GREEN CHEMISTRY
CHALLENGE 2012

One-Component UV Curable Waterborne Polyurethane Coatings

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- One-component (1K) UV Curable Waterborne Polyurethanes will see a significant technical event with a US Patent Publication during June 2012[15].
- This project is not eligible for either the "Academic" or "Small Business" category.
- The most applicable focus area for the 1K UV Curable Waterborne Polyurethane coatings project is: the use of alternative reaction conditions for green chemistry that have a reduced impact on human health and the environment, i.e., reduction in the use of solvents (VOC) and volatile hazardous air pollutants (VHAPS).
- BMS Scientists in the United States took the 1K UV Curable Waterborne Polyurethane raw material and developed end use style formulations and patents that were given to multiple paint companies for development of ultra- low VOC and VHAPS formulations for use in the following coating markets: OEM wood[1], aerospace[2], site applied flooring[3, 4], special effects coatings[5, 6, 7], sun shine cure deck coatings[8] and wet strength paper[15].

1K UV Curable Waterborne Polyurethane based Coatings

Technical Abstract:

In the 1980's Bayer MaterialScience LLC (BMS) developed Water Based Unsaturated Polyesters that were UV or peroxide curable. A paper presented in 1992 reviews the use of this technology and the source reduction of VOC and VHAPS[9]. Unfortunately, this technology did not displace the acid catalyzed -nitrocellulose lacquer systems. In 1992 two-component (2K) water based polyurethane coatings developed by Bayer entered the wood coatings market with both technical and commercial success. This success resulted in the displacement of high VOC and VHAPS coating systems and won the 2000 Presidential Green Chemistry Award. However, the use of this new coating technology was limited by the user-friendliness and slow drying speeds, especially on automated wood coating lines.

With Bayer's commitment to the development of environmentally friendly technologies, BMS continued to pursue new approaches to develop technology that enables the reduction of VOC and VHAPs in coating applications with the introduction in 1999 of a 1K UV Curable Waterborne Polyurethane [10]. The original market development for this product was for the wood market.
In recent years, 1K UV Curable Waterborne Polyurethanes have gained an increasing market share. Renowned manufacturers of office furniture advertise the fact that with such systems their products are low on emissions and environmentally compatible. Large furniture companies are increasingly specifying the use of coating systems with low or no solvent. Such requirements can be met very cost-effectively with coatings based on these raw materials that cure in just seconds under UV light[11]. Emerging markets have been identified since the wood coatings market has accepted the 1K UV Curable Waterborne Polyurethane. These new markets include: aerospace and defense, site applied UV cure flooring, sun shine cure wood decking, special effects coatings and wet strength papers. Since the introduction of this coating technology, the commercial use of this coating system in place of acid catalyzed varnishes - nitrocellulose lacquers resulted in the source reduction of 50-90% for VOC and 50-99% for VHAPS, which in turn is equivalent to the removal of (2007 - 2011) 2.6 million lbs. of organic solvents and 49,000 lbs. of formaldehyde from the US environment[12].

Project Description: One-Component (1K) UV Curable-Waterborne Polyurethane Coatings Meeting the scope and focus area of the Presidential Green Chemistry Challenge

One-component (1K) UV Curable waterborne polyurethane coatings are an outstanding example of the use of alternative reaction conditions for green chemistry. This is accomplished by replacing most or all of the volatile organic compounds (VOC) and volatile hazardous air pollutants (VHAPs) contributing solvents used in conventional 2K solvent-borne coatings with water as the carrier. This may seem an obvious thing to do, but due to the particular chemistry of the reactive components of polyurethane, it is not at all straightforward. A measure of the novelty and

significance of this technology is the number of related patents (25+) granted since we introduced it in 1999[1, 7] as well as the number of research papers published and presented at major national conferences (100+) by ourselves as well as academicians and researchers from other companies.

Two-component solvent-borne polyurethanes have long been considered in many application areas the benchmark for high-performance coatings systems. The attributes that make these systems so attractive are fast cure under ambient or bake conditions, high-gloss and mirror-like finishes, hardness or flexibility as desired, chemical and solvent resistance, and excellent weathering when aliphatic polyisocyanates are used. But the traditional carrier has been organic solvent which, upon cure, is freed into the environment as VOC and VHAPS material. Use of high-solids systems reduces this problem to an extent, but does not go far enough.

One component polyurethane dispersions (PUDs) can impart the properties of polyurethane coatings from a waterborne system containing less organic solvent. They are fully reacted, high-molecular-weight polyurethanes, which are most commonly ionically modified for water dispersibility. They are only lightly cross-linked, however, so as to maintain dispersion stability and low film-forming temperatures. Property development depends on hydrogen bonding, physical entanglements and proper coalescence during film formation. Because of low levels of crosslinking, chemical and solvent resistance is generally not equivalent to that seen in films based on two-component solvent-borne polyurethane. However, 1K UV Curable Waterborne Polyurethane coatings represent a further refinement of this technology since they allow cross-linking to occur during the UV cure process, improving film properties as well as the curing speed. Additionally, manufacturing procedures used for one-component (1K) UV Curable Waterborne Polyurethane coatings are done via the "Acetone Process" which eliminates the need for a co-solvent during production resulting in a nearly VOC free raw material[13].

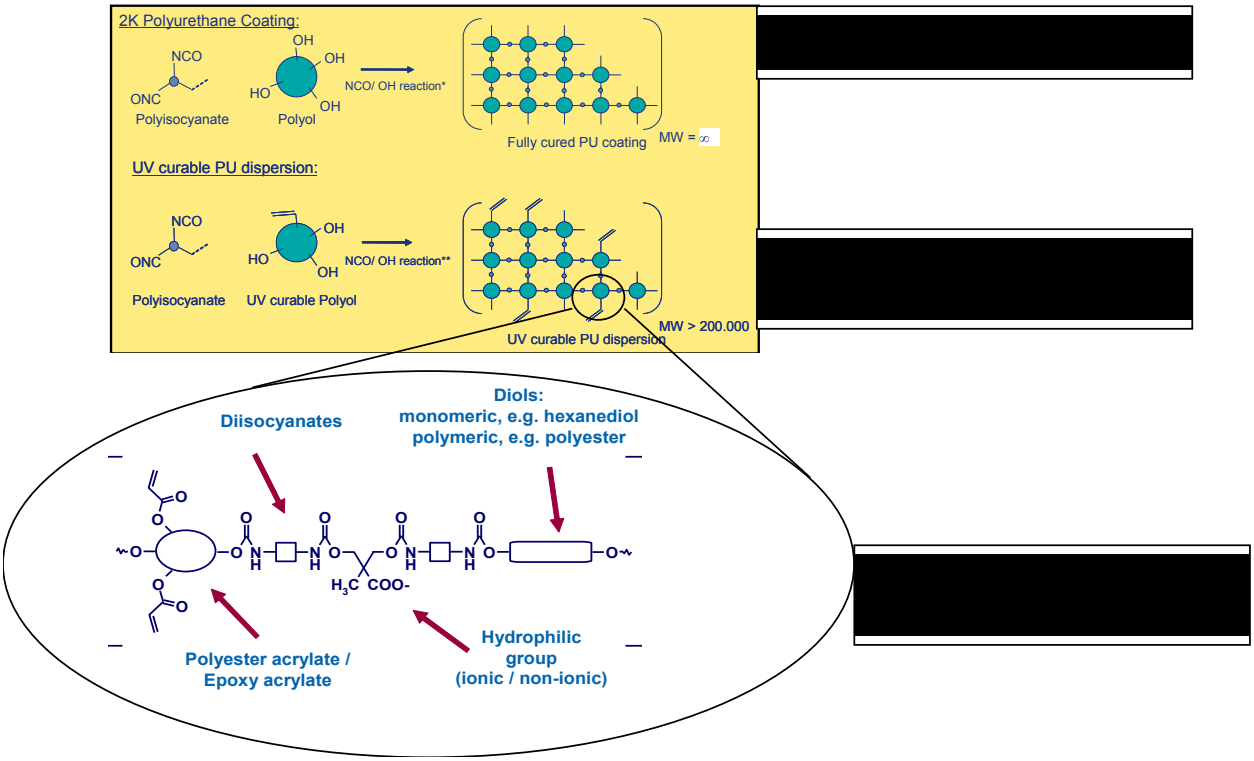
Innovation and Scientific Merit

The development, introduction and acceptance of the 1K UV Curable Waterborne Polyurethane coatings technology was a difficult process. The first product introduced to the US Market was the TSCA listed Bayhydrol® UV 2282 with the intended purpose of reducing the amount of VOC and VHAPS in the wood coatings market. The dominant technology in wood in 1999 was solvent based 2K amino conversion varnishes. The introduction of the Bayhydrol UV 2282 created a steep learning curve due to the dramatic move away from solvents and the need to add a UV curing light source to cross-link the polymer. In addition the use of UV cure, water based sealers resulted in issues with wood grain raising that manifested itself in cosmetically poor looking wood finishes.

To master this new chemistry BMS scientists had to develop a polymer chemistry that could be formulated in water at is production facility where any potentially hazardous raw materials used in the process could be consumed resulting in a 1K UV Curable Waterborne Polyurethane raw material. This substantial up-stream development efforts by BMS scientists attests to BMS' commitment to make the ultimate green chemistry work for the coating industry.

The roots of the 1K UV Curable waterborne Polyurethanes stem directly from technology developed by BMS where a polyisocyanate and a polyol combine in a 2 K reaction creating a polyurethane. This is classic PU chemisrty utilized by a multitude of coatings users in the US today(Reaction Scheme #1). BMS scientists were able to take this known reaction and carry it out in a BMS production facility. The resultant polyisocyanate prepolymer was then reacted with a UV curable polyol through a NCO/OH reaction to form the 1K UV Curable Waterborne Polyurethane. This process develops a high MW (> 200,000 g/mol) polymer in water without any residual isocyanate monomer or polyisocyanate prepolymer. This product also has ultra low VOC since it was carried out using the BMS proprietary acetone process which removes the acetone carrier at the end of the product manufacturing process.

Reaction Scheme: 1K UV Curable Waterborne Polyurethane Coatings reaction scheme



In this process the acetone used to manufacture polyisocyanate prepolymer is distilled away out of the product (Reaction Scheme #2). [13]These unique products demonstrate film properties after dewatering such as Pendulum hardness values in the range of 5 to 60 seconds which increase after UV curing to values that range from 63 to 168 seconds. This wide range of the coating values are mimicked by the T_gs (°C) that range from -80 to +90 (Reaction scheme #3). This kind of varability is only obtainable with the use of hard segments and soft segements that are locked into the polymer backbone and the acrylate functionality that is only possible with this kind of polyurethane technology.

Human Health and Environmental Benefit of One-Component UV Curable Waterborne Polyurethane Coatings

VOCs and HAPs. As a result of the Clean Air Act of 1990, an increased emphasis is being placed on reducing the emissions of volatile organic compounds. Many industries contribute to the amount of pollutants in the atmosphere, including the coatings industry, which uses over 4 billion pounds of organic solvents each year. For example, the nitrocellulose lacquers traditionally used in wood coatings applications often have VOC levels in excess of 6 lbs./gallon. Some of the solvents and the byproducts given off by the chemistry used in these coatings are being particularly regulated as VHAPs.

To help promote a cleaner environment, ultra-low VOC and VHAPs, 1K UV Curable Waterborne Polyurethane coatings are designed to be not only chemically resistant, but also comparable in price to many competitive technologies. Bayer's TSCA-listed 1K UV Curable Waterborne Polyurethane, Bayhydrol ® UV 2282, is one of these competitive technologies. Compared to 2K solvent-borne amino conversion varnishes or nitrocellulose lacquers, 1K UV Curable Waterborne Polyurethane coatings can reduce VOCs and VHAPs 50-99%.

Solvent odor. Not only are solvent emissions environmentally disfavored, they can be hazardous and create unwanted odors when emitted in interior spaces from recently applied architectural coatings. Coatings based on1K UV Curable Waterborne Polyurethanes offer solvent emissions on the order of 0.2 lb/gal with no solvent odor. This low solvent level is important for site applied floor coatings which must be fast drying, abrasion resistant, and generate very little odor after application.

Summary of Health and Environmental Benefits. It is apparent that the work done on the 1K UV Curable Waterborne Polyurethanes over the past several years has resulted in a technology that provides the following health and environmental benefits:

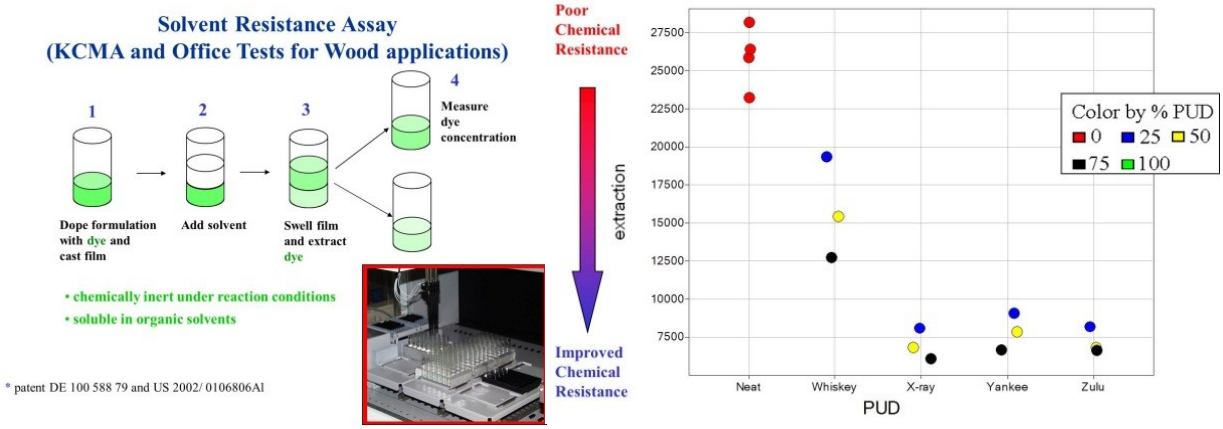
1. Source reduction in the amount of VOC in the range of 50-90%
2. Source reduction in the amount of HAPs in the range of 50-99%
3. Reduction of the amount of chemical byproduct evolution from the film in interior and furniture applications
4. Provide rugged interior and exterior coatings with no solvent odor
5. Offer a waterborne coating system that meets all performance requirements for a variety of coatings markets.

Applicability of 1K UV Curable Waterborne Polyurethane coatings in Industry and Society

OEM Wood Coatings. New environmental initiatives such as CARB, Greenguard™, LEED, and level™ have brought a renewed focus to the emission of VOC's and VHAPs. These new environmental standards, along with economic pressure to be more cost effective, and the need to maintain quality, are important factors when selecting wood coatings. Consumers seek to purchase items that are not only made in an environmentally friendly manner, but do not emit VOC's, formaldehyde or other chemicals.

The wood coatings market was the first to accept the 1K UV Curable Waterborne Polyurethane coatings as an answer to the needs of ultra- low VOCs and VHAPS. The average VOC of the coatings used in the wood coatings market is approximately 3.5 lb/gal; thus an ultra- low 0.2 lbs/gal VOC coating can dramatically impact the total VOC emission for a production site. VOC, however, rarely is the only justification for the manufacturers to apply a new green technology. Film performance is the key.

Graphic 1: Solvent Resistance Assay for 1K UV Curable Waterborne Polyurethane Based Wood Coating



Studies are typically done when raw material suppliers and coatings suppliers need evidence to convince themselves and the OEM wood manufacturer of both the perceived and economic value of converting to a green technology. In this case the problem is so complex for the raw material supplier that he must call on tools that are typically not used in the wood coatings market. The traditional tests are the KCMA and office institutional test protocol. BMS scientists were forced to reduce the development cycle time to be able to screen thousands of formulations so that that the optimal solution could be recommended to their paint suppliers. This technique, known as 'High Throughput Screening" (HTS), was utilized to compare the new green technologies ability to meet the film performance values[14]. Graphic 1 is a depiction of these screening tests. Testing was done robotically utilizing a 50:50 blend of ethanol and water while exposing the test film for 10 minutes to this solution.

Studies were done comparing a waterborne acrylic, a competitive alternative technology to solvent-borne coatings, against a 1K UV Curable Waterborne Polyurethane. In this case the water based acrylic did not perform very well on its own. With the utilization of the 1K UV Curable Waterborne Polyurethane based Coatings a blending scenario was developed that brought the system up to an acceptable chemical resistance level. Paint suppliers will often utilize less expensive acrylic raw materials to reduce the overall cost performance of the system.

In addition to excellent appearance and barrier properties, the1K UV Curable Waterborne Polyurethane based Coatings formulations have none of the pot-life issues that many contemporary wood coatings possess. There is no solvent odor and the VOC is equal to or less than 0.2 lb/gal. Our laboratory has demonstrated and our paint customers have confirmed that 1K UV Curable Waterborne Polyurethane coatings, when properly formulated, have film characteristics similar to those of solvent-borne coatings. These properties include high and low gloss variability, good balance of flexibility and hardness, good abrasion and chemical resistance, and good outdoor weather ability.

Source Reduction in VOC and VHAPS for WOOD Coatings OEM: With the introduction of the 1K UV Curable Waterborne Polyurethanes directly competing against amino conversion varnishes in the wood coatings market this technology was able to remove 2.6 million lbs of organic solvents (VOC) and 49,000 lbs. of formaldehyde (VHAPS) for the period 2007 to 2011 from the US environment.

Site Applied Floor Coatings. Unlike other market areas where regulations governing VOC is the driving force in solvent reduction, the key factor in site applied floor coatings is elimination of solvent odor and the rapid return to service.

Therefore, for site applied floor applications a coating with a VOC of 1.0 lb/gal may be just as undesirable as one with 3.5 lb/gal. One potential solution to solve this unmet need is to use two-component waterborne coatings which has virtually no co-solvent in the formulation. These formulations are based on water-dispersible polyisocyanates and waterborne polyesters or blends of waterborne polyester and polyacrylate. Both pigmented and clear floor coating formulations with VOCs of 0.1 lb/gal or under provide the combination of chemical and scuff resistance, gloss retention, toughness, easy application, long life and good clean ability required in a high quality floor coating. However, the curing of the coating still requires significant amount of time before the floor can be used under the normal conditions. To address the curing speed challenge, BMS has introduced 1K UV Curable Waterborne Polyurethane floor coating technology based on UV Curable Polyurethane Dispersions . This technology offers a 1K system with rapid cure and low odor. This allows the contractor to offer both a green chemistry solution and rapid return to service. Facilities such as hospitals, schools, parking garages and hotels, where the customer can't wait for the paint to dry, are amazed at how fast the job can be completed. In many of these environments, exposure to VOC and VHAPS for personnel working in these facilities can be dramatically reduced.

Special Effects Coatings/Emerging Applications. In the U.S., an emerging market segment is in the area of special effect coatings. These coatings provide the soft, luxurious look and feel of leather to hard plastic interior automobile surfaces such as instrument panels and air bag covers. Two-component solvent-borne polyurethane has long been used in these applications, but the 1K UV Curable Polyurethane Dispersion based Coatings are being considered. The 1K UV Curable Waterborne Polyurethane based Coatings offer the same or better performance of its 2K counterpart. In our laboratories, developmental formulations based on a 1K UV Curable Waterborne Polyurethane based Coatings containing only 0.02 lb/gal VOC provide excellent properties and a softer "feel" than the conventional two-component solvent-borne system with 5.0 lb/gal VOC.

Sun Shine Cure Deck Coatings/Emerging Applications. This new emerging application was developed around the idea of using the light of the sun to activate this unique 1K chemistry. Today's wood deck market is estimated to be at 140 MM lbs. of coatings. These coatings are dominated by low solid's solvent containing alkyds or acrylics. Most deck coatings are applied on an annual basis emitting large amounts of VOC into the environment. BMS scientists identified the following attributes for this unique cured deck coating to include: 1K (unlimited work-life, no mixing of components and no waste), no special curing equipment, easily applied/user-friendly (brush, roll or spray), low VOC/low odor, excellent properties/durability (chemical resistance, weather able, scuff resistance), and rapid return of service (convenient for end user, increased productivity for contractor/applicator). The results concluded that sun shine will cure the 1K UV Curable Waterborne Polyurethane to give acceptable level of performance at a VOC of 0.2 lbs/gal VOC[8] Several paint companies have taken on this concept and have this type of system under field performance evaluations.

Military/Emerging Applications. 2K solvent-borne polyurethanes have traditionally been used in military applications because the extreme environments that the equipment operates in dictate the use a high performance coating. The performance criteria include flat coatings with camouflage requirements, corrosion protection, chemical and chemical agent protection, flexibility, and exterior durability. 2K water-reducible polyurethane coatings based on hydroxyl-functional polyurethane dispersions and hydrophilically modified polyisocyanates are being evaluated for military use due to the necessity to reduce VOCs to comply with the Clean Air Act. Depending on how the various manufacturers produce the coating, applied VOC is between 1.3 and 1.8 lb/gal as compared to solvent-borne systems with VOC of 2.8 lb/gal or greater.

More recently, development work in this application has focused on a 1K UV Curable Waterborne Polyurethane based Coatings. A paper to be presented in 2012 out- lines the current need for coatings to be ready for use under the 72 hour cure schedule[2]. This imposed wait time for a 2K coating to cure is the primary reason for the US military interest in UV cure technology. Mission readiness can't be dependent on waiting for paint to dry. The paper describes the 1K UV Curable Waterborne Polyurethane based Coatings performance attributes to MIL-PRF-85285 which evaluates aerospace topcoats for chemical resistance, flexibility, weather ability, and water resistance. The paper will show that the 1K UV Curable Waterborne Polyurethane Dispersion based Coatings met the MIL-PRF-85285 performance specification except for gloss and did not go above a ΔE value of 1 in the weathering category. This performance for a 1K UV Curable Waterborne Polyurethane is impressive in that this raw material was never designed for use in an aerospace top coat.

Graphic 2: MIL-PRF-85285 1K UV Curable Waterborne Polyurethane Based White Aerospace Coating

Gloss White Coatings Properties

Test	85285 Spec	UV-PUD Coating
GE Impact Test	≥ 60%	60%
Dry / Wet Adhesion	≥ 4B / 4A	4B / 4A
Gloss	60° ≥ 90	80
Initial Pencil Hardness	≥ 2B	HB/F
Mobil Jet Oil	-2 pencils	-1
Hydraulic Fluid	-2 pencils	-1
JP-8 Jet Fuel	-2 pencils	-2
Humidity Resistance after 14 days ambient	30 days	No blisters

Bayer MaterialScience

Weathering

Number of Hours	60° Gloss	ΔE
0	75	---
500	68	0.66
1000	63	0.70
1500	57	0.76
2000	56	0.70
3000	53	0.72

Wet Strength Papers/Emerging Applications: A new and emerging technology for the 1K UV Curable Waterborne Polyurethane is in the use of paper wet strength. A US patent application scheduled for publication in 2012 describes its ability to impart sizing and/or wet strength to papers and paperboards. [15]

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