

OIL-MODIFIED URETHANES FOR CLEAR WOOD FINISHES: DISTINCTION OR EXTINCTION?

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Conventional solvent-based oil-modified urethanes (OMU) have been a mainstay in wood flooring and clear varnish applications for many years. Since their introduction into the United States in the early 1950s, their usage has grown steadily. They find application in the toughest environments, like gymnasium and athletic floors, as well as clear varnishes for hardwood floors in homes, offices, and other public buildings. While favored by the professional flooring contractor, they also are used by the do-it-yourself (DIY) homeowner, for everything from floors to cabinet refinishing to wood furniture restoration.

The features that have made this technology so popular over the years include ease of application, fast dry, excellent long-term durability, and reasonable cost. There are very few resin and varnish systems that can provide the ease of use, appearance, dry time, early mar and scuff resistance, abrasion resistance, and household stain and chemical resistance of a solventborne oil-modified urethane varnish.

Currently, conventional solvent-based oil-modified urethanes, with all of their features and benefits, are facing extinction in the marketplace. The cause: implementation of volatile organic compound (VOC) regulations. The top performing solvent-based oil-modified urethanes have a hefty 520–550 gram/liter VOC. Regulations that will take effect in the northeastern United States in 2005 and in the Los Angeles area of California in 2006 call for VOCs of 350 g/L and 275 g/L, respectively.

Questions that are addressed in this article include:

- (1) What is an oil-modified urethane, and why is it so popular for wood floor coatings?
- (2) What are the VOC regulations? When do they take effect?

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(3) What test methods were used to determine alternative technology performance?

(4) What are the alternatives to solvent-based OMU technology?

(5) How do the alternatives compare to the best of the solvent OMU technologies (550 g/L)?

(6) Is oil-modified urethane technology doomed to extinction, or do the VOC-compliant alternatives provide an opportunity for distinction?

SOLVENTBORNE OIL-MODIFIED URETHANES

Applications

Solventborne oil-modified urethanes are used extensively in the wood floor finish market. Wood floor finishes range from gym floors, which are typically maple, to home and office floors, which are usually red or white oak. The National Wood Flooring Manufacturers Association (NOFMA) has a recommended regimen for finishing wood floors. Included is the need to let the wood acclimate to the climate of the building where it is installed, as well as a sanding regimen from coarse to fine sandpaper before applying the coating. The sanding media can be either sandpaper, steel wool (never used with waterborne coatings though, due to rusting and film discoloration), or a screen/fiber pad on a disc buffing machine. NOFMA recommends coating the wood right after sanding, within the same day. Coating immediately after sanding minimizes the tendency for grain raising. Between coats, screening and dust removal (vacuum and tack cloth) are specified.

The varnish is applied by pad applicator (or some variation, like a squeegee), brush, or roller. Care has to be taken not to overwork the wet varnish, which may result in bubbles. The varnish needs to dry quickly, but, on the other hand, must have excellent wet edge and workability. Oil-modified urethanes, like other technologies that are reviewed in this report, are very effective at balancing dry time with wet edge and workability.

These preparation and application methods are notable in the discussion of alternate technologies, particularly waterborne. In the NOFMA procedures, oil-modified urethanes are cited for their ease of application—easiest compared to all of the other technologies, like waterborne and acid-catalyzed systems.

Chemistry

Oil-modified urethanes are an addition reaction of an isocyanate with a hydroxyl-bearing fatty acid modified ester. The isocyanate typically used is toluene diisocyanate (TDI). The drying oil is reacted with a polyhydric alcohol like glycerol or pentaerythritol, forming polyol-modified vegetable oil or polyol-modified fatty

acid. Isocyanates react readily with alcohols/polyols, resulting in the formation of the oil-modified urethane. The generic structure of an OMU is shown in Figure 1.

Key characteristics that dictate the performance of the oil-modified urethane: urethane content, oil content, and oil type. Higher levels of isocyanate, or less oil, result in higher molecular weight polymers that are harder, faster drying, and more chemical resistant. Due to the higher molecular weight, they also tend to be higher in viscosity. To get to a useable viscosity, more solvent (lower solids) is needed. More solvent means higher VOC—as high as 550 g/L.

Oil selection is also critical to OMU performance. One of the most common oils used in these polymers is linseed. Linseed is a drying oil that provides fast dry, good hardness, and respectable flexibility properties; it also tends to yellow more than some of the semi-drying alternatives. Popular and frequently used semi-drying oils are soya and sunflower. The semi-drying oils are used in varnishes where a lighter color (less yellow) is desired.

Another critical aspect of oil-modified urethanes is solvent selection. Mineral spirits is the solvent of choice for architectural varnish OMUs. This is due to evaporation rates (dry times), wet edge, odor, and reasonably low flammability. Any aprotic solvent (no groups that will react with the urethane)—aromatic hydrocarbons, aliphatic hydrocarbons, esters, and ketones—can be used. Some of the stronger aromatic and oxygenated solvents are used in industrial coating applications.

Oil-modified urethane varnishes, after application, cure to fully crosslinked systems. The mechanism is oxidative cure. Oxygen, in conjunction with the double bonds in the oil, undergoes a complex series of reactions leading to crosslinking. The reaction with oxygen is catalyzed by a metal soap drier (see Figure 2). For most modern OMU varnishes, the metal drier of choice is either cobalt or manganese. The faster this oxidative reaction, the faster the film will cure and be able to be

Figure 1—Generic structure of oil-modified urethane and oil.

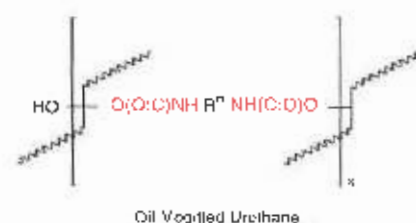
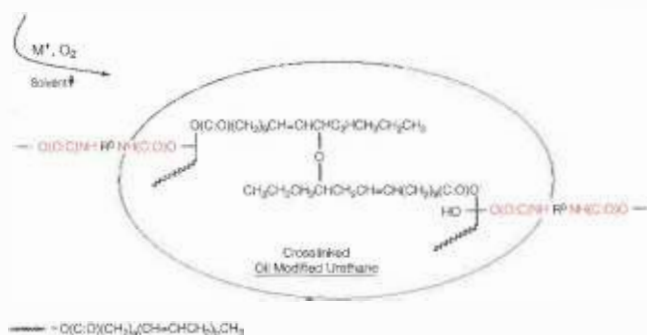


Figure 2—Oxidative cure model of oil-modified urethanes.



put “back-into-service.” Some oil-modified urethane systems, specially formulated with drier accelerators, can be back-in-service in as little as 24 hours. Slower drying oils and lower drier/accelerator levels may lengthen cure to four to seven days. A film with no drier will eventually oxidatively cure on its own, but studies have shown that this process takes a month or more, depending on oil type.

To summarize, solvent-based OMUs are a one-component, self-crosslinking resin and varnish system. They are stable, easy to formulate, and provide a high degree of performance. Later, some non-OMU alternatives to solvent-based oil-modified urethanes are presented. Performance advantages and disadvantages are discussed.

Formulation

Conventional solvent-based oil modified urethanes are very easy to formulate. A typical formulation consists of OMU resin, mineral spirits (or some other suitable aliphatic solvent, depending on drying and open time requirements), metallic drier, and antiskinning agent. Usage levels of metallic drier are relatively low—0.01% metal on resin solids is the norm. The two most common metals used are cobalt and manganese. Cobalt gives faster surface cure, but in solvent-based

Table 1—Clear Varnish Formulation, Conventional Oil-Modified Urethane

Material	Lb	Gal
Conventional solventborne OMU (50% NVW)	576.1	77.86
Mineral spirits	144.0	22.09
Anti-skin (0.2% on resin NVW)	0.6	0.08
6% Cobalt naphthenate (.01% on resin NVW)	0.5	0.06
Totals:	721.2	100.09
Viscosity at 25°C, Gardner-Holdt.....	A-C	
Percent solids, weight/volume.....	40.0/32.7	
Pounds per gallon.....	7.21	
VOC, g/L.....	519	

OMUs, could add slightly more color in both the wet varnish and dry film. Manganese gives more of a through-dry and is slightly lower in overall color than cobalt. If very rapid cure is required (to get faster back-in-service times), an accelerator can be used. Examples of accelerators are commercial products DriRx and Activ8. Optimum use levels for accelerators are a 1:1 molar ratio of accelerator to drier metal. The 1:1 molar ratio, for varnish formulation purposes, is approximately 12 times the weight of pure metal in the drier.

VOC, Grams per Liter

As the formulation in Table 1 shows, the VOC of the conventional OMUs is quite high—519 g/L. The example presented features one of the higher molecular weight, higher urethane level oil-modified urethanes. At the featured VOC, it will have lighter color, quicker dry, the best mar and scuff resistance in the shortest cure time, and it will be the easiest of the solventborne OMUs to flatten (make semigloss and satin finishes).

The longer oil length OMUs are very popular as well. These will formulate to lower VOCs, typically in the 450 g/L region. They have a lower initial viscosity and sharper viscosity reduction curve, hence less solvent is required to achieve specified viscosities—resulting in lower VOC. Dry time and mar and scuff resistance development will be somewhat slower, but still very good compared to other solventborne systems, like alkyds. The longer oil length OMUs will be more difficult to flatten; more flattening agent—like fumed silica—will be required to get a target (lower) gloss.

The discussion of VOC levels is a good introduction to the next part of this article, which reviews current and pending regulations.

VOC REGULATIONS

National Regulation, EPA

The United States Environmental Protection Agency (EPA), in conjunction with the coatings industry, proposed and ultimately formalized in 1998–1999 a series of regulations to limit VOC emissions from architectural and industrial maintenance (site-applied) coatings. These regulations, especially by 2004 standards, are reasonable from a compliance and technology standpoint. In these regulations—40 CFR Part 59, Subpart D—varnishes are listed at a VOC of 450 g/L. A coatings manufacturer making a 500 or 550 g/L varnish could pay exceedance fees, which often resulted in lower cost than reformulating their product line. The national regulations also included tonnage exemptions. The EPA document allows states and regions to impose stricter regulations based on environmental

Figure 3—South Coast Air Quality Management District (SCAQMD).



and meteorological needs. That is where the real difficulty for the coatings industry and varnish manufacturers begins.

South Coast Air Quality Management District

California initiated the original coatings industry VOC regulations, and has continually pushed the VOC regulations lower. Within California, the various regional Air Quality Management Districts (AQMD) can set even lower limits. The lowest limits in the United States are set by the South Coast Air Quality Management District (SCAQMD; see Figure 3), which includes within its jurisdiction Orange County and Los Angeles. The current SCAQMD VOC level for varnishes is 350 g/L. The new proposed limit, Proposed Amended Rule (PAR) 1113, which will go into effect in July 2006, is 275 g/L. In 2006, the South Coast district will do away with the exemption for varnishes in containers of less than one liter in size. Interestingly and ironically, the SCAQMD has cited claims straight from the cans, data sheets, and websites of some of the largest varnish manufacturers as justification for VOC reduction. The claims tout that the reduced VOC water-based varnishes will actually perform better than the solventborne counterparts.

Ozone Transport Commission

Perhaps the larger regulatory threat to conventional solvent-based urethanes, and other higher VOC systems, are those regulations being coordinated by the Ozone Transport Commission (OTC). The OTC is a multi-state organization that focuses on helping their member states reduce ground-level ozone. The OTC membership list includes 12 Mid-Atlantic and Northeastern states, along with the District of Columbia (see Figure 4).

The OTC has recommended several architectural coating VOC reductions. Significant to this article is the pending regulation for varnishes: 350 g/L. This recom-

mendation, already adopted by several states—for example, New Jersey, New York, and Delaware—was set to become law on January 1, 2005. Most of the OTC states (those with the largest populations and most pollution problems) were expected to have this law in place by that time. OTC is providing the exemption for containers of less than one liter.

The OTC regulations—due to timing (early 2005); size of the region in both land mass and population; and California-like limit (350 g/L)—are what is causing the immediate concern among floor finish and varnish manufacturers.

TEST PROCEDURES

The next sections deal with various alternatives—polyurethane and oil-modified urethane types—to conventional OMUs. To help understand the performance of these various systems, this section deals with some of the test methods and parameters that are mentioned in the following sections.

Mar and Scuff Resistance

One of the keys to differentiating performance of the various resins used for clear wood coatings is mar and scuff resistance. There are many tests for mar and scuff resistance—the method presented here is the pendulum scuff test method, as seen in Figure 5. The apparatus consists of a pendulum arm with a weighted hardwood (white oak or maple) block at the end. This is the striking surface to the test panel. The average 20° gloss is read before and after the test. The test consists of hitting the coated panel—either treated steel or maple—four times with the pendulum arm/wood block. Results are expressed as (a) % 20° gloss retained, and (b) visual assessment of the panel (scratching and scuffing). The equipment and method for this

Figure 4—Ozone transport committee, member states.



test was developed by Reichhold. The test development is supported by several statistical experimental designs. Copies of the method are available. Good correlation is seen between pendulum scuff resistance and known quality and scuff resistance of existing commercial and proprietary varnishes.

Taber Abrasion

Taber abrasion is measured by standard varnish test procedures: the instrument arms are weighted with 1000 gram weights. The abrasive wheels are the CS-17 (more abrasive than the CS-10 counterparts). The substrate is the steel panel recommended for the Taber abrader. The initial weight of the panel, and successive weights after 100 cycles, 500 cycles, and 1000 cycles are checked using an analytical balance (four decimal places). Results are expressed in milligrams removed. The reference for this method is ASTM D 4060.

Chemical Resistance

Chemical resistance is performed on the dry films using eight household stains and chemicals. Test chemicals and materials include MEK, olive oil, 409® cleaner, 1% Spic-and-Span cleaning solution, 50% ethanol, white vinegar, water, and 7% ammonia. The test substrates are treated steel and maple. A #65 wire wound rod is used to apply the steel film (approximately 1–1.5 mils dry). Two coats of varnish are brush applied to the maple panel. Each chemical is applied to a two-ply square of heavy duty paper towel on the test film, completely saturating the towel. The towel and solvent/stain are immediately covered with a watch glass. The stain is left on the panel for two hours, after which all stains are removed, and the panel is rinsed and patted dry. The impact of the chemicals is assessed immediately after rinsing. Items affecting the rating of the panel are discoloration (mostly yellowing or whitening, haze development);

blistering; and softening. Each chemical is rated on a scale of 1 to 10, with 10 being "no effect" and 1 being "severe effect and failure" (essentially taking the film out of service). The reference for this test is ASTM D 1308.



Figure 5—Pendulum mark and scuff tester.

Color

Color is an important property, especially when evaluating different oil-modified urethane systems. The color system used is CIELab, with an illumination of D65/10°. From the L, a, b readings, Yellowness Index [calculated as $(142.9 \cdot b)/L$], change in Yellowness Index over time, and Delta E (square root of the sum of the squares of the difference in L, a, b values—test condition versus initial). Color after exposure to light, as well as storage in the dark, are measured. Oil-modified products tend to show more yellowing when stored in the dark. Color panels are stored in a constant temperature (25°C)/humidity (50%) room. ASTM E 313, ASTM D 2244, and ASTM D1925 are references.

Konig Hardness

Konig hardness is the main method used for hardness testing, in reference to this article. Konig hardness measurement is similar in concept to a Sward rocker hardness. The contact points rock back and forth with the Konig pendulum, and the varnish films dampen the rocking motion—like a Sward. The Konig results provide more differentiation between materials. Results with the Konig are expressed in seconds; the longer the pendulum rocks, the harder the test varnish.

Cost Analysis

As part of the evaluation of various technologies, there will be references to cost. Rather than discuss specific prices of raw materials, the following convention and ranges were used:

- (1) Conventional OMU systems—\$15–30/gal.
- (2) Waterborne polyurethane systems—\$30–60/gal.
- (3) High-performance polyurethane systems—\$60–90/gal.

These approximate price ranges are determined through actual purchases and observation at wood flooring distributors, paint stores, and "big box" hardware chains.

NON-OMU ALTERNATIVES TO CONVENTIONAL OIL-MODIFIED URETHANES

As the OTC and South Coast regulations are implemented, are there viable alternatives to meet the demanding new regulations? The next sections present various technologies, with data showing the performance of those technologies versus the 520 g/L conventional solventborne OMU. The first section discusses two waterborne systems: two-component waterborne polyisocyanate varnishes and standard polyurethane dispersion/acrylic varnishes. The later section looks at

Table 2—Waterborne Two-Component Urethane Varnish vs. Solventborne OMU Varnish

Property	Conventional OMU	Waterborne Two-Component
Gloss @ 60°	96	87
Gloss @ 20°	85	69
Gardner dry times, min		
Touch	15	15
Set	30	21
Hard	53	40
Through	82	110
Initial Yellowness Index	16.37	7.29
30 days dark		
Yellowness Index	20.69	6.72
D E	2.78	0.47
Konig, sec		
Overnight	46	72
7 day	90	100
Taber abrasion, mg lost		
500 cycles	56	20
1000 cycles	125	42
Mar & scuff resistance,		
% gloss retained	91%	96%
Stain resistance, total		
rating (8 stains)	63	79

three VOC-compliant OMU technologies: 350 g/L oil-modified urethanes; oil-modified urethanes in exempt solvent—parachlorobenzotrifluoride (PCBTf); and water-based oil modified urethanes. The discussion focuses on the relative advantages and limitations of those technologies. In review, the conventional OMU resin is compared to the three compliant OMU alternatives in several key properties.

Waterborne Two-Component Urethanes vs. Conventional OMUs

Waterborne two-component urethanes, for the purposes of this discussion, are defined as a polyisocyanate that can be reduced in water and combined with a polyurethane dispersion (PUD) polyol or acrylic latex polyol. Another common two-component system (which will not be discussed) is a polyurethane dispersion/acrylic reacted with a polyaziridine crosslinker. The polyisocyanate/PUD polyol is regarded as a high-performance system. Commercial and experimental versions of this system are available in the market.

Waterborne two-component polyurethane systems provide a number of advantages: they have quick development of key properties, particularly mar and scuff resistance, stain resistance, and abrasion resistance. Two-component waterborne systems can be formulated to VOCs at or below 275 g/L. Upon application and aging of the film, they remain water-white, with no yellowing

evident. This might be perceived as an advantage by some varnish companies, but a limitation by others, especially versus solventborne oil-modified urethanes. The OMU's mild ambering over time is said by some to provide warmth to the wood.

In addition to color and color change, the two-component system will provide better abrasion resistance, hardness, and stain resistance versus a conventional OMU system. This is due to a much higher level of urethane in the two-component system. Gloss is lower, and dry-through is slightly slower (see Table 2).

There are some downsides to this technology versus OMUs. First, it is restricted to contractors, and not recommended for (or sold to) the DIY painter. Handling two-component systems, with the need for exacting mix ratios and mixing procedures along with attention to a finite pot life, is generally not for the DIY market. Additionally, polyisocyanates need to be handled with care due to toxicity. Another issue is that more coats are required—generally three to five—for adequate film build. From a varnish formulator perspective, the two-component system is a more complicated formulation (see Table 3). Commercially, these systems are expensive, ranging from \$60–90/gal (compared to \$15–30/gal for an OMU).

Polyurethane Dispersion/Acrylic Varnishes vs. Conventional OMUs

Polyurethane dispersion (PUD)/acrylic blend varnishes cover a wide range of performance. A PUD/acrylic system dries by evaporation of the volatiles (water, neutralizer, and eventually coalescing agent) as the individual particles coalesce to form a continuous film. Unlike the oil-modified urethane and two-component

Table 3—Two-Component Urethane Formulation

	Lb	Gal
Part A:		
PUD polyol (40% NVW)	636.9	72.29
PM acetate	5.0	0.62
Water	123.3	14.81
Associative thickener	4.0	0.46
Wetting surfactant	5.0	0.62
Defoamer	0.4	0.06
<i>Hand mix the following into Part A:</i>		
Part B:		
Water reducible polyisocyanate (80% NVW)	81.2	9.91
PM acetate	10.0	1.24
Totals:	841.4	100.0
Index (NCO:polyol EW)	125%	
NVW, %	38.0%	
NVW, %	33.6%	
VOC, g/L	274	

Table 4—Polyurethane Dispersion/Acrylic Blend System, 40% PUD

Materials	Lb	Gal
Styrene acrylic latex (45% NVW)	401.3	46.45
Water	16.7	2.00
DPM acetate.....	54.2	6.66
Plasticizer	9.0	1.06
<i>Add each material under agitation:</i>		
Water	28.2	3.39
Polyurethane dispersion (35% NVW)	344.0	39.5
Surfactant (surface wetting)	3.0	0.37
Associative thickener.....	4.0	0.46
Defoamer.....	0.5	0.07
Totals:.....	860.9	100.00
Weight/gal, lb.....	8.61	
Weight solids, %.....	35.4	
Ratio of PUD:acrylic	40:60	
VOC:		
lb/gal	2.0	
Grams/liter	242.00	

system, there is no crosslinking of the film after application. The main parameter dictating the durability and resistance of the final varnish is the ratio of polyurethane dispersion to acrylic. Higher levels of polyurethane dispersion (over 50%) give better abrasion resistance and mar and scuff resistance. Higher levels of acrylic or styrene acrylic latex can provide better chemical resistance and lower raw material cost. However, latex modification causes a drop in abrasion resistance and mar and scuff resistance. Higher acrylic

Table 5—PUD/Acrylic Varnish vs. Conventional OMU Varnish

Property	Conventional OMU	PUD/Acrylic
Gloss @ 60°.....	96	87
Gloss @ 20°.....	85	72
Gardner dry times, min		
Touch.....	15	5
Set.....	30	10
Hard.....	53	20
Through.....	82	90
Initial Yellowness Index.....	16.37	7.43
30 days dark		
Yellowness Index	20.69	7.29
DE	2.78	0.09
Konig, sec		
Overnight	46	59
7 day	90	90
Taber abrasion, mg lost		
500 cycles	56	131
1000 cycles	125	198
Scuff resistance,		
% gloss (20°) retained	91%	63%
Stain resistance,		
total rating (8 stains)	63	58

levels will also lower the 20° gloss of the varnish. Performance requirements dictate that a PUD/acrylic blend for flooring applications will have more polyurethane than latex. Conversely, a DIY varnish for general wood coating applications would be fairly high in acrylic.

The latex used in a PUD/acrylic blend system contributes to performance. For example, styrene acrylic latexes, commonly used in industrial maintenance finishes, are known for their outstanding chemical and solvent resistance. Blending a PUD with a harder styrene acrylic will improve chemical resistance. Note that the latex—acrylic or styrene acrylic—has to have the requisite amount of coalescing solvent for optimum performance. Table 4 shows a typical polyurethane dispersion acrylic/styrene acrylic latex blend varnish.

The formulation shows that the harder styrene acrylic requires a high level of coalescent and plasticizer for maximum performance. The coalescing solvent contributes to the VOC, which is still below the lowest 275 g/L target.

The regulators would look at that VOC level of these varnishes, as well as a varnish manufacturer's marketing literature, and question why varnishes have to be made at 520 g/L. That is, why would an oil-modified urethane varnish be preferred, given its higher VOC?

Table 5 shows the performance comparison between the higher VOC OMU and the lower VOC PUD/acrylic system. It is obvious that the PUD acrylic system does not have the mar and scuff resistance, even after a one week dry, that is seen with the OMU. Abrasion resistance is significantly worse with the PUD/acrylic. Glosses, particularly 20° gloss, are lower. The PUD/acrylic has fairly quick dry, although through-dry ("return-to-service time") is actually slightly slower. This could be due to slower evaporation of the coalescing solvent. The PUD/acrylic has respectable chemical and solvent resistance, which could be a function of the latex used. Also notable is that the PUD/acrylic varnish shows no yellowing or color change over time—which again, could be an advantage or a disadvantage depending on the varnish marketing approach taken. One other issue with the PUD/acrylic system: they typically require one to two additional coats of varnish to match the film build of the OMU system. The requirement of additional coats in a waterborne system is a function of a number of things: lower volume solids, lower high shear viscosity, and water soaking into the wood much faster than mineral spirits.

PUD/acrylic waterborne varnishes are intermediate in price range; commercial varnishes range in price from \$30–60/gal. Combine that with the increased number of coats required and PUD/acrylic systems become a much more expensive yet lower performing alternative to conventional oil-modified urethanes.

It should also be noted that PUD/acrylic systems are frequently crosslinked with a polyaziridine in contractor type floor varnishes. This will elevate the performance of the PUD/acrylic system toward the polyisocyanate two-component system. Again, such a system would not be used by a DIY applicator. In addition, the cost would be on a par with the polyisocyanate two-component system (as evidenced by commercial polling and purchases).

OIL-MODIFIED URETHANE ALTERNATIVES TO CONVENTIONAL OIL-MODIFIED URETHANES

The previous section shows two systems that basically bracket the oil-modified urethane varnish: the waterborne two-component polyisocyanate system gives tremendous performance, but at a much higher commercial price. Application is limited to knowledgeable and responsible contractors. The PUD/acrylic blend system is suitable for DIY application, is lower in overall performance, and is still more expensive—both from the number of coats required and the commercial varnish price. Are there VOC-compliant OMUs that meet all, or most, of the properties of the conventional OMUs?

This section looks at three different approaches to providing an oil modified urethane system that is VOC-compliant (less than 350 g/L, and eventually, less than 275 g/L). The approaches are high-solids oil-modified urethanes; conventional oil modified urethanes in exempt solvent; and waterborne oil-modified urethanes. These are all single component, storage stable finishes that can be used by contractors and DIY users alike.

High Solids OMUs vs. Conventional OMUs

Some quick math in a formulation spreadsheet program will indicate that to achieve a 350 g/L varnish, a weight solids of 62% is required. This may sound relatively simple at first—some conventional urethanes are shipped at a 60% NV specification. The second consideration, however, is that the most desirable viscosity range for a solvent-based varnish, especially one that is used in wood flooring applications, is a Gardner Holdt bubble viscosity range of A–C. The Maple Flooring Manufacturers Association (MFMA) specifies viscosities of less than A for heavy duty finishes (Group 2) and A–3 for surface finishes (Group 3). Both areas feature OMU based products. A 60% NV conventional OMU would be in the area of a Z– viscosity.

The question then becomes: how can the viscosity of a conventional OMU be lowered to an acceptable range, at a VOC-compliant solids? The answer is basically to lower the molecular weight of the polymer, thereby depending more on the oxidative cure to gener-

Table 6—High-Solids OMU Varnish

Material	Lb	Gal
High-solids OMU (80% by wt)	610.0	72.79
12% Cobalt drier	0.8	0.10
Accelerator	1.2	0.15
Aluminum (7% AOC)	20.9	2.72
Antiskinning agent	2.0	0.91
Mineral spirits	152.9	23.34
Totals:	787.7	100.00
NVW, %	63.3%	
Viscosity, Gardner-Holdt	C	
VOC, lb/gal	2.88	
VOC, g/L	345.00	

ate crosslink density and molecular weight. Building molecular weight through curing is less effective than building it through manufacture of the polymer—hence, reduced overall performance.

Respectable varnishes can be made using high-solids oil-modified urethanes. To make such a varnish requires good formulating skills, particularly when optimizing the drier package, the most critical formulation aspect in high-solids OMU varnishes. Statistical design of experiments was applied to arrive at the drier package shown in Table 6. Different levels of cobalt drier, different accelerators, and different through driers were all factors in that design.

The formulation (Table 6) shows the complexity of moving from a conventional OMU to a higher solids, VOC-compliant version. There are more ingredients—

Table 7—High-Solids OMU Varnish vs. Conventional OMU Varnish

Property	Conventional OMU	High-Solids OMU
Gloss @ 60°	96	94
Gloss @ 20°	85	87
Gardner dry limes, min		
Touch	15	37
Sol	30	85
Hard	53	240
Through	82	320
Initial Yellowness Index	16.37	28.53
30 days dark		
Yellowness Index	20.69	43.12
DI	2.78	8.80
Konig, sec		
Overnight	46	24
7 day	90	42
Taber abrasion, mg lost		
500 cycles	56	69
Scuff resistance, % gloss retained	91%	87%
Stain resistance, total rating (8 stains)	63	58

Table 8—Clear Varnish Formulation, Based on PCBTf OMU

Material	Lb	Gal
PCBTf-based OMU (40% NVW).....	680.4	69.43
Mineral spirits	114.0	17.40
PCBTf solvent.....	145.9	13.12
Anti-skinning agent	0.6	0.08
6% Cobalt drier (0.01% on resin NV)	0.5	0.06
Totals:.....	941.4	100.09
Viscosity, Gardner-Holdt.....	A	
Non-volatile, % by wt/vol	28.9/32.7	
Wt/gal.....	9.41	
VOC, g/L	275.00	

for example, two driers and an accelerator versus one drier. Due to the higher solids and the recommended ranges of items like through-driers, there are larger quantities of each raw material in the formulation. This adds to the overall raw material cost of the formulation.

Table 7 shows the strengths and limitations of a high-solids OMU system. Most of the properties described are reduced with the high-solids system, supporting the conventional wisdom about reduced molecular weight leading to reduced overall performance. Some of the notable deficiencies are hardness and hardness development over time, reduced abrasion resistance, slightly reduced mar and scuff resistance, and greatly increased yellowing of the film—both initially and after dark storage. While these systems will dry faster than a conventional long oil alkyd, they are significantly slower in dry time than a conventional, high-VOC oil-modified urethane.

It is interesting to note that stain resistance and mar and scuff resistance are only slightly reduced versus the conventional OMU control. Part of this could be due to crosslinking of the [increased] oil. This also reflects improvements that have been made over the old high-solids OMUs. These improvements have occurred over the past few years, as resin suppliers moved to support varnish manufacturers in the face of increasing VOC restrictions.

An advantage to the high-solids technology is increased film build: because the system is higher in solids, every mil of varnish that is applied will have more solids per given volume. A typical high-solids OMU film will require only two coats for a thick, lustrous film. A conventional OMU may require three coats for the same appearance.

There is a caution for high-solids OMUs in film build: at 3 mils wet, the featured dry times and properties were realized. At 6 mils wet and higher, dry time slows considerably—generally to 16+ hours. Surface skinning/curing of thick films can lead to other per-

formance issues, including more yellowing and a decrease in resistance properties.

Cost is an advantage for the high solids OMU—the prediction is that they will still be in the \$15–30/gal conventional oil-modified urethane range. Note that pricing could be somewhat higher, gallon for gallon, due to putting more solids (nonvolatile matter) in the can.

Exempt Solvent-Based OMUs vs. Conventional OMUs

A new group of solvent-based oil-modified urethanes has emerged. These are OMUs based on an exempt solvent—namely parachlorobenzotrifluoride (PCBTf) (Figure 6). PCBTf has the commercial name "Oxsol 100." The EPA and state regulators have determined that PCBTf is not an ozone depleter and hence is exempt from VOC considerations.



Figure 6—Structure of parachlorobenzotrifluoride solvent.

PCBTf has some differences versus the mineral spirits that it is replacing. These differences have to be realized and addressed by the varnish manufacturers. The most obvious issue with PCBTf is readily apparent when you open the can of solvent, resin, or varnish—odor. While odor is a very subjective property, the odor of PCBTf is strong.

Another concern about PCBTf is its cost. It can range from three to six times the cost/pound of mineral spirits. This would put a PCBTf-based OMU firmly in the water-based varnish price range (\$30–60/gal).

The raw material cost of PCBTf is accentuated for the varnish formulator by another interesting aspect of this solvent: it has a very high density. The weight per gallon (in U.S. pounds) of PCBTf is 11.12. Compare that to the density of mineral spirits—6.35 lb/gal. If a formulator is used to formulating to equal weight solids in his varnish, he would have to immediately acclimate to formulating to equal *volume* solids with PCBTf. The conventional wisdom of volume solids being lower than weight solids has to change as well: since PCBTf is more dense than the resin solids, volume solids in a PCBTf-based resin or straight PCBTf-based varnish actually will be higher than the weight solids. Another issue with the higher density of PCBTf is that more *pounds* of solvent (or resin based on the solvent) has to be used to get equal volume yields. This

Table 9—PCBTF-Bases OMU Varnish vs. Conventional OMU Varnish

Property	Conventional OMU	PCBTF OMU
Gloss @ 60°	96	97
Gloss @ 20°	85	85
VOC, g/L	520	275
Gardner dry times, min		
Touch	15	8
Set	30	17
Hard	53	25
Through	82	100
Initial Yellowness Index	16.37	17.16
30 days dark		
Yellowness Index	20.69	20.40
D E	2.78	2.06
Konig, sec		
Overnight	46	52
/ day 90 100		
Taber abrasion, mg lost		
500 cycles	56	53
Scuff resistance,		
% gloss retained	91%	90%
Stain resistance,		
total rating (8 stains)	63	64

contributes to the cost issue with PCBTF, since resin and solvent are sold by the pound, and varnishes are sold by the gallon.

On the other hand, conventional OMUs based on PCBTF allow the formulator tremendous VOC latitude, with minimal, if any, change in performance and durability. PCBTF-containing varnishes can be made at 350 g/L, 275 g/L, and even <10 g/L. VOC is dictated by the ratio of PCBTF solvent to mineral spirits in the formulation.

Table 8, a 275 g/L PCBTF based varnish formulation, illustrates the formulation "oddities" that occur when using PCBTF. Note the weight solids and volume solids, and compare them to the conventional OMU formulation in Table 1. The weight solids in the PCBTF formulation are much lower than the conventional (>10%), while the volume solids are equal. Volume solids control dry film thickness, so formulating to equal volume solids is completely appropriate. The weight per gallon of the 275 g/L formulation is also noteworthy: it is much higher than the conventional OMU formulation in Table 1. One additional formulation note with PCBTF: like water in a latex or waterborne system, PCBTF is an exempt solvent. When calculating VOC, the PCBTF volume must be subtracted from the total volume in the denominator of the VOC calculation (lb of VOC divided by total volume minus volume of exempt solvent). This calculation for exempt solvents, like PCBTF and water, is featured in the regional and national VOC regulations.

The performance of the PCBTF varnish is very similar to the conventional OMU. Due to the faster evaporation rate of PCBTF (0.90) versus mineral spirits (0.13), PCBTF will generally show faster set and dry hard times due to rapid solvent loss. Through dry, which is more oxidative cure related, is not impacted—it is equal to the conventional OMU. Otherwise, the performance—gloss, yellowing, abrasion resistance, mar and scuff resistance, and chemical resistance—is equivalent to the mineral spirits-based oil-modified urethane control (see Table 9).

Water-Based OMUs vs. Conventional OMUs

Water-based oil-modified urethanes have been available for several years, and are starting to grow in popularity as the more stringent VOC regulations are implemented. Water-based OMUs give very similar performance to their conventional solvent-based counterparts at much lower VOCs. The VOC of a typical water-based oil-modified urethane formulation is below 200 g/L.

Other than performance, what are the issues with water-based OMUs? First, versus their solventborne counterparts, water-based OMUs are lower in solids. A typical water-based OMU varnish is 28–30% volume solids. This is lower, but not overwhelmingly so, than the conventional OMU varnish—which is typically around 33% volume solids (see Table 1). Film builds will be slightly less, requiring more coats. While a conventional solventborne system may require two to three coats, the waterborne OMU system will require three to

Table 10—Clear Varnish Based on Waterborne Oil-Modified Urethane

Materials	Lb	Gal
Water-based OMU (33% NV)	758.0	89.18
<i>Premix the following, adding water to Mn drier, before adding</i>		
Water Dispersible Mn drier		
(0.04% on resin NV)	1.1	0.13
Water	25.0	3.00
<i>Premix the following, then add:</i>		
Water	4.2	0.50
Accelerator	1.2	0.15
<i>Add each material under agitation</i>		
Wetting surfactant "A"	3.0	0.39
Wetting surfactant "B"	2.0	0.23
De'aamer	0.5	0.07
Water	52.9	6.35
Totals:	847.9	100.00
NVW, %	30.1%	
NVV, %	29.2%	
Lb/gal	8.48	
VOC, lb/gal	1.56	
VOC, g/L	187.00	

Table 11—Waterborne OMU Varnish vs. Conventional OMU Varnish

Property	Conventional OMU	PCBTF OMU
Gloss @ 60°	96	88
Gloss @ 20°	85	67
VOC, g/L.....	520	187
Gardner dry times, min		
Touch	15	3
Set	30	8
Hard	53	17
Through	82	57
Initial Yellowness Index	16.37	7.54
30 days dark Yellowness Index.....	20.69	12.71
D E 2.78 3.35		
Konig, sec		
Overnight	46	49
7 day	90	79
Taber abrasion, mg lost		
500 cycles	56	34
Scuff resistance, % gloss retained	91%	96%
Stain resistance, total rating (8 stains)	63	61

four coats. A sealer, usually acrylic latex type, is recommended with these systems and other one-component waterborne systems, like the PUD/acrylic system. This minimizes the number of coats of water-based urethane varnish required, bringing it into the same range as solventborne systems (two to three coats). A sealer provides a smoother, higher build appearance for the waterborne OMU, with fewer coats. Fewer coats of waterborne OMU makes the end user's paint cost lower. Sealers also are useful on high tannin woods, like white oak, to block tannins from coming into the topcoats, causing discoloration.

An interesting feature of the water-based OMUs, related to multiple coats for the best appearance, is their dry times. As *Table 11* shows, the dry times are very fast. The applied varnish is dry [hard] enough after one hour to be able to walk on it. The advantage is that the film can be screened or sanded after a few hours, and re-coated. Solvent OMUs typically require an overnight dry before sanding and recoating. With an early start, where two coats of top-coat are required (with a sealer), it would be pos-

sible for a contractor to finish the flooring job in one day.

An issue that is raised routinely about waterborne systems is their tendency to raise the grain. If the recommended NOFMA protocols are followed (see the earlier "Application" section)—with applying the coating immediately after sanding the bare wood and routine sanding/screening after each coat—grain raising is not an issue. Indeed, the water-based OMU looks virtually indistinguishable from its solvent-borne counterpart, once the job is finished (except that, as *Table 11* indicates, it is less yellow).

Another concern, similar to the discussion of the waterborne two-component polyisocyanate system and the PUD/acrylic system, is the complexity of the formulation with waterborne oil-modified urethanes. Issues like recoatability and defoaming—which are non-issues with the solventborne counterparts—need to be taken into consideration. As with the high-solids solventborne OMUs, formulation skill is required to identify and balance the driers, accelerators, surfactants, and defoamers. While the film will dry quickly, adding the right level of driers and accelerators will provide rapid (as little as 24–48 hr) back-in-service times. This means the film will crosslink and develop mar and scuff resistance faster. See *Table 10* for a suggested waterborne OMU formulation.

Table 11 indicates the performance of the waterborne OMU coating previously described. It is slightly lower in gloss, especially 20° gloss, and is slightly lower in one week hardness versus the conventional oil-modified urethane. Otherwise, the properties are equivalent to, and in some cases, better than, the solventborne conventional OMUs. Abrasion resistance is significantly better with the waterborne OMU. Yellowing is less overall, but not the "cold" water-white of a PUD/acrylic system. Mar and scuff resistance is notably better as well. It is interesting to note that the waterborne OMU system shown will develop very good mar and scuff resistance after an overnight dry—an advantage over the con-

Table 12—Comparison of Oil-Modified Urethane Alternatives

Property	Conventional Solventborne OMU	High-Solids Solventborne OMU	PCBTF-Based OMU	Water OMU
VOC, g/L	450-520	350	0-350	<200
Dry time.....	Control	Slower	Faster	Faster
Yellowing.....	Control	More Yellow	Equal	Less Yellow
Film build, coats.....	2-3	2	2-3	2-3, with sealer
Gloss	Control	Equal	Equal	Slightly Lower
Hardness.....	Control	Softer	Equal	Equal
Mar & scuff	Control	Slightly Worse	Equal	Better
Abrasion resistance	Control	Equal	Equal	Better
Chemical resistance	Control	Equal	Equal	Equal
Odor (subjective)	Control	Equal	Stronger	Different
Cost	Control	Slightly Higher	Higher	Higher

ventional solventborne OMUs. Chemical resistance is equivalent to the solventborne system after a one-week cure. Pricing of the waterborne oil-modified urethane systems will fall into the waterborne varnish area—the \$30–60 range.

Comparison of OMU Technology

Several alternatives to conventional oil modified urethanes have been presented. Will the PUD/acrylic systems replace conventional OMUs? Are OMUs bound for extinction? Or are there some distinguishing alternatives to conventional oil-modified urethanes?

Table 12 shows a comparison of the various technologies. Obviously, no OMU technology is a drop-in for existing, high-VOC conventional technologies. There are odor concerns. There are raw material cost/pricing issues. There are formulation issues—generally the compliant systems are tougher to formulate. A look at the actual performance, however, suggests that the compliant OMUs provide many of the same advantages and performance as their higher VOC counterparts. Some of the systems, like PCBTf and waterborne, may actually give improved performance, especially when properly formulated.

CONCLUSION

The question posed in the title of this article remains: Are oil-modified urethanes, a technology used in clear varnishes since the early 1950s, finally headed for extinction, driven out by VOC regulations? The information presented in Table 12 would suggest that extinction for OMUs is not imminent. Advances in exempt solvent technology, waterborne OMU technology, and even 350 g/L high-solids OMU technology indicate that the properties that make oil-modified urethanes desirable—ease of application, quick dry, warm color, mar and scuff resistance, chemical resistance, abrasion resistance, and gloss—are all available in the compliant types.

So the answer is, with proper formulation, VOC-compliant OMU technology will likely keep oil-modified urethanes around for another 50+ years—with distinguished performance over existing conventional OMUs and other non-OMU varnishes.

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