Macromol. Symp. ***187***, *835–844 (2002)*

Stabilizers in Automotive Coatings under Acid Attack

Ulrich Schulz, Kirsten Jansen*, Adalbert Braig***

*Federal Institute for Materials Research and Testing, D 12200 Berlin, Germany

**CIBA SC, CH 4002 Basel, Switzerland

Summary: To examine the action of acid atmospheric precipitation on the light stabilisers in automotive coatings two common clearcoat types (TSA and 2K-PU) blended with commercially available HALS and UVA were subjected to artificial weathering (Acid Dew and Fog test and Acid-free weathering test) and natural weathering outdoors in Jacksonville, FL. Tracing gloss and haze during weathering the test results showed that the influence of acid stress on the long-term performance of the clearcoats depended on the kind of the stabilisation system.

Keywords: coatings; ageing; stabilisation; HALS; gloss; acid resistance

Introduction

Today's automotive coatings are expected to have got long-term weathering performance even when the cars are transported, stored or used in harsh environment with frequent occurrence of acid atmospheric precipitation. There are observations made with clearcoat / basecoat paint systems that surface areas where droplets of acid depositions were present during weathering suffer a faster degradation by UV radiation [1-3]. The reasons for the higher susceptibility of acid attacked surface parts to degradation by UV can be different. Firstly, higher UV sensitive species can be formed as consequence of a chemical reaction of acid with the resin. Secondly, acid deposition can introduce impurities in the coating material as so-called chromophores being able to absorb UV well and transmit the photon energy to the macromolecules easily. Thirdly, light stabilizers like hindered amine light stabilizers (HALS) and ultraviolet light absorbers (UVA), intended to protect the coating system against photo oxidation, can be attacked by acid leading to the formation of non-functioning or water-soluble derivatives. As

© WILEY-VCH Verlag GmbH, 69469 Weinheim, 2002 CCC 1022-1360/00/$ 17.50+.50/0

consequence, the acid attacked surface parts may have lost its shelter against UV radiation. Our work was devoted to the last effect. There is little information about how long the function of light stabilizers is sustained in acid-stressed environment. Usual acid ingredients of atmospheric precipitation are suggested to disable the so-called "parent HALS" to be oxidized to nitroxyl radical necessary to start the radical scavenging mechanism.[4-5] But there is not any reliable information about the progress of this reaction in the field in dependence of the type of HALS and the exposure conditions. Today's most favoured test for assessing the coating behaviour in acid-stressed environment is a 14 weeks lasting outdoor weathering test in Jacksonville, FL. This location is of particular interest for the car manufacturers because it is one of the main ports of the U.S.A. for imported cars and known for frequent occurrence of acid rain and dew generating a typical type of surface damage. Visible acid etch defects can be found immediately after the acid attacks on clearcoats using resins with relatively bad acid resistance. But it is questionable whether acid attacks to the light stabilizers manifest in a noticeable contribution to the visible coating damage caused outdoors in Jacksonville during 14 weeks. It was found in previous examinations that clearcoats using highly acid resistant resins do not experience any visible damage after 14 weeks outdoors in Jacksonville.[6] But the clearcoats may experience an invisible acid-caused damage to the light stabilizers which can lead to catastrophic failure caused by photo oxidation in further years of service. Assessing the influence of acid damaged light stabilizers on the clearcoat lifetime reliably requires to prolong the outdoor exposure test to several years. Such long exposure periods would slow down the introduction of new stabilizer formulations unacceptably. A successful use of appropriate artificial weathering tests to assess the behaviour of light stabilizers in acid-stressed clearcoats is not known till now. Therefore, aim of our examinations was finding answers to following two questions:

1. Is the influence of acid stress on the long-term performance of clearcoats dependent on the kind of the light stabilisers significantly and can such a relationship be assessed by means of an artificial weathering test, like the "Acid Dew and Fog test" (ADF test)?
2. Is a natural short test, like the 14 weeks outdoor exposure in Jacksonville, FL, able to differ the clearcoat samples in relation to the behaviour of the light stabilizers against acid attacks?

Experimental

Two different types of clearcoat were used in this study: a thermosetting acrylic resin (TSA) and a two-part polyurethane (2K-PU) as described in detail in former publication [7]. The coating systems were applied on aluminium panels and cured under production line conditions.

Table 1. Identification of the samples (HPT: Hydroxyphenyltriazine, BTZ: Benzotriazole)

TSA		2K-PU	
Sample	**Stabilization system**	**Sample**	**Stabilization system**
#0	unstabilized	#0	unstabilized
#1	1% HALS 1 (pK-b: 4,4 to 5,5)	#1	1% HALS 1 (pK-b: 4,4 to 5,5)
#2	2% HALS 1	#2	2% HALS 1
#3	1% HALS 2 (pK-b: ca. 10)	#3	1% HALS 3 (pK-b: ca. 12)
#4	2% HALS 2	#4	2% HALS 3
#5	2,5% HPT 1 (UVA 1)	#5	2,5% HPT1 (UVA 1)
#6	2,5% HPT 2 (UVA 2)	#6	1,5% HPT 4 (UVA 4)
#7	2,5% BTZ (UVA 3)	#7	2,5% BTZ (UVA 3)
#8	2,5% HPT 1 + 1% HALS 1	#8	2,5% HPT 1 + 1% HALS 1
#9	2,5% BTZ + 1% HALS 2	#9	1,5% HPT 4 + 1% HALS 1
		#10	2,5% BTZ + 1% HALS 1
		#11	2,5% BTZ + 1% HALS 3

As characterised in table 1 both clearcoat types were blended with commercially available HALS and UVA which were used apart in different concentration (samples 1 to 7) as well as combined with each other (samples 8 to 11). Samples without light stabilizers (samples 1) were examined for comparison. The samples were exposed to artificial weathering (Acid Dew and Fog-Test, ADF-Test in short, and Acid-free weathering test) using a weathering chamber “GLOBAL UV Test” and natural weathering outdoors in Jacksonville, FL. The changes in gloss and haze that are ones oft the most suitable optical properties to detect weathering-caused deterioration on the clearcoat surface were traced during weathering.

The cycle used for the ADF test (see table 2) was characterised by continues UV radiation and changing climatic conditions. The essential feature what the ADF cycle distinguishes from the cycles of the currently used artificial weathering tests is the spraying of an acidic deposition on the sample surface (which is a diluted mixture of sulphuric, nitric and hydrochloric acids) as the first step of the cycle. This spraying simulated the action of acid atmospheric precipitation occurring in industrial urban locations like Jacksonville.

Table 2. The 24 h weathering cycle of the ADF test

Step	Duration	Climatic conditions	
1	short		spraying of the acidic deposition
2	14 hours	dry	9 h at 35°C, 30% RH + 6 h at 60°C, 5% RH with UV
3	4 hours	rain	rinsing with demin. Water, at 35°C with UV
4	6 hours	dry	at 60°C, 5% RH with UV

The cycle of the Acid-free weathering test differed from the ADF cycle only in that the acid wetting at the start was dropped.

Results of artificial weathering

In order to make differences between the stabilisation systems in the behaviour against acid attack by artificial weathering visible it was necessary, first at all, to look for the right balance of the stresses by acid and UV radiation during the test. For this reason two variants of the ADF test differing in the acidity of the solutions (pH 1,5 and pH 2,5 respectively) for the acid wetting of the samples and the exposure period (7 and 70 days respectively) were performed. The specimens which were exposed to the test variant with pH 2,5 over 70 days experienced the tenfold higher UV radiant exposure than the other ones which were subjected to the test variant with pH 1,5 over 7 days. But the specimens experienced the same acid stress expressed by the product of concentration and action time of the acid in both test variants. The haze increase of the TSA samples after the tests was presented in dependence on the kind of the stabilization system in Figure 1. The samples did not show any differences in degradation after the short test variant using the higher acidic solution. The UV radiant exposure proved to be too small for revealing a possible acid-caused damage of the light stabilizers in the weathering results. This test variant was only able to assess the acid resistance of the resin which was the same in all of the 10 samples.

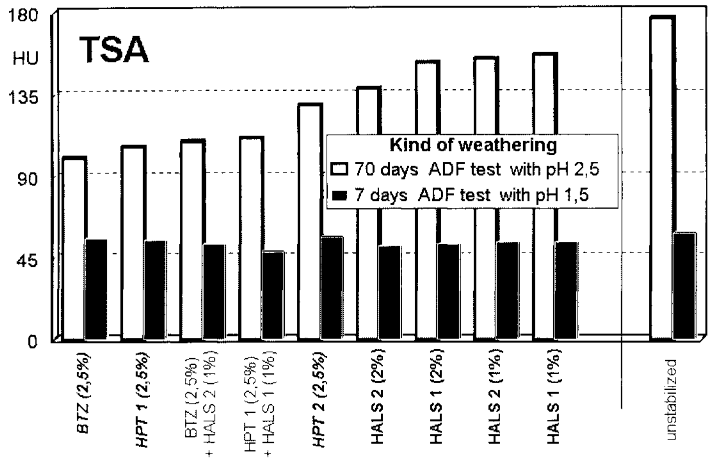

Figure 1. Haze increase (in Haze units HU) after differently long ADF test variants with equal acid stress in dependence of the kind of stabilization

The long test variant using the less acidic solution proved to be a closer approximation to the practice in terms of the ratio of the stresses by acid and UV. It caused higher ageing effects as well as a clear differentiation of the clearcoat samples suggesting that the examined stabilization systems experienced differently strong acid-caused damage which revealed after applying an ample UV radiant exposure only. Therefore, this test variant was used for our further examinations predominantly. The gloss loss of the PU-clearcoat samples was chosen for presentation of the results of the ADF test (variant with pH 2,5) in comparison to that of the Acid-free weathering test. As can be seen in figure 2 the curves for the test without acid stress in the bottom chart, characterising commonly used weathering conditions, revealed a big difference in the long-term performance between the samples containing UV absorbers or not. Finding differences in the efficiency between the UVA containing stabilisation systems each other required a very long exposure period. The curves for the ADF test in the top chart showed that the presence of acid on the surface during weathering accelerated the degradation of the coating significantly.

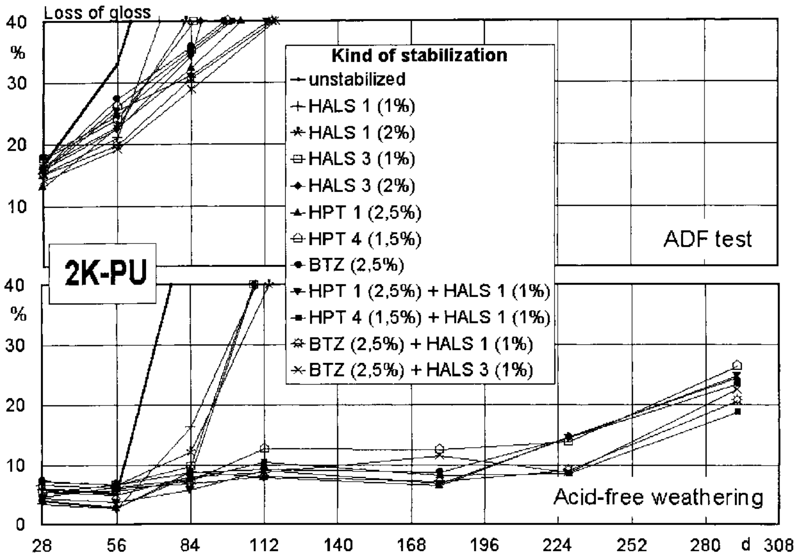

Figure 2. Gloss loss of the PU clearcoat samples upon exposure period

The acid resistance of the resin seemed to be to weak to reveal differences in the stabilizer efficiency under acid stress in the same extent as under acid-free weathering conditions. The state of the samples after 84 days of exposure was chosen to work out differences in the efficiency between the light stabilizers under acid attack. The results of the Acid-free weathering and the ADF-test as well as the differences between the two tests were presented in figure 3. Since the samples differed in the kind of stabilisation only, variations in the extent of the differences between the results of the two tests could only be caused by differences in the acid resistance of the light stabilizers. The samples were arranged in increasing order of the black balks, this means in increasing order of the susceptibility of the stabilisation systems to degradation by acid attack. In the case of the unstabilized sample (most right) the black balk characterised the acid resistance of the resin. Concerning the stabilized samples this would mean that the stabilisation system "BTZ (2,5%) + HALS 3 (1%)" (most left), showing the black balk in about the same extent, did not seem to be influenced by acid. In case of the second sample from the right, blended with 1% HALS 1 only, the gloss loss could be derived from both the acid resistance of the resin and that of the stabiliser in about the same extent. According to general experiences the HALS, known as reactive chemicals, showed the worst acid resistance. The samples using different types and different concentrations of HALS behaved as expected.

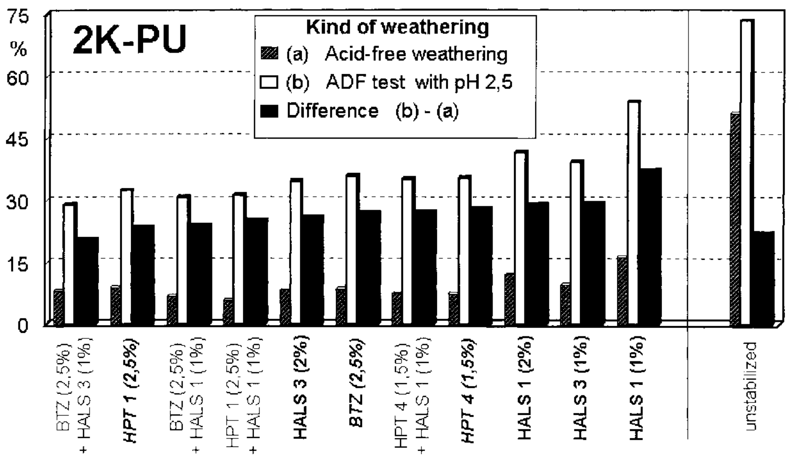

Figure 3. Gloss loss after 84 days of weathering with and without acid stress

This means, the higher the basicity and the lower the concentration the worse the acid resistance. The UVA, known as physically acting light protectors, proved to be more stabile against chemical influences. The samples containing combinations of HALS and UVA behaved better as well as worse than that containing the UA absorber singly. The influence of acid stress also revealed in different rankings in terms of the long-term performance of the samples subjected to the ADF test and the Acid-free weathering respectively.

As can be seen in figure 4 the stabilization system "HPT4 (1,5%) + HALS 1 (1%)" proved to be the worst of the light stabilizer combinations under acid stress but the best one under acid-free conditions. The ADF test results in dependence of the kind of resin were compared in figure 5. As expected the 2K-PU showed the better acid resistance. The light stabilizers behaved equivalently in both resins.

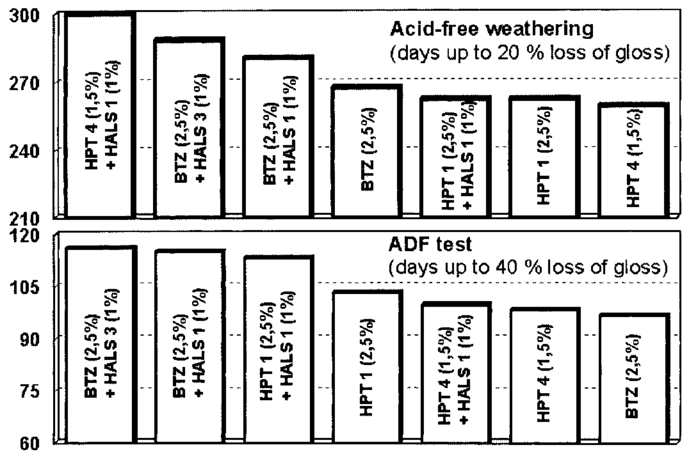

Figure 4. Rankings in long-term performance of the UVA containing PU clearcoat samples subjected to weathering with and without acid stress (ranked from the best to the worst)

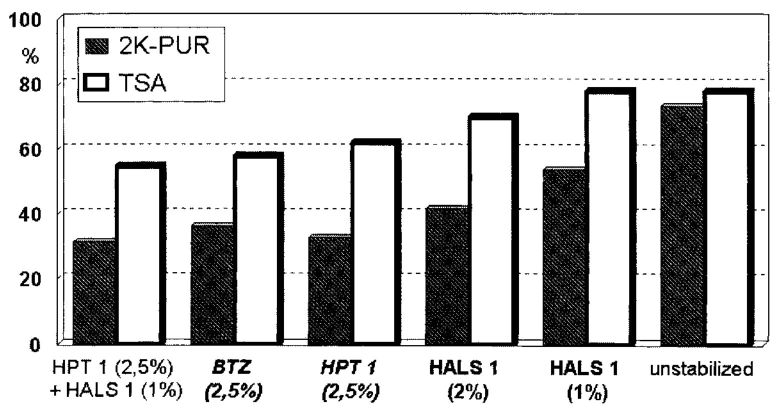

Figure 5. Gloss loss after 84 days of ADF test (pH 2,5) in dependence of the resin

Results of the natural weathering

Gloss loss and haze increase of the PU clearcoat samples after the 14 weeks lasting outdoor weathering in Jacksonville, FL were presented in the figure 6. Only the unstabilized sample differed from the other ones. Significant differences in the behaviour of the stabilised samples could be found neither for the PU nor for the TSA clears. This finding is according to the results of the Acid Dew and Fog test as can be seen in Figure 7.

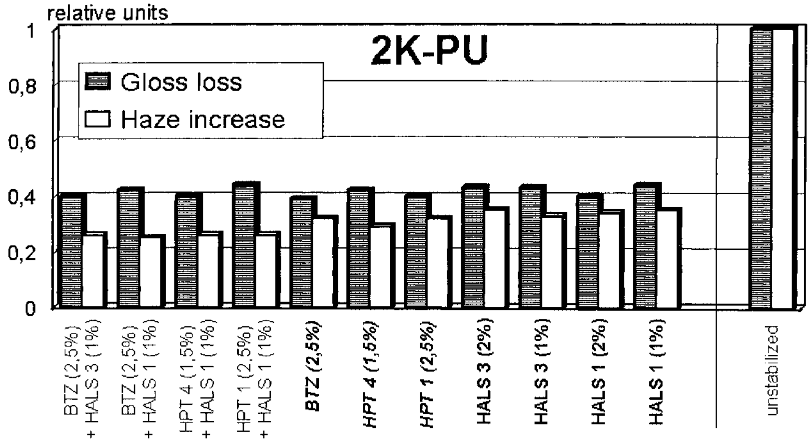

Figure 6. Changes in Gloss and Haze after 14 summer weeks in Jacksonville, FL

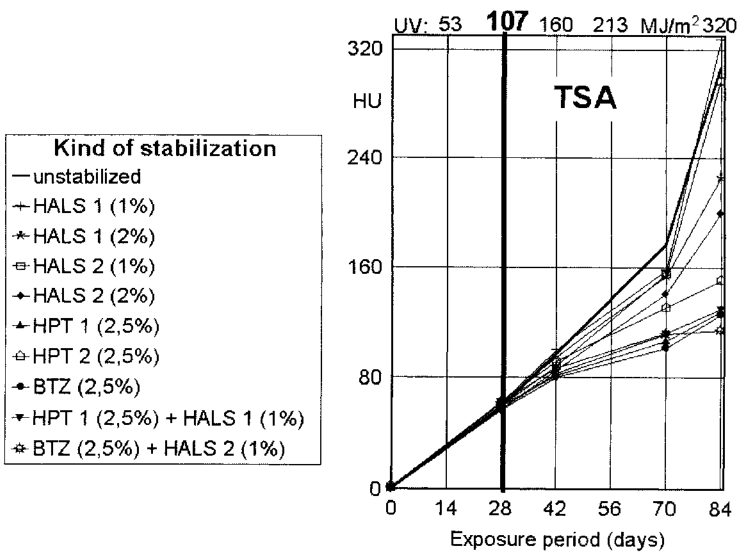

Figure 7. Haze of the TSA samples upon exposure period

The UV radiant exposure of about 107 MJ/m^2 applied naturally during the 14 summer weeks in Florida is marked by the vertically drown thick line in the presentation of the Haze of the TSA samples in the course of the ADF test. The ADF test was also not able to differentiate the samples after applying the equivalent UV radiant exposure (after 28 weathering days).

Conclusions

1. The influence of acid stress on the long-term performance of automotive clearcoats depends on the kind of the stabilisation system. But the lifetime of the commonly used clearcoats in acid-stressed environment, limited by the acid resistance of the resins predominantly, is mostly too short to reveal equivalent differences in the stabilizer efficiency as under acid-free environmental conditions.2. The Acid Dew and Fog test (ADF test) using a solution of pH 2,5 for simulating of the action of acid atmospheric precipitation and performed over 70 days at least proved to be able to determine the influence of acid attack on the efficiency of light stabilisers in automotive clearcoats. The pH 2,5 seems to be the optimal acidity. Higher acidity results in worse selectivity. Lower acidity requires unacceptable prolongation of the test duration.

3. The commonly used 14 weeks outdoor exposure in Jacksonville , FL proved to be too short to make differences in the resistance of light stabilizers against acid attacks visible. This means surviving 14 weeks outdoors in Jacksonville undamaged is no evidence for long-term weathering performance.

References

[1] U. Schulz, P. Trubiroha, U. Schernau, H. Baumgart, *Progress in Organic Coatings* **2000**, *40*, 151

[2] U.Schulz, P. Trubiroha, T. Engbert, T. Klimmasch, *Eropean Coating Journal,* **1999**, *1-2*, 18

[3] U.Schulz, V. Wachtedorf, T. Klimmasch, P. Alers, *Progress in Organic Coatings* **2001**, *42*, 38

[4] .Gugumus, in: *Handbook of Polymer Degradation*, 2^{nd} ed., H. Hamid, Ed., M.Decker, Inc., New York 2001, p.68

[5] A.V. Kucherov, J. L. Gerlock, R. R. Matheson, *Polymer Degradation and Stability*, **2000**, *69*, 1

[6] P. Trubiroha, U. Schulz, V. Wachtendorf, K.Gaszner, *DFO-Technologie-Tage*, **2002**, *50*, 55

[7] V. Dudler, T. Bolle, G. Rytz, *Polymer Degradation and Stability*, **1998**, *60*, 351