Chempol® MPS: High Performing Alkyd Technology for Low VOC Paints and Coatings via Highly Functional Sucrose Esters

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Since 2005, P&G and CCP have collaborated to develop alkyd coatings to support environmental and sustainability initiatives. In 2008, CCP and P&G achieved breakthrough technical innovation which improved performance, and extended the technology broadly to new applications.

<u>Milestones</u>

- March 2007: CCP makes 1st sale of Sefose® 1618U-based alkyd into wood coating application.
- September 2007: P&G and CCP sign a Letter of Intent to collaborate and to tailor the sucrose ester technology for modification of alkyd resins to achieve low VOC paint formulations.
- June 2008: A Joint Development and Supply Agreements are finalized by both companies.
- August 2008: P&G and CCP each conduct successful pilot batch production; P&G on Sefose and CCP on the corresponding Chempol MPS.
- September 2008: Patent applications submitted.
- October 2008: CCP launches Chempol MPS (high performing, low VOC alkyd) and begins actively sampling the coatings industry. Cost Analysis demonstrates Chempol MPS is competitive to conventional alkyds on an equal dry film basis.

In the U.S. the CAS RN 330198-53-3 was assigned to Sefose as part of the PMN process in 2001 and listed on the TSCA Inventory as a commenced PMN substance in early 2002.

<u>Nomination Categories</u>

Primary focus area: **Designing Greener Chemicals**
Secondary focus area: **Greener Synthetic Pathways**

<u>Research and Development</u>

All research & developments leading to Chempol MPS and Sefose were done in the US.

<u>Abstract</u>

CCP and P&G developed new alkyd resin technology, Chempol MPS, that enables formulation of paints and coatings with less than half the amount of VOCs while delivering performance advantages as well, such as fast dry, high gloss, film toughness and increased Renewable Content (RC) in the formulated consumer product. Replacement of conventional alkyd resins by Chempol MPS could

- Reduce VOCs equivalent to emissions from 7,000,000 cars/year
- Reduce ground-level ozone by 590 tons/day or 215,000 tons/year
- Save 900,000 barrels/year of crude oil from solvents and alkyd polymers replaced

For perspective, alkyd resin paints and coatings use large amounts of solvents to solubilize organic components and attain appropriate viscosities. Millions of gallons of these paints/coatings are sold for multiple applications in the U.S. and globally. These solvents are volatile organic compounds (VOCs) that contribute to ground-level ozone formation, a known hazardous gas to humans even at relatively low levels.

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Goal: Develop alkyd coating alternatives that meet performance and environmental goals.

Analysis of Current Alkyd Coatings:

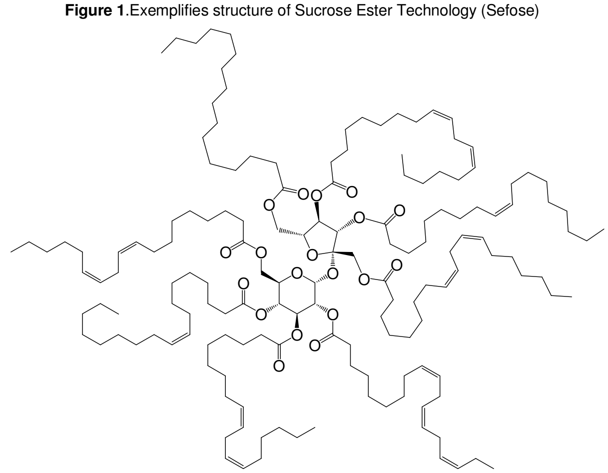
1. Solventborne alkyd coatings continue to be in demand because they are proven to be cost-effective, high performing over a wide range of applications, including architectural finishes, industrial metal and agricultural/construction equipment.
2. They contribute to our societal VOC emissions. Increasing concerns regarding outdoor/indoor air quality and ground-level ozone have spurred R&D efforts to find alternative coating technologies or approaches that lower VOC emissions without compromising performance. A major *challenge* for the industry as a whole.
3. Approaches to low VOC alkyd resins coating formulations exist but invariably have compromised coating performance.
   - In one approach, the molecular weight and viscosity of an alkyd resin is reduced to decrease the need for solvent. As a result, the paint made with it takes much longer to dry[1]; an undesirable feature for many coating applications.
   - Another approach is to use VOC exempt solvents such as t-butyl acetate, acetone, and Oxsol® 100 [1-chloro-4-(trifluoromethyl) benzene]. These solvents tend to be expensive or often have undesired odor and other performance issues.
   - While commercial, low VOC waterborne acrylic latex paints are available, they have performance trade offs that are unfavorable for various coating applications such as short open time, low gloss, and reduced corrosion resistance when compared to solvent alkyd coatings.

Solution: Chempol® MPS, a family of *new alkyd resins* developed by CCP to formulate low VOC solventborne paints and coatings for various applications.

Technology Description

Chempol MPS alkyd resins enabled by Sefose® are the innovative outcome of a *collaborative* effort by P&G and CCP to identify a commercially viable solution to significantly reduce VOC emissions from alkyd coatings without compromising performance. It reflects the commitment of both companies to develop environmentally improved products.

Figure 1.Exemplifies structure of Sucrose Ester Technology (Sefose)



Sefose products are esters prepared from *renewable feedstocks* by esterifying sucrose with fatty acid methyl esters (FAME) via a *solventless* patented process, US6121440

[1] Pourreau, Daniel B. and Scott E. Smyth. "High-Solids Alkyd Resins with Improved Properties Based on Styrene-Allyl Alcohol (SAA) Resinous Polyols." Journal of Coatings Technology, vol. 1/2, February 2004

(Figure 1). The physical properties and reactivity of Sefose has been carefully tailored by controlling its *unique molecular architecture* and *functional density* by choosing the appropriate FAME blends, from natural oils such as soybean and others, to achieve the right fatty acid chain length distribution, *unsaturation* level and degree of esterification.

The customized sucrose ester plays multiple roles in Chempol® MPS. It has been *tailored to work synergistically with alkyd resins when undergoing auto-oxidative polymeric cross-linking*[2] *with other constituents in the applied paint film providing optimal, controllable drying time and enhanced film properties.* Importantly, it:

1) is a *co-reactant* that becomes an integral part of the coating film
2) provides *optimal viscosity control* even for high solids alkyd resin products
3) serves as a very effective *non-volatile* modifier of traditional alkyd resin polymers

Chempol® MPS Performance and Benefits

Background. White paints were made to demonstrate the performance capability and versatility of Chempol MPS. They were made using the same basic starting formulation, (see Table 1), but solvent levels were adjusted as needed to achieve the same in-can viscosity (see Table 3).

Table 1. White Paint Formulation

GRIND	Pounds	Gallons
Alkyd Resin Solids	68	7.8
Mineral Spirits*	67	10.4
Organoclay Thixotrope	4	0.3
Nuosperse 657	3	0.4
TiO_2	303	9.1
Mix above GRIND on high speed for 20 min		
LETDOWN (Premix from above + ingredients below)		
Alkyd Resin Solids	300	34.3
Mineral Spirits*	226	35.1
12% Cobalt Drier	2	0.3
5% Calcium Drier	8	1.0
12% Zirconium Drier	6	0.8
1,10-Phenanthroline (Chelating Drier Enhancer)	3	0.3
Methyl Ethyl Ketoxime (antiskin)	2	0.2
TOTAL	992	100.0

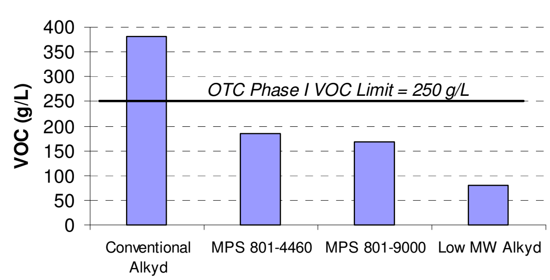
*Mineral Spirits reduced to achieve similar viscosity for each alkyd resin.

Two new commercially available Chempol MPS alkyd resins were compared to a commercial conventional alkyd and an alternative high solids / low molecular weight (HS/LMw) alkyd resin. The conventional alkyd selected is comparable in composition to the Chempol MPS alkyd resin without the Sefose® technology. The paints were formulated to the same pigment to binder ratios and applied at equal dry film thickness for performance evaluation tests (see Table 3).

1. Environmental Impact

VOC Reduction. The *Chempol MPS alkyd paint formulations exhibit reduced VOC levels relative to today's EPA regulations and go beyond the Ozone Transport Commission (OTC) VOC limits proposed for future adoption by the EPA, Fig. 2.* The VOC level for each of the test paint formulations was determined based on the known quantity of solvent added to each formulation to thin the paints to a similar in-can viscosity around 80 KU. The current U.S. EPA national rule places VOC limits at 380 g/L on non-flat high gloss paints. *Chempol MPS 801-4460 and 801-9000 saves 196 g/L and 212 g/L of VOC emissions respectively, a greater than 50% VOC reduction.* The alternative low VOC HS/LMw paint formulation exhibits significant performance shortcomings as discussed in Section 3.

Figure 2. VOC Comparisons



[2] Mallegol, J.; Barry, A. M.; Ciampi, E.; Glover, P. M.; McDonald, P.J.; Keddie, J. L. "Influence of Drier Combination on Through-Drying in Waterborne Alkyd Emulsion Coatings Observed with Magnetic Resonance Profiling." Journal of Coatings Technology., October 2002, 74 (933), pp 113-124; and references within.

Chempol® MPS technology could reduce VOCs by up to 87,000 tons VOC/year[3]*, about 0.41%*[4] *of the total VOC emission in the United States*. This is equivalent to the total annual VOC emissions from over 7,000,000 cars in the U.S.[5] or 648,000 barrels of crude oil[6]. This conclusion is based on the following analysis. Chempol MPS technology would result in VOC reductions in the "long oil" alkyd resin coatings sector which represents 59% of the alkyd coating market[7]. These alkyd coatings account for about 0.77% of all VOC emissions[8]. It is reasonable to assume that current long oil alkyd resin coatings exactly meet the U.S. EPA VOC content requirements. On average, Chempol MPS products will lower VOC content levels of at least 200 g/L. This estimated VOC impact is conservative since the California VOC emissions data used is weighted toward lower VOC coatings due to more restrictive regulations in this state relative to the rest of the U.S.

Ground-Level Ozone Reduction. Anthropomorphic release of VOCs into the atmosphere is one very important factor in determining ground-level ozone levels, but not the only factor. Nitrogen oxides and sunlight generated radicals are also key ingredients in the conversion of oxygen to ozone[9]. Linear reductions in VOC levels do not necessarily produce linear reductions in ozone levels. Nevertheless, reductions in atmospheric VOC levels are a primary focus of the Federal Clean Air Act and our calculations are based on the general presumption that reductions in VOCs released from coatings due to the Chempol MPS technology will result in a linear decrease in ground-level ozone levels.

Ground-level ozone will be reduced by up to about 2.5 tons for each ton of solvent eliminated from alkyd coatings by Chempol MPS technology[10]. *This could mean an ozone reduction of about 589 tons ozone/day.*[11] *This amount of ozone could fill up to 96 hot air balloons per day.*[12] Various solvents, and therefore various VOC species, will be eliminated from alkyd coatings through the use of Chempol MPS and the reactivity's of these VOC species is important in estimating the impact on ozone reduction by the new technology. VOC reactivity scales, such as Maximum Incremental Reactivity (MIR)[13], have been used by CARB and the U.S. EPA[14] to

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[3] As described in footnote 7, the technology might be used in about 317 million lbs of alkyd resin and about 3.05 lbs of alkyds are used in each gallon (e.g., 359.5 lbs alkyd ÷ 118 gal = 3.05 lbs/gal using values from KNG, 2007 page 871, Table 9, totals). Thus about 104 million gallons of alkyd coatings could have this technology per year (i.e., 317 million lbs ÷ 3.05 lbs/gal = 104 million gallons). Chempol MPS could then reduce solvent by about 87,000 tons VOC/year (i.e., 104 million gal/yr x 3.785 L/gal x 200 g VOC /L ÷ 453.6 g VOC/lb VOC ÷ 2,000 lb VOC/ton VOC = 87,000 ton VOC/yr).

[4] 0.77% VOC emissions due to long oil alkyd coatings as described in footnote 8 can be multiplied by the ratio of 200 g/L (VOC reduction due to new technology) to 380 g/L (current VOC emissions) = 0.41%.

[5] An average car in 2002 was responsible for emission of 30.8 g of VOC per day. U.S. DOT Federal Highway Administration. Sources of Vehicle Emissions. Viewed December 5, 2008: http://www.fhwa.dot.gov/environment/aqfactbk/page15.htm.

[6] http://www.eppo.go.th/ref/UNIT-OIL.html. Conversion: 7.45 barrels of crude oil per ton (specific gravity of 33 API taken as average).

[7] 317 million lbs of alkyd resin are used in long oils and this represents 0.59 fraction of the 541 million lbs alkyd market; "The U.S. Paint & Coatings Industry 2006 – 2011: A Multiclient Study" by Kusumger, Nerlfi & Growney, One DeBaun Avenue, C, West Caldwell, NJ 07006 dated September, 2007, p 863.

[8] Estimate developed by Technology Sciences Group using data from the California Air Resources Board which tracks the VOC emissions in annual emissions inventories. Detailed calculations and assumptions not included due to limited space, however available upon request. 30.6 tons of reactive organic gases (ROG)/day emission estimated from alkyd coatings, this is multiplied by 0.59 to give 18.1 tons ROG/day released in California from long oil alkyds and dividing by the total of 2321.39 tons ROG/day = 0.77% of the total daily emission.

[9] For example, see http://www.paintquality.com/ehs/low_voc.html

[10] Estimates developed by Technology Sciences Group using MIR using the average MIR values. Detailed calculations not included due to limited space, but are available upon request. 2.47 g ozone/g VOC, this is equivalent to 2.47 ton ozone/ton VOC.

[11] Calculated as 87,000 ton VOC/yr from footnote 3 ÷ 365 da/yr x 2.47 ton ozone/ton VOC = 589 ton ozone/day.

[12] Volume calculated using Ideal Gas Law using PV = nRT at 1atm and 25^{o}C; hot air ballon average volume = 2832 m^3. http://en.wikipedia.org/wiki/Hot_air_balloon , viewed 12/10/2008.

[13] A variety of scales have been developed based on different nitrogen oxide to VOC ratio presumptions. The MIR scale is the scale preferred by CARB and USEPA. The MIR scale uses a nitrogen oxide level that gives worst-case estimates for ozone production from added VOC. MIR's use 39 different nitrogen oxide to VOC ratios based on historical measurements in 39 different US metropolitan areas (the nitrogen oxide to VOC ratios might not currently represent conditions in those locations) with nitrogen oxide levels adjusted in each model to the level that will give

determine effects of VOC emissions on ozone levels. A variety of VOC solvents are used in alkyd coatings and these VOC range from moderately to highly reactive. Solvent usage is weighted toward mineral spirits since it is the dominant solvent in architectural alkyd coatings. For industrial alkyd coatings, solvent usage is more typically in the family of xylenes[15]. Overall, mineral spirits in alkyd coatings are likely to involve grades with an average MIR of about 1.3 g ozone/g VOC, xylenes with an average MIR of about 8.0 g ozone/g VOC and other solvents with an average MIR of about 1.3 g ozone/g VOC[10].

Increase Renewable Content (RC). *Chempol® MPS paint formulations require less petroleum-based alkyd resin in comparison to paints made with conventional alkyd resins.* The percent renewable content of the paints made was determined by calculating the amount of natural oils and fatty acid-modified sucrose esters in each alkyd resin and then comparing it to the total paint weight. The RC's for the Chempol MPS white paints are 41 and 45% while the conventional long-oil alkyd paint formula has only 24% RC. In contrast, acrylic latex resins, the predominant low VOC technology, have no RC because the raw materials used to make them are derived from petroleum. In Chempol MPS, *Sefose® replaces petroleum-derived raw materials used for making conventional alkyd resins*. If the entire long oil alkyd resin volume were converted to Chempol MPS*, the usage reduction of petroleum-based raw materials translates to 34,900 tons, amounting to an additional annual savings of 260,000 barrels of crude oil*[6].

2. Health & Safety

In Chempol MPS, Sefose replaces solvents commonly used in alkyd resin paint formulations. Table 2 compares safety and toxicity parameters of Sefose and some of these solvents. The solvents have low flash points, are flammable/combustible and show adverse effects. In contrast, Sefose esters have very high flash points, are not flammable/combustible and are fairly innocuous since originally the technology was developed as a food additive[16].

Table 2. Safety Parameters and Codes

Solvent	Flash Point, °C	NFPA Codes: H, F, R	Exposure Limits, ppm	Toxicity
Mineral Spirits	41	1, 2, 0	TWA 100	Lungs. Eyes. Skin. May cause cancer.
Xylene	25	2, 3, 0	TWA 100; STEL 150	Nerves. Liver. Kidney. Blood. Eyes. Heart. Bone Marrow.
n-Butyl Acetate	23	2, 3, 0	TWA 150; STEL 200	Central nervous system.
Sefose	> 250	0, 1, 0	Non volatile	Non Toxic

VOCs have been linked to asthmatic episodes. Acute exposures to petroleum hydrocarbon solvents such as mineral spirits and VM&P naphtha can irritate mucous membranes and cause upper respiratory tract irritation as was seen following acute exposure to high concentrations of Stoddard solvent[17]. Short-term exposure of people to high levels of aromatic solvents such as xylene can cause irritation of the nose and throat, difficulty in breathing, and impaired function of the lungs[18].

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maximum added ozone when additional VOC's are added. Only average MIR values from the 39 models were used in this report for each VOC tested.

[14] Carter, W.P.L. "SAPRC Atmospheric Chemical Mechanisms and VOC Reactivity Scales." http://www.engr.ucr.edu/~carter/SAPRC/. Last update July 7, 2008. Viewed December 4, 2008.

[15] Based on internal CCP knowledge and expertise of alkyd coatings composition in the U.S. coatings industry.

[16] Studies documented in a Food Additive Petition which was accepted by the US FDA and a PMN which was accepted by US EPA.

[17] A hydrocarbon mixture considered to be a subset of mineral spirits. Agency for Toxic Substances and Disease Registry (ATSDR) 2000. Case Studies in Environmental Medicine. Stoddard Solvent Toxicity, Course SS3057. U.S. Dept. of Health and Human Services, Division of Toxicology and Environmental Medicine, 28 p.

[18] ATSDR 2007. Toxicological Profile for Xylene. U.S. Dept. of Health and Human Services, Public Health Service, 385 p.

In addition to respiratory effects, VOC emitting solvents such as mineral spirits, VM&P naphtha, and xylene can cause transient neurologic effects. Irritant contact dermatitis and cardiovascular effects have been also reported. Short-term exposure to volatile aromatic solvents such as xylene delayed response to a visual stimulus, impaired memory, caused stomach discomfort and possible changes in the liver and kidneys demonstrated by abnormal clinical chemistry values[18].

Reduction of indoor VOC levels could be the greatest impact potential from use of Chempol® MPS alkyd resins in paint/coating compositions. Studies conducted using EPA's Total Exposure Assessment Methodology (TEAM) found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside[19]. Because 30% of long-oil alkyd coatings used are for interior architectural projects[7], and assuming an average usage of 10 gallons of paint for each project, over 3 million project sites annually including homes and offices would see reduced pollutant levels as a result of converting from conventional alkyd to Chempol MPS.

3. Paint Performance

In addition to the potential reduction in overall VOC emissions, Chempol MPS enables film performance of applied alkyd coatings previously unattainable with other high solid approaches. For the white paints described in Table 1, the film performance properties were compared based on equivalent dry film thickness. For scrub resistance, block resistance, and dry time evaluation, uniform films were produced in the laboratory using drawdown bars to achieve comparable film thickness. End dry film thicknesses were measured on the scrub resistance panels; the two Chempol MPS alkyd paints and conventional alkyd were in the 1.0-1.1 *mil* range. The HS/LMw alkyd was measured at 1.3 *mil*. Solvent resistance was evaluated by rubbing with a cloth dampened with methyl ethyl ketone (MEK) on steel panels where the test paints had been spray-applied to achieve dry film thicknesses around 2.2 *mil*.

Table 3. Architectural High Gloss Long Oil Alkyd Paint Formulations

Description	CHEMPOL MPS 801-4460	CHEMPOL MPS 801-9000	High Solids / Low Molecular Weight (HS/LMw)	Conventional Alkyd
Sucrose Ester Level	Moderate	High	None	None
Formulation Parameters				
Pigment / Binder Ratio	0.77	0.77	0.79	0.79
% Vol. Solids	76.6	78.6	90.0	50.6
% Organic Renewable Content	41%	45%	42%	24%
Liquid Paint				
Viscosity [KU] (Low Shear in-can viscosity)	80	78	81.3	84.3
Viscosity ICI (High Shear brushing viscosity)	5.8	3.6	7.9	7.3
Gloss [over glass plate]				
20º, 60º	83, 93	84, 93	76, 90	85,92
Dry				
Set to Touch	90 min.	90 min.	7 Hr	50 min.
Dry Hard	4 Hr 15	4 Hr 30	Overnight	7 Hr
Block Resistance, ASTM D4946, 0-10 Scale, 10 = Best score				
Room Temperature	7	8	7	6.5
Elevated Temperature, 52C	5.5	6	3.5	5
Solvent Resistance, Higher Value is Best				
Spray-Applied DFT [mils]	2.2-2.4	2.2-2.3	2.1-2.3	2.1-2.3
MEK 2x Rubs	145	160	75	55

When the Drying performance of the paints was compared, *Chempol MPS achieved Dry Hard[20] faster than both the conventional alkyd and the HS/LMw alkyd (Table 3).* In addition, the paint film of the commercial alternative HS/LMw alkyd paint took by far the longest to reach set to Touch Dry[21] and was still very sticky on the surface after 8 hours. In the alternative HS/LMw

[19] EPA. An introduction to Indoor Air Quality. Organic Gases (Volatile Organic Compounds – VOCs). Accessed Nov. 26, 2008: http://www.epa.gov/iaq/voc.html

[20] Dry Hard condition of a paint film is reached when an object applied under pressure to the paint film no longer leaves a permanent mark or impression on the film surface.

[21] Set to Touch Dry is the time when the wet paint no longer transfers to an object touched lightly to the paint surface.

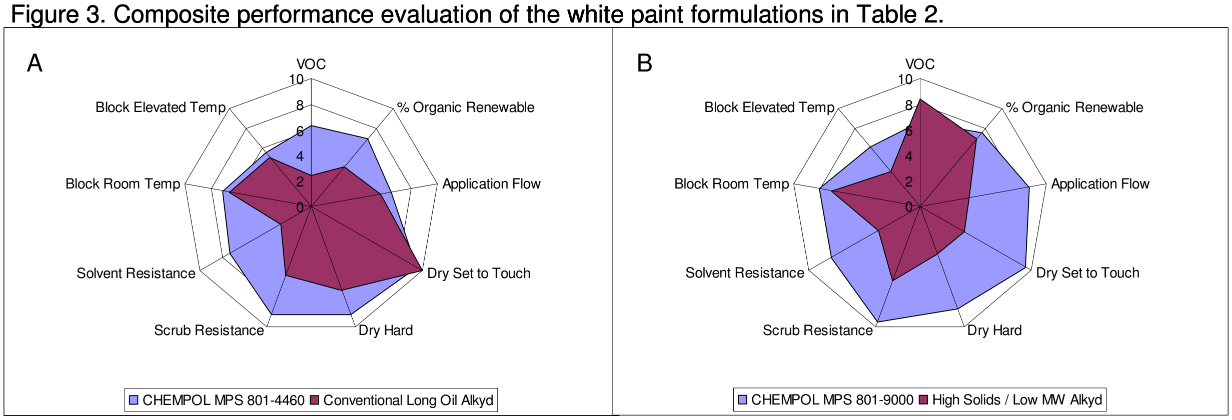
alkyd formulation, the approach manufacturers use to formulate lower VOC alkyd paints, *dry time is severely compromised.*

The Chempol® MPS paints have lower viscosities (ICI viscosities of 5.8 and 3.6) making them relatively easier to apply than the alternative low VOC paint (ICI viscosity of 7.9) and similar to conventional long-oil alkyd coatings (ICI viscosities in the range of 4-7). By contrast, low VOC, high solid paint formulations often display high shear viscosity that creates problems for brushing and rolling applications.

The Chempol MPS paints exhibit significantly enhanced scrub and solvent resistance along with improved block resistance compared with the conventional alkyd and HS/LMw alkyd alternative. Scrub resistance, solvent resistance, and block resistance each demonstrate the physical toughness of a paint film in a different way. The scrub resistance test simulates how a wall-paint withstands scrubbing. Block resistance is a measure of how a paint film will stick to itself after painting is complete; this is a particularly relevant property for wood enamel paints applied to window sashes and door frames where painted surfaces come in contact with each other. Solvent resistance is important in light industrial environment applications.

Chempol MPS alkyd resins exhibit significant paint film performance advantages compared to both the conventional long oil alkyd approach and the high solid / low MW alkyd technology approach. Figure 3 shows the relative composite performance of the tested paints. Each performance vector is indexed from a 0 to 10 score, where 10 is best; thus, greater coverage area indicates better performance. Chart A compares the moderate Sefose®-containing alkyd paint, Chempol MPS 801-4460 with the conventional alkyd; while Chart B compares the higher Sefose-containing alkyd paint, Chempol MPS 801-9000, directly with the HS/LMw alkyd.

Figure 3. Composite performance evaluation of the white paint formulations in Table 2.



Benefit Summary

Long oil alkyd resins, and their paint and coating formulations, have been developed and demonstrated. The assets and expertise to produce the Sefose and Chempol MPS exist to meet the market demand. Commercial adoption of Chempol MPS, while improving paint performance metrics, would have a positive environmental impact by significantly reducing:

- VOC emissions
- formation of ground-level ozone
- use of hazardous solvents, and
- petroleum consumption by using renewable resources