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Scratch Resistance of Paints Degraded by Arid Saharan Environments

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ABSTRACT

In the vast Algerian Sahara, the climate is typically desert, characterized by heat and dryness all year, which contributes to a very pronounced aridity. The aim of this study is to investigate the impact of this arid environment on automotive paints. Four paint samples with different durations of use were tested. Initially, a visualization of the surface condition by optical microscopy and microhardness tests was used. Then, microscratch tests with a progressive loading at a constant sliding speed were carried out to determine the adhesion of the paints. The obtained scratches were analyzed by scanning electron microscopy (SEM). The results show that the microhardness and microscratching resistance of the paints increased to maximum values corresponding to duration of five years. Beyond this duration, an inverse tendency of these characteristics was observed. Compared to the three years sample, the microscratch of this one leads to damage without the delamination of the paint. Prog. Color Colorants Coat. 11 (2018), 233-240© Institute for Color Science and Technology.

1. Introduction

Automotive paints have a decorative and protective function against external environment. Polymer-based paints are used in vehicles [1]. Technological advances tend to use new paint components to meet several requirements such as gloss [2, 3], durability, scratch resistance [4, 5], effects of aggressive environment [6-8] and Corrosion resistance [9, 10].

Currently, automotive paints generally consist of four main layers: electrochemical, primer, color basecoat, and clear coat [11]. Each of these layers has a distinct chemical composition that may contain polymeric binders and pigments as well as inorganic and organic fillers [12]. Since it is in contact with the environment, the transparent layer has an important role against Ultraviolet (UV) radiation which protects the paint surface from the scratching and maintains the paints glossy [4, 6, 8].

The scratch behavior [13] and the degradation of automotive paint layers in the environment have been the focus of several experimental studies [5-7, 14]. These works have shown that the clear coat layer degrades from its outer surface [6] and that its hardness and its elasticity modulus increase with the UV exposure time [7]. Nevertheless, the increase in mechanical characteristics under artificial conditions in the laboratory is more significant than in a natural environment [7]. The increase in weather exposure time strengthens the chemical chain of the paint polymer based and therefore improves the scratch resistance of

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the paint [5]. Several types of damaging by scratching (for example buckling, spallation and cracking) can be observed in paint layer [15]. The main causes of adhesion failure are spallation and buckling of the layers in the case of a ductile substrate materials and a mixture of these two forms of failure added to the elastic recovery in the case of brittle substrates [15].

Christopher et al. [16] and Hamad [17] also indicated that the strengthening of the chemical polymer chain can weaken the paint layer by creating micro cracks. Exposure of polymers to UV and high temperatures alters their elementary molecular chain [18], appearance, and mechanical properties and accelerates their degradation [19].

Temperature also plays an important role in the adhesion of paints [13, 20]. Each daily heating and cooling cycle introduces a mechanical stress due to the mismatch in thermal expansion coefficients between the substrate and the paint [20], so weakening their adhesion. For a range of test temperatures (-80 to +80 °C), the hardness and the critical load of delamination decreased with increasing the temperature [13], a better microscratch behavior was achieved at lower temperatures [2].

In the Algerian Sahara, average annual temperature ranges from -10 to 34 °C (14 to 93 °F), to the extreme temperatures of 49 °C (120 °F) [21]. The daily difference in temperature can reach 44 °C (80 °F) [19]. In addition, this arid climate is characterized by an annual sunshine duration that can reach 3900 h (high plains and Sahara) [22, 23] with an average of 11 hours per day.

This study aims to investigate the effect of the Algerian Sahara arid environment on automotive paints. Paint samples from different years of circulation were collected from the roofs of vehicles of a same brand. These vehicles have been used in a region of southern Algeria characterized by a high intensity of sunshine, high UV radiation and a large temperature gradient. Beforehand, morphological visualization by optical microscopy and mechanical analyses by microhardness tests are carried out on the surface of these paints. Then, microscratch tests are performed using diamond indenters with a same geometry at a constant sliding speed and variable normal load. The obtained scratches are then analyzed by a scanning electron microscopy (SEM). Changes in microhardness, tangential force and critical damage loads are discussed in terms of the applied normal load. Furthermore, the results are discussed in relation to the damage observed by SEM and as a function of the duration of use.

2. Experimental

Four automotive paint samples with four different circulation times of: 3-years (sample-A), 5-years (sample-B), 8-years (sample-C) and 10-years (sample-D) were used. To avoid engine temperature effects, these samples were obtained from the vehicle roof. The paint layers of the used samples are with the same thicknesses on steel panels obtained from vehicles 50 × 50 × 1 mm. Beforehand, optical microscope observations were carried out in order to analyze the surface morphology of the studied paints. The Vickers microhardness of the paints is then determined by a microhardness tester (5100 series BUEHLER Micrometer) in LTDS, Central School of Lyon (ECL), France. For each load test, ranging from 50 to 500 g, five microhardness measurements were made. Microscratch tests were performed at room temperature with a conical diamond indenter angle at the top $2\theta = 120°$ with a radius of the spherical portion R = 200 μm. The tests are conducted with a constant speed (8 mm/min) and a normal progressive force with a displacement speed of 1 mm/min. The machine can measure both the tangential and normal force during the sliding of the indenter (Figure 1). The obtained scratches were analyzed by a Philips XL30 scanning electron microscopy (SEM) in LTDS, Central School of Lyon (ECL), France. It was used in environmental mode to characterize the damage mode in scratches.

3. Results and Discussions

3.1. Optical analysis of the surface

The impact of arid environment on the external morphology of the paint samples was evaluated by optical microscopy. The morphologies are shown in (Figure 2). Figure 2 shows the creation of thin scratches in the clear coat layer. The thickness and the number of these scratches vary with the circulation time. For sample-A (Figure 2a), we note a low number of scratches and the existence of pores in the clear coat layer. The number of scratches becomes larger when the circulation time increases (Figures 2b and 2c). For sample-D, we notice that the scratches are thin but less in number than other samples (Figure 2d). The appearance of the scratches is mainly due to sand storms in the Saharan environment. There are scratches which cannot be healed by reflow and some others disappear completely from the surface [8]. The first ones become more and more visible during further weathering. Acid precipitation accelerates this process due to the interaction between scratching, acid rain and UV radiation [8]. Scratches which disappear completely in the first days of weathering do not leave any traces behind which are sensitive to UV or acid rain [8].

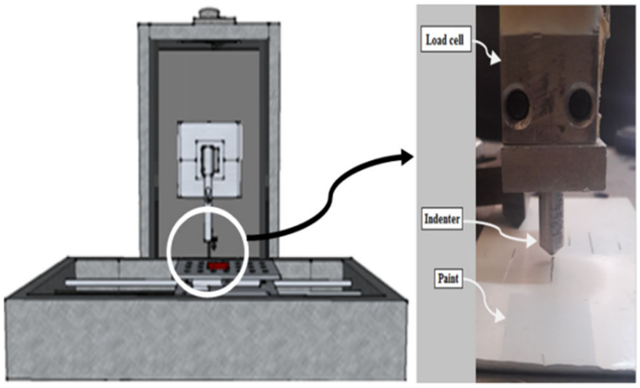

Figure1: Microscratch installation and details of the indenter surface contact.

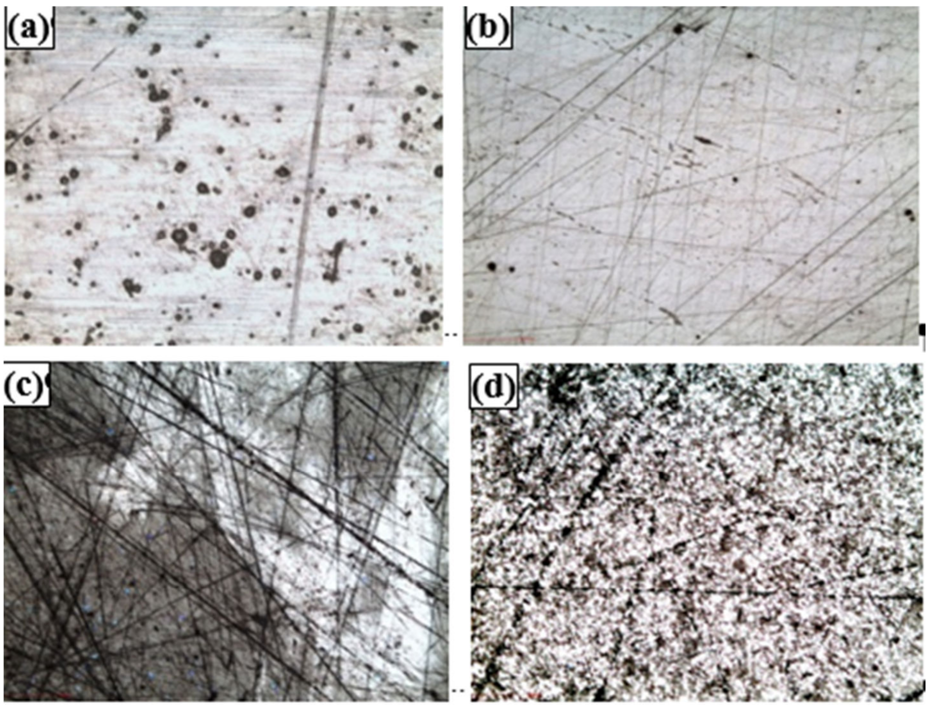

Figure 2: Morphology of paint surfaces according to years of circulation: (a) sample-A, (b) sample-B, (c) sample-C and (d) sample-D.

3.2. Paint microhardness

Vickers microindentation tests with different loads were carried out to characterize the microhardness of the studied paints. Figure 3 shows the obtained microhardness of paints for each type of samples. The influence of the circulation time on the microhardness of paints is very noticeable. For all the test loads, it is noted that the microhardness of the paint for sample-B are higher than the other durations. For all loads, the microhardness increases to maximum values corresponding to the sample-B. Beyond this duration, the microhardness decreases. The exposure of automotive polymer-based clear coat layer to UV increases the cross-linking density [4]. The density also increases with temperature which is the result of polymerization of the clear coat molecular chain [24]. However, this cross-linking takes a limit depending on the duration of UV exposure [2]. After degrading the coatings under aerobic condition, Koen et al. [7] noticed that the hardness and young modulus increase with the duration of exposure. They indicated that the most probable explanation for the increasing of this modulus is related to the oxidation. Oxidation reactions lead to the incorporation of oxygen-containing functional groups into the polymer structure [7]. Nano silica content played an important role on the hardness of polyurethane based clear coat [25], the increasing of nano silica content up to 2% increase the hardness of the polyurethane based clear coat, but, there is a rapid decrease of hardness when the nano silica raised to 5% [25].

3.3. Tangential force

Figure 4 shows the variation in tangential force according to the microscratching normal load for the samples with different durations of circulation. For increasing normal loads up to 10 N, the tangential force increases almost linearly (Figure 4). This load range represents the ploughing mode without cracking or delamination of the material. From this load of 10 N, the tangential force in the case of sample-B continues to have an increasing linear tendency with the increase of the normal load. At a load of about 16 N, a significant drop in the tangential force is noticed for the sample-D (Figure 4). The microscratching of samples B and C is characterized by greater tangential forces compared to other samples. The samples A and D present significant fluctuations in the tangential force, thus proving the formation of first relevant fractures phenomena.

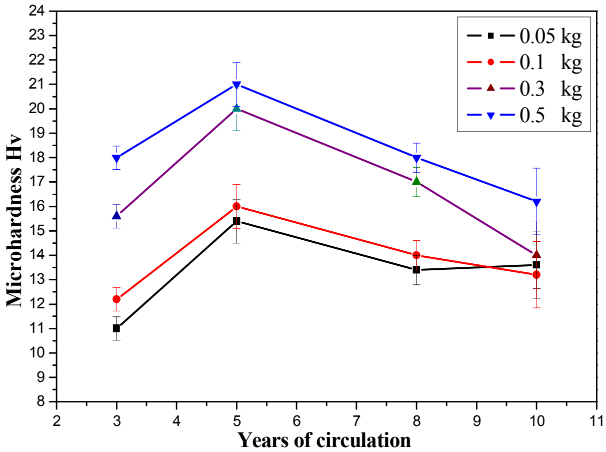

Figure 3: Vickers microhardness, Hv, of studied paints versus duration of use.

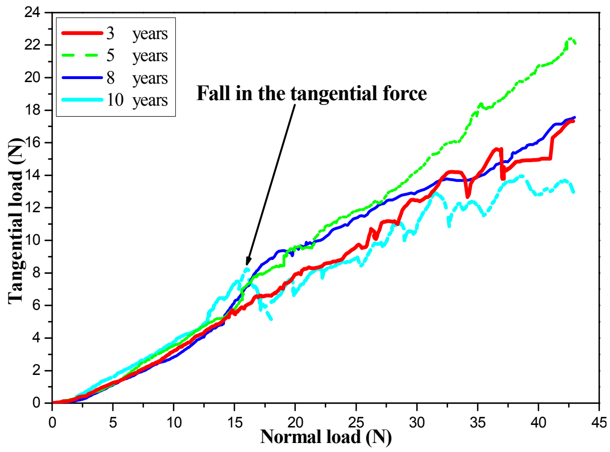

Figure 4: Tangential force according to duration of circulation. Scratching with conical tip (2θ=120°, R = 200 μm) and sliding speed of 8 mm/min.

3.4. Critical loads

Figure 5 shows the values of the three critical loads: ploughing (Lc1), cracking (Lc2) and paint delamination (Lc3) depending on the years of circulation. Compared to other durations, we can deduce that sample-B leads to a significant increase of the critical loads (Lc1 and Lc2) than other durations and, more particularly, that of delamination (Lc3). Despite a short time of circulation (sample-A), critical loads are found lower than in other years (Figure 5). The samples C and D have almost the same critical loads in microscratching test. This result is due to almost the same microhardness (Figure 3). The fact that little changes in first, second and third critical load values could be evidence that little degradation occurs after 8-years and that the UV effect reached its limit [17]. The obtained results show that microhardness and critical loads increase in the first years of use (sample-B). Beyond this period, the microscratching resistance of the studied paints decreases but remains higher than that of more recent paints (Figure 5). For sample-D, they have critical delamination loads (Lc3) of about 16 N which is lower than that of other samples. This may be due to the embrittlement of polymer-based paints after a significant duration of exposure in the arid environment characterized by a high UV intensity and a large temperature gradient [2].

3.5. Discussions

Two forms of damage as a function of normal applied loads and years of circulation were considered. A first state of average loads close to the critical load of the first crack (Figure 6) and a second state of large loads close to the critical load of delamination of the paint layer (Figure 7). The deformation modes of the samples for the different years of use change considerably after the first contact indenter-layer of paint. During the sliding of the indenter, the surface is subjected to a stress field. This stress field depends essentially on the mechanical characteristics of stressed material and the geometry of contact, in particular, the radius of the tip and the angle of attack [26]. An estimation of the indenter layer contact width is obtained by SEM at the level of the appearance of the first cracks (Figure 6). The obtained micrographs and the contact widths revealed that sample-A is characterized by a contact width of ~240 µm (Figure 6a). The sample-B has almost the same contact width (~238 µm) and less cracking (Figure 6b). However, the contact width (~260 µm) and (~302 µm), and the cracking become larger for samples C and D, respectively (Figures 6c and 6d). These results can be attributed to the low microhardness (Figure 3) and low elastic recovery after the passage of the indenter. For this range of normal microscratching forces, a buckling with tensile cracking failure mode dominates the microscratch test.

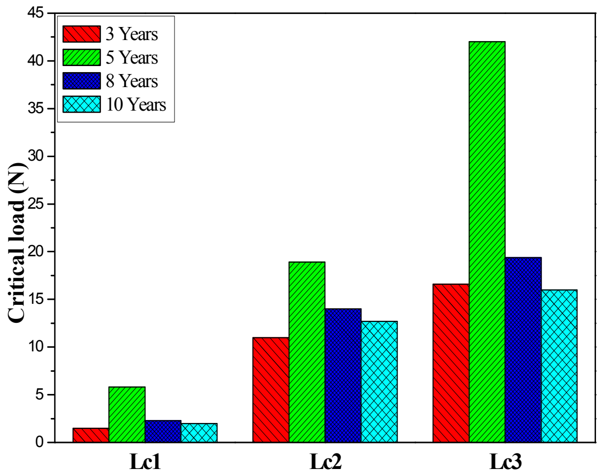

Figure 5: Critical loads versus years of use. Scratching with conical tip (2θ = 120 °, R = 200 µm) and sliding speed of 8 mm/min.

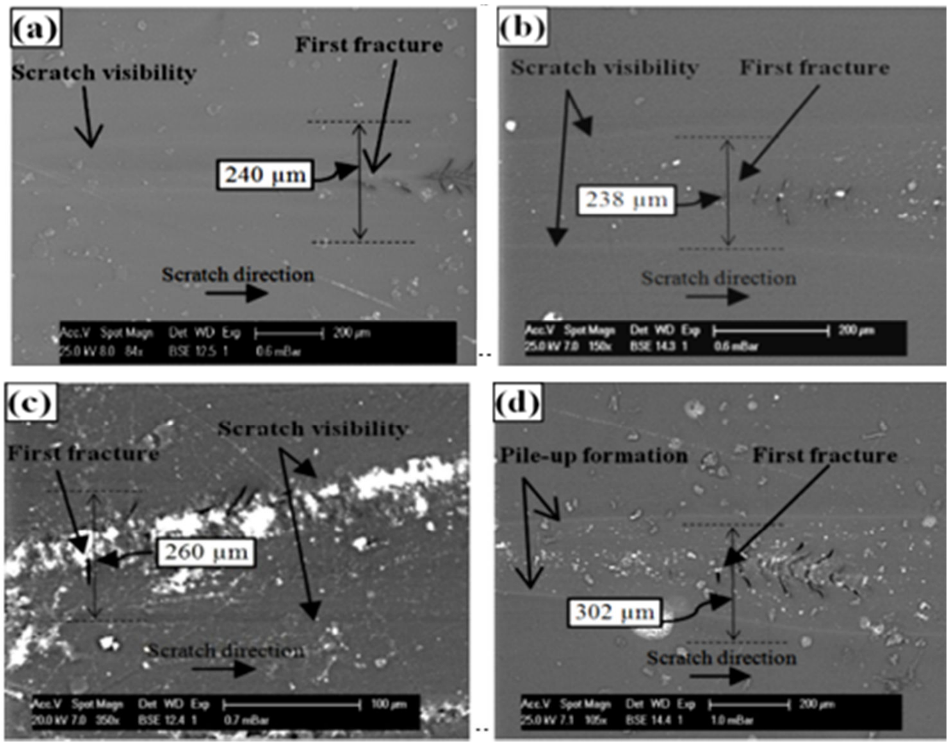

Figure 6: Appearance of the first cracks (Lc2) observed by SEM for different years of use: (a) sample-A, (b) sample-B, (c) sample-C and (d) sample-D.

In addition to the effect of UV, several factors such as temperature gradient [21] and sand storms characteristic of the Sahara region have also important role. During the sliding of the indenter, compressive stresses occur in front of the indenter and tensile stresses occur at the rear of the indenter [27]. When the applied normal load increases, compressive and tensile stresses applied by the indenter overcome the ultimate resistance of the paint, the paint layer begins to deform plastically and almost small circular cracks are formed normally in the scratching direction. This type of damage corresponds to the critical cracking load (Lc2) [28].

The SEM micrographs in Figure 7 show that the paint layer under larger normal loads damages with and without delamination of the paint layer. Indeed, for this range of normal applied forces, the delamination of the material corresponding to the 3rd critical load (Lc3) occurs for the samples A and C (Figures 7a and 7c) and with a significant delamination of the layer, also the substrate is found scratched (Figure 7d). On the other hand, in the case of the sample-B, it is noted that the paint is damaged without delamination and that the cracks are narrower and shorter (Figure 7b).

The impact of the arid environment characterized by high UV intensitie, high temperature and a large temperature gradient has significant influence on the paint layer and its adhesion to its substrate. It is noted that their microhardness and resistance to microscratching varies according to the duration of use. A period of 5-years of use led to better microhardness and microscratch resistance compared to those of other durations. In terms of these properties, there is a beneficial effect of the arid environment but only for durations less than 5-years. The microhardness of the paint and its resistance to delamination decreases beyond a period of 5-years of use (Figures 3 and 5).The UV exposure not only increases the cross-linking density [7, 17] but also creates cracks in the clear coat layer [17].

It thus appears from the obtained results that the arid environment in which the samples have been used leads to improved mechanical properties for less than 5-years. This result is also noticed with accelerated conditions in the laboratory for periods less than one year [5, 7, 8, 17]. However, the durations of use more than 5-years will weaken the adhesion of the paint to the substrate [2] hence, reducing, the critical loads of cracking and delamination.

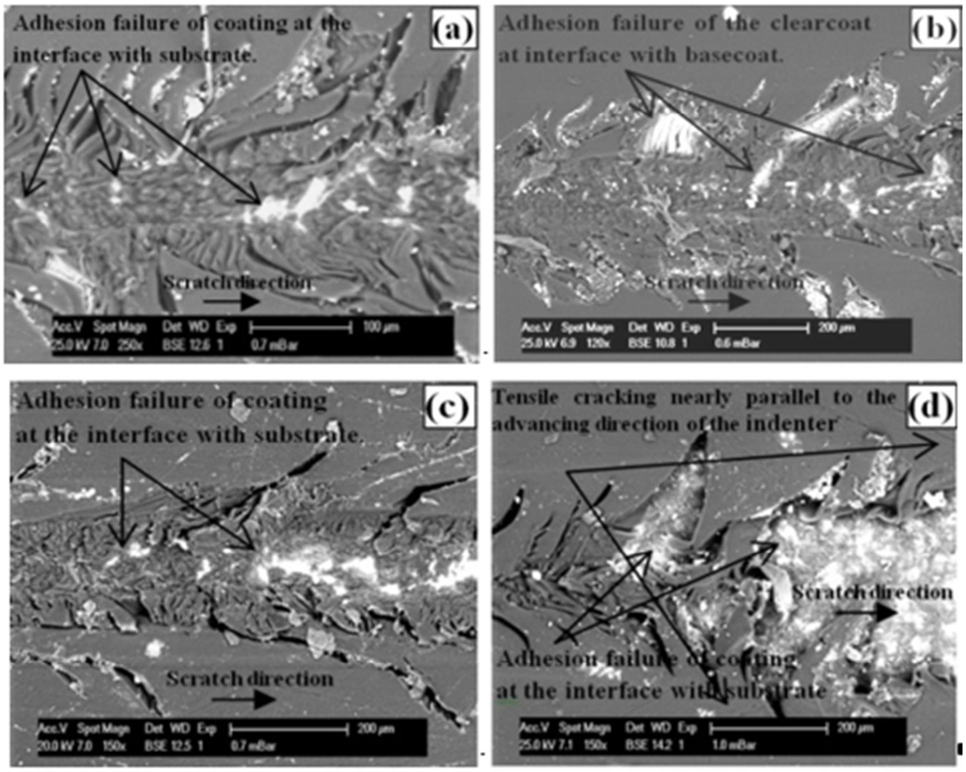

Figure 7: Separation of the paint layer observed by SEM for different years of use: (a) sample-A, (b) sample-B, (c) sample-C and (d) sample-D.

Several forms of paint behavior were observed in scratches, in the middle of the scratch, micro cracks opposed to the scratch direction were dominant (Figure 6), which is also observed by Bull [15]. The cracking of the paint for sample-B (Figure 6b) is less important than that observed in samples C and D (Figures 6c and 6d). Figure 7 shows the transition from the ploughing mode with cracking to the delamination of the paint layer. However, in the case of sample-B, this delamination was not completed (Figure 7b). This improvement in mechanical properties of the paints was obtained after duration of use of 5-years.

4. Conclusion

The aim of this work is to investigate the effect of Algerian Sahara arid environment on morphology and mechanical properties of automotive paints. Four paint samples with different duration of use were examined. The optical examination revealed that in early years of use, scratches with small sizes were initiated in the surface of paint. At duration of 5-years, some of these scratches disappeared completely from the surface, but others become visible. Beyond this duration, scratches which did not disappear from the surface at early time become more visible. The microhardness and scratch resistance of paints in first years of use are lower than those of paints at 5-years of use. Beyond this duration, a decrease of these two properties was noticed. Furthermore, the paint of sample-B shows less damage compared to other ones. Thus, the optimal duration of use is 5-years and not 3-years.

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