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Challenges in developing photocatalytic inks

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ABSTRACT

The paper presents a study on the parameters that influence the stability of photocatalytic ink formulations, to be further deposited on textile substrates. The main features are discussed based on the analysis (composition, structure, rheological parameters) of four commercial inks used in the digital printing on fabrics, outlining the stability as key factor.

Further on, to obtain photocatalytic inks, TiO_2 nanoparticles (Degussa P25, sol–gel) were dispersed in water, water–alcohol, and alcohol; the stability was evaluated using the transmittance spectra. The ink stability was improved and controlled by optimizing the type and amount of various stabilizers: dodecyltrimethylammonium bromide (DTAB), polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), and 2-[2-(2-methoxyethoxy)ethoxy] acetic acid (TODA).

The surface modifications and interactions at the particle/continuous medium/stabilizer interfaces are comparatively discussed. The stabilization mechanisms are proposed considering the influence of the particle concentration, type/dimension and surface charge, and the continuous medium composition and pH.

The photocatalytic activity of the sol–gel TiO_2 was investigated, as dispersed powder and thin film, and comparatively discussed with Degussa (as reference). Based on these results, recommendations on the preparation, characterization and use of titania-based inks were done, outlining PEG and TODA as potential stabilizers.

1. Introduction

Titanium dioxide is one of the most frequently studied materials due to its properties which match a broad field of applications, as photocatalysis (e.g. wastewater treatment and air purification), self–cleaning surfaces, gas sensors, batteries, anti-microbial protection, but also in the biomedical, pharmaceutical, automotive or wood industries, etc. [1–4]. Titania is also one of the main materials used in the efficient solar-energy conversion, both in photovoltaic (as n-type semiconductor) and in solar-thermal applications (as antireflection coatings). Most of these applications use thin layers of titanium dioxide obtained by different deposition/synthesis techniques like PVD [1,4], CVD [4], spray pyrolysis deposition [5,6], doctor blade, dip coating, spin coating [7–10], etc.

A relatively new and cost effective approach is the cold spray deposition of nanoparticle dispersions/inks (i.e. spraying the dispersion on the substrate at room or slightly higher temperature). This allows thin films deposition on flexible substrates with low thermal resistance, on substrates with different geometry and shapes, or on fabrics aiming at self-cleaning and photocatalytic properties. In this last case, applications were identified for specially designed fabrics mainly for military or medical protection suites. The advantages include the reduced costs and the maturity of the deposition technology already existing in the textile industry. Additionally, the nanoparticles can be obtained and optimized in high-temperature processes prior to their dispersion, in conditions that cannot be applied to the deposition substrate.

The problem of ink formulation was firstly defined directly related to the inkjet printing technology (e.g. for textiles), with a focus on the preparation of stable pigment dispersions.

Inorganic pigment based inks are considered prospective colourants due to their advantages: easy deposition on a wide variety of fibres and fabrics, shorter printing duration, lower water and energy consumptions, low environmental impact as compared to dye pigments inks, since they are used as aqueous dispersions.

Basically, a pigment based ink consists of pigment particles/nanoparticles dispersed in a continuous medium, usually water. The key requirements in the ink formulation refer to the homogeneity, the particle dimensions, the viscosity, conductivity and surface tension, and the colour purity, [10–13]. Thus, the printing inks used in the textile industry contain organic pigments up to 20…30% (by weight) and inorganic pigments up to 50% [14].

Particle size is important for avoiding sedimentation, therefore small particles are preferred for obtaining stable inks; the reported values cover a broad range (5…50 μm), depending on the type of pigments and on the printing process [15].

Pigment-based inks suitable for textile printing should have a surface tension ranging from 15 to 45 mN/m, while acceptable viscosities are less than 20 cP at 25 °C for continuous jetting equipment, and

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higher, with a maximum of 30 cP, when the "drop on demand" technique is applied. In digital printing, the pigment ink should have much lower viscosities (1…5 cP) to get high jetting frequency through the small nozzles [16]. In addition, the inks used in fabric printing must have a good colour fastness and light resistance.

Additives are used for tuning the ink properties. Commonly they represent 4…10% in the ink formulation and include: surfactants to reduce the surface tension, thus controlling the droplet stability and improving the wetting behaviour in the deposition process, buffers to control the pH, electrolytes to ensure a good conductivity, biocides to prevent the microbiological degradation of the ink, and binders [11,12]. Binders have multiple roles: they increase the particles — substrate affinity and behave as pigment dispersant thus improving the colour retention. A fairly high binder content in the ink may affect the rheological and mechanical properties, it will increase the viscosity, thus leading to poor jettability. A decrease of the printed textiles softness is also observed [11,13,17]. The most frequently used binders include phenolic resins, styrene/acrylic copolymers, acrylic polymers (e.g. polyacrylamide, PAA), polyvinylpyrrolidone (PVP), octyl-phenol ethoxylates, polyurethane, phosphate esters, and sulfonates [13,17,18].

Hence, ink composition is quite complex; due to commercial reasons the chemical and structural properties of the pigments and additives are usually not disclosed.

Many problems of the ink's formulations are unsolved yet [19,20], especially those related to rheology and stability (particle size and surface charge, additives). Following the ink concept, photocatalytic dispersions/inks (e.g. titania based dispersions) can be prepared and used in cold spraying deposition if a certain stability and the pre-requisites imposed by the spraying nozzle are reached.

The stabilization mechanisms can be electrostatic, based on electrostatic repulsions between the double layers surrounding the particles (when adding electrolytes [21,22]), or steric when large surfactant or polymer molecules adsorb on the particle surface and act as protective barriers against agglomeration [1,23,24]. Combinations of the two mechanisms known as electrosteric stabilization are also possible when polyelectrolytes are used [24,25].

The use of additives (electrolytes, surfactants or binders) increases the stability, but these compounds can interfere with the photocatalytic process (which non-discriminating affects all the organics), with negative consequences on the process efficiency. Thus, the additive amount and type should be optimized considering stability and functionality.

In this paper, four commercial aqueous pigment inks were fully investigated to obtain initial information on the composition, the physicochemical, rheological and structural properties. Based on these, prerequisites for stabilized photocatalytic dispersions are formulated and used in the preparation of titania dispersions, obtained using the standard Degussa P25, and powders obtained following the sol–gel route. The potential of these two photocatalyst powders was comparatively analysed in methylene blue degradation. Further on, the two powders were developed and optimized as inks; the stability of the photocatalytic dispersions is comparatively investigated and discussed, and the stabilization mechanisms of Degussa and sol–gel titanium dioxide particles in different continuous media are proposed. The inks were further deposited on cotton fabrics and the methylene blue photocatalytic removal efficiency of the sol–gel thin films reached far better values (higher than 60%) as compared to the films deposited on glass (less than 20%), under simulated solar radiation.

2. Experimental part

The experiments went through the following stages:

- Commercial inks characterization, to outline the prerequisite properties of stable photocatalytic inks (rheological properties, composition, structure and functional groups, stability);
- Photocatalytic ink formulation: (a) photocatalysts synthesis, and (b) photocatalytic dispersion preparation followed by stability studies;
- Photocatalytic efficiency evaluation for: (a) powders, (b) inks, and (c) thin films deposited from inks on cotton fabrics and on glass.

2.1. Properties of commercial inks

2.1.1. Materials

Four commercial aqueous pigment inkjet inks used in the digital textile printing, with specific colours (yellow, magenta, cyan, black) were investigated in this work. The chemicals were provided by BASF Chemical Company and were used without further purification.

2.1.2. Materials and thin films characterization

The macroscopic physicochemical properties were studied by measuring the density (laboratory pycnometer), the conductivity and pH (Handylab pH/conductivity metre, Schott), the viscosity (rotational viscometer Fungilab, LCP spindle, 100 rpm), and the surface tension (laboratory stalagmometer).

To evaluate the dry solid content, specific amounts of ink (≈ 1 g) were weighted and dried in the oven at 115 °C. Successive drying and weighting cycles were applied until the samples were brought to a constant mass.

The FTIR spectrometry (Spectrometer Vertex V70, Bruker = 600…4500 cm^{-1}, 4 cm^{-1} resolution) was used to obtain basic information on the functional groups in the tested inks, while the UV–Vis transmittance spectra (UV–VIS–NIR spectrometer, Perkin Elmer Lambda 25) were used to evaluate the stability.

2.2. Preparation and characterization of the photocatalytic dispersions

2.2.1. The photocatalytic powders

Two photocatalysts were used as powder to develop dispersions: TiO_2 Degussa P25 (Evonik, Germany) and titanium dioxide prepared via ultra-sonication assisted sol–gel method.

The chemicals used in the sol–gel synthesis were: titanium tetraisopropoxide, TTIP, $Ti[OCH(CH_3)_2]_4$, (97.0%, Sigma-Aldrich); ethanol, C_2H_5OH (99.8%, Chimreactiv), acetylacetone, $C_5H_8O_2$ (99.9%, Alfa Aesar), acetic acid, CH_3COOH (99.8%, Scharlau Chemie).

TiO_2 sol–gel synthesis: the TTIP precursor in the TiO_2 sol–gel synthesis was dissolved in ethanol, followed by the successive addition of acetyl acetone, acetic acid and water under vigorous magnetic stirring, in the volume ratio: TTIP:EtOH:AcAc:HAc:W = 3:5:0.26:0.1:0.6. Acetic acid was used as catalyst, while acetylacetone was added as chelating agent to control the hydrolysis process. The sol was sonicated for 1 h, then aged at room temperature for 48 h, and dried in an oven at 115 °C for 2 h. The resulted powder was annealed at 550 °C for 5 h to eliminate the organic volatile compounds. An increase in the powder crystallinity is also expected.

Photocatalyst characterization: the crystalline structure of the sol–gel powder was investigated using X-ray diffraction (Bruker D8 Discover Diffractometer) and the crystallite dimensions were evaluated by introducing the half-width of the characteristic peaks for anatase and rutile in the Scherrer formula.

The morphological characteristics were investigated using atomic force microscopy (AFM Ntegra Spectra, NT-MDT model BL222RNTE) and scanning electron microscopy (SEM S-3400 N-Hitachi with EDX, Thermo). Energy dispersive X-ray was used to outline the surface elemental composition. Nitrogen adsorption–desorption isotherms were measured at 77 K (Autosorb IQ-MP, Quantachrome analyser) and were used to evaluate the specific/BET surface for the sol–gel TiO_2 and Degussa P25 powders.