International Journal of Adhesion & Adhesives 29 (2009) 240–247

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

FTIR and XPS study of the adsorption of probe molecule used to model alkyd resin adhesion to low carbon aluminum killed steel

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ARTICLE INFO

Article history:
Accepted 23 May 2008
Available online 19 June 2008

Keywords:
XPS
FTIR
Lewis acid–base interaction
Adsorption

ABSTRACT

An important factor in achieving maximum adhesion of a particular coating system to the substrate lies in the proper pre-treatment of the substrate prior to the application of the coating. The Lewis acid–base properties of the outer metal surface play a determining role in many of these applications, and the chemical reactions involved therein. In this work, the Lewis nature of the low carbon aluminum killed (LCAK) substrate has been significantly modified by a chemically activated surface pre-treatment. The wetting properties of the LCAK substrate was determined by contact angle measurements; the coordination of the chemical species on the surface was studied with XPS; FTIR together with the probe molecule ($B(OCH_3)_3$) was used to explain the chemical bonding. The novel combination of contact angle, XPS, FTIR and probe molecule enabled the determination of the Lewis acid–base properties of the LCAK surface before coating. The XPS spectra of the LCAK surface rinsed in warm water show that the surface species differ from that rinsed in tap water. With change in pH, the wettability properties also drastically changed. The probe molecule ($B(OCH_3)_3$) did not bond on the warm water rinsed samples but bonded strongly on tap water rinsed samples as the pH decreased. This research has shown that Lewis acid–base properties can be significantly changed with water temperature and pH, which has important implications for industrial pre-treatment.

1. Introduction

The acidic and basic nature of metal surfaces has been documented [1], but remains a matter of controversy. A variety of techniques have been used to measure acidity including the use of acidic indicators [2], titration with bases using indicators [3] and the measurement of chemisorbed compounds at different temperatures [4]. These techniques have given conflicting and widely differing results for the same materials. Surface acid–base properties are important characteristics, in particular for metal oxides that form on the surface. The acid–base interactions have been widely used in various applications in the chemical industry and the acid–base theory forms a large component of the description of current–surface interaction phenomena [5]. In order to achieve a durable structural adhesion, the formation of this type of chemical bond is necessary and is a strong function of the surface treatment of the substrate.

With this approach to surface interaction phenomena or adhesion phenomena, it is important to characterize and evaluate the chemical sites and, then, to determine their reactivity toward a specific molecule. The acid–base properties of coatings and substrates surfaces are of fundamental significance in adhesion.

Lewis' original formulation of acid–base behavior remains useful and from the late 1940s onward a growing need was felt for its application to adhesion phenomena. Such applications were initiated by Fowkes, starting with a paper in 1964 [6]. Fowkes's work substantially broadens the scope of the original Lewis concepts and merits further discussion in this study.

Many methods are proposed in the literature to understand and quantify the acid–base interactions at the interfaces [7]. It was Fowkes who proposed in the study of adhesion to describe non-dispersive or specific interaction in terms of acid–base or electron donor–acceptor interactions [8,9]. Fowkes then considered these non-dispersive interactions to be identical to electron donor–acceptor or acid–base interactions. Polar molecules used to determine the specific interactions with the solid substrate were characterized by their donor (DN) and acceptor (AN) numbers [10]. The concept of donor–acceptor interactions is an extension of the Lewis acid–base reactions, dealing with coordinate bonds,

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doi:10.1016/j.ijadhadh.2008.05.005

which are formed by sharing a pair of electrons between donor and acceptor species.

Other authors [11,12] have studied the Lewis acid–base phenomena by angular photoelectron spectroscopy and TOF–SIMS methods; however, only give indirect evidence of the formation of chemical bonds during adsorption processes. Leadley and Watts [13] showed usefulness of monochromated XPS, but their adhesion system involved a poly(methyl methacrylate)-oxidized metal (PMMA) interface. While in this present study, a more fundamental approach in terms of the coating system was considered. By using XPS spectroscopy, Watts and co-workers [14,15] showed that the magnitude of Lewis acid–base interactions plays an important part in adhesion.

Coatings can be classified into a number of different categories, but the most convenient system is by chemical composition. Alkyd coatings are widely used for structural bonding purposes, and decorative or labeling containers. Adhesives of this family are a class of polyester coatings derived from the reaction of an alcohol and an acid or acid anhydride. The product will be an ester compound and an acid compound. They are modified with unsaturated fatty acids (from vegetable and plant oils) to give air-drying properties. The unsaturated oils react with oxygen from air, which causes the oils to polymerize or crosslink [16]. All these functions are likely to interact strongly with the basic sites that may be present on the surface of the metallic substrate. These sites can be identified by probing the molecular adsorption and analysis by XPS, SIMS, FTIR, etc., as has been used in combination to determine the chemical nature (Lewis or Brönsted character), the density, and the strength of acid sites at the surface of many solid substrates [17].

Mostly, fully formulated coatings are generally a mixture of large complex molecules, additives and filler materials. As such mixtures are difficult to analyze and to handle, the use of probe molecules was considered for fundamental research purposes [18]. These probe molecules must be representative of some active functions of the coating and also possess a well-established chemical behavior, with respect to their acid–base properties.

In this study, firstly the chemical sites on the low carbon aluminum killed (LCAK) steel substrate were characterized and evaluated. Then the adsorption of boric acid trimethyl ester ($B(OCH_3)_3$), an acidic probe molecule, also representative of ester groups present in organic coatings were investigated. The adsorption of the alkyd coating was then studied. The representative structure of the molecule is shown in Fig. 1. Adsorption was carried out on the standard LCAK surface and on this alloy after different surface treatments.

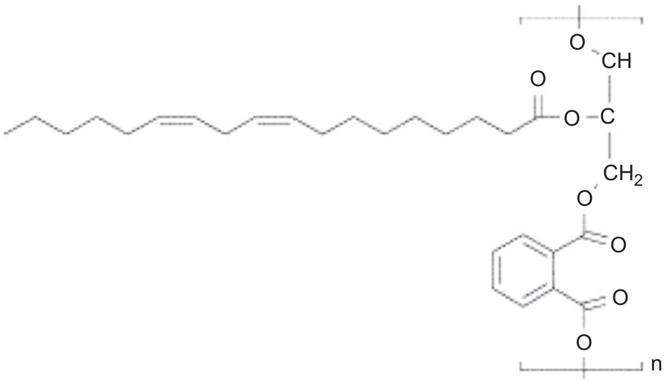

Fig. 1. Schematic alkyd resin used as a binder compound in alkyd coating.

2. Experimental

2.1. Preparation of standard surface

LCAK has been used. The chemical analysis of the steel was determined by spark emission spectrometry. Results are summarized in Table 1. All samples were mounted and polished to a 5 μm finish. The standard sample was washed in HIBITEX (inhibited hydrochloric acid) to remove oxides from the surface layer, rinsed in tap water (aerated) at room temperature to prevent the possibility of organic contamination on the surface, which could influence the wettability and then cleaned with ethanol 99.9% absolute analytical reagent (AR) to remove the water film, followed by a hot-air drying step to prevent corrosion of the surface.

2.2. Warm water treatment of standard surface

The polished sample was rinsed with warm water (de-aerated) at ±40 °C, which was previously boiled for 4 h to remove the oxygen. The surface was then cleaned with ethanol to remove the water film, followed by a hot-air-drying step to prevent corrosion of the surface [19].

2.3. Treatment with acidic and basic solutions

Hydrochloric acid 32% (AR) and sodium hydroxide pellets (AR) aqueous un-buffered solutions representing acidic and basic solutions, respectively, were prepared. The concentrations of the acidic solutions were approximately 1.0, 2.0×10^{-2}, 4.0×10^{-4} and 3.0×10^{-6} mol dm^{-3}, while the concentrations of the basic solutions were approximately 1.0, 1.0×10^{-2}, 2.0×10^{-5} and 4.0×10^{-6} mol dm^{-3}. The pH values for the solutions were measured using a Labotec Orion 410A+ pH-meter with an Orion 91–65 Ag/AgCl electrode that was calibrated with pHs 4 and 10 solutions. pH values of the acidic and basic solutions are summarized in Table 2. Wettability (contact angle) measurements have been performed on the warm water treated LCAK samples as well as the standard LCAK samples, making use of the solutions prepared as in Table 2 as contact liquids for contact measurement. The procedure used to measure the contact angle or wettability is based on the ASTM

Table 1
Trace element composition of low carbon aluminum killed steel in μg g^{-1}

Steel	C	Mn	S	Si	Cu	Ni	Cr	Al
LCAK	0.047	0.2	0.003	0.018	0.008	0.006	0.025	0.059

Table 2
The pH values of the acidic and basic solutions

Approximate concentration (mol dm^{-3})	pH
Acidic solutions	
1	0.8
2.0×10^{-2}	2.5
4.0×10^{-4}	3.6
3.0×10^{-6}	4.1
Basic solutions	
1	13.1
1.0×10^{-2}	12.1
2.0×10^{-5}	10.5
4.0×10^{-6}	9.1