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# Residual stability of polyurethane automotive coatings measured by chemiluminescence and equivalence of Xenotest and Solisi ageing tests

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**Abstract**

Degradation of poly(ester-urethanes) and poly(acrylic-urethanes), as a base for automotive paintings in interior applications, has been studied by chemiluminescence. The samples were clearcoat and black-pigmented paints, unstabilised and stabilized with HALS Tinuvin 292 and UV absorber Tinuvin 1130, exposed to various doses of artificial weathering in Xenotest and Solisi equipment. Chemiluminescence has appeared a powerful tool to evaluate the oxidation stability of various polyurethane systems. From the dependences of oxidation onset temperature on heating rate, the kinetic parameters describing the dependence of induction periods on temperature have been obtained. The kinetic parameters enabled us to calculate the length of the induction period for a chosen temperature, the protection factors of various additives and the residual stability of the polymer after an artificial ageing stress. It has been found that the loss of residual stability with ageing dose obeys a first-order relationship. Equivalence between the two methods of artificial ageing has been determined. The results indicate that the equivalence depends on the polymer composition. The procedure presented here can also be applied for the determination of equivalence of accelerated and field tests so contributing to establishing a reliable correlation between them.


*Keywords:* Chemiluminescence; Polyurethane; Accelerated ageing; Thermo-oxidation; Residual stability; Automotive coating

## 1. Introduction

The combination of oxygen as the reactant and heat as the energy source is a major factor in material degradation. Considering polyurethanes, the effect of light on the rate of degradation should also be taken into account, since they are susceptible to photo-degradation due to a high content of carbonyl groups [1]. The degradation leads to changes in the molecular structure and, consequently, to changes in the chemical and physical properties of materials. In most cases, the oxidation processes occurring in the condensed phase exhibit an induction period which is the stage preceding the main process, where apparently no chemical reaction takes place. The induction period of oxidation is determined as the time of a sudden increase in the oxidation rate [2]. At the end of the induction period, there is often a sudden change of material characteristics, so the length of the induction period is frequently considered to be a measure of material stability. The induction periods, which are often used to compare

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polymer stabilities under given experimental conditions, play an important role in the prediction of long-term durability and service life. Two modes of oxidative induction tests are common; the oxidation induction time (OIT) and the oxidation onset temperature (OOT) [3]. In the case of OIT, the sample is kept at a preset constant temperature and the time of sudden change of measured signal is detected. The OOT is determined as the onset temperature of auto-oxidative reaction while the temperature is raised at a preset heating rate.

In the oxidation of polymers, formation of peroxy radicals mostly takes place during the induction period. According to Russel's mechanism [4], the recombination of secondary peroxy radicals leads to the formation of singlet oxygen and the excited triplet state of carbonyl groups in the polymer chain. Transfer of these excited species to their ground state causes very weak light emission in the visible region:

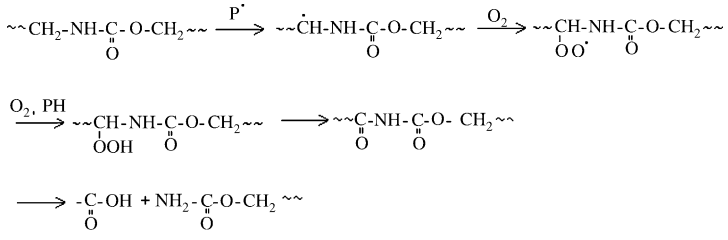
$$2R_1R_2CHOO^{\bullet} \rightarrow R_1R_2CHOH + {}^1O_2 + R_1R_2(C{=}O)* \sim\sim\sim R_1R_2CO + h\nu$$

Chemiluminescence (CL) was first reported by Ashby [5] in 1961, but then devices were too immature to obtain an adequate signal. Nowadays, photomultipliers and slow-scan charge-coupled devices are available, making measurements easier and taking advantages of the CL method's high sensitivity. The rate of formation of peroxy radicals during the induction period is expected to be equal to the rate of their termination by recombination, the CL signal initially being low. At the end of the induction period, the autoacceleration of the oxidation increases the radical concentration and a typical increase of the light emission is observed. Thus, the CL runs can be used to determine the lengths of oxidation induction periods for various materials.

The degradation of polyurethanes has been described by many authors. Objects of their studies were thermoplastics [6–8], foams [9,10], elastomers [11–13], aquatic dispersions [14,15] and coatings. Studies of PUR coatings for exterior applications use techniques like IR spectroscopy [16–18], NMR spectroscopy [17], thermal analysis [17,19,20] and electron microscopy (SEM) [21,22]. Crucial factors for the degradation of coatings for interior application are temperature and UV radiation. The influence of humidity is not as important as it is for exterior coatings. Kinetics of photo-oxidation of PUR coatings were studied by Mielewski et al. [23,24].

Automotive interior coatings are mostly two-component polyurethanes, the polyol component being commonly based on polyester and polyacrylic resins. Particularly soft coatings usually have a soft, leather-like feel and provide surfaces with improved haptic, acoustical and optical properties. Wilhelm and Gardette [25] suggested the mechanism of photo-degradation for polyester-based polyurethanes. It was shown that, upon irradiation at 320 nm, the degradation is brought about only by an induced oxidation of the urethane group (Scheme 1). The polyester segments were shown to be relatively photostable, not contributing to the CL signal. The primarily low photo-initiation rate for polyester coatings was found to increase with exposure time, suggesting that these coatings undergo autocatalytic photo-oxidation [23]. There are two different opinions about polyacrylic-based polyurethanes. According to Mielewski et al. [23], degradation can occur in dependence on the acrylic segments in an autocatalytic way – the initial photo-initiation rate is low, the concentration of chromophores increases during exposure. Dudler and Bolle [26] could not observe a strictly defined induction period, which led them to the conclusion that the degradation of studied coatings does not occur through an autocatalytic mechanism. They tried to analyze the photo-degradation of polyurethane coatings by means of chemiluminescence. It has been shown that the method is suitable for the study of polyurethane degradation; they asserted the potential of this method for the development of a rapid screening test. In general, when comparing the CL-temperature runs of polyurethanes with runs of other materials [27], polyurethanes may be included amongst the strongly luminescent polymers.

In this work, the degradation of poly(ester-urethanes) (EST) and poly(acrylic-urethanes) (ACR), as a base for automotive paintings in interior applications, was studied by chemiluminescence. The samples concerned are clearcoat and black-pigmented paints, unstabilised and stabilized with the most common radical scavenger (HALS) Tinuvin 292 and UV absorber (UVA) Tinuvin 1130, exposed to various doses of artificial weathering.



Scheme 1. Oxidation of polyurethane.