Assessment of Safer and Effective Alternatives to Methylene Chloride for Paint Stripping Products

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I. Introduction

Background

Methylene chloride is a widely used component in paint stripping products. The three major categories of use are industrial (e.g., in a permanent stationary technical installation), professional (e.g., by a tradesman), and consumer (e.g., by a homeowner for do it yourself activities) [1]. Methylene chloride is highly volatile and the primary route of exposure is inhalation. Numerous occupational and consumer deaths during paint stripping operations have resulted from acute methylene chloride poisoning, with 56 reported accidental exposure deaths linked to methylene chloride since 1980 [2]. Methylene chloride can cause acute and chronic effects on the central nervous system. The inhalation of methylene chloride can result in short-term effects such as dizziness, clumsiness, headache, nausea, and numbness of fingers and toes, and long-term effects such as loss of concentration, memory loss, and personality changes [3]. Further, methylene chloride is classified as "reasonably anticipated to be a human carcinogen" by the U.S. National Toxicology Program [4]. Consequently, there is increasing demand for paint stripping products that do not contain methylene chloride.

Several commercially available paint stripping products do not contain methylene chloride; however, their performance is significantly below that of methylene chloride. In addition, , some of the replacement chemicals, such as N-Methyl-2-Pyrrolidone (NMP), introduce other environmental, health, and safety hazards. The Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell (UMass Lowell) undertook a research effort to identify and evaluate safer alternatives to methylene chloride in paint stripping products. TURI had two meetings in 2015 with Savogran to start defining the requirements of the research project. The research objective was the identification and initial evaluation of solvent blends with equal or better paint stripping performance, comparable ingredient costs, and a safer environmental, health, and safety profile than methylene chloride. The primary functional requirements that would need to be satisfied for a solvent blend to replace methylene chloride in general purpose paint stripping products was derived from discussions with paint stripper product manufacturers (e.g. Savogran, Fiberlock Technologies, etc.), furniture refinishers, and available paint stripper-related literature. The primary requirements are the following:

1. Coating stripping performance comparable or equal to methylene chloride.
2. Utilizing solvent blends with appropriate Hansen Solubility Parameters to provide efficacy across a wide range of coatings: paints (oil, latex, lead), varnishes, lacquers, shellacs, epoxies, and polyurethanes.
3. Effectiveness on multiple substrate materials: wood, metal, ceramic, and masonry.

4. Non-flammable or low flammability.
5. Volatile organic compounds (VOC) content less than 50%.
6. Raw material cost less than approximately $0.70 per pound.
7. Does not damage substrate material – will not stain, discolor, or alter the substrate, corrode the metal substrate, or raise the grain on wood substrate.
8. Comprised of chemicals that are safer from an environmental, health, and safety standpoint as compared to methylene chloride.
9. Composed of chemicals that have small molar volumes and low hydrogen bonding values so that they can rapidly penetrate the various polymer coatings [5].

Approach

The research team used Hansen Solubility Parameters in Practice (HSPiP) software to help identify solvent blends with the desired solvency parameters (diffusion, polarity, and hydrogen bonding). The Hansen Solubility Parameters-based approach was an efficient method to rapidly identify safer and effective alternatives to methylene chloride and NMP in paint stripping products.

Hansen Solubility Parameters (HSP) were used to characterize the solvency of methylene chloride and potential alternatives, and are based on three distinctive forms of inter-molecular force:

1) Dispersion forces (δD): All atoms are surrounded by electron "clouds." The electron cloud is, on average, evenly distributed around the atom. At a given instant, however, the electron distribution may be lopsided. This temporary polarization results in attractive interactions with nearby atoms.
2) Polar forces (δP): Dipole moments are created when atoms of the same molecule have different electronegativities.
3) Hydrogen bond forces (δH): This force exists between hydrogen atoms and other atoms present in adjacent molecules.

These three parameters are used to describe solvent and solute interactions. Each parameter can be used as an axis in three-dimensional solubility space so that each solvent and solute can be represented as points and spheres in three-dimensional solubility space. The distance between HSP points in solubility space is calculated as follows:

$$\text{Distance}^2 = 4(\delta D_1-\delta D_2)^2 + (\delta P_1-\delta P_2)^2 + (\delta H_1-\delta H_2)^2$$

HSP values are based on the principle that "like dissolves like," meaning that the closer the solute and solvent are in three-dimensional solubility space, the greater the likelihood that the solvent will be effective. If a single solvent with the desired HSP values does not exist, then mixing together two or three solvents with different HSP values can generate a solvent blend with the desired HSP values [6]. The HSPiP software can be used to quickly scan through thousands of chemicals to find the optimal solvent and solvent blends for the target HSP values. The larger the molecule (molar volume), the more it will affect kinetics and slow down the dissolution reaction. With other things being equal, small solvents dissolve better than large solvents. Smaller molecules penetrate more easily into the polymer network typically present in coating materials. This is one reason that methylene chloride performs so well in paint stripping applications. For the paint stripping process, the size of the molecule is important to enhance the transport through the paint layers, so that the solvent can penetrate the paint and attack the adhesive bond to the substrate [7].

The new solvent blends identified were then evaluated for environmental, health, and safety characteristics, as well as raw material cost. The solvent blends then underwent technical performance testing for paint stripping efficacy on various substrates and coatings at the TURI Laboratory. The initial field-based testing of the solvent blends took place at Belcastro Furniture Restoration during May 2017.

Currently, the U.S. EPA estimates that 1.3 million consumers and 17,600 workers use methylene chloride-based paint stripping products, and 732,000 consumers and 30,300 workers use NMP-based paint stripping products. The potential benefit of a successful outcome for this research is the significant reduction in these exposures [8, 9].

II. Laboratory Testing Results

The TURI Laboratory at UMass Lowell provided the lab space, resources, and oversight needed to complete the laboratory testing. The following summarizes the paint stripper test results for the nine primary functional requirements.

Requirements 1, 2, and 3: Coating stripping performance

One of the testing goals was that the coating stripping performance be comparable to methylene chloride for a wide range of coatings and for multiple substrate materials: wood, metal, ceramic, and masonry. The laboratory testing was completed for wood, metal, and masonry, and the laboratory testing for ceramic substrates will be conducted in the near future.

The ASTM International Standard D6189, "Standard Practice for Evaluating the Efficiency of Chemical Removers for Organic Coatings," was used as a starting point for creating test coupons for this research. The scope of the ASTM D6189 standard is the evaluation of the effectiveness of coatings removers used on clear or pigmented coatings as applied to wood and metal. For the creation of test coupons, the standard requires that three layers of coating be applied to the wood or metal substrate.

To create a more challenging and realistic paint stripping performance test, the test coupons created for this research had the following four additional requirements that were not specified in ASTM International Standard D6189: 1) a primer layer, 2) a minimum of four layers of coatings instead of only three layers, 3) extended thermal aging for 3 weeks in an oven set at 140°F to simulate 11 months of aging, and 4) sanding and alcohol-wiping between each coating layer to better promote adhesion between the coating layers.

For creating the wood test coupons, 3.5 inches wide by 15 inches long planks of white pine wood were first coated with Kilz Original Interior Oil-Based primer and then left to dry at room temperature overnight. The following day, the coupons were then lightly sanded with 100-grit sandpaper to allow the primer layer and the following layer of coating to adhere more tightly. Once sanded, the coupons were then wiped clean with isopropanol. Each coupon was designated a different specific coating such as lacquer, oil-based paint, latex-based paint, epoxy, varnish, or polyurethane. The coating was then applied on top of the primer layer. Each coupon was painted with four layers of its designated top coat, allowing for each layer to dry overnight, be sanded, and cleaned with isopropanol. In addition, a mixed test coupon was created that had an oil primer layer, a latex-based paint layer, an oil-based paint layer, another latex-based paint layer, another oil-based paint layer, and two layers of polyurethane. This mixed coupon created a challenging scenario for paint stripping products. After the test coupons were painted with their final layer of top coat and dried overnight, they were then thermally aged in an oven for three weeks at 140˚F to simulate 11 months of aging.

For the metal test coupons, steel sheets with a galvanized finish were used. Each steel sheet was 12 inches wide, 12 inches long, and 28 gauge thick. The metal test coupons were first coated with a white Rust-oleum Clean Metal Primer. Next, four layers of black Rust-oleum Protective Enamel were applied onto the metal test coupons. Similar to the wood test coupons, the metal test coupons were sanded and wiped clean with isopropanol between each coating layer and the finished coupons were thermally aged in an oven for three weeks at 140˚F.

For the masonry test coupons, masonry (concrete) blocks were used to create the test coupons. Each masonry block was 3.5 inches wide, 7.5 inches long, and 2.25 inches high. Each masonry block was first coated with white Behr Premium Concrete Stain. Next, some masonry coupons were coated with white Behr Masonry, Stucco, and Brick paint, and other masonry coupons were coated with gray Behr Premium Basement and Masonry Waterproofer. Similar to the wood test coupons, the masonry test coupons were sanded and wiped clean with isopropanol between each coating layer and the finished coupons were thermally aged in an oven for three weeks at 140°F.

Following completion of the coupon aging process, rubber gaskets were super-glued onto the aged test coupons to designate the testing areas. The rubber rings enabled the thickened and un-thickened paint stripping solvent blends to remain in one area on the test coupon without flowing to other areas of the test coupon surface. The rubber gaskets used were 3/16 inches high with a 1.5 inch outside diameter and a 1.25 inch inside diameter. This created a test area of approximately 1.23 square inches on the surface of the test coupon. During the test, 1.5 ml of the chemical paint stripper was placed within the test area by pipet. Next, a laboratory watch glass was placed on top of the rubber gasket to ensure that it would not evaporate out of the testing area during the test. This step was conducted to evaluate the new solvent blends that had not yet had evaporation barrier additives included within the formulation. Once the chemical remained in the test area for a pre-determined dwell time, the chemical paint stripper and paint residue was then removed from the testing area using a spatula and paper towel. Then the coating was scraped with a plastic scraper until no more coating material could be easily removed. Figure 1 shows a wood coupon with ring gaskets after testing was completed.

Figure 1: Wood coupon with ring gaskets after testing

After scraping, the testing area was then given a visual rating between 0% and 100% to indicate how much substrate surface had been exposed during the given dwell time. The ratings were estimates provided by a lab technician after visual inspection of the test area. The ratings were provided in increments of 5% since it was not possible for the lab technician to attain any further resolution with the visual estimation process. The rating "0%" was given if the paint stripper removed some coating layer(s) but the substrate surface was still completely covered by a coating. The rating would be "<u>**0%**</u>" in bold and underlined if the paint stripper did not remove any coating at all. The rating "50%" would be given if approximately half of the substrate surface was exposed. The rating "100%" would be given if the substrate surface was completely exposed.

Fourteen different chemical paint removers, ten commercially available and four formulations recently developed by TURI/UMass Lowell, were tested at different dwell times for specific coatings. Of the ten commercially available paint stripping products, three of them contained methylene chloride. The first product was Strypeeze™, from the company Savogran, which is a low methylene chloride content paint stripper. The other two methylene chloride-based paint stripping products, SuperStrip™ from Savogran and KleanStrip™ from W.M. Barr, had high methylene chloride content. The seven commercially available paint stripping products that did not contain any methylene chloride were based on other chemicals such as NMP, benzyl alcohol, and dibasic esters. Table 1 shows the solvents used in the three methylene chloride-based paint strippers, the seven alternative paint strippers without methylene chloride, and the four new UMass Lowell-developed formulations.

Table 1: *Solvents Used in Paint Stripping Products*

Supplier	**Product**	**Primary Component**	**Secondary Component**	**Other Component(s)**
Savogran	Strypeeze™	Methylene chloride	Methanol	Toluene, Acetone
Savogran	Superstrip™	Methylene chloride	Methanol	Toluene
W.M. Barr	KleanStrip™	Methylene chloride	Methanol	-
UMass Lowell	Formulation #4	Methyl Acetate	Dimethyl sulfoxide	Thiophene
UMass Lowell	Formulation B	Methyl Acetate	Dimethyl sulfoxide	Thiophene
UMass Lowell	Formulation F	Methyl Acetate	Dimethyl sulfoxide	None
UMass Lowell	Formulation #9	Acetone	Dimethyl sulfoxide	Thiophene
Eco Safety Prod.	EcoFast™	Benzyl Alcohol	Water	-
Dumond Chem.	Peel Away 7™	Benzyl Alcohol	NMP	-
W.M. Barr	Citristrip™	NMP	Dibasic Esters	Citrus
Sunnyside Corp.	ReadyStrip™	Benzyl Alcohol	NMP	Formic Acid
EZ Strip	EZStrip™	Dibasic Esters	Triethyl Phosphate	Water
Motsenbocker	LiftOff™	Glycol Ether DB	Acetone	-
Dumond Chem.	SmartStrip™	Benzyl Alcohol	Water	-

To determine the dwell time for each type of coating for wood and masonry coupons, the methylene chloride-based strippers were tested at different dwell times until substrate exposure between 65% and 95% was achieved. This target range was selected because it provided a dwell time where the methylene chloride-based stripper was effective at removing the majority of the coating material on the substrate. A target value of 100% would not be helpful because 1) it would not be possible to determine the exact dwell time when 100% coating material removal occurred, and 2) it does not provide the opportunity for non-methylene chloride formulations to potentially exceed methylene chloride's performance. The resultant dwell times vary between coatings because of the range of difficulty to remove the different types of coatings. For example, the oil, varnish, and epoxy coatings are difficult to remove and require longer dwell times for the methylene chloride-based paint strippers to reach the 65%–95% target range. In realistic paint stripping scenarios, it is sometimes recommended that the chemical be reapplied as needed. Reapplication was implemented for the wood coupons with the epoxy, varnish, and oil coatings as well as the mixed coupon. For example, the paint stripper applied on an epoxy coating would have an initial 20 minute dwell time, followed by a scraping, a paint stripper reapplication for a subsequent 10 minute dwell, and then a second scraping. For the metal coupons, there was not a predetermined dwell time, and instead the coupons were scraped after cracking of the coating materials occurred.

The results of the paint stripper performance testing conducted at the TURI Laboratory are shown in Table 2 for wood coupons, in Table 3 for masonry coupons, and Table 4 for metal coupons. The results in the table are for a single test conducted for each coating and paint stripper combination. The test was not designed to provide statistical significance, but rather to ascertain the relative paint stripping effectiveness of the paint strippers.

Table 2: *Laboratory Performance Testing Results for Wood Coupons: % Substrate Exposed*

	Dwell Time (min)	**Strypeeze**	**SuperStrip**	**Klean-Strip**	**UML Form 4**	**UML Form B**	**UML Form F**	**UML Form 9**	**EcoFast**	**Peel Away**	**CitriStrip**	**Ready-Strip**	**EZ Strip**	**Lift Off**	**Smart Strip**
Epoxy	20,10	80	95	95	80	85	75	90	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Shellac	8	65	75	70	70	50	20	0	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Lacquer	10	75	95	85	95	60	65	95	0	0	0	0	0	0	0
Polyur.	10	95	85	85	95	65	70	60	**0**	**0**	**0**	0	**0**	**0**	0
Varnish	20,12	85	85	85	80	75	80	95	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Oil	25,10	95	90	95	70	75	75	50	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Latex	25	85	80	85	70	80	60	15	0	0	0	0	0	0	0
Mixed	20,15	85	90	85	60	65	70	75	0	0	0	0	0	0	0
Avg.		83	87	86	78	69	64	60	0	0	0	0	0	0	0

Table 3*: Laboratory Performance Testing Results for Masonry Coupons: % Substrate Exposed*

	Dwell Time (min)	Strypeeze	SuperStrip	Klean-Strip	UMLForm 4	UML Form B	UML Form F	EcoFast	Peel Away	CitriStrip	Ready-Strip	EZ Strip	Lift Off	Smart Strip
White	7	85	95	95	75	85	65	0	0	20	0	0	0	0
Grey	8	95	99	95	80	70	75	2	0	20	0	0	0	0
Avg.		90	97	95	78	78	70	1	0	20	0	0	0	0

Table 4: *Laboratory Performance Testing Results for Metal Coupons: % Substrate Exposed*

	Strypeeze	Super Strip	Klean-Strip	UML Form 4	UML Form B	UML Form F	EcoFast	Peel Away	CitriStrip	Ready-Strip	EZ Strip	Lift Off	Smart Strip
Dwell time	6 min	5 min	3.5 min	15 min	23 min	30 min	376 min	360 min	225 min	363 min	296 min	288 min	181 min
% Substrate Exposed	85	100	100	100	70	55	60	25	70	50	30	40	50

The results for the three types of substrates (wood, masonry, and metal) were similar in that the UMass Lowell formulations showed a range of paint stripping performance similar to methylene chloride-based paint strippers, and a range of performance significantly better than the non-methylene chloride products currently commercially available. For example, on wood coupons the range of substrate exposure across all types of coatings achieved by the three methylene chloride-based products (Strypeeze, SuperStrip, and KleanStrip) was 65% to 95%. For the UMass Lowell-developed Formulation #4, the range of substrate exposure across all types of coatings was 60% to 95%. For the seven commercially available alternative paint stripper products without methylene chloride, there was zero substrate exposure across all types of coatings.

Requirement 4: Non-flammable or low flammability

The target requirement was to have a solvent blend that was non-flammable with a flash point greater than 100°F. The Occupational Safety and Health Agency (OSHA) and the Consumer Product Safety Commission classify a liquid with a flash point less than 100°F as "Flammable" and a liquid with a flash point greater than 100°F as "Combustible." The flash points for the solvents used in the UMass Lowell Formulations are: methyl acetate 14°F, dimethyl sulfoxide (DMSO) 189°F, and thiophene 30°F. While some components of the new UMass Lowell formulations have flash points less than 100°F, the percentage of the individual solvents used in the overall formulations can be modified to result in flashpoints above 100°F, depending on cost and performance tradeoffs. Flashpoint tests have not yet been completed for the UMass Lowell solvent blends, but will be completed by August 2017.

Requirement 5: Volatile organic compounds (VOC) content less than 50%

All of the UMass Lowell paint stripper formulations have VOC content less than 50% as they contain 50% or greater of VOC-exempt solvents such as methyl acetate, dimethyl carbonate, and acetone.

Requirement 6: Raw material cost less than approximately $0.70 per pound

The alternative solvent blends evaluated under this research were selected g for low raw material cost. To have commercial potential, the cost of the alternative solvent blends must be cost comparable to paint stripping formulations containing methylene chloride. The target cost level for alternatives was to have raw material cost less than approximately $0.70 per pound. Therefore, many solvents were screened out from further consideration due to raw material costs significantly above the target cost level.

It is difficult to obtain exact pricing for solvents because of factors like the quantity of chemicals ordered (i.e. bulk orders of an ISO tank rather than just a 55-gallon drum), different prices from different chemical suppliers, geographic location (domestic or international source of chemicals), and the ongoing price fluctuations of any given solvent. However, based on our best information at the time of this research, Formulation F has an approximate cost ($0.59 per lb) which is below the target cost, Formulation B ($0.73 per pound) is comparable to the target cost, and Formulation 4 ($0.94 per lb) and Formulation 9 ($0.94 per lb) are slightly above the target cost.

Requirement 7: No damage to substrate material

A key requirement for the alternative materials is to not damage the substrate material. This includes staining, discoloring, or altering the substrate, corrosion of the metal substrates, and raising the grain of the wood substrates. Alternative materials that are caustic, acidic, or corrosive would have a high likelihood of damaging the substrate materials. Therefore, the alternative materials were selected based on not having significant caustic, acidic, or corrosive properties. During the performance testing conducted in the TURI laboratory, the substrate surface was thoroughly examined for damage after each paint stripping test for all substrate materials: wood, metal, and masonry. The alternative solvent blends evaluated in this research did not exhibit any damage to the substrate materials during any of the testing conducted on wood, metal, and masonry substrates.

Requirement 8: Environmental, health, and safety

The UMass Lowell-developed formulations were designed to be composed of chemicals that are safer from an environmental, health, and safety standpoint compared to methylene chloride. First, the solvents selected for consideration in the UMass Lowell paint stripping formulations were screened for significant environmental, health, and safety issues by using information provided in safety data sheets and other publicly available chemical hazard sources.

For the solvents that passed this initial screen, the GreenScreen™ for Safer Chemicals was then used as the evaluation tool to provide a more detailed and comprehensive environmental, health, and safety assessment. GreenScreen for Safer Chemicals, developed by Clean Production Action, is a comparative chemical hazard assessment method. In this tool, 20 human health, environmental toxicity, fate, and physical hazard endpoints are evaluated for each chemical. Assessing chemicals is accomplished by examining comprehensive toxicological data, checking GreenScreen specified lists, and using estimated data from suitable analogs or modeled data where measured data are lacking. As a result of this assessment, chemicals are designated with one of the following four Benchmark Levels [10]:

Benchmark 1: Chemical of High Concern - Avoid
Benchmark 2: Use but Search for Safer Substitutes
Benchmark 3: Use but Still Opportunity for Improvement
Benchmark 4: Prefer – Safer Chemical

In 2015, ToxServices conducted GreenScreen assessments for several chemicals used in paint stripping formulations including methanol, methylene chloride, benzyl alcohol, etc. [11]. In 2017, TURI contracted with ToxServices to conduct GreenScreen assessments for the following four chemicals used in the UMass Lowell solvent blends: methyl acetate, thiophene, DMSO, and acetone. The complete report from the 2017 assessment by ToxServices is available on the TURI website. The Benchmark results from the 2015 and 2017 Green Screen analyses by ToxServices are provided in Table 5. The chemicals used in methylene chloride-based paint stripping products (methylene chloride, methanol, and toluene) each received a Benchmark Level 1: "Chemical of High Concern – Avoid." The chemicals used in the new UMass Lowell formulations (acetone, methyl acetate, and DMSO) received Benchmark Levels of 2 or 3, and are, therefore, safer than the three chemicals (methylene chloride, methanol, and toluene) used in methylene chloride-based paint strippers. Thiophene was assigned a preliminary Benchmark Level 2 based on currently available data for eighteen out of the twenty different hazard endpoints assessed. Thiophene received a final score of "U," which means "Unspecified due to Insufficient Data" since there is currently insufficient data in the scientific literature to assess thiophene for two hazard endpoints: carcinogenicity and endocrine activity. Other commonly used chemicals (benzyl alcohol, dibasic esters) for non-methylene chloride paint stripping products have received a Benchmark Level 2. Therefore, all of the paint strippers that do not contain methylene chloride are likely to be safer than the methylene chloride-based strippers. TURI will conduct additional investigation into the potential hazards of the entire solvent blend formulations and the data gaps identified for thiophene.

Table 5: *GreenScreen Benchmark Levels for Chemicals Used in Paint Strippers*

Chemical	Bench-mark	Benchmark Explanation	Benchmark Reason (Primary Hazard Endpoints of Concern)
Methanol	1	Chemical of High Concern – Avoid	"High" developmental toxicity
Methylene chloride	1	Chemical of High Concern - Avoid	"High" carcinogenicity
Toluene	1	Chemical of High Concern – Avoid	"High" reproductive and developmental toxicity
Acetone	2	Use but Search for Safer Substitutes	"Moderate" developmental toxicity, reproductive toxicity, and endocrine activity; and "High" flammability
Benzyl alcohol	2	Use but Search for Safer Substitutes	"Moderate" developmental toxicity; "High" neurotoxicity (repeated dose) and skin sensitization
Dibasic ester mixture (Estasol)	2	Use but Search for Safer Substitutes	"Moderate" developmental toxicity and endocrine activity
Methyl acetate	2	Use but Search for Safer Substitutes	"Moderate" developmental toxicity and endocrine activity; and "High" flammability
DMSO	3	Use but Still Opportunity for Improvement	"Moderate" skin irritation & eye irritation; "Moderate" flammability
Thiophene	U	Data Gaps	Prior to data gap analysis, it was assigned a Benchmark 2. Insufficient data for carcinogenicity and endocrine activity

Requirement 9: Be composed of chemicals that have small molar volumes and low hydrogen bonding values

Paint penetration is an important consideration in removing multiple layers of paint in a single application of a paint stripper. The penetration of the multiple layers of paint and breaking the bond between the paint and substrate make it easy to remove all layers with a scraper. Paint penetration is a function of molar volume and Hansen hydrogen bonding parameter. In general, the smaller the molar volume, the better the paint penetration, and the lower the Hansen hydrogen bonding parameter, the better the paint penetration.

Therefore, the chemicals selected for the alternative formulations were composed of chemicals that have small molar volumes so that they can penetrate the various polymer coatings. Based on the results of numerous tests, it was found that the ability of the solvents to effectively strip multi-layer coatings was significantly decreased after the molar volume size exceeded 80 ml/mol. Methylene chloride has a molar volume of 64 ml/mol. The solvents chosen for the alternative formulations, DMSO (71 ml/mol), acetone (71 ml/mol), methyl acetate (70 ml/mol), and thiophene (79 ml/mol), have molar volume sizes comparable to or less than 80 ml/mol. The molar volume size is much greater than 80 ml/mol for many of the chemicals typically found in commercially available alternative paint stripping formulations: NMP (96 ml/mol), benzyl alcohol (104 ml/mol), dimethyl succinate (135 ml/mol), dimethyl glutarate (152 ml/mol), d-Limonene (163 ml/mol), dimethyl adipate (168 ml/mol), and triethyl phosphate (171 ml/mol).

Although water has a low molar volume, it has a high hydrogen bonding Hansen Solubility Parameter of 42.3 $MPa^{1/2}$, and therefore is not an effective penetrant of polymer matrices found in coating materials. Methylene chloride has a low hydrogen bonding Hansen Solubility Parameter of 7.1 $MPa^{1/2}$and a low molar volume, which makes it an effective penetrator of coating materials. The solvents used in the UMass Lowell formulations all have low hydrogen bonding Hansen Solubility Parameters: methyl acetate (7.6 $MPa^{1/2}$), DMSO (10.2 $MPa^{1/2}$), and thiophene (7.8 $MPa^{1/2}$).

III. Field-based Testing Results

Field testing for one of the new paint stripping formulations developed by UMass Lowell was conducted on May 19, 2017. The field testing took place at the Belcastro Furniture Restoration facility located in Tyngsboro, Massachusetts. Belcastro Furniture Restoration has been doing antique repair, refinishing and restoration for over 40 years, and has been working with the Massachusetts Office of Technical Assistance and Technology and the Toxics Use Reduction Institute to find safer and effective alternatives to methylene chloride. For the field testing, a decorative column was used that had several layers of lead-based paint and was approximately 115 years old (Figure 2).

Figure 2: Decorative column with lead-based paint

The two paint stripper materials used during the field testing are shown in Table 6.

Table 6: *Paint Stripper Materials*

Product	Supplier	Ingredients
B7 Industrial Paint Remover	Benco Sales Inc., Crossville, TN	Methylene chloride 70%–80% Methanol 5%–15% 2-Butoxyethanol 1%–10% 2-Methoxymethylethoxpropanol 1%–3% Wetting agent and wax 1%–5%
Formulation #4	University of Massachusetts Lowell	Methyl acetate Dimethyl sulfoxide (DMSO) Thiophene

The two paint stripper materials were applied by the Belcastro operator to the decorative column using paint brushes. The methylene chloride-based paint stripper was applied to the left side of the decorative column, and Formulation #4 was applied to the right side of the decorative column. The initial application of the paint stripper materials can be seen in Figure 3.

Figure 3: Initial application of paint stripping materials
(B7 on left side, Formulation #4 on right side)

The paint removal method conducted by the Belcastro operator consisted of the following iterative process:

1. Apply the paint stripping materials onto the surface of the decorative column.
2. Allow the paint stripper to remain on the surface of the column for a few minutes.
3. Scrub the area with ScotchBrite™ scouring pads and wire brushes.
4. Wipe the area clean with a cloth rag so that photos could be taken.

Steps 1–4 were repeated several times so that photos could be taken after 20 minutes, 29 minutes, 34 minutes, and 39 minutes of testing. These photos can be seen in Figures 4–7. The testing was concluded after 39 minutes from the initial application of the paint stripping materials. A single Belcastro operator conducted the tests for the B7 and Formulation #4 paint strippers at the same time by alternating efforts to allow the paint stripper on one side to dwell on the surface, while scraping the other side. Separate paint brushes, ScotchBrite scouring pads, and wire brushes were used for the two different paint stripping materials to prevent cross contamination during the testing.

Figure 4: Testing results after 20 minutes (B7 on left side, Formulation #4 on right side)

Figure 5: Testing results after 29 minutes (B7 on left side, Formulation #4 on right side)

Figure 6: Testing results after 34 minutes (B7 on left side, Formulation #4 on right side)

Figure 7: Testing results after 39 minutes (B7 on left side, Formulation #4 on right side)

The Belcastro operator made the following observations during the field test:

- There were several layers of lead paint on the decorative column. (The cream, brown, white, and grey colored paint layers are visible in Figures 3–6.)
- The methylene chloride-based product made the paint more gummy during the removal process than the Formulation #4 did.

- Formulation #4 seemed to evaporate faster than the methylene chloride-based product. (Unlike with many commercially available paint stripping formulations such as B7 used by the operator, Formulation #4 does not yet contain an evaporation barrier additive.)
- Some areas of wood substrate are exposed as a result of the testing for both the methylene chloride-based product and Formulation #4.
- Overall, the two paint stripping products performed approximately equally for removing the lead paint from the wood substrate.

Additional field testing will be conducted at Belcastro Furniture Restoration once an evaporation barrier has been added to the UMass Lowell paint stripping formulations.

IV. Conclusions and Next Steps

Performance testing at the TURI Laboratory was conducted for a variety of coating materials on wood, masonry, and metal substrates. The testing results showed that the new solvent blends developed by UMass Lowell, comprising various combinations and amounts of methyl acetate, dimethyl sulfoxide, thiophene, and other solvents, worked comparably to methylene chloride-based paint strippers and significantly better than other commercially available alternatives based on chemicals such as NMP, benzyl alcohol, and dibasic esters. In addition, the UMass Lowell formulations without thiophene are likely safer than methylene chloride from an environmental, health, and safety standpoint. Thiophene was assigned a preliminary Benchmark Level 2; however, there is currently insufficient data publicly available to assess thiophene for carcinogenicity and endocrine activity. Therefore, the UMass Lowell formulations with thiophene will be further investigated to address the current data gaps.

The field testing conducted at Belcastro Furniture Restoration provided results that indicate that one of the new solvent blends developed by UMass Lowell performs comparably with methylene chloride-based paint strippers for multi-layer lead paint on wood substrate applications.

Further research and testing is needed to build on the successful paint stripper solvent blend formulations already developed. Paint stripper products typically comprise 95% to 98% solvent blends and 2% to 5% chemical additives. TURI identified and evaluated suitable solvent blends to meet the solvency functionality provided by methylene chloride within a paint stripping product. To enhance the overall performance of paint stripping products, formulations routinely contain chemical additives that perform the following functions [12]:

- Activator: an additive that increases the penetration of the solvent or solvent blend into the coating matrix.
- Evaporation inhibitor: an additive used to reduce evaporation of the solvent and increase contact time with the coating and substrate.
- Thickener: an additive used to increase the viscosity of the product so that it can remain in place for use on vertical surfaces.
- Corrosion inhibitor: an additive used to ensure the stability of the stripper in its packaging or to protect the substrate.
- Surfactants/rinsing agent: an additive used to wet or penetrate the coating surface.
- Colorant: an additive used to provide color to the formulation to make it easier to locate where the paint stripper has been applied on the substrate.

The next steps for the research include the identification and evaluation of the other additive ingredients of a complete paint stripping formulation. Once viable additive chemicals with acceptable environmental, health, and safety characteristics have been determined, we will conduct performance testing of the completed paint stripping formulations at the TURI laboratory and at a furniture refinishing facility.

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