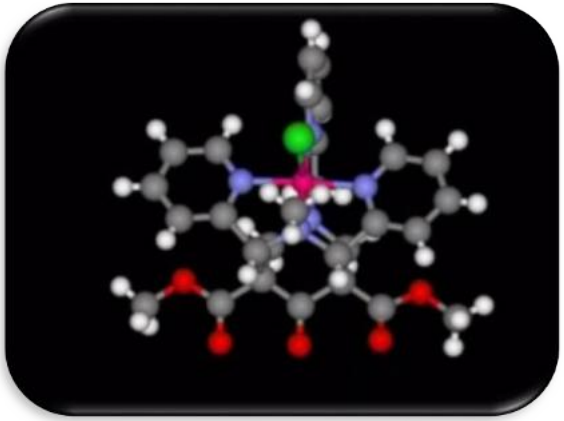


Why Borchi® OXY-Coat?

- Iron complex – new technology (standard iron carboxylates: not enough performance)
- High activity in alkyd systems
- Addition rate of iron is very low: up to 100 times lower than cobalt
- notorious yellowing of alkyds is minimized with FeLT-based driers
- good performance in cold and humid weather
- Applicable in a wide range of coatings systems that dry oxidatively
- Developed initially for consumer products (detergency)

=enough data to register by REACh without assimilation with other driers

Borchi® OXY-Coat is sometime a little bit more difficult to use **but it is not only a replacement** it is a new technology bringing extension of alkyd properties



Iron based paint catalyst FeLT containing a polydentate Ligand:
Borchi® OXY-Coat product range

Borchi® OXY Series: Why the best long term choice?

- ✓ **Borchi® OXY Series:** no REACh registration issue expected / no additional charges

soon ……

Primary Driers

- ✓ Coming discussions (REACH 31/05/2018)
  - Manganese driers?? **31/05/18 →start REACh discussions**
  - **Accelerated** Manganese driers??? **31/05/18 →start REACh discussions**
    with additional possible issues on the complexing agents themselves
  - Vanadium based driers????????? 31/05/18? ….? Business case show no great interest to spend money on this nearly empty Reach dossier
- ✓ Cobalt carbox CLP: Repr. 2, H361d
  suspected of damaging the unborn child

  Pending discussion ….. + Carciogenic 1b!!!!!

  already banned in Offset inks, packaging, OEM automotive, Ecolabels…and more and more sectors will follow

History of Co-Replacement Development

Borchers can supply:

Cobalt octoate, neodecanoate, naphtenate, boroacylates:
as long you would/could buy

Manganese octoate, neodecanoate:
only for primers and dark colors (due to his brown colour)

Accelerated Manganese:
suits quite well in solventborne, incl. long oils – but not 100% sure about future after 05/2018

Vanadium drier: don't worth to invest for REACh registration due to lack of data and limited system where it works

Iron octoate: too limited activity at room temperature

Iron Ligand **FeLt** (Borchi OXY Coat / BOC):
the more long-term – the best for DIY, even easier and better than cobalt on several technical perspectives

Borchi® OXY Series

Borchi® OXY – Coat is 100 times more active than cobalt driers.

That leads to a more sensitive product (to adsorption, to skin) – not a drop-in solution ☹

But we developed additional delivery forms and complement tools (ie. Borchi® OXY Synergist for the high solids) and also provide methodology for screening with Guidelines

Borchi® OXY – Coat 1101

- ✓ Solvent: water
- ✓ Standard for waterborne systems – no VOC

Borchi® OXY - Coat

- ✓ Solvent: PG
- ✓ "Universal" for solventborne and waterborne systems

Borchi® OXY - Coat 1310

- ✓ Solvent: DPM
- ✓ Standard for solventborne systems
- ✓ Incl. for thix resins, where PG has a negative influence on viscosity

Formulation Guideline

- The BOC series of driers is similar to Cobalt siccativated systems in that secondary driers, feeder driers and/or wetting and dispersing agents are needed to improve drying results

- Steps to optimize a formulation with BOC:

1. Ladder Study
2. Improve Through Dry
3. Increase Surface Dry / Avoid Loss of Dry
4. Anti-Skinning

- Different approaches for solventborne and waterborne systems

Formulation Guideline – Solventborne Systems

1) Ladder Study

- Try different concentrations

0.5%
BOC 1310 or BOC

1.0%
BOC 1310 or BOC

2) Insufficient Through Dry

- Add Zirconium and/or Calcium

0.5% BOC 1310 or BOC
+ 1% OS Zr 18

0.5% BOC 1310 or BOC
+ 1% OS Ca 10, basic

0.5% BOC 1310 or BOC
+ 1% OS Zr 18
+ 1% OS Ca 10, basic

3) Insufficient Surface Dry or Loss of Dry?

- Add W & D agents to the mill base

+ Borchi® Gen 0650 (mill base)

+ Borchi® Gen ND plus (mill base)

4) Anti-Skinning?

- Add AAS

+ 0.2% AAS 0444

All dosages are calculated on total formulation

Formulation Guideline – Waterborne Systems

- Waterborne systems are easier to dry
- Normally less BOC is needed
- Usually systems contain already enough wetting and dispersing agents

1) Ladder Study

- Try different concentrations

0.10% BOC 1101

0.25% BOC 1101

0.50% BOC 1101

2) Insufficient Through Dry?

- Add Zirconium or Zinc

0.25% BOC 1101
+ 0.5% Zr 10 aqua

0.25% BOC 1101
+ 0.5% Deca Zn 10 aqua

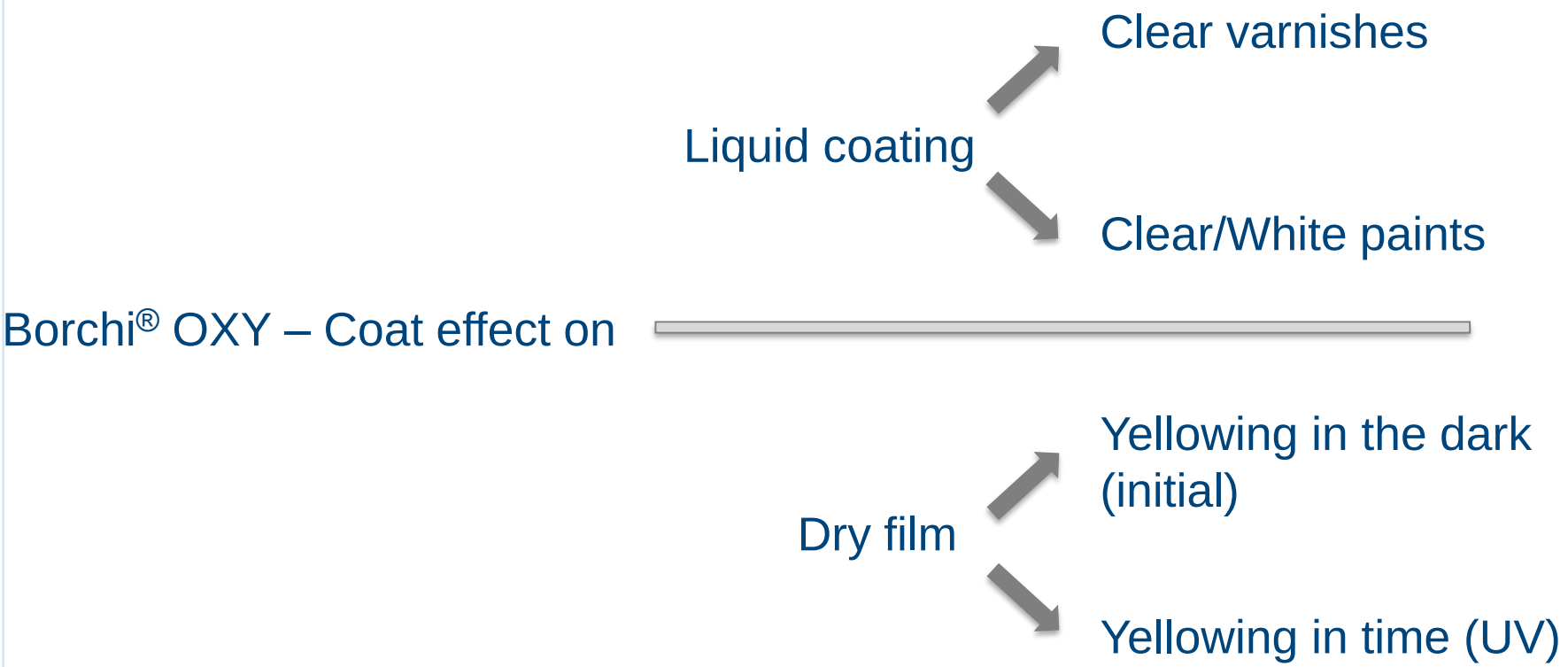
3) Anti-Skinning?

- Normally not necessary in waterborne systems. If desired add Ascinin® Anti-Skin

0.10% AAS 0445

All dosages are calculated on total formulation

Discoloration ("yellowing"of Paint Formulation)



Discoloration (“yellowing”of Paint Formulation)

Borchi® OXY – Coat has an extremely low influence on the liquid color of the system compared to other standard driers. This is visible in the liquid formulation as well as in the dried film.

Test system is based on longoil alkyd.

Binder	Binder + 0.5% BOC 1310	Binder + Cobalt drier	Binder + Competitor, Mn based

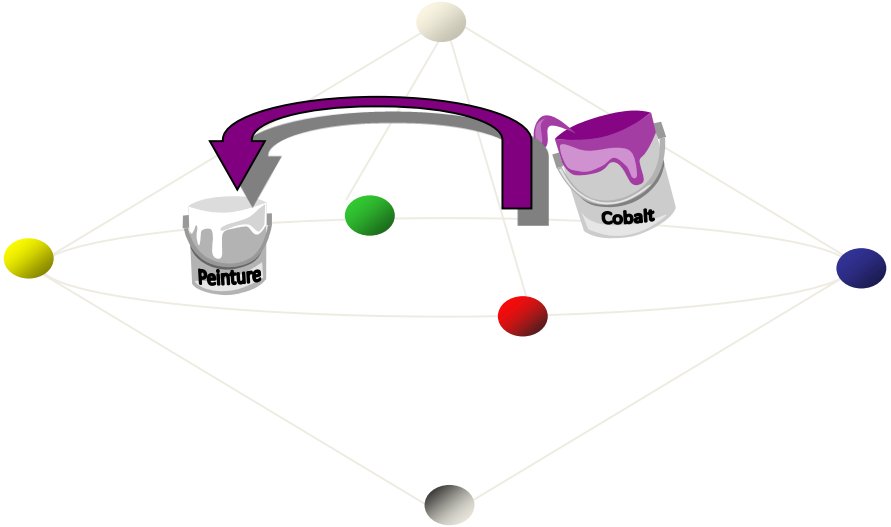
Test system based on longoil alkyd (soy) for metal and wood application.

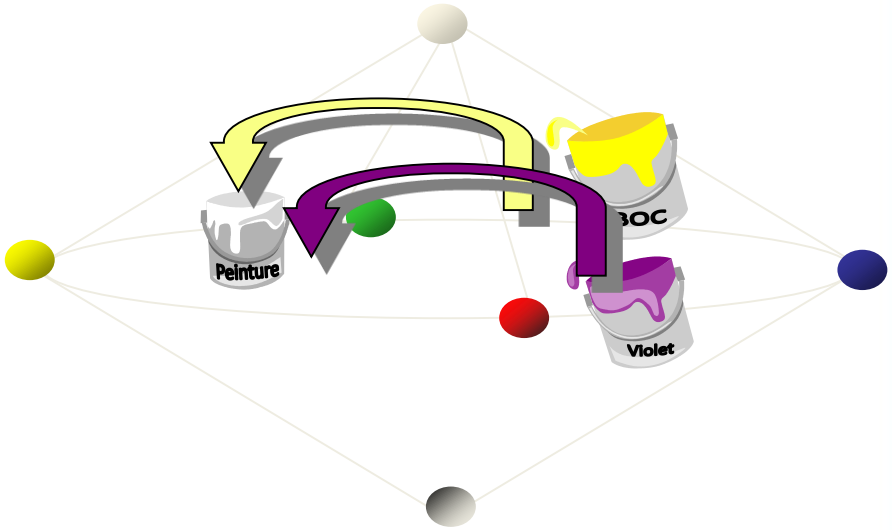
Binder	Binder + 0.4% BOC 1310	Binder + 0.5% Competitor, Mn based	Binder + 0.1% Borchers® Dry 0411 HS (our accelerated Mn)

This is very positive for clear coats for sure,

Discoloration (“yellowing”of Paint Formulation) - White

Borchi® OXY – Coat (BOC) is yellow/brown light by itself
(but much clearer than Manganese)
By this way it is slightly negative for white paints because don’t bring the brightening effect of cobalt (that compensate the yellow tone of binder)





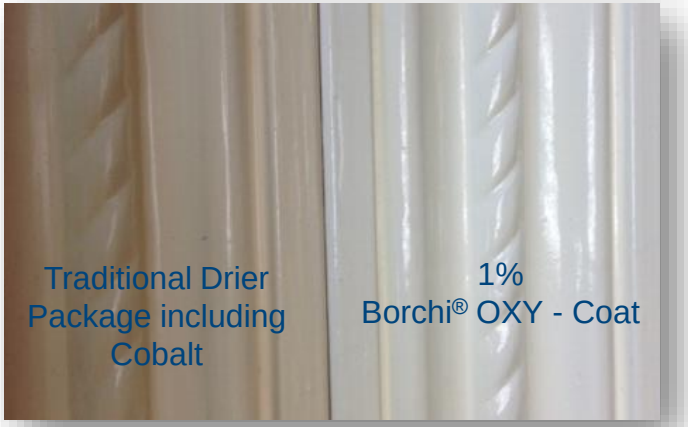
With Borchi® OXY – Coat need to provide this brightening or calibrate the base paint in tinting systems: quite easy with a tiny amount of violet pigment

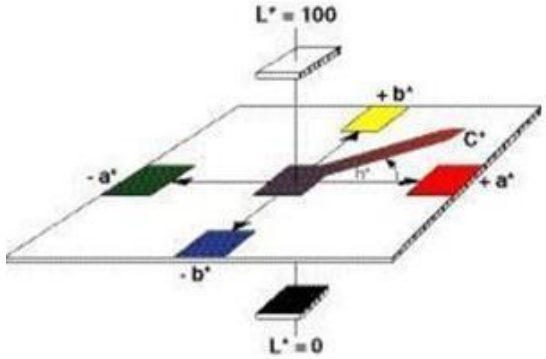
[that is not possible to do with Mn because too dark yellow or brown that will lead to a dirty white]

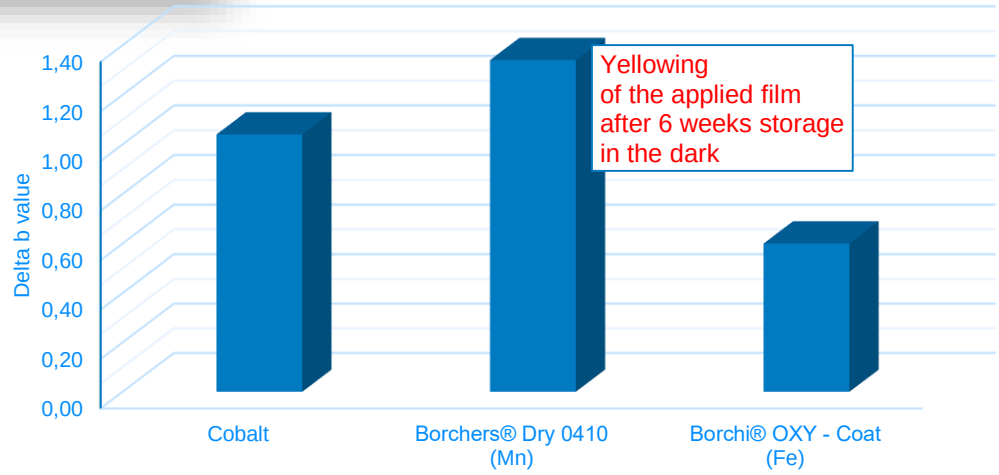
Yellowing during drying (yellowing in the dark)

Borchi® OXY – Coat has an extremely low influence on the colour of the system compared to other standard driers

Test System:
Beckosol AQ 206
8% TiO_2 Tint Paste
Wood panels







Test Formulation – Long Oil Alkyd Resin

Test Formulation	Description	[%]
Synthalat SF 653	Long-oil drying alkyd resin	64,00
Pigment Paste *1		16,00
Testbenzin D 40	Solvent	20,00
Total		100,00

*1 Pigment Paste	Description	[%]
Kronos 2360	Titanium Dioxide	65,00
Aerosil R972	Anti-Settling	0,50
Borch® Gen 1252	Wetting and Dispersing	31,50
MPA	Solvent	3,00
Total		100,00

Additon Rates Driers & Anti-Skins		[%]
		on total formulation
Borchi® OXY - Coat	Primary Drier	0,25
Octa Soligen® Calcium 10, basic	Secondary Drier	0,10
Octa Soligen® Zirconium 18	Secondary Drier	0,50
Ascinin® Anti Skin 0444	Anti-Skin	0,10
Borchi® Nox M2	Anti-Skin	0,30

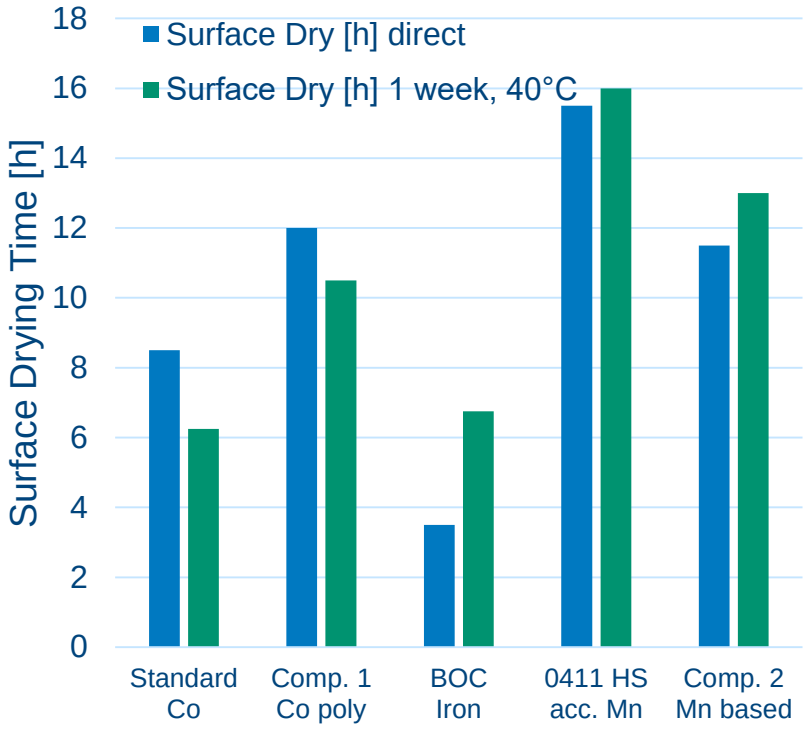
Test Formulation – Long Oil Alkyd Resin

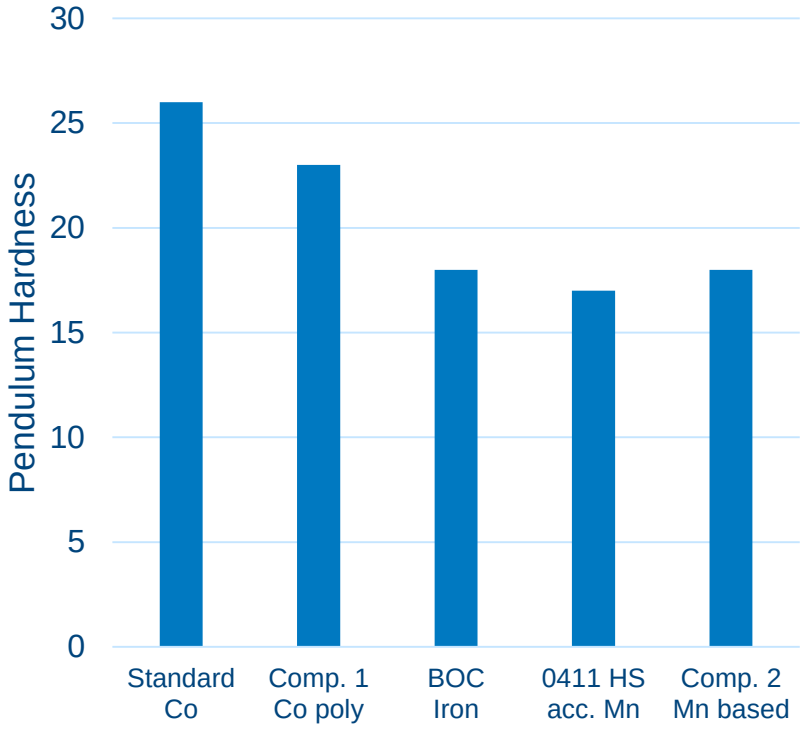
- ✓ Variation of test formulation with different primary driers

Primary Driers	Description	Addition Rates Primary Driers (As supplied, calculated on total formulation)	Secondary Driers	Anti-Skinning
Octa-Soligen® Cobalt 10	Cobalt carboxylate	0,50 %	Zirconium Barium Zinc	Ascinin® Anti-Skin 0444 Borchi® Nox M2
Competitor 1	Cobalt polymer	0,50 %		
Borchi® OXY – Coat	Iron complex	0,25 %	Zirconium Calcium	
Borchers® Dry 0411 HS	accelerated Manganese	0,14 %	Zirconium Calcium	
Competitor 2	Manganese based	0,14 %		

Lab Results – Long Oil Alkyd Resin

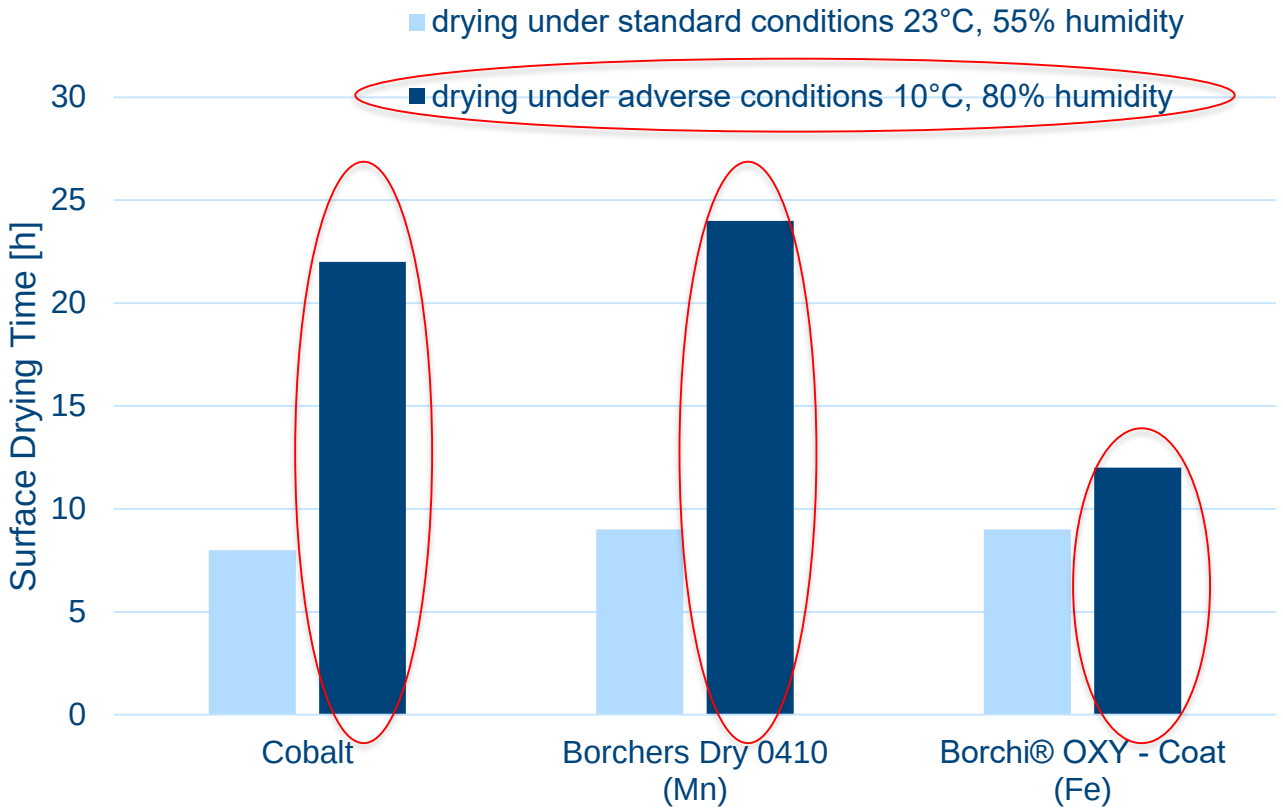
- ✓ Borchi® OXY – Coat drying time is comparable to cobalt standard
- ✓ Manganese based driers show longer drying time compared to cobalt
- ✓ Borchi® OXY – Coat hardness is lower compared to Cobalt, but comparable with other cobalt replacements





Drying Time of a HS Alkyd Resin – Adverse Conditions

Borchi® OXY – Coat exhibit shorter dry times under adverse conditions compared to standard drier systems



Test system:
White pigmented system based on high solids alkyd for low VOC

Borchi® OXY Series: the limits

In water

- ✓ Easy replacement
- ✓ Plenty of technical benefits
- ✓ Cost-effective vs Cobalt

In short & medium oil lengh and classic long oil

- ✓ More difficult replacement (sensitive to other ingredients like pigments, fillers, matting agents…)
- ✓ Several technical benefits
- ✓ Possible to work Cobalt/oxime-free

In long oil / high solid applied by brush roller when long storage needed

- ✓ often difficult to get right balance drying properties / storage stability moreover when needed to be MEKO-free (concern when applied by brush but not so difficult when applied by spray)
- ✓ Some tools can help:
  - Borchi OXY Synergist
  - Crosslinkers
  - other tools under development!!!!!!!

Thank You for Your Attention

For more information visit our homepage: www.borchers.com

Or contact one of our sites

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