Performance by Design:
Abrasion and Scratch Resistance UV/EB Curable Sealers and Topcoats

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ABSTRACT:

An optimized UV cured topcoat and a sealer combining good scratch and abrasion resistance for wood was developed. A combination of screening, ladder and experimental design technique was used. First 12 urethane acrylate oligomers were screened for abrasion and scratch resistance and the four best oligomers were chosen for a ladder study incorporating additives like reactive waxes, silica and alumina. Using statistical design of experiments, an optimized sealer and topcoat formulation was uncovered. Results of these experiments showed that a combination of a topcoat consisting of an urethane acrylate oligomer, reactive wax and non reactive silica cured on a sealer (polyurethane based sealer) gave very good combined abrasion and scratch resistance properties.

INTRODUCTION:

The main technologies used for wood coatings (sealers and topcoats) are acid cured melamines, nitrocellulose lacquers, polyurethanes (solvent based), water based acrylics and polyurethane dispersions, unsaturated polyesters and near 100% solids radiation curable oligomer acrylates. Key performance properties for wood coatings are scratch and abrasion resistance. Other properties such as chemical, stain, moisture resistance and weatherability, while important serve specific end-use needs like kitchen/bath cabinets, office furniture or pre finished flooring.

The objective of this work was to formulate an abrasion and scratch resistant UV curable sealer and top coat for wood. In doing so a formulator typically has to address two major questions.

1. What performance properties do my formulary ingredients contribute to the coating?

2. What test methods will be used (specified by the end-user) to know that I have a coating meeting or exceeding my customer's expectations?

Typically, the abrasion resistance of a coating is measured using the widely accepted test method ASTM D4060. The test consists of mounting a coated disk on a rotating wheel that is abraded by coarse wheels of standard hardness under known weight. A gravimetric determination is then made based on the weight change of a specimen over a specific number of cycles, or as an average rate over a specific number of cycles (mg/cycle) or as the number of cycles required to wear-through a specific coating thickness. But there is no one universally accepted technique to measure scratch resistance. Koleske[1] reports three different ways in which materials are scratched when being tested for mar resistance:

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1. Single scratches made with a needle or other sharp instrument (Diamond or Hoffmann scratch test).
2. A large number of scratches made by abrasive particles falling or impinging on the specimen (Falling sand test)
3. A large number of fine scratches made by an abrasive medium being rubbed against the specimen, call scuffing. (Steel wool test).

In tests 2 and 3, the results are similar in that there is a loss of gloss or haze produced on the surface of the specimen being tested. We used methods 1 and 3 described above.

The work is divided into three parts. First we measured the abrasion and scratch resistance of a series of urethane acrylates individually. In the second part we selected the four best performing oligomers and tested them with functional additives in a ladder study. Finally, in the third part, we optimized a complete formulation for a wood sealer and a topcoat using experimental design methods, identifying not only the best additives but also their levels and interactions with other formulary components.

METHODS

1. Abrasion resistance testing was performed per ASTM D4060 using 500 gram loads on CS-17 wheels. Abrasion rate testing was done for 100 cycles while abrasion resistance was measured at 1000 cycles or as specified in the graphs.

2. Scratch resistance was measured using three different techniques.

    a. Hoffman scratch/mar tests were done per ASTM D2197.
    b. Steel wool marring/gloss retention was measured before and after twenty double rubs with #2 grade steel wool covering a ball-peen hammer.
    c. The Taber Shear/Scratch tester measured the scratch resistance of a coating by recording the weight required for a diamond-tip stylus to break the coating surface while rotating at a constant rate.

3. Coefficient of friction of coatings was measured using a Thwing-Albert friction/peel tester. A 700 gram sled was modified with #2 grade steel wool and was pulled along the surface of each coating at 12 inches per minute.

4. Microhardness tests were done using a Fischerscope HC100. This nondestructive test measured the microhardness and visco-elastic properties of selected urethane acrylates under controlled stress conditions.

5. Gloss measurements were made using a BYK Gardner Micro-Tri-Gloss meter. All gloss readings were taken at 60°.

6. Viscosity measurements were conducted using a Brookfield viscometer model LVT at 25 ^{o}C.

7. Coatings - All coated films were prepared on phosphate treated steel at specified coating thicknesses for Parts 1 & 2. In Part 3, coatings were applied to roll-coated oak

panels at 20 -30 microns using Model D-72250 Burkle roll coater. Each test panel was sanded before and after using an epoxy primer coat. Afterwards, two sealer and two topcoats were then applied to each panel curing each panel after each coat.

8. Curing - All curing was performed on a LESCO EBS with conveyor using a medium pressure mercury bulb at a total energy of 662 mJ as supplied by Primarc UV.

MATERIALS

The urethane acrylates and additives evaluated in this work are listed in Tables 1 and 2, respectively.

Table 1 - Urethane Acrylate Properties

Urethane Acrylates	Trade name	Saturation	Tensile Strength (kPa)	Elongation (%)	Modulus (kPa)	Glass Transition (°C)
UA-6008	Photomer® 6008	Aliphatic	47,050	8	941,800	47
UA-6010	Photomer® 6010	Aliphatic	14,190	45	122,600	-7
UA-6019	Photomer® 6019	Aliphatic	56,400	8	117,500	51
UA-6184	Photomer® 6184	Aliphatic	37,100	8	855,300	53
UA-6210	Photomer® 6210	Aliphatic	9700	40	82,400	32
UA-6217	Photomer® 6217	Aliphatic	22,400	27	83,400	35
UA-6230	Photomer® 6230	Aliphatic	7300	69	15,100	2
UA-6363	Photomer® 6363	Aromatic	13,600	32	108,200	28
UA-6572	Photomer® 6572	Aromatic	6700	86	9800	-29
UA-6891	Photomer® 6891	Aliphatic	13,700	60	62,300	28
UA-6892	Photomer® 6892	Aliphatic	9000	47	22,100	14
UA-6893	Photomer® 6893	Aliphatic	18,900	42	337,300	41
PE-5432	Photomer® 5432	Aliphatic	22,500	10	566,100	47

Table 2 - Filler Descriptions

Fillers	Trade Name	Properties
Wax-1	Perenol® UV wax	Reactive
Wax-2	Behenyl Acrylate	Reactive
Wax-3	Acumist® A-18	Non-Reactive
Wax-4	Ceridust® TP 5091	Reactive
Silica-1	Syloid® 222	Non-Reactive
Silica-2	Aerosil® R7200	Reactive
Silica-3	Syloid® RAD2105	Non-Reactive
Silica-4	Tamisil® 15	Non-Reactive
Alumina-1	Spacerite® S3	Non-Reactive
Alumina-2	Spacerite® S11	Non-Reactive
Alumina-3	Spacerite® S23	Non-Reactive

RESULTS

Part I –The abrasion resistance, Hoffman and steel wool scratch resistance of a series of urethane acrylates are depicted in Figures 1, 2 and 3 respectively. The data from these

Figure 1 - Abrasion resistance of urethane acrylate oligomers

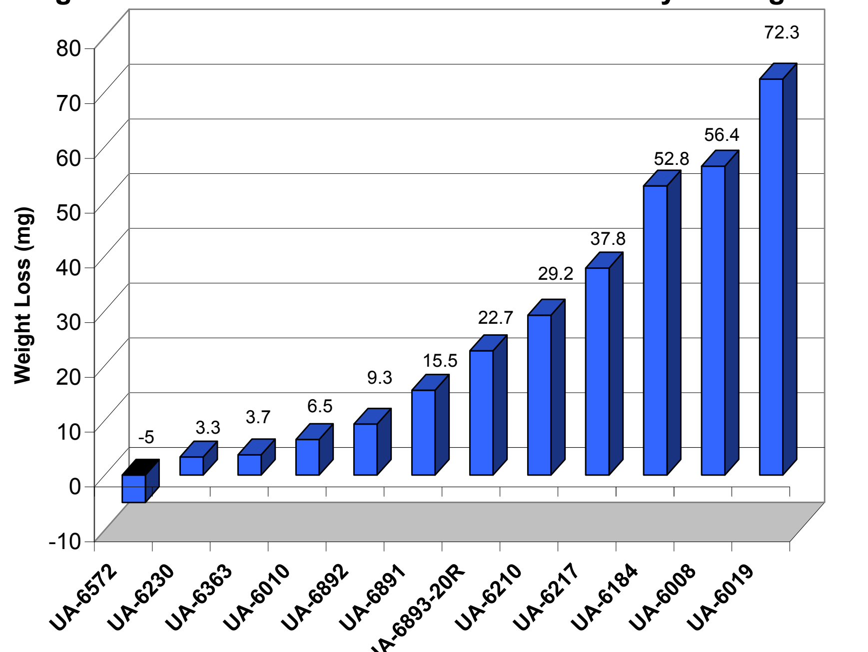


Figure 1 - Hoffman scratch resistance of urethane acrylate oligomers

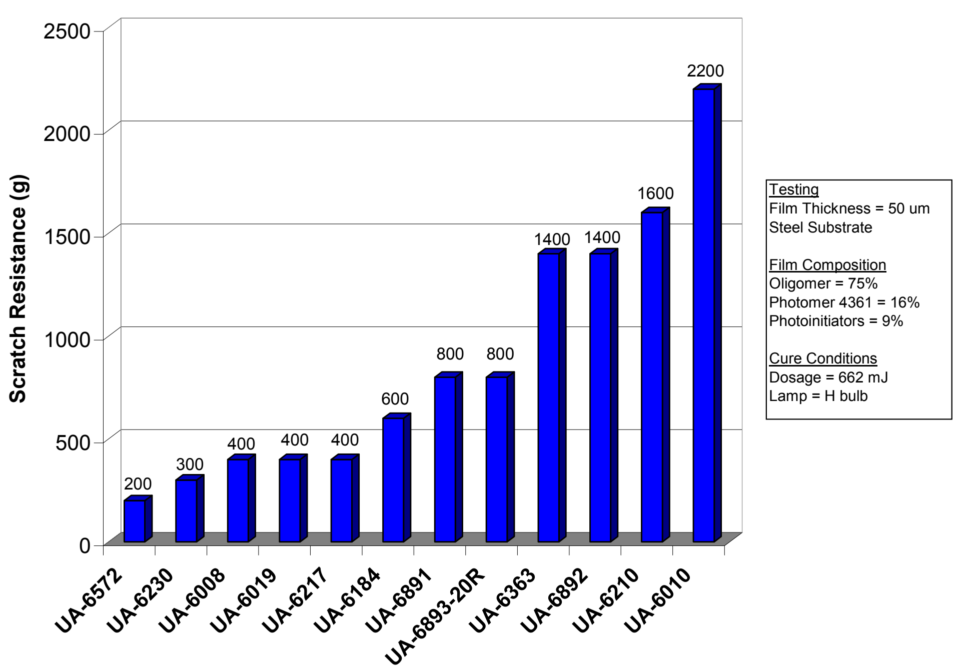
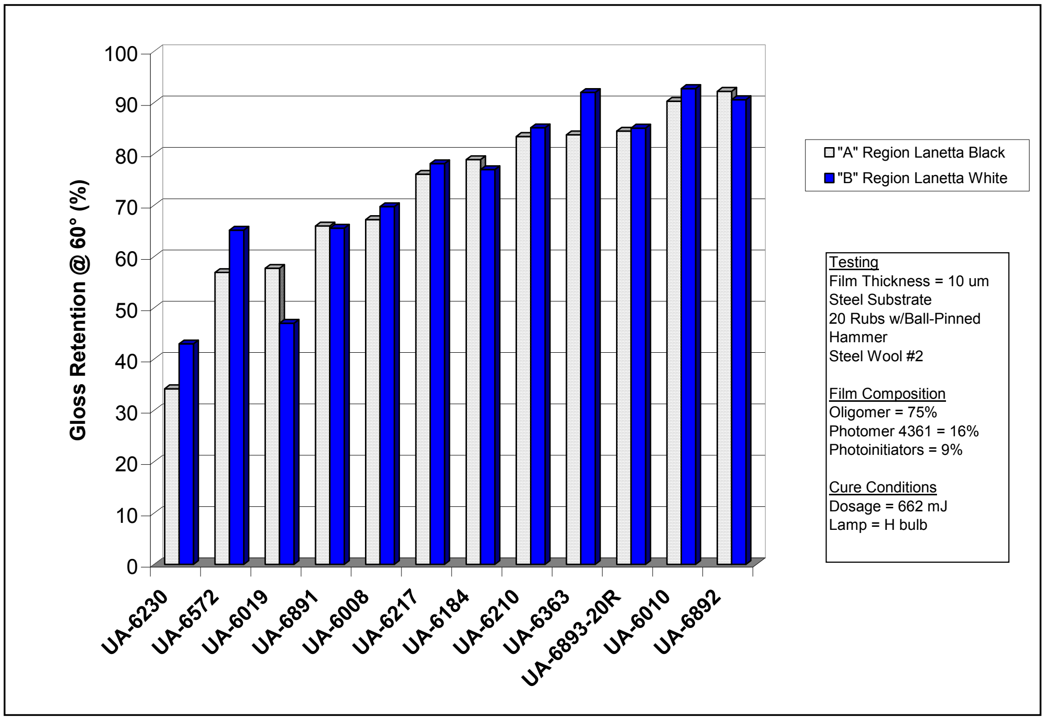


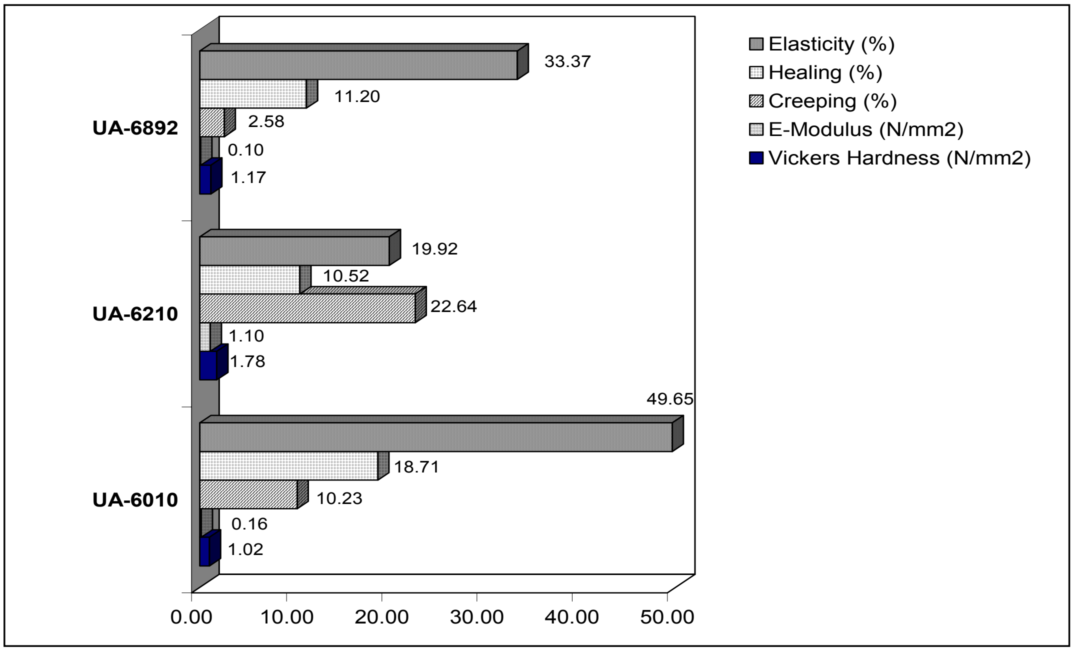
Figure 2 - Gloss retention after steel wool scratch test for urethane acrylate oligomers



graphs indicate that the aliphatic urethane acrylates UA 6010, UA 6210, UA 6892 and UA 6363 possess the best combination of high abrasion (low mg/cycle of weight loss) and high scratch resistance (High values of Hoffmann scratch resistance and gloss retention after steel wool scratch test). These four oligomers were chosen for further study.

Micro-hardness testing has been defined as the "measurement of damage depth and recovery of damage depth of a coating after exposure to a single point indentor."[2] The elasticity of a coating is an indication of the coating's viscoelastic behavior under a controlled stress. Creep is the time resolved strain exerted by a coating under low stress conditions. Healing describes the coating's upward force exerted after removing a downward stress. Hardness and modulus relate to compressibility of the coating. Micro-hardness data for three of the four urethane acrylate products was measured (Figure 4). Figure 4 shows UA-6210 has the lowest percentage of elasticity with excellent creeping and moderate healing performance. In addition, UA-6210 had the highest modulus and hardness among the urethane acrylate products compared and so is a good candidate for further study.

Figure 3 – Microhardness tests data for urethane acrylate oligomers



<u>Part II</u>: Study of abrasion and scratch resistance of urethane acrylates with additives

The scratch resistance and abrasion rate of the four selected urethane acrylates were compared in the presence of eight additives. The functional additives included two waxes, three types of silica, and three aluminum oxides.

The results of abrasion and scratch resistance tests are presented in Figures 5 and 6. Based on Figure 5, scratch resistance was enhanced using waxes and silica but not with alumina. Figure 6 suggests abrasion rate was enhanced using silica and alumina but not with waxes. At face value there appears to be a formulating challenge. To get high abrasion resistance, the use of alumina might deter our efforts to get high scratch resistance using waxes. Either we could use silica alone as a filler to get a single coat system or use the insight that scratch resistance is needed only in the thin top coat while abrasion is needed in the sealer coat. By splitting the performance requirements between the sealer and the topcoat, the aim is to get the best of both properties. The poor performance of UA-6363 in both scratch resistance and abrasion rate testing eliminated it from further work in this study.

<u>Part III:</u> Optimization using experimental design

In designing performance, the ultimate goal is to have robust formulations where the reasons for good performance are understood and predictable within limits. Since the palette of available materials is very wide, we first screened out poorly performing oligomers. Then choosing the best four oligomers we discovered that the choice of fillers and additives impacts abrasion and scratch resistance. In doing so we narrowed the design space. So instead of using a "vary one factor at a time method" we used an experimental design. This technique is

Figure 4 - Change in gloss for urethane acrylates with functional additives

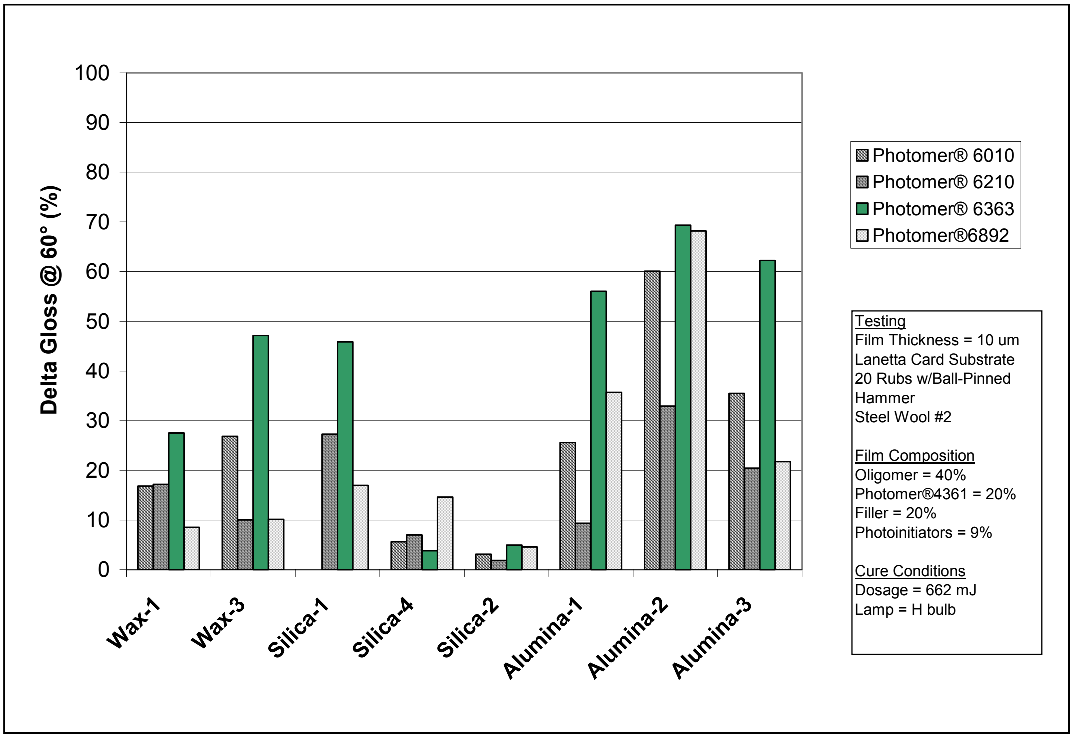
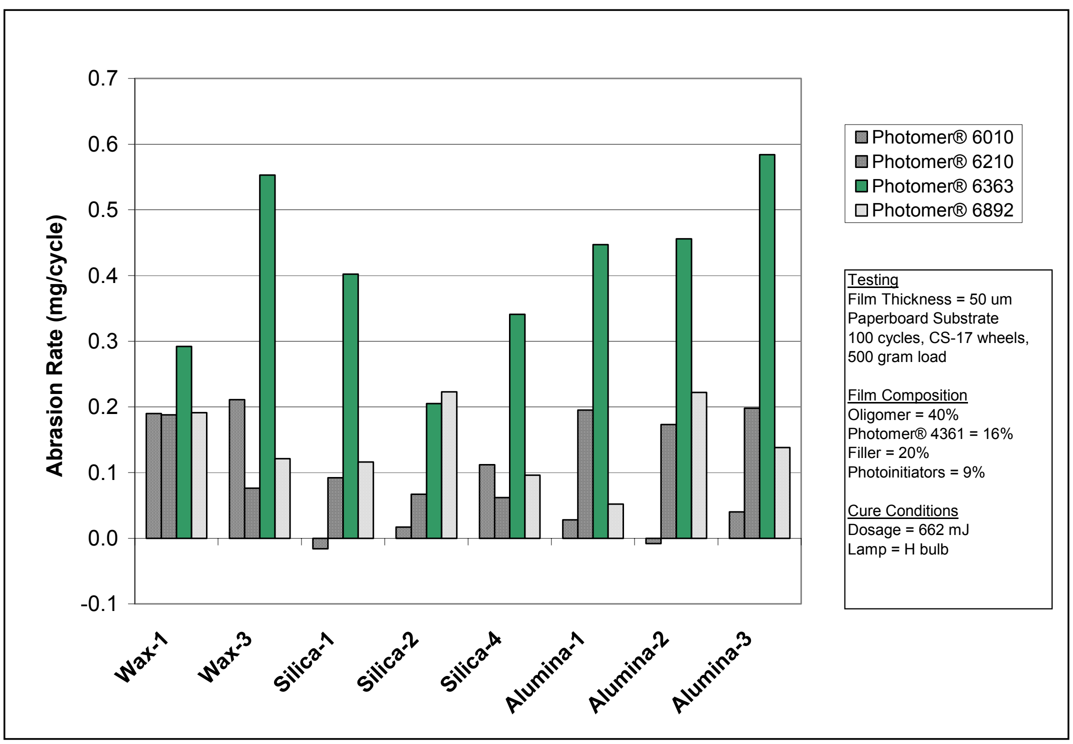


Figure 5 - Abrasion rate for urethane acrylates with functional additives



useful in gaining insights into which components and what extent they synergistically or divergently affect the desired performance.

A two level, three factorial model was built using Design-Ease software where the three factors were the two urethane acrylates UA-6210 and UA-6892 (best performers from Parts I and II), two types of silica (silica 2 and 3) and two waxes (waxes 1 and 2). Our design space consisted of 64 formulations (three factors, two levels, $2^{n,}$ n=3, 8 formulations per set times 8 sets). The design responses compared 60° gloss before and after steel wool scratch test, abrasion rate, and coefficient of friction for UV cured coatings by varying the three factors (Table 1) simultaneously. The design limits are shown in the Table 3 below.

Table 3 - Design Limits

Variables	Concentration (Low)	Concentration (High)
Urethane Acrylates	20 wt%	50 wt%
Silica	2 wt%	20 wt%
Wax	2 wt%	10 wt%

Each set was labeled according to its corresponding urethane acrylate oligomer followed by an alphabetical designation A through D. Tables 4 and 5 identify the design sets, variables, responses, significant factor interactions and desirability of optimized formulations.

An analysis of variance of the factors showed key significant interactions, i.e. Two or more factors simultaneously determine the outcome of a response. As an example, in Table 4, with 6210A, we see that the abrasion rate is affected by the wax and silica whereas the gloss loss after silica steel wool scratch resistance test is affected by wax and the urethane acrylate oligomer. Further, using the software we input our desired features (constraints), namely: high scratch resistance, i.e. high 60 °gloss retention after steel wool scratch test, low abrasion rate (low wt. loss after 100 cycles of test using CS 17 wheels and 500g load) and low coefficient of friction.

Within these constraints the software optimizes the formulations and delivers a desirability value. A high number means that a formulation so chosen would give the required performance with a high level of probability. Thus a formulation containing UA-6210 (Table 6, 92% desirability), silica 2 and wax 1 is expected to give optimum performance. In contrast to UA-6210, all the datasets with oligomer UA6892 gave lower desirability (69% max.) values. As a result only UA6210, Wax-2, and Silica-3 were chosen for the final formulations. One optimized formulation (Topcoat 1) containing oligomer UA6210 is given in Table 6. Two other formulations were prepared to see if reactive waxes that were not a part of the originally designed study would also helpful in improving abrasion resistance. An amine synergist (Photomer® 4967), dispersing aid (Texaphor® UV20) and leveling agent (Perenol® S4) were used in both topcoat and sealer formulations.

Table 4 – Photomer 6210 Design Models

Photomer® ID	Variables	Steel Wool C.O.F	Gloss @ 60°	Abrasion Rate	Desirability
6210A	Wax-2 Silica-2	Interactions Wax and Silica	Interactions Wax and Urethane Acrylate	Interactions Wax and Silica	64.3%
6210B	Wax-2 Silica-3	Interactions Wax and Silica	Single Component Wax	Interactions Wax and Urethane Acrylate	**92.7%**
6210C	Wax-3 Silica-2	None	None	None	71.3%
6210D	Wax-3 Silica-3	None	None	None	61.5%

Table 5 – Photomer 6892 Design Models

Photomer® ID	Variables	Steel Wool C.O.F	Gloss @ 60°	Abrasion Rate	Desirability
6892A	Wax-2 Silica-2	None	None	Single Component Wax	62.4%
6892B	Wax-2 Silica-3	Single Components Urethane Acrylate or Wax	None	Interactions Urethane Acrylate and Wax	52.7%
6892C	Wax-3 Silica-2	None	Single Components Wax or Silica	None	**68.8%**
6892D	Wax-3 Silica-3	Single Component Urethane Acrylate	Single Components Wax or Silica	Single Components Wax or Silica	66.7%

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Table 6 – Topcoat Formulations

Components	Topcoat1	Topcoat2	Topcoat3
UA-6210	43.63	43.63	43.63
Silica-3	17.45	17.45	17.45
Wax-2	1.75	0.00	0.00
Wax-1	0.00	1.75	0.00
Wax-4	0.00	0.00	1.75
(3EO)TMPTA	12.74	12.74	12.74
TRPGDA	12.74	12.74	12.74
Liquid benzophenone	1.75	1.75	1.75
Benzil dimethyl ketal	1.75	1.75	1.75
Amine Synergist	7.85	7.85	7.85
Dispersing Agent	0.17	0.17	0.17
Leveling Aid	0.17	0.17	0.17
Total (wt.%)	100.00	100.00	100.00

A similar experimental design as discussed above was conducted to uncover optimized sealer formulations. In this design, we chose a polyester acrylate PE-5432 and a urethane acrylate UA-6010, two silicas (Silica-2 and Silica-3) and two types of alumina (Alumina-1 and Alumina-2). After a similar analysis as shown above, two optimized formulations were uncovered (Table 5).

Table 7– Sealer Formulations

Components	Sealer1	Sealer2
PE-5432	50.00	0
UA-6010	0	50.00
Silica-3	2.00	2.00
Alumina-2	2.00	2.00
EOTMPTA	10.72	10.72
TRPGDA	25.88	25.88
Liquid Benzophenone	2.00	2.00
Tribenzoyl phosphine oxide	2.00	2.00
Amine Synergist	5.00	5.00
Dispersing Agent	0.20	0.20
Leveling Aid	0.20	0.20
Total (wt.g)	100.00	100.00

In the final step we used the knowledge gained from Tables 6 and 7, coated oak wood veneer panels with the optimized sealer and topcoat via bench-top roll coater. The results of testing from these three UV cured panels are shown in Table 8.

Table 8 – Part Four Results

Sealer Type	Topcoat Type	Diamond Scratch Resistance (grams)	Steel Wool C.O.F. Kinetic-Static	Hoffman Scratch Resistance (grams)	Steel Wool Gloss Retention (%)	Abrasion Resistance 2500 cycles, CS-17, 500 mg
PE Sealer 1	Topcoat 1	130	0.388/0.312	200	91	**188.5**
PE Sealer 1	Topcoat 2	110	0.357/0.305	130	92	635.9
PE Sealer 1	Topcoat 3	90	0.318/0.266	110	100	653.4
UA Sealer 2	Topcoat 1	**200**	0.370/0.296	**700**	95	**271.1**
UA Sealer 2	Topcoat 2	**190**	0.362/0.308	**500**	95	614.4
UA Sealer 2	Topcoat 3	160	0.356/0.304	400	91	669.8

Top-coat scratch resistance was enhanced using Topcoat 1 or Topcoat 2 over a polyurethane based sealer coat (Sealer 2). Best abrasion resistance but only modest scratch resistance was obtained using the Topcoat1/Sealer1 combination. This also shows that not all reactive waxes enhance abrasion resistance in UV curable topcoats (example Topcoat1/Sealer1 and Topcoat2/Sealer1). Clearly, the predicted responses from the experimental design cannot be universally applied to all reactive waxes. This means that the experimental design is useful in optimizing a formulation only within a given system and not necessarily across different systems.

Previously published reports indicted that reactive silica was shown to improve abrasion resistance in UV cured topcoats[3]. However, in this work, the best combination of scratch and abrasion resistance is obtained from a combination Topcoat1/Sealer2 system. This system consisted of two different polyurethane acrylates, non-reactive silica, and a reactive wax. Even though our desirability equation was designed under a constraint to get low C.O.F, in reality we noticed that the best performing combinations for topcoat sealer system was from coatings that had high coefficient of friction values.

Conclusions:

The designed performance of a formulated UV coating for wood is highlighted in this work. The work demonstrated how the final coating performance varied with the composition of the sealer coat and topcoat. Through the use of initial screening and ladder study, four urethane acrylates with best combination of scratch and abrasion resistance were chosen and it was determined that both scratch and abrasion was enhanced by silica in both sealer and top coats. A designed experimental approach resulted in optimized formulations for the topcoat and the sealer. Both the silica and certain reactive waxes like behenyl acrylate interacted together to enhance scratch resistance in the topcoat. A combination of alumina and non-reactive silica enhanced abrasion resistance of sealers. An optimized sealer/topcoat combination was produced having very low abrasion rate and high scratch resistance

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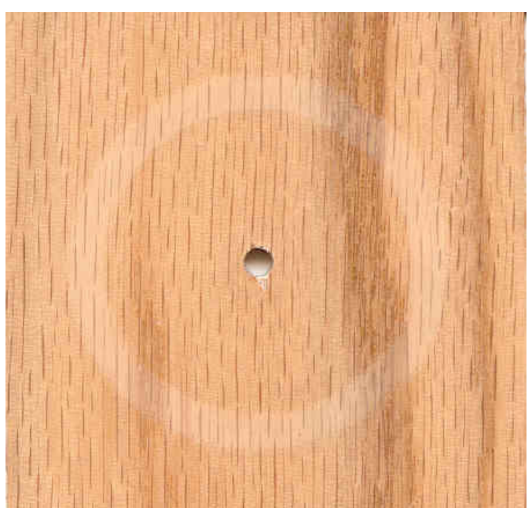
APPENDIX

Photomer® 5432 Sealer

Photomer® 6010 Sealer



Topcoat 1 & Photomer® 6010 Sealer

TRADEMARKS

Photomer®	Cognis Corporation
Perenol®	Cognis Corporation
Texaphor®	Cognis Corporation
Acumist®	Honeywell Corporation
Tamisil®	Unimin Specialty Minerals
Aerosil®	Degussa Corporation
Specerite®	Alcoa Corporation
Ceridust®	Clairant Specialty Chemicals

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[1] Koleske, J. V, "Paint and Coating Testing Manual", 14th Edition of the Gardener-Sward Handbook, ASTM, Philadelphia, PA, 1995, page 579.

[2] Ryntz, R. A., Britz, D., "Scratch Resistance Behavior of Automotive Plastic Coatings" *Journal of Coating Technology*, Vol. 74, No. 925, page 77

[3] Baba, A., Takahashi, T., Eriyama, Y., Ukachi, T., "Development of UV Curable Hard Coatings with Acrylic Functionalized Silica Particles", Japan Synthetic Rubber Co. Ltd., Japan