UV Stabilisation of Powder Clear Coats

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Summary: Powder coatings are gaining importance in exterior applications such as automotive and architectural finishes. The use of additives in powder coating formulations enhance the durability of the coating by reducing the effects of harmful UV light and providing high temperature stability during processing and curing. Customers` increased demands for better retention of aesthetical and mechanical properties has prompted the development of new additives dedicated to powder coatings.

This paper presents an overview of the performance of light stabilizers used in powder coatings.

Key words: powder clear coats; UV absorber; hindered amine light stabilizers; weathering

1. Introduction

Overall development of the technology is mainly due to so called five E's associated to powder coatings: Excellence of finish, Environmental friendliness, Economics, Energy savings, Ease of application. The latest technology advances in powder coatings stimulate further the growth by allowing outlet in new applications such as automotive clear coats or highly durable architectural finish. Powder clear coats are forward looking for the automotive industry as it is said by Johann Thaler from BMW [1]. Since 1996 these coatings are successfully used in series as clear top coat by this company. This development has been accessible thanks to new binders systems like polyacrylate used in combination with light stabilizers like UV Absorber (UVA) and hindered amine light stabilizers (HALS). Polyacrylate is a binder of choice for transparent finishes with general properties such as high transparency, excellent flow and acceptable durability. Light stabilizers extend the life of such coatings to more than 5 years Florida exposure and meet the demand from the automotive industry [2, 3]. These high performance coatings match the quality of liquid paints and so their use will grow more and more in the automotive industry for car bodies and components like wheel rims. In Europe the highest growth rates in powder coatings segments are quoted for polyacrylate powder coatings over the next five years [4]. The first large scale practical application of powder coating in general industry has been seen with bicycle frame [5].

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Currently the most common powder coatings used for exterior applications in industrial applications and architectural finishes are based on polyester (PES) binder systems. One of the main restraints to the development of these coatings are their limited durability where classical terephthalic acid PES resins are used. However in this area significant improvement have been achieved with the development of so called "super durable" polyesters. Lifetime of these super durable resins have been enhanced by use of appropriate light stabilizers. The aim of this paper is to show the prolonged life of powder clear coats via the use of light stabilizers. Artificial and outdoor weathering demonstrates the combined protective action of different UV absorbers (UVA) and hindered amine light stabilizers (HALS). To have a representative view of the market for powder clear coats (automotive and general exterior applications) four binder systems were chosen: two polyacrylates based on glycidylmethacrylate (GMA) and two based on polyester / triglycidylisocyanurate (PES / TGIC).

Light stabilizers

Coatings used outdoor are exposed to detrimental processes initiated mainly by the UV portion of solar radiation, gaseous pollutants and acid rain. According to the intended end use, service life up to five or even ten years may be required. High performance coatings must be protected by stabilizers in order to withstand a harsh environment during its life time. The best protection for high quality clear coatings is obtained by using a combination of UVA and HALS [6-8]. The filter effect of the UVA protects the substrate mainly against color change and photochemical polymer degradation, which in turn leads to delamination and loss of mechanical properties. HALS prevent surface degradation and protects the coating against loss of gloss and cracking. The four most important UV absorber classes are benzophenone, oxalanilide, benzotriazole and hydroxyphenyl-s-triazine, benzotriazoles are the most widely used for polymers and paints [9]. The mechanism of action of UVA is the absorption of UV-light and its rapid conversion into harmless energy e.g. heat. Absorbance follow the Lambert-Beer Law:

$$E = Abs = \varepsilon \cdot c \cdot d, \text{ where} \quad (1)$$

E = extinction; Abs = absorbance; ε = extinction coefficient [$L \cdot Mol^{-1} \cdot cm^{-1}$]; c = concentration [$Mol \cdot L^{-1}$]; d = (film-, cell) thickness [cm].

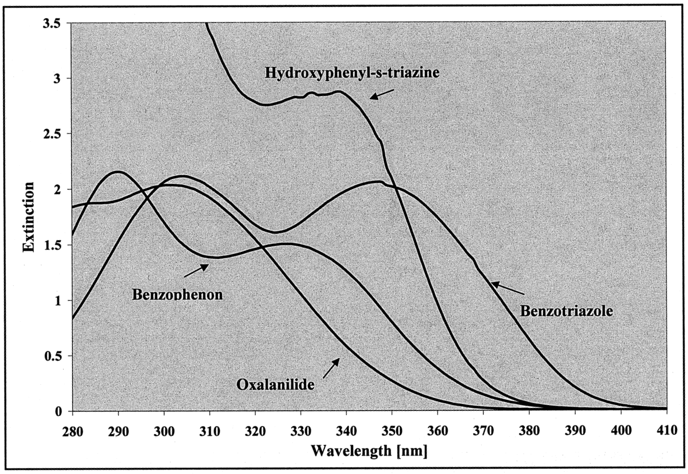

Figure 1: Absorption spectra of different UV absorber classes, c=1.4x10-4 mol/l in chloroform.

The initial extinction of UVA's is directly proportional to the extinction coefficient ε, the concentration c and the film thickness of the clear coating.

The extinction coefficient ε is usually given at the wavelength corresponding to the maximum of absorption of the product. Table 1 shows the ε of each UVA used in this work. The absorption profile of the UVA's plays also an important role. Figure 1 shows the absorption spectra of the UVA's participating in the study.

Table 1: Extinction coefficients ε of different UVA at maximum long wave absorption (λmax), c=1.4x10-4 mol/l in chloroform

UV Absorber	λ_{max} [nm]	ε [$L \cdot Mol^{-1} \cdot cm^{-1}$]
Hydroxyphenyl-s-triazine (UVA1)	339	~21700
Benzotriazole (UVA2)	346	~15600
Benzophenone (UVA3)	327	~10700
Oxalanilide (UVA4)	301	~14500

The strongest absorption in UVB (290-320nm) is achieved with hydroxyphenyl-s-triazine (UVA1), followed by oxalanilide (UVA4), benzotriazole (UVA2) and benzophenone (UVA3). The best coverage in UVA (320-390 nm) is achieved with UVA 2 and UVA 1 whereas UVA 3 and 4 show a relatively low absorption in that part of the spectrum. An other parameter crucial in UV Absorber selection is photo-stability, it is of paramount importance to keep in the film enough active product to ensure proper extinction. From that respect UVA1 and UVA2 have a definitive advantage when it comes to long exposure.

Sterically hindered amines (HALS) are almost exclusively derivatives of 2,2,6,6-tetramethylpiperidine which is responsible for the stabilization effect of these compounds. The "Desinov Cycle" (see figure 2) present a possible action mechanism for HALS. After activation step conversion of >N-R to >NO* (nitroxyl radical) is trapping of radical build within the polymer matrix begin. As the reaction proceeds further with a peroxide radical the nitroxyl radical is re-generated.

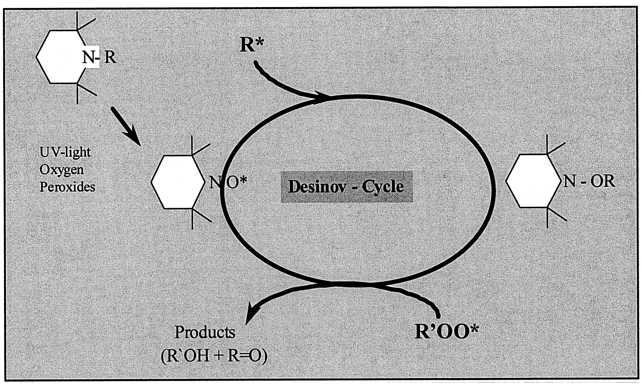

Figure 2: The 'Desinov Cycle'.

The substitution of the nitrogen atom in piperidine derivatives play an important role in HALS efficacy. Experiments carried out in liquid clear coatings [10-11] have shown the effect of the nitrogen substitution on the >NO* formation. These experiments have demonstrated that peroxide radicals were formed right at the start of weathering. Their concentration start to decrease when a sufficient number of nitroxyl radicals is present in the coating. The faster the conversion of >N-R to <NO* the earlier the protection against free radicals start.

Unlike UV absorber, the efficiency of HALS does not depend on coating thickness and radical scavenging take place throughout the film.

2. Experimental

All powder clear coats were mixed in a large kitchen cutter and extruded twice using a Prism 16 mm twin screw extruder, at 80-110°C barrel temperature.

Table 2: Basic formulations for GMA powder clear coat

Components	**GMA 1**	**GMA 2**
Synthacryl VSC 1436 / Additol VXL 1381	96.2	--
Almatex PD 7610 / Dodecanoid acid		94.5
Additol XL 490	0.5	1.5
Benzoin	0.3	--
Worlee Add 902	--	1
UVA	**2**	**2**
HALS	**1**	**1**
Sum	***100***	***100***
Curing	*30' 140°C*	*30' 160°C*

The materials were milled in a Retsch ultracentrifugation mill and sieved through a 125µm sieve.

The clear coats were sprayed onto panels pre-coated with silver metallic aqueous basecoat (30' 130°C) and cured in an electric oven (see table 2, 3). The dry film thickness after cure was approx. 60 mµ.

Table 3: Basic formulations for TGIC powder clear coat

Components	**PES 1 / TGIC**	**PES 2 / TGIC**
Uralac P 5000 / Araldit PT 810 (TGIC)	96.5	_
Crylcoat 2988 / Araldit PT 810 (TGIC)	_	96.5
Resiflow PV 88	1	1
Benzoin	0.5	0.5
UVA	***1***	***1***
HALS	***1***	***1***
Sum	***100***	***100***
Curing	*15' 195°C*	*15' 195°C*

In this work four formulations were used for evaluation of the different type of UVA and HALS. Detailed formulations are provided in table 2 and 3. GMA 1 is a system used for general industrial paints.

GMA 2 is especially suited for high performance automotive coatings. For TGIC system used in the architectural and general industry two types of polyester were chosen: a standard polyester as PES 1 and a super durable polyester as PES 2.

Light stabilizers tested were: hydroxyphenyl triazine (UVA 1), benzotriazole (UVA 2), benzophenone (UVA 3), oxalanilide (UVA 4), HALS 1 and HALS 2. The chemical formulae are shown in figure 3 and 4. All these UVA's and HALS are solid and have at 200°C less than 1% loss of weight, this was determined by TGA (30°C – 300°C, heat rate = 10°C / min). GMA 1 was prepared with all UVA's in combination with HALS 1. GMA 2 was stabilized with UVA 1 and UVA 2 in combination with HALS 2. Both TGIC powder clear coats were tested with UVA 1 and UVA 2 in combination with both HALS .

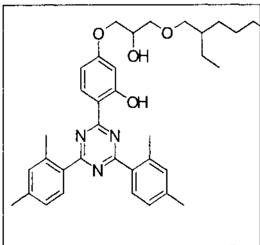	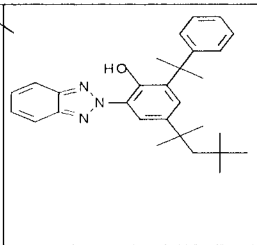	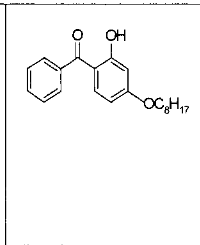	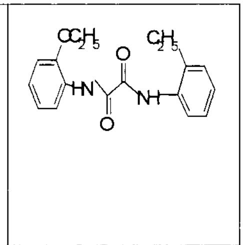
UVA 1 m. pt – 74°C	UVA 2 m. pt – 113°C	UVA 3 m. pt – 48°C	UVA 4 m. pt – 124°C

Figure 3: chemical structure of the different UVA used in this study.

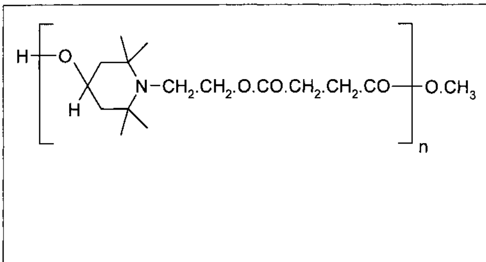	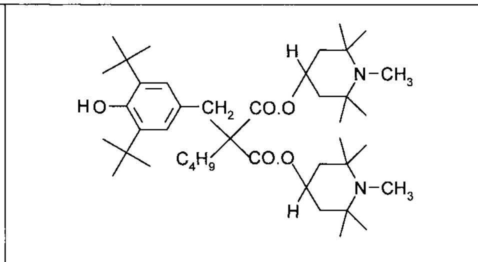
HALS 1 m. pt – 74°C	HALS 2 m. pt – 146°C

Figure 4: chemical structure of the different HALS used in this study.

Bake-over resistance was assessed by measurement of the Yellowness Index (YI), the higher the YI measured is the higher the risk of yellowing of the coating during bake-over.

All powder clear coats were exposed to accelerated and natural weathering. The outdoor exposure was carried out in South Florida (5° / black box, unheated). Accelerated weathering was carried out by UVCON (cycle: 8h light at 70°C; 4 h condensation at 50°C; 0,67 W / m^2 QUV-B radiation at 313 nm). Criteria used to assess coatings performance were: 20° gloss according to DIN 67530, Yellowness Index (YI) according to ASTM D 1925.

3. Results

3.1 GMA powder clear coats

Polyacrylate powder coatings based on GMA combined with carboxylic or anhydride hardeners lead to powder coatings with excellent flow and transparency. GMA 1 cured with an anhydrid hardener is a common powder coating system used for industrial applications. GMA 2 cured with a carboxyl hardener is a standard system targeted to the automotive industry.

Different types of UVA

Lightstabilization with commercial UV absorbers like benzotriazole, benzophenone, oxalanilide (UVA 2; 3; 4) and a newly commercialized hydroxyphenyl triazine (UVA 1) in combination with HALS 1 were tested in a powder clear coat GMA 1. Natural and accelerated weathering results are shown in figure 5-6. In both exposure methods the hydroxyphenyl triazine UV-absorber gave the best performance in term of gloss retention.

Performance gap between the different UVA classes is broader when it comes to colour retention (figure 7). Benzotriazole and hydroxyphenyl triazine show in this test clearly better performance

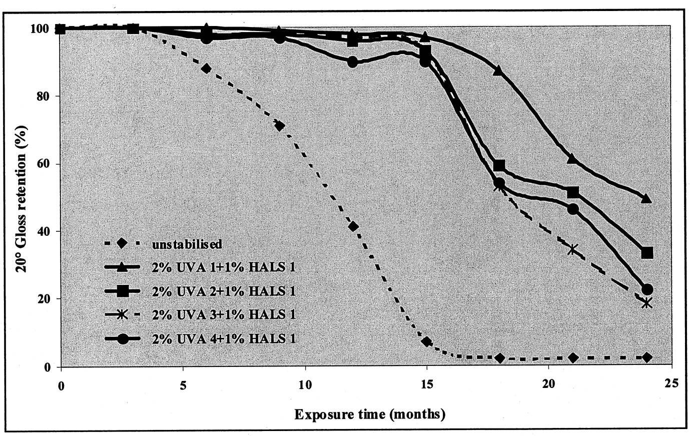

Figure 5: Florida exposure of GMA 1 in combination with different types of UVA.

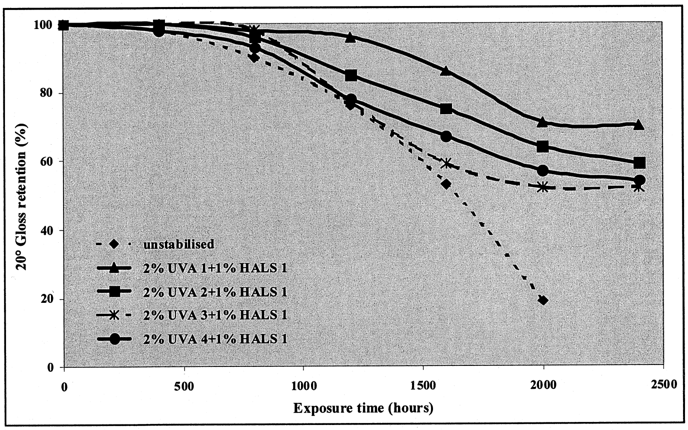

Figure 6: Accelerated weathering (UVCON) of stabilized and unstabilized GMA 1.

Performance gap between the different UVA classes is broader when it comes to colour retention (figure 7). Benzotriazole and hydroxyphenyl triazine show in this test clearly better performance compared to oxanilide and a benzophenone type. Limited differentiation in term of gloss retention and important gaps observed in term of color deviation confirm the contribution of HALS toward stabilization of coating surface whereas the variable part (UVA) has a major impact on color stabilization.

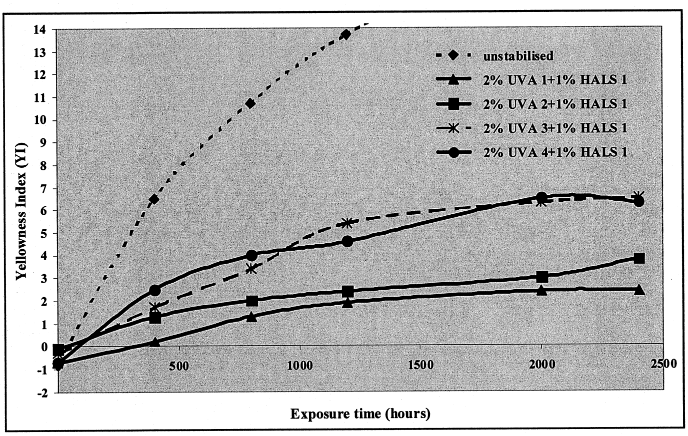

Figure 7: Color retention (UVCON) of stabilized and non-stabilized GMA 1.

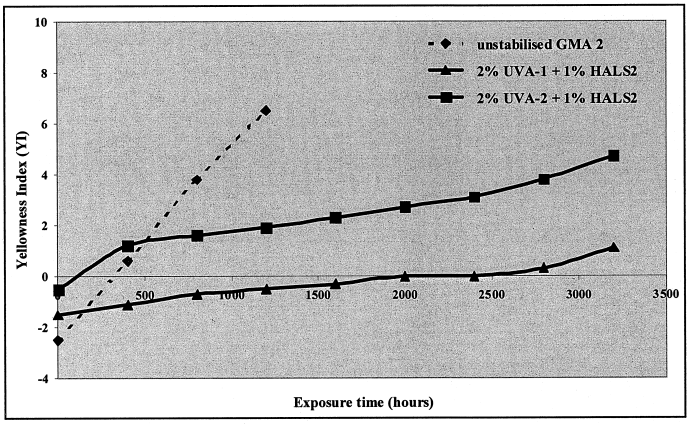

Figure 8: Color retention (UVCON) of stabilized and non-stabilized GMA 2.

In GMA 2 HALS 1 could not be incorporated due to incompatibility with the binder. The lowest influence on initial color and the minimum YI development was achieved through the use of UVA 1 (figure 8). In this case the strong extinction of UVA 1 in UVB and slightly inferior absorbance in long UVA wavelength compared to UVA 2 is an advantage. A consequence is a lower initial color versus UVA 2 and better efficacy to filter the most damaging part of UV spectrum. GMA 1 and 2 without additives per-form both at relatively low level, worthwhile to mention that improvements reached by addition of light stabilizers may vary considerably from one binder system to the other as illustrated in figure 9.

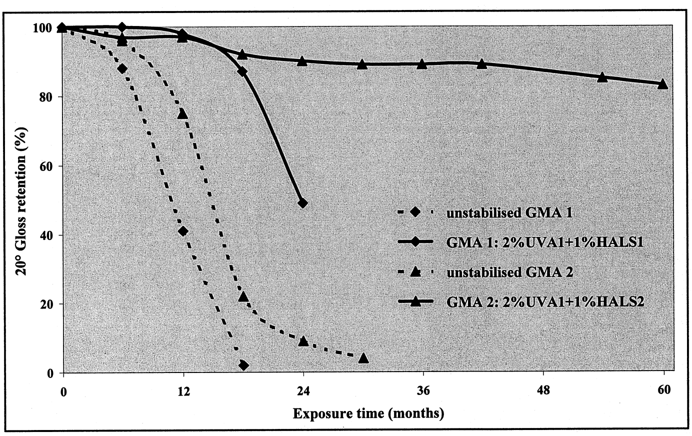

Figure 9: Comparison between GMA 1 and GMA 2 after Florida exposure.

Bake-over resistance

Figure 10 shows a comparison of the Yellowness Index between normal cured and baked-over powder clear coats of GMA 2 applied over silver metallic aqueous basecoat. In this system the contribution of UVA 1 to the initial YI upon normal cure is minimum compared to UVA 2 .

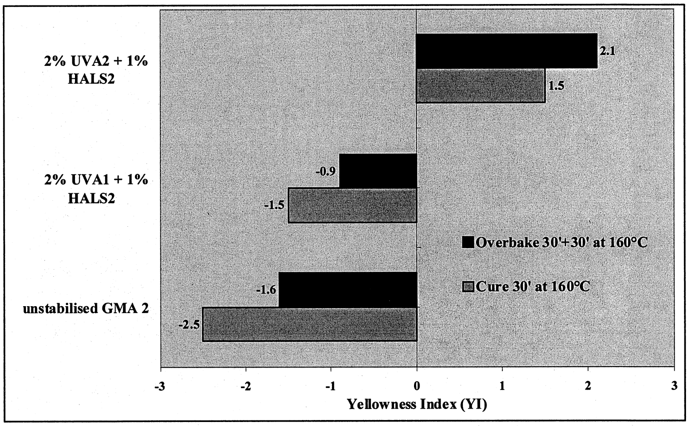

Figure 10: Influence of light stabilizer on thermal stability of GMA 2 powder clear coat upon silver metallic basecoat.

It is a definitive advantage for this high performance coating when applied over light colored basecoat. This is due to the fact that the triazine UVA 1 is slightly blue shifted in comparison to benzotriazole UVA 2. The color deviation in case of bake-over is reduced as HALS 2 contain a phenolic anti-oxidant moiety and prevents yellowing by auto-oxidation.

3.2 TGIC powder clear coats

TGIC powder coatings are still popular in architectural and general industrial paints used outdoor. In Europe these systems are labeled with 'T' (toxic) since 1998. There are several alternatives that can possibly replace TGIC [12]. TGIC and alternatives react with standard polyester resins (PES 1) based on terephthalic acid. Further development of these polyesters led to super durable polyesters (PES 2) based on Isophthalic acid with better durability but weaker mechanical properties [13].

Different types of HALS and UVA

Table 4: Florida exposure of PES 1 in combination with different type of HALS and UVA

Stabilizer	20° Gloss after ... Months		
	0	12	21
unstabilised PES 1	99	46	
1% UVA 1	100	75	15
1% UVA 1 + 1% HALS 1	100	79	22
1% UVA 1 + 1% HALS 2	100	79	20
1% UVA 2	100	65	5
1% UVA 2 + 1% HALS 1	98	71	11
1% UVA 2 + 1% HALS 2	100	69	8

In both polyester systems PES 1 and PES 2 the two types of HALS were combined with UVA 1 and UVA 2 to assess the effect of different stabilizers on weathering.

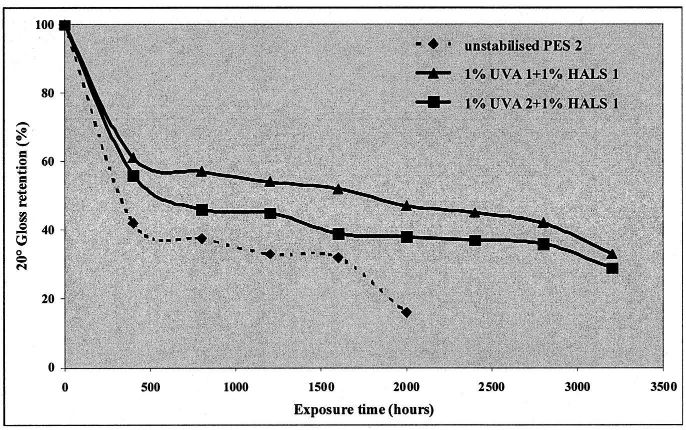

Figure 11: Accelerated weathering (UVCON) of stabilized and non-stabilized.

With the standard polyester system (PES 1) limited differentiation was seen in accelerated weathering between the different systems. Outdoor exposure data begins to show the effects of stabilization as demonstrated in table 4. UVA 1 show with and without combination of HALS better performance than UVA 2 (see table 4). However it is clear that limited improvement can be achieved through the use of additives in standard PES resins.

In the case of super durable PES resins all performances are clearly improved and UVA 1 outperform UVA 2 again (figure 11-12).

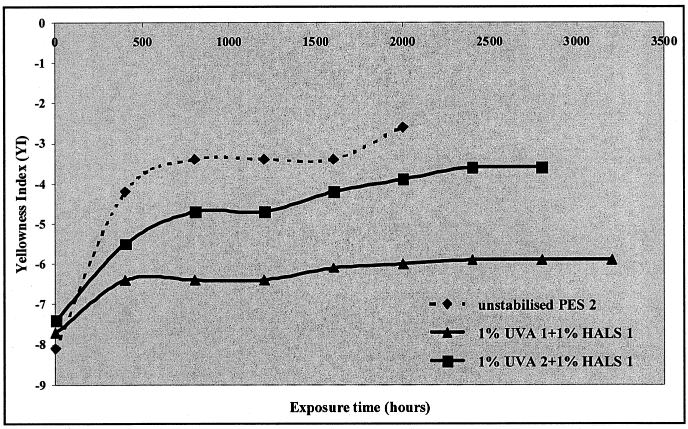

Figure 12: Color retention (UVCON) of stabilized and non-stabilized PES 2.

In addition the comparison between stabilized and un-stabilized coatings is particularly advantageous by the inclusion of additives (figure 13).

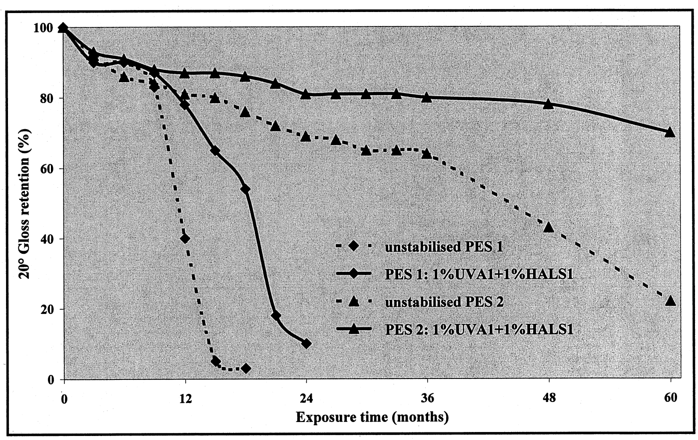

Figure 13: Comparison between PES 1 and PES 2 after Florida exposure.

4. Conclusion

The efficiency of light stabilizers in acrylates and super durable PES clear coat is confirmed in both artificial and outdoor exposure tests.

With the UV-absorber types the hydroxyphenyl triazine (UVA1) exhibits overall the best performance in term of gloss and color retention. Because of its ease of incorporation (low melting point), its slight contribution to the initial color and its great color retention performance this UV Absorber is dedicated to high quality powder coatings.

Additives have a valuable contribution provided that they are used in high performance binders!

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