EXPANDED APPLICATIONS AND
Alkyd Coatings Using High-

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> This article shows that advanced high-performance catalysts can improve almost all performance criteria of an alkyd-based coating.

Introduction

Alkyd-based coatings cure via both physical and chemical drying processes. The natural drying time of an alkyd can be weeks to months, which is not desirable from a practical point of view. In practice, the chemical crosslinking process is accelerated using catalysts, commonly referred to as driers. Generally, these are transition metal complexes with organic ligands. The most widely known and commonly used driers are based on cobalt carboxylates. While cobalt driers lead to highly crosslinked hard films, cobalt-based siccatives have recently faced reclassification as class 1b carcinogens by the Cobalt REACH consortium,[1] a nonprofit group tasked with preparing the registration dossiers

ENHANCED DURABILITY OF

-Performance Catalysts

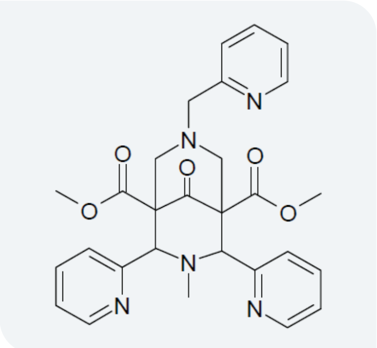
for cobalt and cobalt compounds. As a carcinogen, cobalt that is used to cure coatings and inks can be a risk to human health as humans can be in frequent contact with these substances (especially when applying paints or scraping off old paint layers). Many regions recognize that the use of cobalt in this industry must be reduced as part of a movement toward a sustainable future.

The two leading technologies to replace cobalt driers are based on either manganese or iron. Manganese carboxylates (Mn^{3+}) have long been known to exhibit good drying activity, although generally to a somewhat lesser degree than that observed with cobalt. Furthermore, the formation of Mn^{3+} species often leads to a brown coloration of the formulation, which precludes its use at high levels or in light-colored coatings.

Most iron driers show poor activity, especially in relation to cobalt or manganese analogs at ambient temperatures. Iron carboxylates work well at high temperatures and are often used in stoving enamels where curing occurs at 80–250 °C. Iron has a distinct yellow-brown color that can lead to significant discoloration in light-colored formulations as well.

An exception to this is the recent invention of an iron-bispidon complex (**Figure 1**), which shows vastly improved catalytic activity at very low iron weight percentages (wt %).[2] For example, in a medium-oil alkyd resin, the level of iron needed to obtain a good level of curing activity can be reduced

FIGURE 1
Bispidon structure, dimethyl 3-methyl-9-oxo-2,4-di(pyridin-2-yl)-7-(pyridin-2-ylmethyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate.



from 0.08 wt % on resin solids, a typical drier loading for many formulations, to 0.0007 iron wt % on resin solids.[3] As a result of this low dosage, color intensity in a paint formulation is greatly reduced, often to a level below that of cobalt-based coatings.

Fe-bispidon complexes have emerged as a preeminent cobalt alternative for the drying of waterborne and solventborne alkyd paints. Due to very high efficiency at low metal wt %, these complexes are often referred to as High-Performance Catalysts (HPC). When tested in model systems, HPCs often provide superior performance in drying speed as well as many physical coating properties when compared with cobalt-based driers.[4-6] While model systems provide valuable insight into the underlying chemistry, the goal in this study was to understand the effect of HPCs on the chemistry and coating properties of real-world alkyd paint formulations made with industry-leading resins. A series of experiments was conducted to determine the optimum dosage of HPCs for four commercially available alkyd emulsions using representative formulations of the types used in architectural trim paints. These formulations were then evaluated in an array of standard industry tests versus equivalent cobalt-catalyzed formulations. Differences in the types and levels of chemical crosslinks were studied through Fourier Transform Infrared (FTIR) spectroscopy experiments on cured films. Possible variations in the β-scission reaction pathway were evaluated through gas chromatography/mass spectroscopy (GC/MS).

Finally, to demonstrate the relevance of these formulations for architectural trim applications, a section of popular commercial alkyd and acrylic paints was benchmarked and compared.

Materials and Methods

Coatings were applied at a wet thickness of 4 mils (100 µm) / dry film thickness of 2 mils (50 µm) using a standard drawdown bar unless otherwise noted. Cobalt-catalyzed formulations were used as controls, and as such, the cobalt-loading levels and use of additional additives such as zirconium, calcium, or other organic accelerators were taken from recommendations by the requisite resin suppliers and were thus assumed to be at or near optimal levels. Optimal loading levels for HPCs were determined experimentally through ladder studies for each resin and were based on additive wt % on resin solids.

Dry Times

Dry times were determined over a Mylar® substrate using Gardco circular dry-time recorders set to 24-hour durations. Set-to-touch (ST) time is defined as the point where the stylus no longer leaves a clean, smooth line through the coating surface. Tack-free (TF) time is defined as the point where the stylus no longer ruptures or tears the film. Through-dry (TD) time is defined as the point where the coating is no longer marked or indented by the stylus. Dry-time testing was conducted in duplicate, and the final values reported were the average of two measurements.

Hardness Testing

Coating hardness was determined over a glass substrate via a TQC Pendulum Hardness Tester using the König method described in ISO 1522. Each measurement was taken three times, and the final value was the average of those measurements rounded to the nearest whole number.

Scrub Testing

Scrub testing was conducted using the cycles-to-failure method reported in ASTM D2486 via a TQC Washability tester using 6½” x 17” black Leneta scrub panels.

Washability Testing

Washability testing was conducted following the method reported in ASTM D3450 via a TQC Washability tester using 6 ½” x 17” white Leneta scrub panels. Stains were applied in a 1” stripe perpendicular to the direction of cleaning and allowed to age for one day prior to cleaning. Panels were exposed to 100 total cycles with non-abrasive media reapplied every 25 cycles. Color values were measured using an X-rite MA9X Spectrophotometer, and results were reported as the difference in ΔE between the unstained coating and the cleaned area.

Blocking Test

A blocking test was conducted according to ASTM D4946 using sealed Leneta test charts at a wet film thickness of 6 mils (150 µm).

Corrosion Testing

Corrosion resistance was evaluated according to ASTM B117 using a Singleton Salt Spray Chamber. Films were cast onto 3” x 6” cold-rolled steel panels at a wet film thickness of 4 mils (100 µm) and cured for 7 days prior to being placed into the chamber. They were removed after 120 hours and evaluated.

TABLE 1
Resins Used in Trim Paint Formulations

Polymer Type	Chemistry	Applications
Resin 1—Alkyd Emulsion	Short Oil	High-gloss trim paints, wall and ceiling paints, light industrial, direct-to-metal, wood stains
Resin 2—Alkyd Emulsion	Medium Oil	Interior and exterior architectural enamels, decorative finishes
Resin 3—Alkyd Emulsion	Medium Oil	High-gloss trim paints, wall and ceiling paints, light industrial, direct-to-metal, wood stains
Resin 4—Alkyd Emulsion	Polyurethane-Modified	High-gloss trim paints, interior and exterior architectural enamels
Resin 5—Acrylic Emulsion	Styrene Acrylic	High-gloss trim paints, wall and ceiling paints, light industrial, direct-to-metal, wood stains

Accelerated Weathering

Accelerated weathering testing was conducted following ASTM D4787 using a Q-Lab QUV Accelerated Weathering Tester. Films were cast onto 3" x 6" aluminum panels at a wet film thickness of 4 mils (100 µm) and allowed to cure for 7 days prior to being placed into the chamber. Exposure time was 336 hours at 0.89 W/(m^2·nm) at a wavelength of 340 nm. Gloss and color measurements were made after the panels were removed and compared against their initial values.

GC/MS

Coating samples were analyzed by thermal desorption GC-MS for differences in volatiles such as aldehydes, hydrocarbons, and ketones. 100 mg samples were allowed to cure for 24 hours in aluminum pans. The pans were then transferred to a MicroChamber apparatus held at 65 °C with a 100 mL/min flow of nitrogen. The effluent was sampled for 15 minutes with a Tenax TA thermal desorption tube. The tube was then swapped for a 2,4-DNPH cartridge and sampled for 30 minutes. The Tenax tubes were analyzed by GC-MS for general volatiles, and the DNPH cartridges were eluted with acetonitrile and analyzed by UPLC-MS for aldehydes and ketones.

FTIR Testing

Films were cast onto 3" x 6" aluminum panels at a wet film thickness of 4 mils (100 µm) and allowed to cure for 7 days. Samples were then analyzed using a Perkins-Elmer Spectrum 2 FTIR with a diamond crystal.

Discussion and Results

Five waterborne resins were chosen to create industry-relevant architectural trim paint formulations (**Table 1**). The optimized formulations based on HPC are listed in **Table 2**, and formulations based on cobalt-catalysts and an acrylic resin are listed in **Table 3**.

TABLE 2
Optimized High-Performance Catalyst (HPC) Formulations

Material	wt %			
	Resin 1	Resin 2	Resin 3	Resin 4
Grind				
D.I. water	12.35	12.16	12.35	11.65
HEUR*—High Shear	3.10	3.00	2.50	2.20
HEUR—Mid Shear	1.55	0.50	0.70	0.50
Dispersant	0.77	0.75	0.75	0.70
2-Amino-2-methyl-1-propanol	0.03	0.03	0.03	0.03
Rutile TiO_2	21.60	24.00	23.50	24.00
Nepheline syenite	7.20	7.00	7.70	4.20
Letdown				
Resin	52.00	51.00	51.00	55.30
HPC	0.40	0.40	0.30	0.42
12% Zirconium carboxylate	1.00	1.16	1.17	1.00

*Hydrophobically modified ethylene oxide urethane

TABLE 3
Optimized Cobalt and Acrylic Formulations

Material	wt %				
	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5
Grind					
Deionized water	12.35	12.16	12.35	11.65	15.00
HEUR—High Shear	3.10	3.00	2.50	2.20	0.75
HEUR—Mid Shear	1.55	0.50	0.70	0.50	0.30
Dispersant	0.77	0.75	0.75	0.70	0.75
2-amino-2-methyl-1-propanol	0.03	0.03	0.03	0.03	0.03
Rutile TiO_2	21.60	24.00	23.50	24.00	23.50
Nepheline syenite	7.20	7.00	7.70	4.20	4.00
Letdown					
Resin	52.00	51.00	51.00	55.30	51.00
5% Cobalt carboxylate	0.23	0.23		0.23	
12% Zirconium carboxylate	0.245	0.245		0.245	
Combination drier Co: 2.5%, Zn: 2.5%, Zr: 6%			0.575		
2,2'-Bipyridyl (30%)	0.05	0.05		0.05	
Glycol ether DPnB					2.50
Flash-rust inhibitor					0.20

FIGURE 2
Dry times for paint formulations in standard conditions (23 °C and 50% relative humidity). ST = Set-to-touch, TF = Tack-free, TD = Through-dry.

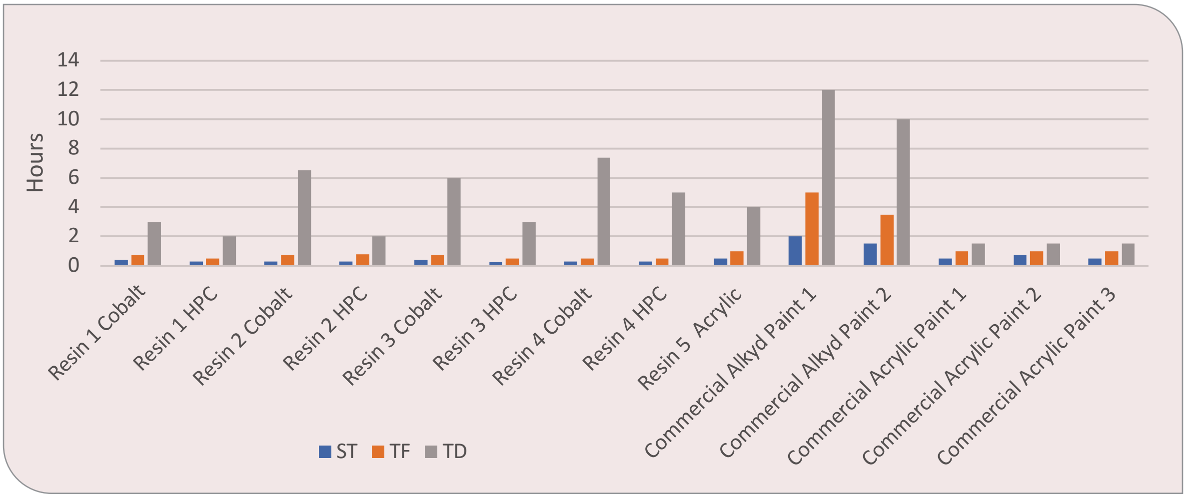


FIGURE 3
Dry times for paint formulations in adverse conditions (10 °C and 80% relative humidity). ST = Set-to-touch, TF = Tack-free, TD = Through-dry.

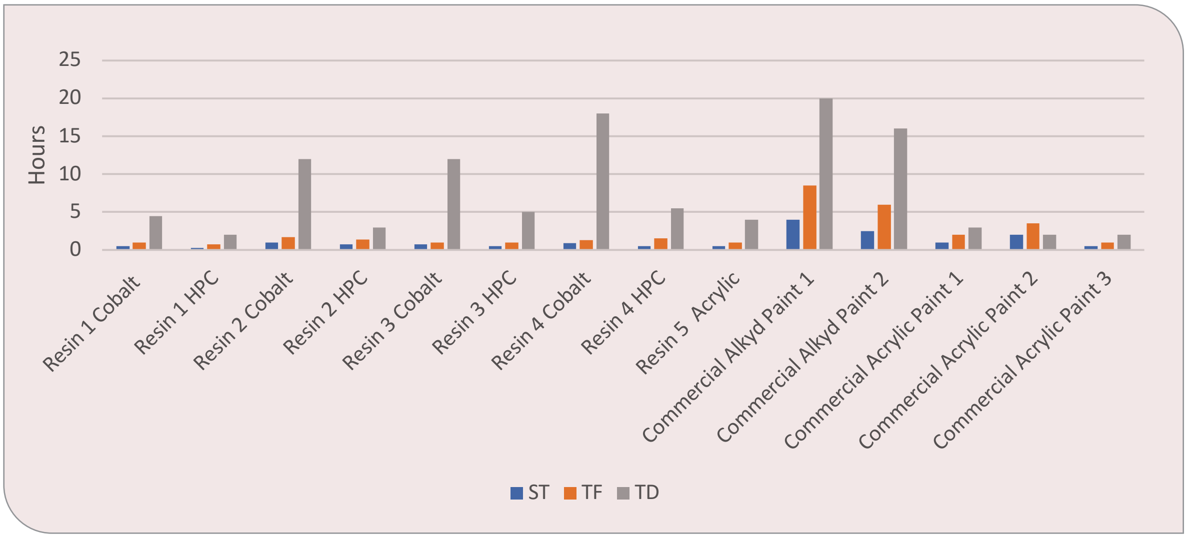
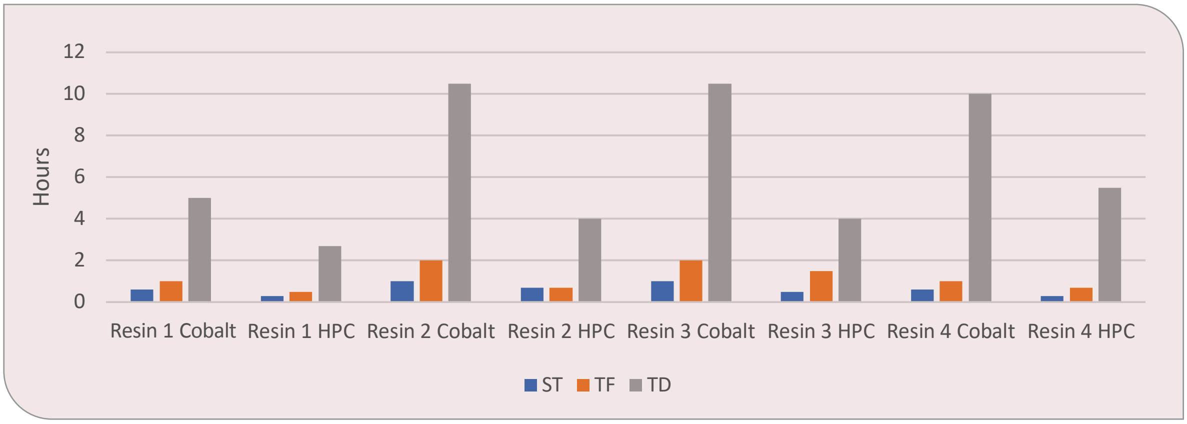


FIGURE 4
Dry times for alkyd formulations in standard conditions (23 °C and 50% relative humidity) after 14 days of heat aging at 50 °C. ST = Set-to-touch, TF = Tack-free, TD = Through-dry.



Dry times were tested for all systems under standard conditions (**Figure 2**). In this test, a clear advantage was evident for HPC-catalyzed coatings, which showed a 50–75% reduction in dry time compared with cobalt-catalyzed systems and commercial alkyd paints. In some cases, the dry time for HPC alkyds was similar to the acrylic products.

Dry times were also tested under adverse low-temperature, high-humidity conditions (**Figure 3**). HPC-catalyzed alkyds showed dry times that were 50–75% faster than comparable cobalt-catalyzed alkyds and again similar to the acrylic products.

Finally, the effect of heat aging was evaluated for cobalt- and HPC-catalyzed alkyds (**Figure 4**). The cobalt-based coatings showed a substantial increase in dry times, whereas the dry times for HPC systems were virtually unchanged.

A numerical summary of all dry-time testing can be seen in **Table 4**, which shows superior drying performance for HPC under all evaluated conditions.

The hardness of all coating systems was tested quantitatively using a König pendulum (**Figure 5** and **Table 5**). Overall, HPC was found to produce hard coatings with similar results to those produced using cobalt. The commercial products showed a range of different hardness values, likely corresponding to the glass transition temperatures of the source polymers.

TABLE 4
Dry Times in Hours for Evaluated Systems

Standard Conditions	DT	TF	TD	Adverse Conditions	DT	TF	TD	After Aging	DT	TF	TD
Resin 1 Cobalt	0.4	0.75	3.0	Resin 1 Cobalt	0.5	1	4.5	Resin 1 Cobalt	0.6	1.0	5.0
Resin 1 HPC	0.3	0.5	2.0	Resin 1 HPC	0.3	0.75	2.0	Resin 1 HPC	0.3	0.5	2.7
Resin 2 Cobalt	0.3	0.75	6.5	Resin 2 Cobalt	1.0	1.7	12	Resin 2 Cobalt	1.0	2.0	10.5
Resin 2 HPC	0.3	0.8	2.0	Resin 2 HPC	0.75	1.4	3.0	Resin 2 HPC	0.7	0.7	4.0
Resin 3 Cobalt	0.4	0.75	6.0	Resin 3 Cobalt	0.75	1	12	Resin 3 Cobalt	1.0	2.0	10.5
Resin 3 HPC	0.25	0.5	3.0	Resin 3 HPC	0.5	1	5.0	Resin 3 HPC	0.5	1.5	4.0
Resin 4 Cobalt	0.3	0.5	7.4	Resin 4 Cobalt	0.9	1.3	18	Resin 4 Cobalt	0.6	1.0	10.0
Resin 4 HPC	0.3	0.5	5.0	Resin 4 HPC	0.5	1.5	5.5	Resin 4 HPC	0.3	0.7	5.5
Resin 5 Acrylic	0.5	1.0	4.0	Resin 5 Acrylic	0.5	1.0	4.0				
Commercial Alkyd Paint 1	2.0	5.0	12	Commercial Alkyd Paint 1	4.0	8.5	20				
Commercial Alkyd Paint 2	1.5	3.5	10	Commercial Alkyd Paint 2	2.5	6.0	16				
Commercial Acrylic Paint 1	0.5	1.0	1.5	Commercial Acrylic Paint 1	1.0	2.0	3.0				
Commercial Acrylic Paint 2	0.75	1.0	1.5	Commercial Acrylic Paint 2	2.0	3.5	2.0				
Commercial Acrylic Paint 3	0.5	1.0	1.5	Commercial Acrylic Paint 3	0.5	1.0	2.0				

FIGURE 5
König hardness results for paint formulations conducted in standard conditions (23 °C and 50% relative humidity).

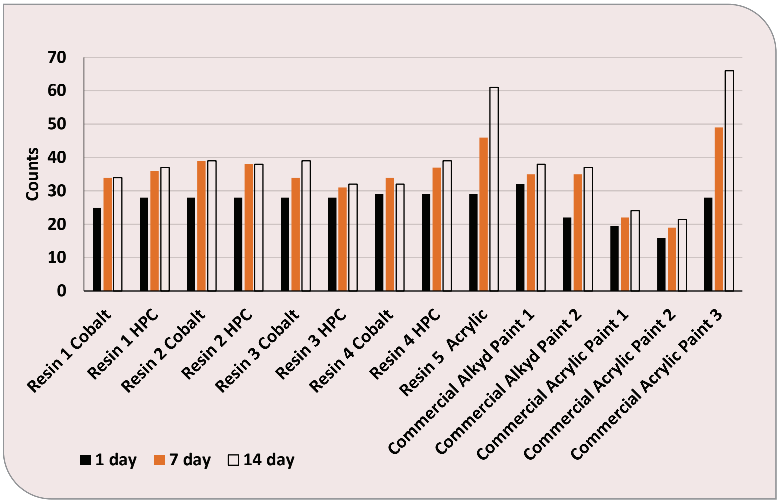


TABLE 5
König Hardness Results Conducted in Standard Conditions (23 °C and 50% Relative Humidity)

Standard Conditions	1 day	7 days	14 days
Resin 1 Cobalt	25	34	34
Resin 1 HPC	28	36	37
Resin 2 Cobalt	28	39	39
Resin 2 HPC	28	38	38
Resin 3 Cobalt	28	34	39
Resin 3 HPC	28	31	32
Resin 4 Cobalt	29	34	32
Resin 4 HPC	29	37	39
Resin 5 Acrylic	29	46	61
Commercial Alkyd Paint 1	32	35	38
Commercial Alkyd Paint 2	22	35	37
Commercial Acrylic Paint 1	20	22	24
Commercial Acrylic Paint 2	16	19	22
Commercial Acrylic Paint 3	28	49	66

FIGURE 6
Scrub testing results for paint formulations.

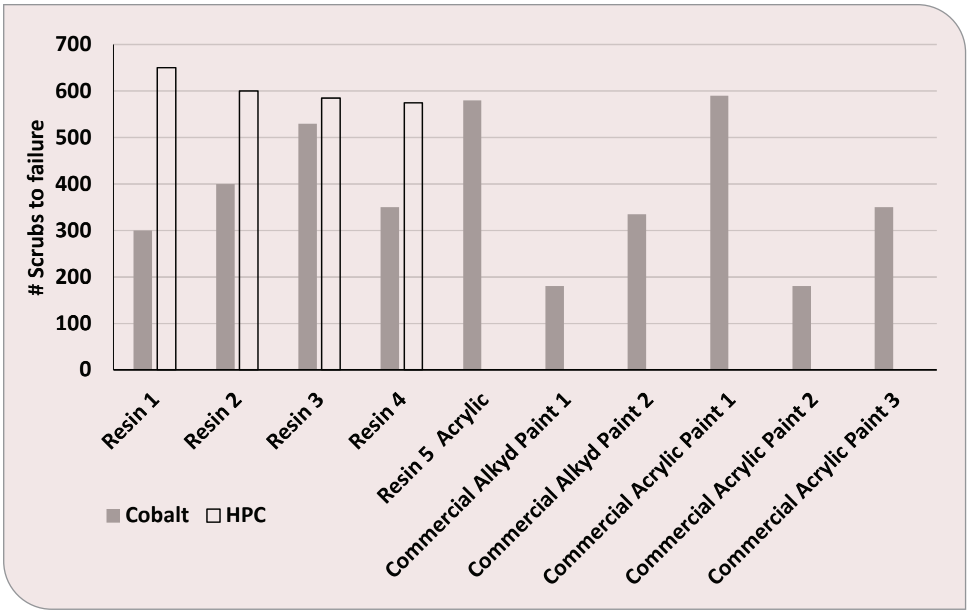


FIGURE 7
Washability testing results.

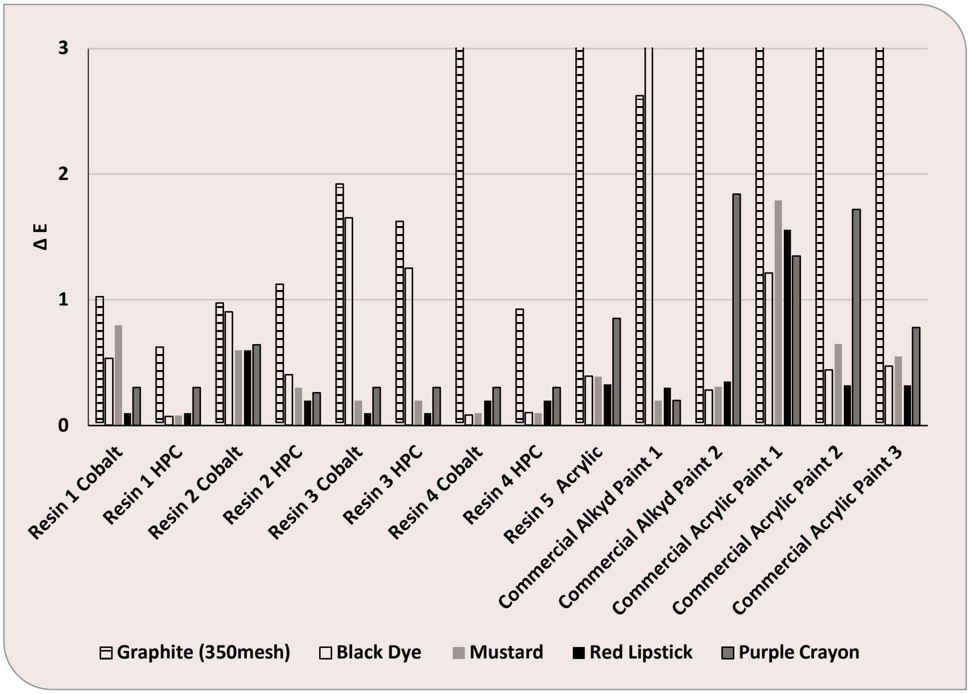


TABLE 6
Numerical Washability Results, ΔE

	Graphite (350 mesh)	Black Dye	Mustard	Red Lipstick	Purple Crayon
Resin 1 Cobalt	1	0.53	0.8	0.1	0.3
Resin 1 HPC	0.6	0.07	0.08	0.1	0.3
Resin 2 Cobalt	0.95	0.9	0.6	0.6	0.64
Resin 2 HPC	1.1	0.4	0.3	0.2	0.26
Resin 3 Cobalt	1.9	1.65	0.2	0.1	0.3
Resin 3 HPC	1.6	1.25	0.2	0.1	0.3
Resin 4 Cobalt	3.6	0.08	0.1	0.2	0.3
Resin 4 HPC	0.9	0.1	0.1	0.2	0.3
Resin 5 Acrylic	3.64	0.39	0.39	0.33	0.85
Commercial Alkyd Paint 1	2.6	7.8	0.2	0.3	0.2
Commercial Alkyd Paint 2	28.96	0.28	0.31	0.35	1.84
Commercial Acrylic Paint 1	22.94	1.21	1.79	1.56	1.35
Commercial Acrylic Paint 2	49.26	0.44	0.65	0.32	1.72
Commercial Acrylic Paint 3	12.97	0.47	0.55	0.32	0.78

Scrub testing illustrated the enhanced durability of HPC-catalyzed alkyds with improvements ranging from 10% to more than 100% (**Figure 6**). Additionally, HPC-cured coatings showed equal or greater performance than the commercial paints showed in most cases.

HPC-based coatings demonstrated enhanced washability and stain resistance when compared to what cobalt-catalyzed systems and commercial paints demonstrated (**Figure** 7 and **Table 6**). It is possible that some of the differences between the commercial paints and the experimental formulations were due to variances in formulation and gloss levels across different brands and manufacturers; the significant washability and scrub improvements observed in resins 1–5, in which formula composition and gloss level were identical (save the catalyst), indicate that the HPC improved durability performance.

Blocking tests showed no changes in performance based on the catalyst (**Figure 8**). All systems performed well, with the exception of the acrylic formulation (resin 5).

Accelerated weathering showed significant differentiation in yellowing and gloss retention across the different formulations and products. After 336 hours of QUV exposure, substantial yellowing was observed in all cobalt-catalyzed formulations as well as both commercial alkyd paints (**Figure 9** and **Table** 7). These coatings showed a strong increase in b* values, ranging from 1.5 to 5.5 units. Conversely, the HPC-based paints showed very little yellowing, ranging only from 0.3 to 0.5 units, very similar to the acrylic systems, which are typically known for lightfastness.

FIGURE 8
Blocking test results.

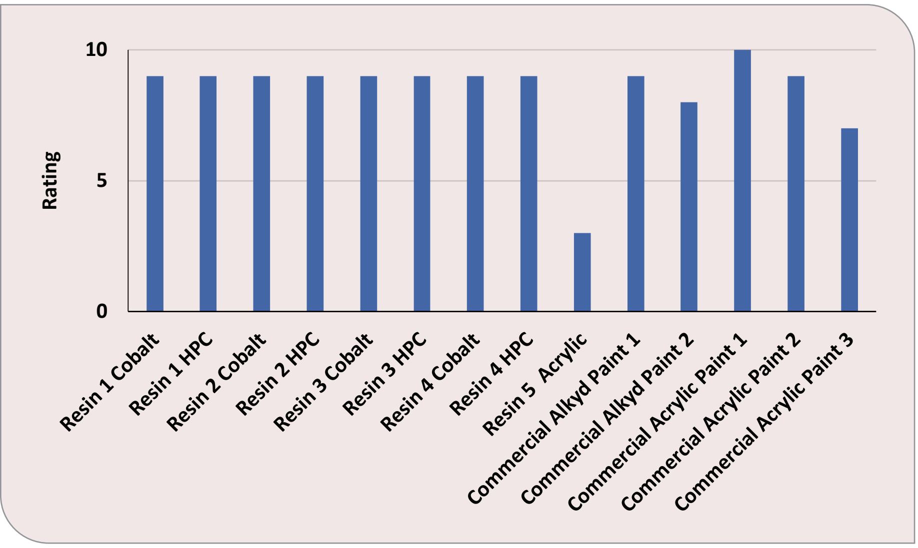


FIGURE 9
Yellowing after 336 hours QUV exposure represented by Δb*.

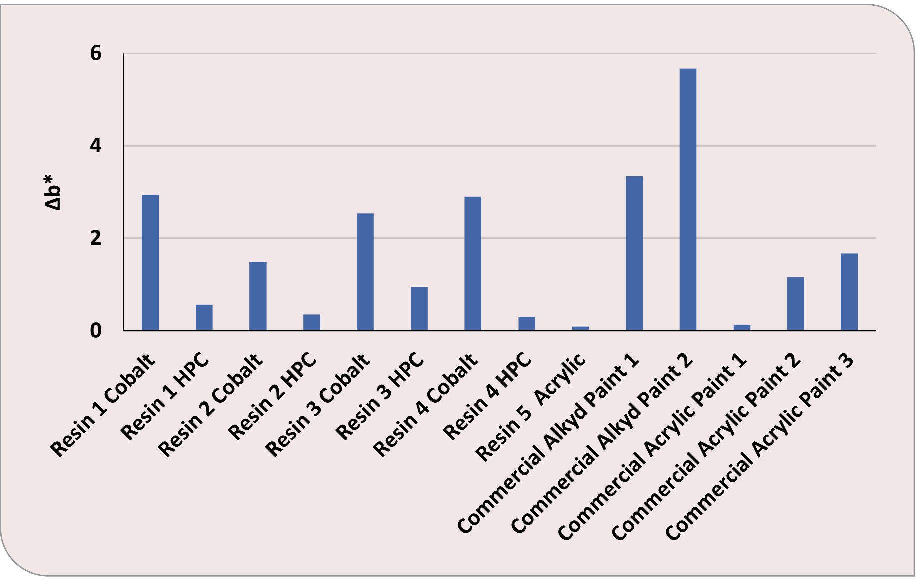


TABLE 7
b* Values After 336 Hours QUV Exposure

	b* initial	b* QUV	Δb*
Resin 1 Cobalt	-0.44	2.5	2.94
Resin 1 HPC	-1.56	-1.0	0.56
Resin 2 Cobalt	0.51	2.0	1.49
Resin 2 HPC	0.35	0.7	0.35
Resin 3 Cobalt	-0.74	1.8	2.54
Resin 3 HPC	-1.74	-0.8	0.94
Resin 4 Cobalt	-0.90	2.0	2.90
Resin 4 HPC	0.25	0.55	0.30
Resin 5 Acrylic	-0.36	-0.45	0.09
Commercial Alkyd Paint 1	-1.54	1.8	3.34
Commercial Alkyd Paint 2	0.17	5.84	5.67
Commercial Acrylic Paint 1	-0.54	-0.41	0.13
Commercial Acrylic Paint 2	-0.94	0.22	1.16
Commercial Acrylic Paint 3	-0.21	1.46	1.67

HPC provided a sizable improvement in corrosion resistance when compared with cobalt and the other systems. It showed reduced field corrosion, lower scribe creep, and less blistering.

Unsurprisingly, a similar trend was observed in gloss retention (**Figure 10** and **Table 8**). All cobalt-catalyzed systems and four out of the five commercial products showed significant gloss loss ranging from 11% to 36%. HPC-based coatings showed excellent gloss stability, losing only between 2% and 5% of their initial values.

Corrosion testing showed significant differentiation between HPC, cobalt, and the commercial paints (**Figure 11**). HPC provided a sizable improvement in corrosion resistance when compared with cobalt and the other systems. It showed reduced field corrosion, lower scribe creep, and less blistering. All commercial paints showed very poor corrosion protection regardless of resin chemistry. It should be noted that none of the experimental formulations used corrosion inhibitors of any kind, with the exception of the acrylic (resin 5), which required a flash-rust inhibitor.

To gain insight into possible sources for the observed difference in performance

FIGURE 10
Change in 60° gloss values after 336 hours QUV exposure.

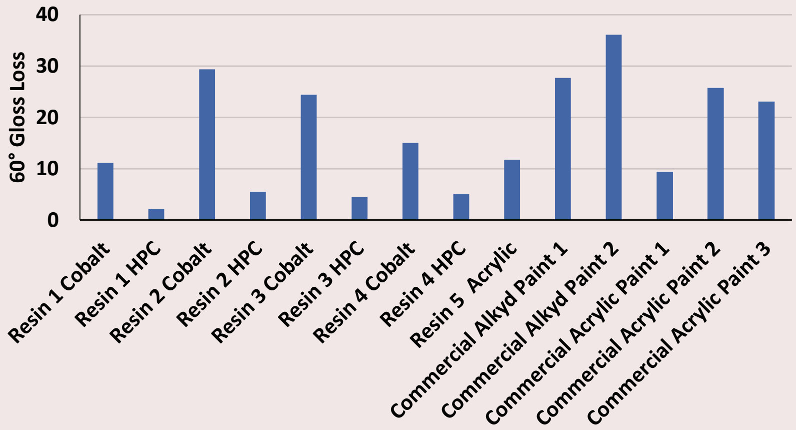
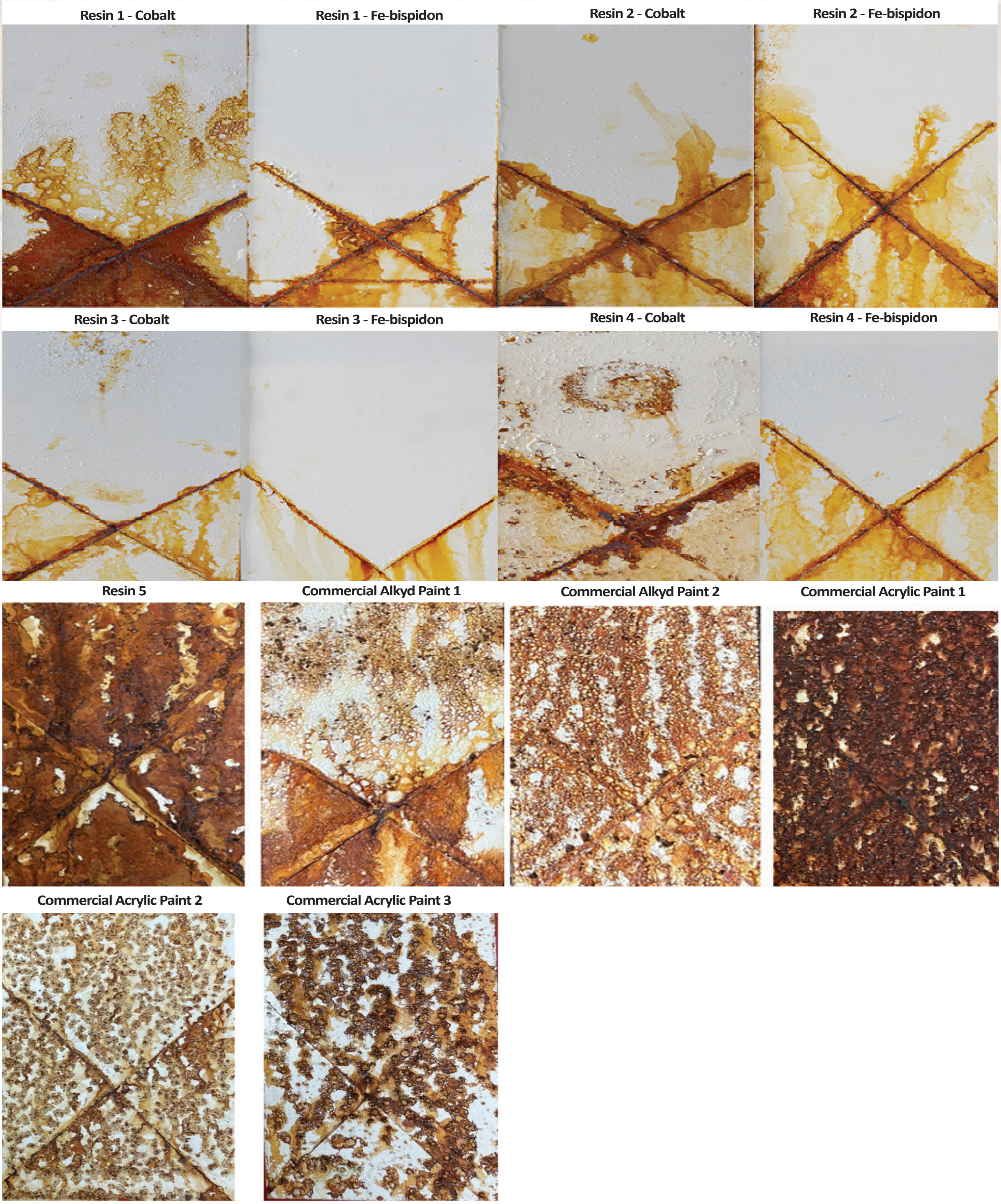


TABLE 8
60° Gloss Values After 336 Hours QUV Exposure

	Initial Gloss	Gloss after QUV	% Gloss Loss
Resin 1 Cobalt	45	40.0	11.1
Resin 1 HPC	45	44.0	2.2
Resin 2 Cobalt	46	32.5	29.3
Resin 2 HPC	46	43.5	5.4
Resin 3 Cobalt	45	34.0	24.4
Resin 3 HPC	45	43.0	4.4
Resin 4 Cobalt	48	40.8	15.0
Resin 4 HPC	48	45.6	5.0
Resin 5 Acrylic	51	45.0	11.8
Commercial Alkyd Paint 1	30	21.7	27.7
Commercial Alkyd Paint 2	33	21.1	36.1
Commercial Acrylic Paint 1	33	29.9	9.4
Commercial Acrylic Paint 2	45	33.4	25.8
Commercial Acrylic Paint 3	75	57.7	23.1

FIGURE 11
Corrosion results after 120 hours of salt-spray exposure.



Resin 1 - Cobalt

Resin 1 - Fe-bispidon

Resin 2 - Cobalt

Resin 2 - Fe-bispidon

Resin 3 - Cobalt

Resin 3 - Fe-bispidon

Resin 4 - Cobalt

Resin 4 - Fe-bispidon

Resin 5

Commercial Alkyd Paint 1

Commercial Alkyd Paint 2

Commercial Acrylic Paint 1

Commercial Acrylic Paint 2

Commercial Acrylic Paint 3

between coatings formulations that differ only in catalyst type, the chemical compositions of HPC- and cobalt-cured films were evaluated through FTIR spectroscopy. During auto-oxidation, the unsaturated fatty acids in alkyd paints react with molecular oxygen from the air to form alkyl hydroperoxides. Subsequent decomposition of these alkyl hydroperoxides yields alkoxy and per-oxy radicals.[7,8] Radical addition and recombination result in crosslinking, and eventually, extended networks are formed (**Figure 12**).[9]

In cobalt-catalyzed oxidation, carbon–carbon termination reactions are not usually observed; most often, ether or peroxide crosslinks are the prevailing termination result.[10,11]

The formation of carbonyl and ester groups can also occur from the combination of alkoxyl and hydroxy radicals or the oxidation of fatty acids.[12] For practical coating applications, ether, ester, and peroxide crosslinks are less desirable than carbon-carbon bonds. Peroxide crosslinks decompose slowly over time and can facilitate additional oxidation reactions, which lead to film embrittlement. Ester bonds are susceptible to hydrolysis and degradation through weathering. Ether crosslinks may show reduced chemical and abrasion resistance.

TABLE 9
Peak Heights and Peak Height Differences for Resin 1 and Resin 3 FTIR

Bond Type	C-C	C=O	C-O	C=C
	Absorbance			
Wavenumber	2,925	1,720	1,255	973
Resin 1—HPC	0.1014	0.3715	0.3853	0.0256
Resin 1—Cobalt	0.0864	0.3971	0.4102	0.0268
% Change HPC vs. Co	+14.80%	-6.90%	-14.50%	-4.70%
Resin 3—HPC	0.1013	0.4478	0.4609	0.0203
Resin 3—Cobalt	0.0887	0.4742	0.4778	0.0216
% Change HPC vs. Co	+12.40%	-5.90%	-3.70%	-6.40%

FTIR absorption spectra for resin 1 and resin 3 showed notable differences in peak heights for HPC- and cobalt-catalyzed films (**Table 9**, **Figures 13** and **14**).

At 2,925 cm^{-1}, which is attributed to a CH_2-CH_3 stretch, the HPC-catalyzed films showed a 12.4–14.8% greater peak height. At 1,720 cm^{-1} and 1,255 cm^{-1}, which are attributed to a C=O stretch and a C-O-C stretch, respectively, a reduction in peak height is observed in HPC-catalyzed films compared with cobalt. This may be

FIGURE 12
Model representation of the oxidative drying pathway for an alkyd polymer.[9]

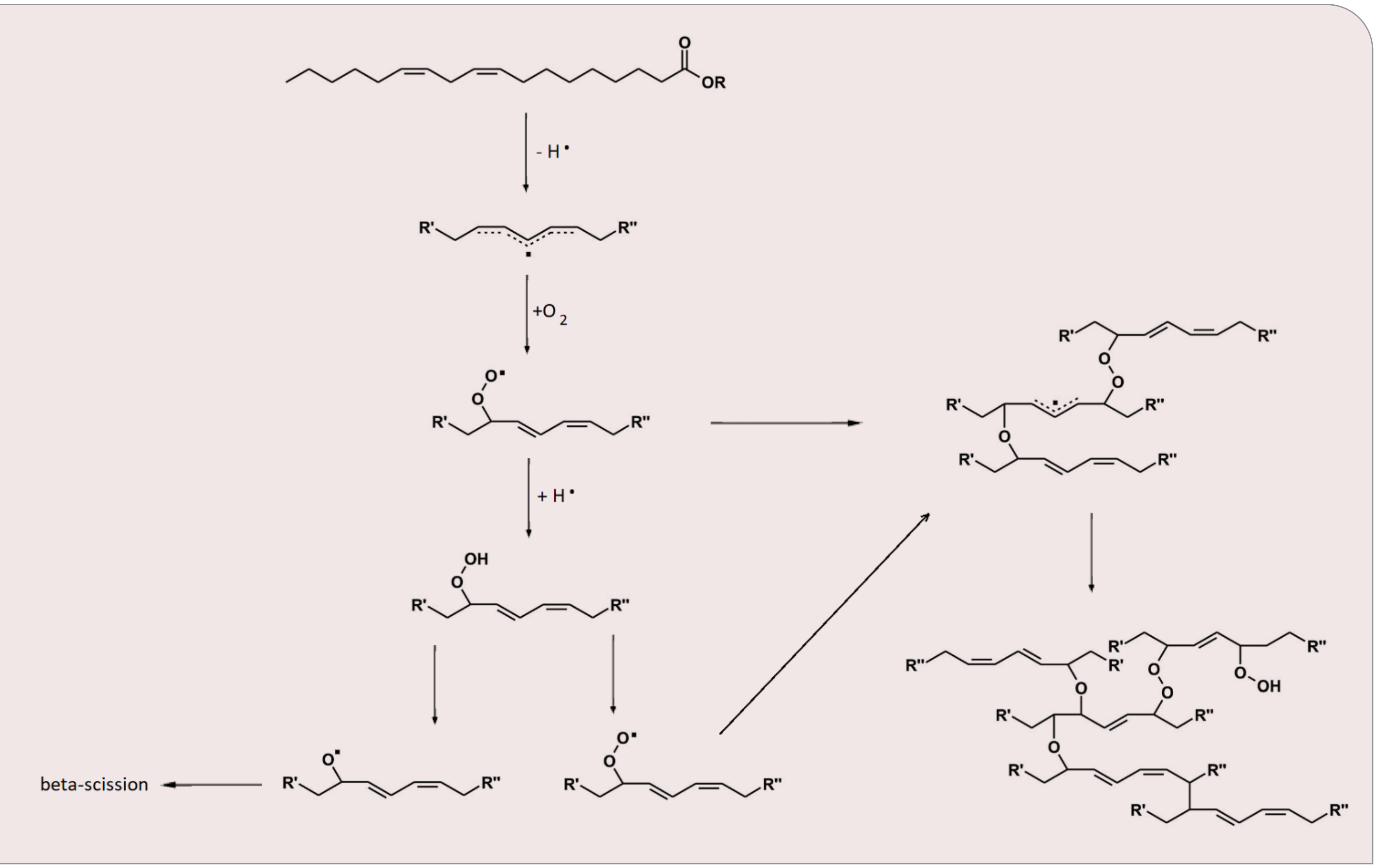


FIGURE 13
Resin 1 FTIR spectra, black = HPC, red = cobalt.

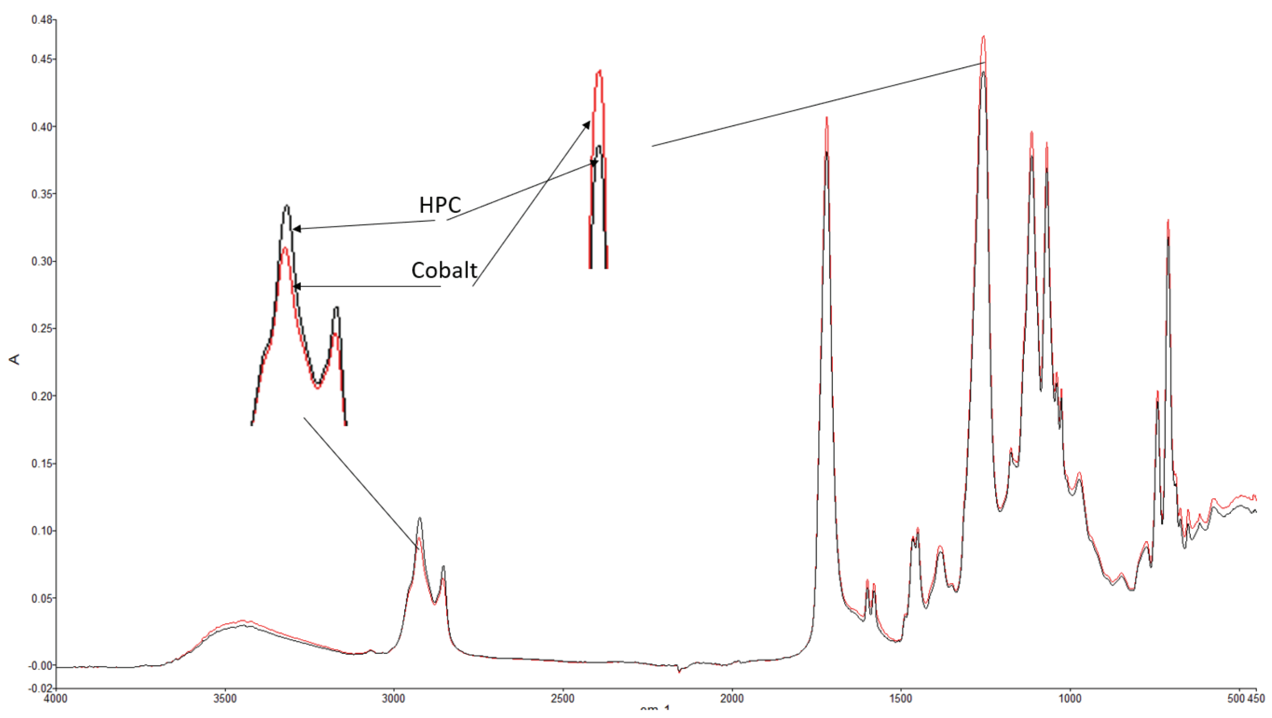
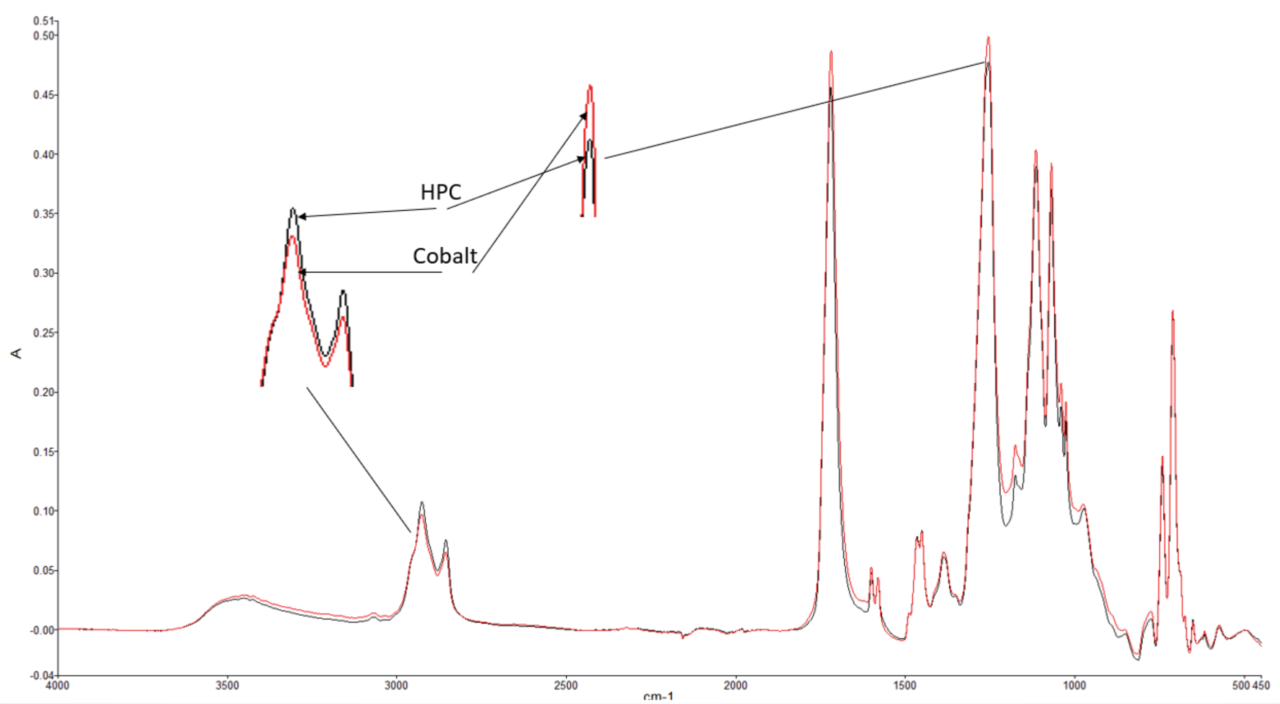


FIGURE 14
Resin 3 FTIR spectra, black = HPC, red = cobalt.



HPC-based alkyd coatings outperformed not only commercial alkyd-based paints but also acrylic-based commercial paints in most tests.

evidence that more C-C crosslinks and fewer ether and ester bonds were formed during the curing process in the presence of the HPC. Finally, at 973 cm^{-1}, which is attributed to a C=CH out of plane deformation, the HPC showed 4.7–6.4% less peak height than cobalt. This may indicate less residual unsaturation and a higher conversion rate for HPC-based coatings.

The final inquiry was to investigate possible differences in the β-scission pathway for HPC versus those for cobalt catalysts. The β-scission side reaction for alkyds leads to the formation of small-molecule volatile organic compounds (VOCs) such as aldehydes, ketones, and hydrocarbons. β-scission occurs when a hydroxyl group, which is formed after the hydrogen abstraction, oxygen uptake, and peroxide decomposition steps, is alpha to conjugated alkenes.[13] Differences in β-scission products were analyzed by thermal desorption GC-MS for resin 1 and resin 3 (**Figures 15** and **16**, **Tables 10** and **11**).

Differences were found in both the amount and types of volatile species evolved. HPC-catalyzed coatings showed not only fewer emissions overall but also lower levels of dangerous compounds such as formaldehyde, with approximately half the level seen in cobalt-based formulations.

FIGURE 15
GC/MS emissions for Resin 1.

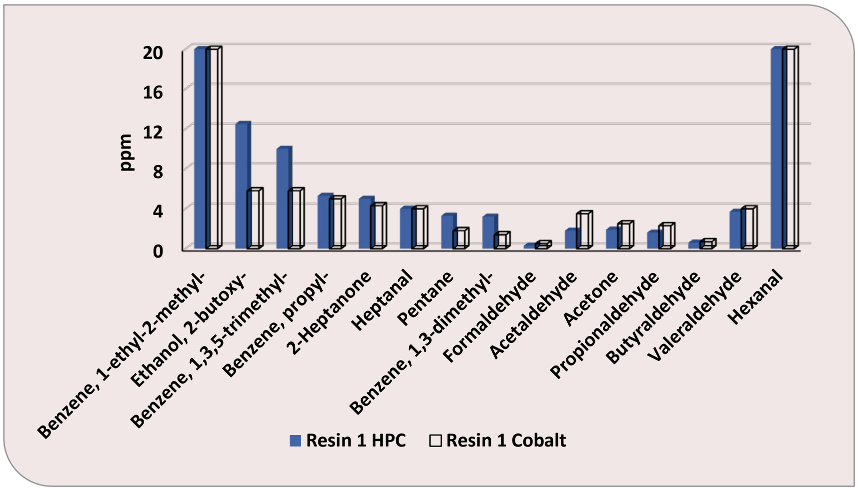


FIGURE 16
GC/MS emissions for Resin 3.

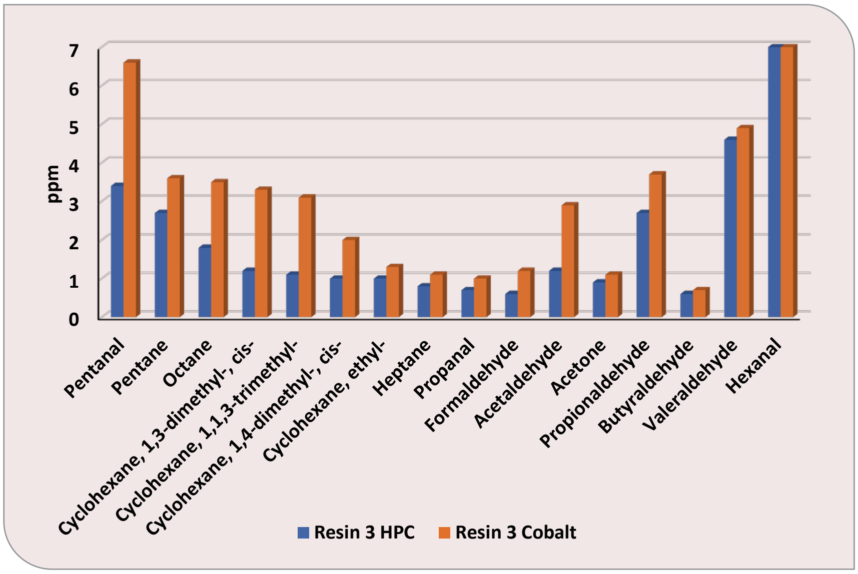


TABLE 10
Resin 1 Emissions

	Resin 1 HPC	Resin 1 Cobalt
Benzene, 1-ethyl-2-methyl-	29.7	26.6
Ethanol, 2-butoxy-	12.5	5.8
Benzene, 1,3,5-trimethyl-	10	5.8
Benzene, propyl-	5.3	5.0
2-Heptanone	5.0	4.3
Heptanal	4.0	4.0
Pentane	3.3	1.8
Benzene, 1,3-dimethyl-	3.2	1.4
Formaldehyde	0.3	0.5
Acetaldehyde	1.8	3.5
Acetone	1.9	2.5
Propionaldehyde	1.6	2.3
Butyraldehyde	0.6	0.7
Valeraldehyde	3.7	4.0
Hexanal	45	64.4
Total	127.9	132.6

TABLE 11
Resin 3 Emissions

	Resin 3 HPC	Resin 3 Cobalt
Pentanal	3.4	6.6
Pentane	2.7	3.6
Octane	1.8	3.5
Cyclohexane, 1,3-dimethyl-, *cis-*	1.2	3.3
Cyclohexane, 1,1,3-trimethyl-	1.1	3.1
Cyclohexane, 1,4-dimethyl-, *cis-*	1.0	2.0
Cyclohexane, ethyl-	1.0	1.3
Heptane	0.8	1.1
Propanal	0.7	1.0
Formaldehyde	0.6	1.2
Acetaldehyde	1.2	2.9
Acetone	0.9	1.1
Propionaldehyde	2.7	3.7
Butyraldehyde	0.6	0.7
Valeraldehyde	4.6	4.9
Hexanal	57.7	50.6
Total	82	90.6

Conclusions

The results presented in this work support the idea that, for oxidative crosslinked polymers, catalyst choice can affect fundamental coating properties. HPCs showed performance advantages over cobalt-catalyzed formulations in areas such as dry times, scrub resistance, stain resistance, and washability. They also demonstrated reduced yellowing, better gloss retention in QUV, and superior corrosion resistance, while maintaining high hardness and good blocking performance. Analysis of FTIR spectra provided evidence that HPCs can affect the types and levels of crosslinks that form during curing. It is theorized that HPCs may create a higher percentage of carbon-carbon bonds and fewer ester and ether bonds than cobalt-catalyzed paints do. Furthermore, HPC-based alkyd coatings outperformed not only commercial alkyd-based paints but acrylic-based commercial paints in most tests. In sum, it is now possible to meet or exceed the high-performance requirements that modern consumers demand when using bio-renewable, zero-VOC, sustainable alkyd-based coatings by formulating with advanced, sustainable HPCs. ❊

To learn more, please visit borchers.com/HPCs or contact borchersinfo@milliken.com.

References

1. Cobalt REACH Consortium. Cobalt REACH Consortium (CoRC). http://cobaltreachconsortium.org (accessed August 7, 2019).
2. Simpson, N.; Maaijen, K.; Roelofsen, Y.; and Hage, R. The Evolution of Catalysis for Alkyd Coatings: Responding to Impending Cobalt Reclassification with Very Active Iron and Manganese Catalysts, Using Polydentate Nitrogen Donor Ligands. *Catalysts*, 2019, 9, 825.
3. De Boer, J.W.; Wesenhagen, P.V.; Wenker, E.C.M.; Maaijen, K.; Gol, F.; Gibbs, H.; and Hage, R. The Quest for Cobalt-Free Alkyd Paint Driers. *Eur J Inorg Chem*, 2013, 21, 3581-3591.
4. Gibbs, H.; Gol, F.; Hage, R.; and Wesenhagen, P.V. Oral presentation at the European Coating Show. 2009. Nürnberg, Germany.
5. Gibbs, H. Oral presentation at the European Coating Show. 2011. Nürnberg, Germany. www.borchers.com. (Borchi Oxy Coat).
6. Müller, B.; Poth, U. *Coatings Formulation,* 2nd edition. Vincentz Network. Hannover, Germany, 2011, 89-95.
7. Bieleman, J.H. Driers. *Chimia*, 2002, 56, 184-190.
8. Van Gorkum, R.; Bouwman, E. The Oxidative Drying of Alkyd Paint Catalyzed by Metal Complexes. *Coord Chem Rev,* 2005, 249 (17-18), 1709-1728.
9. Soucek, M.D.; Khattab, T.; and Wu, J. Review of autoxidation and driers. *Prog Org Coat,* 2012, 73(4), 435-454.
10. Heaton, F.W., and Uril, N. The Aerobic Oxidation of Unsaturated Fatty Acids and their Esters: Cobalt Stearate-Catalyzed Oxidation of Linoleic Acid. *J Lipid Res,* 1961, 152-160.
11. Hellgren, A.C.; Wallin, M.; Weissenborn, P.K.; McDonald, P.J.; Glover, P.M.; and Keddie, J.L. New Techniques for Determining the Extent of Crosslinking in Coatings. *Prog Org Coat,* 2001, 43, 85-98.
12. Mallégol, J.; Gardette, J.-L.; and Lemaire, J. Long-term Behavior of Oil-Based Varnishes and Paints I. Spectroscopic Analysis of Curing Drying Oils. *J Am Oil Chem Soc,* 1999, 76, 967-976.
13. Porter, N.A.; Lehman, L.S.; Weber, B.A.; and Smith, K.J. Unified Mechanism for Polyunsaturated Fatty Acid Autoxidation. Competition of Peroxy Radical Hydrogen Atom Abstraction, .beta.-scission, and Cyclization. *J Am Chem Soc.,* 1981, 103 (21), 6447-6455.