

A guide for MEKO compliance and 'future-proofing' alkyds

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Alkyd-based paints are experiencing a revival in the coatings industry due to their bio-renewability, cost-effectiveness and overall good performance in many applications. As the industry increases sustainability standards for paint formulations, a hurdle for alkyd coatings remains in the raw materials required to formulate a paint, namely cobalt catalysts and methyl ethyl ketoxime (MEKO) anti-skinning agents.

These two materials face increasing regulatory changes, which will simultaneously increase the burden on formulators developing label-free paint. MEKO's toxicity makes it challenging for formulators to meet safe exposure limits due to its volatility and additionally, MEKO and cobalt have been classified as carcinogens. In this paper, we discuss non-toxic alternatives to both materials, focusing on the path to reformulation with data demonstrating the performance benefits of Borchers' cobalt and MEKO alternatives.

Background on alkyd coatings

Alkyd-based coatings dry via autoxidation when oxygen reacts with points of unsaturation based on fatty acids in the resin. This process can be prolonged if unaided, so cobalt-based catalysts are utilised as oxidative catalysts to speed the curing of alkyd resins. Since cobalt catalysts are reactive to oxygen, an anti-skinning agent such as MEKO is often required to prevent the paint surface from forming a film (called 'skin'). Therefore, many alkyd-based paint formulations are dependent on cobalt for adequate curing and on MEKO for storage stability.

The regulatory case on cobalt & MEKO

Regulatory pressure on cobalt and MEKO is not a new topic in the coatings industry. However, regulation changes have been increasing in frequency and severity since 2020. The European Commission recently published (in ATP 15 part 3 Annex VI) the entry of MEKO with the classification of 1B carcinogen with a concentration limit at $\geq 0.1\%$.

This classification will take effect on 1 March 2022. From this date onward, formulators cannot use MEKO if they want to create label-free products if it meets or exceeds the concentration limits. This directive, coupled with the many protocols required for handling the raw material based on its hazard pictograms (Figure 1), is a significant regulatory push to remove this raw material from alkyd formulations.

The continued risk assessments on cobalt and its compounds by European Authorities will see more reclassifications with new stringent label requirements. Many carboxylate salts, including 2-ethylhexanoate, are already classified CMRs (carcinogenic, mutagenic or toxic to reproduction), and a proposal for the restriction of some cobalt salts is still under discussion. The European Chemicals Agency (ECHA) concluded in its 2019 draft proposal that soluble cobalt salts are to be treated as non-threshold Carcinogens Category 1B under REACH. Additional cobalt-containing compounds are under consideration to be classified as 1B carcinogens by no later than 2023, and an Occupational Exposure Limit (OEL) of 0.1 mg/kg has been proposed and is set to come into effect by 2023. These considerations include concentration limits set by the European Commission.

Hazard Pictograms – MEKO	
Current Classification	New Classification

Figure 1: Hazard pictograms for MEKO

Evaluation paths for MEKO replacement

With these regulatory requirements in mind, formulators must plan and test to reformulate alkyd coatings without MEKO by the March 2022 deadline. Before directly replacing MEKO in a traditional alkyd formulation containing cobalt, formulators should consider the potential reclassification of cobalt-containing materials to future-proof the formulation from additional regulatory directives. Reformulation option 1 is to remove MEKO without adjusting your current cobalt-containing drier package. If

this path is taken, there is a risk of having to reformulate one year later which wastes valuable lab resources and time.

Furthermore, MEKO-free anti-skinning agents can differ in efficiency and dosage with cobalt driers compared to cobalt-free technologies. The preferred anti-skinning agent for replacing MEKO in a cobalt-containing formula might be different from the optimal anti-skinning agent for cobalt-free driers, making the first formulation step redundant. It is Borchers' recommendation to consider both cobalt and MEKO replacement at the same time.

Borchers' high-performance catalysts and MEKO-free anti-skinning agents

Borchers offers safe and environmentally friendly alternatives to both cobalt and MEKO that aid in formulating a more sustainable alkyd coating. High-performance catalysts (HPC) are next-generation driers that are superior in sustainability and performance compared to metal carboxylates. These solutions are based on patented organometallic ligand technologies. Borchers' HPC products include Borchi® OXY-Coat variations for waterborne and solventborne systems and the newly developed Borchi Dragon for high solids or long oil alkyd paints. These products are globally registered, REACH compliant, alkylphenol ethoxylate (APEO)-free, and volatile organic compound (VOC)-free (in waterborne systems). Compared to cobalt carboxylates, the efficiency of HPCs is so high that less oxygen is needed to promote oxidative cure throughout the film, not just on the surface. This advantage allows for faster cure rates and lowered or no dependency on secondary driers, such as zirconium or strontium, to provide through-drying in the system. Additional benefits that Borchers' HPCs bring to alkyd coatings, aside from improved labelling, include excellent drying under adverse conditions and reduced or no yellowing over time.

Borchers also offers a line of MEKO-free anti-skinning agents that can be classified as oxime-containing (Borchi Nox and Borchi Shield) or oxime/phenol-free (Ascinin®). When formulating with these products, the optimised dosage of the HPC must first be determined by testing it alone in the paint to verify drying performance. Once the dosage of HPC is set, the anti-skinning agents should be tested in a ladder study if the system is skinning. Advantages to testing the HPC alone also include the potential not to require anti-skinning agents in the formulation if no skinning is found.

Highlighting performance benefits

To showcase the performance benefits of a MEKO- and cobalt-free formulation that utilises Borchers' products, tests were conducted in a solventborne high gloss white trim paint based on a high solids long oil alkyd. The control formulation included the standard drier package - cobalt, zirconium and calcium carboxylates with MEKO. The Borchers-recommended formulation included Borchi OXY-Coat, calcium carboxylate and Ascinin Anti-Skin 1240, making the formulation cobalt-free and MEKO/oxime/phenol-free. Performance benefits of the Borchers-recommended formulation included faster drying time (Figure 2), with the formulation curing about 30% faster than the cobalt control. Another benefit can be seen in the yellowing performance. Yellowing is a standard performance limitation of cobalt-containing drier packages. In the graph shown in Figure 3, the yellowing of the control formulation doubled, whereas the Borchi OXY-Coat and Ascinin Anti-Skin 1240 formulation provided lower yellowing over time.

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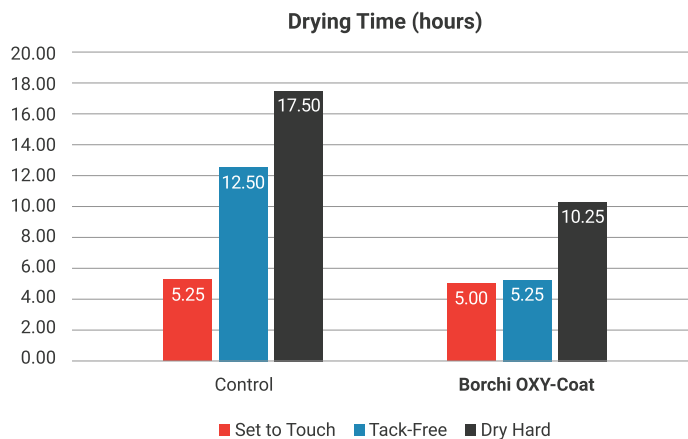


Figure 2: Drying time performance: cobalt control vs. Borchi OXY-Coat (Gardco Circular Dry Time Recorder)

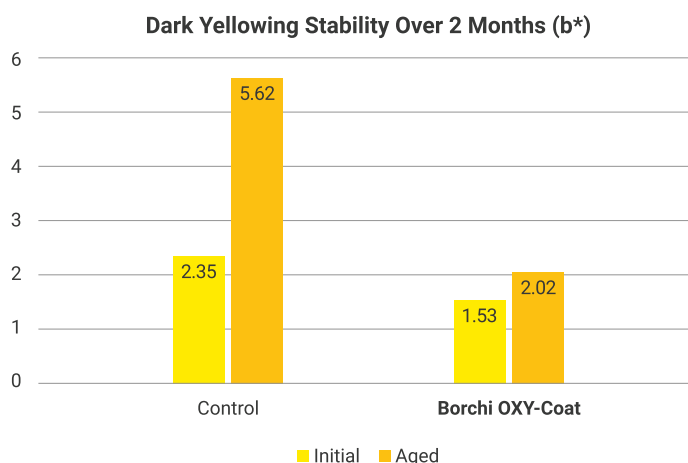


Figure 3: Yellowing performance: cobalt control vs. Borchi OXY-Coat (XRite MA 94)

Conclusions

New regulations on MEKO and cobalt are expected to significantly impact the coatings industry within a short window of time. While MEKO regulations will be established sooner, replacing both MEKO anti-skinning agents and cobalt catalysts with safer alternatives during the same reformulation project will save time, provide sustainable formulations from a product stewardship standpoint, and enhance overall performance in alkyd paints.

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