

New Radiation-Curable Polyurethane Dispersions For Outdoor Application On Wood

MICHEL TIELEMANS

*Cytec Surface Specialties
Anderlecht street 33
B-1620 Drogenbos
Tel : +32.2.3345578
Fax : +32.2.3783944
Michel.Tielemans@cytec.com*

JEAN-PIERRE BLEUS

*Cytec Surface Specialties
Anderlecht street 33
B-1620 Drogenbos
Tel : +32.2.3345922
Fax: +32.2.3783944
Jean-Pierre.Bleus@cytec.com*

ABSTRACT

Radiation curable polyurethane dispersions (called UV-PUD) have benefited over the last years from a continuous growth in a market that recognizes in them a high-end performance for innovative markets. These products combine the advantage of (i) the polyurethane chemistry (ii) the radiation curing technology and (iii) the physico-chemistry of aqueous colloidal dispersions.

The chemical structure of UV-PUDs is presented in the framework of new coating developments for improved outdoor resistance. These coatings offer a competitive advantage for certain industrial applications on wood, like joinery. The mechanisms of polymer degradation are shortly summarized. In particular, the model chemical structure of an unsaturated polyurethane is outlined and the essential chemical modifications of the backbone are described for promoting an increased resistance to hydrolysis and ultraviolet light. The polymer modifications involve the stoichiometric replacement of diisocyanates and several linear telechelic diols based on polyesters, polyethers, polyacrylates, polybutadienes, polycarbonates and polysiloxanes. The comparative effect of dimethylol propionic acid against dimethylol butanoic acid is also reported. Finally, the influence of critical additives like UV-absorbers, light stabilizers (HALS) and photo-initiators are outlined using electron beam curing as a comparison against UV-irradiation.

The formulation of the aqueous dispersion and its application on wood by spraying are described in detail. The mechanical and chemical resistance of the coatings is assessed using a standard protocol. The test method for artificial weathering uses repeated cycles of ultraviolet light with defined temperature & relative humidity patterns (Atlas C4000 Weather-O-Meter). It is inspired by the indications of the European directive EN927.

The comparative aging results of the coatings are statistically analyzed by determining a critical time (t_c) linked *either* to the significant apparition of defects on the wood surface *or* to the complete destruction of the sample. The results are accompanied by pictures that visually show the evolution of the samples during the test. Some aging correlations have been made with the same coatings on a neutral, treated metallic substrate and with free films submitted to mechanical analysis.

In the case of a polyester-based unsaturated polyurethane model, the use of photo-initiators reduces considerably the life time of the coated sample while, surprisingly, no significant improvement has been recorded following the use of UV-absorber and light stabilizers (HALS) in the coating. The best performances were obtained with a particular polycarbonate-based variant. In that case, it was possible to significantly increase the longevity of the coated wood in our test conditions, while presenting a similar level of mechanical and chemical performance.

INTRODUCTION

The coating technologies having a lower chemical impact on environment & health are gradually dominating the market with, as a consequence, the development of innovative waterborne polymers with good standards of performance for many industries.

Some of the most promising developments within the whole waterborne polymer family involve radiation-curable polyurethane dispersions (called UV-PUD) [1, 2, 3]. These products benefit from a continuous growth within the coating market that recognizes, on top of lower energy requirements, their high-end performance and strong potential. They are positioned at the interface between different chemistries and technologies [4] and, hence, their unique features take advantage from *both* polyurethane polymers and radiation curing technology while their colloidal nature in water differentiates them from their 100% equivalents. As such, they should contribute largely to sustain the growth in markets where the penetration of radiation curing is still low.

UV-PUD's are colloidal dispersions that comply with the expected reduction of volatile organic compounds and whose stability is mainly ensured by the electrostatic repulsion between the anionic polymer at the surface of these particles [5]. The dispersion is in essence a metastable and heterogeneous, multi-phase system where the drifts from an ideal model underlines an infinite morphological complexity [6]. Their *rheology* is governed by a complex relationship between (i) the solid contents of the dispersion (ii) the particle size distribution and morphology (iii) the pH. It is particularly favorable for robust low-viscosity applications like spray or gravure. Their *film formation* is also beneficial with a low minimum film formation temperature (MFFT) that does not require the use of coalescing agents and that results in the formation of a coating becoming physically dry after water evaporation and particle coalescence. These properties are very peculiar for waterborne polymer dispersions that become very hard and resistant after the crosslinking process.

UV-PUD's are intrinsically true polyurethane polymers having hard urethane and urea domains with strong hydrogen bonding which, together with the acrylate crosslinking ability, give the material its hardness and resistance - whilst the softer domains serve as buffer zones and account for the flexibility and the elongation. As a consequence, a superior balance in chemical resistance and mechanical properties is obtained due to the lower crosslinking density and the higher average molecular weight between crosslink points. It is obvious that a radiation-cured coating becomes harder and more rigid when the number of reacted acrylic double bonds increases and that the chemical and solvent resistance increase accordingly. The influence of the crosslinking density and the molecular weight between crosslinking on the coating performance was reported elsewhere [7, 8].

The waterborne polymers require an easy & robust application onto the substrate to form a continuous film that binds the substrate in such an intimate manner that the coating and the substrate are becoming one new single element with an increasing value in the eyes of the customer. In this condition, the coating primarily offers a strong advantage related to the protection and the valorisation of the substrate. Additionally, it is required to display long-lasting features after aging or weathering. Among all the substrates covered by industrial coatings, wood takes an important economical position [9] on the side of plastic, metal, glass, concrete, textile, etc.

The wood substrate is a natural porous material consisting mainly of cellulosic fibres and lignin. In order to compete with other building materials, the durability of wooden constructions must be increased significantly while preserving or even enhancing their natural appearance. Wood is not dimensionally stable and is very vulnerable to surface deterioration through fungal, microbial, moisture and light degradation as well as to tannin staining. As such, the wood substrate continues to present a challenge for efficient protective coatings in terms of esthetical and qualitative performance, more typically for outdoor applications. The outdoor wooden joinery is a big wood market sub-segment that includes applications like window frames, doors, shutters and panels. Today, it is still mostly based on conventional (non radiation curable) waterborne technologies (acrylics, alkyds) but specific needs for improved productivity and performance are identified in the high-end part of this market.

A radiation-curable polyurethane dispersion especially designed for outdoor resistance can offer to the outdoor joinery industry the productivity benefits of radiation curing that provides higher cure speed with the possibility to allow the rapid stacking of coated items. The coating displays a superior mechanical & chemical resistance suitable to protect high quality wooden materials from challenging usage conditions. At the same time, it presents the advantages of waterborne polymers that allow easy and safe applications (sprayability, low volatile organic content, absence of irritancy). To meet the market demands, durable clear coats are required that reduce photochemical degradation and moisture uptake - as a dynamic equilibrium between water & water-vapour absorption and desorption. The coating must have a good dimensional stability to avoid film failure (cracking) and loss of adhesion (flaking, peeling, blistering) arising from mechanical solicitations (scratch), from thermal effects (freeze thaw) and from the penetration of water and its accumulation at the coating interface [10].

It is shown since many years that the adhesion offered by a coating on wood is linked to the good penetration of the polymer into the wood structure, which comprises the mechanical interlocking inside the porosity of the substrate. This condition is depending in turn on the polymer characteristics like its viscosity and molecular weight (flow) as well as its polarity (wetting). A good adhesion between two materials is thus also the consequence of high attraction forces at their interface as figured by the two components which account for the total adhesion forces at the interface, i.e. the polar component and the dispersive component (Van der Waals forces). The particle size plays also an important role in the case of polymer dispersions in order to develop these intimate mechanical and physico-chemical bonding interactions [11].

This paper discloses the chemistry to upgrade the outdoor performance of UV-PUD's and will demonstrate that the resulting high-resistant and ecologically-appealing products are particularly interesting in the case of outdoor wood application.

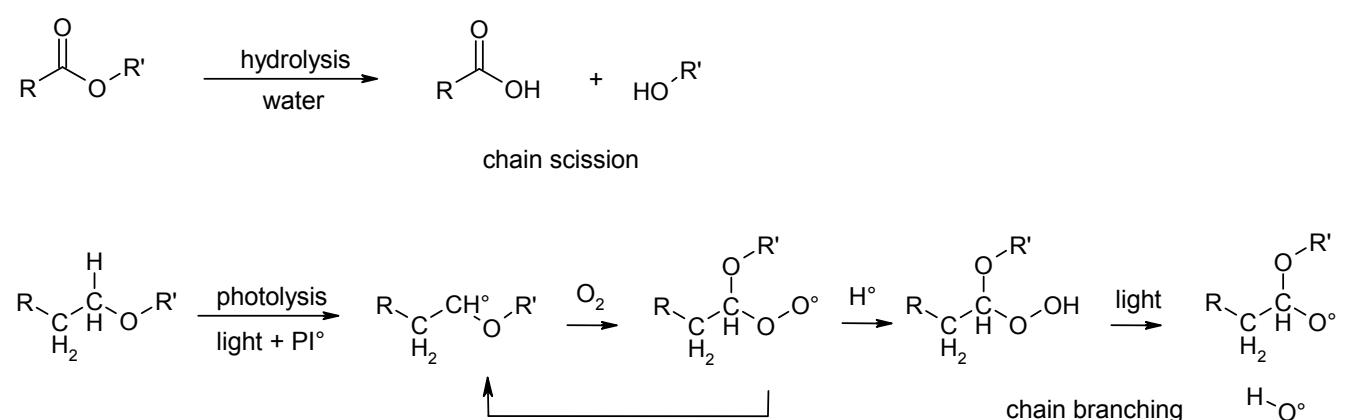
BASIC PRINCIPLES OF POLYMER AGING

In a natural outdoor environment, the primary factors affecting a coating are linked to temperature, humidity, light, oxygen and the various atmospheric pollutants. All these factors generally combine in complex synergistic effects that affect both the coating surface and the bulk. The major degradation pathways that explain the weathering of a coating are twofold: *hydrolysis* and *photolysis* that result in a dramatic modification of the polymeric material due

to either chain scission and/or chain branching and crosslinking [12, 13]. These phenomenon's are responsible for a deep modification of the physico-chemical properties of the material that degrades in becoming (for instance) hard and brittle. Macroscopic observations often indicate a loss of adhesion on the substrate and the creation of defects that allow water to penetrate to the substrate surface that it then deteriorates.

The hydrolysis commonly affects the polymer by scission at their ester, amide, urethane, urea and/or carbonate linkages. The polyester linkage is particularly sensitive in that aspect. Its hydrolysis primarily reduces the molecular weight of the polymer and forms carboxylic acids and alcohols that are not chemically inert and that can further participate to the degradation process. This is reported in the Figure 1.

Figure 1. Hydrolytic and photolytic degradation pathways of a polyester- and polyether-based polyurethane



The photolysis commonly involves a free radical photo-oxidation process. The formation of free radicals happens by the homolytic rupture of covalent bonds due to the interaction of the polymer matrix with light and/or heat, but the residual free radicals from a photo-initiator are also an additional source. This reaction is particularly prevalent with ether functions where the *alpha*-hydrogen against oxygen are well known to be labile for abstraction by radicals. Once these free radicals have been formed, they react with oxygen to form a peroxy radical. These radicals can in turn abstract hydrogen's from the polymer to form hydroperoxides and a new radical. This cyclic mechanism happens until two radicals are coupled in a termination reaction with an increase of the crosslink density. The hydroperoxides further decompose by homolytic rupture of the oxygen – oxygen linkage that restart the cycle and create branching. Radical coupling between polymers are creating excessive crosslinking at the polymer surface causing micro-cracks that change the surface morphology and reduce gloss, create penetration channels for water, etc. This mechanism is also reported in Figure 1.

The nature of the polymer takes a very important role. The level of hydrolysable function in the polymer (esters, amides, urethanes, ureas, carbonates...) is directly accountable for the hydrolysis pathway. The same is true for the photolysable functions (especially ethers) but it is noticeable that branched polyesters having more secondary and tertiary hydrogen's available for abstraction, also contribute to the photolysis. The residual acrylic double bonds that are still present at a certain level even in fully crosslinked material where chain mobility is

becoming extremely low, do also contribute to crosslinking and to the increase of hardness generally observed during weathering.

The crosslinking density of the coating has also an impact on degradation [14]. A highly crosslinked network reduces the rate of oxygen (and water) uptake and limits the surface photolysis (and hydrolysis). This is particularly the case for all the polymers described in this study, which have been crosslinked after irradiation with ultraviolet light or electron beam.

The additives that reduce the effect of the photolysis pathway are found in two categories. First the radical scavengers, under which the widely used category of hindered amine light stabilizers (HALS), play a curative role in capturing the radicals and transform them into photo-stable products. Secondly, the light absorbers that present a high molar extinction coefficient in the Beer-Lambert relation and play a preventive role by reducing the effect of the light in the bulk of the material.

Although the most reliable information on the outdoor behavior of a coated substrate is obtained from the natural exposure in a harsh outdoor environment (like Arizona or Florida), these tests require long durations to deliver a conclusion and are generally incompatible with the efficient study of structural modifications of a polymer. Hence, it is of common use to develop new polymers based on the results from laboratory accelerated weathering tests [15]. This has already been done for urethane acrylates used in 100% formulations [16, 17].

MODIFICATION OF THE POLYURETHANE STRUCTURE

Many compositional variants have been described in the literature in order to obtain a stable colloidal dispersion of an acrylated polyurethane polymer. In most of the cases, several basic structural elements need to be present in order to obtain a balanced level of properties, namely (a) at least one diisocyanate (b) at least one diol (c) at least one hydrophilic diol capable to disperse the polymer in water and to ensure its colloidal stability (d) at least one unsaturated alcohol and/or diol capable to bind to the polymer.

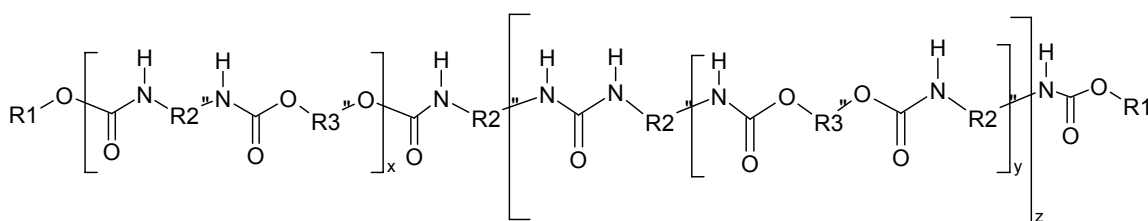
We have used a model process for our study that was versatile enough to encompass a wide range of composition variants based on (a), (b), (c) and (d). In a *first step*, a low molecular weight polyurethane pre-polymer is synthesized in a low boiling point solvent (typically acetone) from a diisocyanate and from long & short chain diols. Long-chain diols are selected from polyester diols, polycaprolactone diols, polyether diols, polyacrylate diols, polycarbonate diols and polysiloxane diols in order to provide the flexible segments of the polymer. Short-chain functional diols are used to provide the enhanced ionic character required for water dispersibility. In a *second step*, the carboxylated, isocyanate-terminated polyurethane pre-polymer is capped with an hydroxylated, acrylated molecule. During a *third step*, the pre-polymer is then dispersed into water under high shear mixing and after the neutralization of the carboxylic acid functions with a tertiary amine. In a *forth step*, the low boiling point solvent is stripped out under vacuum.

The modeled structure of the UV-PUD is represented in Figure 2. The left side of the molecule is accountable for the end-capped polyurethane ($x = 1-3$, $z = 0$) while the right site between the large brackets represents the fraction of the polymers that have been naturally

chain extended in water through the hydrolysis of the remaining isocyanates and the formation of an urea ($x = y = 1-3, z = 1$). It is very easy from this model to highlight the permitted structural variants from R1, R2 and R3. In all our variants, we have changed only one structural parameter at the time, keeping the equivalent ratios between the isocyanates and the alcohols constant both in the stage 1 (urethanisation) and in the stage 2 (capping). The isocyanate content is followed by titrimetry during all the synthesis. By doing this way, the stoichiometry of the polymer variants is always under control and only the weight proportions of the different components may vary due to their difference in equivalent weights. Also the nature and the stoichiometry of the neutralization has not been modified.

All the variants have been made from a starting model polymer based on the use of 4,4'-dicyclohexylmethane diisocyanate (H12MDI) as component (a), a polyester diol made from adipic acid and neopentyl glycol as component (b), dimethylol propionic acid as component (c) and pentaerythritol triacrylate as component (d). It is referred in the text as dispersion A'.

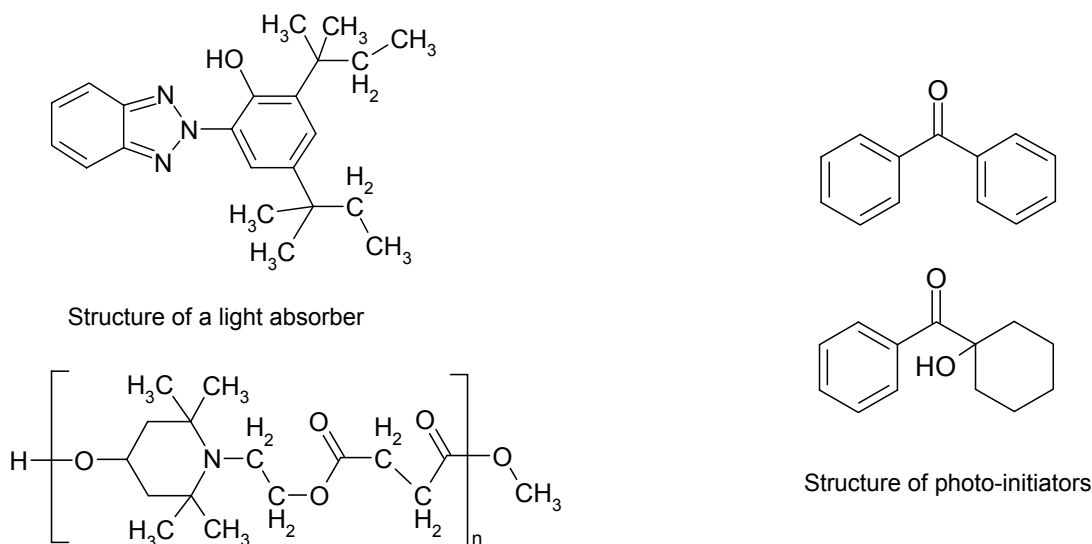
Figure 2. Model structure of an UV-PUD



A significant number of polymer variants have been made but due to the big number of syntheses that has been done, it was decided to select only those being the most representative of their category. The goal of these polymer modifications was to provide a polymer that was prone to enhance the weathering properties in the frame of the known degradation pathways described earlier. We looked essentially for a higher hydrolytic resistance offered either by the backbone linkage or by an increased hydrophobicity or water repellency. We looked also for a higher photolytic resistance offered by specific additives known in the state of the art, like the light absorbers or light stabilizers. All our products contain the same amount of light absorber and hindered amine light stabilizer (HALS) additives added during the synthesis process, except model-dispersion A (similar to A') where they are absent. All the polymers have also been formulated with benzophenone-type photoinitiators. The structure of these additives is outlined in Figure 3.

The first series of variants implied the choice of diisocyanates whose effects on outdoor weathering has already been described [18]. We replaced stoichiometrically the 4,4'-dicyclohexylmethane diisocyanate (H12MDI) by isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) which constitute the majority of commercial aliphatic diisocyanates. The tetramethylxylene diisocyanate (TMXDI) contains an aromatic ring not linked directly to the isocyanate group, which is imparting specific and very interesting properties to the molecule [19]. The commercial aromatic diisocyanates, like toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI), were not considered due to their demonstrated poor performance for weathering. Model-dispersions B, C and D correspond to these modifications, see Table 1.

Figure 3. Model structure of additives used in this study



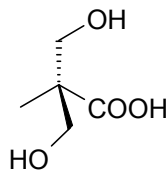
Structure of a Hindered Amine Light Stabilizer (HALS)

The second series of variants implied the wide choice of the polyols. Their model structure is exemplified in the Figure 4. These macrodiols are generally referred to as soft segments in the polyurethane and are thus essential building blocks for these polymers used in coating applications. The amount and nature of the polyol component incorporated in the synthesis of polyurethanes exhibit the most significant influence on the end properties of the resulting products. This allows a broad spectra of features ranging, e.g. from hard to soft, from hydrophilic to hydrophobic. We looked at the possibility to combine the desired mechanical and chemical properties with a good weathering resistance at the same time.

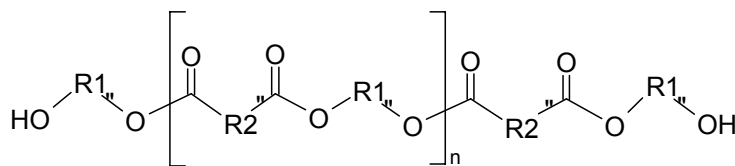
We replaced stoichiometrically the dimethylolpropionic acid (DMPA) by the dimethylolbutanoic acid (DMBA). On top of several process advantages known for the second, it was tempting to consider that the increase of hydrophobicity on the molecule bearing the ionisable carboxylic group could be favorable to reduce the hydrolytic degradation pathway. This corresponds to model-dispersion E, see Table 1.

The polyester backbone has the reputation of being sensitive to hydrolysis but with some exceptions. For that reason, we replaced the standard polyester by a polycaprolactone with a higher backbone hydrophobicity coming from the choice of the diol molecule chosen as initiator (R3 in the Figure 4). Polyesters made from ortho-phthalic acid were also reported to increase hydrolytic resistance in a much higher level than isophthalic and terephthalic acids [20]. The polyester backbone can also be modified by the use of a fatty acid dimer or the like. These polyols claim for high hydrolytic stability, good flexibility and water & solvent resistance. Those fatty acids with low unsaturation level are naturally better towards oxidation and present a good color retention suitable for outdoor exposure. This corresponds to model-dispersion F and G, see Table 1.

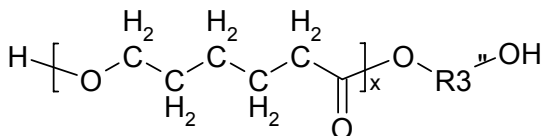
Figure 4. Model structure of several polyols used in this study



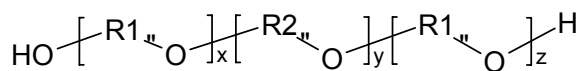
Dimethylol propionic acid



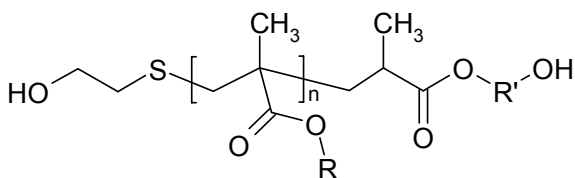
Typical structure of a polyester diol



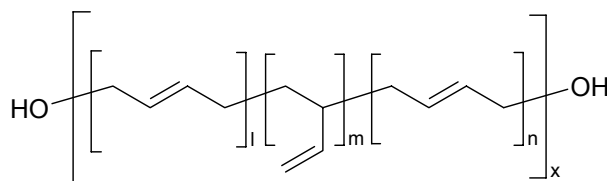
Typical structure of a polycaprolactone diol



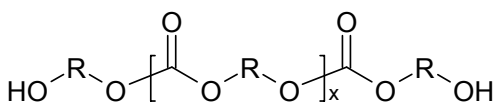
Typical structure of a polyether diol



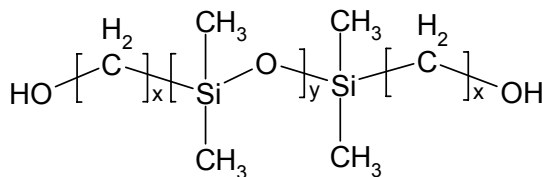
Typical structure of a polyacrylate diol



Typical structure of a polybutadiene diol



Typical structure of a polycarbonate diol



Typical structure of a polysiloxane diol

The polyether backbone has proven records of good hydrolytic stability but, on the other hand, it is generally quite weak for photolytic degradation. The explanation is generally linked to the presence of the labile hydrogen in the alpha position of the oxygen from the ether linkage and to the photo-initiated homolytic rupture of this bond (see before). The most hydrophobic structures between the polyethers (R1, R2 in the figure 4) were however quite interesting to consider, like the polytetramethylene glycol. Some structures have linear or branched block structures ($x, y, z \neq 0$) that can add some diversity in the structure and upgrade the properties. This corresponds to model-dispersion H, see Table 1.

The polyacrylate backbone displays generally a good performance for outdoor resistance. It is however more a challenge to obtain low molecular weight polyacrylate diols with telechelic functionality, since the random distribution of hydroxy groups is the rule. *Alpha, omega*-polymethacrylate diols can however be obtained by the free radical polymerization of methacrylates in the presence of hydroxylated mercaptans used as chain transfer agent and

followed by the selective end-group transesterification with a diol [21]. It is convenient to use 2-mercaptoethanol as transfer agent. The choice of the methacrylate side chain (R in the figure 4) and the capping diol (R' in the figure) permit several compositional variations. This corresponds to model-dispersion I, see Table 1.

The polybutadiene backbone presents a very hydrophobic structure. They are claimed to be incorporated in polyurethanes to provide a high hydrolysis resistance in extreme acidic or alkaline conditions and good mechanical properties for flexibility. The structure (see figure 4) displays a multi-block structure with various molecular weights possible. This corresponds to model-dispersion J, see Table 1.

The polycarbonate backbone is known to combine excellent hydrolytic and photolytic resistance within a wide range of structures. The choice of the diol (R in the figure 4) can provide a certain number of grades and molecular weights, and several diols can also be combined in the same oligomer. This corresponds to model-dispersion K, see Table 1.

The polysiloxane backbone is claimed to bring some of the basic features of silicones in a polyurethane polymer, e.g. increased hydrophobicity and water repellency as well as release properties. The polysiloxane is quite resistant to hydrolysis and photolysis. Special grades display a telechelic functionality where the spacer length at both sides of the molecule (x in the figure 4) can be tailor-made. This corresponds to model-dispersion L. Worth to mention, this is the only case where the amount of this oligomer has been intentionally limited to 10% in weight, the standard polyester of this study being added to guarantee the usual stoichiometry. This corresponds to model-dispersion L, see Table 1.

Another backbone modification that has not been encompassed in this study involves the use of fluorinated building blocks that generally provide strong beneficial surface modifications linked to a low surface energy [22].

Table 1. Characteristics of synthesized polyurethane dispersions

	isocyanate	diol	solids (%)	viscosity (mPa.s)	pH	particles (nm)	stability 60°C (days)
A	H12MDI	polyester	35.0	40	7.0	29	>10
A'	H12MDI	polyester	35.0	50	7.5	50	>10
B	IPDI	polyester	35.0	74	7.7	67	>10
C	HDI	polyester	35.0	2240	7.8	75	>10
D	TMXDI	polyester	33.0	20	7.2	76	>10
E	H12MDI	(polyester)	35.0	48	7.6	35	>10
F	H12MDI	polycaprolactone	35.0	64	7.4	31	>10
G	H12MDI	<polyester>	35.0	48	7.1	51	>10
H	H12MDI	polyether	35.0	46	7.1	38	>10
I	H12MDI	polyacrylate	35.0	38	6.9	31	>10
J	H12MDI	polybutadiene	35.0	52	6.9	202	<10
K	H12MDI	polycarbonate	35.0	67	7.5	26	>10
L	H12MDI	Polysiloxane	35.0	28	7.1	125	>10

The characteristics of the synthesis described here above are summarized in Table 1. The solid content is expressed in percent using a gravimetric method (2H, 120°C). The viscosity is measured in mPa.s using a Brookfield viscosimeter at 50 rpm and 25°C. The mean particle size is recorded using a Malvern Autosizer Lo-C equipment and is expressed in nm. The

colloidal stability is approached qualitatively by placing a sample of dispersion in an oven at 60°C and looking for the time of apparition of a significant deposit resulting from a destabilization.

APPLICATION AND TESTING ON WOOD

The additives used for the formulation of water-based compositions are an essential tool to provide the good application and performance of the coating on wood. All the model-syntheses have been formulated with the aim to obtain a robust product for spray coating. The standard formulation used in all cases is described in Table 2.

A photo-initiator (Additol BCPK) has been used to allow efficient crosslinking under UV-light; as such, its use is mandatory in the formulation. A rheology modifier (Ucecoat XE430, hydrophobic ethoxylated urethane nature) is also used in order to obtain a viscosity of about 1200 mPa.s (Brookfield, 20°C). Although relatively high, this viscosity was providing a smooth application on wood by air spray without any sagging problem on vertical panels. The amount of thickener may vary somewhat in the formulation in order to obtain the target viscosity. A matting agent (Acemat TS100, silica dispersion) has been used in order to deliver a low gloss coating around 20% (60° angle). A wax dispersion (Aquamat 208) is incorporated in order to enhance some surface properties of the coating as scratch resistance and matting level. A defoaming agent (Byk 025) is used to minimize foaming problems and related coating defects after spraying. Finally, a wetting agent (Emulat S793) is beneficial to reduce the surface tension of the formulation and promote a good wetting of the wood without defects. All these additives provide a coating with a good aesthetical quality able to cover nicely the wood surface and to ensure its protection without defects like “orange peel”, “pin holes” and “fish eyes” that depress the coating performance.

Table 2. Formulation of polyurethane dispersions

DISPERSION A-L	100 parts	Polyurethane dispersion	Cytec Surface Specialties
ADDITOL BCPK	1.5 parts	Photo-initiator	Cytec Surface Specialties
UCECOAT XE430	2.0 parts	Rheology modifier	Cytec Surface Specialties
ACEMAT TS100	1.5 parts	Matting agent	Degussa
AQUAMAT 208	3.0 parts	Matting / scratch resistance agent	Byk Chemie
BYK 025	0.1 parts	Defoaming agent	Byk Chemie
EMULAT S793	0.3 parts	Wetting agent	Cytec Surface Specialties

The testing involved in this study has been inspired by European Standard EN927 “Paints & varnishes – coatings materials and coating systems for exterior wood” which is composed actually by 5 published parts, namely (1) classification & selection (2) performance areas (3) natural weathering test (4) assessment of water-vapor permeability (5) assessment of liquid-water permeability. The part (6) about artificial weathering - particularly interesting for this study - has to our knowledge not been published prior to the start of our investigations, although a draft version has been published in German (December 2004). Although recognizing the interest of standardized methods [23], we have often replaced the standard protocols with own methods that have been providing proven value for the earlier comparison of coatings on wood material. Our protocols are described below.

The substrates used for this study are plain pine wood for the artificial weathering and beech for the chemical & mechanical resistance tests.

The preparation of the wood for artificial weathering involved 4 separate steps that were aligned as much as possible to the conditions practiced in the real world. The pine wood was selected because of its ability to evidence early degradations in aging conditions.

The solid pine wood is first cut in 140 x 59 x 18 mm pieces, the edges & corners are rounded and the surface is sanded with a 150 grit paper.

An impregnation primer is applied onto the wood by dipping in a formulated commercial waterborne acrylic latex (copolymer methylmethacrylate : butylacrylate) diluted at 20% solids in order to obtain a 100 g/m² wet coating. The layer is physically dried at ambient temperature.

An intermediate coat is then similarly applied onto the coated wood by dipping in another formulated commercial waterborne acrylic latex (copolymer methylmethacrylate : butylacrylate) diluted at 20% solids in order to obtain a 100 g/m² wet coating. The layer is physically dried at ambient temperature. The surface is sanded with a 320 grit paper.

A top coat constituted by the above formulation of the A-L polyurethane dispersions is applied on the vertical wood panels at a thickness of 150 g/m² wet by using a spray technique. A uniform and defect-free application without sagging is obtained in those conditions. The coating is dried at room temperature and is followed by a treatment at 40°C. The radiation curing happens by passing the panels at a slow speed of 5 m/min under 2 mercury lamps of 80 W/cm in order to ensure full crosslinking. In one case, an electron-beam irradiation (e.g. 50 kGy, 250 kv) was performed on a formulation containing no photo-initiator.

The artificial weathering on coated wood has been performed using an Atlas CI 4000 Xenon Weather-O-meter fitted with filtered 6500 watt Xenon arc lamps. The aging cycles have been fixed at 1H30 with irradiation at 0.55 W/m², 50°C and 50% relative humidity, followed by a condensation period of 0H30 with irradiation at 0.55 W/m², 50°C and 95% relative humidity. The samples have been grouped in series with a least 2 replicates per product together with a reference polymer. The artificial aging was assessed every 250 hours and photographs were taken for each individual panel. The sample were taken out of the equipment after a complete wood degradation of when the test reached a duration of 3000 hours.

The artificial weathering on free films has been made using either a Votsch VC4034 climate oven at 85°C and 95% humidity or an irradiation chamber fitted with an Ultra Vitalux 230V E27/ES 300W ultraviolet lamp with a target of 5 days, 10 days and 15 days each. The free films were maintained on a flat glass surface above a piece of Teflon in order to avoid the irreversible curling of the films. The samples were submitted to mechanical analysis. Tensile properties were measured with a Zwick Z010 elongation testing machine at cross-head speed of 50 mm/min. and at room temperature. Rectangular-shaped specimens of 3 cm by 1 cm were cut from films for the tests using 3 -7 independent measurements for each film if the degradation of the film permitted.

The free films were prepared with a thickness of 100 μ dry by making the appropriate wet film on a release paper using knife coating directly on a Werner-Mathis ventilated oven for 2 minutes at 60°C. The film is then kept overnight in a standard ventilated oven at 60°C until complete dryness. The free film was cured 3 times at 5 m/min under a lamp of 80 W/cm. The dispersions for free film were each time formulated with 1.5% of ADDITOL BCPK (photo-initiator), 1% of Byk 346 (wetting agent) and a quantity of Ucecoat XE430 1:1 in water (thickener) in order to get a viscosity around 1000 mPa.s.

The preparation of the beech wood for performance testing implied 3 subsequent applications of the same formulated A-L polyurethane dispersions by spraying on the vertical wood panels to obtain a thickness of 75 g/m² wet. Each coating layer is dried at room temperature and is followed by a treatment at 40°C. The radiation curing happens after the 3 applications by passing the panels at a speed of 5 m/min under 2 mercury lamps of 80 W/cm. A uniform and defect-free application without sagging is obtained in those conditions.

The stain resistance of a coating is assessed by putting a test substance on the coating, covered with a microscope glass and left for 4 hours. The test substances used are a commercial glass cleaning product, ammonia 5%, ethanol 20%, butyl glycol, water, ketchup, mustard, red wine, coffee, javel water 9%, acetic acid and eosine 2%. The stains are washed with a couple of rubs using a tissue saturated with isopropanol. The remaining stains are assessed visually using a 0-5 scale, 0 = best. A low value (0) is expected to provide the best protection against any household product spillage.

The adhesion was measured after cross-cut and hatch; the damage to the coating due to adhesion loss is expressed in a 0-5 scale, 0 = best. A low value (0) is necessary to ensure a strong permanent bond between the coating and the substrate.

The scratch resistance has been measured using the Erichsen test equipment and expressed as the minimum force applied to the pencil in order to scratch the surface. The value is expressed in Newton. High values are indicative of a hard surface prone to protect the wood surface in an efficient manner.

The blocking has been assessed by putting the coated wood panels side by side and applying a pressure equivalent to 500 kg/m² at a temperature of 40°C during 16 hours.

The gloss of the coated wood was measured using a Gardner gloss meter with an incident light of 60° angle. The possibility to match a wide range of gloss values as a consequence of the formulation and coating conditions are perceived as an advantage in many markets.

RESULTS AND DISCUSSION

In a first instance, all the coated wood panels have been submitted to the artificial weathering of the Xenon Weather-O-meter with the conditions described earlier.

The coated wood often presented some differences in aging behavior for a given coating. This spread of results is accountable for the natural & porous nature of the material and a statistical analysis is required to detect the tendencies of the aging data. We found it relevant

to determine 2 types of critical times (t_c), one linked to the apparition of visual defects on the wood surface and another corresponding to the visual perception of a complete degradation of the sample. The times are integers of 250 hours which corresponds to the periodicity of the assessments. The values recorded correspond to the mean of at least 2 samples. They are reported in the Table 3.

Table 3. Critical times of degradation (t_c) in hours for coated wood (beech)

	A	A'	A''	B	C	D	E	F	G	H	I	J	K	L	IS
t_c #1	875	875	1500	375	500	375	625	1125	625	625	500	####	1625	625	950
t_c #2	2500	1750	2500	1125	750	1625	2250	2125	1375	1625	1250	####	2875	1125	2350

Conscious of the relative irreproducibility of the data, we were however certain of their value to detect significant trends and discriminate between the different polymers used for this study in the same practical way that would use the end user.

It is possible to see that the reference product (A') of our study does behave honorably towards the acrylic industry standard (IS) used as a benchmark. Nevertheless, the limitation clearly appears for this reference product that has not been optimized for outdoor application.

The product without the light absorber & stabilizer additives (A) does not perform worse than the previous, even at the contrary. A tentative explanation is that the hydrolytic degradation pathway is by far prevalent in a polyester-based polyurethane so that the additives play only a minor role in the minor photolytic degradation pathway. This assumption is comforted by the results obtained on free films and described below.

The product without the photo-initiator (A'') cured by electron beam provides a strong improvement of the aging behavior. This result was not surprising considering that the photo-initiator, mandatory when UV light is used for crosslinking, stays partially unaffected in the cured film and acts as a source of radical during the whole life of the coating exposed to light. Perspectives are thus opened to reduce the level or adapt the nature of the photoinitiator to make it the most suitable for aging.

The effect of the diisocyanate (B, C, D) was not found to be determining for the aging performance. No better result could be found than that obtained with H12MDI (A'). The use of the pseudo-aromatic TMXDI (D) does not result in a dramatic decrease of the aging performance, especially for the second critical time.

The switch from dimethylol propionic acid to dimethylol butanoic acid (E) shows a trend for a minor improvement of the aging performance, especially on the second critical time. The use of a polycaprolactone backbone (F) shows a more evident trend for improvement which is not the case for the fatty polyester backbone (G).

The polyether backbone (H) presents an overall *status quo* while the polyacrylate backbone (I) does not respond at all to the legitimate expectations that we placed in it.

The polybutadiene backbone (J) is the sole modification that resulted in a dispersion with high particle size and with poor colloidal stability. As a consequence, it was decided to restrict its use in the aging test.

The polycarbonate backbone (K) provides the most evident upgrade of the aging performance, with a significant improvement of both critical times.

Finally, the incorporation of a silicone in the backbone (L) surprisingly depresses the aging performances.

All the results obtained are placed in the perspective of the industry standard (IS) used as a benchmark. As such, it is important to consider that only the polycarbonate backbone (K) largely over perform the acrylic latex (IS) for aging.

Considering as evidence that the polycarbonate backbone (K) was the best candidate, we performed the chemical and mechanical tests on beech wood as outlined in the previous chapter, taking the polyester backbone (A') as the reference together with the industry standard (IS). The results are disclosed in Table 4.

Table 4. Mechanical resistance and chemical resistance after 4 hours (DIN 68 861) for coated wood (beech)

* best = 0	Cleaning product	Ammonia 5%	Ethanol 20%	Butyl glycol	Water	ketchup	Mustard	Red wine	Coffee	Javel 9%	Acetic acid	Eosine 2%	Adhesion	Scratch, Erichsen	Scratch, nail	Blocking
	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	N	0*-5	0*-5
A	0	0	0	5	0	0	0	0	0	0	0	0	1	21	0	0
K	0	0	0	0	0	0	0	0	0	0	0	0	0	18	0	0
IS	4	4	0	5	0	0	2	2	2	3	0	3	0	12	5	1

There is a clear superiority of the two UV-PUD's for all the stain tests, and it is possible to see that the polycarbonate backbone (K) is even slightly better than the polyester (A') in our tests – in particular for the severe butyl glycol stain. The superiority of the radiation-cured materials is also clearly evident for the scratch resistance measured by the Erichsen test but also with the nail scratch test. The superiority in blocking resistance is only slightly visible however. This surprising effect is probably due to the formulation of the ready-to-use industry benchmark. The adhesion is good to excellent in any case.

Figure 5. Artificial weathering (Xenon) of coated wood (pine) after 2000 hours, from left to right: polycarbonate(K), polyester (A) and acrylic latex (industry standard)

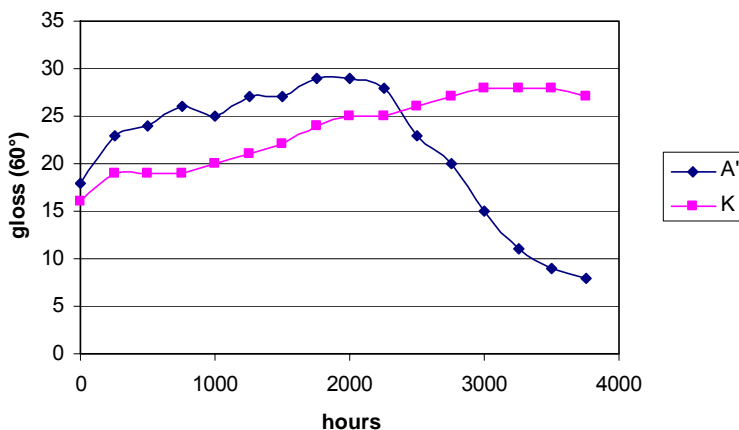


As an illustration, we present the photographs of the polycarbonate backbone (K) compared with the polyester (A') and the industry standard (IS) after aging of 2000 hours in the Xenon test. Only the first coating presents no degradation while the second is already quite damaged by the appearance of big white areas on the wood surface and the third presents the first evidences for the same evolution. They are shown in the Figure 5.

The polycarbonate (K) and the polyester (A') have also been tested on a neutral substrate in order to separate the influence of the wood from that of the pure coatings. The neutral substrate that we selected is made from metal pieces covered with a white pigmented super-durable polyester film. The coated plates have been submitted to the Xenon test in the same conditions as the wood panels. The gloss retention was followed over time and measured every 250 hours. This evolution is presented in Figure 6.

Although the initial gloss of the 2 coatings is quite similar at the start, they all show an increase of the gloss up to a point where the degradation occurs and that the gloss decreases. The maximum was found to be at about 3750 hours for the polyester (K) and 2000 hours for the polyether (A'). We believe that the initial increase of the gloss is due to the relaxation of the coating as a consequence to the increased temperature of the test. The decrease of gloss is due to the visible coating degradation with surface defects similar to chalking and orange peel.

Figure 6. Artificial weathering (Xenon) of coated panels (neutral) up to 4000 hours

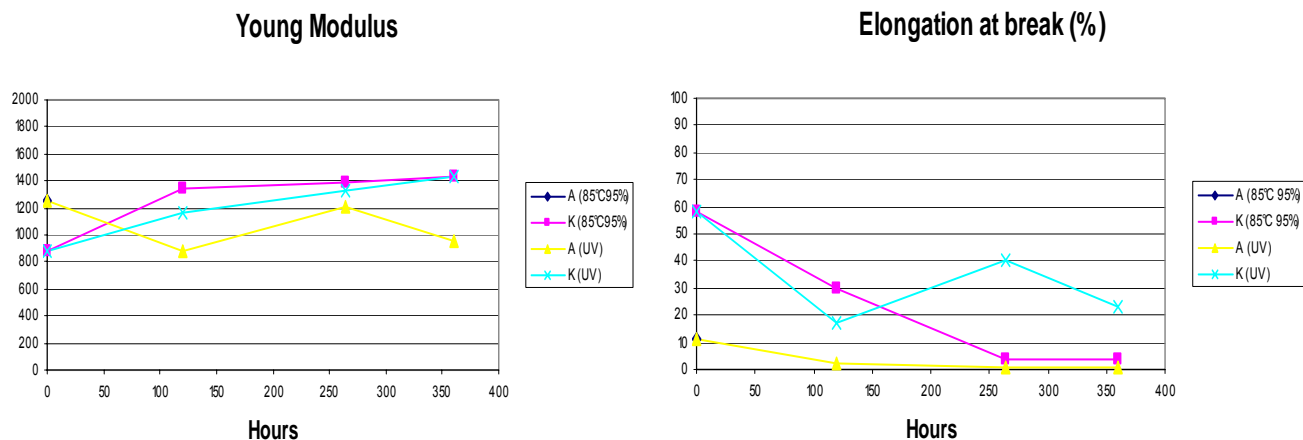


It is extremely interesting to consider that these critical times of degradation are both significantly superior to those t_c measured with the wood panels with identical aging conditions. This suggests some mechanisms of degradation that first involve a modification of the coating barrier properties affecting in turn the wood surface due to the water penetration – then secondly involve the destruction of the coating and the wood surface accordingly.

In order to further understand the mechanisms of degradation, we tried to separate the hydrolytic and photolytic pathways by submitting free films of polycarbonate (K) and polyester (A') in a climate oven (no light) and in an irradiation box (no humidity) - considering the

thermal degradation as secondary. The results of the evolution of mechanical properties – Young modulus and elongation at break – under the 2 conditions are described in Figure 7.

Figure 7. Artificial weathering (climate oven, ultraviolet light) of 100 μ films



The initial values of mechanical analysis indicate that the polyester (A') is slightly harder than the polycarbonate (K). The hydrolytic and photolytic degradations make the films always become stiffer as shown by the evolution of Young modulus and elongation at break, except for the cases where a more erratic evolution is recorded – e.g. Young modulus evolution of polyester (A') under UV light.

The predominant effect of hydrolysis over photolysis is clearly demonstrated in the case of the polyester backbone (A') since the films are becoming so brittle and damaged that they can not be handled anymore for mechanical analysis; as a consequence, they do not appear in the graphs of Figure 7. The hydrolysis is present but far less pronounced in the case of the polycarbonate (K).

CONCLUSIONS

Wood is a natural porous substrate that degrades easily under exterior conditions. It is the reason why it is preferably covered with a coating that enhances its appearance and protects it from mechanical & chemical aggressions. It is shown in this study that suitable polycarbonate-based radiation-curable polyurethane dispersions provide high end performance in case of exterior exposure compared with acrylic industry standards. Moreover, the waterborne nature of the polymer presents a low viscosity that permits a robust and safe application by spray, the product being almost free of volatile organic solvents (VOC) and non-irritant for skin and eyes. It is also free of tack after drying and before curing. Such a product is thus particularly recommended for use as transparent top coat for wood joinery where excellent outdoor resistance is essential.

The weathering is a multi-path degradation process leaded mainly by hydrolysis and photolysis. Radiation curable polyurethane dispersions present a wide variety of compositions out of several chemical building blocks that include the nature of the diisocyanate as well as

the long & short chain diols. Depending on the choice of these building blocks, it is possible to tailor-make new products that present a significantly improved weathering resistance compared with an industry standard in an accelerated Xenon test based on a top-coated wood panel having conventional acrylic primer & intermediate coats. The use of a polycarbonate backbone presents the biggest improvement of the aging resistance. In this case, it is demonstrated that the mechanical & chemical resistance is maintained at the same high level superior to an acrylic industry standard. The use of a photo-initiator is found to be detrimental to aging compared with the same polymer without photo-initiator and cured by electron beam. In the case of a polyester backbone reference, the use of light stabilizer and light absorber do not bring the expected improvement of the aging. This can be attributed to the predominance of the hydrolytic degradation over the photolytic degradation as demonstrated with the use of free cured films submitted to humidity or ultraviolet light. It is shown that the degradation of the coated wood happens prior to the degradation of the coating placed on a neutral substrate. This observation suggests that a modification of the coating barrier properties towards water would happen during the aging process before that the destruction of the coating accounts for the damage.

ACKNOWLEDGEMENTS

The author's wish to thank all the colleagues who were involved at different stages of this study including Business Unit, Technical Service & Development, Engineering, Production, Regulatory Affairs and Intellectual Property. They were all participating with their expertise & commitment to the development of this new exciting technology. Thanks to Jean-Claude Vanovervelt in his role of Scientific Advisor. Special thanks go to those collaborators who realized all the heavy synthesis work and application trials, namely Vincent Renard, Marcus Vandermercken, Jimmy Tereran and Christian Stesman.

REFERENCES

1. K.Tharanikkarasu and B.K.Kim, "Aqueous Dispersions of Polyurethane Ionomers", Prog. Rubber and Plastics Technol. (1997) 13(1), 26-55.
2. K. L. Noble, "Waterborne Polyurethanes", Progress in Organic Coatings (1997) 32, 131-136.
3. M.Moss, "Water-based UV-curable Coatings", Coatings World (1999) 33-37.
4. K.Buysens, M.Tielemans and Th.Randoux, "Radiation Curable Coatings: a Variety of Technology for a Variety of Applications", Pitture e Vernici – European Coatings (2002) 19, 78, 27.
5. M.Tielemans, P.Roose, Philippe De Groote, Jean-Claude Vanovervelt, "Colloidal Stability of Surfactant-free Radiation Curable Polyurethane Dispersions", Progress in Organic Coatings 55 (2006) 128-136.
6. Alex Lubnin & al. "Nanostructured, Nonuniform and Core-Shell Polyurethane Dispersions" Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium (2005), 32nd, 190-206
7. R. Schwalm, "Crosslinking Effect on Mechanical Properties of UV-Curable coatings", Polymer Paint Color Journal (1999) 189, 4421.
8. F.Masson, C.Decker, T.Jaworek, R.Schwalm, "UV-Radiation Curing of Waterbased Urethane-Acrylate Coatings", Progress in Organic Coatings (2000) 39, 115-126.
9. K.Pianoforte, "The Wood Coatings Market", Coatings World (February 2005), 22-26.

10. M. de Meijer & al. "Mechanism of Failure in Exterior Wood Coatings" Proceedings of the International Woodcoating Congress (2002), 3d, 28-30.
11. F.H.Chung, "Unified Theory and Guidelines of Adhesion, Journal of Applied Polymer Science (1991) 42, 1319-1331.
12. G.Genskens, "Degradation & Stabilization of Polymers, Applied Science Publisher, 1997.
13. J.W.Martin, Double Liaison (1996) 479-480, 22-31 "Durabilité des revêtements Organiques : Etat de l'Art ».
14. D.R.Bauer, Journal of Coatings Technology (1994) 66, 835, 57.
15. C.Decker & al. J. Polym. Sci., Polym. Chem. Ed. (1991), 29, 739.
16. B. Yang, "Weathering resistant oligomers for long-term applications", Modern Paint and Coatings (1996), 86(5), 40-42,44,46 .
17. T.E. Cauffman, Modern Paint and Coatings (1995), 85(6), 32-4, 36, 38, 40 "Formulating urethane acrylate coatings to reduce degradation"
18. L.Byoung-Hoo & all. Polymer Degradation and Stability 91 (2006) 1025-1035 "Influence of isocyanate type of acrylated urethane oligomer and of additives on weathering of UV-cured films".
19. M.Tielemans, V.Renard, S.Smeets, S.Piazza, J.C.Vanovervelt, "New Perspectives for Radiation-Curable Polyurethane Dispersions, Double Liaison (2003) Vol. 5, 36-44 and the proceedings from M.Tielemans, V.Renard, S.Smeets, J.P.Bleus, J.C.Vanovervelt, "New Waterborne Radiation-Curable Polyurethanes for Wood & Plastic Materials (2003) Forum de la Connaissance, Paris.
20. D.K. Hillshafer, Angewandte Macromol Chem, 261, 173-188 (1998) "Ortho-phthalic esters for non-foam polyurethanes"
21. G.Reusmann & coll. Verfkroniek, 74, 25-28 (2001) "Polymethacrylate diols, "New building blocks to modify resins for coatings"
22. R.bongiovanni & all. Progress in Organic Coatings 45 (2002) 359-363 "High Performance UV-cured Coatings for Wood Protection".
23. E.R.Miller & al. "Quality Assurance for Exterior Wood Coatings through European & British Standards, Surface Coatings Internat. Coatings J. (2006) 89, 96-99.

BIOGRAPHIES



Michel Tielemans was born in Brussels in 1962. He obtained a Ph.D in organic chemistry from Brussels University in 1988. He joined Procter & Gamble as Product Development Chemist in 1989 and moved the same year to UCB. He has been a Research Scientist in the field of acrylic latexes before becoming a Group Leader. Later, he could extend his expertise of waterborne polymers with the development polyurethane dispersions where he is still active today. His current research projects mainly covers waterborne radiation-curing coatings for wood, plastics, metal. He is the author of several patents and articles in the field. In 2005, the chemical specialty sector of UCB became part of Cytec.



Jean-Pierre Bleus was born in 1949. In 1971, he became Bachelor in chemistry from the University of Liège (Belgium). He joined UCB in 1974 as Research Chemist in the Acrylics & Adhesives department for two years. From 1976 to 1993 he worked in the wood furniture finishing at Reliance who was purchased later on by AKZO. Since 1993, he is working as TS&D Engineer Radcure for UCB, who became Cytec Surface Specialties in 2005.

