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Behaviour of different removers on permanent anti-graffiti organic coatings



S. Rossi*, M. Fedel, S. Petrolli, F. Deflorian

Department of Industrial Engineering, University of Trento, via Sommarive n. 9, 38123 Trento, Italy

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1. Introduction

The problem of graffiti was originated in the second half of the last century and it is producing a lot of damages to urban furniture, buildings and transport means bodyworks. The graffiti removal cost is very high. As a consequence, due to this problem, the coating industry has developed permanent solutions to this problem minimising the cleaning costs [1–6]. For the urban administration and private citizen, the damage caused by graffiti presents considerable costs. In 2006, the Tennessee Department of Transportation spent more than 240,000 dollars on removing graffiti along its roads and bridges [7]. Las Vegas, with a population of about 1.7 million spent more than 3 million dollars each year cleaning up graffiti [8]. In 2007, in Australia the rolling stock graffiti removal cost was 12 million dollars and 8 million dollars for railway infrastructures [9].

The anti-graffiti coatings have to maintain over time the effectiveness in the graffiti removal minimising the colour and gloss changes due to the cleaning action. The coating must be thermally and chemically stable and solar radiation resistant. Moreover environmental compatibility and economic factors has to be considered as well. Considering metallic surfaces and components, there are two kinds of anti-graffiti products. The sacrificial one is removed during

* Corresponding author. E-mail address: stefano.rossi@unitn.it (S. Rossi). Graffiti removal presents high costs in street furniture, transport and architectural facades. Considering painted metallic surfaces, the removal has to be easy and not modify the protective and the aesthetic properties. The study of the interaction between paint and remover and the effects on the anti-graffiti properties is the aim of this paper. Two kinds of polyurethane organic coatings, indicated for metallic substrates, and two different surface finishing were considered. This kind of organic coatings shows a very good corrosion properties connected with the low water uptake together a very interesting aesthetical aspect. The behaviour of methylethylketone, xylene and an aliphatic and aromatic solvent mixture, before and after accelerated weathering, was evaluated. MEK was proven to be particularly aggressive. The wrinkled finishing shows strong criticality.

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the cleaning. The permanent system is not solubilized by the remover adopted to clean the graffiti. In this way the permanent antigraffiti coatings maintain their capacity to be cleaned also for more cleaning cycles. The choice of a permanent anti-graffiti coating involves a bigger initial cost, repaid in the following years with a faster and more effective cleanings. The sacrificial solutions are often waxes based coatings that are removed with the graffiti using hot water jet [3]. In order to decrease the graffiti paints adhesion and to ensure a greater durability, fluorinated resins are used [4].

Generally the permanent anti-graffiti products are enamels or polyurethane coatings. Vitreous enamels have the advantage to be chemically inert with organic solvents used in the remover but present some critical issues as brittleness, difficult application on irregular surface and expensiveness [10]. This kind of layer is used in railway stations or subways very prone to vandalism. The polyurethane coatings are spreading because of their aesthetical and technical performance [4,5]. The anti-graffiti behaviour sometimes is obtained using fluorocarbon functional groups [6]. The strong C-F chemical bond has a low interaction with the graffiti paint molecules. In this way it is possible to decrease the surface energy and the permeation of polar and non-polar solvent into the coating [10]. Polyurethane resins show good mechanical properties and chemical resistance necessary to resist the solvent attack and guarantee a high corrosion resistance [11–13]. These properties are correlated to the strong cross-linking between isocyanates and polyols [14]. The critical aspect is the UV radiation resistance. In the last years a lot of solutions were investigated [5,15–19]. The powder application process, applied on metallic substrates, allows working in absence of solvent (Volatile Organic Compound – VOC-very low) with benefits for environmental sustainability. Moreover it is possible to recover the powder waste (efficiency greater than 95%) and the application plant is cheaper and less energy-consuming than the one adopted for the solvent paint [19–21].

The anti-graffiti coatings are a quite recent product, so there are not a lot of literatures about it. The study of the interaction between the coating and the removers and, as a consequence, the effects on the anti-graffiti properties is the aim of this paper. Removers prescribed by the ASTM D6578-13 [22] standard (methylethylketone and xylene), and a remover made of a mixture of aliphatic and aromatic compounds were exploited.

Two different formulations and two different surface finishing were considered. A widely used polyurethane anti-graffiti powder coating was modified while changing the chemistry of the polyol (hydroxylated polyester resin) or changing the additives to reach a different surface finishing. In this way it was possible to analyse the influence of these parameters on the anti-graffiti properties. Anti-graffiti properties were evaluated measuring the aesthetical properties variation such as colour and gloss. In addition to the anti-graffiti properties evaluation on an original surface, the accelerated weathered surface was considered too. The weathering was obtained with a cycle test made of exposure to UV radiation and water condensation. The artificial accelerated ageing was performed with UV-B radiation, according to ASTM G154-12a standard [23], in order to appreciate a polyurethane coating degradation in a reasonable time. Anti-graffiti properties during exposure time were investigated.

2. Material and methods

Aluminium alloy AA 1050 (min 99.50% Al) panels obtained from a rolled coil, were used as substrate. These sheets have 75 mm \times 150 mm and 0.6 mm of thick, characterised by a smooth surface (Ra 30 μ m) without defect or surface porosity. The surface was degreased introducing the aluminium panel in a becker with acetone for 10 min with ultrasound stirring. The powder coating was applied with a spray gun followed by 20 min at 190 °C as curing process. The studied samples with their characteristics are reported in Table 1.

Two formulations are based on a polyester resin with a high number of –OH groups in order to minimise the free volume. This allows the coating to have high chemical resistance and less solvent penetration [24]. The TPA formulation differs from IPA for the monomers adopted to obtain the polyester hydroxylated resin. The isophtalic acid (IPA) creates a compact structure due to the different angle bond imposed to the polymeric chain during the crosslinking [15,24]. The terephtalic acid (TPA) is cheaper and easier to process [14]. The NCO/OH ratio is stoichiometric. The polymeric powders were produced in laboratory of Akzo Nobel Italy (Como Italy). The wrinkled surface is obtained by the addition

Table 1

Composition of the studied samples.

SAMPLE	TPA_S	TPA_W	IPA_S
Surface finishing	Smooth	Wrinkled	Smooth
Resin	Hydroxylated polyester resin based on terephtalic acid and neopentylglycol		Hydroxylated polyester resin based on isophtalic acid and neopentylglycol
Hardener	Polyisocyanate adduct blocked with caprolactam and uretidione		
Additive	Wrinkled wax		



Fig. 1. Mask used to reproduce the graffiti on the painted surface.

of a low density polyethylene wax. The colour of the samples is RAL 7035, according with standard RAL colour system [25] obtained adding titanium dioxide (PW6), yellow iron oxide (PB77) and carbon black (PB77). The amount of pigments is of about 30 wt%, most of which is by titanium dioxide. Standard commercial fillers, aluminosilicates and barium sulphate (average dimension of about 4 μ m) are added about 1%_{wt}.

The anti-graffiti properties were evaluated according to ASTM D6578-13 standard. A solvent-based acrylic spray (AREXONS Acril colour [26], red RAL 3000 [25]) was used to draw the graffiti, as indicated in the cited ASTM standard. This acrylic-based thermoplastic paint is insoluble in water but easily soluble in polar organic solvents, such as esters and ketones. In order to limit the

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