Surface Tension Modification of NMP-based Paint Strippers

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ABSTRACT

The increasing awareness of exposure to traditional paint strippers has prompted a search for alternative products. One group of such alternatives are formulations based on N-Methylpyrrolidone (NMP). In comparing NMP-based paint removers with more volatile products, the primary trade-offs are stripping speed versus solvent inhalation, and product cost versus usage cost. NMP-based paint removers work at a slower rate, but have dramatically lower vapor pressures thus reducing the chances of solvent inhalation. In addition, by lowering the surface tension of these NMP formulas, the time required for their use may be decreased by as much as 40%. Regarding cost, NMP blends may be more expensive to purchase, but approximately 40% less product is required to achieve similar stripping results.

INTRODUCTION

The solvents traditionally used in paint strippers include methylene chloride, methanol, acetone, and methyl ethyl ketone. In evaluating stripping speed, these products have some common properties that play a key role in their ability to quickly remove paint.

All of these solvents consist of **small, non-complex molecules.** This allows fast and efficient solvent penetration of the cured paint or coating.

They all have **high vapor pressures** resulting in **fast evaporation rates.** The quick evaporation of solvent aids in lifting paint from the substrate.

They also have **low surface tensions.** This allows them to quickly "wet out" all surfaces, fill any surface pores, and begin immediate penetration of the paint film.

In combination, these properties result in paint stripping formulas that can quickly and effectively remove most common paints and coatings.

NMP, in comparison, has relatively different properties of molecular size, vapor pressure, and surface tension that result in slower stripping times.

NMP is a larger molecule. As such, NMP simply requires more time to penetrate a given coating.

NMP has a lower vapor pressure. After penetration of the coating, highly volatile solvents will lift paint as they flash back through the paint film. The low volatility of NMP slows this lifting process.

NMP has a higher surface tension. The surface tension of NMP is nearly double that of other paint stripper solvents.

Table 1 - Solvent Property Data

	Vapor Pressure (mm Hg)	Surface Tension (Dynes/cm)	Reference Temperature (°C)
Methylene Cl	340	26.5	20/20
Methanol	100	22.6	21/20
Acetone	185	22.3	20/20
MEK	70	24.6	20/20
NMP	0.24	42.0	20/24

If any of these key properties could be modified, perhaps the stripping speed of NMP could be improved as well. Molecular size is fixed, and although vapor pressures and surface tensions can be reduced through increasing temperature, this is not a common practice in most paint stripping applications. However, through the addition of an appropriate surfactant, the surface tension of NMP blends may be modified to improve stripping speed.

PRODUCT DESCRIPTION

Composition

Five NMP-based formulas were reviewed in this study to determine their effectiveness as paint strippers. The compositions of these five blends with their respective flash points are listed in the following table. (Note: Flash points were determined by ASTM method D-56, Tag Closed Cup.)

Table 2 - Paint Stripper Formulas

	#1	#2	#3	#4	#5
NMP[1]	31.0%	60.0%	80.0%	12.0%	50.0%
Hisol® 15[2]	50.0%				
EEP[3]	17.9%	13.9%		6.7%	
DBE[4]		25.0%	12.0%	80.0%	36.0%
Dowanol®TPM[5]			7.0%		13.0%
Methocel®311[6]	1.1%	1.1%	1.0%		1.0%
Klucel®H-PR[7]				1.3%	
Flash Point	133°F	168°F	182°F	176°F	186°F

For safety considerations, cosolvents were chosen so that low volatility and high flash point would be maintained in the final blend. As required, cellulosic thickeners were added to increase viscosity. Further information on the blending and use of these formulas is available in the BASF publication, "**Formulating Paint Strippers with N-Methylpyrrolidone.**"

Applications

All of these formulations demonstrated good paint stripping ability in the removal of commonly used paints and coatings. During testing, performance data were developed on the ability of these products to strip acrylic latex, alkyd, polyurethane, and epoxy coatings from wood substrates.

Use of NMP paint strippers is similar to that of any other stripper. The product is simply applied to the substrate with a brush or roller and given sufficient time to penetrate the coating. Using a thickened version will allow the stripping of walls or ceilings.

Following application, the residual stripper, paint flakes and dissolved pigment are easily removed using a standard plastic or metal scraper.

Since all of these products will slowly evaporate, the following procedure is recommended to ensure complete removal of the spent solvent from the surface:

Step 1: After the stripper and paint have been scraped from the surface, wipe the area clean with a cloth or absorbent towel.

Step 2: Using a wet cloth or towel, clean any residual formula from the surface. As these products rinse well with water, any residual solvent is easily removed.

Step 3: Using a dry cloth or towel, remove any excess moisture, and then allow the surface to air dry for several minutes.

In most applications, a single application of the stripper is sufficient, even when stripping thick (multiple) paint layers.

Hazards

As stated earlier, one of the primary trade-offs between NMP and traditional strippers is stripping speed versus solvent inhalation. One method for judging the relative risk of inhalation is by comparing the ratios of equilibrium vapor concentration (EVC) to permissible exposure limit (PEL, 8 hour average) for each solvent. This data is listed in Table 3.

Table 3 - Vapor Concentration Data (@ 20°C)

	EVC (ppm)	PEL (ppm)	Ratio
Methylene Cl	450,000	500	900
Methanol	130,000	200	650
Acetone	240,000	750	320
MEK	92,000	200	460
NMP	300	100*	3
Hisol® 15	1,300	100	13
EEP	1,400	50*	28
DBE	260	10*	26
Dowanol®TPM	25	-	-

*Denotes producer's recommendation.

Higher ratio values indicate relatively higher risks of inhalation exposure. For instance, NMP's ratio of three versus methylene chloride's ratio of 900 indicates that the risk of inhaling a concentration of methylene chloride above the recommended PEL is 300 (900/3) times more likely than when using NMP under the same conditions.

In other words, NMP provides the user with a greater margin of safety from inhalation as compared to the more common paint stripper solvents.

As with any solvent, the use of gloves is essential to prevent severe drying and potential blistering of exposed skin. It is recommended that rubber gloves be worn during any use of these products. Should any exposed skin come into contact with an NMP blend, immediately rinse the exposed area with water. Also, it is strongly recommended that these products be used in well ventilated areas and that goggles be worn throughout the stripping process.

The NMP blends tested in this study have flash points in the range of 140° - 200°F. As such, all of these compositions result in combustible, but not flammable, mixtures.

PRODUCT PERFORMANCE

Effectiveness

NMP-based formulas will effectively strip the following coatings:

- Acrylic latex gloss enamel
- Household epoxy spray paint
- Polyurethane gloss enamel
- High gloss polyurethane wood finish
- Tallow oil alkyd spray paint

In this study, the above coatings were stripped from wood. The effectiveness of these formulas to strip similar coatings from other substrates (i.e. metal, plastic, glass, concrete) should be equivalent.

Time Requirements

With sufficient time, NMP blends can be quite effective paint strippers. In some cases, these blends required longer contact time than required by conventional stripping formulations.

In general, the longer working times were required when stripping higher crosslinked coatings. For certain blends, lowering the surface tension resulted in noticeably faster stripping of these more complex coatings.

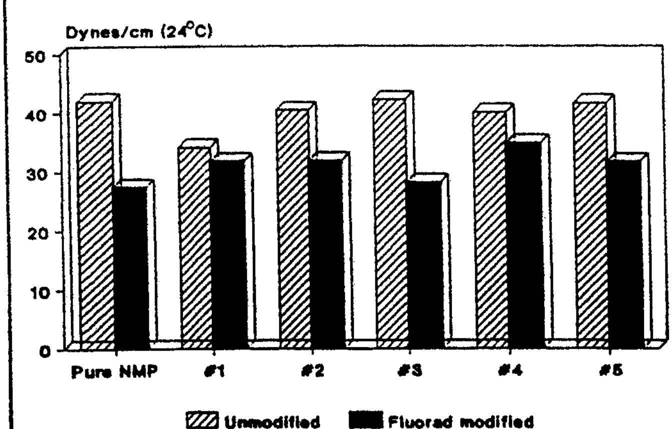
To quantify the impact that surface tension has on stripping speed, the original five formulas were modified with a nonionic surfactant, Fluorad® FC-430. Shown in Table 4 are the original formulas modified to contain 0.2 wt% of Fluorad® FC-430. Flashpoints of the new mixtures are listed as well.

Table 4 - Paint Stripper Formulas using Fluorad®

	#1	#2	#3	#4	#5
NMP[1]	31.0%	59.8%	79.8%	12.0%	49.8%
Hisol® 15[2]	50.0%				
EEP[3]	17.7%	13.9%		6.7%	
DBE[4]		25.0%	12.0%	79.8%	36.0%
Dowanol® TPM[5]			7.0%		13.0%
Methocel® 311[5]	1.1%	1.1%	1.0%		1.0%
Klucel® H-PR[6]				1.3%	
Fluorad®[7]	0.2%	0.2%	0.2%	0.2%	0.2%
Flash Point	138°F	174°F	184°F	180°F	194°F

After addition of the surfactant, each modified formula was compared to the original, unmodified version. The results of these tests are shown in Figure 1.

Figure 1 - Surfactant Induced Surface Tension Reduction



Formulas	#1	#2	#3	#4	#5
Unmodified	34.2	40.5	42.3	40.1	41.7
+Fluorad®[7]	31.8	31.9	28.2	34.9	31.7

NMP Pure	42.0
NMP + 0.2% Fluorad®	27.5

Table 5 - Comparative Stripping Times (minutes)					
	Alkyd (3 layers)	Urethane Enamel (2 layers)	Household Epoxy (2 layers)	Acrylic Latex (2 layers)	Urethane Finish (1 layer)
Formula #1:					
Unmodified	6-7	33	17	7-8	9
+ 0.2% Fluorad	7	33-34	16	7-8	8-9
Formula #2:					
Unmodified	<5	23	19	7-8	6
+ 0.2% Fluorad	5	20	13	7-8	6-7
Formula #3:					
Unmodified	7-8	26	14-15	7-8	4
+ 0.2% Fluorad	7-8	19	9	7-8	4-5
Formula #4:					
Unmodified	7-8	110	24	7-8	100
+ 0.2% Fluorad	7-8	67	20	7-8	96
Formula #5					
Unmodified	7-8	42	17	7-8	9
+ 0.2% Fluorad	7-8	28-29	14-15	7-8	8-9
Methylene Chloride Formula					
Zip-Strip[8]	2.0	2.0	1.5	2.0	1.5

To measure relative performance, tests were conducted to observe the time required to lift various coatings from wood at room temperature. The modified NMP blends were tested against the original formulas, as well as Zip-Strip, a common methylene chloride-based product. Table 5 above lists the results of these tests.

In actual use, those blends modified with Fluorad® demonstrated a noticeable improvement in stripping speed when removing urethane enamel and household epoxy, the more complex of the coatings tested. This increase in efficiency is illustrated by Figures 2 & 3.

It should be noted that even after reducing the time required to strip urethane enamel and household epoxy, the NMP formulas are slower than the methylene chloride product. Again, the trade-off is one of stripping speed versus the possibility of solvent inhalation. NMP works slower, but provides the user a working environment containing less solvent vapor.

Figure 2 - Urethane Stripping Time Improvement

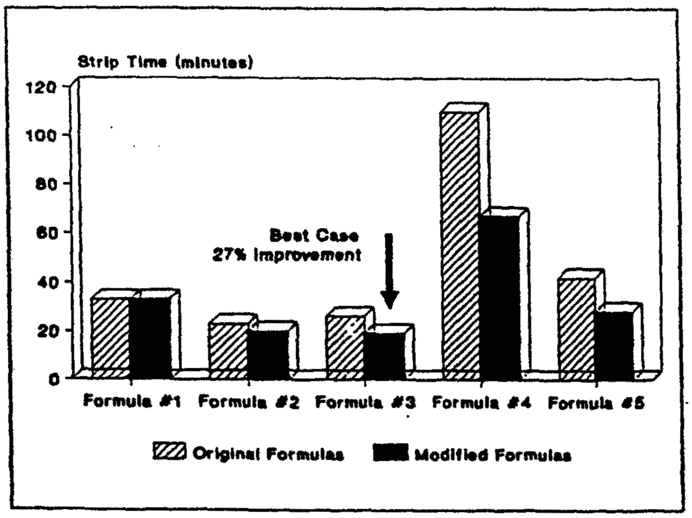
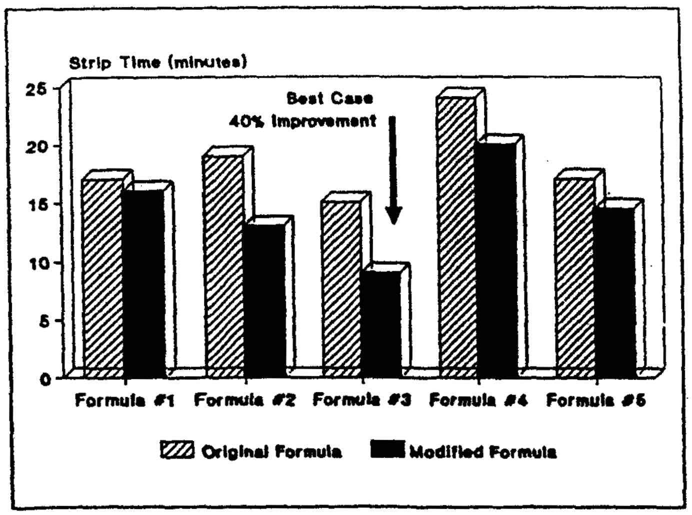


Figure 3 - Epoxy Stripping Time Improvement



WASTE MANAGEMENT

Material Recyclability

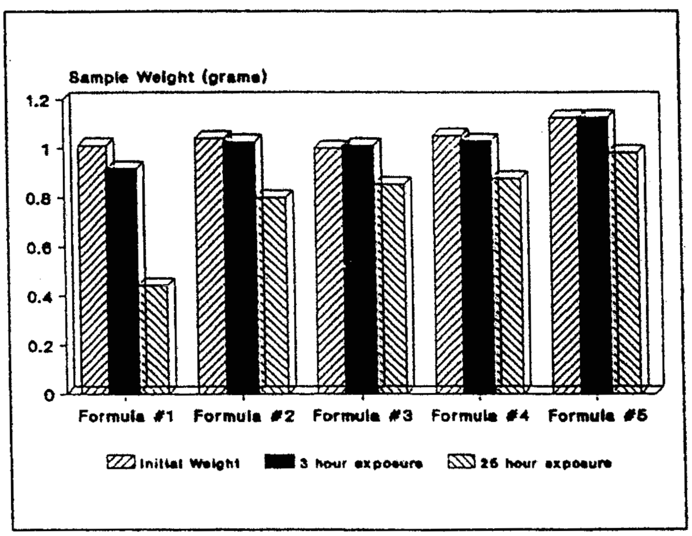
A significant amount of the spent stripper is potentially reuseable solvent. However, as this is a thickened mixture, conventional distillation techniques of recovery are unrealistic. Any paper waste collected during use of the product further compounds the issue of recycling by distillation.

If a sufficient volume of thickened residue were isolated, a filter press could be used to separate the spent solvent. This solvent could then be recycled via distillation and reused.

Waste Generation

All of the compounds used in these NMP-based formulas have low vapor pressures. Until physically removed, a large volume of residue will remain on the substrate even after an extended period of time.

Figure 4 - Product Remains on Substrate



As shown in Figure 5, relatively minor amounts of the stripper will evaporate from the substrate, even after 25 hours.

In normal use, 15-30 minutes should be sufficient to remove most coatings. However, as further illustrated by Figure 6, 98% of the stripper formulation will remain on the surface even after three hours. Most importantly, this low volatility significantly reduces the possibility of solvent inhalation.

Figure 5 - Evaporation Loss is Minimal (long term)

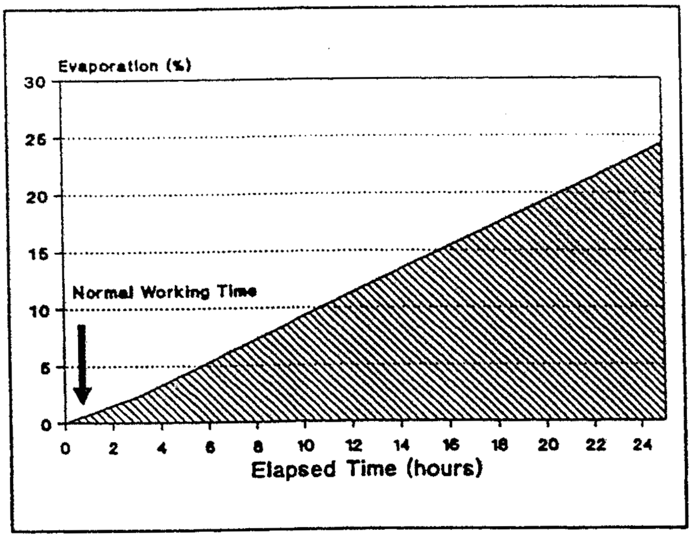
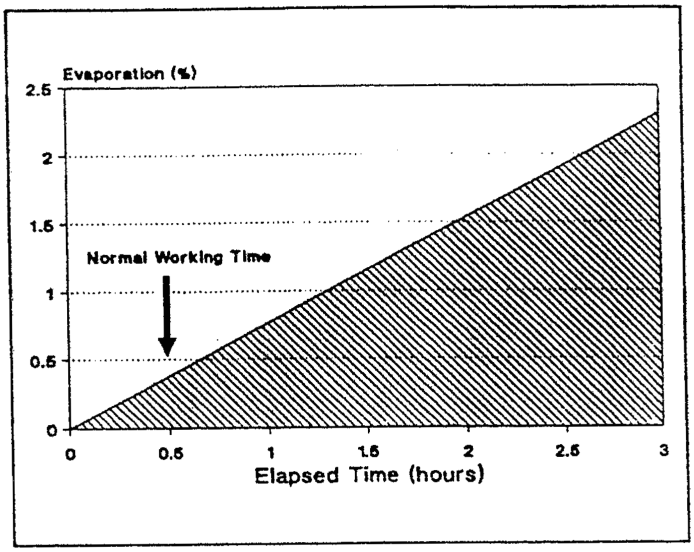


Figure 6 - Evaporation Loss is Minimal (short term)



Waste Disposal

In using these products, it is recommended that the solvent/paint residue as well as any paper or cloth debris be deposited in a thick-walled polyethylene or polyvinylidene chloride bag.

In those areas of the country where household chemicals are sorted from other household garbage, these bags of residue should be separated for proper disposal.

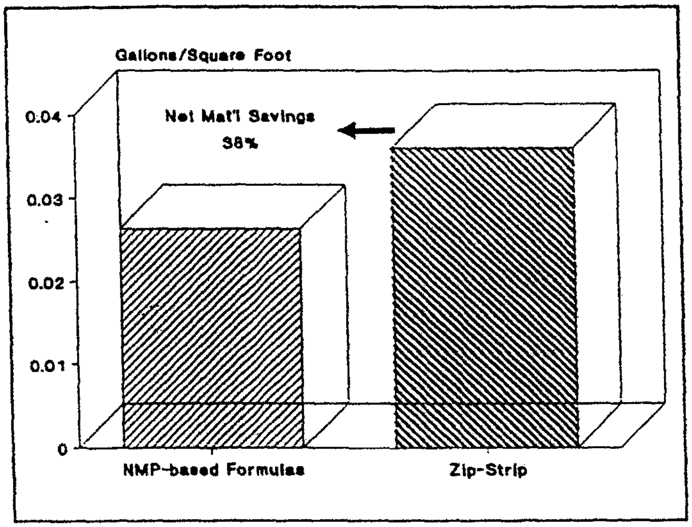
STRIPPING COST

Another factor when developing NMP blends is usage cost. Each of the five coatings examined in this study was removed in a single application of an NMP blend. The methylene chloride product, Zip-Strip, also removed each coating in a single application.

However, the volume of the NMP blend required for a single coat was approximately 38% less than that required of Zip-Strip. This represents a substantial savings in actual material required to strip any given surface area.

NMP strippers may be more expensive per gallon than traditional products. But, less product will be required to achieve similar results.

Figure 7 - NMP Blends are more Efficient



SUMMARY

The search for alternative paint strippers will likely include several alternative solvents. In comparison to traditional paint strippers, the primary differences are issues of stripping speed versus the possibility of solvent inhalation, and product cost versus usage cost.

NMP blends work slower than traditional paint strippers, but NMP generates less solvent vapor during the stripping operation than do the more common paint stripper solvents.

NMP blends may be more expensive per gallon, but they will cover more surface area per gallon than will traditional paint strippers.

In evaluating replacements for traditional solvents, these trade-offs must be carefully reviewed prior to the selection and use of an alternative paint stripper. In some applications, stripping speeds of NMP-based formulas can be improved through lowering the surface tensions of the blends.

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Product Information Brochure: Fluorad® Coatings Additives FC-430, FC-431, 3M Industrial Chemical Products Division, issued 11/89.

SOURCES

1. BASF Corporation
   Parsippany, NJ
2. Ashland Chemical Company
   Columbus, OH
3. Eastman Chemical Products, Inc.
   Kingsport, TN
4. Dow Chemical Company
   Midland, MI
5. E.I. duPont de Nemours & Company
   Wilmington, DE
6. Hercules, Inc.
   Wilmington, DE
7. 3M Industrial Chemical Products Division
   St. Paul, MN
8. Star Bronze Company
   Alliance, OH

Appendix A: Sample Preparation

(3) Layers of Alkyd:

A 2" x 8" x 10" piece of white pine board was sanded and then cleaned of all dust. The board was then spray painted with three thick coats of alkyd spray paint with 24 hours drying time between each application.

Coat 1: a green Tallow oil alkyd spray paint manufactured for Hardware Wholesalers, Inc. (HWI) 2012 green HWI No. 789-855, Lot #F033.

Coat 2: a brown Tallow oil alkyd spray paint manufactured for Hardware Wholesalers, Inc. (HWI) 2036 brown HWI No. 789-757, Lot #6174-2734.

Coat 3: the same green described above.

Reference: BASF Laboratory notebook - August 27, 1988.

(2) Layers of Household Epoxy:

A 2" x 8" x 10" piece of pressure-treated wood was sanded and then cleaned of all dust. Two coats of epoxy spray paint were applied to the surface. A drying time of 72 hours was allowed between coats. Before application of the second coat, the first coat was lightly sanded and cleaned of all dust.

Coat 1: NYBCO Epoxy Spray Paint Code #1901 Appliance Snow White, lot # CP-81, manufactured by: New York Bronze Powder Co., Inc., Elizabeth, NJ.

Coat 2: NYBCO Epoxy Spray Paint Code #1912 Coffee Brown, lot # BC-72, manufactured by: New York Bronze Powder Co., Inc., Elizabeth, NJ.

Reference: BASF Laboratory notebook - September 19, 1988.

(2) Layers of Acrylic Latex Enamel:

A 2" x 6" x 8" piece of white pine board was sanded and then cleaned of all dust. The board was then painted with two coats of acrylic latex gloss enamel. The paints were applied with a polyester bristle brush. A 24 hour dry time was allowed between each application. Also, the surface of the first coat was lightly sanded and cleaned before the second coat was applied.

Coat 1: JET-DRI® Acrylic Latex Gloss Enamel Code #00, Gloss White lot #AEA10 13E048, manufactured by: Desoto, Inc. Des Plaines, IL.

Coat 2: JET-DRI® Acrylic Latex Gloss Enamel Code #33, Azure Blue, manufactured by: Desoto, Inc., Des Plaines, IL.

Reference: BASF Laboratory notebook - September 19, 1988.

(2) Layers of Urethane Enamel:

A 2" x 6" x 8" piece of white pine board was sanded and then cleaned of all dust. The board was then painted with two coats of urethane enamel. The paints were applied with a polyester bristle brush. Coat # 1 was lightly sanded and cleaned of all dust prior to application of the second coat, 24 hours later.

Coat 1: JET-DRI® Polyurethane Gloss Enamel Code #17 Autumn Brown Lot #AE112 13048, manufactured by: Desoto, Inc., Gainesville, TX.

Coat 2: JET-DRI® Polyurethane Gloss Enamel Code #00 Gloss White Lot #AE 132 13E033, manufactured by: Desoto, Inc., Gainesville, TX.

Reference: BASF Laboratory notebook - September 19, 1988.

(1) Layer of Urethane Wood Finish:

A 2" x 6" x 24" piece of white pine board was sanded and then cleaned of all dust. The board was then painted with polyurethane stain, which was covered with a urethane high gloss top coat. Both stain and top coat were applied with a polyester bristle brush. Time between application of stain and top coat was 24 hours. The stain coat was very lightly sanded and cleaned of dust prior to top coat application.

Stain: High gloss polyurethane varnish stain Code # 61, Dark Oak Lot # 7568500612, manufactured by: Red Devil Paints and Chemicals, an Insilco Company, Mt. Vernon, NY.

Top Coat: High Gloss Polyurethane Code #70 , Clear lot # 75685 00702 , manufactured by: Red Devil Paints and Chemicals, an Insilco Company, Mt. Vernon, NY.

Reference: BASF Laboratory notebook - September 19, 1988.

JET-DRI® is a registered trademark of Desoto, Inc., Des Plaines, IL.

Appendix B: Surface Coverage Comparison

Zip-Strip Sample

A piece of finished oak board was measured and weighed. A coating of Zip-Strip was then applied with a polyester bristle brush. The total surface of the wood was coated with the same thickness of the stripper. (All thin spots in the Zip-Strip layer were filled in.) A single application was required to lift the finish that was on the surface of the oak substrate. The resin system of the finish was not known.

Measurement of board: 6" x 4" x 3/4"
Weight of board alone: 227.51g
Weight of board + Zip Strip: 254.62g

a. 6" x 4" = 24 in^2 of surface coated with Zip-Strip
b. 27.11g at 1.181 g/cc = 22.955 cc/24 in^2
c. 144 in^2 = 1 square foot = 137.73 cc

NMP Formula Sample

A piece of finished oak cut from the same board described above was measured and weighed. A coating of Formulation 4 (see Table 2) was applied with a polyester bristle brush. The total surface of the wood was coated with the same thickness of stripper. A single application was required to lift the finish away from the oak.

Measurement of board: 9 5/16" x 4" x 3/4"
Weight of board alone: 291.37g
Weight of board + Formulation 4: 319.58

a. 9 5/16 x 4" = 37.25 square inches coated with Formulation 4
b. 28.21g at 1.0962g/cc = 25.73 cc/37.25 in^2
c. 144 in^2 = 1 square foot = 99.46 cc

1000 cc = 1 liter = 1.057 quarts

NMP technology will cover 38.05 square ft/gallon (single application)

1000cc/99.46cc = X sq ft/sq ft
X = 10.054 square ft / liter
10.054 sq ft/X = 1.057 quarts/4 quarts
X = 38.05 square ft/gallon

Zip-Strip will cover 27.48 square ft/gallon (single application)

1000cc/137.73cc = X sq ft/sq ft
X = 7.26 square ft/liter
7.26 sq ft/X = 1.057 quarts/4 quarts
X= 27.48 square ft/gallon

A gallon of NMP formula will cover 38.46% more surface area than a gallon of Zip-Strip.