A Waterborne for Every Reason:

The Expanding Capability and Applicability of Waterborne Resins.

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Introduction

The lure of waterborne coatings and their more environmentally friendly profiles continues to draw customers. The growth is constant, but stills seems pocketed to certain fields. The explanations for the selected growth are as varied as the industries. However, inherent weaknesses, perceived or otherwise, are most commonly the cause of the lack of adoption. This paper details a new approach toward waterborne resin design with the hope of removing some of those obstacles.

Design

Initially, the goal was to design resins that would both speed the removal of water and reduce the amount of water trapped in the thickening resin. These are two common basic desires. They are also two of the first aversions pointed to by solvent-borne practioners investigating a switch. Many parameters were studied in an attempt to meet these first conditions. We decided upon polyurethane chemistry. Then varied building blocks components, changed molecular weights, investigated acid functional groups, and the choice of neutralizing amine.

Through a simultaneous combination of those factors, a new line of waterborne polyurethane resins has been formed. Their drying times are desirably short, though certainly affected by processing conditions (table 1). In addition, we find the clarity and gloss of the resultant films are visually better than previous versions (table 2) and a sure sign that the resins are affecting drying time.

Thickness (dry film)(μm)	**<5**	**5-15**	**15-20**	**20-30**
Oven time (60C)	<3	3-5 m	5-7 m	7-10 m

Table 1. Representative drying speed of line of resins

As we would expect, the drying times are related to film builds sprayed out. At ~40% solids, these are the sought after faster drying speeds and resultant properties.

Thickness (dry film)(μ m)	10	10	10	10
Oven time (60C)	0 min	1 min	3 min	5 min
Gloss after UV curing	not cured	70	85	95

Table 2. The effect on gloss from quick, low-temperature drying of new waterborne resin.

Using these quick drying principles, we were then able to alter the building blocks enough so that differentiated products were obtained, all of which have similar drying profiles. But the more serendipitous discovery was that the collateral properties of these new resins were often superior to previous versions. Identified improvements include better and wider adhesion profiles, greater coating integrity, and better compatibility.

Results and Discussion

Primer (6166W)

With this resin we hoped to get good wetting and adhesion, the compatibility to do color rendering, toughness, and easy water cleanup. We found adhesion to not only wood but PVC and PET as well. For wood cross-sectional analysis of wood suggested that this resin had excellent penetration of the wood fiber.

Figure 1. Photos showing adhesion of a layered system where new primer is used. Also showing adhesion after coin scratch, another unique check on adhesion. Wood grain wetting is also nice here.

Figure 1 shows an adhesion check on wood. This is for a primer with clearcoat over top, so this also demonstrates intercoat adhesion with this primer. The coin scratch is actually a fairly good but indirect way to test adhesion of your primer, as it demands the coatings to "flex" under the weight of the coin, but not so much that it either tears or loses adhesion. You can also note from both photos the difference in color; there was no limit found as to the level of colorant that could be added. In these pictures, the richness of the wood grain demonstrates the desired, excellent wetting and resultant adhesion.

Easy cleanup is another ancillary request from roller, blade, or brush applicators as their shifts and breaks often cause resin in the paint lines to harden. Therefore, the ability to quickly soften and clean left-over resin is often highly desirable. To test if this primer had this ability, we sprayed out the resin on a PVC panel and dried it for 30m at 60C. This greatly exceeds its dry time and the coating is presumable harder than it might get in a production setting. The cooled panel was still tacky, as demonstrated by finger drag in figure 2a. Then the panel was placed in a room temperature water bath for 1 minute, 2b. Visible softening was noticeable without any mechanical assistance. Gentle stirring with the panel in the water then quickly removed the coating from PVC (see figure 2). This phenomenon where a resin loses water efficiently and completely but then redissolves quickly in excess water after it has dried is hard to explain. Apparently, the choice of resin parameters has aided in both uptake and removal of water.

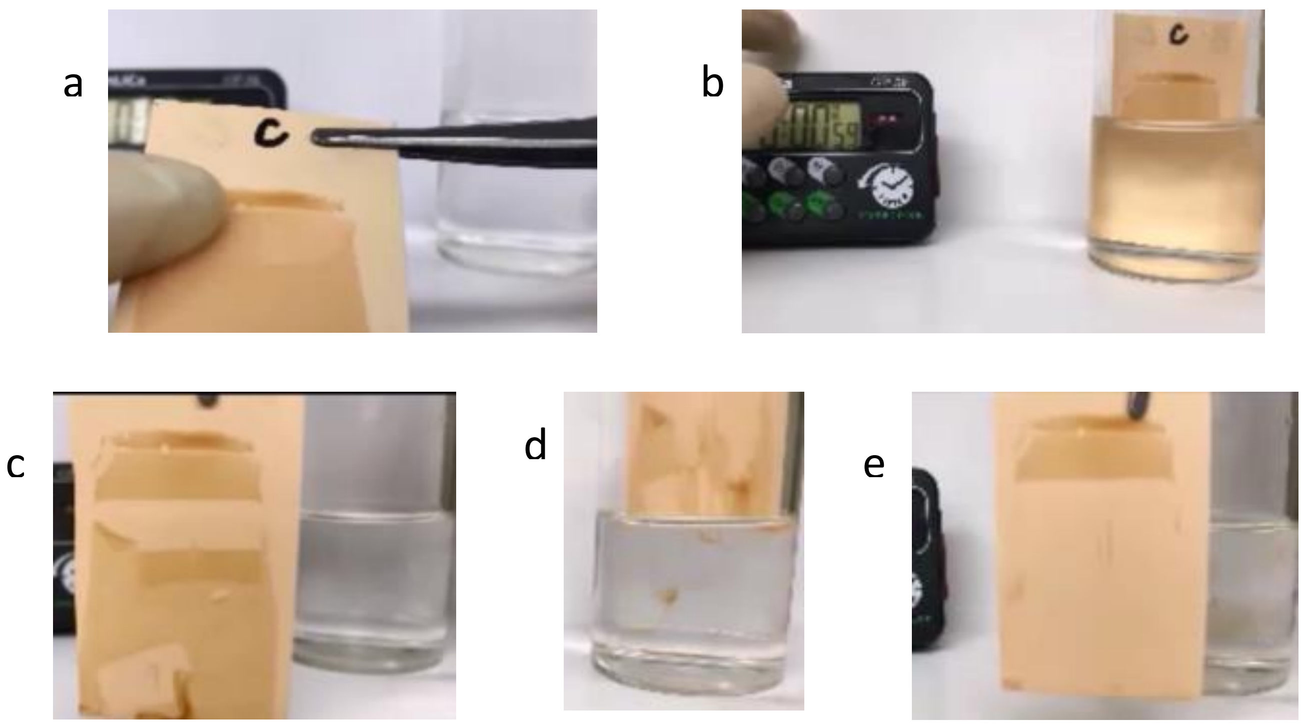


Figure 2. Demonstration of easy clean process. a) after 30m bake not tack-free b) set to soak 60s RT c) after 60s soak no agitation d) after to two simple dips e) after 3 second swirl

Hard Coat for Wood (DR-W496-1)

After adhesion, we sought to identify if this genre of resin design could provide the needed properties in a topcoat. In general, chemical resistance(s) and various types of scratch resistance are requested/required. We used a common three-coat application system to test the capabilities of the hard coat (figure 3). Then we applied a number of different iterations to also test a number of different subsidiary properties (table 3). Testing was then performed on the combinations (table 4).

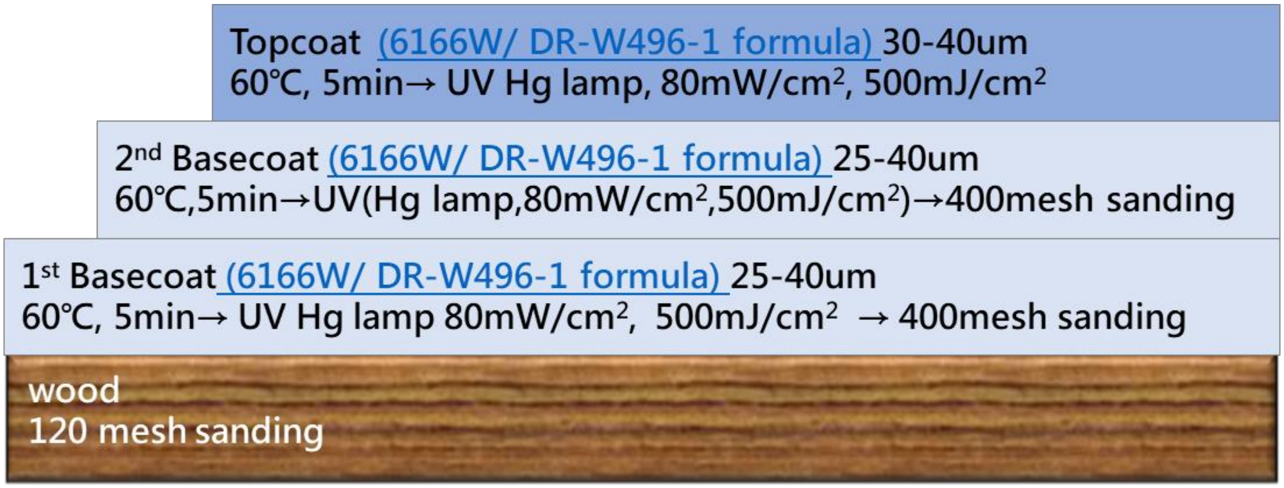


Figure 3. Example of three tier coating system.

Example	#1	#2	#3	#4
Topcoat	DR-W496-1	6166W	DR-W496-1	DR-W496-1 +6166W
Basecoat	DR-W496-1	6166W	6166W	DR-W496-1 +6166W
Basecoat	DR-W496-1	6166W	6166W	DR-W496-1 +6166W

Table 3. Wood conversion application formulation.

Items	#1 All Hardcoat	#2 All Primer	#3 Primer then Hardcoat	#4 All 50%+50%Mix
Adhesion (3M, #600)	5B	5B	5B	5B
Hardness on glass	4H	HB~F	2H	H
Water Resistance(24hr) No Change	PASS	PASS	PASS	PASS
50% Ethanol Resistance (24h) No Change	PASS	PASS	PASS	PASS
24hr Stain Resistance (coffee, red wine, tomato catsup, orange juice, mustard)	PASS	PASS	PASS	PASS

Table 4. Testing results of three tier panel coat systems.

There are many interesting things to notice in this data. First, the all hard coat system (all DR-W496-1) has adhesion both to the substrate and intercoat adhesion. These are both properties that are typically difficult to achieve when the crosslinking has increased. Clearly the changes instituted for quick drying have brought unexpected properties to other facets of the coating. In a similar surprise, the all primer system has a surprising amount hardness for a primer. A common characteristic of primers is flexibility (often referred to as soft) so as to achieve maximum mechanical adhesion. Our primer has excellent adhesion but still demonstrates a modest amount of toughness. The third application shows that the two resin systems can be layered with good intercoat adhesion. It also shows that the hardness is intermediate between the all primer and the all hard coat versions. It is our experience that a system like this is better for many adhesion tests like coin scratch, where a certain amount of flex is desirable. The last combination demonstrates that the two systems are compatible and can produce other intermediary properties. We believe this could give the formulators more latitude to tailor the exact properties for their products. More evidence that this three tier systems are fully coalesced is demonstrated with the passing of the chemical resistance tests we chose. Given the previously demonstrated easy-clean properties, it is important to see that once it is UV cured, the resultant coatings are resistant to water or solvent.

Tack Free (DR-W425 & DR-W482)

In many application settings the need to have a tack free resin, after application and flash time, is required. For UV, this can often happen on 3-D parts or in overspray areas where the light doesn't sufficiently reach to achieve full cure. This new genre of resin has been modified to have some thermal cure. This provides enough cure after a heated flash to create a tack free system before UV cure. The two resins created in this category have sufficiently different flow and thermal cure parameters that they can produce very different appearances. This is true even when the standard three-tier wood application method is utilized. Each layer is ~30 micron thick, flashed 5 min at 60C, cured with ~900mJ/cm^2, with sanding after each of the first two layers. In these configurations, these coatings are able to pass a variety of common tests see table 5. The two tack-free resins retain good adhesion, good coin scratch and other chemical resistances common for our new category of waterborne resins.

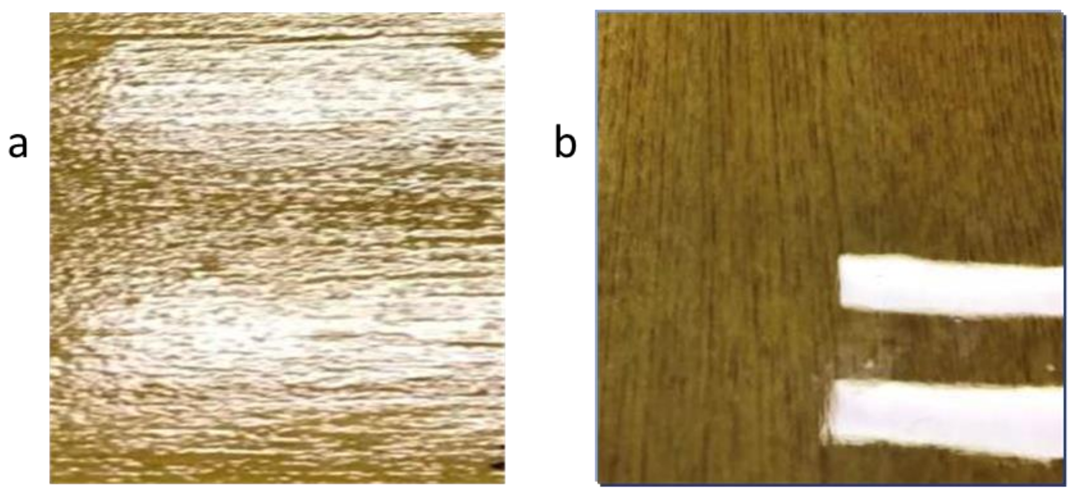


Figure 4. a) DR-W425 tack-free, textured surface. b) DR-W482 tack free high gloss surface

Tests	DR-W425	DR-W482
Gloss (60°)	75-85	85-95
Adhesion(3M, #600)	5B	5B
Coin Scratch Resistance	Excellent	Good
Acetone, drop on surface maintain wetting 10min	PASS	PASS
Ammonia$_{(aq)}$, drop on surface maintain wetting 60min	PASS	PASS
Ethyl alcohol(50%, drop on surface maintain wetting 24hr)	PASS	PASS
Stain Resistance(coffee, red wine, tomato catsup, orange juice, mustard, drop on surface maintain wetting 24hr)	PASS	PASS

Table 5. Resistance tests on the three-layer, tack-free systems

Plastic (DR-W470 & DR-W485s)

Trying to probe the limits of what this new genre of waterborne coatings can achieve, two additional resin modifications were made to enhance application to plastic. Both resins have adhesion to ABS, PC, and PC/ABS and can capably incorporate effect substances. The second resin, 485s, distinguishes itself with a higher acrylate density and the corresponding greater crosslinking.

A high and low gloss version of DR-U470 was made, ~15 micron DFT, 5 minute 60C flash, and ~1000 mJ/cm^2 cure. Two versions with sample formulas are seen in figure 5 and table 6.

High Gloss

Low Gloss

Figure 5. Single layer coatings on ABS. The pictures are taken simultaneously, i.e., under the same light.

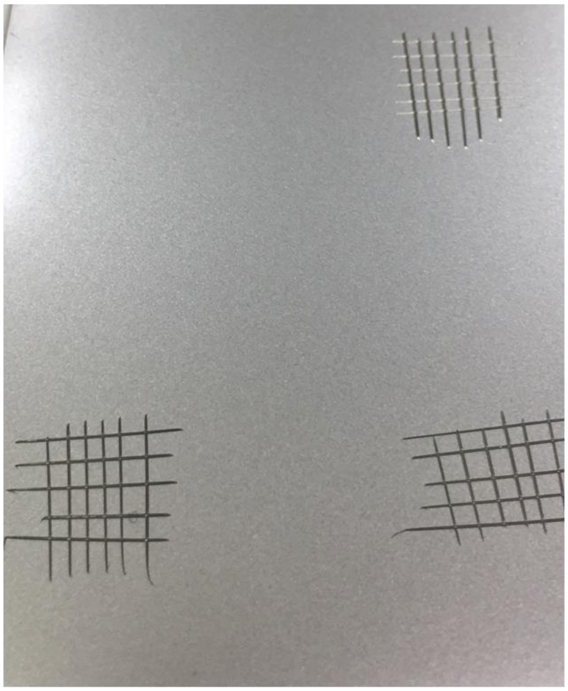
Formulation	High Gloss	Low Gloss
Etercure DR-W470	97.5	91.8
Byk 192 (dispersing)	-	0.2
Ceraflour 920 (matte)	-	6
PI 1173/TPO (1:1)	-	1
PI 1173/BP (1:1)	2.5	1
Test	**High Gloss**	**Low Gloss**
Adhesion	5B	5B
Gloss 60	92-95	20-30
Pencil Hardness, 500g	4H	4H
RCA, 175g	>1000	>1000
Water Resist (70C,30m)	PASS	PASS
Water Resist (37C, 48h)	PASS	PASS
50% EtOH (25C, 48h)	PASS	PASS
Recoatability	PASS	PASS

Table 6. Formulas of DR-W470 with and without flat, then testing of these coatings.

This class of resins also exhibit good adhesion. The addition of wax matte agent appears to only affect the gloss of the coating, as all other tests are indistinguishable. Lower glosses are achievable but will need to be researched on a case-to-case basis. The ethanol test here distinguishes this resin positively from previous generations. It further demonstrates the higher coating integrity within this new category of waterborne resins. These coatings also retain the relatively hard features, yet remains recoatable, which is a fascinating dichotomy.

If further crosslinking is desired, another version of plastic's resin was made with additional acrylates per base molecule, DR-W485s. The result not only gives harder, more impervious coatings, it has also been found to provide good orientation for flake additives. The higher acrylate density also gives greater confidence in monocoat solutions using this resin. Figure 6 demonstrates the effectiveness of this resin in making an aluminum flake coating at ~ 10% aluminum loading.

a



b

Item	Result
Metallic appearance	Excellent
thickness(um)	10-13
hardness(500g)	4H
gloss(60°)	82.5
L value	73-74
Adhesion(ABS/PC)	5B
Water resistance (70°C, 1hr)	5B
RCA Test (175g)	>300

Figure 6. Demonstration of an aluminum flake panel with testing in DR-W485s

Conclusions

The initial goal was to make waterborne resins that dried faster and clearer. That goal was accomplished in this work. However, along with those properties have come other unexpected desirable properties. These include good adhesion over a broad range of substrates, relatively greater levels of compatibility with co-resins or co-solvents or effect substances, and good resistance properties. The new resins amazingly maintain an interesting mix of hardness and flexibility while displaying easy clean properties. All of these favorable properties have been found within a general framework which still allows differentiation of resin chemistry and properties. We feel that this new genre of waterborne coatings will provide the formulators with the flexibility to attain markets previously unreachable with waterborne solutions.