

## Competitive adsorption of (phosphorylated) ethoxylated styrene oxide polymer and polyacrylic acid on silica coated iron oxide pigment



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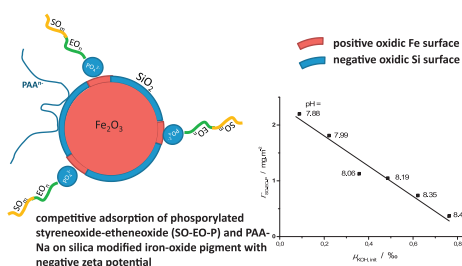
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### HIGHLIGHTS

- Adsorption of anionic polymeric surfactants on silica-modified  $\text{Fe}_2\text{O}_3$  pigment with negative zeta potential.
- This is due to the presence of positive oxydic iron sites.
- Styrene oxide–ethyleneoxide– $\text{PO}_4^{2-}$  (SO–EO–P) adsorbs, only caused by electrostatics.
- Polyacrylic acid sodium salt (PANa) also adsorbs; not lowered by SO–EO–P.
- SO–EO–P adsorption is lowered by PANa.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The colloidal stabilization in waterbased paint is poorly understood due to its complexity in composition, usually containing mixtures of particles and of surface active agents (“dispersants”). In this study we make a step forward by analyzing the competitive adsorption of a few widely used dispersants on a typical inorganic pigment (70 nm sized  $\text{Fe}_2\text{O}_3$ -based red pigment; surface treated with silica; negative zeta potential at  $\text{pH} \sim 7$ ). The supposition is that any particle type in paint needs sufficient adsorbed dispersant in order to be stable. Thus, we investigate, for two combinations of two dispersants, how they mutually affect their adsorption at that pigment. Also the “single” adsorption of these dispersants was investigated, thus in the absence of the other. The dispersants are an anionic, polyacrylic acid sodium salt (“PANa”;  $M_w = 15,000$  Da) in combination with a  $M_w = 1500$  Da blockcopolymer of styrene oxide (SO) and ethoxylene (EO), either or not endcapped by a phosphate group (P). The adsorption behavior was analyzed by size exclusion chromatography of the processed supernatant of the pigment dispersion. PANa and SO–EO–P adsorb for electrostatic reasons while SO–EO has affinity only to an organic surface. PANa and SO–EO–P show regular single adsorption with a plateau starting at the critical micelle concentration (cmc). SO–EO shows single adsorption only beyond its cmc based on the adsorption of full micelles. When in competition, with SO–EP–P/PANa the adsorption of SO–EO–P is lowered by  $\sim 65\%$  while that of PANa is unchanged. With SO–EO/PANa the surface active species behave like in single adsorption below the cmc, but beyond the cmc a complicated phase separation occurs that cannot be based on mixed micelles. The adsorption data of PANa are compromised by depletion of PANa from interstices between particles. The anionic dispersants adsorb to the silicium oxide coated iron oxide pigment with negative surface potential because of the presence of a pH dependent relatively small number of positive iron oxide surface sites.

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## 1. Introduction

The colloidal stability of pigment particles in a paint system is essential for the quality and durability of the coating made of that paint. Traditionally, pigments and a resin were dissolved or dispersed in an organic solvent. However, environmental concerns led to legislation aiming at reducing the use of organic solvents. As a result, several low-solvent or solventless types of paint systems have been developed. A major low-solvent paint type is based on polymer latex and usually contains also other colloid-sized additives, such as color pigments, surface active agents and other additives. When compared with solvent-based paints, these water-based types contain more types of dispersed particles, which makes controlling their colloidal stability more difficult. Also the types of dispersing agents are completely different (although some refer to these surface active agents with the generic name surfactants, it may be confusing to do so in the case of polymeric species; that is why we will usually denote them by “dispersant”). A typical paint system consists of latex, white pigment, at least one color pigment (but typically a number of them) together with dispersants for each type of dispersed particle. Thus, often at least three surfactants are competing in their adsorption on the particles. Note that also other surface active agents like anti foamers, wetting and leveling agents may be used. While high quality paints are indeed available, the understanding of how the different dispersants involved cooperate or compete is still poor.

Many studies in the past were directly related to adsorption of a single dispersant and a single particle type [1–7]; for titania pigments they were reviewed in ref. [8]. Additionally, the adsorption behavior of a specific combination of a surfactant (i.e., a low molar mass dispersant) and a polymer was investigated [9]. On the other hand, the competition between native and alumina coated silica particles for the adsorption of a single nonionic polymer was investigated [10]. Most of these adsorption studies were carried out on model systems. This means that in these cases the surface can be well defined with respect to both chemical and geometrical properties, while also the molar mass of the dispersant is well defined. The aim of this research is to investigate the adsorption behavior of polymeric dispersants on real pigment particles as used in paint systems. These systems are not model systems but are rather complex because the geometry of pigment particles is not well defined and their surface has usually been chemically modified. Some research in this field has been performed on titanium dioxide pigment particles [11–14]. We will consistently use the word “pigment” in connection with such an inorganic oxide particle in order to remind the reader that the colloidal properties of such a particle may considerably deviate if compared to a pure particle, especially because they usually have been surface-modified.

While our ultimate goal is to understand why all these types of particles can together be colloidally stable in a waterborne paint, it is not feasible to study such a system in its full complexity. Therefore we will assume that particles in a paint do usually need adsorbed dispersant in order to be colloidally stable (although coverage is not a guarantee for colloidal stabilization in a mixed dispersion, we will suppose this as we believe that this usually the case). This allows us to learn about the paint stability by studying the adsorption for a single particle type in the presence of mixtures of dispersant.

The method of stabilizing a latex is intimately related to its production process which generally comprises commercially sensitive information. For white pigments it is known that they are often stabilized by the anionic polyacrylic acid sodium salt [11–15]. Therefore we decided to start focusing at color pigments. As these pigments fall apart in inorganics and organics, both of which are often used, we decided to consider one type of each class. While an organic pigment was the subject of a previous study [16], in the

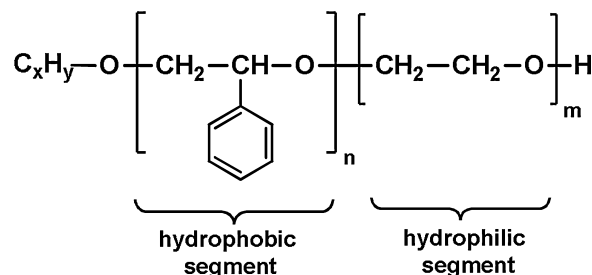


Fig. 1. Structural formula of SO-EO and SO-EO-P. In the latter case the terminal hydrogen is replaced by a phosphate group ( $m \cong 20$  and  $n \cong 5$ ).

present study we will consider an inorganic pigment. We selected an iron oxide pigment ( $\text{Fe}_2\text{O}_3$ ) because these pigments are made in a large range of color shades and are abundantly applied; its surface had been treated with silica by the manufacturer.

In a previous paper [16] we focused on the case of white pigment ( $\text{TiO}_2$ ) in combination with an organic color pigment. The sodium salt of polyacrylic acid (PANA) was considered to be an adequate, often used stabilizer for  $\text{TiO}_2$  while non-ionic styrene oxide-ethylene oxide blockcopolymer (SO-EO) was used to stabilize the color pigment. In that study the adsorption of these two surface active agents on the organic pigment was investigated, both how they adsorb in the absence and how they adsorb in the presence of the other. The present adsorption study considers how dispersants adsorb at an inorganic  $\text{Fe}_2\text{O}_3$  color pigment and their interactions. On recommendation of the manufacturer of SO-EO, the dispersant SO-EO-P was selected (i.e., SO-EO to which a phosphate group was attached) because it is known to have good affinity to  $\text{Fe}_2\text{O}_3$  pigment and for this reason used quite often in practice. An advantage of specifically this dispersant is that its molecular structure can be well compared with that of SO-EO. Thus, we will analyze and discuss the adsorption behavior on our iron oxide pigment surface for a number of dispersant systems, for PANA, SO-EO, SO-EO-P, PANA/SO-EO and PANA/SO-EO-P.

## 2. Experimental

### 2.1. Materials

As a typical inorganic pigment for waterborne paints we used Ferroside Orange 204 M, ex. Rockwood Pigments Italia S.p.A. Divisione SILO. This is an iron oxide pigment. According to the manufacturer, it has a density of  $4900 \text{ kg/m}^3$ , a specific surface of  $2.0 \times 10^4 \text{ m}^2/\text{kg}$ , a predominant particle size of 70 nm and a combined content of silica and alumina of <1%. XPS analysis in our laboratory, using a ESCALab 220i-XL electron spectrometer from VG Scientific with 300 W Al-K $\alpha$  radiation, confirmed the presence of silica at a level of the order of 1% while alumina was not been traceable. The conclusion is that this pigment had been surface treated with silica only.

Three polymeric surface active agents were employed. The common dispersant in competitive adsorption experiments was polyacrylic acid with a molar mass of 15,000 Da (Sigma Aldrich; 35% solution of its sodium salt). Such polyacrylate anion is commonly used as dispersant for titanium dioxide, the usual white pigment in paint systems. This sodium polyacrylate will be denoted as PANA [11–14].

The second dispersant used is a block-copolymer consisting of a block of styrene oxide groups and a block of ethoxylene groups (SO-EO), with a molar mass of 1500 Da (Tego Dispers 650 ex. Tego, Essen, Germany); its structure is given in Fig. 1. The lengths  $m$  and  $n$  of the hydrophilic and hydrophobic block lengths (see Fig. 1) are

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