6. PHOTOCHEMISTRY

6.1. Lectures

L01 EPR AND UV/VIS STUDY ON PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE POWDERS

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Introduction

The detoxification of polluted water by semiconductor photocatalysis based on the photoexcitation of titanium dioxide is nowadays accepted as promising technique also for industrial applications.^{1–3} The degradation of a variety of toxic organic contaminants is initiated by non-selective attack of hydroxyl radicals generated upon ultra-band gap irradiation of TiO₂.

Our investigations are oriented on monitoring the photogenerated paramagnetic intermediates in titanium dioxide suspensions by Electron Paramagnetic Resonance (EPR) spectroscopy. The quantum efficiency of UVA-induced photocatalytic processes was evaluated.

Experimental

Titanium dioxide Aeroxide[®] P25 kindly provided by Degussa Company (Evonik Degussa, Germany) was used in all experiments. The formation of free radical species upon irradiation of TiO₂ suspensions in aerated aqueous media was monitored using spin trapping agents 5,5-dimethyl-1-pyrroline N-oxide (DMPO; Aldrich) and 5-(diisopropoxy-phosphoryl)-5-methyl-1-pyrroline N-oxide (DIPPMPO; Alexis[®] Biochemicals). Semi-stable free radicals 4-hydroxy-2,2,6,6tetramethylpiperidine N-oxyl (Tempol), cation radical of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS⁺⁺) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) were also used to monitor TiO₂ photocatalytic activity by a continuous decrease of radical concentrations upon irradiation.

UV/VIS Spectra of Titanium Dioxide Suspensions

UV/VIS spectra of TiO₂ aqueous suspensions in the wavelength interval 240–600 nm were recorded using a UV/VIS spectrometer UV-3600 (Shimadzu, Japan) with a large integrating sphere assembly using transmittance measurement accessory. TiO₂ suspensions with low concentrations $(0.01-0.1 \text{ mg TiO}_2 \text{ ml}^{-1}, \text{ i.e.}, 1 \times 10^{-5} \text{--}1 \times 10^{-4} \text{ g cm}^{-3})$ were used in UV/VIS experiments. Titania suspensions prepared instantly before recording UV/VIS spectra were sonicated

1 minute (Ultrasonic Compact Cleaner TESON 1, Tesla, Slovak Republic), and then UV/VIS spectra were measured in duplicate. The suspensions were not stirred during spectrophotometrical measurements. The values of absorption and scattering coefficients at the individual wavelengths ($\Delta l = 5$ nm) were evaluated from the experimental data by a least-squares minimization procedure (Scientist[®], Micro-Math) using Kubelka-Munk model of diffuse reflectance and transmission in accordance with refs.^{4,5}.

EPR Photochemical Experiments

The suspensions of TiO₂ containing spin trapping agents (DMPO and DIPPMPO) or semi-stable radicals (Tempol, ABTS⁺⁺ and DPPH) were prepared instantly before EPR measurements. The stock TiO₂ suspension (1 mg ml⁻¹) was homogenized in ultrasonic bath for 1 minute before dilution to final concentration of $0.5 \text{ mg TiO}_2 \text{ ml}^{-1}$. Then the suspensions were carefully mixed by slight air stream and immediately transferred to a small quartz flat cell (WG 808-Q, Wilmad-LabGlass, USA; optical cell length 0.045 cm) optimized for the TE₁₀₂ (ER 4102 ST) rectangular EPR cavity (Bruker, Germany). The samples were irradiated at 295 K directly in the EPR resonator, and EPR spectra were recorded in situ using EMX X-band EPR spectrometer (Bruker). As an irradiation source HPA 400/30S lamp (400 W, Philips; UVA irradiance of 5 mW cm⁻²) was used. A Pyrex glass filter (thickness of 1 mm) was applied to eliminate radiation wavelengths below 300 nm. The first spectrum in the time-course of EPR spectra was measured without radiation, and subsequently we started the exposure, monitoring ten spectra upon continuous irradiation.

Results

UV/VIS Spectra of Titanium Dioxide Suspensions

The spectrophotometrically monitored extinction in heterogeneous titanium dioxide aqueous suspensions represents combination of absorption and scattering phenomena caused by particles. Fig. 1 shows the experimental extinc-



Fig. 1. The set of UV/VIS spectra measured in aqueous suspensions of Aeroxide[®] P25 with increasing concentration. The numbers specify TiO2 concentration in 10^{-5} g cm⁻³

tion spectra of Aeroxide[®] P25 in aqueous suspensions with increased concentrations measured in wavelength interval 240–600 nm.



Fig. 2. The dependence of extinction at selected wavelengths upon product of TiO₂ concentration and cell length obtained for Aeroxide[®] P25 aqueous suspensions. The symbols represent experimental data and dotted lines were evaluated by least-squares minimization procedure using Kubelka-Munk absorption and scattering model



Fig. 3. Experimental (-) and simulated (--) EPR spectra obtained in aerated irradiated Aeroxide[®] P25 suspensions in the presence of spin trapping agents DMPO and DIPPMPO. Magnetic field sweep: a) 7 mT; b) 15 mT

The structure of Aeroxide® P25 sample comprises a mixture of crystalline polymorphs with 80 % anatase and 20 % rutile³. The energy band gap value of anatase ($E_{bg} = 3.2 \text{ eV}$), and rutile ($E_{bg} = 3.02 \text{ eV}$) correspond to absorption threshold at 384 and 410 nm, respectively. Consequently, extinction observed in the visible region, originates exclusively from the scattering on titania nanoparticles. It should be noted here that the extinction data observed for wavelengths 1>410 nm are in good accordance with Rayleigh scattering (extinction = $k \times 1^{-4}$). The extinction spectra of Aeroxide[®] P25 measured at various loadings were used for numerical evaluation of absorption and scattering coefficients at individual wavelength in accordance with Kubelka-Munk model of diffuse reflectance and transmission^{4,5}. Our experiments confirmed a significant contribution of scattering phenomena in the region 240-400 nm, in accordance with previously published results.⁶ The values of absorption and scattering coefficients calculated from the extinction data were used for the construction of UV/VIS absorption and scattering spectra of Aeroxide[®] P25 in the wavelength interval 240–600 nm.

The sets of experimental results obtained at 310, 365, 405 and 500 nm, along with corresponding fittings to Kubelka-Munk model illustrates Fig. 2. The calculated absorption spectra of Aeroxide[®] P25 was used to find amount of absorbed UV radiation (300–400 nm) under the given experimental conditions (incident radiation flux in EPR cavity 6.6×10^{-8} Einstein s⁻¹; absorbed radiation flux 6.5×10^{-9} Einstein s⁻¹). Finally the quantum efficiency of photoinduced radical processes monitored by *in situ* EPR spectroscopy was evaluated⁷.

Photochemical In Situ EPR Experiments

The photoinduced formation of reactive oxygen-centered free radicals in the aerated aqueous suspensions of Aeroxide[®] P25 was investigated using EPR spin trapping technique, a method for indirect detection of short-living radicals. Upon UV irradiation of aerated TiO₂ suspensions in the presence of DMPO, typical four-line EPR spectra were monitored, which are characterized with spin Hamiltonian parameters $a_{\rm N} = a_{\rm H}^{\ \beta} = 1.49$ mT and g = 2.0058, and are representative of the hydroxyl radical added to DMPO ('DMPO-OH; Fig. 3.a). The formation of hydroxyl radical adducts was evidenced also using DIPPMPO, as during photoexcitation of P25 in aqueous media dominates EPR spectrum with $a_{\rm N} = 1.407$ mT, $a_{\rm H}^{\ \beta} = 1.320$ mT, $a_{\rm p} = 4.665$; g = 2.0058, characteristic of hydroxyl radical adduct ('DIPPMPO-OH; Fig. 3.b).

The paramagnetic signals of 'DMPO–OH may be produced directly by the addition of photoproduced hydroxyl radicals. However, we cannot exclude an alternative mechanism assuming spin trap oxidation by photogenerated holes to cation-radical DMPO⁺⁺, which hydrolyses in the aqueous media to 'DMPO–OH without direct hydroxyl radical formation⁸. The formal initial rate of photoinitiated 'DMPO–OH formation was evaluated from double integrated EPR spectra monitored upon continuous UV exposure. The data obtained were used for the calculation of quantum efficiency of 'DMPO–OH formation ($\eta_{\text{-DMPO-OH}} = (7.6 \pm 0.8) \times 10^{-4}$).

The photoinduced elimination of semi-stable free radicals (Tempol, DPPH, ABTS⁺⁺) in titanium dioxide suspensions represents an alternative technique of photoactivity testing⁸.

The principle of the detection of reactive free radical formation using Tempol is based on monitoring the decrease in EPR intensity resulting from the interaction of its $>N-O^{\circ}$ group with the photogenerated reactive radical species, as well as singlet oxygen⁹. The EPR spectrum of Tempol under the given experimental conditions presents a three-line signal characterized by hyperfine splitting $a_N = 1.70$ mT and g = 2.0060. The decrease of Tempol concentration monitored upon irradiation in aerated aqueous suspension of Aeroxide[®] P25 was described by the formal first-order kinetic model (Fig. 4.), and the evaluated initial rate was used in the calcu-



Fig. 4. Changes in concentration of semi-stable radicals monitored upon irradiation of Tempol, DPPH and ABTS⁺⁺ in Aeroxide[®] P25 suspensions. The symbols represent experi¬mental data and dotted lines were evaluated by least-squares minimization procedure using first-order kinetic model

lation of photocatalytic process quantum efficiency ($\eta_{Tempol} = 0.0013 \pm 0.0001$).

The photocatalytic experiments with DPPH were due to its lower water solubility performed in mixed water/ethanol (1:1; v/v.) solvent. We observed limited photochemical stability of DPPH upon irradiation also in TiO₂-free solutions, but the addition of Aeroxide[®] P25 considerably increased the rate of DPPH termination (Fig. 4.). It should be noted here that the mechanism of DPPH photocatalytic decomposition may be very complex, as DPPH molecules are capable of reacting with photogenerated electrons and hydroxyl radicals simultaneously. Probably, also from ethanol photogenerated hydroxyethyl radicals may react with DPPH producing diamagnetic products, and, consequently, the evaluated value of quantum efficiency reached the highest value ($\eta_{DPPH} = 0.02$ 2 ± 0.002).

The EPR spectrum of ABTS⁺⁺ is characterized by a complex hyperfine structure, but the higher value of the modulation amplitude used in the EPR spectrometer settings facilitates monitoring it as a single-line signal (g = 2.0036). The irradiation of ABTS⁺⁺ in aqueous suspensions of Aeroxide[®] P25 caused efficient elimination of paramagnetic signal (Fig. 4). Our previous UV/VIS investigations of photoinduced ABTS⁺⁺ reaction in TiO₂ suspensions confirmed the decrease of ABTS⁺⁺ selective absorption bands at 735 and 415 nm, coupled with the simultaneous growth of ABTS

absorption at 340 nm. These data are in good correlation with photocatalytic reduction of cation-radical ABTS⁺⁺ to ABTS.⁸ The initial rate of ABTS⁺⁺ reduction evaluated from EPR spectra monitored upon irradiation in P25 aqueous suspensions served as a basis for computation of quantum efficiency ($\eta_{ABTS}^{++} = 0.011 \pm 0.001$).

Conclusions

Kubelka-Munk analysis of UV/VIS spectra measured in aqueous TiO₂ suspensions confirmed significant contribution of Aeroxide[®] P25 scattering in ultra-band gap wavelength interval 240–400 nm; the extinction data observed for wavelengths 1 > 410 nm are in good accordance with Rayleigh scattering on nanoparticles. EPR spin trapping technique and semi-stable radical eliminations were used to monitor photoinduced generation of reactive radical intermediates in Aeroxide[®] P25 suspensions, and the differences in evaluated quantum efficiencies reflected the variation of photocatalytic reaction mechanisms.

Dedicated to Prof. Andrej Staško on the occasion of his 70th birthday.

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L02 PHOTOCATALYTIC DEGRADATION OF FORMIC ACID ON TIO, THIN LAYERS

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Introduction

Environmental pollution is becoming more and more serious. Catalysis under UV irradiation, called photocatalysis, is attracting a great deal of attention from environmental purification point of view¹. Titanium dioxide (TiO₂) photocatalysis has been focused on the elimination of toxic and hazardous organic substances and metals in wastewater, drinking water and air, which is important for the protection of the environment². Heterogenous photocatalysis is a process based on the excitation of a semiconductor by light of energy equal to or higher than the bynd gap one. This excitation generates electron-hole pairs which can give rise to redox reactions with species adsorbed on the catalyst surface³. Among the warious semiconductors, TiO₂ is the most suitable photocatalyst because of its high activity, photostability and availability. Anyway, serious practical problems arise from the use of TiO₂ powders in the photocatalytic process – the need for post treatment separation in a slurry system. A key technology for the practical application of photocatalysis to environmental problems is the immobilization of TiO₂ as thin film on a solid substrate (even if normally the film-type photocatalysts have low surface areas and their intrinsic photocatalytic activity is usually smaller than of the powders).

 TiO_2 films have been often prepared by expensive methods as pulsed laser deposition, reactive evaporation and chemical vapour deposition. Low cost preparation methods are the sol-gel process including dip-coating, spin-coating and micropiezo jet as the final step of preparation. Sol-gel method usually requires a thermal post-treatment in order to eliminate organics present in the films or to induce crystallization of the deposited material. An important requirement for improving the TiO_2 photocatalytic activity is to increase its specific surface area, which is certainly dependent on the crystal size. It is known that the smaller the catalyst is, the larger will be its specific surface area. Nevertheless, if the particles are very small, the charge carrier recombination is more probable. Thus the particle size must be optimized.

Formic acid (FA) was choosen because of simple mechanism of degradation: it undergoes a direct mineralisation to CO_2 and H_2O without the formation of any stable intermediate species⁴. Moreover, it also represents a possible final step in the photodegradation of more complex organic compounds.

Experimental

Preparation of TiO, Thin Films

Borosilicate glass plates $(30 \times 30 \times 2 \text{ mm})$, Verre Equipements, France) were chosen as a substrate for immobilization of TiO₂ thin films. TiO₂ layers were prepared using following organometallic precursor in sol-gel process: a mixture of absolute ethanol (85 ml) and acetylacetone (3.8 ml) was added to titanium(IV) propoxide (10.3 ml) under continuous stirring, a small amount of water (0.69 ml) in ethanol was dropped at last to the previously mixed solution.

Depositions of thin films were realized by dip-coating method (withdrawal speed 120 mm min⁻¹) and by micropiezo jet. In the case of micropiezo jet one cartidge of desk-top printer (EPSON R220) was filled with sol. The substrate was fixed into the holder for CD and it was printed by sol. It was possible to choose the area covered of substrate by sol or the quality of printing. The amount of printed precursor (i.e layer thickness) was determined by the gray level (dot area) of printed images. We used 2 printing speeds: slow at 720 DPI and rapid one at 360 DPI. These values are given by the printer driver setup. In the next stage, the coated substrates were dried for 30 min. at 110 °C and then calcinated for 4 hours at 450 °C with temperature ramp of 3 °C min⁻¹ which allowed us to obtain TiO₂ predominantly in anatase form.

Fig. 1. Picture from optical microscope, TiO_2 thin films prepared by dip coating method. 2 layers at the edge (upper) and 4 layers at the edge (down)

Formic Acid Photocatalytic Degradation

The formic acid reaction solution was prepared with initial concentration of 20, 50, 100, 200 and 400 mg dm⁻³. The degradation process took place at ambient temperature in a Pyrex reactor (100 ml) with 30 ml of reaction solution under constant stirring. Before the reaction, the FA solution in the reactor was stirred during 30 min in obscurity to reach the solution adsorption equilibrium in contact with TiO₂ surface. During the FA photocatalytic oxidation with concentration ranging from 20 to 400 mg dm⁻³, 0.5 ml of reaction solution was sampled every one hour for HPLC analysis. The total reaction time was 7 h. The UV irradiation was provided by high pressure mercury lamp (Philips HPK–125 W).

In order to determine the kinetic behavior of formic acid degradation on TiO_2 films, the initial reaction rate was estimated up to 120 min of irradiation time. The obtained values of reaction rate for various FA initial concentrations were treated using Langmuir-Hinshelwood (L-H) model.

$$v = \mathbf{k} \cdot \boldsymbol{\theta} = \frac{\mathbf{k} \cdot \mathbf{K} \cdot \boldsymbol{c}}{1 + \mathbf{K} \cdot \boldsymbol{c}}$$
, (per gram of photocatalyst) (1)

where k is the rate constant, θ is coverage degreese of surface active sites, K is adsorption constant and *c* is the initial concentration of reagents in the solution⁵.



Fig. 2. Picture from optical microscope, TiO₂ thin films prepared micropiezo jet by rapid (upper) and slow (down) mode

Results

Characterization of TiO₂ Thin Films Prepared by Optical Microscope

The TiO₂ thin films deposited on the borosilicate glass plates were optically transparent and they adhered well to the glass substrate after the calcination process. In the case of TiO₂ layers prepared by dip-coating method, the layers are homogenous and without cracks in the middle of a coated surface, whereas the homogeneity gets worse towards the edge of glass. The TiO₂ film quality slightly decreased with increasing layer number, in the case of 4 layers some cracks is appeared in the film structure (Fig. 1.).

The second method for preparation TiO_2 thin films was the newly adopted picropiezo jet. Surface morfology of prepared thin film greatly depends on the print setting. The TiO_2 prepared by micropiezo jet by rapid mode have smooth and flat surface, cracks are observed when sol loading exceeded 90% dot area. On the other hand, the layers prepared by slow mode are uneven and discontinuous (Fig. 2.).

Degradation of Formic Acid in Aqueous Phase

At first we will discused TiO_2 thin films prepared by dipcoating method. The reaction rate constants k depend strongly on TiO_2 layer number (i.e. layer thickness) whereas the adsorption constants decrease. The same behaviour we observed for two values of irradiance (7.7 and 4.6 mW cm⁻²). The thicker TiO_2 film effectively absorbs the radiation, the holes can better oxidize FA (Fig. 3.).



Fig. 3. Comparison of Langmuir-Hinshelwood parameters for different intensity of irradiance

We observed the same characteristics in the case of thin films prepared by micropiezo jet (Fig. 4.). The photocatalytic activity grows with the value of dot area. It is caused by the growing amount of deposited TiO_2 and the thickness of TiO_2 thin film. Roughness of surface has a positive influence on the adsorption of FA on the surface of TiO_2 . We observed decrease of adsorption constant for 60 % slow mode. It could be induced by too low coverage of substrate by TiO_2 .



Fig. 4. Comparison of Langmuir-Hinshelwood parameters for TiO₂ thin films prepared by picropiezo jet

From the L-H model (1) we calculated the coverage of surface active sites θ by FA for different FA initial concentration (Table I and Table II). We can see that the pollutant adsorption on TiO₂ surface increased with increasing FA concentration. We observed a decrease in FA adsorption with increasing number of TiO₂ layers or sol loading. It almost achieved the value of 1 for FA initial concentration of 8.7 mmol dm⁻³. That is nearly all active sites on TiO₂ surface were covered by FA molecules, which correlates well with obtained L-H kinetic behavior.

Table I

The coverage degree for different FA initial concentration, different iirradiance and for (1-4) TiO₂ layers

c FA[mmol	7.7 mW cm ⁻²			4.6 mW cm ⁻²		
dm ⁻³]	1	2	4	1	2	4
8.7	0.95	0.94	0.91	0.95	0.93	0.88
4.3	0.90	0.89	0.83	0.90	0.86	0.79
2.1	0.82	0.81	0.71	0.82	0.76	0.65
1.1	0.70	0.67	0.55	0.69	0.61	0.48
0.4	0.48	0.45	0.32	0.47	0.39	0.27

Table II

The	coverage	degree	for	different	FA	initial	concentration
and	for TiO ₂ th	nin films	s pre	pared by	mic	ropiezc	jet

c FA[mmol		Rapid			Slow	
dm ⁻³]	100%	80%	60%	100%	80%	60%
8.7	0.81	0.83	0.85	0.91	0.92	0.92
4.3	0.68	0.71	0.74	0.83	0.85	0.85
2.1	0.51	0.55	0.59	0.71	0.73	0.74
1.1	0.34	0.38	0.42	0.55	0.58	0.59
0.4	0.17	0.19	0.22	0.32	0.35	0.37

Conclusions

We prepared TiO_2 thin layers on borosilicate glass plates by dip coating method a newly by micropiezo jet. TiO_2 thin films prepared by dip-coating method are homogenous and transparent as well as films prepared by micropiezo jet by rapid mode. In the case of TiO_2 thin films prepared by slow mode, the layers are uneven and discontinuous, partial coverage of substrate with and without TiO_2 is observed.

The photocatalytic efficiency of prepared coatings was evaluated by the photooxidation of FA. The kinetic parameters of FA disappearance, reaction rate constant and adsorption constant, corresponded to Langmuir-Hinshelwood behavior. It was found that the photocatalytic activity grows with the value of dot area or number of layers (i.e. thickness of film).

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L03 KINETIC OF DEGRADATION OF HISTORICAL DOCUMENTS CONTAINING IRON-GALL INKS

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Introduction

Deterioration of paper documents containing iron-gall inks is supposed to be a combination of two degradation pathways – acid hydrolysis of cellulose and oxidative degradation of cellulose. Iron gall inks contain transition metals, such as iron and copper, catalyzing the radical oxidation of the substrate, as well as acids, catalyzing its hydrolysis^{1,2}. Transition metals are capable to enter Fenton and Fenton-like type of reactions^{3,4} and catalyze homolytic decomposition of peroxides with production of hydroxyl radicals. Hydroxyl radicals can oxidize cellulose and induce degradation of cellulose⁵.

Content and ratio of transition metals in historical irongall inks recipes vary. In addition to iron the most notable transition metal is cooper and the molar ration of the iron cooper to iron in these recipes get the value up to 0.7(ref.⁶). It was found that even trace amounts of cooper induce significant destruction of paper substrate⁷. The catalytic action of cooper in Fenton and Fenton-like reactions predominate over the catalytic action of iron^{6,8} and the catalytic action of iron and cooper is additive⁶.

The influence of transitional metals in iron-gall inks on the rate of degradation and change of optical properties of aged model documents were studied in this paper.

Experimental

Model ink systems were prepared according to the suggestion of Neevel². The molar ratio of transition metal:tannine (5.5:1) and the amount of gum arabic $(4.71 \text{ g} 150 \text{ ml}^{-1})$ were kept constant. Seven model inks with the ratio of copper:iron 0 (without cooper), 0.025, 0.05, 0.10, 0.25, 0.40 (A1–A6) and model ink containing only Cu without iron (A7) were used in this study. Used chemicals: tannic acid (Sigma Aldrich), ferric sulphate heptahydrate (Lachema, Czech Rep.), cupric sulphate pentahydrate (Lachema, Czech Rep.), gum arabic (Sigma-Aldrich), cupriethylene-diamine (Sigma-Aldrich), deionised water. Water solutions of inks were applied on substrate after 15 days free staying in dark.

Whatman filter paper No. 1 (purified cotton linter cellulose) was used as a model substrate. Using a computer-guided plotter with a refillable plotter pen each ink was applied in rectangles (12×5 cm) and then left to dry at room temperature. The average ink amount per sample was 0.008 g cm⁻². Samples with pH values lying in four different regions (~ 3, ~ 4, ~ 5, ~ 6) were obtained by short immersion (2–3 s) of inked paper samples into the diluted solutions of sodium hydroxide (from 0.25M to 0.40M, as appropriate for particular sample to obtain required pH)). The samples were submitted to accelerated ageing in closed vessels at 90 °C according to the method described by Lojewski and Baranski⁹.

The degree of polymerization (DP) of samples was determined viscometrically using cupriethylene-diamine as a solvent¹⁰. Degree of polymerization was calculated from viscometric data using Mark-Houwink-Sakurada equation and the constants according to Evans and Wallis^{11,12}. Rate constants "k" of degradation of paper samples was calculated by least squares fitting of the plot DP vs. time using Ekenstam equation for degradation of linear polymers¹³:

$$(1/DP_t) = (1/DP_o) + k t$$
 (1)

where DP_t and DP_o are degrees of polymerization at the beginning of ageing and after time "t" of ageing, respectively.

Colorimetric measurements were performed using spectrocolorimeter GretagMacbeth Spectrolino keeping the standard condition for graphic arts measurements (geometry 45/0, D50 illumination, 2° standard observer, measurement without polarizing filter, black background) according to the standard¹⁴. Standard error of the colorimetric measurements was less than 1.0 (in ΔE^*_{ab}).

Results and Discussion

The rates constants of degradation of samples containing model inks at various pH are shown on the Fig. 1.



Fig. 1. Rate constants of degradation vs. ratio Cu : Fe (A1-A7) and pH

The rate constants of degradation are significantly higher at the pH value around 3, the ratio Cu: Fe in inks does not significantly affect the rate of degradation. With increasing pH the rate of degradation descends and depends on the ratio Cu: Fe in inks. Samples with higher content of copper in the inks exhibit higher constant of degradation at the same pH value.

The color changes of selected samples during ageing are on the Fig. 2.



Fig. 2. Samples of inks (A1, A3, A6) at the ageing time of 0, 1, 2, 3, 4 and 24 hours, pH 3

The colorimetric changes of the samples during ageing can be summarize as follow. CIE Lab lightness of samples aged at the pH range 3 increases with prolonged ageing and this bleaching is steepest for the samples with higher content of copper (Figs. 3.–5.). At the same time CIE Lab chroma increases from small initial values (1.8) to the values up to 20 and CIE Lab hue angle is shifted from 280 ° to 76 ° (corresponds to the shift from grey to brown-yellowish color). More significant changes of chroma and hue angle during ageing were observed for the samples with higher content of cooper. The nature of these changes suggests that oxidative reactions of the iron-gall ink take place in addition to the degradation of cellulose fibers.



Fig. 3. Changes of colorimetric parameters (CIELab) during ageing; sample A1, pH 3

Colorimetric changes of samples aged in higher pH ranges follow the above trend, but were less significant (color difference $DE^*_{ab} < 3.5$). Lower extend of changes of color corresponds to the lower rate of degradation in these pH ranges

In order to asses the role of hydrolytic degradation and the catalytic influence of transitional metals, the rate constants of degradation of pure substrate (Whatman paper) without ink deposition at various pH were determined (Fig. 6.).

As follows from the Figs. 6 and 7., the degradation of the samples containing iron gall inks is significantly higher than the degradation of samples of the pure substrate



Fig. 4. Changes of colorimetric parameters (CIELab) during ageing; sample A3, pH 3



Fig. 5. Changes of colorimetric parameters (CIELab) during ageing; sample A6, pH 3

of the same pH. While the increasing of pH value of pure substrate to 3 increased the rate constant of degradation about 4-times, the change of pH value from 6 to 3 for the sample with ink A1 increased the rate constant of degradation about 20-times. This can be considered as evidence, that the accelerated degradation of samples containing transitional metals is not caused simple by increased acidity but that specific degradation reactions of cellulose fibers catalyzed by transitional metals play significant role.

Conclusions

The rate of degradation of samples of paper with irongall inks containing copper and iron in various ratios is the highest at the lowest pH values (around 3) and the value of rate constant of degradation does not depend significantly on the content of cooper in the ink in this pH range. Rate of degradation of the samples in less acidic regions is lower and depends on the content of cooper. The degradation of samples



Fig. 6. Rates constants of degradation of substrate (Whatman paper) without ink deposition at various pH and without pH adjustment (natural substrate)

with inks with higher ratio copper: iron is faster, what may be caused by more significant oxidative degradation.

Accelerated degradation of samples containing transitional metals is not caused simple by increased acidity but that specific degradation reactions of cellulose fibers catalyzed by transitional metals play significant role.

Changes of colorimetric parameters during degradation of studied samples provide further indication of the running oxidation reactions.

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Fig. 7. Rate constants of samples from Fig. 6 compared with rate constants of degradation of sample A1

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L04 PHOTOCHEMICAL TRANSFORMATION OF ANTICANCER DRUG IRINOTECAN

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Introduction

The camptothecin family of anticancer medicines has a unique mechanism of action directed to the inhibition of topoisomerase I (Topo I). It was previously shown that camptothecin (CPT) inhibits Topo I via the formation of ternary complex, in which the biologically active lactone ring of CPT stabilizes an irreversible Topo I/DNA covalent complex. Camptothecin molecule contains conjugated system of π -electrons representing a potential basis for UVA photoexcitation resulting in the reactive free radical species generation (e.g., ROS - Reactive Oxygen Species), which are responsible for lightmediated DNA cleavage. Consequently, alternative mechanisms of DNA damage upon the simultaneous application of CPT, Topo I and UV radiation ($\lambda = 365$ nm) were considered. A number of photoactive compounds require the contribution of a metal ion for the DNA cleavage event, therefore the biological activity of irradiated CPT has been tested also in the presence of Cu(II) ions^{1,2}. Our previous investigations were oriented on study of interaction of CPT with Cu(II) and Fe(III) ions upon irradiation. The results obtained confirm the participation of these ions in the photoinitiated activation of camptothecin accompanied with the formation of reactive radical species^{3,4}.

Irinotecan (CPT-11 or Camptosar[®]) is a watersoluble semisynthetic analogue of the natural alkaloid camptothecin. The structure of CPT-11 is shown in Fig. 1.



Fig. 1. Structure of irinotecan (CPT-11)

Irinotecan is a pro-drug, converted *in vivo* to its active metabolite. CPT-11 interfere with Topoisomerase I and cancer cells death appears to result from DNA strand breaks caused by the formation of cleavable complexes.

Our investigation was focused on photochemical transformations of CPT-11 in aqueous and dimethylsulfoxide (DMSO) solutions, and on its photoactivation in the presence of equimolar amounts of Cu(II) ions monitored by EPR spectroscopy.

Experimental

Irinotecan hydrochloride (CPT-11, Fig. 1) and cupric chloride were applied in photochemical experiments. 5,5-Dimethyl–1-pyrroline N-oxide (DMPO) and α -(4-pyridyl-1-Oxide)-N-*tert*-butylnitrone (POBN) were used as spin trapping agents, 2,2,6,6-tetramethyl-4-piperidinol (TEM-POL) was applied as spin label. The selective oxidation of 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP) *via* singlet oxygen to the paramagnetic nitroxyl radical oxyl (TEMPOL) was utilized for ¹O₂ detection by EPR spectroscopy.

The stock solutions of CPT-11 and CuCl₂ (both 2×10^{-3} mol dm⁻³) were prepared in redistilled water or dimethylsulfoxide. The CPT-11 (150 µl) were mixed with identical volume of solvent (water or DMSO) or 150 µl Cu(II) ions (to obtain equimolar solution CPT-11: Cu(II)) and 50 µl of aqueous or DMSO solutions of spin traps/spin label were added prior to irradiation. The prepared solutions were saturated by argon or air, filled in the quartz flat cell optimized for the Bruker TE₁₀₂ EPR cavity.

The X-band EPR spectra were recorded at EPR Bruker EMX spectrometer equipped with a TE₁₀₂ (ER 4102ST) resonator. Samples were irradiated at 295 K *in situ* using HPA 400/30S lamp (400 W, $\lambda_{max} = 365$ nm, Philips, UVA irradiance 10 mW cm⁻²). A Pyrex glass filter was applied to eliminate the radiation wavelengths below 300 nm. The simulations of the individual components in the complex EPR spectra were calculated using WinEPR and SimFonia programs (Bruker). The experimental EPR spectra were fitted as the linear combinations of these individual simulations using a least-squares minimization procedure with the Scientist Program (MicroMath).

Results

The EPR spin trapping technique enables to evidence reactive short-lived free radicals adding them to spin trapping agent under the formation of more stable paramagnetic products (spin adducts). The EPR spectrum of adducts brings information on type of reactive radical trapped.

DMPO. The dimethylsulfoxide solvent is well known for its ability to stabilize super-oxide anion radical. The EPR spectra measured after 10 min of irradiation of CPT-11 in DMSO solutions under air in the presence of DMPO confirmed the formation of two radical adducts (Fig. 2.). The spin Hamiltonian parameters of EPR signals obtained by simulation analysis revealed the generation of 'DMPO- O_2^- , characterized by hyperfine splittings $a_N = 1.274$ mT, $a_H^{\beta} = 1.035$ mT, $a_H^{\gamma} = 0.137$ mT and g-value = 2.0058(ref.⁵). This EPR signal dominates in the experimental spectrum (relative concentration 80 %), and is produced immediately after beginning of irradiation. Additionally, a minor EPR signal was observed, attributed to 'DMPO-OCH₃ adduct ($a_N = 1.330$ mT, $a_H^{\beta} = 0.794$ mT, $a_H^{\gamma} = 0.155$ mT and g-value = 2.0058)⁵.



Fig. 2. Experimental (solid line) and simulated (dotted line) EPR spectra (magnetic field sweep 7.5 mT) obtained after 10 minutes of a continuous irradiation of system CPT-11/DMPO/ DMSO/air. Initial concentration: c_0 (CPT-11) = 0.86 mmol dm⁻³ and c_0 (DMPO) = 30 mmol dm⁻³

The formation of superoxide anion radicals upon photoexcitation of CPT-11 in DMSO solvent was unambiguously confirmed by the addition of enzyme superoxide dismutase (SOD) into the solution, which caused a significant decrease of $DMPO-O_2^-$ EPR intensity by the competitive reaction of SOD with O_2^{--} .

The production of 'DMPO–OCH₃ adduct was established previously in aerated DMSO systems producing oxygencentered free radicals ($O_2^{\bullet-}$, 'OH). Probably, the generation of this minor adduct reflected the reaction of ROS with solvent producing 'CH₃ radicals, which are in the presence of molecular oxygen transformed to CH₃OO[•] and trapped as 'DMPO–OCH₃.

It should be noted here that the application of DMPO was not possible in systems containing Cu(II) ions and DMSO solvent, due to the formation of paramagnetic species even after mixing of individual solutions before irradiation, so the identification of photo-induced radical adducts was limited.

TEMPOL. The principle of the detection of reactive free radical formation using TEMPOL and its derivatives is based on monitoring the decrease in its EPR intensity resulting from the interaction of its $>N-O^{\circ}$ group with the generated reactive radical species, as well as singlet oxygen (Eqs. 1–4)⁶:

 $>N-O^{\bullet}+^{\bullet}OH \rightarrow >N^{+}=O+OH^{-}$ (1)

$$>N-O'+OH \rightarrow >NOOH \rightarrow >NH+O_2$$
 (2)

$$>N-O'+R \rightarrow >NO-R$$
 (3)

$$>N-O' + {}^{1}O_{2} \rightarrow \text{products and/or quenching}$$
 (4)

The EPR spectrum of TEMPOL in DMSO solvent in the presence of oxygen represents three-line signal characterized with hyperfine splitting $a_N = 1.573$ mT and g = 2.0060, as il-

lustrates inset in Fig. 3.a. Irradiation of TEMPOL in DMSO solution under air or argon confirmed its photochemical stability under given experimental conditions, as only negligible decrease of EPR signal was observed. The situation was similar if TEMPOL was irradiated in the presence Cu(II) ions. However, the addition of CPT-11 to the reaction system under air or argon led to the decrease of TEMPOL signal.



Fig. 3. TEMPOL relative concentration monitored upon continuous irradiation (λ >300 nm) of DMSO solutions in the presence CPT-11 and/or Cu(II) ions (c_0 (TEMPOL) = 43 µmol dm⁻³) under air (a) and argon (b). Inset represents experimental and simulated EPR spectrum of TEMPOL in DMSO (magnetic field sweep 6 mT). Initial concentrations of CPT-11 and Cu(II) ions (in mmol dm⁻³): $\blacksquare c_0$ (CPT-11) = 0, c_0 (Cu(II)) = 0; • c_0 (CPT-11) = 0, c_0 (Cu(II)) = 0.86; $\blacktriangle c_0$ (CPT-11) = 0.86; c_0 (CPT-11) = 0.86

The addition of equimolar amount of Cu(II) ions into CPT-11 solution and subsequent irradiation led to the decrease of TEMPOL signal which was less pronounced than in system with only CPT-11. The termination of TEMPOL signal in the presence of CPT-11 indicated the formation of reactive radical species which can react with TEMPOL, forming diamagnetic products. The presence of Cu(II) ions in reaction systems with CPT-11 could cause the competitive reactions, e.g., reoxidation of Cu(II) (Eqs 5, 6):

$$Cu(II) + O_2^{\bullet} \rightarrow Cu(I) + O_2 \tag{5}$$

$$Cu(I) + O_2 \rightarrow Cu(II) + O_2^{-}$$
(6)

Additionally, the formation of singlet oxygen ${}^{1}O_{2}$ was confirmed, as irradiation of CPT-11 in the presence of TMP resulted to the formation of TEMPOL radical.

Conclusions

The work was focused on spectroscopic characterization of photoinitiated processes of irinotecan. Radical formation in the photoactivated system with CPT-11 and CPT-11/Cu(II) was monitored by spin traps DMPO and POBN under inert atmosphere and also in the presence of oxygen. DMPO was used for confirmation of photoinduced reactive radical species formation in DMSO solutions and POBN in aqueous solutions, respectively. Semi-stable free radical TEMPOL was used to verify the production of radicals upon irradiation. Dedicated to Prof. Andrej Staško on the occasion of his 70th birthday.

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Introduction

Photocatalysis on TiO₂ has received much attention during last two decades. If TiO₂ absorbs a quantum of UV radiation of sufficient energy ($\lambda < 400 \text{ nm}$), an electron is excited into the valence band and an electron-hole pair is created. The potentials of electron and hole are strong enough to oxidize water to hydroxyl radicals and reduce molecular O2. Resulting reactive oxygen species (ROS) are very powerful oxidizing agents and readily attack any organic matter in their proximity until it is totally cleaved to CO₂ and water. Numerous applications utilizing this process for water purification, toxic waste treatment, air purification and deodorizing have been proposed and some successfully marketed. The same process can be applied for the design of self-cleaning and self-disinfecting surfaces. Moreover, the oxygen vacancy creation and subsequent photo-corrosion on irradiated surfaces of TiO₂ convert the surface to superhydrophilic nature, which further enhances its self-cleaning ability.

Photocatalytic systems based on slurryied powder of TiO_2 offer excellent performance due to their very high catalyst surface area. Upon immobilization, the free surface of catalyst inevitably decreases, resulting into a loss of catalytic performance. Nevertheless, immobilized TiO_2 is the preferred form of photocatalyst. for industrial application. The need of removing powder photocatalyst can prohibitively complicate any process.

So far, several forms of immobilized powder TiO_2 were reported, featuring glass, silica gel, quartz, stainless steel, titanium, paper and many other materials as support. There are many methods of TiO_2 powder immobilization, such as suspension dip-coating, electrophoretic coating, spray coating, etc. However, inferior optical and mechanical properties or resulting films restrict the use of these materials only to some type of applications, such as photocatalytic reactors.

Sol-gel technique represents a totally different approach to the preparation of TiO_2 thin layers. Sol-gel is one of the most successful techniques for preparing nanosized metallic oxide materials with high photocatalytic activities. By tailoring the chemical structure of primary precursor and carefully controlling the processing parameters, nanocrystalline products with very high level of chemical purity can be achieved. In sol-gel processes, TiO_2 is usually prepared by the reactions of hydrolysis and polycondensation of titanium alkoxides, Ti(OR)n to form oxopolymers, which are then transformed into an tridimensional network.

In this way, thin, compact and transparent layers of TiO_2 can be conveniently produced. Such layers find their use in

the design of "smart" surfaces, such as self-cleaning glass sheets and tiles, mirrors with antifogging effect, self-disinfecting material etc. However, a suitable method for liquid sol application is needed in order to obtain a thin layer with excellent properties.

There are two traditional method of thin layer preparation from liquid precursors: spin-coating and dip-coating. Spin-coating method uses centrifugal force to form a film of liquid precursor: a sufficient volume of precursor is placed onto the support which is then rotated at a high speed. The liquid is spread by centrifugal force and a wet film of precursor is formed. The thickness of the resulting wet film depends mainly on the angular velocity of substrate rotation, precursor viscosity, precursor concentration and solvent evaporation rate¹. In contrary, dip coating is based on dipping the substrate into liquid precursor and pulling it out at constant speed. Again, viscosity, concentration, solvent volatility and speed of pulling influence the resulting film thickness. The faster we pull, the thicker the film is.

Both these methods are widely used, yet they are burdened by several significant disadvantages, as summarized in Table I. Firstly, the coated area is rather limited. In the case of spin coating, this limitation is due to the centrifugal force. Substrates larger than a few centimeters simply can not be rotated at several thousands rpm. The area of dip coated substrates is usually also limited to centimeter scale, although devices handling large substrates up to meter size are known. Secondly, the efficiency of precursor use is extremely poor. In both spin- and dip-coating, most of the precursor is wasted, and only few percents are actually used to build up the film. Moreover, dip-coating gives us substrates coated from both sides, which is not always desired. Thirdly, both these methods are very sensitive to surface defects. A surface defect can produce traces and streaks and degrade large areas of cauted substrate. At last, these classic methods on their own are not capable of selective deposition ("patterning"), i.e. the whole area of substrate is coated.

Table I Method comparison (adopted from², modified by authors)

	Spin	Dip	Inkjet
Precursor use efficiency Coated area	~ 95 % wasted ~ cm	~ 95 % wasted ~ dm	$\sim 5 \%$ wasted $\sim m$
Sensitivity to surface defects	\bigcirc	\bigcirc	\odot
Possibility of "patterning"		(\odot

Because of these problems and limitations, a more robust method of liquid precursor application has been searched for. Inkjet printing is apparently a very good candidate for this task. In a conventional inkjet printer, small droplets of low viscosity ink are ejected from a print head and fall onto printed substrated³. The movement of the print head and the substrate is precisely controlled by computer and so is the volume of ejected droplets and their loading per unit area. If we are able to replace the ink with a liquid precursor and printing paper with suitable substrate, we obtain a very robust device for the precursor deposition.

Naturally, both the printer and precursor must fulfill certain requirements in order to be employed as a thin layer deposition tool. The printer has to be able to handle rigid media so that solid materials can be used as layer support. The precursor must be of a very low viscosity (less than 20 mPa s) and must not damage the printer. If solid particles are present in the precursor, their diameter must be well below the print head nozzle diameter (50–20 μ m typically) and their aggregation must be prevented. Despite these limitations, inkjet printing has been successfully used for the deposition of a wide variety of liquid precursors, such as conducting polymers⁴, metallic nanoparticles dispersions⁵, metallic precursor solutions⁶, enzymes, various catalyst nanoparticles dispersions etc.

Experimental

Sol and Substrate Preparation

Sol-gel technique was applied to titanium dioxide thin films preparation using titanium(IV) propoxide as titanium precursors.

40 ml of ethanol was mixed with 3.8 ml acetylacetone. This mixture was then dropwise added to 10.3 ml titanium(IV)tetraisopropoxide (TTIP). Finally, 45 ml of ethanol was mixed with 0.69 ml water and this mixture was again dropwise added to the sol composition. Prepared sol was stored in an airtight bottle in darkness at 5 °C.

Borosilicate glass plates with sizes of $30 \times 30 \times 2$ mm (Verre Equipements, France) were chosen as a substrate for immobilization of TiO₂ thin films. This type of glass contains only 4.2 % wt. Na₂O and 0.1 % wt. of CaO. Before the preparation of the thin films, each glass was pre-treated in order to eliminate any dust, grease and other residues using an aqueous solution of industrial surfactant and dried under air flow.

Sol Application

Sol application was performed in a novel inovative way utilizing a modified office inkjet printer (Epson R220). Original ink cartridges were removed from the printer and the ink tubing and printhead were flushed and purged with anhydrous propanol. Flushing with anhydrous propanol is extremely important in order to remove any remaining aqueous ink. If this step is omitted or performed incompletely, the titanium sol will hydrolyse upon contact with residual water and precipitated TiO_2 will clog the print head nozzles.

"Virgin empty" spongeless carts were supplied by MIS Associates, USA. Titanium sol was filtered frough $0.2 \,\mu m$ mesh size syringe filter and loaded into one "virgin empty" cart. This cart was installed into the printer in the black position while the remaining positions were occupied by the same carts filled with dummy ink (a mixture consisting of water,

propanol, surfactant and colorant). After a series of head cleaning cycles a perfect nozzle check pattern was obtained. Cleaned glass plates were then mounted into a modified CD holder, fed into the printer and printed with "black only" driver setting. The colour of the printed pattern was varied in different levels of grey (100%, 90%, 80%, 70%, 60%) and thus glasses with correspoding *relative sol loading value* were printed.

Two print setting were adopted – *rapid* and *slow* (see Table II). The resolution, print speed and media settings were varied and their influence on the resulting TiO_2 layer properties was evaluated.

Table II Print setting

	Rapid	Slow
Media Settings	Plain paper	CD Premium Surface
Resolution	360	720
Highspeed	yes	no
printing	(= bidirectional	(= unidirectional
F0	printing)	printing)
Absolute	appr. 1 cm ² s ^{-1}	appr. $0.05 \text{ cm}^2 \text{ s}^{-1}$
printing speed	"FF • • • • •	Tr

Layer Treatment

After the previous procedure, the coated glass plates were dried in the oven at 110 °C for 30 min. Finally, the deposited layers were thermally treated in a calcination furnace at 450 °C for 4 hours with ramp of 3 °C min⁻¹ to obtain the transparent photocatalytically active titanium dioxide films in anatase presupposed phase.

Study of Printed Layers Properties

Optical and SEM imaging was performed in an ordinary manner on a Nikon Eclipse E200 optical microscope equippend with Nikon D200 digital camera and Hitachi S4700 FESEM scanning electronic microscope. Recorded electronic images were also used to evaluate the layer thickness.

Surface Analysis was performed on Sanning Probe Microscopy NTegra Prima/Aura (NT-MDT).

Photocatalytic performance was evaluted by recording the dechloration rate of 2,6-dichloroindophenol (DCIP). The reaction took place in a simple single-plate reactor where the solution was circulated through a siphon by a centrifugal pump. The siphon ensured a constant level of solution over the catalyst plate during the whole reaction despite decreasing volume due to sampling. UV radiation was delivered by Philips HPA – 400 W metal halogen lamp and the intensity was 2.4 mW cm⁻².

The DICP concentration was determined by UV-VIS spectrophotometry at 600 nm. Samples were taken at 20 minutes intervals. Formal first order kinetic model was adopted and the reaction rate constants were calculated.

Results

Layer Structure and Morphology

As far as the layer morphology is concerned, we can clearly see that there are principal differences between rapid and slow printed layers, no matter what the sol loading is. The rapid printed layers are very smooth and compact up to 80 % of sol loading (see Fig. 1.). When the sol loading value exceeds this threshold, cracking occurs (See Fig. 2.).



Fig. 1. 80 % sol loading, rapid printing



Fig. 2. 100 % sol loading, rapid printing

On the other hand, the slow-printed layers show completely different structure – their surface is very grooved and rough. It clearly keeps the structure of individual drops. When the sol loading value is low, we can clearly see the patterns of individual drops (see Fig. 3.). When the sol loading value increases, this pattern is still present and some cracing occurs in very thick regions (Fig. 4.).

A more detailed view is provides by the SEM imaging. Here we get a closer look at the cracks and it is also possible to estimate the thickness of the layers (Fig. 6.).

The differences in the layer structure are caused by the different speed of sol ejection: During rapid printing, the sol ejection rate is faster then solvent evaporation, and therefor a liquid film is formed on the substrate. Only then the solvent evaporates, leaving a "dry" layer of gel. However, during slow printing, the sol ejection rate is very small and the rate of evaporation exceeds it. Therefore a solig gel is formed



Fig. 3. 60 % sol loading, slow printing



Fig. 4. 100 % sol loading, slow printing



Fig. 5. 100 % sol loading, rapid printing

on the substrate already during printing and the last drops of sol are deposited onto dried gel. Therefore a distinctive structure develops and the resulting layer is very rough.

The roughness prepared layers was in much greater detail observed by AFM. Unfortunately, the roughness of slow printed layers was too high to be observable by our device, therefore a direct comparison is not possible at the moment. The AFM record for the rapid layer reveal a very



Fig. 6. A crack detail, 100 % sol loading, rapid printing

smooth surface whose roughness is comparable to the roughness of support glass.



Fig. 7. AFM record of 100% sol loading, rapid printed layer

Photocatalytic Performance

Fig. 7 shows the overall results for the DCIP dechloration experiment. We can clearly see that the dechloration rate increases with increasing sol loading. However, the there is a difference in the slope of this dependency. We believe that this difference can be explained by the differences in layer homogeneity. While the rapidly printed layers are very smooth and compact, the slow printed layers are grooved and rough. Therefore the catalyst surface is basically constant in the case of rapid printing and only the thickness of the layer changes. On the other hand, in the case of slow printing, both the average layer thickness and interface surface increases as sol loading increases.

Conclusion

In this letter, we demonstrate the benefits of using inkjet printing technology for the preparation of TiO_2 thin layers.



Fig. 8. Reaction rate constant comparison

By utilizing the well know sol-gel chemistry used so far for spin- and dip coated layers of TiO_2 together with the wide deposition possibilities offered by inkjet printing, we are able pro prepare thin layers of TiO_2 in a very effective and clean way with minimum waste. The structure of prepared layers greatly depends on the printing conditions: If the sol ejection rate is faster then solvent evaporation, a smooth compact layer is produced. On the other hand, when the solvent evaporation rate is grater than sol ejection, we obtain highly structured and porous layer.

Slowly printed layers have structured and grooved surface giving them opaque matt apperance, but their photocatalytic performance is superior compared to rapidly printed layers. We believe this is mainly due to greater catalyst interface area. On the other hand, rapidly printed layers have better optical properties – they are glossy and transparent. However, the smooth surface results into lower mass exchange rate and therefore their photocatalytic performace is lower.

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L06 PROMISING PERSPECTIVES IN PHOTOCATALYSIS

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Introduction

Heterogeneous Photocatalysis based on titania originated some 40 years ago but the interest of industry for environmental applications emerged only 10 years ago. These applications mainly concerned self-cleaning materials and water and air purification and standardisation is now required. In France, French AFNOR created the B44-A photocatalytic commission in September 2007, which is composed of scientists from National and from industry.

Researches in the field of the Photocatalysis are now one of the major for remediable energy. This is a technology which took a considerable rise during these last 10 years. It is particularly well adapted to answer the new environmental stakes, insofar as she proposes solutions of for clean treatments to fight effectively against environmental pollution. The photocatalysis is a technique based on oxydo-reduction (Redox) processes, particularly well appropriate to the treatment of environmental pollution. It is quoted in the last report/ratio of the Ministry for Industry relating to "key technologies 2010" like as one of the technologies carrying for the economic development in France. These applications mainly concerned self-cleaning materials and water and air purification and standardisation is now required. In this particularly favorable context, AFNOR, the French Agency for Standardization, which has, in particular, for the mission of promoting emergent technologies and to supporting their development, has just created the Commission of Standardization named Photocatalysis B44A. At the time of during the launch the meeting of launching on May 11, 2007 which brought together some 30 people persons met, among which whom people from industry, representatives of the public authorities and scientific experts of from academic research. The scope of applications selected is relatively broad, taking into account the multiple applications considered, such as the air cleaning, the elimination of the odors, the coating materials to create self-cleaning surfaces (glass, metals, concretes, cements...), the purification, potabilisation and detoxification of water, etc. It was initially decided, to focus the work of standardization of the Commission on the applications of the photocatalysis in the field of the on air treatment.

After the presentation of the commission of standardization AFNOR "B44A" the principle of photocatalysis and the active species generated at the surface of a photocatalyst will be presented under different reaction conditions (liquid phase (water, solvents) and gas phase), corresponding to dedicated applications such as air and water treatments, self-cleaning materials, fine chemistry. Hydrogen production will be also introduced. The comparison of reaction mechanisms occurring in aqueous and gaseous phases is made possible by identifying the intermediate products formed during the degradation of pollutants in both phases. The prediction of reaction pathways in aqueous phase is based on the attack by OH[•] radicals on different families of organic pollutants and subsequently verified by the experiments. Some applications of photocatalysis (decoloration of dyes, detoxification of water, use of solar energy, air treatment (VOC and odor removal), self-cleaning materials), developed at IRCELYON will be presented and put in realistic perspectives.

Principle of Photocatalysis and Active Species

Photocatalysis is based on the double aptitude of the photocatalyst (essentially titania) to simultaneously adsorb reactants and to absorb efficient photons.

When a divided semiconductor is illuminated with photons of energy higher than or equal to its band gap energy, photo-electrons e^- and photo-holes h^+ are created. The electron is then extracted from the valence band (VB) to the conduction band (CB). This process results in a positive region in the VB (Hole h^+) and a free electron (e^-) in the CB (1). Mechanisms for the primary events occurring at the catalyst surface have been described.^{1–3}

$$TiO_2 + h\upsilon \rightarrow TiO_2 + e^-(CB) + h^+(VB)$$
(1)

Reactants can adsorb and react either with electrons (acceptor molecules such as O_2) or with holes (donor molecules).

The hole, at the catalyst surface, reacts with donor molecules such as hydroxyl ions (OH⁻) and adsorbs water (case of presence of water) to form free radicals (OH[•]). (Eqs. (2) and (3)):

$$\operatorname{FiO}_{2}(h^{+}) + \operatorname{OH}^{-} \to \operatorname{TiO}_{2} + \operatorname{OH}^{\bullet}, \qquad (2)$$

$$\operatorname{TiO}_{2}(h^{+}) + \operatorname{H}_{2}\operatorname{O}_{\mathrm{ads}} \to \operatorname{TiO}_{2} + \operatorname{OH}^{\bullet} + \operatorname{H}^{+}, \qquad (3)$$

or directly with reactants (mainly in absence of water) to form $R^{\boldsymbol{+}\boldsymbol{*}}$

$$\operatorname{TiO}_{2}(h^{+}) + R \to \operatorname{TiO}_{2} + R^{+\bullet}.$$
 (4)

The CB electron reduces oxygen to the superoxide ion: O_2^{-} (Eq. (5)). This reaction prevents the e⁻/h⁺ recombination, in the absence of other electron acceptors.

$$O_2 + e \rightarrow O_2^{-}$$
 (5)

Water Treatment vs. Air Treatment

In aqueous phase, the further reduction of O_2^{\bullet} produces H_2O_2 , as described in (6):

$$O_2^{\bullet-} + e_- + 2H^+ \rightarrow H_2O_2 \tag{6}$$

The superoxide ion and its protonated form subsequently dismute to yield hydrogen peroxide or a peroxide anion (Eqs. (7)–(9)):

$$O_2^{\bullet-} + H^+ \to HO_2^{\bullet} \tag{7}$$

$$O_2^{\bullet-} + 4HO_2^{\bullet} \rightarrow 2OH^{\bullet} + 3O_2 + H_2O_2$$
 (8)

$$2HO_2 \rightarrow O_2 + H_2O_2 \tag{9}$$

Hydrogen peroxide can also react with superoxyde *via* the Harber-Weiss reaction (10) or through the reduction of H_2O_2 by the CB e⁻ (11) (Ref.⁴)

$$O_2^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + OH^- + O_2 \tag{10}$$

$$H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^-$$
(11)

On the other hand, recombination of OH[•] radicals can lead to the production of hydrogen peroxide (12):

$$OH^{\bullet} + OH^{\bullet} \to H_2O_2 \tag{12}$$

In gas phase, organic radicals formed R^+ can react with superoxyde O_2^- or directly with O_2 to formed oxidised compounds and in situ water, which allow to obtained a total mineralization by indirect formation of hydroxyl radical (13), (14).

$$R^{+} + O_2 - \to Ox \tag{13}$$

$$R^{+\bullet} + O_2 \to Ox \tag{14}$$

These types of reactions can also be observed in aqueous phase⁵.

Principle of Self Cleaning Materials

Self cleaning materials are based on the photocatalytic and superhydrophilic properties (case of glass)^{6,7} of a submicronic layer of photocatalyst TiO₂, deposited on their surface. Active species photogenerated, described previously (3) and (5) (OH, O₂-...) are able to eliminate the organic stains adsorbed on the glass surface by slow combustion at ambient temperature. Moreover, the photogeneration of these radicals induces simultaneously a phenomenon of "superhydrophilicity" on the surface of the TiO₂ layer, which takes part in the self-cleaning property of glasses, in the presence of water (rain). The proposed mechanisme occurring is presented on Fig. 1.



Fig. 1. Superhydrophilicity of TiO₂

Superhydrophilicity is due to the formation of hydroxyl group on the surface of catalyst. This superhydrophilicity can occur only in the case of humide atmosphere.

Fines Chemicals vs. Environmental Catalysis

Indeed photocatalysis is alternatively able to induce mild and selective oxidation reactions and total oxidation reactions leading most elements to their higher oxidation state, in particular leading organic carbon to the +4 oxidation state in CO_2 .

This is mainly due to the *absence* (mild oxidations) and to the *presence* (total oxidation) of water. In the first case, the active species is a neutral atomic O^{*} species⁸ whereas in the presence of water (or humid air), OH[•] radicals (2nd best universal oxidant) lead to total oxidation. Their formation is summarized in Table I.

Hydrogen Production

Scientists all over the world are very interested in hydrogen gas as the most promising energy resources to overcome the future energy crisis.

The photocatalytic decomposition of water into hydrogen and oxygen has been regarded as one of the most potential approaches ever since Fujishima and Honda reported the photoelectrochemical water splitting using a TiO_2 electrode⁹.

When the surface of the TiO_2 electrode was illuminated, electrons flowed from it to the platinum counter electrode. The oxidation reaction (oxygen gas evolution) occurs at the TiO_2 electrode and a reduction reaction (hydrogen gas evolution) occurs at the Pt electrode.

The principles of photoelectrochemical water splitting have been used to guide the design of particulate systems for photocatalytic water splitting. For example, a TiO_2 particle with a small amount of Pt deposited on it is essentially a miniature photoelectrochemical cell, on which water is oxidized at the bare oxide and is reduced at the Pt-covered area to achieve the desired overall reaction.

However, particulate photocatalytic systems have the disadvantages to imply a separation of charge carriers not as efficient as with an electrode system. In addition, the back reaction between the evolved hydrogen and oxygen gases can take place. This was a problem in early work with TiO₂/Pt photocatalysts. Since, photocatalytic water splitting has been studied intensively over the past several decades. A variety of metal oxides have been examined as powder photocatalysts. These materials include transition metal oxides containing metal ions of Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, or Ta⁵⁺ with d⁰ electronic configuration and typical metal oxides having metal ions of Ga³⁺, In³⁺, Ge⁴⁺, Sn⁴⁺ or Sb⁵⁺ with d¹⁰ electronic configuration The record efficiency of 18.3 %, achieved on a AlGaAs/ Si-RuO²/Pt system, is very encouraging. However, these systems are so expensive that the cost of the hydrogen fuel produced would not be competitive with other regenerative types of energy. Heterogeneous photocatalysis could provide

Table I

Features	Fine Chemicals	Environmental Catalysis
Main reaction	Mild oxidation	Total oxidation
Initial selectivity	100%	No selectivity
Final products for organics	>C=O	CO_2
Medium	Dry medium	Water, Humid air
Active species	O^*	OH•
Reaction of Formation		$(\text{TiO}_2) + \text{hv} \rightarrow \text{e}^- + \text{h}^+$
Reaction of Formation	$O^{-}_{(ads)} + h^{+} \rightarrow O^{*}_{(ads)}$	$(H_2O \leftrightarrow H^+ + OH^-) + h^+ \rightarrow H^+ + OH^{\bullet}$

a low-cost route for production of H_2 fuel, if the photocatalyst were able to utilize solar energy efficiently¹⁰.

Generally, the other studies showing the photocatalytic H_2 production was initially evolved from a CH_3OH-H_2O and the mechanism implied is resume below¹¹.

- $\begin{array}{l} R-CH_2OH_{(liq)} + (2 \text{ sites on } TiO_2) \rightarrow R-CH_2O^-_{(ads)} + H^+_{(ads)} \\ \bullet \quad \text{Electron transfer to metal particles as for CDIE} \\ e^- + (Pt) \leftrightarrow e_{-_{Pt}} \end{array}$
- Reaction of holes h⁺ with chemisorbed alcoholate anions

 $h^+ + R - CH_2O^- \rightarrow R - CH_2O^\bullet$

- Release of a hydrogen atom and formation of a carbonyl-containing molecule (presently an aldehyde)
 R-CH₂O[•] → R-CHO + H[•]
- Reverse spillover of H[•] atoms back to the metal particle probably as protons
 H[•] → H⁺ + e⁻
- Neutralization of protons at metal particles containing an excess of electrons "nano-cathodic – (like process)" H⁺ + e⁻_{Pt} → H[•] (Pt)
- Recombination of H• atoms and evolution in the gas phase
 - $2\mathrm{H}^{\bullet}_{(\mathrm{Pt})} \rightarrow \mathrm{H}_{2}(\mathrm{g})$

Research Field in Photocatalysis Developed at IRCE-LYON

Water Treatment

Removal of organic compounds – Comparison and/or coupling with other advanced oxidation processes

Removal of a large number of organic compounds such as phenolic compounds^{12,13}, pesticides^{14–16}, dyes^{17,18} has been successfully degraded and chemical pathways identified in our laboratory. Their kinetics or chemical pathways compared to other advanced oxidation technologies^{19–21} such as H_2O_2 –UV, H_2O_2 –Fe²⁺, O_3 and ultrasound^{22,23}. We have also shown that the combination between photocatalysis with these different advanced oxidation processes can improve their efficiency. For exemple the electronic affinity of ozone favor the (e[–], h⁺) separation and the formation of actIve species.

The efficiency of supported TiO_2 has been evaluated and demonstrated strongly decreased the photocatalytic degradation of non-neutral compounds. This decrease has been

attributed to the presence of silica binder which decreases the adsorption of anionic compound on the photocatalyst by electrostatic repulsion.

Fate of nitrogen group

Nitrogen has always been a complex element in chemistry because of its apparent inertness as N₂, and of its multiple oxidation states, ranging from -3 to +5. Nitro-compounds were found to decompose into nitrite, easily oxidized into nitrate. Amino groups have been found to decompose into ammonium ions, slowly oxidizable into nitrate. Eventually, nitrogen atoms incorporated into triazinic aromatic rings were found to resist oxidation, remaining in their -3 oxidation state. This was showed by a partial oxo-degradation of s-triazine into cyanuric acid C₃H₃O₃N₃. Fortunately, cyanuric acid is innocuous because of its very high stability. It constitutes one of the very few examples of organics resisting photocatalytic degradation at room temperature. This is due (i) to the three bonds of N atoms involved in the aromatic ring skeleton (i.e. without aliphatic substituents) and (ii) to the maximum formal oxidation state of carbon (+4), already reached in C₃H₃O₃N₃. Concerning the degradation of (-N=N-) azogroups, the mass balance in *n*-containing final products could not be obtained in aqueous phase analyses considering only the formation of NO₃⁻ and NH₄⁺. However, this mass balance can be obtained quantifying N2 evolution, and show that azogroups is mainly transformed into nitrogen gas. For example, N2 evolution from Congo Red (the "terror" of printers and of paper-makers) is given in Fig. 2. During its photocatalytic



Fig. 2. Kinetics of n-containing compound evolution, either in the aqueous or the gas phase during the photocatalytic degradation of Congo Red dye

degradation the total nitrogen balance could be permanently established.

In the case of Amaranth a prohibited cancerigen alimentary dye or Reactive Black 5, the 100 % gaseous N2 expected could not be reached. The only 85 % and 70 % of N2 obtained were due to the presence of a hydrazone isomeric form shown below.



Prediction of chemical pathways – Impact of electronic density

Several studies mentioned the importance of electronic density on initial attack of hydroxyl radical, considering their electrophilic characters but also the importance of adsorption.^{24–27} Taking into account these works, we used the CAChe software and the semi-empirical MOPAC package to calculate Frontier electron densities and point charges of all individual atoms in different structures (triazolidine²⁸, Imazapyr²⁹ and diuron.

Then we correlated these values with experimental results and showed that we can predict the main initial intermediates products taking into account the attack of OH[•] radical on the highest electronic density.

For example, electronic density can explain that amine group is mainly transformed into nitrate in the case of ammelide whereas amine group are transformed into ammonium in the case of amino-phenol (Fig. 3.)

However, this approach is a global approach and it does not explain for exemple if the monochlorohydroxylated compounds which are mainly formed in the case of diuron are obtained abstraction of hydrogen and hydroxylation or addition of OH[•] on the cycle and then dechlorination.

For these reasons DFT calculations have been established to determine the enthalpy of formation of each compounds considering attack by OH[•] radical on each atom.

Removal of micro-Organisms

Obtaining a clean air or a drinking water does not pass only by the elimination of the polluting species of chemical origin (dyes, pesticides, hydrocarbons,...), it requires also the elimination of the pollutants of biological origin (virus, bacteria, mushroom, yeast...). This operation is called disinfection or sterilization.

At IRCELYON, we work on the study of a photocatalytic disinfection process which has the advantages of proceeding at room temperature and atmospheric pressure without addition of chemical reagents and to allow a total CO_2 mineralization and H_2O . Our studies aim to better understand the mechanisms of action of the reactive species $HO^{\bullet}, O_2^{\bullet}, HO_2^{\bullet}$, produced on the surface of the irradiated photocatalyst.

The studies began with Escherichia coli, a model micro– Organism representative of the bacteria. Correlations between chemical analyzes and biochemical are studied by determi-



Fig. 3. fate of nitrogen in the photocatalytic degradation of 3-amino-phenol and ammelide



Fig. 4. Electronic microscopy of a suspension of *E. coli* bacteria in contact with the catalyst TiO, Degussa P–25

nation of the photocatalytic oxidation in vitro of the nucleic acids (DNA, ARN). The first results, under UV-A irradiation



Fig. 5. Picture of gel electrophoresis from I: Intracellular sample, E: Extracellular sample of suspension of *E. coli* treated by UVA photocatalysis at different exposure times (0–240 min). The bands correspond to (1) chromosomic DNA, (2) 23S rRNA and (3) 16S rRNA. M: DNA molecular weight marker

in the presence of a photocatalysor TiO_2 , show the importance of the contact between micro-organisms and nanoparticules of the catalyst (Fig. 4.) which leads to the perforation of the membrane and the loss of cultivability. In parallel one observes the formation of ions ammonium and organic acids, the progressive degradation of the ARN and DNA (Fig. 5.) and the absence of nucleic acids in solution.

Used of solar energy

Various contaminants (phenol, 4-chlorophenol, 2,4-D, benzofurane, malic acid, formatanate, Congo Red,...) previously studied in our laboratory, were later photodegraded in the solar pilot plant at the "Plataforma Solar de Almeria" (PSA, Spain) and it was demonstrated that the kinetic results obtained with micro-photoreactors at laboratory scale could be extrapolated to pilot photoreactors having capacities of several hundred litres by using a circulating suspension of titania. The variation in photo-efficiency under high solar flux, as well as possible thermal effects of solar light, has also been studied.³⁰ Some years later, European program AQUA-CAT allows us to developed and test a totally autonomous solar photoreactor, presented in Fig. 6., able to potabilize water by decontamination (chemicals) but also disinfection (bacteria).



Fig. 6. AQUACAT autonomous solar photoreactor prototype for water potabilization

Air Treatment

Removal of Organic Molecules - Comparison of Reaction Mechanisms Occurring in Aqueous and Gaseous Phases

Conventional technologies for removing VOCs from the polluted air stream involved adsorption by activated carbon, biofiltration and bioscrubbling, thermal oxidation and incineration which encounter the drawbacks to be non destructive and/or expensive because of high-energy requirements and/ or consumption of chemicals. A highly promising method for the destruction of VOC is photocatalytic oxidation. It offers several advantages, in comparison to the other processes, such as the destruction of organic contaminants rather than their transfer from a phase to another one, a complete mine-







(b)



Main mechanism of MTBE photocatalytic degradation in aqueous (a) or gaseous phase (b)

ralisation into carbon dioxyde and water and a wide range of VOC can be treated. Its efficiency has been demonstrated for removing a large number of VOC. In our laboratory we have shown the efficiency of the degradation of different odorous compounds^{31,32} and even for the total mineralization of triple carbon-carbon bonding³³.

Moreover, utilization of this process is energetically interesting because it operates at ambient temperature and the use of solar energy to initiate photocatalytic oxidation reactions is possible.

The photocatalytic reaction mechanism is few studied in gas phase and the role of water on the mechanism not really well established. The study of humidity on mechanism of acetylene photocatalytic degradation reveals that in dry air, acetylene is slowly degraded and mainly reacts with photogenerated holes.

The comparison of the reaction mechanisms occurring in gas and aqueous phases in the photocatalytic degradation of methyl-tertio-butyl ether (MTBE), a volatile organic compound (VOC) used as a substitute for tetraethyl-lead in gasoline agree with

In aqueous phase, the main pathway is the attack on the methoxy group of MTBE by OH[•] and in a less extend by HO_2^{\bullet} to form tertio butyl formiate and tertio butanol while in gaz phase the attack mainly occur by hole on methyl of tertio bytyl.

In Scheme1 are represented the main mechanism of attack of MTBE in aqueous phase (a) and gaz phase (b)

Improvement of Photocatalysis by Coupling With Adsorbant or Cold Plasma

In our laboratory, we also work on the improvement of the photocatalytic efficiency. In air treatment, we have first tested the effect of the presence of adsorbant such as zeolithe and secondly coupled photocatalysis with non-thermal plasma.

Contrary that it will be mentioned in the literature, our results reveals that no improvement of VOC degradation occurs in presence of TiO_2 + activated carbon whereas zeolite improves the efficiency of TiO_2 supported on non woven fibre; These improvement is attributed a better dispersion on TiO_2 on fibre (Fig. 7.).

The initial reasons for coupling plasma and photocatalysis were that the photocatalysis was expected favour the total mineralization of VOC into CO_2 by decreasing intermediate compound formed in plasma reaction but also used UV generated by plasma, due to excited nitrogene relaxation, as well as activated species such as ozone, which are able to, are activate photocatalytic material.

Our results reveals that an improved of efficiency is observed when materials are present in plasma discharge. However, this improvement is mainly due to the presence of a porous material. It means that UV generated by plasma is not sufficient to activate photocatalyst.



Fig. 7. (a) Adsorption and photodegradation of acetylene on TiO_2 coupled with adsorbing material or not and (b) Photoproduction of CO₂ by TiO₂ coupled with activated carbon

Studies performed using additional UV indicates that a synergy is observed between plasma and photocatalysis, less CO is detected and the formation of carbon dioxide is improved. Moreover, the photocatalytic material is less easily poisoned by intermediate compounds formed due to its regeneration by plasma.

Removal of Virus

The efficiency of a photocatalytic reactor against the avian influenza virus using an aerosol flow of about 40 m³ h⁻¹ and about 10^3 CFU ml⁻¹ (CFU: Colony Forming Unit) have been tested. Since the A/H5N1 virus is strongly pathogenic,



Fig. 8. Photos of experimental device used to test the efficiency of BUXAIR reactor against the avian influenza virus

the tests were performed on the A/H5N2 strain of the virus, chosen as the conventional research model for the A/H5N1 strain. A reference was made using no irradiation flux. The experimental set was represented in Fig. 8.

Titration results are presented in the Fig. 9.a,b. Without UV-light, we observe a 0.7 log (or 80%) reduction of the number of viruses. The addition of UV-light led to a complete elimination of viruses titrated at entry up to a 3.1 log.



Virus inactivation test in normal conditions (UV+Photocatalysis)



Fig. 9. (a) Virus inactivation tested in the Imutube photoreactor in dark conditions. Air flow: 40 m3/h; (b) Virus inactivation tested in the Imutube photoreactor in UV + photocatalyst

Self Cleaning Materials

Present Challenges in Photocatalysis

The number of publications on photocatalysis presently increases exponentially, especially from emerging countries and from the community of materials. Experts are now confronted by new challenges. Some of them concern the following points:

- Are we "condemned" to exclusively work with titania?
- Can TiO₂ be photosensitized in the visible by doping? (It is already known that cationic doping is not efficient and rather detrimental whereas anionic doping is under investigation).
- Can we find a new photocatalyst different from TiO₂ and directly active in the visible?

- Is photocatalysis suitable for preparative Fine Chemistry?
- Is photocatalysis enough bactericide in water and in air?
- Can Photocatalysis be employed as a new medical tool ("cancericide effect,....")?
- Are we able to define a few standardized and globally accepted tests for each photocatalytic application?

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L07 PHOTOCATALYTIC PROPERTIES OF TIO₂ AND PHOTOSENSITIZING MATERIALS FOR BACTERICIDAL APPLICATIONS

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Introduction

Several water disinfection technologies are available, such as chlorination and ozonation. However, in addition to their high costs, they can lead to the formation of harmful disinfection by-products (DBPs), among which the most dangerous are the trihalomethanes (THMs), well-known for their high carcinogenic potential¹.

Among the new oxidation methods or "Advanced Oxidation Processes" (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of pollutants at ambient temperature and atmospheric pressure using a cheap photocatalyst, TiO₂, having the possibility of using a part of solar energy as the UV source. Its principle is based on the formation of highly reactive oxygen species (ROS), such as OH[•], O₂^{•-} HO₂[•], capable of destroying chemical and biological water contaminants, under irradiation of semiconductor particles (photocatalyst) with photons of energy higher than or equal to its band gap energy. TiO2 mediated photocatalysis has been widely investigated for a large number of organic contaminants. Their degradation pathway and their mineralization has been reported^{2,3}. Nowadays, interest is directed to the use of this technique in water disinfection. Photocatalytic oxidation as a technique for microbial disinfection was first demonstrated by Matsunaga et al.⁴ using TiO₂-Pt photocatalyst. Since the effects of various parameters (nature of support, nature of photocatalyst, light power, initial concentration) on the photocatalytic efficiency have been studied^{5,6}

Other types of catalysts begin to appear for desinfection, such as photosensitizing materials which generate singlet oxygen under UV but also visible light. Singlet molecular oxygen (abbreviated ${}^{1}O_{2}$) is the lowest electronic excited state of molecular oxygen. It can be readily generated by energy

transfer from electronically excited dyes to ground state dioxygen, following a photochemical process called sensitization in which the excited state of the sensitizer, mostly in its triplet state, is quenched by molecular oxygen yielding singlet oxygen. Singlet oxygen is a short-lived highly reactive species that is known to inactivate air- or water-carried bacteria efficiently^{7,8}.

In this work, we compared the photoinduced deactivation of the model bacteria *Escherichia coli* K–12 (*E. coli*) using industrial TiO₂ photocatalysts, Degussa P25 and Millennium PC500, either suspended or supported and photosensitizers supported on silica (organic molecules derived from quinone, benzophenone, or 9,10-dicyanoanthracene). The influence of parameters, such as the nature and amount of the sensitizer or TiO₂ and of the irradiation intensity was investigated.

Experimental

Materials

Two industrial and commercial TiO_2 , Degussa P25 and Millennium PC–500 and four sensitizers (9,10-Dicyanoan-thracene (DCA), anthraquinone (ANT), 4-benzoyl benzoic acid (4-BB) and a new photosensitizers named X) prepared on silica⁹ were used in suspension. PC–500 coated on Ahlstrom paper and commercialized by Ahlstrom firm under the reference 1048 was used as supported TiO₂.

Bacterial Strain and Growth Media The bacteria strain used was *E. coli* K12 PHL 1273 containing a green Fluorescent protein (gfp) in ADN which enhanced the synthesis of fimbriae.

Aliquots of the overnight cultures were inoculated into fresh medium and incubated aerobically at 37 °C until the stationary growth phase was reached (15 h). Growth was monitored by optical density (OD) at 600 nm. Bacterial cells were harvested by centrifugation at 500 rpm for 10 min at 4 °C. The bacterial pellet was subsequently washed three times with the Mili-Q water. Cell suspensions were inoculated in the solution in a Pyrex cylindrical reactor to the required cell density corresponding to 10^7 – 10^8 colony forming units per millilitre (CFUml⁻¹). Serial dilutions were prepared if necessary in the solution and 100 µl samples were plated on Plate-Count-Agar (PCA, Merck, Germany). Plates were incubated at 37 °C for 24 h before the bacterial counting was carried out.

Photoreactor and Light Sources

The reactor consisted on a batch Pyrex cylindrical (100 cm^3) inside which 20 ml of *E. coli* aqueous solution was put into contact with the photocatalyst. The directly irradiated side of the reactor was the bottom window suprasil disk, 3 cm diameter. The light source was a HPK 125 W Philips mercury lamp, cooled with a water circulation. The irradiation spectrum was cutt–Off below 340 nm using a Corning 0.52 filter. All reactions were carried out at ambient temperature.

Results and Discussions

Efficiency of TiO,

Fig.1 represents the inactivation of *E. coli* strain in presence of the two titania photocatalysts in slurry and of supported PC–500.

In suspension, TiO₂ PC–500 is much more efficient than TiO₂ P25 to inactivate *E. coli*. However, its efficiency decreases when it is supported due to the lower contact between catalyst and bacteria¹⁰.

The more important efficiency of the PC–500 as a function of time can be explained by considering the evolution of the pH (from 6.5 to 5 after 3 hours) during the photocatalytic inactivation of *E. coli*. In this case more TiO_2 surface is positively charged. TiO₂ PC–500 should be more efficient than P25 due to the presence of more negative charges on its surface, at the working pH, taking into account the isoelectric point (IEP) of both catalysts (IEP = 7 for P–25 and 6.2 for PC 500).

Another hypothesis could also be suggested considering the smaller PC–500 particles, which could more easily penetrate between fimbriae and help more quickly to perforate the membrane. However, PC–500 particles were more agglomerated those of P25 as found by D.Gumy⁵. This hypothesis seems less probable than that based on surface charges.



Fig. 1. Inactivation of *E. coli* 1273 strain in presence of 1 gdm⁻³ of TiO₂ Degussa P25 or TiO₂ Millennium PC-500 using a 3.85 mW cm⁻²

The effect of the amount of TiO_2 (P-25) and of light intensity show:

(*i*) that the optimal concentration of TiO_2 found to inactivate *E*-*coli* was 0.25 g dm⁻³. Above this value a scattering effect of titania occurs,

(*ii*) by increasing the intensity from 0.48 to 3.85 mW cm⁻², the time necessary to totally inactivate *E*–*coli* decreased from 180 to 90minutes and seems reach a plateau above 4 mW cm⁻².

Efficiency of Photosensitizers - Comparison with TiO₂

The efficiencies of the photosensitizers supported on silica elaborated by the sol-gel method, to inactivate *E.coli* are presented on Fig. 2.

Contrary to the results observed with TiO_2 , with all the sensitizing materials a lag period is observed which can be attributed to the self-defense of the micro–Organism against active species such as ${}^{1}\text{O}_2$ (no OH• radical can be formed with these sensitizers).



Fig. 2. Efficiencies of used photosensitizers

Several parameters can influence the results obtained with these sensitizing materials, such as the nature and the concentration of the photosensitizer in the material, its method of preparation (inclusion for SG0, grafting in the xerogel for SG1 or post-grafting for SG2), or its specifice surface area. For exemple, with an original sensitizer × prepared in the lab (patent pending), it is found that a material obtained by post-grafting of the photosensitizer on silica xerogel (SG2-X) presents a higher efficiency than the same material prepared by grafting during the sol-gel process (SG1-X), itself more efficient than the material obtained by inclusion of the photosensitizer in the xerogel (SG0-X). However the se nsitizer × concentration decreases for these three materials in the order SG2>SG1>SG0 (27, 10 and 0,6 µmol g⁻¹ respectively). Moreover, the increase of photosensitizer amount in the experiment leads to an increased efficiency. Comparing now different sensitizers, it is observed that SG0-DCA and SG0-X, prepared by inclusion of the sensitizer with roughly the same concentration (0,2 and 0,6 μ mol g⁻¹ respectively, gives the lowest efficiency. The most efficient material is an anthraquinone grafted material, SG2-ANT, with a much higher sensitizer concentration (250 µmol g⁻¹). However, additional work is needed to further correlate the known quantum yield for ¹O₂ production and the inactivation order¹¹.

Compared to DEGUSSA P25 TiO_2 , the efficiency of the photosensitizing materials is less important and a noticeable lag time before inactivation is observed. However the study of this type of catalysts to inactivate bacteria should be developed considering their potentiality to be activated by solar light.

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L08 INTERACTIONS IN IRON GALL INKS IN AIR AND NITROGEN ATMOSPHERE

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Introduction

One of the most commonly used writing and drawing materials applied from the ancient times through Middle Ages until the modern times were the iron gall inks. In Europe they were highly used from the beginning of 11th century until the end of 20th century. The libraries and archives all over the world contain enormous amount of books (notes of Leonardo da Vinci), manuscripts, documents (US constitution proposal) and musical compositions (scores of J. S. Bach), which were written with iron gall inks.

For the preparation of iron gall inks, galls (from the chemical point of view these are polyphenols), vitriol (iron(II) sulphate), gum arabic, and as a solvent, water, sometimes wine, beer or vinegar were used. Sometimes pigments or copper (II) sulphate were added into these inks. The mixture of polyphenols with iron(II) sulphate contained complexes, which were in many cases dark coloured, while the black colour was the result of the exposure to air¹. The manufactured inks exhibited very low pH values and represented real danger of the damage for the carrier onto which they were applied. The chemical character of inks remained very important due to the conservation problems and is very important for solving problems with the corrosion of the paper carrier. The damages included the browning of handwriting, the paper breaking, holes in carriers and the total loss of documents caused by the corrosion.

The important component that can influence the reaction between iron ions and phenolic acid is gum arabic, a binder used in the production of the ink. V. Rouchon Quilet observed in her work, that this binder might inhibit the degradation of the paper by iron gall inks².

Several authors have studied the structure of iron gall pigments. Wunderlich assumed that formed complex contained iron octahedrally coordinated with six oxygen atoms in four molecules of gallic acid¹. The iron chelation properties of phenolic acids are very important also for living organism. According to authors Mabrour J. et al., plants tannins, which were used also in the ink preparation were the mixtures of several compounds (tannic acid, gallic acid and ellagic acid) and with iron cations or other metal ions were able to create chelates that composed of 3 phenolic acid units attached to one iron ion.

The evaluation of the metal chelation properties of phenolic acid has been usually done by means of UV VIS absorption spectroscopy, analysing the shifts of UV bands of polyphenolic compounds and the formation of new bands in the visible region³.

Building on the knowledge about historical inks obtained from literature we prepared the model systems compound of gallic acid, ferrous sulphate and gum Arabic. We investigated the reaction of gallic acid with Fe(II) ions. The complex formation in the solution on air and in nitrogen atmosphere was monitored by UV VIS spectroscopy. At the same time we monitored pH value of the solutions.

Experimental

Gallic acid (3,4,5-trihydroxybenzoic acid) monohydrate, p.a. and gum arabic, p.a. were obtained from Sigma-Aldrich, ferrous sulphate ($FeSO_4 \cdot 7H_2O$) was purchased from Lachema Brno (Czech Republic).

We followed the historical recipe to prepare the model inks.⁴ Prepared solution of gallic acid $(3.6 \times 10^{-4} \text{ mol dm}^{-3})$ and ferrous sulphate $(1.8-7.2 \times 10^{-4} \text{ mol dm}^{-3})$ in gum arabic solution (1 g of gum arabic 100 ml⁻¹ water) were mixed immediately before the measurement. The samples were closed in the quartz cell and stored in the dark.

The solutions for study of complex formation in nitrogen atmosphere were continuously bubbled with nitrogen gas for 15 minutes before mixing. After the addition of ferrous sulphate to gallic acid, the samples were saturated with nitrogen again and then closed in quartz cell.

The UV VIS spectra of gallic acid and the changes in the spectra after addition of ferrous sulphate were recorded on UV VIS spectrophotometer PU 8800 (Philips, United Kingdom). The UV VIS spectra were measured in the wavelength range of 200–800 nm vs. a reagent blank containing gum arabic at specified concentrations in the cell (length = 1 cm). The pH measurements were carried out on the digital pH meter (Jenway 3510, United Kingdom).

Results

The UV VIS spectra of the colour complex occurrence on air were investigated in the solution of gum arabic (1 % wt.),





gallic acid $(3.6 \times 10^{-4} \text{ mol dm}^{-3})$ and three concentrations of ferrous sulphate (1.8, 3.6 and $7.2 \times 10^{-4} \text{ mol dm}^{-3}$). The new absorbance band with maxima between 560 and 590 nm was formed after the addition of ferrous sulphate to gallic acid $(3.6 \times 10^{-4} \text{ mol dm}^{-3})$ in gum arabic solution (Fig. 1.). This increase in absorbance indicated that gallic acid chelated iron and produced the complex that gives a colour absorbed in the visible range. The complex formation was slow and continued several hours up to several days, because the delimited reaction was the formation of unstable complex Fe(II) - gallic acid, that was the first step in the formation of the coloured Fe(III) complex. Simultaneously we observed the batochrome shift of absorbance maxima from 260 nm to 280 nm, immediately after the addition of Fe(II) ions and after 4 hours of the interaction of ink components (Fig. 1.). This shift could be caused by the structural changes in the gallic acid molecule as a consequence of the complex formation with Fe or the partial oxidation of gallic acid by the hydroxyl radicals produced via Fenton mechanism in the presence of Fe.



Fig. 2. Increase of absorbance at 560–590 nm after addition of FeSO₄ to gallic acid ([gallic acid]₀ = $1.8 \times 10^{-4} \mod \text{dm}^{-3}$) in solutions with various content of Fe(II) ions ([FeSO₄]₀ = $7.2 \times 10^{-4} \mod \text{dm}^{-3} \blacktriangle$, $3.6 \times 10^{-4} \mod \text{dm}^{-3} \blacksquare$, $1.8 \times 10^{-4} \mod \text{dm}^{-3} \blacklozenge$) on air.

The experimental time dependencies (absorbance at 560 nm) shown in Fig. 2. were fitted by a non-linear least-squares method to the general exponential function (Scientist, MicroMath), and the formal initial rate of the complex formation

$$R_{in} = \left(\frac{dA_{\lambda_{max}}}{dt}\right)_{t \to 0}$$
(1)

was calculated using the evaluated exponential function parameters.⁵ The Fig. 2. showed that the highest rate was reached for the highest concentration of $FeSO_4$.

From Table I is evident that the initial rate of the complex formation and absorbance maxima at 560–590 nm of solutions measured in the presence of air oxygen reached after 3 hours of complex formation decreased with decline of Fe(II) contents in the solution.

Tal	ble	Ι

The influence of initial Fe(II) concentration and atmosphere on complex formation ([gallic acid]₀ = $3.6 \times 10^{-4} \text{ mol dm}^{-3}$, [gum arabic] = 1 % wt.); R_{in} – initial rate of complex formation; A_{3h} – absorbance at 560 nm after 3 hours

Fe:GA	$R_{in}[min^{-1}]$	R _{correlation}	A _{3h}
2:1/air	0.00658	0.993	0.555
1:1/air	0.00557	0.997	0.443
1:2/air	0.00362	0.997	0.312
2:1/N ₂	0.00075	0.997	0.343
$1:1/N_{2}$	0.00078	0.999	0.330
$1:2/N_{2}$			0.007

Parallely with the changes in the UV VIS spectra the differences in pH values of the solutions were observed. The regression in pH value occurred in the range of 4.6 to 4.1–4.3, but it was not strongly dependent on the amount of added $FeSO_4$. The decline in pH value was caused by the production of sulphuric acid that was released during the complex formation or by the oxidation of excess iron(II) sulphate by oxygen in air.



Fig. 3. UV VIS spectra of complex formation after the addition of FeSO_4 to gallic acid ($[\text{FeSO}_4]_0 = 7.2 \times 10^{-4} \text{ mol dm}^{-3}$; [gallic acid] $_0 = 3.6 \times 10^{-4} \text{ mol dm}^{-3}$) at various time after mixing of components (0, 30, 60, 120, 180 min), bubbling with N₂ only immediately after prepaeration.

The differences in UV VIS spectra were investigated in the same solutions in nitrogen atmosphere (Figs. 3., 4., Table I)), while the samples were bubbled with nitrogen gas only right after preparation, then closed in cell and repeatedly measured. In this case the flow of coloured complex formation was very similar to the ones with ratio $FeSO_4$: gallic acid 2:1 and 1:1, while in both cases the significant slow down of reaction in the beginning was observed. After 60 min the significant rise of absorbance took place, the absorbance in visible region after 4 hours was in case of 1:1 ratio close to the value measured without nitrogen. As the solutions were not bubbled continually, we can assume that because of untightiness diffusion of air oxygen into measuring cell could took place which caused creation of coloured complex.



Fig. 4. Increase of absorbance at 560–590 nm with time after addition of FeSO_4 to gallic acid ([gallic acid]_0 = $1.8 \times 10^{-4} \mod \text{dm}^{-3}$) in solutions with various content of Fe(II) ions ([FeSO₄]_0 = $7.2 \times 10^{-4} \mod \text{dm}^{-3} \blacktriangle$, $3.6 \times 10^{-4} \mod \text{dm}^{-3} \blacksquare$, $1.8 \times 10^{-4} \mod \text{dm}^{-3} \blacklozenge$), bubbling with N₂ only after preparation

In sample with access of gallic acid the creation of coloured complex was not observed. In this sample also change in pH during reaction did not occurred, while we observed decrease of pH approximately about 0.2 unit in the first two samples.

So that inert atmosphere was not damaged, all three observed samples were bubbled with nitrogen not only before start of measurement, but also between individual measurements. (Fig. 5) In this case only minimal changes of absorbance in visible region during measurement were determined. The absorbance in sample with the highest content of Fe(II)ions increased about 0.011 during 4 hours, in sample with equimolar content of components about 0.004 and in last sample it did not changed. Coloured complex is not created without presence of oxygen.

Conclusions

The use of UV VIS spectroscopy positively indicates the complex formation due to the absorbance increase at 650 nm and is suitable for the complex stability testing. The complex formation is most effective in solution with excess of Fe(II)



Fig. 5. UV VIS spectra of complex formation after the addition of FeSO_4 to gallic acid ([FeSO₄]₀ = $7.2 \times 10^{-4} \text{ mol dm}^{-3}$; [gallic acid]₀ = $3.6 \times 10^{-4} \text{ mol dm}^{-3}$) at various time after mixing of components (0, 60, 120, 240 min), bubbling with N₂ continual

ions. The reduction in the concentration of Fe(II) ions in the solution causes the retardation of the complex formation.

The complex formation in inert atmosphere is strongly decelerated considering its formation on air, the role of oxygen is determining for colour complex formation.

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L13 STUDY OF INFLUENCE OF IRON-GALL INKS COMPOSITION ON PROPERTIES OF HISTORICAL DOCUMENTS

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Introduction

Iron gall inks applied on documents represent serious problem regarding conservation and preservation of documents. Problem is frequently caused by different kinds of materials and recipes used for ink preparation. Quantitative ratio of ink main components - gallic acid and ferrous sulphate - was considerably different for particular recipes. Chosen 104 historical recipes from 15th-19th century contained more iron as was necessary for creating of colour complex¹, some of them even contained hydrochloric acid or sulfuric acid to reach instant colouration and to improve solubility of pigments². In 18th century it was discovered that inks with the best qualitative properties were with the ratio of gall (source of gallic acid) and green vitriol (Iron (II) sulfate heptahydrate) 3:1. If the ratio for FeSO₄ increases, ink is instable³. In 19th century the unification of manufacture methods of iron gall inks was noticed. Recipes contained only pure compounds - ferrous salts and gallic or tannic acids mixed in stechiometric ratios.

The aim of this work was to investigate changes of paper with applied iron gall ink under accelerated ageing for different molar compositions of main components.

Experimental

Six inks (listed in Table I) with different ratios of gallic acid (Sigma - Aldrich Lambda Life) and ferrous sulphate (Lachema Brno) and constant amount of additives - gum Arabic (Sigma - Aldrich Lambda Life) and sodium benzoate (Lachema Brno) were prepared. Inks were applied on paper Whatman (Whatman Laboratory Division, Maidstone, England, Cat No 1001917, mass per area 90 gm⁻², pH 7) by immersing in solution, removing extra liquid using filter paper and roller with constant pressure; the mass per area addition was 7.35 gm⁻². After drying on air samples were conditioned at 23 °C and RH 50 % during 24 hours. Consequently accelerated ageing was applied in covered bottles at 90 °C at different times 1, 4, 8, 14, 24 hours⁴. Following chemicals and devices were used for experiments and measurements: cupri-ethylene-diamine (Sigma - Aldrich), capillary viscosimeter according to norm ISO 5351/1 for determination of limit viscosity number, device for thermal analysis Mettler Toledo, optic fiber spectrophotometer HR 4000 CG (Ocean Optics Inc.), spectrophotometer SpectroDens A504009 Premium (Techkon).

Table I Composition of iron gall inks

Ink	Gallic acid, GAL [mol dm ⁻³]	FeSO4 [mol dm ⁻³]	Ratio Fe: GAL
AT1	0.10	0.00	0
AT2	0.08	0.02	0.25
AT3	0.06	0.04	0.67
AT4	0.04	0.06	1.5
AT5	0.02	0.08	4
AT6	0.00	0.10	_

Results

Changes of physical and chemical properties of prepared samples caused by accelerated ageing were investigated. Attention was focused on estimation of degree of polymerization of a carrier material (method of limit viscosity number determination), determination of rate constant of depolymerization and thermal analysis – estimation of thermal stability. Using spectrophotometry in VIS/NIR area we tried to determine the course of degradation of inks. Colour changes of inks were also monitored.

The degree of polymerization (DP) of samples was determined viscometrically using cupri-ethylene-diamine as a solvent⁵. Degree of polymerization was calculated from viscometric data using Mark-Houwink-Sakurada equation with the constants (a, K) according to^{6,7}. Rate constants "k" of degradation of paper samples was calculated by least squares fitting of the plot DP *vs*. time using Ekenstam equation for degradation of linear polymers⁸.

$$(1/DP_t) - (1/DP_o) = k \cdot t,$$
 (1)

where DP_t and DP_o are degrees of polymerization at the beginning of ageing and after time "t" of ageing, respectively.

The degree of polymerization during ageing in all cases decreased and differences were in between 1,500–900 (Fig. 1.). Decrease of DP of AT1–AT6 was much more considerable as of only paper Whatman. As Fig. 2. showed,



Fig. 1. Decrease of polymerization degree during ageing; Whatman in comparison with samples AT2 and AT4 (by Ekenstam equation)



Fig. 2. Rate constants of degradation vs. ratio Fe:GAL (AT1 -AT6)



Fig. 3. Dependence of temperature of decomposition on molar ratio of Fe: gallic acid. Samples after 24 hours ageing

depolymerzation rate was considerably higher for samples AT3, AT4 and AT5. Inks with molar ratio greater or equal to 0.67 were destructing substrates faster than others. Inks which didn't contain any of complex components (AT1, AT6) weren't so aggressive to paper.

Basis of thermogravimetric analysis (TGA) consisted of warming of samples with constant rate according to controlled temperature programme in inert N₂ atmosphere and monitoring of the weight changes as a function of temperature (TG curve). Differences in material weight as a function of temperature and proportion of this change represented thermal stability of material. Samples with no ageing and maximum time of ageing were measured. Fig. 3. represented dependency of decay temperature T_d on ink composition and it showed that increasing content of iron decreased thermal stability of samples (lower value of T_d means that degradation takes course earlier).

Series of dependencies of Kubelka-Munk function (reflectance, KM) on wave number (λ) were obtained by measuring spectra in area 380–1,050 nm (VIS/NIR) of paper samples with applied iron gall inks with different ratio of gallic acid and iron for all chosen times of ageing. For evaluation of KM spectra method of factor analysis was used⁸. As a first step analysis of main components was done and



Fig. 4. Changes of colorimetric parameter ΔE^*_{ab} (CIELab) during ageing; all samples



Fig. 5. Changes of colorimetric parameter ΔL^* during ageing; sample AT3

number of linear independent components in spectra was determined. These components correspond to chemical individuals that manifested in measured spectra. Analysis of main components was performed using CVD-TFA method (method of cross verification using factor analysis)⁹. Series of all spectra (non-aged and aged for all times) composed 4 independent components, series of spectra for non-aged samples represented 3 independent components, series of spectra for maximum ageing time (24 hours) represented 3 independent components and combined series of spectra composed of maximum aged and non-aged samples represented 4 independent components. The most probable explanation for these results was that in spectra of non-aged samples existed 3 chemical components, during ageing occurred formation of one new component and another was vanishing. In series of spectra of maximally aged samples occurred 3 chemical components. This method however didn't allow identify their composition.

Regarding colour axis of colour space L^* , a^* , b^* were measured and recalculated to C^* characterizing chroma of colour and h^* representing hue angle (quality of saturation). Total colour difference was calculated from values L^* , a^* , b^* and represented differences between aged and original paper samples. Total colour difference increased according to ageing and in maximum time values total colour difference was in range 3–15 (Fig. 4.). Samples with inks AT4 and AT5 were the most inferior to ageing, the values of colour difference of inks AT1–AT3 and AT6 were acceptable (max. value 4). On the basis of these results regarding influence of ink composition on optical properties of samples it could be assumed that higher ratio of iron to gallic acid caused more considerable changes in colour of samples.

According to analysis of axis changes in colour space interesting behavior of lightness (L^*) was observed. From the beginning value L^* was slightly decreasing for all samples then break occurred and lightness started to increase (Fig. 5.). It could be caused by initial ink colouration (complex formation) on substrate which turned into bleaching (degradation of pigment structure). Chroma (C^*) gradually slightly decreased (saturation was decreasing), value of hue angle of colour tone (h^*) wasn't changing noticeably during ageing.

Conclusions

According to results it could be assumed that inks with ratio of iron:gallic acid greater than 0.67 behaved considerably destructive on paper substrate which proved negative effect of extra iron in writing inks.

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L14 AN OVERVIEW OF INKJET PRINTOUTS ACCELERATED AGEING METHODS

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Introduction

Nowadays, digital photography is the mainstream photographic technology. It is not a new concept, it was invented by Sony in 1981, but it has taken approximately 20 years for the technology to develop into the mainstream business that it is today.

Inkjet printing has become one of the major imaging technologies used in digital printing applications. The versatility of inkjet has led to an ever increasing number of applications for this technology. Inkjet has now diversified into the business/network, wide format, photo realistic and textile printing applications. These require better image durability in order to provide a print performance as good as existing photographic, lithographic, screen or offset printing technologies. For many of these applications the print must be stable for many years for archiving or the preservation of an image exposed to the environment. The light stability of prints is of particular importance and the improvement of the photo stability of inkjet prints is an important goal^{1,2}.

This paper describes the various factors that affect the permanence of inkjet printouts. Accelerated test methods are described with respect to past and current standards that are widely used in imaging industry.

Image Permanence Light Fastness Tests

Standardized image permanence tests serve a number of important purposes:

- to provide guidance to consumers in selecting the longest-lasting materials which otherwise meet their needs in terms of cost, image quality, print size and convenience,
- to provide printer, ink, and paper manufacturers' research & development departments image permanence test methods to help evaluate and improve the longevity of future products,
- to enable manufacturers to understand their position in the marketplace relative to their competitors,
- to provide manufacturers image permanence data for use in promoting their products to customers,
- to provide museums and archives with data concerning the true stability properties of the imaging materials in their collections so that right conditions of the duration of display and storage can be implemented to achieve long-term preservation of the materials in their original, unchanged form.

There are several approaches for determining the light fastness of printouts. The simplest and most realistic would be to expose the print sample to actual daylight. This would indicate true lifetime of the printouts under real time conditions. However, there are many problems associated with such methods as the time taken to achieve results. The alternative, accelerated exposure testing methods have become well established allowing reproducible results to be produced in short time scales. Various standard procedures are available for accelerated ageing which detail sample type and preparation, equipment, exposure conditions, measurement and evaluation of the results^{2,3}.

Attitude to Evaluation of Inkjet Light Fastness Tests

There were two main types of progress in evaluation of inkjet printouts light fastness tests. The first used the existing standards for photographic materials and continued tracking changes of light fastness with densitometric measurements. Status A (for transparencies and reflection prints) and Status M (for negatives) densitometric filter sets were optimized for specific colorant systems of photographic materials. The second way tried to use evaluation of light fastness tests of textiles and dyes with simultaneously tested blue wool references. Light fastness was evaluated by noting on the scale of blue wool standards and rating the standard which has undergone a similar change to that of the print specimen^{4,5}.

History of Accelerated Ageing Methods

First ANSI standard for testing the permanence of color photographs was ANSI PH1.42–1969 – American National Standard Method for Comparing the Color Stabilities of Photographs. This standard did not contain "predictive" tests that could be reported in terms of years of display or the years of storage under specified conditions. It specified a series of comparative tests, including a 5.4 klx glass-filtered xenon arc test to simulate indoor display. It also included tests to simulate use in slide projectors, fluorescent viewers and direct sunlight through window glass. This early standard specified starting densities of both 1.0 and 0.5. It never achieved significant use and during the 1980's was more or less abandoned by manufacturers as well as independent labs³.

ISO 2835: Prints and Printing Inks – Assessment of Light Fastness was published in 1974. It also did not contain "predictive" tests but it described an outdoor glass-filtered daylight test of printouts together with a standard range of eight blue dyes on wool cloth. For accelerated tests it recommended high pressure xenon lamps, light sources with spectral energy distribution very different from daylight were not permissible. Light fastness was evaluated using grey scale for assessing changes in color and blue wool references⁵.

ANSI IT9.9–1990 – American National Standard for Imaging Materials – Method for Measuring was published in 1990. This document specified five comparative tests for light fading stability. The light fading tests included both 6.0 klx glass-filtered cool white fluorescent and xenon arc tests to simulate indoor display conditions. Cautions were given with regard to possible reciprocity failures in accelerated light stability tests, and it was recommended that tests also be conducted at 1.0 klx to asses this problem. A single starting density of 1.0 was specified, but like the previous ANSI standard (PH1.42–1969), it did not specify limits of acceptability for dye fading, color balance shift, or stain formation. These important factors were left to the user to determine.

Described ANSI standard (IT9.9-1990) was adopted with little change by ISO in 1993 as ISO 10977:1993 - Photography – Processed Photographic Colour Films and Paper Prints - Methods for Measuring Image Stability. Light stability test methods were almost the same. Five light stability tests were described: 6 klx simulated indoor indirect daylight test through window glass (xenon arc lamp), 6 klx glass-filtered fluorescent room illumination test, 3 klx incandescent tungsten room illumination test, 100 klx simulated outdoor sunlight test (xenon arc lamp) and intermittent tungstenhalogen lamp slide projection test. 1 klx test for determining reciprocity failure exhibition of materials was recommended too^{3,6}. Standard window glass was specified by relative spectral transmittance of float glass, together with relative spectral distributions of light sources used in light stability test methods (Fig. 1.).



Fig. 1. Illuminants and glass window specification: cool white fluorescent lamp F-6, incandescent tungsten CIE illuminant A, outdoor daylight CIE illuminant D65, indoor indirect daylight ID65 and relative transmittance of standard window glass

In xenon arc simulated outdoor sunlight test light/dark cycles were recommended to provide good correlation with results obtained in some outdoor tests. The sample temperature during both cycles was mentioned too.

ANSI IT9.9–1996 replaced the further ANSI standard from 1990. It continued to specify a 6.0 klx illumination level for indoor light stability tests, and also specified a single starting density of 1.0(ref.³). In the same year an important document was published: ISO 13655:1996 – Graphic Technology – Spectral Measurement and Colorimetric Computation for Graphic Arts Images. This standard defined a methodology for reflection and transmission spectral measurement and colorimetric parameter computation for graphic images⁷. It did not interest in light fastness tests factually, but the methodology defined here was used for evaluation of color changes in these tests later.

In 1997 first edition of ISO 12040:1997 – Graphic Technology – Prints and Printing Inks – Assessment of Light Fastness Using Filtered Xenon Arc Light was published. The method for evaluating light fastness using blue wool references corresponded with the method given by ISO 2835. It described an accelerated test method by specifying the light source and filters for daylight simulation as well as exposure of the test samples to artificial daylight⁸.

Other documents dealing with theme of printouts accelerated tests were ASTM standards. ASTM D 3424 - Standard Test Methods for Evaluating the Relative Lightfastness and Weatherability of Printed Matter was published in 1998 and revised in 2001. It described a series of lightfastness tests using natural or artificial light sources. Accelerated tests were constructed to simulate outdoor weathering, daylight through window glass (both xenon arc apparatus and enclosed carbon-arc apparatus) and indoor lighting in combination with window filtered daylight (fluorescent lamp). Illumination conditions were described in W m⁻² nm⁻¹ at specified wavelength value (340 nm) for xenon arc lamp or in Wh m⁻² for fluorescent lamp apparatus⁹.

In 2005 ASTM F 2366 – Standard Practise for Determining the Relative Lightfastness of Inkjet Prints Exposed to Window Filtered Daylight Using a Xenon Arc Light Apparatus was brought out. It recommended conditions of the test: an irradiance level of xenon arc lamp, the temperature (black panel or chamber air) and relative humidity. It also described the evaluation of changes in color and optical density in the printed samples. Color changes were determined either visually by comparison with the unexposed specimens or instrumentally by comparison with the color of the same specimen prior to exposure and reported as color difference, ΔE^*_{ab} (1).

$$\Delta E_{ab}^{*} = \sqrt{(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2}}$$
(1)

Using of spectrophotometer or colorimeter with the CIE 1964 (10°) Supplementary Standard Observer and Standard Illuminant D65 or the CIE 1931 (2°) Standard Observer and Standard Illuminant C was suggested^{9,10}.

The last mentioned document is ISO 18909: 2006 – Photography – Processed Photographic Colour Films and Paper Prints – Methods for Measuring Image Stability which was published in 2006. It replaced the further ISO standard (ISO 10977) and continued in inconvenient densitometric evaluations of inkjet printouts.

Evaluation Methods Progress

Modern digital printing systems employ a wide variety of pigment or dyebased colorants with markedly different spectral properties, and some use more than cyan, magenta, yellow, and black colorants to achieve enhanced color gamut and improved continuous tone properties. In the current digital era of highly diverse colorant sets, even within a single technology class such as inkjet materials, we can no longer rely on reasonable consistency of neutral gray patch fabrication based on specified densitometric aim points. Additionally, the historical ANSI and ISO test methods only tracked losses of density from a single initial aim point of 1.0, although more starting aim points were allowed. The traditional dyebased chromogenic systems lost density uniformly across their full tonal scale, resulting in a more or less parallel shift (light fade) or linear slope change (thermal ageing) over the majority of the densitometric curve.

Today, this type of performance cannot be assumed. Catalytic fading, non-uniform printed dot dispersions and using three, four, six, seven, eight (or more) ink colorant sets with different blending levels means that the full tonal scale performance cannot be reliably inferred from measurements of just one or two initial density points, the full tonal scale behavior should be evaluated. Densitometry is no longer wholly appropriate method for measuring image quality of modern imaging systems⁴.

While densitometry has long been the process control data of choice for the photo finishing and printing industries, the digital imaging market is now rapidly embracing a colormanaged workflow. It is based on colorimetric characterization of monitors, printers and scanners. With regard to these facts it is better to produce samples for pictorial image quality studies using colorimetric methods rather than densitometric methods.

Some concerns have been raised that ΔE^*_{ab} says something about magnitude but not direction of color change. However, to generate color change one must collect the LAB data, and thus direction of change results are available if one desires to examine these trends.

Conclusions

Lightfastness tests are important guides in the area of material durability. They help both manufacturers and consumers to find out, make or buy a high-quality product. High requirements for information about inkjet print durability resulted in efforts to make the predictive test methods. Accelerated ageing tests are trying to answer these requirements. Nowadays, xenon arc lamps are predominantly used to simulate outdoor illumination or daylight filtered through window glass and white fluorescent lamps to simulate indoor illumination conditions. One have to be careful about possibility of the accelerated light stability tests reciprocity failures.

The testing and measurement of image stability is a very complex science. Standards provide recommendations and

guidance on interpreting and using test data generated by the testing methods. However, these are only general recommendations and guidance because images in general have a wide range of stability requirements based on intended application, and are stored or displayed under a vast range of conditions.

As we work more and more with non-traditional photographic media (inkjet), using densitometry may lead to results that do not correlate well with actual pictorial image changes. Nowadays, attention is given to using the colorimetric characterization of image quality studies. There are some problems about CIELAB data evaluating, but new models of the colour difference are still being developed.

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- ASTM F 2366-05 Standard Practise for Determining the Relative Lightfastness of Inkjet Prints Exposed to Window Filtered Daylight Using a Xenon Arc Light Apparatus.
L15 SUBJECTIVE AND OBJECTIVE EVALUATION OF RECOGNISABILITY OF BLACK **CHARACTERS ON PAPER**

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Introduction

Visibility and recognisability of text is the key factor, influencing the information intake from printed media, billboards and other sources. As follows from several recently published papers, its importance is still increasing with the development of new technologies of spreading out the information (e.g., internet or cellular phone technology). On the other hand, a lack of attention is paid to the text visibility and recognisability, as only few published papers deal with an objective method for its determination/evaluation, respectively until present.1-9

The background/foreground colour contrasts, as well as the luminance of carrier are considered to be the key factors with significant impact on text visibility and recognisability. Further on, the visibility and recognisability of achromatic documents influences besides the previously mentioned also the following visual factors: letter size and style, text effects used, screen resolution, and, additionally, adaptability of reader/observer on the text displayed on screen.

The development of objective method for visibility and recognisability evaluation and prediction is of great importance. It can be later on applied for further paper quality controlling/improvement process, to affect the preferences of printing offices (to use paper of certain grades and luminance); for paper recyclation processes optimization; deacidification, modification, coating, encapsulation, scission or different conservation technologies; effect of processes of deacidification of old books and archive documents; and last but not least, to improve the communication between papermaking and printing industry and their clients/customers.

In order to obtain the objective valuable method for visibility and recognisability evaluation, it is important to find unambiguous answers on the question of the dependence or mutual correlation between subjective assessment of visibility and recognisability and the objective foreground/background contrast measurement, keeping the letter size and style constant. Additionally, the impact of carrier ageing, e.g., paper acidic hydrolysis induced destruction, as well as the influence of modern developed deacidification and stabilization procedures applied for the historical/archival document conservation and protection¹⁰, on their visibility and recognisability is still not satisfactory proven and verified.

The aim of this work is to determine the influence of contrast between text character and background (foreground/ background optical contrast) and other factors on monochromatic text visibility and recognisability and to present new valuable method of its evaluation from simultaneous comparative subjective (human observers) and objective (spectrophotometric) measurements of optical contrast. Moreover, we propose here the objective method for the determination of visibility and recognisability of documents and its prediction in aged documents in respect to all previously mentioned significant objective factors.

Experimental

Samples Characterisation

Commercial white office paper Maestro was used in all experiments. Sets of randomly generated standard black colour letters of Latin alphabet (size, 12 pt; style, Times New Roman regular (Microsoft Office[®] 2003)) creating the strings of constant length, printed using commercially available colour printer, (nominal resolution, 600 DPI) were printed out on paper sheet. Standardized black letters are defined in CIE L*a*b* system as follows:

$$L_{c}^{*} = 30.668, a_{c}^{*} = 0.714, b_{c}^{*} = -0.18$$
 (1)

Subjective Visibility and Recognisability Evaluation Observers

Ten undergraduates of an average age of 20 years with standard visual acuity and correct colour recognisability without any previous experiences with such type of testing were used as observers. Five sets of randomly generated text strings of identical length were used during the measurement with one observer. The character of strings excluded the factor of potential learning process.

FGHIJT	3 Z Y V S F R E	81K08KD1	Y FG W Q O P V	BMNKL2
K L T 2 U 3	EWQZYPU	VYUOPM	8 S 9 5 4 7 W A	рүссхви
POU2RE	57891456	RBVYXZV	UBKLFDS	OULITD

Fig. 1. An example of the text string used in visibility and recognisability tests. (Contrast: background 0 % B_{h.MS Word}, text 100 % B_{b MS Word}).

Typical set of generated text string is shown on Fig. 1. Two trained observers moreover estimated the distinction in borders using the method of magnitude estimation as previously suggested in ref.¹. Observers were tested to the ability to correctly recognize (read) 10 randomly selected letters from the generated strings for each contrast scale (Table I).

Evaluation of the influence of document contrast on its visibility and recognisability

Psychophysical method was used to measure the number and percentage of correctly recognized characters (R_{a}) at the same background/foreground contrast of documents:

Observers were asked to recognize 10 randomly selected characters from different text strings for each contrast between text characters and background. The distance l_i (cm) between the observer and text was changed continuously either to the distance l_{100,i} at which still 100 % of the text was recognized correctly, or to $l_{0,i}$, with 0 % of correctly recognized letters. Using this approach, the dependence of correctly recognized letters on the distance for each colour contrast was obtained. The so obtained "absolute" individual visibility and recognisability functions $R_{S_i} = f(l')$ was normalized, in order to minimize the influence of external factors (e.g., light direction, source or intensity). Each l_i value was related to the value of l_{100} , obtained for the text string written on 100% white background (0 % B_{b, MS Word}, Table I). The so-obtained values of l'i were used for the contrast dependent visibility and recognisability evaluation.

Objective Visibility and Recognisability Evaluation

The same text samples as utilised in subjective visibility and recognisability tests were analysed by commercially available spectrophotometer Minolta CR 200. CIE colour parameters L^{*}, a, and b for both, text characters (L^{*}_C, a_C, b_C) and for background (L^{*}_B, a^{*}_B, b^{*}_B, using the cylindrically shaped gape collector (gape size, 3 mm) without any filters and software correction applications. From these values the colour difference ΔE_{C-B} between the text and its background as a basic evaluation parameter was calculated using the following equation:

$$\Delta E_{C-B} = \sqrt{\left(L_C^* - L_B^*\right)^2 + \left(a_C^* - a_B^*\right)^2 + \left(b_C^* - b_B^*\right)^2} (2)$$

Statistical Analysis and Data Correlation

The dependencies of l'_i and ΔE_{C-B} on text visibility and recognisability as well as the mutual correlation between these parameters were fitted to the proper mathematical function using the non-linear regression analysis. The statistical parameters of the calculation procedure (R squared, coefficient of determination and correlation, P) serve for the quality of correlation consideration.

Results

Typical dependence of averaged visibility and recognisability on relative distance from an object, obtained for different background/foreground contrasts (ΔE_{C-B}) from typical observers, is depicted on Fig. 2. For the better visualization of the text recognisability dependence on foreground/ background contrasts, the obtained dependencies for each contrast were averaged and the maximum achieved distance at which just the 100% successful recognisability was achieved ($l_{100\%}$) at each contrast value was evaluated. As we have found, the continuous background "darkening" causes the gradual luminance decrease. We moreover found, that text visibility and recognisability increases significantly in the

Table I

A set of different background/foreground contrast, ΔE values obtained from (2), and subjective evaluation of the same colour system. The different contrasts between background and printed text (foreground) were achieved using Microsoft Office Word[®] 2003 software grey scale, setting the ratio of black colour (Bb, MS Word) to 0 % (100 % white); 5 %; 10 %; 20 %; 30 %; 40 %; 50 %; 60 %; 70 %; 80 %; 90 %; 95 %; and 100 % (totally black), respectively, as it is listed bellow

Background shading set by MS Word® Software	Blackness B _{b MSWord®} [%]	ΔE_{C-B}	ΔE_{C-B} , visual evaluation
- ,	100	0.0	negligible
FGHIJ	95	6.1	significant
FGHIJ	90	8.2	great
FGHIJ	80	15.7	considerable
FGHIJ	70	20.4	considerable
FGHIJ	60	28.3	considerable
FGHIJ	50	36.5	considerable
FGHIJ	40	40.6	considerable
FGHIJ	30	48.0	considerable
FGHIJ	20	53.1	considerable
FGHIJ	10	60.2	considerable
FGHIJ	5	64.5	considerable
FGHIJ	0	64.7	considerable



Fig. 2. The dependence of text recognisability(R_s ; %) on the relative distance from observer (l'; m), evaluated from visual test for different colour contrasts $B_{b, MS Word}$

range of $\rm B_{b,\,MS\,Word}$ % <10–30>, in comparison to pure white background.

The further addition of black colour (% $B_{b, MS Word}$) into background does not influence the text visibility and reco-

gnisability in any way, as the maximum distance for 100% correctness of reading is in fact, the same as if the text is printed on white background (0 % $B_{b, MS Word}$). As a result of additional darkening, the visibility and recognisability and correctness of text recognition dramatically decreases and at 95 % $B_{b, MS Word}$, which is in fact, almost pure black background of similar hue and saturation as the text in fore-ground, the correctness fallen down close to zero.

The dependence of visibility and recognisability on text background is better visible, when the relative distance, $R_{\rm e}$, is plotted versus the foreground/background colour difference ΔE_{C-R} , evaluated from spectrophotometric measurements, as it is clearly depicted on Fig. 3. for the same observer. The opinion that text recognisability is in linear dependence to the optical contrast, is widely spread out. In contrary to this assumption, we found that the dependence between the visual subjective recognisability/visibility and recognisability and optical contrast ΔE_{C-B} is not linear in the whole range of ΔE_{C-B} $_{R}$, as is finally clearly demonstrated on Fig. 3. (theoretical course 1). At lower ΔE_{C-B} (up to 30%) the linearly growing dependence of visibility and recognisability on colour contrast is observed, while on the contrary at higher $\Delta E_{C,R}$ the saturation of text visibility and recognisability is observed, or the visibility and recognisability slightly decreases.

From the data presented on Fig. 3., the region of improved recognisability might be delimited. At optical contrast e.g., $\Delta E_{C-B} = 64.7$, $L_B^* = 93.2$ and $B_{b MSWord} = 0$ % the value of relative visual recognisability/visibility and recognisability reaches the value $R_s = 0.983$. If the optical contrast decrease of e.g., to $\Delta E_{C-B} = 53.1$, the R_s value increased to the value of 1.02. It means that in spite of lowered optical contrast between the foreground text and background, reader/observer is able to recognize the printed character from the longer distance than at higher optical contrast.

Data obtained in subjective visibility and recognisability tests served for the re-calculation and transformation of optical



Fig. 3. The representative dependence of text visibility and recognisability (expressed as Rs) on the colour difference (ΔE_{C-B}), evaluated from spectrophotometric measurements, whitness of background (L_B^*) and blackness ($B_{b\ MSWord}$; %). 1 – theoretical course, 2 – measuring course

colour difference (ΔE_{C-B}) on the objective optical-device predictable visual recognisability/visibility and recognisability, expressed by the following mathematical equation:

$$R_{s} = \left[1 - \left(\frac{\Delta E_{c-B} - 56.4}{56.4}\right)^{2}\right]^{0.87},$$
(3)

which correlates well with experimental data. As follows from the data presented, change in relative recognisability is significantly dependent on the initial optical contrast, i.e. on the optical contrast of non-modified document.

Conclusions

Based on the results presented, we can conclude that the visibility and recognisability of text printed on white background (i.e., freshly produced paper just after the industrial whitening), is even worse than those, printed on grey or shaded papers. This fact can find effective application in paper recycling industry, which is nowadays of growing importance, with one of the key problems of recycled paper whitening without the influence on its mechanical or physical properties.

The evaluation of text visibility and recognisability of printed documents based on both subjective and objective assessment is presented in this paper for the first time. Objective easy-to-use methods of paper visibility and recognisability evaluation based on tristimulus values measurements are presented, based either on the relative visibility and recognisability and optical contrasts or on their relative indexes dependencies, respectively. As follows from results presented, the dependence of recognisability and visibility of printed text on respective background optical contrast has not the linear character, i.e., the higher optical contrast ("white background") can even make the visibility and recognisability of text worse than that printed on lower contrast background.

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L16 PIGMENTS FOR PHOTOCATALYTIC PAINTS

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Introduction

During recent years environmental problems play an important role in the applications of titania pigments. These include the use of their photocatalytic behavior in the development of self-cleaning surfaces for buildings, i.e. antisoiling and antifungal growth and NO_x emissions reduction. In terms of self-cleaning paints, the idea is to limit the oxidation and chalking of the paint film to the very near surface layers such that over time with weathering rain water will wash the top layer leaving an underlying clean fresh surface. In this regard, mixtures of pigmentary rutile and nanoparticle anatase pigments appear to provide the best option, with the former inducing some level of base stability, whereas the presence of the latter gives rise to surface activity¹.

It is well known¹ that photocatalytic paints should contain two types of titania at minumum, pigmentary grade rutile serving as effective UV filter and nanocrystalline anatase serving as the photocatalytic component responsible for the photocatalytic function of the paint. Whereas the function of the pigment grade rutile in paints is well known and long time experience exists with this kind of material, the effect of nanocrystalline anatase is much less investigated till now. We expect that this kind of material should possess high photacatlytic activity and should be easily dispergable in the paint medium. We suppose that these demands should be fulfilled by anatase with particle size below ~ 80 nm or anatase/rutile mixtures with the same particle size. The synthetic procedure should be acceptable from environmental point of view and should be technologically viable at acceptable price.

Experimental

Synthesis of Hydrated Titania Gel Samples

Aqueous solution of titanyl sulphate containing 33 g dm⁻³ of TiOSO₄ was slowly neutralized with 26% aqueous NH₃ melting ice bath under stirring with magnetic stirrer; the desired pH was achieved within 20 min. After the pH was reached, the suspension was stirred for additional 30 min. The obtained precipitate was filtered off and repeatedly dispersed in water until no anions were detected. Finally, the product was washed out with distilled water and isopropyl alcohol and dried at 40 °C in air. The samples denoted as AP and RP were prepared by adding of equimolar amount of 26% aqueous NH₃ to the TiOSO₄ solution at 80 °C; moreover, the RP sample contains also 5% of rutile nuclei.

In order to assess photocatalytic properties of the catalysts, kinetics of 4-chlorophenol (4-CP) decay in an aerated aqueous suspension of photocatalyst was measured. The irradiation experiments were performed in a home-made laboratory photoreactor. Probes of irradiated suspension (1 ml) are taken at desired irradiation times and analyzed by HPLC. The HPLC experiments were run on a Merck device with L-6200 Intelligent Pump, L–3000 Photo Diode Array Detector and D–2500 Chromato-Integrator. Mobile phase methanol/water (2:3, v/v) and a Merck column LiChro-CART 125–4 filled with LiChrosphere 100 RP–18 (5 mm) were used. Injection loop was 20 ml, and a flow rate of 1 ml min⁻¹ and detection wavelength of 280 nm was applied^{2,3}.

Structural morphology of the samples was revealed by SEM (scanning electron microscopy). A Philips XL 30 CP microscope equipped with EDX (energy dispersive X-ray), Robinson, SE (secondary electron) and BSE (back-scattered electron) detectors was used. TEM observation was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB6 cathode, 1.7 Å point resolution) with an EDX (energy dispersive X-ray) detector attached. Samples were reground in agate mortar, the powder was dispersed in ethanol and the suspension was treated in ultrasound for 10 min. A drop of very dilute suspension was placed on a carbon-coated Cu grid and allowed to dry by evaporation at ambient temperature.

Powder X-ray diffraction (XRD) was used for monitoring the phase composition of the samples. Unit-cell parameters, crystallite size, and weight fractions of phases were calculated by the Rietveld method. X-ray powder diffraction of annealed samples was performed on a Siemens D5005 diffractometer (Bruker AXS, Germany) using Cu Ka radiation (40 kV, 30 mA) and a diffracted beam monochromator. Qualitative phase analysis was performed with High Score software package (PANalytical, the Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, Germany, version 8.0), and JCPDS PDF–2 database. For quantitative phase analysis, Diffrac-Plus Topas software package (Bruker AXS, Germany, version 2.1) with structural models based on ICSD database was used.

Surface area of the samples was determined from nitrogen adsorption-desorption isotherms at liquid nitrogen temperature using a Coulter SA 3100 instrument with 15 min

Table I Properties of the initial titania gels

Sample	Preparation pH	Surface area [m ² g ⁻¹]	Content of S [% wt.]	Wt. loss by annealing to 1200 °C [% wt.]
TIG 7	3	140	4.9	32
TIG 8	6	180	1.6	24.8
TIG 9	8	260	0.2	20.3
AP	(7)	76	2.7	21.7
RP	(7)	78	2.8	20.8

lasting outgas at 120 °C. The surface area was calculated by BET method while the pore size distribution was determined by BJH method.

Results

The characteristics of the studied titania gels are given in Table I. The results given in this Table show that all prepared hydrated titania gel samples contain remarkable content of sulphate anions (given as S content). The content of SO_4^{2-} decreases with increasing precipitation pH; at higher pH values can be prepared saples practically free of bound sulphate anions. All synthesised samples show rather high surface area, increasing with increase of the precipitation pH.

Fig. 1. shows X-ray diffraction pattern of the starting hydrated titania. The samples precipitated at higher temperature (AP and RP) contain mostly nanocrystalline anatase whereas the samples prepared at melting ice temperature TIG 7–9 are practically amorphous with signs of crystallinity at the sample TIG 7 prepared at the lowest pH 7.



Fig. 1. XRD patterns of the precipitated titania gels. a -sample RP; b - sample AP; c - sample TIG 7; d - sample TIG 8; e - sample TIG 9

Typical microstructure of the initial gels is shown on the Fig. 2. The micrograph A shows the initial sample; we can observe small (4–5 nm) crystalline zonnes randomly oriented which are surrounded by amorphous material. After annealing at 800 °C (Fig 2.B), the material is crystalline with typical crystal size in range 50–80 nm. Detail examination show that particular crystals consist of ~ 5 nm domains indicating that the crystals were formed in a self-assembly process of seeds.

It is well known that annealing of hydrated amorphous or nanocrystalline titania gels results in growth of crystalline anatase particles, at tempearture higher than 800 °C transformattion of anatase to rutile occurs. This proces has been described earlier for nanocrystalline hydrated anatse prepared by homogeneous precipitation with urea². The behaviour of our samples is similar to the earlier described system but we observed that the phase composition of the



Fig. 2. TEM micrograph of the starting gel TIG 7 (A) and of its annealing product at 800 °C (B)

annealed product depends significantly on the conditions of preparation of the starting gel. Fig. 2. shows the dependence of the anatase content in the annealed hydrated titania gels on preparation temperature (the rest to 100 % is rutile). We can see on this Fig. that the transition temperature from anatase to rutile is situated between 800–1,100 °C, depending on the preparation conditions of the initial gel. The lowest transition temperature was found for the RP sample (containing rutile seeds), the highest for the sample AP (prepared at 80 °C). The anatase to rutile transition of the TIG samples lies between these samples, the lower is for the TIG 7 sample prepared in weakly acidic medium whereas the higher is for the TIG 9 sample prepared in weakly alkaline medium.

The growth of the crystals during annealing is shown on the Fig. 4. We can observe continuous growth of particles during annealing in range 5–200 nm. The results presented on Figs. 3. and 4. showed that, depending on the conditions of synthesis of the starting gels (pH and temperature) and the annealing mode, both particle size and phase composition can be adjusted in rather wide range.



Fig. 3. Anatase to rutile transition of the precipitated titania gels. a – sample RP; b – sample TIG 7; c – sample TIG 8; d – sample TIG 9; e – sample AP

The photocatalytic activity of the annealing products of the sample AP determined by decomposition of 4-chlorophenol as model reactant are given on Fig. 5. We can observe on this Fig. that the activity of some tested materials is rather high, even exceeding the Degussa P–25 material (often used



Fig. 4. Dependence of the particle size of TiO₂ on the annealing temperature for different starting titania gels



Fig. 5. Photodecomposition of 4 chlorophenol on various photocatalysts. 1 – starting AP sample; 2 – sample AP annealed at 700 °C for 30 min; 3 – sample AP annealed at 700 °C for 8 h; 4 – sample AP annealed at 800 °C for 30 min; 5 – sample AP annealed at 800 °C for 8 h; 6 – sample AP annealed at 900 °C for 30 min; 7 – sample DEGUSSA P–25

as standard photocatalyst for comparative assessment of photocatalytic activity).

The dependence of the 1st order rate constant of photocatalyzed decomposition of 4-chlorophenol on the annealing temperature for the sample AP is given on Fig. 6. We



Fig. 6. Dependence of photoactivity of the annealed AP sample on the annealing temperature

can observe sharp peak at this graph in temperature range 800-900 °C (transition temperature anatase – rutile for this sample).

Conclusions

The described synthetic procedure for preparation of photocatalytic titanium oxide is suitable for preparation of highly active nanocrystalline material; the process enables to set both particle size and anatase/rutile ratio by controlling the parameters of synthesis. The materials were successfully tested as photoactive component in photocatalytic paints.

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L17 PHOTOLYSIS OF ARENE–IRON PHOTOINITIATORS

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Introduction

Already 100 years ago G. Ciamcian predicted exploitation of photochemistry reactions in industry: "I do not believe that the industry should wait any longer before taking advantage of the chemical effects produced by light"¹. But Roloff complain, that "large photochemical production processes are still extremely rare" in eighties². Nowadays the systems cured by UV radiation, or energy-rich radiation in general, are used in many branches of industry.

Arene–iron photoinitiators are investigated relatively long time^{2,3}, their synthesis published Nesmeyanov in 1963⁴, but only one is commercially available: $(\eta^5-2,4$ -cyclopentadien–1-yl)[(1,2,3,4,5,6- η)-(1-methylethyl)-benzene]-ferrous hexa-fluorophosphate (under the commercial name Irgacure 261 by Ciba Speciality Chemicals). New types of arene–iron complexes are synthesized and tested as initiators for radical⁵, hybrid⁶ or mainly cationic polymerizations.^{5–10} and others

Photolysis of twelve arene-iron compounds was studied in this paper. The capability of initiation of UV polymerization was investigated previously for some of these compounds by fotocalorimetry⁷ or FTIR^{9,10}.

Experimental

Materials

Eleven arene-iron salts were synthesized by exchanging the ferrocene ligand or by nucleophilic substitution reaction⁷.

A mixture of ferrocene, aluminium chloride, aluminium powder in the excess of relevant arene (benzene for B, 1,3,5-trimethylbenzene – TMB, hexamethylbenzene – HMB, 1,4-diisopropylbenzene – DIPB, 1,3,5-triisopropyl-benzene - TIPB, chlorobenzene - CB, 4 methylphenol - PMP, phenyl ether - DPO and biphenyl -BP) was refluxed under nitrogen for 15 hours. After cooling, the mixture was treated with ice gradually added with constant stirring. After the end of exothermic reaction, the mixture was filtered and the phases of filtrate separated. The organic portion was extracted with water; the combined aqueous phases were extracted with diethyl ether and added to a concentrated solution of potassium hexafluorophosphate in water. The mixture was stirred, and then kept in a refrigerator for several hours. The precipitated solid was collected by filtration and dried. The raw product was purified by recrystallization from an acetone-ether mixture.

In the case of nucleophilic substitution reaction a mixture of sodium hydride, isopropyl alcohol (for IPOB, resp. *n*-propyl alcohol for NPOB) and tetrahydrofuran was stirred under inert atmosphere for about 10 min, whereupon mixture of CB (η^5 -cyclopentadien–1-yl) [(η^6)-chlorobenzene]-Fe(II) hexafluoro-phosphate) and tetrahydrofuran was added. The mixture was stirred at room temperature under argon in darkness for 24 hours, whereupon it was concentrated by evaporating the solvent and treated with potassium hexafluorophosphate in water. After shaking, dichloromethane was added followed by solution of hydrochloric acid for adjustment of pH. After separation, the aqueous layer was extracted with little amount of dichloromethane; the combined organic phases were dried with salt brine, and evaporated until almost dry. The brown-red tar formed was dissolved in dichloromethane, and the product was precipitated by addition of diethyl ether.

Initiator IPB was not synthesized but commercially available initiator (Irgacure 261) by Ciba Speciality Chemicals was used. Structure formulas of tested initiators are shown in Fig. 1.



Fig. 1. Structure formulas of tested initiators

Experimental Apparatus and Measurement Method

UV-VIS absorption spectra and photolysis of photoinitiators were monitored by UV-VIS spectrometer Specord 210 (Analytik JenaAG, Germany) in solutions of photoinitiators in acetonitrile at room temperature. The molar absorption coefficients were calculated using the Lambert-Beer's law. Photolysis of photoinitiators (concentration of 2×10^{-4} mol dm⁻³) was followed by decreasing the absorption bands after irradiation by high-pressure mercury lamp (CE Green Spot from UV Source Inc., USA). The intensity of irradiation was 500 mW cm⁻² (in the spectral region 258–380 nm). The normalized absorbance A_n was calculated by (1):

$$A_{n} = (A_{0} - A_{t})/(A_{0} - A_{\infty}), \tag{1}$$

where A_0 is absorbance of measured band before the irradiation, A_{∞} is absorbance after the final photolysis and A_t is absorbance after the irradiation time t.

The dependence of normalized absorbance on the irradiation dose was described by (2) for first-order reaction:

$$A_{n} = P_{1}(1 - e^{-P_{2}E}), \qquad (2)$$

where P_1 is maximal normalized absorbance, P_2 is rate of decomposition after irradiation and E is the irradiation dose [mJ cm⁻²]. From (3), $E_{1/2}$ can be calculated as the energy needed to achieve the half photodecomposition.

$$E_{1/2} = \ln 2/P_2$$
 (3)

The degree of photodecomposition X_p of initiators for irradiation dose E was calculated from (4):

$$X_{p} = A_{p}/P_{1} \tag{4}$$

Results

Photolysis spectra of [Cyclopentadien-Fe–arene] PF_6 photoinitiators are on Fig. 2. The concentration of photoinitiators in acetonitrile was 2×10^{-4} mol dm⁻³ and irradiation dose was 0–1,600 mJ cm⁻². Arrows mark the change of absorption bands during the UV exposure. Isoabsorptive points indicate that photoinitiators photodecomposition proceeded selectively without side reactions.

The degree of initiators decomposition caused by UV irradiation was evaluated from absorption changes at such wavelengths, where only respective initiators absorb (not products of its photodecomposition): 243 nm for B, CB, DIPB, DPO, IPB, IPOB, PMP, and NPOB, 245 nm for HMB, TIPB and TMB. The photolysis absorption spectra of BP are different from other tested initiators. Biphenyl produced during decomposition of BP has strong absorption band at 250 nm (Fig. 3.). From this reason, the absorption band at 290 nm was chosen.

Type of ligand has influence on absorption spectra and rate of decomposition of photoinitiators. The lowest absorption was found out for initiator B, the highest absorption for initiators with electronegative atoms in ligands. Rate of decomposition is also higher in present of ether, halogen or alcohol group. Course of decomposition was slower if methyl or propyl substituent were used on arene ligand. After UV irradiation arene ligand is released and band 243 nm decreases (except BP).



Fig. 2. Absorption spectra of photoinitiators in acetonitrile (concentration of 2×10^{-4} mol dm⁻³) measured after UV exposure

The dependences of photoinitiator normalized absorbance A_n (1) on UV dose were fitted by non-linear regression according to (2). The non-linear regressions were treated by software OriginPro. The adequacy of proposed regression model with experimental data and the reliability of parameter estimates P_1 and P_2 found (Table I) were examined by the goodness-of-fit test. The determination coefficients R^2 are equal to 99.5 % or better. Applying (3) to the data according to the regression criterion, the energy needed to achieve of photodecomposition of 0.5 ($E_{1/2}$) has been estimated (Table I). Comparing the values of $E_{1/2}$ or P_2 it is apparent that speed of decomposition is higher in present of alcohol,

ether or halogen group on arene ligand. Course of decomposition was slower if methyl and propyl groups were used.



Fig. 3. Absorption spectra of initiators (BP and DPO) and abs. spectra of correspond ligands produced by photolysis

Table I Decomposition of initiators (solution in acetonitrile)

initiator	λ[nm]	$[dm^{-3}mol^{-1}] \\ cm^{-1}]$	P ₁	$\begin{array}{c} P_2\\ [cm^2mJ^{-1}]\end{array}$	E _{1/2} [mJ cm ⁻²]
IPB	243	11,858	1.046	0.0020	333
DIPB	243	12,024	1.055	0.0020	347
CB	243	14,830	1.020	0.0025	275
NPOB	243	16,040	1.008	0.0028	270
DPO	243	14,399	0.996	0.0035	194
PMP	243	8,043	1.008	0.0038	185
HMB	245	11,494	1.241	0.0011	645
TIPB	245	8,438	1.079	0.0017	402
TMP	245	9,254	1.036	0.0021	321
IPOB	243	13,796	1.088	0.0030	227
В	243	7,048	1.107	0.0016	406
BP	290	5,432	0.982	0.0089	71

Normalized absorbances were recalculated by (4) and the degree of photodecomposition X_p of initiators for irradiation dose E was obtained (Fig. 4.). There is apparent influence of type of ligand on the course of photolysis of photoinitiators. The sequence of initiators names in legend correspond with speed of photolysis (for initiator BP different absorption band was evaluated, so comparing with others initiators is questionable).

Conclusions

The molar absorption coefficients and degree of photodecomposition of prepared initiators was determined. Types of used ligands influence the absorption spectrum of photoinitioator, rate of decomposition and UV dose needed for achieving of $E_{1/2}$. Initiators with alcohol, ether or halogen



Fig. 4. Dependence of degree of initiators decomposition on UV dose

substituents on ligands have higher molar absorption coefficients and decomposition of them are accelerated. The found results of decomposition efficiency correspond with results of polymerization initiation efficiency in epoxide and vinyle-ther binders^{9,10}.

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L18 KINETICS OF OXIDATIVE PROCESSES ON INKJET-PRINTED THIN LAYERS OF TITANIUM DIOXIDE

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Introduction

As the photogenerated active oxygen species are formed at the irradiated TiO_2 surface, this system can be utilized for microbes deactivation instead of the conventional methods such as UV irradiation, heat treatment or chemical disinfectant application.

The mechanism for bactericidal activity of photocatalytic oxidation was firstly¹ proposed by Matsunaga et al. in 1985. In this pioneer study, they showed that coenzyme A taking part in many biochemical processes is photoelectrochemically oxidized, which leads to the inhibition of cellular transpiration and eventually cell death. Most studies of photocatalytic microbe inactivation are focused on bacteria^{2–16}, less on viruses¹⁷, yiest^{18,19} and fungus^{20,21}. As most of the bacteria-focused studies deals with *Escherichia coli*, this species was proposed as a standard microorganism for normalised testing of the photocatalytic activity of various substrates. One reason for this choice is definitely the fact that the presence of this bacteria indicates the contamination of water by feaces.

The mechanism for bactericidal effect of photocatalytic process on TiO₂ was in detail described on *E. coli*: Maness²² et al. proposed, that *E. coli* was killed by the process known as lipid peroxidation. They propose that the first step is the interaction of oxidation products generated by irradiated titanium dioxide with microorganism cell wall. Here the initial oxidative damage takes place. Despite having the cell wall damaged, the cell is still viable. After the erosion of cell wall, an attack onto the cell membrane takes place as the polyunsaturated phospholipids are the main components of bacterial cell membrane.

The formation of malondialdehyde was also observed, indicating the oxidative decomposition of lipids in protoplasm. This is a highly reactive compound capable of damaging proteins, nuleic acids and bases. Due to the severe erosion of membrane structures the vital biochemical processes such as respiration, semipermaeability and oxidative phosphorilation are slowed down and evetually terminated, resulting in ultimate cell death.

Sunada et al.²⁴ studied the destruction of *Escherichia coli* entotoxine which is an integral component of cell membrane by titanium dioxide. They proved that the cell death was accompanied by the endotoxine degradation and concluded, that the photocatalytic ptocess onto a TiO₂ thin film includes the destruction of outer bacterial mebrane.

Some differences in the susceptibility of various microorganisms to the photocatalityc stress can be observed. The differences are especially apparent between gram-positive and gram-negative bacteria. The gram-positive ones, although being less structurally complex then the gram-negative ones, are encapsulated by a thick peptidoglycanous layer. Similarly fungi and yiest are less sensitive to the photocatalitic attack because of their strong eucariotic cellular wall representing relatively strong resisting barirrier agaist the reactive oxygen radicals generate on the surface of irradiated titanium dioxide.

Electrons reduce adsorsobed oxygen to superoxide radicals (O_2^{\bullet}) . Electron holes exidies OH groups into hydroxyl radical HO[•], which then act as the main oxidizing agents. The heterogeneous photocatalytic process then consists of a series of reactions which may be expressed by the following set of equations:

$$\text{TiO}_2 \xrightarrow{k\nu} \text{TiO}_2(\mathbf{c}_{cb}^-, \mathbf{h}_{yb}^+) \longrightarrow \text{recombination}$$
(1)

$$TiO_{2}(h_{vb}^{+}) + H_{2}O_{ads} \longrightarrow TiO_{2} + HO_{ads}^{\bullet} + H^{+}$$
(2)

$$\operatorname{TiO}_{2}(h_{vb}^{+}) + \operatorname{HO}_{ads}^{-} \longrightarrow \operatorname{TiO}_{2} + \operatorname{HO}_{ads}^{\bullet}$$
(3)

$$\operatorname{TiO}_{2}(\mathbf{h}_{vb}^{+}) + \mathbf{D}_{ads} \longrightarrow \operatorname{TiO}_{2} + \mathbf{D}_{ads}^{+}$$
(4)

$$HO^{\bullet} + D_{ads} \longrightarrow D_{oxid}$$
(5)

$$TiO_{2}(e_{cb}^{-}) + A_{ads} \longrightarrow TiO_{2} + A_{ads}^{-}$$
(6)

Here, **A** stands for the electron acceptor and **D** electron donor. In most cases, a complete mineralization of organic substrate takes place and CO_2 a H_2O are the final products. Dissolved oxygen is the usual acceptor in aqueous media, being transformed into superoxide anion-radicals ($O_2^{\bullet-}$), which can further initiate the formation of hydroxyl radical HO[•]:

$$\operatorname{TiO}_{2}(\mathbf{e}_{cb}^{-}) + \mathcal{O}_{2_{ads}} + \mathrm{H}^{+} \longrightarrow \operatorname{TiO}_{2} + \mathrm{HO}_{2}^{\bullet} \underbrace{\longrightarrow} \mathcal{O}_{2}^{\bullet-} + \mathrm{H}^{+} (7)$$

Although the photocatalytic inactivation of microorganism is not suitable for the decomposition of a large quantity of matter in a short time, it became a highly effective measure to eliminate lower concentration of microorganisms and especially to prevent their further growth.

Generally, several different disinfection kinetic models are used in order to describe the microorganism killing²⁶. The first empiric model for experimental data fitting was proposed by Chick and Watson in 1908:

$$\ln\frac{N}{N_0} = -k c^n t , \qquad (8)$$

where N_0 and N corresponds to initial and remaining microorganism population, respectively, k is inactivation rate constant, t is reaction time, c is disinfection agent concentration and n is reaction order. In most cases n equals 1, causing the deactivation of microorganism to become a first-order reaction. The Chick-Watson model was modified considering two different kinetic constants, k_1 describing the rate of microbial disinfection and k_2 taking into account the biocide concentration decrease:

$$\ln \frac{N}{N_0} = -\frac{k_1 c^n}{nk_2} \left[1 - \exp(-nk_2 t) \right]$$
(9)

In 1972, the kinetic model of Hom was developed, which assumes a general equation for disinfection:

$$\ln \frac{N}{N_0} = -\mathbf{k} \ c^m t^h \ , \tag{10}$$

where k is the disinfection rate constant, c is the concentration of biocide, m is the Hom dilution coefficient, t is elapsed time and h is the Hom time exponent²⁹. It should be noted that if h equals 1, then the equation reduces to that of the Chick-Watson model.

Some authors, who studied UV disinfection of wastewater, tried to replace the concentration of disinfectant in the previous equation (10) with the intensity φ of UV radiation³¹. Then the expression of the rate N/N_0 becomes:

$$\ln \frac{N}{N_0} = -k \; \phi^* t = -k \; H \; , \qquad (11)$$

where t is time of exposure and then the product $\varphi \times t$ gives the total exposure dose $H[Jm^{-2}]$.

Horie and co-authors assumed that cell deactivation obeys a second-order reaction between cells and oxidative radicals, and the death of a cell is caused by *n* times reactions on the basis of a series-event model. They derived complex equation for rate constant k' of photocatalytic disinfection in slury of titanium dioxide taking into acount titanium dioxide concentration and incident light intensity²⁵.

Unfortunatelly, these equagtions doesn't obeys fully to experimental data of photocatalytic disnfection of yeasts on immobilized titanium dioxide layer.

The most popular way of titanium dioxide thin layer preparation is sol-gel method. Usually the substrates are coated by dip-coating or spin-coating method. But each of them has some drawbacks. It would be very convenient to prepare these layers by way similar to spray coating. Inkjet printing is apparently a very good candidate for this task. In a conventional inkjet printer, small droplets of low viscosity ink are ejected from a print head and fall onto printed substrate. If we are able to replace the ink with a liquid precursor and printing paper with a suitable substrate, we obtain a very robust device for the precursor deposition.

By utilizing the well know sol-gel chemistry used so far spin- and dip coated layers of TiO_2 with the wide deposition possibilities offered by inkjet printing, we are able to prepare photocatalytically active thin layers of TiO_2 in a very effective and clean way with minimum waste.

Experimental

Sol-gel technique was applied to titanium dioxide thin films preparation using titanium(IV) propoxide as titanium precursors. Soda lime glass plates with sizes of $50 \times 50 \times 1.5$ mm were used as a substrate for TiO₂ thin films after treatment for surface sodium ions leaching.

Sol application was performed in a novel innovative way utilizing a modified office inkjet printer with empty carts. Cleaned glass plates were then mounted into a modified CD holder, fed into the printer and printed with "black only" driver setting. The colour of the printed pattern was varied in different shades of grey (100%, 95%, 90%, 80%, 70%, 60%) and thus glasses with varying sol loading were printed. The resolution, print speed and media settings were also varied and their influence on the resulting TiO₂ layer properties was evaluated. Two way of printer setting were chosen for thin layer of TiO₂ preparation – slow (S) and rapid (R). The sample marked as 100 R corresponds to 100 % of sol loadings printed by rapid way.

After coating, the glass plates were dried in the oven at 110 °C for 30 min and finally at 450 °C for 4 hours.

Photocatalytic killing of yeast Candida vini and Candida tropicalis were performed to study the antimicrobial properties of prepared TiO₂ layers. The yeast cells have spherical or oval, sometimes cylindrical or elongated shape of $3.0-5.5 \times 4.0-9.0 \ \mu m$ in size. Generally, Candida is the most common cause of opportunistic mycoses (Candidiasis) worldwide. This type of endogenous infection mostly arises from overgrowth of the fungus inhabiting in the normal flora.

The yeast culture for the photocatalytic test was prepared as follows: 1 ml of yeast culture cultivated for 24 h in GPY liquid nutrient media was diluted with 9 ml of deionized water and centrifuged for 5 min at 4,000 rpm. The supernatant was separated from yeast sediment and centrifugation was repeated once again with 10 ml of deionized water. After last changing of liquid, the pure yeast suspension in water was well homogenized using minishaker. 30 µl of this suspension was dropped onto 15 min pre-irradiated TiO₂ film on glass plate and spread by micropipette for better contact of yeasts with photocatalyst surface. The sample was then put on reflective surface in Petri dish and covered by quartz plate in order to maintain a constant humidity during reaction. The sample was irradiated by four fluorescent lamps Sylvania Lynx-S 11 W with a maximum of energy at 365 nm. Irradiance of 1 mW cm⁻² was maintained by lamp distance adjustment.

The irradiated samples were analyzed by epi-fluorescent microscopy using Acridine orange dye: 40 μ l of 1.8×10^{-4} M Acridine orange (in phosphate buffer with pH 6) was added to 30 μ l drop of irradiated sample placed in Petri dish. The Acridine orange dye is capable to bind to DNA in dead cell and so in epi-fluorescence microscope this complex emits red light. Then the dead cells appear as red and live cells as green in colour. A random selection of 20 places on a sample was recorded by Pixelink PL–A662 CCD camera (Pixelink Canada) and images were processed by Lucia software. On each image, the number of live and dead cells was calculated and expressed as the survival ratio (SR), i.e. number of live cells divided by total number of cells in each image using following formula:

$$SR = \frac{N_{\text{live}}}{N_{\text{live+dead}}}$$
(12)

The obtained survival ratio was averaged and processed by statistical methods.

Results

By the described method of thin layer of titanium dioxide we prepared layers predominantly with crystaline structure proved by Raman spectroscopy (Fig. 1.). The Raman spectroscopic measurements of TiO_2 calcinated films revealed the anatase phase to be dominant with the small portion of rutile.



Fig. 1. Raman spectra of printed layer of titanium dioxide 95R



Fig. 2. Titanium dioxide layers: Smooth surface of rapidly printed sample 95 R (left) and structured surface of slow printed sample 95 S

The different amount of sol printed on glass surface and two different way of sol printing resulted in various surface structure, layer homogeneity and porosity. The surface structure varied from smooth surface of fast printed layers to wrinkly surface of slow printed layers (Fig. 2.). Maximum thickness was 212 nm. The smooth layer was formed by 30 nm particles of titanium dioxide. However, this smooth layer contained cracks smaller than 700 nm (Fig. 3.).

We found that process of yeast photokilling does not significantly depend on way of printing if the surface is fully covered by TiO₂. Generally, a damage of membrane needs



Fig. 3. SEM microphotography of sample 95 R

a certain time and we observed the induction period. When a membrane was perforated, the second period occurred during which the microorganism inactivation was accelerated.

The presence of plateau in the later period of reaction was found during yeast inactivation. Inner cell components present outside the cells cause the competition between these molecules and bacteria as regards the rective oxygen species. We found similar results for both used cells of *Candida tropicalis* and *Candida vini*.



Fig. 4. Photocatalytic inactiovation of yeast *Candida vini* on slow printed titanium dioxide layer

Conclusions

It was found that printed layers show photocatalytic activity. The prepared lyaers were thiner than 200 nm and transparent. Their properties were proved by phtocatalytic inactivation of yeasts. This process does not depend on the way of sol delivery by inkjet printer if the glass surface is fully covered.

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L20 A STUDY ON THE THICKNESS HOMOGENEITY AND REFRACTIVE INDEX OF THIN ORGANIC LAYERS

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Introduction

This paper deals with the utilization of optical and interference microscopy for the study of thin film layers. We present a new and very simple method for the determination of refractive indexes of transparent layers based on interference phenomena. Both thin layer thickness and refractive index can be determined by this method.

We used this method for a complex analysis of sandwich and gap structures of organic semiconductor components (e.g. ITO/PEDOT/DPP/Alq3/Al) prepared by a combination of following procedures: vacuum vapour deposition and/or spin coating and/or inkjet printing. A series of photographs of one sample was recorded and analysed which gave us the thicknesses of individual layers, their homogeneity and their refractive indexes.

Recorded images were processed by means of image analysis (correlative and fractal analysis). Image analysis was performed using application HarFA (Harmonic and Fractal Image Analyser), which has a wide potential of use not only for image analysis but for analysis of video clips, signals and numerical data as well.

Results obtained by image analysis methods were confirmed and eventually further extended by ellipsometric measurements, which is unfortunately more time consuming and challenging.

Experimental

Sample Preparing

Within the context of development of new cheap organic materials suitable for optoelectronic applications (e.g. photovoltaic cells, light emitting diodes, etc.) new techniques of their cheap production are looked for. The preparation of thin films structures by means of various methods, e.g. spin coating, vacuum evaporation or inkjet printing seems to be very perspective techniques. Structures prepared for electronic applications are mostly multilayered with a complicated structure, see Fig. 1.

It is possible to prepare complex structure of electronic component by means of suitable combination of all three procedures.

For example, structure at Fig. 1. consists of conductive thin film ITO (indium tin oxide) deposited on a glass substrate.

The other two films are composed of PEDOT (poly(3,4ethylenedioxythiophene)) and semi conductive derivative DPP (diketo pyrrolo pyrrole). These work as an active photoconductive element. It is possible to prepare these from solutions and/or dispersions by means of inkjet printer and/or spin coating, respectively.



Fig. 1. Example of multilayered structure for electronic applications

Last two films consist of Alq3 (tris (8-hydroxyquinoline) and aluminium. Alq3 works as an interlayer between active semiconductor DPP and contact electrode (Al) and both layers are prepared by vacuum vapor deposition.

It is apparent that functionality of electronic component prepared in this way is dependent on the quality of prepared films, this means on homogeneity of their thickness, on their mutual contact (adhesion) and on their time and mechanical stability.

In this respect the films prepared from solution are crucial. In the case of these films it is necessary to ensure good adhesion to underlying film (for PEDOT it is ITO), to prevent agglomeration of dispersing particles and crystallization¹.

Image Data Recording

Image analysis methods can be with advantageously utilized for the quality assessment of films prepared in this way. It is possible to use them for surface quality assessment in combination with optical microscope and digital camera. Film thickness determination is possible in combination with an interference microscope. It is also possible to determine refractive index of organic materials^{2–3} using suitable interpretation of recorded results.

For example, it is possible to use the software HarFA developed by authors of this contribution for image analysis. It is necessary to eliminate image errors caused by e.g. non-homogeneity of the light, by non-linear transfer of brightness (gamma correction), and by thermal noise^{4–6}.



Fig. 2. Principle of image data recording

Interference microscope Interphako (Carl Zeiss Jena) is used for the film thickness measurement. The principle of the measurement is based on the phase shift between beams reflected from the surface of the thin organic film and evaporated Al refractive layers. Film structure is demonstrated at Fig. 3. This phase shift is in a good agreement with double thickness of the film, as demonstrated at Fig. 3. (on the top).



Fig. 3. Principle of thickness layer measurements with using of interference microscope

Using splitting and three-dimensional shift of two parts of the Fig. and their subsequent composition it is possible to get interferential images such as those at Fig. 4.



Fig. 4. Interference microscope images (from the "air" side) for edge of ITO (on the left) and DPP (on the right)



Fig. 5. Interference microscope images (from the "glass" side) for edge of ITO (on the left) and DPP (on the right)

The details for two edges at aluminium contact are for ITO layer (on the left) and for DPP (on the right side). The shift of the interference line at the edge is in agreement with the Fig. 3. A similar image can be observed from the bottom

side of the sample – from the "glass" side. The results are presented at Fig. 5. We can see that shift on the edge is greater than when it is observed from the "air" side of the sample (Fig. 4.).

Data Analysis

The analysis performed by HarFA consists of the following steps:

- Recording of image sequences (videos) of electrical contact from the side "air" and "glass (*Open video, File types: Images*). This step was set for more effective analysis.
- Selection of interesting part of interference images, at the place of main interference maxima (the square 512×512 pixels was selected).
- Selection of proper colour space for analysis (the *Brightness*, not threshold *not BW* settings was select).
- Making of two videos (from "air" and from "glass" side) which was consist from interference image sequences (*Save square video as...*)
- Processing of correlation analysis for selected frames of videos. Selected part was vertical rectangle 256×512 pixels at the frame middle (*Correlation*). The results were saved as images (see Fig. 6.) and as data files (see Fig. 7.).



Fig. 6. The results of correlation analysis – sharpen lines of the same phase on the image: the split of ITO edge from the "air" (on top) and from the "glass" (bottom) measuring

The saved data were further statistical processed by a very simple procedure. The average values of all lines were calculated and a rotation leading to horizontal zero reference line was performed. The average shift of the split and average wavelength (in pixels) from the shift of lines was calculated. The results of these very simple calculations are at Fig. 8. for ITO from "air" and "glass" side.

The thickness and refractive index of DPP and ITO can be immediately from these dependences determined. The results of calculations are summarized in Table I. The values were calculated as the average values of all pixels at the edge (Fig. 7.). The uncertainty of these values is very small; the errors are caused by the homogeneity of the measured surface.

The thickness was calculated from the known wave length $\lambda = 512$ nm, refractive index from the simple equation $n = \Delta s / \Delta l$, where Δs is so called optical line and Δl real line of the light. The profile of average phase line shift for the whole contact is presented on Fig. 8.



Fig. 7. The phase lines of the ITO edge split from the "air" side measuring



Fig. 8. The corrected phase lines of the ITO edge split from the both "air" and "glass" side measuring



Fig. 9. The profile of average phase line

The imperfect groves created by cutting to DPP layer give in maxima the same shifts of phase as the second ege (DPP). The right changes of the phase are caused by inhomogeneties on the end of glass.

Results

We can see from the results at the Table I that the ITO layer is thinner and its homogeneity is lower than DPP layer. Also refractive index value is more accurately for ITO layer.

These results confirm the dependences of refractive indexes and thicknesses on the split position of layer edge on Fig. 10. and Fig. 11. We can see that the homogeneity of the ITO thickness is greater than the momogeneity of DPP and Table I:

The refractive index and thickness parameters of ITO and DPP layers ($\lambda = 512 \text{ nm}$)

Parameter	ITO layer	DPP layer
Sample thickness [nm]	38 ± 1	80 ± 5
Optical thickness [nm]	66 ± 3	107 ± 18
Refractive index [-]	1.73 ± 0.05	1.34 ± 0.15



Fig. 10. The refractive index both ITO and DPP layer calculated from edge split reason



Fig. 11. The thickness both ITO and DPP layer calculated from edge split reason

also the refractive index is more constant. The results are in agreement with data from ref.⁷.

Conclusions

The new very simple and quick method for the determining of layer thickness and their refractive index was presented. The other advantages are that the calculation of refractive index is not dependent on the surrounding layers but only on the layer with edge. This fact is advantage in contrast to ellipsometry.

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6.2. Posters

P01 THE STUDY OF TIO₂ THIN FILMS PHOTOCATALYTIC ACTIVITY ON DEGRADATION OF YEAST AND DYE POLLUTANTS

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Introduction

Among various oxide semiconductor photocatalysts, titanium dioxide (TiO_2) appears to be a promising and important prospect for use in environmental purification, because of its strong oxidizing power, photoinduced hydrophilicity, nontoxicity and long-term photostability. TiO₂ shows excellent photocatalytic activity for oxidative degradation of environmental pollutants¹.

The first description of antimicrobial effect of TiO_2 film was published by Japanese professor Matunago and colleagues in 1985. At the beginning of the photocatalytic reaction, highly reactive groups containing oxygen atoms (ROS – reactive oxygen species) are formed. These ROS produced by photocatalysis cause different type of damage in live organisms. After a hydroxyl radical attack, the outer membrane is partially destroyed. There is no important change of cell viability during this process, but membrane permeability towards ROS is changed. At this stage, ROS can attack the cytoplasmic membrane more easily, which results in the lipid membrane peroxidation and subsequent cell death².

Experimental

Preparation of TiO, Thin Film

The substrates used as film supports were soda-lime glass plates. Boiling the glass plates in sulfuric acid removes the surface sodium ions and therefore the photoactivity of the film can be improved.

Transparent TiO₂ layers were immobilised on glass plates using sol-gel method with titanium tetraisopropoxide in ethanol as precursor. Depositions of thin films were realized by dip-coating method with withdrawal speed 120 mm min⁻¹. In the next stage, the coated substrates were dryed for 30 min. at 110 °C and then calcinated for 4 hours at 450 °C with temperature ramp of 3 °C min⁻¹.

Photooxidation of 2,6-

dichloroindophenol

The photocatalytic activity of the TiO₂ films was evaluated by examining the oxidation rate of water solution 2,6-DCIP (2×10^{-5} mol dm⁻³) upon UV irradiation (2.4 mW cm⁻², solar lamp Philips HPA-400 W) in a desk reactor. The concentration decrease of 2,6-DCIP was determinated spectrophotometrically. A photochemical dechloration of 2,6-DCIP is a reaction of first order kinetics.

Antimicrobial Efect of TiO₂ Thin Film

Photocatalytic killing of yeasts *Candida tropicalis* and *Candida albicans* were performed to study the antimicrobial properties of TiO_2 films. These yeasts belong to the class of Ascomycetes, the family of Saccharomycetaceae and the kingdom of Fungi. Generally, *Candida* is the most common cause of opportunistic mycoses (Candidiasis) worldwide. This type of endogenous infection mostly arises from overgrowth of the fungus inhabiting normal flora. *C. albicans* is the most frequently encountered medical pathogen, the second one is *C. tropicalis*.

The yeast culture for the photocatalytic test was prepared as follows: 1 ml of yeast culture cultivated for 24 h in GPY liquid nutrient media was diluted with 9 ml of deionized water and centrifuged for 5 min at 4,000 rpm. The supernatant was separated from yeast sediment and centrifugation was repeated once again with 10 ml of deionized water. After the last change of liquid, the pure yeast suspension in water was well homogenized using minishaker. 30 µl of this suspension was dropped onto 15 min pre-irradiated TiO₂ film on glass plate and spread for better contact of yeasts with photocatalyst surface. The sample was put in Petri dish and covered by quartz plate. The UV irradiation was provided by fluorescent lamp Sylvania Lynx-S 11 W with intensity 1.5 mW cm⁻². After exposure suspension of yeasts, 40 ml of 1.8×10^{-4} moldm⁻³ Acridine Orange was added to the drop of irradiated sample. Nicon Eclipse 200 with epifluorescent adapter equipped with Camera Pixelink Canada was used for dead and live cell resolution and calculation. It was calculated survival ratio of yeasts.

$$SR = \frac{N_{live}}{N_{live+dead}}$$
(1)

Results

Photooxidation of 2,6-DCIP

Fig. 1. shows that the number of layers (i.e. thickness) influences the photocatalytic activity. The higher number of TiO_2 thin layers is, the higher the photocatalytic activity is. But in the case of 4 layers, the photocatalytic activity is smaller due to its large thickness. The layer is too thick, so the generation of electrons and holes proceed deep in the semiconductor layers, and therefore they can't get to the surface and participace the reaction. It causes the decrease of photocatalytic activity.

Antimicrobial efect of TiO₂ thin film

The reaction was performed only in deionized water without the nutrient compounds to avoid their influence on yeast degradation process.

The dependence of *Candida tropicalis* and *Candida albicans* survival ratio on irradiation time and TiO₂ layer



Fig. 1. The influence of number of TiO_2 thin films on the photocatalytic efficiency 2,6-DCIP



Fig. 2. The survival ratio of *Candida tropicalis* during irradiation

number is demonstrated at the following figures (Fig. 2. and Fig. 3.). It can be seen, there is no antimicrobial activity during UV irradiation of yeast suspension when the photoca-talyst is absent.

Concerning the induction period, it is decreasing with increasing number of TiO_2 layer.

In the case of *Candida albicans*, we observed worse antimicrobial efficiency (Fig. 3.) therefore longer time of irradiation is necessary to kill them.



Fig. 3. The survival ratio of *Candida albicans* during irradiation

Conclusions

We prepared TiO_2 thin films on soda-lime glass plates by dip coating method. Films are homogenous and transparent.

The photocatalytic efficiency of prepared coatings was evaluated on photocatalytic oxidation 2,6-DCIP in aqueous phase, as well as on killing of microorganisms, *Candida tropicalis* and *Candida albicans* yeasts.

We found that the number of layers (i.e thickness) positively influences the photocatalytic oxidation of 2,6-DCIP.

Concerning the microorganisms killing, *Candida tropicalis* and *Candida albicans* were selected for determination of TiO_2 thin film antimicrobial properties, because they represent the most frequently encountered medical pathogen, causes the opportunistic mycoses. We observed that the photocatalytic degradation rate increases with increasing TiO_2 film thickness.

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P02 USING OF VIS-NIR FIBRE OPTICS REFLECTANCE SPECTRA FOR IDENTIFICATION OF IRON-GALL INKS IN HISTORICAL DOCUMENTS

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Introduction

The identification of brown-grey inks is of importance to understand the history and aesthetics of an object, to evaluate the risks involved with its use, and to judge the effects of conservation treatments. Drawings may contain different browngrey shades side-by-side, which could be due to the use of different drawing inks. Traditionally, to obtain brown-grey shades, bistre, sepia, carbon black and iron gall inks were used¹. Iron gall inks contain transition metals, such as iron and copper, catalyzing the radical oxidation of the substrate, as well as acids, catalysing its hydrolysis². These degradation processes, generally known as "ink corrosion", lead to the formation of fluorescent and brown degradation products, followed by mechanical weakening of the paper and formation of cracks. If none of these phenomena are observed, it is not easy to visually distinguish iron gall inks from other, potentially less aggressive, brown-grey inks.

Different instrumental analytical methods, e.g. SEM/ EDX, XRF or FTIR have been applied to identify inks³. As most collection keeping institutes do not have access to these techniques, there is a need for "hands-on" methods that do not require sampling or transport of the object outside the institute. Nowadays, Fibre-Optics Reflectance Spectrometers (FORS) have reached dimensions which allow them to be transported easily to the objects to be measured.

It was shown, that brown-grey inks can be distinguished by the reflectance spectra obtained from visually comparable shades of sepia, bistre and iron gall inks, processed by chemometric factor analysis method⁴. In this paper previously developed method of factor analysis was used to process VIS-NIR fibre optics reflectance spectra measured on historical drawings and documents with grey-brown inks and identification of iron gall inks.

Computational and Experimental

Previously developed chemometric detector for identification of iron gall inks in the VIS-NIR spectral region⁴ was used. Reference data set consists of 132 spectra of samples of iron gall inks. Chemometric detector is based on the testing of correspondence of studied individual spectrum with the database. This testing was performed by the method of the Factor Analysis – namely Target Factor Analysis⁵ was used. This method evaluates the deviation, call AET parameter, of tested spectrum from the projection of tested spectrum into the factor space of database spectra set. Great value of AET parameter indicates that the tested spectrum does not correspond to the database. On the other hand, low value of AET parameter indicates, that the tested spectrum corresponds to the spectra of databases. In this case we select the value of AET = 0.006 as a threshold (corresponds to the statistically evaluated reproducibility of the measurement of the database spectra).

Spectra of studied historical documents and drawings were measured with the fibre optics spectrophotometer system Ocean Optics consisting of Hi-Res spectrometer HR 4000CG-UV-NIR, UV-VIS-NIR light source DH-2000-BAL and standard reflectance accessory with 45 °/45 ° geometry. Spectra were measured at the region 500–1,050 nm. For each measurement, the detector was calibrated on the blank paper near to the inked area. In this way, changes in spectral reflectance due to ageing of the substrate were largely excluded. Original reflectance spectra were transformed into Kubelka-Munk⁷ spectra. Kubelka-Munk spectra are generally preferred in the methods using linear algebra⁸. Also, each spectrum was normalized to have maximum value equal one, to enhance shape analysis.

Results and Discussion

The presence of iron gall inks was tested in the set of drawings from collection of Slovak National Gallery. Example of the analysis of VIS-NIR spectra of the drawing from 16th century is on Fig. 1.

The spectra were measured at the four locations and AET parameters indicate that the iron gall ink was used. This result is supported by the results of XRF analysis confirming the presence of iron.

The analysis of document from 19th century is on Fig. 2. VIS-NIR spectra were measured at two positions.

The AET value at of the spectrum at location A indicates that the iron gall ink was used for signature (this finding was supported by the colorimetric spot test⁹), the spectrum at location B absorbs practically all VIS-NIR light, what



Fig. 1. Sitting Evangelist, Bartolomeo Passarotti, 1550–1590, Slovak National Gallery, Bratislava, Slovak Republic, Inventory No. K 96



Fig. 2. Document from 19th century, Slovak National Archives, Bratislava, Slovak Republic

indicates the probable presence of some kind of carbon black (Chinese) ink.

The attempt to use the detector to analyse the ink on the parchment is on the Fig. 3. The average spectrum of the typefaces corresponds to the iron gall inks spectra according to the low value of the AET parameter.

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P03 THE INFLUENCE OF PHOTOINITIATORS AND ADITIVES ON THE PHOTOCHEMICAL SPEED OF METHACRYLATED PVAL

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Introduction

Cross-linking is a vital tool for modification of existing polymers to achieve new and improved materials. Cross-linked gels often have different properties based on the type of cross-linking method used (chemical, physical or ionical cross-linking), as well as the fact that each method brings with it is own limitations and benefits depending on the desired use and application of the gels¹.

PVAI is largely used for the production of fiber (vinylon), film, in the paper industry, in the textile sizing, as a modifier of thermosetting resins, as pressure-sensitive adhesives, emulsifier, ect. The final properties of PVAI mainly depend on the properties of its parent polymer, poly(vinylacetate), its polymerization conditions and degree of hydrolysis. Crosslinking as well as modification of PVAI through its hydroxyl groups open new domain of application for this material².

Experimental

This study deals with the cross-linking reaction of methacrylated PVAl by the UV initiated non-linear polymerisation in the solid phase. For this purpose the modified PVAl had to be prepared.

Preparation of Modified PVA1

PVAI was dissolved in a mixture of DMSO and DMFA at 95 °C. Then the temperature was lowered to 70 °C. GMA and KOH ethanolic solution were added dropwise. Upon the addition of KOH, the solution changed color to yellow. After 1 hour the mixture was cooled down to room temperature and the deionized water was added. PVAI modified in this way was precipitated in ethanol and finelly washed in acetone. During this reaction a tricomponent copolymer poly(vinylalcohol-co-vinylacetate-co-vinylhydroxyprophylmethacrylate) was created.

Cross-Linking of MPVA1

A thin layer of methacrylated PVAl solution was spincoated onto anodized aluminium plates. The coating mixture consisted of mPVAl (20 % wt.), water, surfactant and a variable amount of photoinitiators. We used three types of photoinitiators (Igacure 2959, Irgacure 2100, Irgacure 819) and their concentration was changed from 0.5 % wt. to 4 % wt. (this concentration was recommended by producer).

The spin-coated plates were exposed by UV radiation, developed in the deionized water and dyed in a Saturn Blue L4G solution. Each step of the aluminium plate was measured by a densitometer. We observed the influence of photoinitiators type and concentration on the photochemical speed *S*. The photochemical speed was calculated according to the mathematical formula:

$$S = \frac{1}{H_n^{0.5}},$$
 (1)

where $H_n^{0.5}$ is a exposure at the normalised optical density 0.5. The value of the exposure was determined from the densitometrical measurement.

Crosslinking Above the Glass Transition Temperature

Besides the study of cross-linking below the glass transition temperature (T_g) , we also investigated the kinetics of cross-linking reaction above T_g . In order to performe the cross-linking reaction above T_g , we added different types and concentration of plasticizers and we studied the dependence of this substances on the photochemical speed.

Glycerol and poly(ethylenglycol) (PEG) were used as plasticizers. We compared their plasticizing effect. The photochemical speed was determined in the same way as in case when the reaction runs below T_{o} .

Results

Modification of PVA1

The modified PVAl was prepared using GMA. The theoretical stechiometric degree of modification should have been 4 % mol. The real degree of the conversion was determined by UV-VIS spectroscopy³.

Firstly, the calibration curve was constructed. The molar absorption coeficient was found out from its direction. If we knew the value of the molar absorption coeficient, the degree of conversion could be worked out. Prepared mPVAI had the degree of conversion 3.83 % mol.

The Influence of Initiators on the Photochemical Speed

The optical densities for each field of the aluminium plates were found out from the densitometrical measurement. The dependence $D_n = \log H$ was constructed. D_n is a normalized value of optical density, which was calculated as the quotient of the constituent fields of aluminium plates optical density and the full cross-linking field optical density. The value of $H_n^{0.5}$ was determined from this dependence and now we were able to calculated the photochemical speed by the formula (1).

The goal of our work was to obtain a higher *S* using two different photoinitiators (I 2100 and I 819) instead of I 2959. The spectral sensitivity of I 2959 is in the far region of UV radiation and we wanted to shift the spectral sensitivity of the studied system up to longer wavelengths because of better utilization of a radiation energy.

We didn't reach this goal probably because the coating compositions with I 2100 and I 819 had the character of

microheterogenous mixtures. A stable emulsion was prepared in case I 2100 and a suspension was formed yet using I 819.

The results *S*, for each added initiators amount, are presented in Table I and we observe the comparison of *S* all using photoinitiators in Fig. 1. We can see that the *S* is the biggest for I 2959 and the smallest for I 819.

Table I

The photochemical speed of using commercial photoinitiators

Concentration of initiators [% wt.]	<i>S</i> of I 2959 [cm ² J ⁻¹]	$\frac{S \text{ of I } 2100}{[\text{cm}^2 \text{J}^{-1}]}$	S of I 815 $[cm^2 J^{-1}]$
0.5	4,281.44	769.84	45.96
1.0	1,379.69	566.07	26.62
2.0	1,033.33	237.53	11.95
4.0	652.74	102.91	8.38



Fig. 1. The dependence $D_n = \log H$ for all using photoinitiators, for initiators concentration 4 % wt.

Cross-Linking Above the T

For the system with the plasticizers (glycerol and PEG), the photochemical speed *S* was determined in the same way as in the previous case. This photochemical speed was compared with *S* for the system without the plasticizer. A huge increase of *S* was observed in system with glycerol (about $50 \times$).

The highest increase was achieved for glycerol concentration 5 % wt. When the concentration of plasticizer rises up above 5 % wt., the S decreases. This happens

Table II

The pho	tochemica	l speed of	f systems	with p	lasticizers
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Concentration of	Sglycerol	S _{PEG}
plasticizers [% wt.]	$[cm^2 J^{-1}]$	$[cm^2 J^{-1}]$
0	1,379.69	1,379.69
2	9,399.18	3,013.21
4	44,869.37	3,693.69
6	11,097.60	2,286.60
8	3,280.65	946.37

due to a huge increase of polymer free volume, which causes the moving away of macromolecular chains. The outgrowth is a disappearance of nearly all interaction.

The same results were reached also in case with PEG but S was grown up only three times. The overview of established speed can be observed in Table II. The comparison of PEG and glycero effect is noticed in Fig. 2.



Fig. 2. The comparison of photochemical speed for two different plasticizers

Conclusions

We synthesised mPVAl with the degree of conversion about 4 % mol. which secures a compromise between the system solubility in water and the content of double bonds in this system.

Our effort was to shift the spectral sensitivity up from UVC area the region of longer wavelength. This goal was accomplished but it doesn't lead to the rise of photochemical speed. It is probably caused by very slow radical transfer which comes as consequence of non-homogenous coated mixture. The coated system had heterogenous character due to limited miscibility of using compounds.

We also investigate the change of photochemical speed after plasticizer addition. We discovered that glycerol is better plasticizer than PEG because S grows up till $50 \times$ in system with this plasticizer.

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P04 TiO₂ BASED SENSOR WITH NANOSTRUCTURED SURFACE FOR GAS DETECTION

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Introduction

On the field of environmental protection, many efforts have been done in few past years to produce a highly sensitive system for atmospheric pollutant monitoring using semiconductor metal oxide (SMO) materials¹. More recently, the research was aimed to develope a nanostructured surface of sensing electrode in order to sufficiently increase its effective surface area and hence its sensitivity². This nanostructure formation can be easily realized through a thin nanoporous Al₂O₂ template created e.g. on gold electrode. Such prepared metal nanostructures (nanowires, nanotubes, etc.) can be further modified by immobilization of previously mentioned semiconducting material. TiO2 was found to be one of the efficient agents for this purpose, in particular for detection of different gases: O₂, H₂, CO, NH₃ as well as hydrocarbons^{3,4}. Analogous to photocatalysis, the anatase phase is expected to play more important role in this case than the rutile^{5,6}. Some investigators also observed a positive effect of doping the titania sensors with metals like Au, Pt, Nb, Cu or Cr^{7,8}.

Concerning the preparation of solid gas sensor from semiconducting material, sol-gel procedure belongs among widely used techniques despite of high precursor price and poor shelf-life of prepared sols^{9,10}. However, this process allows a good control of surface properties such as composition, thickness and topology. A deposition of TiO₂ onto electrode with nanostructured surface can be then effected using dip-coating or drop-coating method. It is supposed the smaller size of semiconductor particles results in better sensitivity. Moreover, TiO₂ component should have a sufficiently porous structure.

Experimental

Preparation of Au Nanorods

Nanorod-structured surface of Au electrode was fabricated using an anodisk purchased from Whatman, which consists of Al_2O_3 template sputtered on thin Au substrate. Au deposition conditions were set as follows:

- electrolyte composition of 6 g dm⁻³ of $K[Au(CN)_2]$ and 2.32 g dm⁻³ of H_3BO_3 ,
- electrolyte temperature of 50 °C,
- current density of 0.25 mA cm⁻².

The deposition time t (s) of Au was calculated from following relationship:

$$m_{Au} = 1.2 \times 10^{-6} \cdot t \cdot \frac{I}{S},$$
 (1)

where m_{Au} [g] corresponds to amount of deposited Au and *I/S* is a current density [mA cm⁻²]. From preliminary experiments, the electrodeposition times of about 500 and 2,000 s are needed to produce Au nanorods with approximate length of 1 µm using 20 and 100 nm Al₂O₃ pore size, respectively. Finally, Al₂O₃ template was eliminated by dissolving in NaOH.

The obtained Au nanorods were characterized by SEM.

Fixation of Au Nanosensor

Such prepared Au nanosensor was fixed on corundum plate with thick-film platinum meander heater using glass paste.

Deposition of TiO₂ Nanostructures

Next step was aimed to immobilization of TiO₂ coatings by sol-gel technology starting from titanium tetrapropoxide precursor, ethanol as solvent and acetyl-acetone as stabilizing agent. The concentration of Ti was 0.35 mol dm⁻³. The sol was simply dropped onto Au surface of sensor with comblike structure (Fig. 1), then dried at 110 °C in oven and finally annealed at 450 °C in a furnace. Also these samples were analyzed using SEM. Raman and FTIR-ATR spectroscopies were employed to characterize TiO₂ phase constitution.



Fig. 1. Schematic illustration of gold-nanorod electrochemical gas sensor with comb-like structure

Results

As can be seen from SEM characterization (Fig. 2), Au nanorods reached the presupposed length of about 1 μ m and thickness of 0.1 μ m.

Raman spectroscopic measurement showed the TiO_2 structures are predominantly in anatase phase with a small portion of rutile and organic contaminants originated from precursor (Fig. 3)¹¹. The study of annealing temperature influence revealed that a composition of amorphous and rutile phase dominates in TiO₂ film dried only at 110 °C.

In addition, the presence of carbonate was also detected in samples prepared at 450 °C taking the FTIR-ATR spectra (Fig. 4). The scientists suppose the elimination of this residue detected at 1,380 cm⁻¹ requires the temperature as high as 600 °C(ref.¹²).



Fig. 2. SEM image of gold nanorods electrodeposited through Al₂O₃ template



Fig. 3. Raman spectra of TiO₂ annealed at 110 °C and 450 °C

Conclusions

At higher annealing temperature, anatase was found to be the majority phase in TiO_2 structure, while at lower one, TiO_2 was rather in the rutile form mixed with amorphous phase. Some organic and inorganic residues were also detected even after calcination at 450 °C.

Due to impedance spectroscopic measurement, we can assume our TiO_2 structures are homogenous and suitable for detection of various gases.

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Fig. 4. FTIR-ATR spectrum of TiO, annealed at 450 °C

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P05 IMAGE ANALYSIS OF OFFSET LITHOGRAPHY PRINTS

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Introduction

Three methods of image analysis and densitometry were employed in this study to characterize influence of paper quality to quality of prints. Image analysis methods investigate the quality of printed details. The size and ink influence of printed 2% screen dots were measured by analysis of particles. Modulation transfer function (MTF) and fractal analysis were used for inspection of print edge. The 5 coated and 5 uncoated offset printing papers were tested for inspecting quality of similar samples.

Experimental Part

Screen dot size, fragmentation, fluctuation of colour (Fig. 2.) and missing dots were measured.

MTF was obtained from print edge for full printed patches¹ (Fig. 3.).

Fractal analysis method was based on Box Counting method² (Fig. 4., eq. (1)).

$$\ln N_{BBW}(1/\varepsilon) = \ln(K_{BBW}) + D_{BBW}\ln(1/\varepsilon)$$
(1)

where ε is cell size of square net, N_{BBW} is number of black and partially black cells (Fig. 4.), D_{BBW} is fractal dimension.

Results and Discussion

Image Analysis of 2% Screen Dots Area of screen dots

Average area of screen dot of coated samples is above of ideal screen dot size $(436 \ \mu m^2)$ – from 509 to 608 μm^2



Fig. 1. Construction of measuring equipment

Fig. 2. Fragmented screen dot (a), fluctuation of ink inside screen dot (b)

(b)

(a)



Fig. 3. Procedure to obtain MTF, ESF/LSF – edge/line spread function, R – reflectance, u – space frequency,×– measured distance



Fig. 4. Box Counting method

(Fig. 5.) that refers to dot gain. The biggest dot gain is by the sample 2, can be classified as the best, because of less possibility of missing dots.

Mostly opposite situation is for the uncoated paper. The lowest dot gain is by sample 6.



Fig. 5. Average area of screen dots

Fragmented and missing screen dots

From the Fig. 6. we can conclude that uncoated samples are more predisposed to fragmentation of screen dots and to occurrence of missing screen dots. Average frequency of screen dot fragmentation is for coated samples markedly lower as for uncoated samples.



Fig. 6. Average frequency of fragmented screen dots

From Figs. 7. and 8. can we draw the same conclusion as for the frequency of fragmented screen dots – higher amount of missing screen dots in uncoated samples. Black prints were the best, more resistant to missing dots as all other colour prints. We can observe more missing screen dots for cyan, magenta and then for yellow colour.

For all colours we can conclude that sample 4 is the best among the coated samples and sample 7 and 8 are the best among the uncoated samples.

Modulation Transfer Function

Space frequency value suggests that the samples 2 and 3 for face side and the sample 4 for reverse side are of higher quality (Fig. 9.). The lower quality sample was the sample 6.



Fig. 7. Frequency of missing screen dots, face side



Fig. 8. Frequency of missing screen dots, reverse side

Fractal Analysis of Prints

The results of fractal analysis clearly divided the studied samples into two groups (Fig. 10.) – coated and uncoated printing papers. The order of quality of the samples was the same for face and reverse side of printing papers – the best sample 4, the lowest quality sample 10.

Densitometry

The parameters of Walker-Fetsko eq. $(2)^3$, except of print smoothness parameter *k*, gain expected values for coated and uncoated papers, with exception of samples 2 and 5 (face and reverse side).



Fig. 9. The average space frequency u



Fig. 10. The average value of fractal dimension

$$y = (1 - e^{-kx}) \{ b(1 - e^{-x/b}) + f[x - b(1 - e^{-x/b})] \}$$
(2)

where y – the amount of ink transferred to paper [gm⁻²], x – the origin amount of ink on printing plate, k, f and b – constants obtained from graphical dependence.

The parameters of Tolenaar-Oittinen eq. (3) are more consistent. The parameters of steepness m and the parameters of sharpness radius n determined from the curve of ink consumption have markedly higher values for the coated papers.

$$D = D_{\infty} \left(1 - \mathrm{e}^{-my^n} \right) \tag{3}$$

where D_{∞} – optical density for $y \rightarrow \infty$.

The trend of increasing trapping with increasing total porosity and decreasing with increasing average radius of pores for uncoated papers was observed. The opposite trend was observed for the coated papers. Interesting correlation of linear regression between trapping and solid density of inks of primary colours for the coated papers was found - 86.4 %.

The dot gain value $\Delta A_{T}(50 \%)$ decreases with increasing total porosity and decreases with increasing gloss and average radius of pores. No such correlation was found for uncoated papers.

We tried also to relate image analysis parameters and densitometry values. The 96% correlation of linear regression of black solid density for face and reverse side of coated papers and fractal dimension D_{BBW} confirms that image analysis is a useful method for evaluation of quality printing.

Summary

Expected correlation of densitometry values and properties of offset printing paper samples was not tight and for uncoated papers was almost none. The differences in the groups of papers were very small and taking into account errors of measurements were statistically insignificant. Dissipation of values is mostly lower for the coated papers, which refer to more homogenous surface of these samples.

Image analysis methods allowed to classify quality of samples: the sample 4 and 2 belongs to the best quality and the sample 10 and 6 belongs to the least quality printing paper.

The correlation of classical parameters of printing quality for black printing ink and parameters obtained by the methods of image analysis was investigated. Good correlations found for fractal dimension and parameters of surface roughness suggest the possible application and potential of further development.

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P06 COLOR FIDELITY OF REPRODUCTION OF HISTORICAL DOCUMENTS

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Introduction

The aim of this study was ability of colour reproduction of historical documents by commercial semi-professional reproduction system. Colour management systems (CMS) and colour profiles (ICC profiles) of input/output devices were used. The quality of capture and printing operations was evaluated by colour difference value^{1,2}.

Experimental Part

Capturing devices – CCD cameras Olympus C 7070 WZ, Fujifilm FinePix S7000, Nikon D50; scanner HP ScanJet 8300.

Output device – Epson Stylus PHOTO R2400, solvent based ink K4.

Measurement devices – spectrophotometers TECHKON SpectroDens, Spectroscan.

Lightning – two light SoLux, 4,700 K, 28,000 lx in position of sample, 45 $^{\circ}/0^{\circ}$.

Ink-jet papers – Epson Archival Matter, Epson Premium Semigloss Photo, Epson Premium Glossy Photo, Ilford Smooth Pearl.

Test targets – analogue target IT8.7/2, Kodak Ektacolor Paper, $5^{"} \times 7^{"}$, 264 patches; digital target TC9.18 RGB, 918 patches.

Conversion of SRGB Colour Space to CIE L*a*b* Colour Space

Exact definition of colour space sRGB permit transformation of sRGB values to CIE $L^*a^*b^*$ colour space for evaluating of colour difference².

Calculation of XYZ colour values based on matrix equation 1 with previous modification of sRGB values².

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}_{D50} = \begin{bmatrix} 0,4361 & 0,3851 & 0,1431 \\ 0,2225 & 0,7169 & 0,0606 \\ 0,0139 & 0,0971 & 0,7141 \end{bmatrix}_{D50} \begin{bmatrix} R_{sRGB} \\ G_{sRGB} \\ B_{sRGB} \end{bmatrix}$$
(1)

XYZ colour coordinates was transformed to CIE $L^*a^*b^*$ colour coordinates and average colour difference values of test patches was calculated with respect to the original values.

Results and Discussion

The first step of digitizing process was test of different exposure conditions of digital cameras/scanner on reproduction of colour from original (264 colour patches) to captured



Fig. 1. Exposure time shift, CIE L*a*b* colour space, digital camera Fujifilm, D50WS, dark grey – underexposure, light grey – overexposure, gray – right exposure, black – test target

picture. The selection of exact white balance value was based on grey balance of captured pictures. Table I shows the influence of saturation on the colour difference value. Artificial saturation of colour increased colour difference value. Influence of exposure time on colour shift can be observed from Fig. 1. The best colour correlation to original was obtained for overexposed captured pictures. Colour profiles were prepared for all captured pictures and average colour differences of patches were calculated (Table I) before (ΔE^*_{ab1}) and after (ΔE^*_{ab2}) applying of ICC profiles.

The lowest average colour difference before applying ICC profile was obtained for Fujifilm digital camera, followed by Olympus and Nikon cameras respectively. After

Table I

Average colour differences ΔE^*_{ab} for all digital cameras, the picture name define white balance (colour temperature), saturation (S – satured, WS – without saturation), overexposed pictures (O)

	Fujifilm			
Picture name	ΔE^*_{ab1}	ΔE^*_{ab2}		
D50SO	14.2	9.5		
D50WSO	11.1	8.2		
D42SO	17.1	9.6		
D42WSO	14.1	9.4		
	Nikon			
Picture name	ΔE^*_{ab1}	ΔE^*_{ab2}		
D50SO	15.3	11.4		
D50WSO	13.8	11.2		
D65SO	16.1	9.3		
D65WSO	14.4	9.3		
Olympus				
Picture name	ΔE^*_{ab1}	ΔE^*_{ab2}		
D50WSO	8.6	9.5		
D42WSO	12.8	10.6		

Photochemistry

applying of ICC profile camera Fujifilm was the best followed by Nikon and Olympus cameras.

We try to set the white balance to custom mode. The results were better only in the case without using of ICC profile.

The average colour difference values for scanner (Table II) refer to better colour reproduction using embedded scanner profiling program.

The lowest average colour difference before applying ICC profile was obtained for Fujifilm digital camera, followed by Olympus and Nikon cameras respectively. After applying of ICC profile camera Fujifilm was the best followed by Nikon and Olympus cameras.

We try to set the white balance to custom mode. The results were better only in the case without using of ICC profile.

The average colour difference values for scanner (Table II) refer to better colour reproduction using embedded scanner profiling program.

Table II

Average colour differences ΔE^*_{ab} , scanner HP

ΔE^*_{ab} without CMS	ΔE [*] _{ab} with ICC profile of ProfileMaker	ΔE^*_{ab} ICC profile of embedded program
12.64	6.38	4.13

The next step was printing captured images using different print conditions to minimize colour difference values. Before printing we prepare ICC profiles for different paper substrates.

Table III shows decreasing average colour difference of prints using ICC profile of printer.

Average colour difference depends on gamut size of test charts (Table III, TC9.18, IT8.7/2.

Fig. 3 shows the relations of gamuts of historical poster and capturing devices (represented by test chart). Colour gamut of 264 colour patches test chart is bigger as colour gamut of historical poster.

Table III

Average colour differences ΔE^*_{ab} , Epson printer, digital test charts TC9.18 and IT8.7/2

Paper type	ΔE^*_{ab} without ICC profile	ΔE^*_{ab} with ICC profile TC9.18	$\begin{array}{c} \Delta E^*_{ab} \\ \text{with} \\ \text{ICC} \\ \text{profile} \\ \text{IT8.7/2} \end{array}$
Epson Archival Matte	34.50	18.50	9.81
Epson Premium Glossy Photo	29.87	16.56	8.72
Epson Premium Semigloss Photo	29.89	16.55	8.34
Ilford Smooth Pearl	30.39	16.68	9.22



Fig. 2. The sample of historical poster, 43 measured points, 50×70 cm, 1925–1930, Fujifilm



Fig. 3. Historical poster (gray) and test chart (black), CIE $L^*a^*b^*$ colour space

Conclusion

Quality of digitized image represented by average colour difference of colour patches of digital cameras/scanner was the best for scanner $-\Delta E^*_{ab} = 4.1$. Ink-jet printer reproduced cameras images with $\Delta E^*_{ab} = 16$ for 918 patches and $\Delta E^*_{ab} = 9$ for 264 patches, result for the scanner was the best $-\Delta E^*_{ab} = 4.1-6.5$. In our case the colours of historical poster were inside the gamut space of tested input devices and mostly inside of gamut space of output device, therefore we can predict reproduction almost without any loss of colour

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information caused by adaptation of out-of-gamut colours within of obtained colour difference range.

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P07 IMPROVEMENT OF BARRIER PROPERTIES OF PAPER USING PHOTOCHEMICALLY MODIFIED POLYMER LAYERS

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Introduction

The materials based on cellulose fibers (paper, card board) are sensitive to humidity and oxygen. Properties of packagings made of these materials may be improved by functionalization of paper surfaces. In combination with the characteristics of the basic materials, additional property profiles for different applications may be envisaged. Inorganicorganic hybrid polymers (ORMOCER®s: Trademark of the Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e. V., Munich) are well-suited for the specific functionalization of different polymer and paper surfaces. These materials are water-based or dispersed in nontoxic solvents. Curing is performed photochemically or thermally at relatively low temperatures. Resulting layers are transparent, sturdy and chemically stable. The gas permeability of coated papers is significantly reduced and barrier properties to water vapour and odours are enhanced¹.

Papers and boards have to comply with certain demands for a successfull application of inorganic-organic hybrid polymers. The coated substrate should have a smooth, compact and non-porous surface preventing the low-viscosity coating solution penetrating deep into the paper profile and enabling even and homogeneous coating. The surface tension value should be above 40 mN m^{-1} in order to ensure a good wettability. The application of a coating primer might be necessary to fulfil these demands. With respect to the prospect application of these materials in the packaging industry, it is necessary to ensure these materials poses barrier properties and at the same time they are biodegradable and environmentally friendly.

These special material properties can be ensured by using hydrophilic water-based coating materials and a photochemical curing. Such systems feature multiple advantages, such as low VOC emission, low irrability, high speed curing, high gloss of cured coatings and simple processing. However, drying prior to curing is necessary².

Poly (vinyl alcohol) (PVAl), is a water soluble, filmforming, biodegradable polymer, unfortunately with insufficient resistance to water and water vapour. It is believed that modification of PVA by various organic moieties can significantly improve the barrier properties of coatings prepared from these modified grades of PVAl thus widening the application possibilities in the packaging industry.

The goal of this work was to study the ways of improving barrier properties of paper by coating it with hybrid inorganic-organic polymer ORMOCER®s. A primer consisting of UV-curable PVAl containing methacrylate moieties (poly(vinyl alcohol-co-vinyl hydroxypropyl methacrylate))) was used for planarization of the substrate. The composition of both active layers was optimized and water the vapour permeability was determined gravimetrically.

Experimental

Materials

Poly(vinyl alcohol) Sloviol 8-98 (NCHZ, Slovakia), glycidylmethacrylate (GMA, Merck, Germany), N,N-dimethylformamid (DMF, Lachema, Czech Republic), dimethyl sulfoxide (DMSO, Merck, Germany), ORMOCER (Fraunhofer Gesellschaft zur Forderung der angewandten Forschung, Munich, Germany), Irgacure 2959 (Ciba, Switzerland), Irgacure 184 (Ciba, Switzerland), Ethanol (Merck, Germany) and Acetone (Merck, Germany) were used.

Preparation of Poly(vinyl Alcohol) Derivative

10 g PVAl was dissolved at 90 °C in a mixed solvent (50 ml DMF and 50 ml DMSO). After complete dissolution, the mixture was cooled to 70 °C and 1 ml of GMA and 2.5 ml of 5 % wt. ethanolic solution of KOH was added dropwise. Mixture was kept at 70 °C for an hour and constantly agitated. Then it was cooled to ambient temperature, diluted with 25 ml of water and the product was precipitated into an excess of ethanol. The precipitate (PVAl-GMA) was collected, washed in acetone and dried to constant weight at room temperature³.

Polymerization Kinetics Measurement

Samples were prepared by mixing the photoinitiator initiator Irgacure 184 with ORMOCER[®]s and Irgacure 2959 an with aqueous solution of modified PVAI (PVAI-GMA) in varying ratios. These coating compositions were coated onto aluminum plates and cured at the light intensity 12 mW cm⁻² (medium pressure mercury vapour lamp, 250 W).

Polymerization kinetics was evaluated on the basis of FTIR spectroscopy measurements (spectrophotometer Excalibur Digilab FTS 3000MX, USA). The absorption band at the frequency of 1,635 cm⁻¹ corresponding to the C=C bonds, was monitored. The monomer conversion × was determined on the basis of decrease of the absorption band intensity according to

$$X = 1 - \frac{\left[A_{\lambda}\right]_{0}}{\left[A_{\lambda}\right]_{k}}, \qquad (1)$$

where $[A_{\lambda}]_0$ and $[A_{\lambda}]_t$ is the absorbance measured at the chosen wavelength before and after the exposure to UV light for the time t, respectively. The values of maximum conversion X_{max} were obtained from the plots of \times and R_{p} vs. time.

The water Vapour Permeability Measurement

The watervapour permeability (WVP) was quantified according to a German standard DIN 53 122 and determined as an amount of the water vapour in grams passed through paper sample of a certain thickness within 24 hours at the temperature of 20–23 °C and relative humidity of 85 % provided by saturated KCl solution. Water vapour was quantitative absorbed on silicagel.

Results

In order to optimize the coating compositions we prepared samples of ORMOCER[®]s containing 1, 3 and 5 % wt. of Irgacure 184. During the curing process, a decrease of absorbance can be observed in the bands characteristc for carbon-carbon double bond (810 a 1635 cm⁻¹). As shown in Figure 1, the initial rate of curing is the fastest for 5 % wt. content of photoinitiator, where 70 % conversion is achieved within 40 s. Sample containing 3 % wt. of initiator takes 2 minutes to reach the same conversion while sample containing 1 % wt. of initiator takes 5 minutes. However, in the case of all three samples the curing process was completed and the conversion reached 88–90 %.



Fig. 1. Influence of exposition dosage (ED) on the UV curing of ORMOCER[®]s at various Irgacure 184 concentrations (1 % \blacksquare , 3% \blacktriangle and 5 % \blacklozenge ; layer thickness 10 µm) at the light intensity 28 mW cm⁻²

The modification reaction performed on PVAl lead to the epoxide ring opening and the attachment of hydroxypropyl methacrylate moieties onto the PVAl macromolecular backbone. Therefore the UV curing process will be performed through radical polymerization of methacrylate groups in the lateral moieties.

As the modified product was soluble in water, also water soluble initiator was chosen (Irgacure 2959). Samples were not cured immediately after coating, but solvent water had to be evaporated first. Similarly to ORMOCER[®]s, samples of containing 1, 3 and 5 % wt. of Irgacure 2959 were prepared.



Fig. 2. Influence of exposition dosage (ED) on the UV curing of PVAGMA at various Irgacure 2959 concentrations (1 % \blacksquare , 3% \blacktriangle and 5 % \blacklozenge ; layer thickness 10 µm) at the light intensity 12 mW cm⁻²

The highest conversion was achieved with 3% wt. of initiator, sufficient curing was observed also in the case of 5% wt. composition. However, in the case of 1% wt. composition sufficient conversion can not be reached even after substantial extension of curing time.

Water vapour permeability (WVP) is a very important property of packaging materials. We determined the WVP of a paper and also observed the changes in WVP after coating with ORMOCER[®]-lacquer. Some samples featured an intercoating of PVAI-GMA, applied as s planarizing primer. With respect to the results of primary double bond conversion study, we used 3 % wt. of photoinitiators for both systems and coatings were cured for 5 minutes, this corresponds to the exposure dose 8.4 Jm⁻². WVP was determined gravimetrically and the results are summarised in Table I.

As presented in Table I, the WVP was basically not altered by coating with PVAI-GMA. After curing this coating, the WVP decreased by 34 %. A similar value was achieved by coating the paper with the ORMOCER[®]-coating and curing. Significant decrease in WVP was achieved when the primer coating of PVAI-GMA was used. Since WVP is not a material constant, its value depends on the least permeable component of a system. Therefore it is possible to conclude that the 68 % decrease of WVP in the case of triple system with both coatings cured is caused by

Table I

Water vapour permeability for paper coated with photochemicall active polymers (uncured u, cured c)

Sample	WVP[gm ⁻² day ⁻¹]
Paper	1,200
Paper/PVAGMA(u)	1,150
Paper/PVAGMA(c)	800
Paper/ORMOCER®s(c)	750
Paper/PVAGMA(u)/ORMOCER®s(c)	600
Paper/PVAGMA(c)/ORMOCER®s(c)	390

higher smoothness and pore closing resulting from the effect of the primer. As a direct consequence, the second layer of ORMOCER[®]s is more even and homogeneous and therefore its barrier effect is more pronounced.

Conclusions

The UV curable polymer films were prepared by addition of radical-type photoinitiators to ORMOCER and PVAI-GMA. According to spectroscopic monitoring of the curing process, optimal curing conditions were determined (3 % wt. of photoinitiator for both polymers, exposure dose 8.4 J m⁻². Paper coated with PVAI-GMA primer and ORMOCER active layer features significantly lower WVP – a decrease by 68 % comparing with uncoated paper was observed.

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P08 INFLUENCE OF AGEING ON OPTICAL PROPERTIES OF ARYLMETHANE DYES

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Introduction

Arylmethane dyes represent one of the oldest manmade dyestuffs. Primarily, Fuchsin and Methyl Violet were manufactured at the end of the 19th century. A milestone in the synthesis of arylmethane dyestuffs was the discovery (by Michler in 1867) of the reaction of phosgene with dimethylaniline. Based on this reaction, Caro and Kern prepared Crystal Violet in 1883. Fisher described, in 1887, the process of preparing Malachite Green, which is still employed on an industrial scale^{1,2}. Later, other types of arylmethane dyes were prepared on the basis of hydroxyl triphenylmethane and xanthene compounds, and additionally acidic triphenylmethane dyes obtained by sulphonation of basic dyestuffs.

Damage to archive documents (bleaching, colour changes, total loss) written with tools based on arylmethane dyes, initiated the study of processes responsible for these devastating changes. The knowledge of the mechanisms of these processes opens new possibilities for the stabilization and preservation of such documents.

As arylmethane dyes in inks are water-soluble, it is essential that they are protected if aqueous conservation treatment is undertaken. Fixatives used for such a purpose must meet certain criteria (besides being able to fix the dye). In particular they must not change (or only by a minimal amount) the optical appearance of the object, i.e. neither cause colouring nor damage of the support material nor decrease the aging resistance of the dye-paper complex. The reversibility of the whole process, i.e. the possibility of removing the agent from the support, should also be taken into an account³.

Experimental

In our experiments we used acidic, partly groundwood containing paper produced by Slavošovské Papierne (Slavošovce, Slovak Rep.)

The colorants used in the tests were arylmethane dyes (Basic Red 9, Acid Green 16). Basic Blue 9 (Methylene Blue) is a phenotiazine dye with poor lightfastness. The dyes were provided from TRIADE, Netherlands.

The fixatives used were following:

Fixing agent from Neschen company, Germany, suspension consisting of 1,2 % Mesitol NBS (Bayer AG) and 6 % Rewin EL (Chemische Fabrik Tübingen), pH = 6.2 (further marked as Neschen).

Sandofix WE – (Sandoz AG), 10% water solution, pH = 4.1.



Fig. 1. Colour Fastness of Acid Green 16 after ageing; (a) – fixation, (b) – fixation and deacidification

Cyclododecane $C_{12}H_{24}$, solution prepared from 5 g cyclododecane and 40 g toluene.

Deacidification solution (aqueous solution of a mixture of magnesium and calcium bicarbonates, pH = 7.4) was prepared from 17 g MgCO₃ and 2 g CaCO₃ per 1 dm³ of water saturated with gaseous carbon dioxide. The samples were prepared as follows: paper rectangles measuring 7×12 cm were coloured wit solutions of different dyes (1 ml) and air dried at room temperature. Colorants Basic Red 9 (Basic Fuchsin), Acid Green 16 and Basic Blue 9 (Methylene Blue) were used as 0.2% solution in a mixture of distilled water and ethanol (1:1). Paper samples were immersed for 2 minutes into solutions of Neschen and Sandofix fixing agent, while cyclododecane was applied by brush on both sides on the samples.

The samples were submitted to accelerated aging by moist heat at 80 °C and 65 % RH in a climatic chamber (Feutron GmbH, Greiz, Germany (0, 3, 6, 12, 24 days). The properties of the paper samples were measured according to the Slovak Technical Standards (STN) and STN ISO Standards. A spectrophotometer Spectrolino (Gretag Macbeth AG, Regensdorf, Schwitzerland) was used for measurements of the colour components ΔL^* , Δa^* , Δb^* before and after accelerated aging on coloured paper, after fixing and after fixing and deacidification treatments.
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Fig. 2. Colour Fastness of Basic Red 9 after ageing; (a) – fixation, (b) – fixation and deacidification

Results

Accelerated aging of coloured paper provided complex problems because during the aging procedure the chemical and mechanical properties of the paper, as well as of the arylmethane components are changing simultaneously.

Fig. 1. presents dependency of total colour difference changes for paper coloured with 0.1% Acid Green 16, after moist heat aging. Despite an initial increase of ΔE^* caused by the fixatives, especially by cyclododecane, it can be seen that all three fixing agents caused a significant decrease after 24 days of this aging, for Sandofix and cyclododecane there was a colourfastness improvement of about 35%. After the deacidification of samples fixed by cyclododecane another decrease (49%) was observed down to $\Delta E^*_{ab} = 11.0$ after 24 days of accelerated aging (Fig. 1.).

Fig. 2. shows the the behaviour of Basic Red 9 dye applied to paper as 0.1% ethanolic solution after moist heat aging. Moist heat fastness of the dye was improved after fixing and deacidification. This was particularly apparent from the decrease of total colour difference after 12 and 24 days of accelerated aging compared to aged, unfixed paper.

Moist heat accelerated aging of paper coloured with 0.2% Basic Blue 9 solution caused a decrease of ΔE^*_{ab} for all three fixing agents compared to non-fixed samples. The best fixing effects was shown by Sandofix (38% decrease). All three fixing agents caused about a 40% decrease of ΔE^*_{ab} after deacidification of the fixed paper samples (Fig. 3.).



Fig. 3. Colour Fastness of Basic Blue 9 after ageing; (a) – fixation, (b) – fixation and deacidification

Conclusions

It is possible to suppose that one universal fixing agent will have same beneficial effect on all types of dye of all archival documents.

The best lightfastness of arylmethane dyes, after being fixed with cyclododecane was shown to be Acid Green 16 and Basic Red 9 (decrease about 25 %) and followed by deacidification, Acid Green 16 and Basic Blue 9 (decrease about 46 %).

After fixing with Neschen fixing agent or Sandofix respectively and subsequent deacidification, the best light-

Table I

Total colour difference (ΔE^*_{ab}) of the coloured samples after accelerated aging (24 days) by moist heat at 80 °C and 65% RH

	Acid Green 16	Basic Red 9	Basic Blue 9
Coloured paper	32.3	39.5	23.8
Fixed by Neschen	27.7	30.1	22.6
Neschen + deacidification	23.5	29.0	13.4
Fixed by Sandofix	24.2	24.2	14.8
Sandofix + deacidification	26.3	28.0	14.7
Fixed by cyclododecane	24.1	28.6	20.8
Cyclododecane + deacidification	16.6	28.6	13.3

fastness was seen on the sample of Basic Blue 9 (decrease 44 %).

The highest resistance towards moist accelerated aging after being fixed using cyclododecane and was recorded for Acid Green 16. Good lightfastness of arylmethane dyes, after being fixed with cyclododecane and then deacidified we have seen in samples of Acid Green 16 and Basic Blue 9.

After fixing with Neschen and Sandofix fixing agents, the highest resistance towards moist accelerated aging was seen in samples of Basic Blue 9. This work has been supported by Slovak Grant Agency VEGA (project VEGA 1/0800/08) and project MVTS COST D42/08.

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P09 INVESTIGATION OF DECOMPOSITION OF PHOTOINITIATORS

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Introduction

One of the most important part of UV cured systems are photoinitiators. The initiator plays a key role in that it governs both the rate of initiation and the penetration of incident light into the sample, and therefore controls the depth of cure. The rate of polymerization depends initially on the reactivity of the functional group, its concentration and the viscosity of the resin¹. The present range of commercial photoinitiators has absorptions that covers the whole spectrum of UV and near visible light and allows the efficient formulation for majority of UV curing applications. More recent developments in photoinitiator technology are addressing particular problems that have risen in UV curing, such as that of migration from coatings into foodstuffs, etc. and the introduction of polymeric photoinitiators to counter this effect.

In this work were investigated properties (absorption spectra and molar absorption coefficients, rate of photodecomposition, number of photodecomposition products) of four photoinitiators. Two of them are commercially available initiators (Irgacure 2959, Irgacure 261) and the other two are new prepared photoinitiators (HP1 and CB). CB is cationic organometallic photoinitiator and HP1 is hybrid photoinitiator which can efficiently initiate polymerization reaction of both free radical and cationic polymerization². The detailed synthesis of HP1 was described in previously publicated works^{3,4} and synthesis of CB in works^{5,6}. The investigated photoinitiators are shown in Fig. 1.

Experimental

UV-VIS Spectroscopy

UV-VIS absorption spectra and photolysis of photoinitiators were monitored by UV-VIS spectrometer Specord 210 (Analytik Jena AG, Germany) in solutions of photoinitiators in acetonitrile at room temperature. The molar absorption coefficients were calculated using the Lambert-Beer's law. Photolysis of photoinitiators (concentration of 1×10^{-4} mol dm⁻³) was followed by decreasing the absorption bands after irradiation by high-pressure mercury lamp (CE Green Spot from UV Source Inc., USA). The intensity of irradiation was 500 mW cm⁻² (in the spectral region 258–380 nm). The normalized absorbance A_n was calculated by equation:

$$A_{n} = (A_{0} - A_{t})/(A_{0} - A_{\infty}), \qquad (1)$$



Fig. 1. Prepared photoinitiators HP1 and CB and commercial photoinitiators Irgacure 261 and Irgacure 2959

where A_0 is absorbance of measured band before the irradiation, A_{∞} is absorbance after the final photolysis and A_t is absorbance after the irradiation time t.

The dependence of normalized absorbance on the irradiation dose was described by (2) for first-order reaction:

$$A_{n} = P_{1}(1 - e^{-P_{2}E}), \qquad (2)$$

where P_1 is maximal normalized absorbance, P_2 is rate of decomposition after irradiation and E is the irradiation dose (mJ cm⁻²). From equation (3), $E_{1/2}$ can be calculated as the energy needed to achieve the half photodecomposition.

$$E_{1/2} = \ln 2/P_2$$
 (3)

The degree of photodecomposition X_p of initiators for irradiation dose E was calculated from (4):

$$X_{p} = A_{n}/P_{1}$$
(4)

Determination of the Number of Decomposition Products after UV Photolysis by Factor Analysis

The photolysis absorption spectra of solutions of studied photoinitiators in acetonitrile were used for the determination of the number of components k in the solution by factor analysis in the INDICES algorithm. The INDICES^{7,8} determines the number of dominant components present in the equilibrium mixture. In this algorithm the various indicator function Principal Components PC(k) techniques were developed to deduce the exact size of the true component space and can be classified into two general categories: (i) precise methods based upon the knowledge of the experimental error of the absorbance data, $s_{inst}(A)$, and (ii) approximate methods requiring no knowledge of the experimental error, $s_{inst}(A)$. In general, more precise and most inclining methods are based on the first criterion concerning the procedure of finding the point where the slope of the indicator function PC(k) = f(k) changes. Each "real" factor corresponding to an actual absorbing component in solution will cause a dramatic decrease in PC(k) value, whereas superfluous factors cause only very small decreases. Elbergali et al.⁹ proposed a modification of index methods using derivatives to improve identification of the number of components. The second derivative SD(k) – the number of components in solution is equal to k where SD(k) has its first maximum (except k = 2). The third derivative TD(k) – the number of components in solution is equal to k where TD(k) has its first minimum (except k = 2). The derivatives ratio ROD(k) – the number of components in solution is equal to k where SD(k) has its first maximum (except k = 2). The derivatives ratio ROD(k) – the number of components in solution is equal to k where SD(k) has its first maximum (except k = 2).

Results

UV-VIS Spectroscopy

UV spectra of all investigated photoinitiators are shown on Fig. 2. Molar absorption coefficients at the most important emission wavelengths of the medium-pressure mercury lamp are summarized in Table I. The absorption spectrum of prepared cationic photoinitiator CB is similar to the spectrum of commercial cationic photoinitiator Irgacure 261. The exchange of isopropyl ligand by chlorine caused hypsochromic shifts from 391 nm to 377 nm and from 456 nm to 446 nm. Photoinitiator HP1 has higher molar absorption coefficients for all main emission bands of medium-pressure mercury lamp than the other tested photoinitiators (with exception of initiator Irgacure 2959 and emission band 303 nm; Table I). This is useful for commercial applications, because medium-pressure mercury lamp is often used as UV source for curing of inks, varnishes, etc.

Table I

Molar absorption coefficients ε [dm³mol⁻¹cm⁻¹] of photoinitiators in acetonitrile at the most important emission wavelengths of the medium-pressure mercury lamp

Photoinitiator	253 nm	303 nm	313 nm	365 nm
HP1	15,443	1,652	898	194
CB	7,129	366	242	48
Irg. 261	7,051	452	316	91
Irg. 2959	5,270	1,725	421	14

Photolysis of Initiators

The photolytic decomposition of initiators after UV irradiation was investigated by UV-VIS spectroscopy. Photolysis spectra of initiators are on Fig. 3. The concentration of photoinitiators was 1×10^{-4} mol dm⁻³ in acetonitrile and irradiation dose was 0-3,600 mJ cm⁻². Arrows mark the change of absorption bands during the UV exposure. Isoabsorptive points indicate that photoinitiators photodecomposition proceeded selectively without side reactions.

The degree of photoinitiators decomposition caused by UV irradiation was evaluated from absorption changes at such wavelengths, where only respective photoinitiator absorb (not products of its photodecomposition): 243 nm for CB, 243 nm for Irgacure 261 and 290 nm for Irgacure 2959. In case of HP1, it was difficult to analyse the decomposition spectra due to overlapping of spectra of adduct and products of photolytic reaction. Therefore it was not possible to find



Fig. 2. Absorption spectra of photoinitiators in acetonitrile (concentrations 1×10^{-4} and 2×10^{-2} mol dm⁻³)



Fig. 3. Absorption spectra of photoinitiators in acetonitrile (concentration of 1×10^{-4} moldm⁻³) measured after UV exposure

the wavelength corresponding only to the decomposition of radical or cationic part of molecule. For the basic information about photolysis of HP1, the wavelength 196 nm was chosen.

The dependences of photoinitiator normalized absorbance A_n (1) on UV dose were fitted by non-linear regression according to (2) (Fig. 4.). The non-linear regressions were treated by software STATISTICA. The adequacy of proposed regression model with experimental data and the reliability of parameter estimates P_1 and P_2 found (Table II) were examined by the goodness-of-fit test. The determination coefficients R^2 are equal to 99.6 % or better. Applying (3) to the data according to the regression criterion, the energy needed to achieve of photodecomposition of 0.5 ($E_{1/2}$) has been estimated (Table II). Comparing the values of $E_{1/2}$ it is apparent





Fig. 4. Dependence of normalized absorbance of initiators on UV dose

Table II

Estimated parameters $P^{}_1$ and $P^{}_2,\,E^{}_{1/2}\,[mJ\,cm^{-2}]$ and determination coefficient R^2

	HP1 (196 nm)	CB (243 nm)	Irg. 261 (243 nm)	Irg. 2959 (290 nm)
P ₁	0.986	1.024	1.008	1.0526
P_2	$3.3 imes10^{-3}$	1.37×10^{-3}	1.32×10^{-3}	4.1×10^{-3}
R_2	0.9960	0.9981	0,9990	0.9991
E _{1/2}	210	506	525	169

that prepared hybrid photoinitiator HP1 and free radical photoinitiator Irgacure 2959 needs approximately 3 times less energy for the decomposition (with high-pressure mercury lamp as UV source) and the rate of photolysis is faster as compared to cationic photoinitiators (Irgacure 261 or CB).

Normalized absorbances were recalculated by Equation 4 and the degree of photodecomposition X_p of initiators for irradiation dose E was obtained (Fig. 5.). From Fig. 5. is apparent that the course of photolysis of prepared hybrid photoinitiator HP1 is very similar to that of radical initiator Irgacure 2959 and the photolysis of these initiators is much faster than photolysis of cationic initiators CB and Irgacure 261.

Determination of the Number of Decomposition Products after UV Photolysis by Factor Analysis

The photolytic absorption spectra of photoinitiators (Fig. 3.) were used as absorption matrix for determination of number of components k in solution (after photolysis). For INDICES methods on Fig. 6 (the residual standard deviation – RSD, the root mean square error – RMS, the third derivative – TD and derivatives ratio – ROD), the dashed line denotes the value of the instrumental error, $s_{inst}(A)$. The best



Fig. 5. Dependence of degree of initiators decomposition on UV dose

approximation of $s_{inst}(A)$ for hybrid initiator HP1 was found for k = 5. The indices methods and their derivatives lead to estimation of five light absorbing components in the photolysis reaction system (Fig. 6.). One of them is original HP1 and the others are decomposition products. The estimated number of components (adduct and products) corresponds to the results of mass spectrometry (analysed was sample of HP1 in acetonitrile after UV photolysis). With this analytical method were detected four decomposition products with molecular weights of 218, 232, 477 and 654 g mol⁻¹.

Analysis of INDICES methods for cationic photoinitiator Irgacure 261 leads to an estimation of three light absorbing components in the photolysis reaction system.



Fig. 6. The logarithmic dependence of representative functions of INDICES algorithm as a function of the number of principal components (k) for the absorbance matrix of photolysis equilibria of hybrid initiator HP1

One of them is Irgacure 261 and the others are products of photoinitiator decomposition (isopropyl benzene and ferrocene), which corresponds to conclusions that have been published elsewhere¹⁰. During the decomposition of Irgacure 261, inorganic compound $Fe(PF_6)_2$ is also formed (non-absorbing in measured UV region).



Fig. 7. Suggested photodecomposition schema of prepared initiator CB

All index methods proved three light absorbing components of CB photolytic equilibria (CB, ferrocene and chlorobenzene). Prepared cationic initiator CB has similar structure as cationic photoinitiator Irgacure 261 and results of factor analysis (number of decomposition products) are for both initiators the same. From UV-VIS spectra and information from literature^{10,11} about photodecomposition of iron-arene complexes it can be assumed that the reaction mechanism of the decomposition of CB under UV light is similar as for Irgacure 261. The suggested decomposition schema of initiator CB is on Fig. 7. For free radical photoinitiator Irgacure 2959, the INDICES methods prove that there are four light absorbing components in the photolysis equilibria mixture. The molecular weights of individual photolysis products of Irgacure 2959 detected by mass spectrometry are 166, 314, 330 and 478 gmol⁻¹, respectively. Photolysis products of initiators Irgacure 261 and CB were not detected, which is probably caused by low molecular weights of expected decomposition products resulting in the low sensitivity of measurement with the ion trap analyzer.

Conclusions

The photodecomposition rate of prepared hybrid photoinitiator is similar to radical initiator Irgacure 2959. These two initiators need approximately 3 times less energy (highpressure mercury lamp as UV source) than cationic organometallic photoinitiators Irgacure 261 and CB to achieve half photodecomposition. The estimated number of photodecomposition products of initiators after UV photolysis by factor analysis show good correlation with results published elsewhere^{10,11} about photodecomposition of organometallic initiators or obtain from mass spectrometry.

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P11 STUDY OF STABILIZATION OF DOCUMENTS CONTAINING IRON GALL INKS BY TREATMENT OF ATMOSPHERIC DBD N₂ PLASMA

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Introduction

Problems of iron gall inks corrosive effect on paper support is solved in conservation practice by basic treatment of endangered documents in deacidification solutions of Mg or Ca salts¹. However, this treatment is not sufficient and for preservation of acceptable practical properties some other processing – like application of reinforcing agents, antioxidants or some substances which can remove excessive mobile forms of present transitional metals (iron)². In recent times also favourable influence of plasma treatment on paper support leading to improvement of its mechanical properties were proven³.

The aim of this work was study of application techniques of chitosan as reinforcing substance of alkaline nature with anti-microbiological effect for processing of paper containing iron gall ink followed by its treatment in dielectric barrier discharge (low-temperature plasma). The influence of potassium iodide – as antioxidant agent – on changes of some properties of treated papers was followed as well.

Experimental

Iron gall ink prepared according to the recipe⁴ was applied to wood-free filter Whatman paper No. 1 (Cat No. 1001917), producer Whatman Laboratory Division, Maidstone, England, basis weight 90 gm⁻², pH 7, with the help of plotter (HI-1117E Image Maker, Houston Instrument) in quantity of 2.65 ± 0.05 gm⁻². In order to get a model of older writig, samples were artificially aged in a closed space⁵ during 4 hours and they were named as "C" (control).

Tested samples were treated by different techniques:

- Technique A: impregnation by 0.5 % wt. of chitosan solution (Sigma-Aldrich, USA) in 0.1 moldm⁻³ acetic acid for 10 minutes, pressing out of excessive modification agent on an inert support and drying. The samples designation: CHA.
- Technique B: continual modification in chitosan solution (for about 5 s) and drying at ambient conditions. The samples designation: CHB.
- Technique C: technique A continuing with activation of samples surface by plasma – (atmospheric plasma surface treatment technique) (DBD in N₂ atmosphere at atmospheric pressure: 15 kV, 5 kHz, 0.1 Wm-¹², duration of action 5 s, N₂ flow rate 5 dm³ min⁻¹)⁶. The samples designation: CHP.

• Technique D: activation of paper surface by plasma under the same conditions as above mentioned technique C and subsequent application of technique B. The samples designation: PCH.

Before application of chitosan and plasma, one part of samples was immersed in 0.01 mol dm⁻³ solution of KI (Lachema Brno, Czech Republic) for 1 minute and dried between two filter paper sheets at the given pressure. The samples are marked as KI CHP (made by technique C) and KI PCH (made by technique D).

After modification the samples were pre-conditioned in bottles and artificially aged at 90 °C according to Bégin-Kaminska method⁵ during 0, 2, 4, 8 and 24 hours. After ageing they were again air-conditioned (24 hours, 23 °C, 50 % RH) and tested for changes mechanical properties caused by modification treatment. They were folding endurance (MIT method according to ASTM D 2176, Tinius Olsen, 3 N, cross direction, average of 10 measurements with standard deviation 35 ± 5 %) and zero-span breaking length (equipment FDP 40).

Results

Influence of Technique of Chitosan Application

It was found out by gravimetry that the amount of chitosan deposited by two different procedures A and B described above in experimental part was the same $(1.80 \pm 0.02 \text{ gm}^{-2})$. From Fig. 1. it can be seen that longer impregnation time with pressing out of modification solution (CHA) significantly increases folding endurance. For samples with shorter impregnation time but without pressing (CHB) increase of double folds was recorded comparing to the original sample, however after 2 hours of accelerated ageing the differences were negligible. It can be explained by penetrating of chitosan throughout the whole volume of sample during longer impregnating time while at the shorter time it rests mostly on the sample surface.



Fig. 1. Folding endurance of samples modificated with chitosan by two different methods in aging time

Influence of Technique of Chitosan Application and Plasma Treatment

Longer time of impregnation by chitosan followed by their treatment in plasma (technique C) seems to be more suitable (Fig. 2.a), however in the presence of KI the situation is reversed – the more suitable is plasma treatment before application of chitosan (technique D), Fig. 2.b. In that case also shorter time of impregnation by chitosan improves mechanical properties of samples. The presence of potassium iodide is unambiguously appropriate in the system. It can be suppose that plasma activates the carrier material and forms reactive spots in paper in paper already before process of chemical modification and thus stronger bonds between cellulose and chitosan can be created (by crosslinking).



Fig. 2. Dependence of folding endurance on aging time; (a) – Influence of technique of chitosan and plasma application, (b) – Influence of technique of chitosan and plasma application at presence of KI

M o d i f i c a t i o n T r e a t m e n t E f f i c i e n c y Changes of mechanical properties after modification treatment expressed by ratio of followed value of modified sample to the value of non-modified sample in certain time of ageing, called often as coefficient of permanence S confirms efficiency of selected treatment comparing to non-modified sample.

Fig. s 3, 4 express changes and results of folding endurance and zero-span breaking length for all tested modification systems applied to the samples according to the modifi-



Fig. 3. Coefficient of stability of folding endurance as dependence of aging time



Fig. 4. Coefficient of stability of zero-span breaking length as dependence of aging time

cation technique B. They confirm improvement of zero-span breaking length for all modified systems during ageing time in approximately the same extent (2-8x) and also improvement of folding endurance for the most suitable systems KICH and KICHP where coefficient of permanence reached in its maximum values around 30.

Conclusions

The work was concentrated on enhancement of strength and stability of historical paper documents treated in dielectric barrier discharge (DBD) at atmospheric pressure in combination with natural polymer chitosan and/or anti-oxidizing agent. Choise of suitable modification matter and combinations of application techniques was realised.

Implementation of appropriate system for chemical modification containing antioxidant and strengthening component relatively resistant to ageing is more important than application of plasma treatment; modification systems containing potassium iodide and chitosan appeared to be suitable.

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P12 THE INFLUENCE OF RECEIVING LAYER COMPOSITION ON INKJET PRINT LIGHTFASTNESS

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Introduction

Papers for inkjet printing can be divided into several categories according to their printing quality or segment of application. On one hand, multipurpose office papers treated with a surface sizing agent and starch are designed for lowand middle-end applications. On the other hand, inkjet papers with high quality demands must be coated using specialty pigments and additives^{1,2}. For printing high-quality photographic images, special media are used as the substrate. Currently, there are two types of special media, namely swellable polymers (based on PVAl or gelatin) and microporous media (both silica and alumina types)³.

In many cases fillers can have a marked influence on the thermal and photochemical stability of the polymer material. They can exhibit a protective effect or alternatively they may be photoactive and sensitise the photochemical breakdown of the polymer. Research activities about the photochemical properties of titanium dioxide (TiO₂) deal with studying photochemical activity of TiO₂ in order to convert harmful organic wasteproducts into harmless environmentally acceptable materials. Another deals with minimising the photocatalytic activity of TiO₂ in order to enhance the durability of organic substrates such as polymers and coatings⁴.

To enhance the durability, stabilizer additives such as ultraviolet light absorbers (UVAs) and hindered amine light stabilizers (HALS) are added to the coatings formulation⁵. One of the typical photostabilizing actions proposed for a polymer system containing HALS⁶ is showed on Fig. 1.



Fig. 1. Typical photostabilizing action of HALS in the polymer system

For printing, the three subtractive primary colours of yellow (Y), magenta (M) and cyan (C) are used. These colours are chosen because they produce the maximum number of colours by mixing (i.e. the maximum colour gamut). They can produce ca. 85 % of the 16.7 million colours theoretically possible. Inkjet dyes have to fulfil several requirements, most importantly hue (colour), vividnes, operability (reliability) and safety. Anionic water-soluble dyes (Dye-SO₃⁻) are the dyes of choice for inkjet printers³.



Fig. 2. Acid Red 52, Gamma Acid Magenta and H-acid dyes

Magenta dyes usually have the lowest lightfastness in inkjet and, indeed, in most other colour applications. The most commonly used magenta dyes for desktop inkjet printers are C. I. Acid Red 52, the H-acid dyes and dyes based on Gamma acid (they exist only in the azo form and due to higher lightfastness, compared to the other magenta dyes, they have found use in photographic applications)⁷.

Experimental

Anatase pigments are generally more photoactive than the rutile types⁴, what is the reason why TiO_2 of rutile type was used. It was dispersed into 5% wt. solution of poly (vinylalcohol) (PVAl) in 4:1 ratio. 0, 2 and 8 % wt. of water soluble stabiliser Eversorb AQ1 (blend of HALS and UVAs) was added into final dispersions. Filter paper was used as a substrate for prepared receiving layers. Layers were prepared by spreading the dispersion through a screen printing form by a blade.

Test charts were printed by Epson Stylus Photo R220 printer by dye-based inks with resolution720 DPI. Ink set MIS Dyebase for Epson printers containing C, M, Y, K, LC and LM cartridges was used (supplied by MIS Associates Inc., USA). Test chart consisted of cyan, magenta, yellow and black colour printed with 100% and 50% dot area.

CIE L*a*b* coordinates of print samples were measured by spectrophotometer Gretag Macbeth Spectrolino with illuminant D65 and filter D65. The specimens were irradiated by metal-halide lamp to reach the same exposure dose. Values of temperature, relative humidity and irradiance were taken through the exposures. Relationship (1) describes calculation of total colour difference ΔE_{ab}^{*} . Colour changes were evaluated from measuring after each exposure.

$$\Delta E_{ab}^{*} = \sqrt{(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2}}$$
(1)

Results

The efect of TiO_2 added into print layers was studied using microscop Nicon Eclipse E200 and camera Nicon D200. In many plastics applications, the primary use of TiO_2 is as an opacifier⁴. In addition, it improved print quality of specimens (Fig. 3.).



Fig. 3. Specimens coated with PVAI (a) and with dispersion of TiO₂ in PVAI (b)

Only magenta ink results were evaluated (100% and 50% dot area). Total exposure dose acquired by irradiation was 50.6 J cm⁻², average temperature and relative humidity values were 27.7 °C and 24.8 %.



Fig. 4. Values of total colour difference: (1) – layer with TiO_2 printed with 50% dot area, (2) – layer with TiO_2 printed with 100% dot area, (3) – layer without TiO_2 printed with 50% dot area, (4) – layer without TiO₂ printed with 100% dot area

Fig. 4. shows values of total colour differences calculated for magenta ink specimens at the end of the experiment. Fig. 5. and Fig. 6. represent receiving layers with TiO_2 filler use. The total colour difference values exceed 5 after first

exposure already. The growth of ΔE_{ab}^* values is smallest in the case of 8% addition of AQ1 stabilizer.



Fig. 5. Receiving layer with TiO₂ and 50% dot area print



Fig. 6. Receiving layer with TiO₂ and 100% dot area print

Fig. 7. and Fig. 8. represent receiving layers without TiO, filler use. The total colour difference values begun to



rise from the lower levels (less than 3). The growth of ΔE_{ab}^{*} values is smallest in the case of 8% addition of AQ1 stabilizer again.



Fig. 8. Receiving layer without TiO_2 , with 100% dot area print

Conclusions

Addition of TiO_2 into receiveng layers improved print quality and opacity of printouts, however, it decreased their lightfastnees. 50% dot area printouts faded more quickly than 100% once. An increased proportion of colour overprint and a catalytic fading can be the reason of this behaviour.

Stabilizer AQ1 had a positive influence on the lightfastness of printouts. 2% AQ1 addition decreased the progress of fading and 8% addition had even better impact on this process.

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P13 PHOTOPOLYMERIZATION OF MONOMERS WITH TWO DIFFERENT REACTIVE GROUPS

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Introduction

Glycidyl methacrylate (GMA) and 3,4-epoxy-1-butene (vinyl oxirane, butadiene monoxide, BMO) rank among monomers having two different functional groups able to polymerize by two distinct mechanisms – free radical (methacrylate and vinyl groups) and cationic (epoxy group), resp. Using suitable photoinitiators so-called hybrid photopolymerization occurs, interesting from theoretical point of view.^{1–3}

Photopolymerization of GMA or mixtures of GMA with another monomers is of practical meaning as well because it gives technical useful products⁴. The oligomers prepared mainly by cationic polymerization of epoxy groups of monomers like glycidyl vinyl ether (GVE) and BMO can advantageously be used in vehicle systems^{5,11}.

The aim of this work was the study of the photopolymerization kinetics of bifunctional monomers in the presence of the free radical and cationic photoinitiators as well as their mixtures using Fourier transform infrared (FTIR) spectroscopy, mostly with transmission technique.

Experimental

Materials

Glycidyl methacrylate – Sigma-Aldrich (USA), purity >97 % wt., stabilized by 0.005 % wt. p-methoxyphenol, bp 192–197 °C

Glycidyl vinyl ether – Sigma-Aldrich, purity 97 % wt., bp 139 °C

Butadiene monoxide -3,4-epoxy-1-butene, Sigma-Aldrich, purity 98 % wt., bp 65–66 °C

Irgacure 250 – (4-methylphenyl)[4-(2-methylpropyl) phenyl] iodonium hexafluorophosphate, Ciba-Geigy (Switzerland), a 75 % wt. solution of the active substance in propylene carbonate

Quantacure ITX – 2-isopropylthioxanthone, Great Lakes Fine Chemicals (USA), mp 62-77 °C

All the chemicals were used as purchased without any further purification.

Measurements

CE GREEN SPOT (UV Source Inc., USA) – UV radiation 300–480 nm (max. at 365 nm) source was high-pressure mercury arc lamp (100 W). UV light was guided through optical-fibre cable (diameter 5 mm), output delivery was 5 W. The distance of the optical-fibre waveguide outlet from the sample was 20 mm.

Radiometr Compact (UV Process Supply, USA) was used to calibration of UV source in the spectral range

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258–380 nm (max. at 365 nm). With this device the radiation energy relative to surface up to maximum $20,000 \text{ mJ cm}^{-2}$ can be measured.

AVATAR 320 (Nicolet Instrument Corp., USA) – FTIR spektrofotometer (beamspliter KBr, detector DTGS KBr). Our measurements were carried out at the resolution 4 (in this case the distance of the two points in the spectrum is 1.929 cm^{-1}) using transmission, reflection and ATR (Attenuated total reflection) techniques. In all cases 32 scans were recorded and averaged.

Measurements

The photopolymerization experiments were carried out at the laboratory temperature, the average room temperature was 21 °C. For transmission technique use the defined amount of reaction mixture was placed on the grade silicon window and immediately overlayed by covering teflon foil $60 \mu m$ thick. The UV exposition was interrupted by samples analysis, time intervals between expositions were about 0.5 min. GMA reaction mixtures with photoinitiators were polymerized using specular reflexion technique and ATR technique as well. Within the photopolymerization in closed reaction space the thickness of the layer varied in the range of 5 to 7 μm .

The reactive groups concentration was determined on the basis of the respective absorption peaks areas for epoxy group and the methacrylic or vinyl double bond. As internal standard the carbonyl group absorption peak (1,719 cm⁻¹) only with GMA could be used. This peak does not change in the photopolymerization conditions. The results usually are the averaged three to five repeated analysis. The reactive groups conversion extent was expressed according to following equation^{7,8}

$$x = (P_0 - P_t) / P_0, \tag{1}$$

where P_0 , P_t are the sample absorbances before the UV exposition and after the irradiation total time t.

Results

FTIR spectra of the monomers used are shown in Fig. 1. During the polymerization in the presence of the free radical initiator (Quantacure ITX) the absorbances (areas) of the three peaks in the wavenumbers regions 800-950 cm⁻¹ and 1,600-1,750 cm⁻¹ are subsequently relatively falling. The peak at 944 cm⁻¹ corresponds with methacrylate double bond of GMA⁹, the second one at 1620 cm⁻¹ indicates the presence of the vinylether double bond in GVE¹⁰ and the third one at 1,641 cm⁻¹ is charakteristic for the vinyl double bonds in BMO¹¹. In contrast to this, initiating the monomers polymerization using the cationic photoinitiator Irgacure 250 the peaks areas at 909 cm⁻¹, 903 cm⁻¹ a 818 cm⁻¹ ^{12,9,11} are relatively falling. These peaks correspond with epoxy groups of GMA, GVE a BMO. In the presence of the cationic photoinitiator further the absorption peaks at 1,620 a 1,641 cm⁻¹ are falling.





Fig. 1. FTIR spectra of the studied monomers mixtures with photoinitiátors before UV exposition

The experimental time-conversion curves (some typical examples are in Fig. 2.) as a rule satisfy the *n*-order kinetic equations⁶

$$\frac{dx}{dt} = k x^m (1-x)^n \tag{2}$$

$$\frac{dx}{dt} = (k_1 + k_2 x^m)(1 - x)^n$$
(3)

very well. In these relations k, k_1 and k_2 are the reaction rate constants, n represents the reaction order and m denotes the autocatalytic exponent.

The free radical initiator concentration in the reaction mixture does not affect the attained conversion of the methacrylate double bonds in GMA which exceeded 90 % in every case. However, the necessary total irradiation time reduces as the photoinitiator concentration increases until 1.67 % mol. The vinyl double bonds conversion in BMO with the free radical initiator (~ 1.1 % mol) reached 45 % after the total irradiation time of 172 s. In the presence of the free radical photoinitiator GVE polymerizes very slowly, the vinyl ether double bonds conversion does not exceed 5 % even after irradiation time of 200 s (Fig. 2.).

During the cationic photopolymerization of the epoxy groups in GVE and BMO the reduction of the vinyl ether and vinyl absorption bands, resp. takes place at the same time. In both these cases the double bonds conversions attained are lower than those of epoxy groups. It was shown¹¹ that the BMO cationic photopolymerization proceed mainly by the oxirane ring opening. In our experiments GVE reacted in a similar manner, however the vinyl ether bond conversion in the initial polymerization stage was higher than the epoxy group conversion. Generally it holds however that the more reactive oxirane monomers are characterized by lower polymerization rate compared with the vinyl ether monomers¹³. During the GVE polymerization in the presence of the catio-



Fig. 2. Conversion curves of the double bonds (C=C) in the presence of ~1.1 % mol. QUANTACURE ITX and the epoxy groups (ES) in the presence of ~0.13 % mol. IRGACURE 250

nic photoinitiator the mutual interference of the both reaction groups apparently occurs.

Markedly different results were obtained in monitoring the cationic photopolymerization of GMA. In oxirane ringopening polymerization the conversions up max. 20 % were observed (Fig. 2.). On the contrary, with the increasing cationic photoinitiator concentration the polymerization rate of the methacrylate double bonds expressively rises. For example in the presence of 0.45 % mol IRGACURE 250 reach the conversion of the methacrylate double bonds 90 % after irradiation time 252 s. In comparison with GVE and BMO monomers the cationic photopolymerization of GMA in the closed thin layers is retarded hard. This matter of fact can be explained by very low reactivity of the glycidyl methacrylate epoxy groups in the experimental conditions applied. During irradiation then enforced the radical intermediates produced in diaryl iodonium salt decomposition as well.

In investigation of the hybrid monomers photopolymerization was found that the conversion curves are of the same type as those obtained in the presence of the cationic initiator alone. In every hybrid photopolymerization experiment, the initiation system was the ratio 1:1% mol mixture of the free radical and cationic photoinitiators. In the case of the GMA photopolymerization the dominate reaction is the double bond polymerization again. The free radical photoinitiator addition to the cationic one enables the appreciable irradiation time shortening. Fig. 3. shows the dependence of the sum total conversions of the both functional groups vs. the hybrid initiation system concentration and irradiation time for all the monomers investigated.

Through the transmission and specular reflection techniques applied on the GMA photopolymerization in the closed thin layers with the free radical or cationic iniciators very similar results were obtained. The GMA photopolymerization monitored by the ATR technique proceeded in the air presence. This accelerated the cationic polymerization which became the dominant reaction and the epoxy group conversion reached considerably higher values.



Fig. 3. The sum total conversions of the epoxy groups and double bonds of the monomers investigated in the presence of the hybrid photoinitiator system (mol. ratio 1:1). 1 - GMA, 2 - GVE, 3 - BMO

Conclusions

Experimental results shows the glycidyl methacrylate and butadiene monoxide monomers are able to polymerize in the presence of both the free radical and cationic photoinitiators. Within the glycidyl methacrylate photopolymerization in the closed thin layers the dominant reaction center is the methacrylate double bond even with diaryl iodonium salt photoinitiator. Glycidyl vinyl ether provides homopolymers only with the cationic photoinitiator and after irradiation finishing the conversions of the both functional groups reach the similar values. The substantial acceleration of the investigated monomers curing can be reached in the hybrid systems using suitable combination of the cationic and free radical initiators. The used mathematical models described the experimental data very well and could be applied on all the kinetic data obtained.

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P14 A NEW APPROACH TO INKJET PRINTS LIGHTFASTNESS EVALUATION

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Introduction

The majority of printers used for colour printing in offices and homes today are inkjet printers. Inkjet is a digital printing process where the ink is ejected directly onto a substrate from a jet device driven by electronic signals. Due to its ability to print on a wide variety of substrates, inkjet technology is also increasingly being used in industrial printing and in the package printing industry.

According to the ink application it is possible to classify the inks frequently used and a method of their drying in a receiving layer: aqueous ink – absorption and evaporation, oil-based ink – absorption, UV-curable ink – absorption and the time available before cure and hot-melt/phase change – freezing.

The ink designed for ordinary portable inkjet printers can contain more than 20 various compounds, playing an important role for final printout quality. Main components of an aqueous/solvent based inkjet ink are: colorant, which gives the ink its primary function – absorbing light of a particular wavelength band (2–8 %), carrier fluid which dissolves or suspends the colorant (35–80 %), surfactant lowering the surface tension of the ink to promote wetting (0.1–2.0 %), humectant which inhibits evaporation (10–30 %), penetrant which promotes penetration of the ink into the paper structure for the purpose of accelerating ambient drying (1–5 %), dye solubilizer promoting dye solubility in the primary carrier fluid (2–5 %), anti cockle additive which reduces the interaction with paper fibres which otherwise leads to paper cockle and curl (20–50 %).

An ideal paper for inkjet printing should possess the following properties: sufficient hold out of ink dye on the surface to provide high optical print density, quick absorption of ink carrier liquid for fast drying, to prevent feathering and bleeding, low colour-to-colour bleed (well-defined diffusion of the ink), low strike-through and water- and light-fastness.

The printout fading is caused by many factors as for example chemical compounds in air (mainly aggressive ozone)¹, higher temperature, air humidity and light. The ultraviolet light is surely the most dangerous enemy of inkjet printouts. Very similar impact can be observed in the case incandescent light illumination. Any printouts should be never exposed to higher temperatures or left on moisty places.

The light fading^{2,3} should be determined by exposure dose. But it was found that this process doesn't fulfil the reciprocity law. Colour photos exposed to low intensity irradiation for a long time are often more damaged than those exposed to high irradiation for a short time with the same exposure dose.

The absorption of direct sunlight can be very dangerous for dye molecule. Its excitation can lead to forming of colourless products. Moreover, reactive oxygen radical present in illuminated layer can decompose the image dye.

The reaction pathway of the ink-forming azo dye depends on the chemical environment in which the dye molecules are bound. This environment is determined mainly by the print medium, ink-forming components and surrounding atmosphere. Depending on these conditions the dye molecule can be either reduced or oxidised. The azo dye molecule can be reduced to corresponding colourless amines in the presence of hydrogen donor. This reaction speeds up when the hydrogen donor or the azo dye itself is in the excited state. Excited dye molecules are unstable and therefore are easily degraded. The reducing hydrogen can originate from alcoholes, amines, ketones, carboxylic acids, ethers and esters. The azo dye molecules existing in hydrazone tautomeric forms attacked by singlet oxygen undergo the oxidative degradation pathway. An unstable peroxide molecule originates from this reaction. The peroxide decomposes spontaneously while nitrogen is released from the azo group. Reaction products can be coloured.

Experimental

The following inkjet paper were used: Ilford Galery Smooth Gloss – high glossy paper with microporous receiving layer, enabling fast drying of surface layer, Epson Archival Matt – matte coated paper designed for archival purposes, Ilford Galery Classic Gloss – high glossy paper with swellable polymer layer, Foma 1224 – matte coated paper for everyday printing. The test targets TC9.18 (X-Rite) were printed by printer EPSON R220 on samples of inkjet papers using dye-based inkset ESC-R200–4 (MIS Dyebase). These samples were irradiated in Q-SUN-Xe1-B (Q-PANEL) xenon chamber. Spectral irradiance was set to 0.68 W m⁻² at 340 nm. The test targets were measured using spectrophotometer Spectrolino (X-rite) and evaluated by ProfileMaker 5.0 software.

Results

Main drawback of inkjet printing technology compared to classic silver halide photography is the overlap and mixing of individual inks in the receiving layer.

The illumination of inkjet printed photographs causes fading of individual inks with different rates – this process is called catalytic fading. During this process one ink or its decomposition products can serve as a catalyst for the second ink degradation. The results are unexpective colour shifts of printed pictures.

Test target TC9.18 with 918 patches enables to judge the results of accelerated ageing of ink overlaps. The main advantage of a great test target is the possibility to calculate ICC profile and subsequently to express the gamut in CIE $L^*a^*b^*$ colour space. Similarly, we evaluate the cross-sections through the gamut body at various lightness levels in CIE $L^*a^*b^*$ colour space. In most cases, it is sufficient to represent the gamut as the cross-section of CIE $L^*a^*b^*$ colour space in 50% level of lightness (L50), eventually in 25% and 75% level (Fig. 1.). The other way of accelerated ageing results presentation consists of gamut volume calculation.



Fig. 1. An accelerated ageing test of FOMA 1224 before (yellow lines) and after 33 hours (white lines): cross-sections of CIE $L^*a^*b^*$ colour space at L25 (left), L50 (middle) and L75 (right)

After exposure dose of 80.3 kJ m^{-2} at 340 nm, we observed a considerable fading of all papers used in this test. This process is illustrated in Fig. 2 by means of counts of colour differences ΔE^*_{ab} . The distribution of colour differences ΔE^*_{ab} is narrow for papers with high resitance to fading, whereas the broader distributions indicate low lightfastness of tested inkjet papers.



Fig. 2. The counts of colour differences values ΔE^*_{ab} after 33 hours of accelerated ageing test measured on 918 patches of TC9.18

All tested papers possesed a similar gamut, after accelerated ageing we found their gamut to be much smaller. Irradiation during accelerated ageing caused the loss of vivid colours printed by overlapping inks containing yellow ink. This is well visible on gamuts comparison (Fig. 4.).

Conclusions

From the presented results we can conclude that the highest image stability was observed on both Ilford papers. These papers showed the least colour fading of all tested papers. Colour gamut comparisons and the evaluation of colour differences distribution can significantly support the complex assessment of inkjet prints lightfastness.



Fig. 3. A cross-section of CIE L*a*b* colour space at L50 before test: Ilford Galery Smooth Gloss – red line, Epson Archival Matt – yellow line, Ilford Galery Classic Gloss – white line and Foma 1224 – gray line



Fig. 4. A cross-section of CIE L*a*b* colour space at L50L after 33 hours of accelerated ageing test: Ilford Galery Smooth Gloss – red line, Epson Archival Matt – yellow line, Ilford Galery Classic Gloss – white line and Foma 1224 – gray line

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