How to Achieve Faster Dry Times and More with High-performance Catalysts in Low-VOC Alkyd Coatings

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The alkyd coating market continues to face increasing challenges as government bodies and environmental agencies establish new volatile organic content (VOC) and regulatory restrictions. In many cases, reformulation is necessary to meet low-VOC requirements, which may cause adverse effects in the final coating, such as slow dry times, increasingly complex formulations, and poor coating performance.

Formulators can overcome such performance obstacles in sustainable coatings by using the proper high-performance catalyst (HPC). This unique technology can meet VOC requirements, outperform standard metal carboxylates across multiple resin platforms, and may eliminate the need for complex drier packages.

INTRODUCTION

Alkyd resins are oil-based polyesters created by reacting alcohol and acid, which can further be modified through the addition of unsaturated oils. These oils can vary in length and branching, which will create different coating properties, allowing for high diversity and tailoring for specific applications. Alkyds form a film by undergoing a crosslinking reaction in the presence of oxygen in the surrounding air at sites of unsaturation in the fatty acids. If unaided, this autooxidative process can be extremely slow.

The application of alkyds spans a multitude of different market segments, from architectural to industrial, and can be used on various substrates, including wood and metal. The versatility of these resins keeps them relevant in the coatings market as new chemistries are continually being developed. Since the original synthesis in the 1900s, alkyds have faced increasing regulations, driving developments of more sustainable alkyd chemistries.

It is well documented that the emission of potentially harmful VOCs has resulted in an increase in the number of health problems such as asthma, allergies, and other breathing problems as well as environmental concerns associated with global warming.

The health and environmental hazards related to these potentially harmful VOCs have prompted government agencies to enact stringent regulations. The increase in public awareness regarding environmental effects and health issues drives the demand for low-VOC paints and coatings, which has led to the development of low-solvent, solvent-free, and waterborne coatings. Low-VOC paints and coatings typically use water as a carrier instead of petroleum solvents. In some cases, specialized solvents, such as de-aromatized (aromatic content less than 1%) solvents, are used to reduce VOC content.

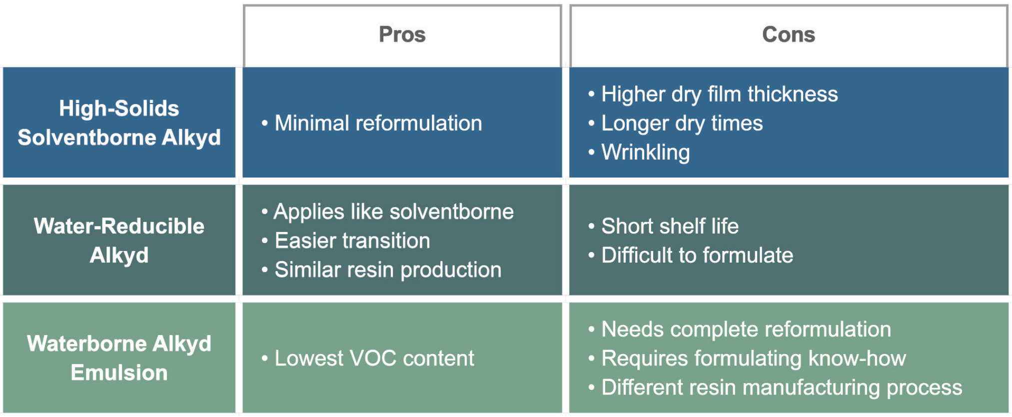
To comply with these increasing regulations, there are three paths that formulators can choose when working with alkyd coatings.

The first path is to increase the solids content, reducing VOCs in solventborne alkyd formulations. This is the most straightforward choice, as it typically requires a minimal amount of reformulation. Resin manufacturers can increase solids in two ways. Manufacturers can keep the same molecular weight and reduce solvent content. However, viscosity will increase, leading to potential differences in application performance and increased film thickness, resulting in wrinkling. To keep viscosity similar, manufacturers can decrease the molecular weight of the resin and solvent content, but this could negatively affect drying and performance properties.

The second path is to move from a pure solventborne alkyd to a water-reducible alkyd. Formulators often choose this path because of the similarity in paint application to high-VOC solventborne alkyds. Manufacturers can also continue to use the same industrial equipment, and the resin is easy to produce. Water-reducible alkyds are created by incorporating carboxylic-acid groups into the structure. These acid groups are then neutralized with amines to enable solubility in water. Although these types of alkyds are high in solids, 70–75% by weight, they still have relatively high levels of VOCs, primarily hydrophilic glycol ether solvents.

The third path is to use waterborne alkyd emulsions. This technology was engineered to have extremely low VOC levels that are significantly lower than water-reducible or high-solids solventborne alkyd coatings. Initially, waterborne alkyds did not have the same chemical resistance, ease of application, or shelf stability as solventborne alkyds. However, through years of development and adjustments, the properties of waterborne alkyds have become like that of solventborne alkyds. This is due in part to utilizing the correct additives in the full coating formulation to increase corrosion resistance, shelf stability, and other performance properties. This can be a difficult transition for coating manufacturers because nearly all materials and additives will need to change from what is traditionally used in high-VOC solventborne coating formulations.

FIGURE 1—Paths to Lowering VOC Levels in Alkyd Coatings



	Pros	Cons
High-Solids Solventborne Alkyd	• Minimal reformulation	• Higher dry film thickness • Longer dry times • Wrinkling
Water-Reducible Alkyd	• Applies like solventborne • Easier transition • Similar resin production	• Short shelf life • Difficult to formulate
Waterborne Alkyd Emulsion	• Lowest VOC content	• Needs complete reformulation • Requires formulating know-how • Different resin manufacturing process

All three options have pros and cons (*Figure 1*), as well as potential adverse consequences when the VOC level of a formulation is reduced. Longer dry times, reduced shelf life, wrinkling, and increased formulation complexity are common challenges formulators need to overcome with these technologies. By utilizing HPCs, formulators are achieving low-VOC targets while maintaining paint quality and meeting customer demands.

HPCs are a unique technology that can outperform typical metal carboxylates in oxidatively cured alkyd systems. They are patented organometallic ligand technologies (WO2012093250A1) that work differently from traditional metal driers. There are many environmental benefits such as being cobalt-free, APEO-free, and CMR-free materials. HPCs are also compliant with the European Union's Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH). These catalysts are globally registered and can be used in both solventborne and waterborne applications, making them highly versatile. This article will discuss one case study from each of the three low-VOC alkyd formulation paths that showcase the use of HPCs to overcome performance challenges.

EXPERIMENTAL PRACTICES

The experimental practices described in this article are specific to Borchers' internal laboratory procedures. Each system is unique and requires individualized testing and optimization to meet target values. At times, changes to the procedures are necessary depending on the coating application and end goals.

HOW TO FORMULATE WITH HPCs

Formulating with HPCs is different from working with a traditional cobalt-containing drier package. Cobalt is considered a surface drier, which means that it works primarily on the interface between the coating surface and the surrounding environment. Because of this, cobalt needs to be combined with other secondary or through driers to facilitate crosslinking throughout the body of the coating. Borchers' HPCs work as both surface and through driers, meaning that, in many cases, formulation complexity can be reduced by switching to HPCs.

The first step in the reformulation process is to conduct a ladder study at 0.5%, 1.0%, 1.5%, and 2.0% catalyst on resin solids (*Table 1*) to determine if coating specifications are met for dry time, hardness, antiskinning behavior, etc. If the formulation does not meet all necessary properties, the next testing phase is to evaluate secondary driers.

Secondary driers are tested in combination with the best primary drier loading level at 0.25% and 0.50% active metal on resin solids. Although there are many secondary drier options, the most common is zirconium. Once the formulation is optimized for the best dry time, additional performance criteria are evaluated as needed.

TABLE 1—Primary Drier Optimization Example

Primary Drier Optimization
High-Performance Catalyst (HPC) Ladder Study

Material	% HPC On Resin Solids			
	0.50	1.00	1.50	2.00
Fully Formulated Coating (75% Resin Solids)	100.000	100.000	100.000	100.000
HPC	0.225	0.450	0.675	0.900
Total Weight	100.225	100.450	100.675	100.900

In pigmented systems, an additional step is required to prevent loss of dry (LOD). LOD is the undesirable effect of a coating dry time increase on storage. For example, on the day a sample is made, the dry time could be four hours. After the same sample has aged for a few weeks, the dry time could increase on storage to be 8, 12, 24 hours, or longer. This LOD performance is due to the adsorption of driers onto the surface of the pigment. To prevent this adsorption from occurring, calcium can be used as a sacrificial drier, preventing the primary and secondary driers from being lost to the pigment. Calcium is evaluated at 0.25% and 0.50% active metal on resin solids.

Finally, if skinning occurs in a solventborne system, antiskinning agents will need to be tested. Skinning is a process in which a thin solid layer forms on top of the coating surface. This happens because the alkyd begins to cross-link when in contact with oxygen in the container. Antiskinning agents create a barrier that blocks oxygen from reaching the unsaturation in the alkyd during storage. These products are screened at 0.2%, 0.4%, and 0.6% on total formulation. Enough antiskinning agent should be added to prevent skin formation without negatively affecting the dry time. Typically, the more antiskinning agent used, the slower the dry time.

Sample Preparation

When optimizing a drier formulation, the first step is sample preparation. This is done by making a fully formulated paint without adding any driers or antiskinning agents. The driers are added to the paint and mixed until well incorporated. The samples will then need to "sweat-in" for 24 hours before moving to the dry-time evaluation stage.

Dry-time Evaluations

When evaluating dry times, environmental conditions are critical. For example, coatings typically dry quicker in hot, dry environments than in cold, humid environments. For this reason, evaluations are conducted in temperature and humidity-controlled conditions. Standard evaluation conditions are 23 °C, with 50% relative humidity. The evaluations presented in this article followed ASTM D 5895; all coatings were applied at 3-mils wet-film thickness, with a bird bar, over a mylar substrate. Once the paint is applied on the substrate, the drawdown is placed into the humidity chamber to evaluate dry time.

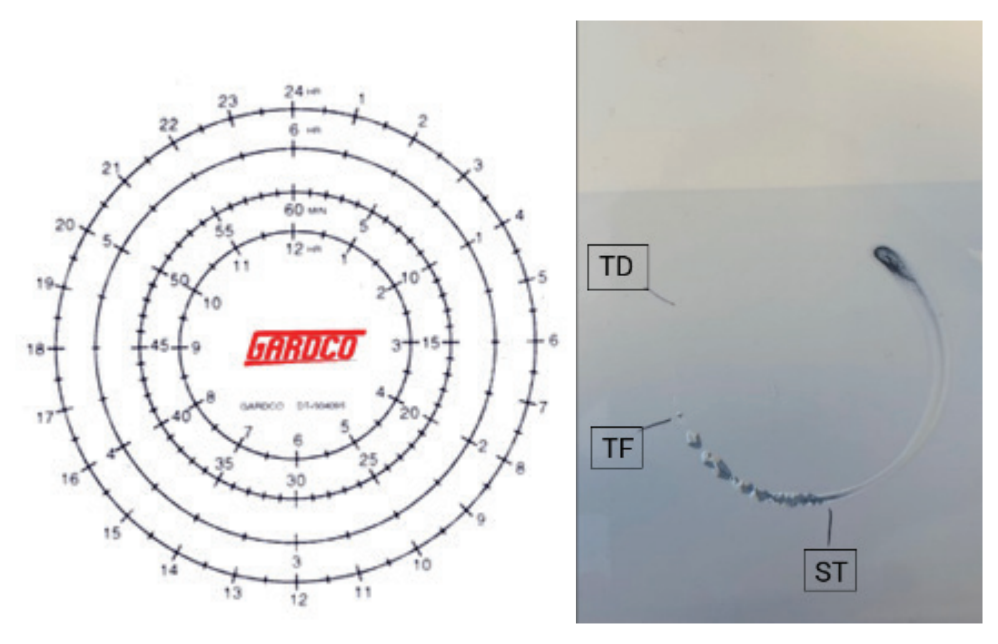
Dry times are evaluated with a Gardco Quadracycle drying time recorder. The recorder moves around in a circle over a set amount of time. The instrument can measure dry times in 1-, 6-, 12-, or 24-hour increments, depending on the estimated drying time of the coating. Each sample is evaluated in duplicate. After the circular dry recorder has completed its cycle, samples are removed from the chamber and read using the Gardco template (*Figure 2*). When reading dry times, three primary stages of drying are evaluated: set to touch (ST), tack-free (TF), and through dry (TD) (*Figure 2*).

At the ST stage, the paint is just beginning to dry. TF begins to show rupturing of the coating where the Teflon ball is tearing at the curing film. Finally, TD is when the film is completely cured and no longer leaves any mark on the surface. The dry times of the different drier combinations should be compared, followed by secondary evaluations.

Hardness

Following ASTM D 4366, coating hardness can be tested by making a 4-mil drawdown over a glass substrate. The hardness of the coating is read as a development over time, typically at 1, 3, and 7 days. Longer amounts of time up to 14, 21, or 28 days (about four weeks) can also be included, if necessary, for

FIGURE 2—Gardco Circular Dry-time Recorder Template and Drying Time Example



the specific application. The instrument used is a TQC Sheen Pendulum Hardness Tester using a König pendulum. Results are reported in oscillations or seconds, in which a higher number indicates a harder coating.

Yellowing

Yellowing is evaluated by reading the color of a 3-mil drawdown over a mylar substrate. The instrument used for this test is an X-Rite MA94, which reports results as L*a*b* values. For color, b* is the value used to assess yellowness. A higher b* value indicates a yellower coating.

Loss of Dry (LOD)

LOD is evaluated by taking a 20 g sample and placing it in a sealed vial. The vial is placed in an oven for two weeks at 50 °C. After this time, the sample is removed from the oven.

Once the sample has reached a constant temperature, a dry-time evaluation is performed once more, as described in the procedure above (the difference between the initial dry time and the dry time after two weeks at 50 °C). A large difference between the dry times of the initial and aged samples signifies a severe LOD.

Skinning

Skinning in solventborne coatings is evaluated using the LOD sample and by observing the surface of the coating after one week and two weeks at 50 °C. The rating system used is a scale of 0, where no skin is visible, to 6, where the coating is completely gelled. Anything over a 0 rating is unacceptable in most cases.

Adhesion

For a coating to fulfill its function of protecting a surface, it must remain adhered to the substrate. To test this property, an adhesion test is performed following ASTM D3359-09 method B, crosscut. The substrate for this evaluation is ACT Cold Rolled Steel Bonderite 1000 Parcolene 60. In this test, the film is cast over a metal substrate and allowed to cure for 7 days. After that time, the film is scored using a 5x5 grid. Pressure tape is then firmly adhered to the area and pulled off at a 90° angle from the substrate. The adhesion is rated by assessing how much of the coating has been removed by the tape. Coating performance is considered inferior if a substantial amount of the coating appears on the tape.

Water Resistance

In many industrial coating applications, the film is exposed to outdoor elements such as rain. This exposure to water can cause degradation in the coating; therefore, water exposure can help to predict the service life of the coating itself. Water resistance can be evaluated following ASTM D870-09, "Standard Practice for Testing Water Resistance of Coatings Using Water Immersion."

The substrate for this evaluation is ACT Cold Rolled Steel Bonderite 1000 Parcolene 60. The coating should be cast onto a metal substrate and allowed to dry for seven days. After that time, the panel is placed three-quarters of the way into a water bath at 38 °C. After three days, the panels are removed from the water bath and evaluated for surface defects and blistering. The less deformation of the coating surface, the better the result.

RESULTS AND DISCUSSION

High-solids Solventborne Alkyd Case Study

The formulation that was tested for a high-solids solventborne alkyd at 275g/L VOC was based on an oil-modified urethane resin from Polynt-Reichhold, UROTUF F275-M-75. This resin is primarily used in an interior wood-floor finishes, so adhesion and water resistance were not tested. The starting point formulation utilized a standard cobalt-containing drier package (*Table 2*) that suffered from slow drying times and yellow undertone. Using the process described above, the formulation was optimized at 1.0% Borchi® Dragon HPC on resin solids. Utilizing one HPC instead of the three drying components in the standard drier package resulted in a much simpler formulation.

The primary benefit delivered from this optimization was a decrease in TD time from 8.5 hours, with the cobalt control drier package, to 3.1 hours with 1.0% Borchi Dragon on resin solids (*Figure 3*), resulting in a 63% reduction in dry time. The same trend was observed with LOD testing, where the HPC formulation was 41% faster than the cobalt-containing formulation (*Figure 4*).

A secondary benefit was reduced yellowing (*Figure 5*). The original cobalt-containing formulation had an

TABLE 2—UROTUF F275-M-75 Cobalt Control and Optimized HPC Drier Formulations

High-Solids Solventborne Alkyd Formulation				
Supplier	**Function**	**Material**	**Cobalt Control**	**1% Borchi Dragon HPC**
Polynt-Reichhold	*Oil-Modified Urethane Resin*	**UROTUF F275-M-75**	68.31	68.31
Klean Strip	*Solvent*	**Mineral Spirits**	15.67	15.67
Borchers	*Cobalt Drier*	**12% Cobalt Hex-Cem**	1.06	0.00
Borchers	*Chelating Agent*	**Dri-RX HF**	2.73	0.00
Borchers	*Anti-Skinning Agent*	**Skino #2**	1.71	0.00
Dow Inc.	*Solvent*	**DOWSIL 244 Fluid**	15.02	15.02
Borchers	*High-Performance Catalyst*	**Borchi Dragon**	0.00	0.51
		Total Weight	105.50	100.51

FIGURE 3—Dry-time Comparison for High-solids Solventborne Alkyd Formulation

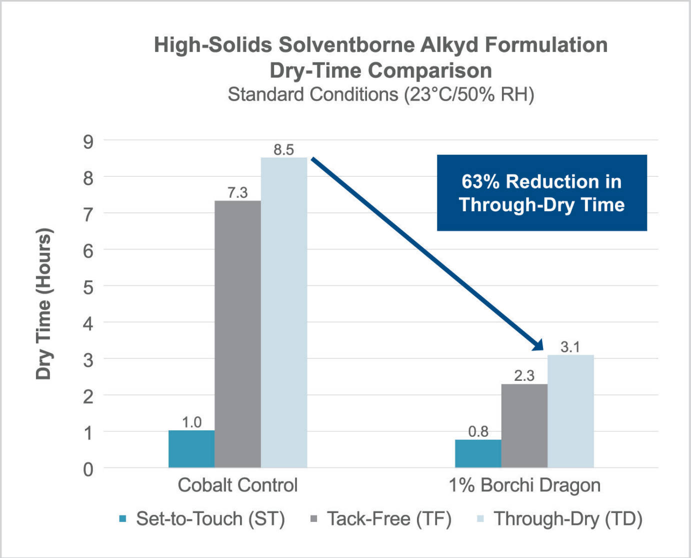


FIGURE 4—LOD Comparison for High-solids Solventborne Alkyd Formulation

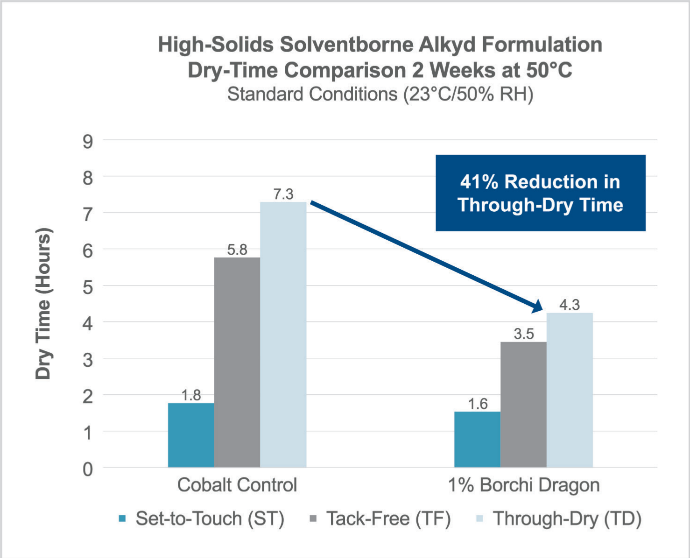
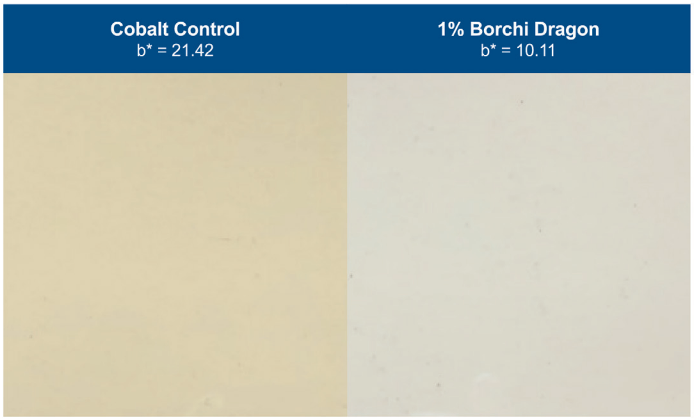


FIGURE 5—Drawdown Over White Background for High-solids Solventborne Alkyd Formulation



extremely yellow undertone that is undesirable in clear wood coatings. In the example, a 3-mil film was applied with a drawdown bar over a transparent mylar substrate. When placed over a white background, the b* value for the cobalt-containing control was 21.42 units. By optimizing the HPC formulation, the yellowness was substantially decreased by 10 units.

Hardness, the last parameter observed, is critical in wood coatings. *Figure 6* shows that the HPC formulation had a similar hardness profile at 1, 3, and 7 days. This demonstrates coating performance properties were maintained when switching from cobalt to 1.0% Borchi Dragon HPC.

Water-reducible Alkyd Case Study

The water-reducible alkyd formulation (*Table 3*) was based on YPWA-01W70, a Yoo-Point resin from China. The control utilized a combination drier containing cobalt and other metals. The formulation was optimized using Borchi OXY-Coat 1101 HPC at 1.0% on resin solids.

FIGURE 6—Hardness Development for High-solids Solventborne Alkyd Formulation

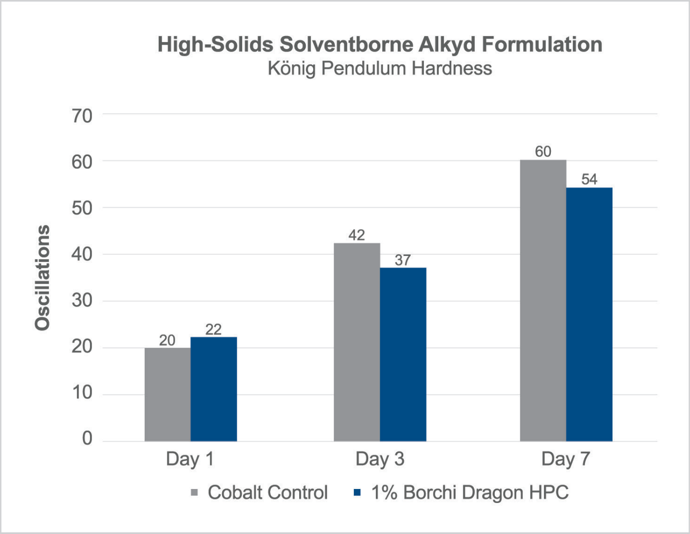


TABLE 3—YPWA-01W70 Cobalt Control and Optimized HPC Drier Formulations

Water-Reducible Alkyd Formulation				
Supplier	**Function**	**Material**	**Cobalt Control**	**1% Borchi OXY-Coat 1101 HPC**
Borchers	*Pigment Dispersant*	**Borchi Gen 1252**	0.63	0.63
N/A	*Solvent*	**Deionized Water**	8.25	8.25
Angus	*Amino Alcohol*	**AMP-95**	0.06	0.06
Borchers	*Defoamer*	**Borchers AF 1171**	0.06	0.06
LB Group	*Titanium Dioxide Pigment*	**Lomon R-996**	21.00	21.00
Grind to Hegman 7				
Yoo-Point	*Waterborne Alkyd Modified Acrylic*	**YPWA-01W70**	35.00	35.00
Angus	*Amino Alcohol*	**AMP-95**	0.14	0.14
N/A	*Solvent*	**Deionized Water**	34.72	34.72
Borchers	*Rheology Modifier*	**Borchi Gel 0620**	0.14	0.14
TOD	Cobalt-Containing Combination Drier	**WD016**	0.25	0.00
Borchers	*High-Performance Catalyst*	**Borchi OXY-Coat 1101**	0.00	0.25
		Total Weight	100.25	100.25

There were several benefits found through this optimization, including adhesion and water resistance. As most water-reducible coatings are used in the industrial sector, these are two vital parameters. *Figure 7* shows a 7-day dry adhesion comparison between the cobalt-containing drier package and the HPC drier package. The tape removed less of the HPC-containing coating compared to the cobalt-containing formulation, showing improved performance of the coating.

A similar trend was observed for water resistance, in which the HPC formulation showed better performance (*Figure 8*). The example below was tested 7 days after applying the coating and was soaked for 3 days. By using an optimized HPC formulation, the performance properties of the final coating were improved, as evidenced

FIGURE 7—7-Day Dry-adhesion Comparison for Water-reducible Alkyd Formulation

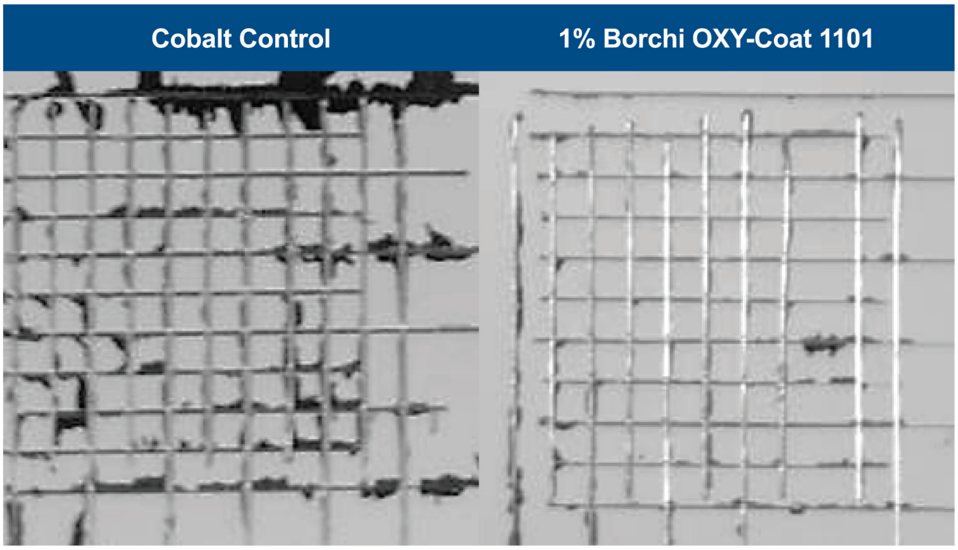
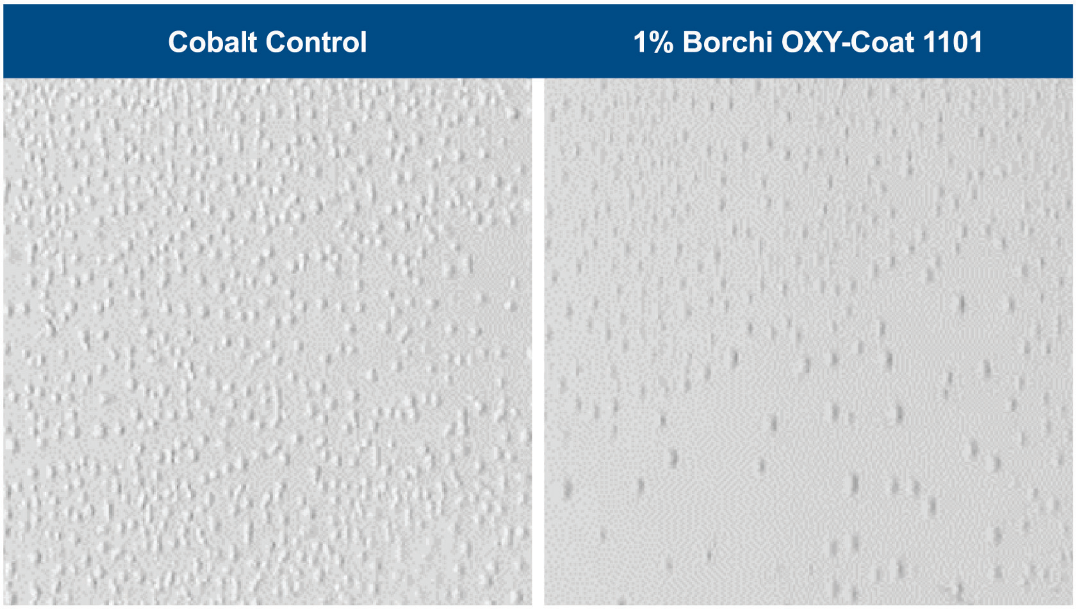


FIGURE 8—7-Day Dry, 3-Day Water-soak Comparison for Water-reducible Alkyd Formulation



by a reduction in film defects and blistering.

Dry times (*Figure 9*) for both the cobalt-containing and HPC formulations were equivalent. The TD time was approximately 6 hours. There was a slight improvement of 0.3 hours observed with the HPC control, but it was not significant. The same results were seen in LOD testing (*Figure 10*) where the dry times were equal with cobalt and 1.0% HPC.

Color (*Figure 11*) for both formulations was very similar. The b* value for both coatings was about 2 units with the HPC formulation having a 0.06 unit lower value. A difference this small is not observable with the human eye.

The sample with 1.0% Borchi OXY-Coat had lower hardness at both 1 day and 7 days compared to cobalt (*Figure 12*). Day 3 hardness was not evaluated for these formulations.

FIGURE 9—Dry-time Comparison for Water-reducible Alkyd Formulation

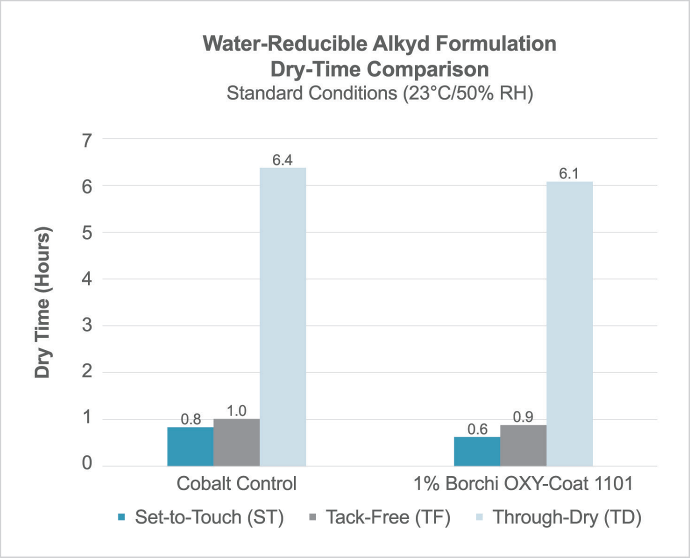


FIGURE 10—LOD Comparison for Water-reducible Alkyd Formulation

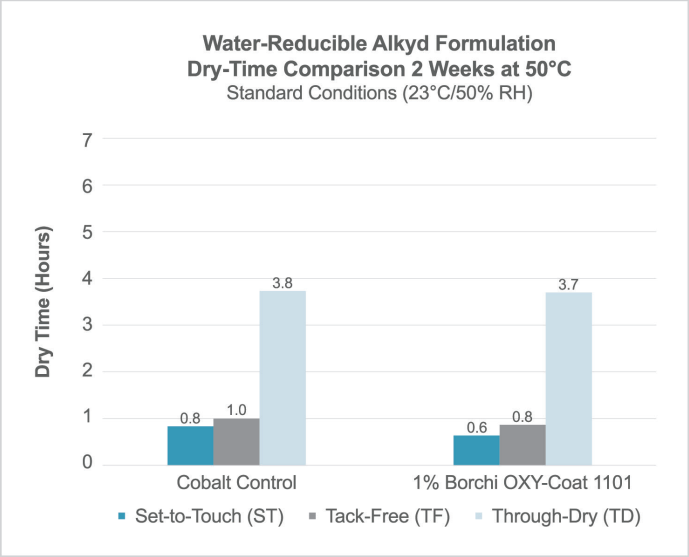


FIGURE 11—Drawdown Over Black Leneta for Water-reducible Alkyd Formulation

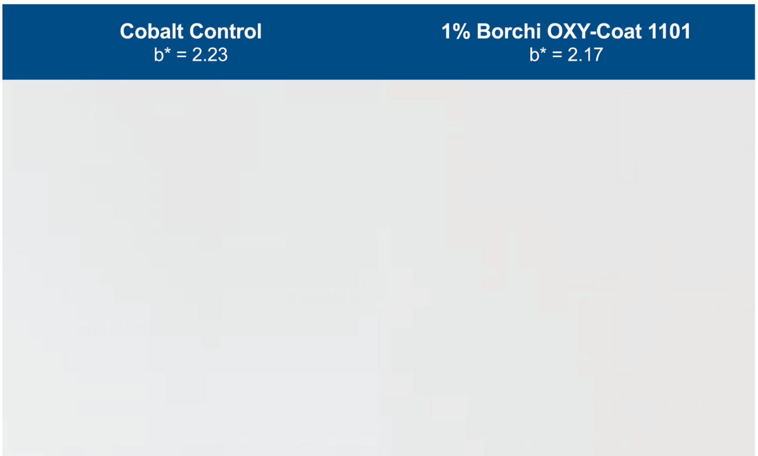


FIGURE 12—Hardness Development for Water-reducible Alkyd Formulation

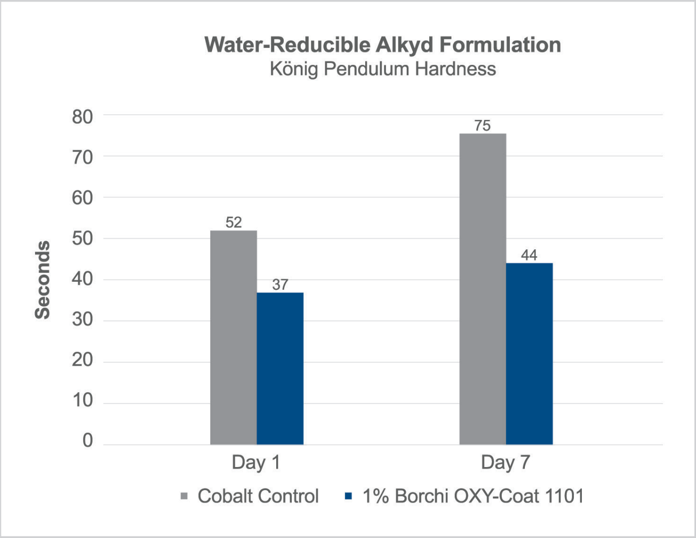
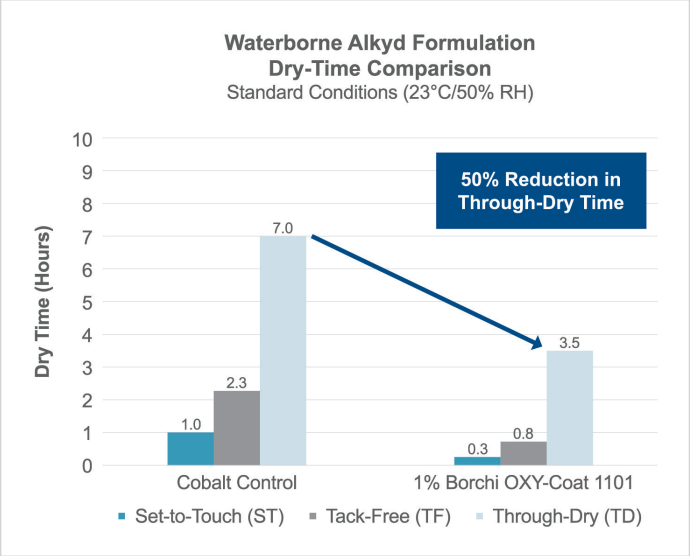


TABLE 4—Uradil AZ-760 Cobalt Control and Optimized HPC Drier Formulations

Waterborne Alkyd Formulation				
Supplier	**Function**	**Material**	**Cobalt Control**	**1% Borchi OXY-Coat 1101 HPC**
N/A	*Solvent*	**Deionized Water**	5.53	8.36
Borchers	*Defoamer*	**Borchers AF 1171**	0.11	0.11
Dow Inc.	*Rheology Modifier*	**Acrysol RM 8W**	0.47	0.47
Angus	*Amino Alcohol*	**AMP-95**	0.02	0.02
BYK	*Dispersant*	**DISPERBYK-190**	3.64	0.00
Borchers	*Dispersant*	**Borchi Gen 1252**	0.00	1.45
Venator	*Titanium Dioxide Pigment*	**Tioxide TR90**	25.96	25.96
Covestro Coating Resins	*Waterborne Alkyd Emulsion*	**Uradil AZ-760**	56.13	56.13
N/A	*Solvent*	**Deionized Water**	4.63	4.63
Grind to Hegman 7				
Borchers	*Cobalt-Containing Combination Drier*	**Octa-Soligen 421 Aqua**	0.65	0.00
N/A	*Solvent*	**Deionized Water**	0.65	0.00
Troy Corporation	*Wetting Additive*	**Troysol LAC**	0.09	0.09
Borchers	*Flow and Leveling Additive*	**Borchi Gol 1570**	0.14	0.14
ICL Phosphate Specialty	*Corrosion Inhibitor*	**Halox 570**	2.46	2.46
Dow Inc.	*Rheology Modifier*	**Acrysol RM-2020**	0.17	0.17
Borchers	*High-Performance Catalyst*	**Borchi OXY-Coat 1101**	0.00	0.30
		Total Weight	100.65	100.30

FIGURE 13—Dry-time Comparison for Waterborne Alkyd Formulation



Waterborne Alkyd Case Study

The waterborne alkyd formulation at 13.46 g/L VOC was based on Covestro Coating Resins' Uradil AZ-760 medium oil soybean alkyd emulsion based on soybean fatty acids. The starting point formulation utilized a cobalt-containing combination drier that included additional metals. This formulation was optimized using Borchi Gen 1252 pigment dispersant and 1.0% Borchi OXY-Coat 1101 on resin solids (*Table 4*). Adhesion was not evaluated for these formulations. The benefits observed in this optimization included faster dry times, improved LOD, reduced yellowing, and enhanced water resistance. The sample with 1.0% Borchi OXY-Coat 1101 had lower hardness compared to cobalt.

The initial TD time of the starting point formulation was 7.0 hours; by optimizing the formulation, the dry time was cut in half to 3.5 hours (*Figure 13*). This trend was maintained on heat age stability, where the TD time on LOD with HPC was half of the TD time with cobalt (*Figure 14*).

An additional benefit provided to the final coating formulation included a 1.5-unit reduction in b* value, which resulted in a brighter, cleaner white paint color (*Figure 15*).

Hardness development with HPC was slightly lower compared to the cobalt-containing formulation (*Figure 16*). This trend was consistently observed at 1, 3, and 7 days.

Finally, water resistance was greatly improved, showing almost no deformation or blistering with the HPC-optimized formulation (*Figure 17*). This test was performed seven days after applying the coating and soaked for 24 hours in water.

CONCLUSION

Health and environmental hazards related to VOCs have resulted in stringent regulations enacted by governments and environmental agencies. The growth in public awareness regarding environmental effects and health issues is driving the demand for low-VOC paints and coatings. To meet these increasingly rigorous regulations, there are three paths that formulators

FIGURE 14—LOD Comparison for Waterborne Alkyd Formulation

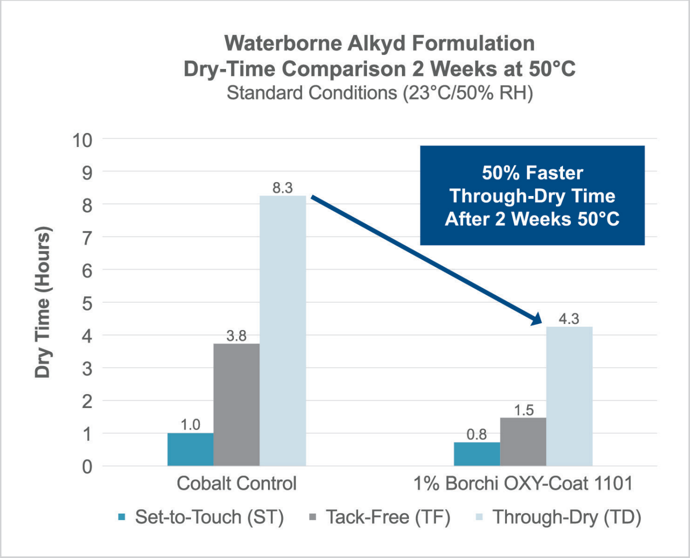


FIGURE 15—Drawdown over Black Leneta for Waterborne Alkyd Formulation

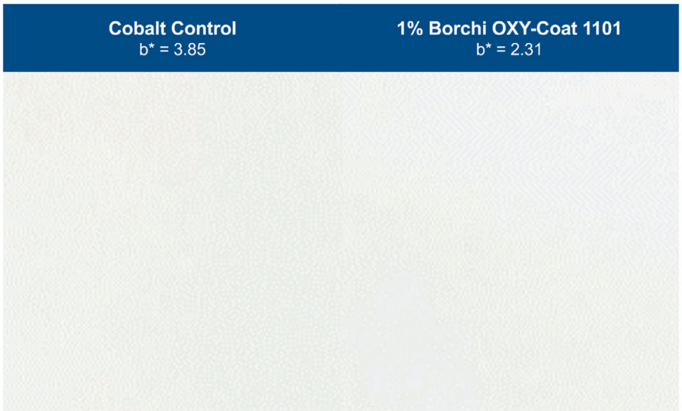


FIGURE 16—Hardness Development for Waterborne Alkyd Formulation

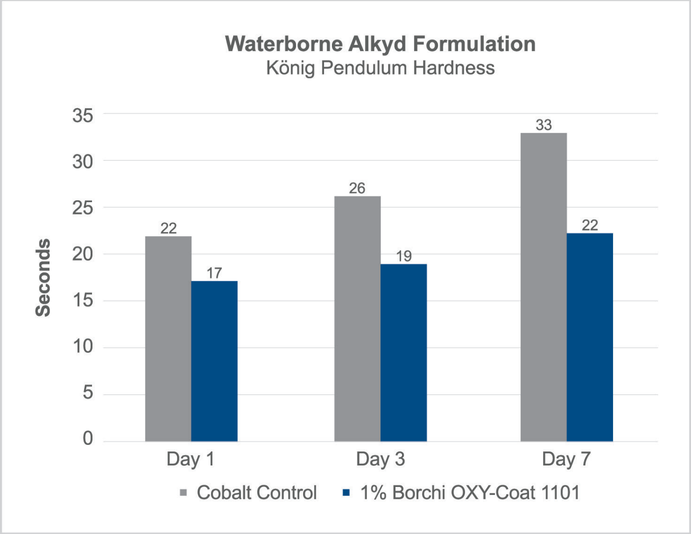
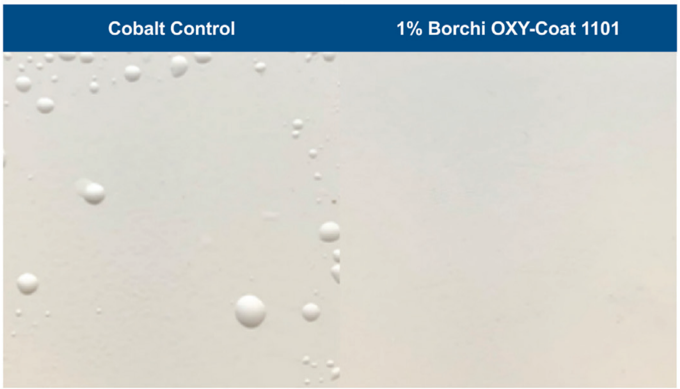


FIGURE 17—7-Day Dry, 3-Day Water-soak Comparison for Waterborne Alkyd Formulation



can choose when working with alkyd coatings: 1) high-solids solventborne, 2) water-reducible, and 3) waterborne.

These three formulating paths face various challenges, including long dry times, reduced shelf life, wrinkling, and increasing formulation complexity. Utilizing HPCs helps overcome these challenges in low-VOC alkyd coatings. The results from the HPC-containing alkyd formulations discussed in this article demonstrate that formulators can achieve their low-VOC targets while maintaining paint quality and meeting customer demands. ❊

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