Progress in Organic Coatings 66 (2009) 281–290

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Use of analytical techniques to reveal the influence of chemical structure of clearcoat on its biological degradation caused by bird-droppings

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ARTICLE INFO

Article history:
Received 3 July 2009
Accepted 4 August 2009

Keywords:
Bird-droppings
Clearcoat
FTIR spectroscopy
Hydrolytic reactions

ABSTRACT

There are various biological materials which may repetitively deposit on a painted automotive body during its service life, causing possible local defects. This study is an attempt to reveal the mechanism of degradation caused by bird-droppings and to compare the performance of clearcoats having various resin/hardener ratios. Two different testing methods varying in aging conditions, of the effect of natural bird-droppings, were applied to two types of clearcoats. Variations in chemical structure were characterized by the aid of FTIR spectroscopy and DMTA analysis. Also, in order to establish an experimentally viable procedure to assess such an effect, synthetic countertype of bird-droppings (pancreatin) was used to simulate this natural phenomenon.

The results revealed that a digestive enzyme (lipase) present in bird-droppings, can induce the hydrolysis reaction of coating polymer leading to a locally distributed etched surface. It was also found that the clearcoat containing higher ratios of melamine cross-linker had poorer performance against bird-droppings in spite of having a greater cross-linking density.

1. Introduction

Most studies in the field of automotive coatings show that the main properties envisaged are attributed to their appearance and aesthetic aspects as well as their protective behavior against environmental factors during the service life. These factors can be categorized as mechanical and chemical ones. The former (e.g. mar, scratch and stone chipping) are those which may only cause mechanical deformation. Chemical factors (e.g. sunlight, humidity, acid rain and biological substances), however, are those that affect the chemical structure of the coating, resulting in variations of surface quality such as appearance as well as other physico-chemical characteristics.

The reasonably appropriate properties such as high hardness, modulus, high glass transition temperature and excellent transparency of acrylic melamine systems have lead to the considerable usage of this resin combination to be the dominant coating system in automotive industries [1]. The monomer types of acrylic resin, the functional groups of melamine cross-linker and the acrylic/melamine ratio, are the main factors which affect the curing (and inevitably the performance) in the resultant coating. However, due to the presence of esteric and etheric linkages in the structure of these resins, the occurrence of hydrolytic reaction seems probable, leading to inferior chemical and weathering resistance [1].

Although, the influence of sunlight, humidity and acid rain on automotive coatings, especially on clearcoat has been studied thoroughly [2–9], the effect of biological materials has not been dealt with in more details [10]. In this regard, an automotive coating is repeatedly exposed to different biological materials such as bird-droppings, tree gums and insect bodies. Therefore, the investigation of the influence of such materials and the coating degradation mechanism seems essential. Stevani et al. [10] studied the influence of dragonfly eggs, a native insect of north and south America, on an acrylic melamine automotive clearcoat. They found that hydrogen peroxide released during hardening of eggs, oxidizes the cysteine and cystine residues present in the egg protein, leading to the formation of sulfinic and sulfonic acids.

In our previous work [11], we studied the effect of bird-dropping on various aspects of an automotive clearcoat including physical, mechanical and aesthetic properties. In this study, we try to reveal the effect of bird-droppings on the chemistry behind this degradation for two types of acrylic melamine clear coats differing in melamine ratio. To develop a new method for evaluation of the coating against natural bird-droppings, pancreatin was also used to simulate the effect of this biological compound. FTIR spectroscopy was conducted to discuss the degradation of the coating as a result of the biologically induced hydrolysis reaction occurring in aging experiments.

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doi:10.1016/j.porgcoat.2009.08.003

2. Experimental

2.1. Coating preparation

The coatings used in this study constitutes a multi-layer automotive system applied on steel panels which had been previously phosphated in a three cationic phosphate bath. Then, an epoxy-amine electro deposition (ED) coating was applied and cured at 180 °C for 20 min, followed by applying a polyester melamine primer cured at 140 °C for 20 min. After that a black basecoat layer was applied, followed by application of a clearcoat layer through a wet-on-wet method. Two different partially methylated acrylic/melamine clearcoats (C1 and C2) were utilized differing in acrylic: melamine ratio being 70:30 and 80:20, respectively. The curing process of basecoat/clearcoat was done simultaneously at 140 °C for 20 min.

2.2. Biological materials

Two biological substances were employed; i.e. natural bird-droppings and its synthetic equivalent, pancreatin. The natural bird-droppings were collected from a sparrow and the synthetic one was purchased from MERCK and used as received. A slurry of both bird-droppings and pancreatin were prepared. Their pHs were 6.3 and 6.25, respectively.

2.3. Aging of clearcoats

As the biological materials affect the coating both in aged state (exposed to environment) and in freshly applied state, the aging conditions used to study the effect of these materials included a pre-aging and post-aging as follows.

2.3.1. Pre-aging

Pre-aging means that before the exposure of clearcoat to biological attack a four-stage aging process is performed. This multi-stage aging was conducted according to PSA D27 5415 standard. The details of stages have been explained in our previous paper [11]. In summary, these stages are schematically presented in Fig. 1.

As shown in Fig. 1, before depositing of biological substances, a series of samples were set aside to assess the effect of pre-aging on both clearcoats.

2.3.2. Post-aging

In this method, the coatings were subjected to both aging and biological attacks simultaneously. The aim of this method was to study the synergistic effect of aging and biological material. This method is also described in Fig. 1.

2.4. Instrumentation

2.4.1. Dynamic mechanical thermal analysis (DMTA)

In order to evaluate the network structure of clearcoat after curing, the cross-linking density of clearcoats was determined using DMTA. For this, the two final layers (basecoat and clearcoats) were applied on glass slides from which free films were prepared.

The cross-linking density was calculated by equation $\nu_e = E/3RT$; where R is gas constant coefficient, E and T are minimum storage modulus at the rubbery zone plateau and its corresponding temperature, respectively. DMTA was carried out using a Tritec2000 model, working at frequency of 1 Hz, temperature range from −30 °C to 180 °C and scanning rate of 10 °C/min.

2.4.2. FTIR spectroscopy

In order to follow the chemical variations of clearcoats caused by curing, pre-aging and biological attack, FTIR spectroscopy was car-

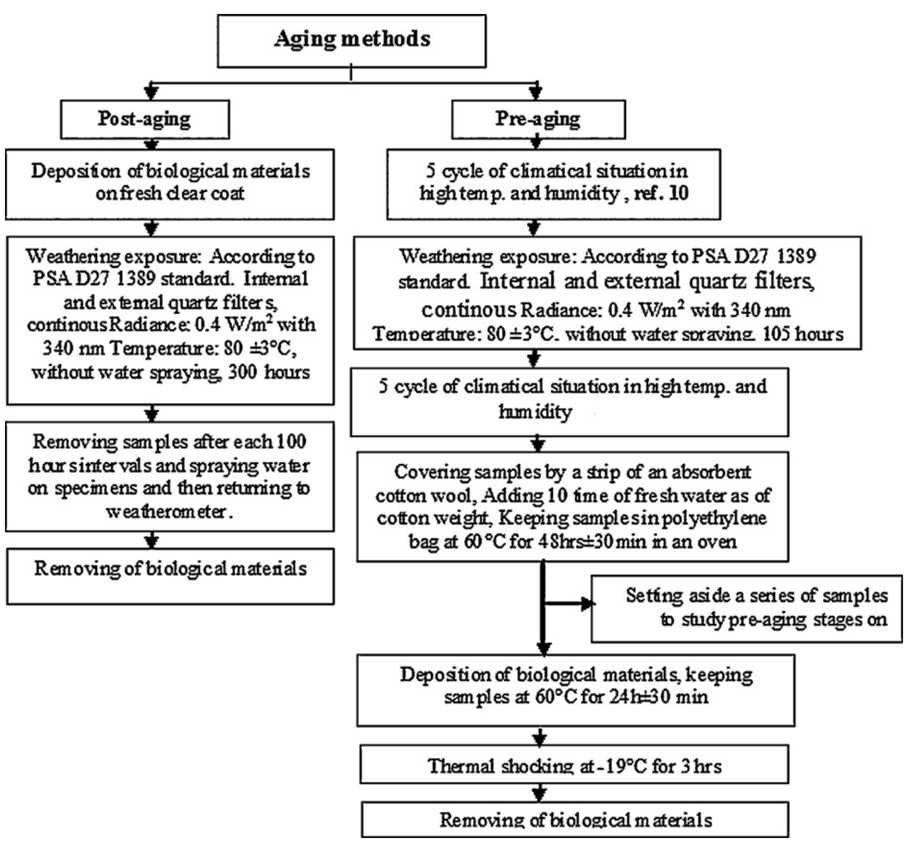

Fig. 1. Different stages of post- and pre-aging processes.