Light Stability and Gas Fading on Nanoporous Ink-Jet Materials

Rolf Steiger, Pierre-Alain Brugger and Martin Staiger
ILFORD IMAGING Switzerland GmbH
Marly, Switzerland

Abstract

The **light stability** of various ink-jet dyes has been studied on several types of nanoporous, nanocrystalline ink-jet materials (γ-Al_2O_3, ZrO_2, SiO_2, AlOOH, rare-earth doped Al-oxides). The following parameters influencing light stability will be discussed: chemical properties of the metal oxides, pore diameter, pore volume, surface charge (sign and density), dye adsorption, dye aggregation and dilution in inks. Catalytic fading in nanoporous media is in relation with porosity. Various methods to increase the light stability of inks in such media are discussed. A possible mechanism to explain the photolytic degradation of ink-jet dyes in nanoporous materials is proposed. **Gas fading** was studied using different environmental gases under well defined conditions. The **overall stability** of inks in nanoporous media depends on other parameters than in polymer layers. Therefore, improvements in nanoporous layers were also made using other tools.

Introduction

Ink-jet dyes in **nanoporous media** show two kinds of instability, which must both be considered if long term stability of printed images in these materials is discussed.

The first instability is the **photo oxidation of imaging dyes,** which follows, in the best case, about the same kinetics as in media containing swelling polymers as ink receiving layers.

Another, far more dramatic effect, which is almost absent in swelling polymers, is a relatively fast oxidation of imaging dyes in normal environment. This process, often called **gas fading,** occurs in the absence of light, and always preceedes photooxidation.

Both effects are discussed below, as well as their relative contribution to the long-term stability of images in nanoporous media. **Gas fading experiments** were carried out by exposing printed images to various environmental gases (without light) under well known conditions of temperature, humidity and partial pressure.

Light Stability In Nanoporous Media

It is well known[1] that absorption spectra of dyes contain information on the geometrical arrangement of dye chromophores in dye aggregates. However, the **number** of individual dye molecules within dye aggregates has little influence on absorption spectra if more than about 10 dye monomers per aggregate are present.[1] Absorption spectra of dyes show similar features in polymer layers and in nanoporous metal oxide coatings on transparent base.[2] The spectral ratio between aggregated and deaggregated species[2] is not drastically different (ARCHIVA inks), although in **polymeric** ink-jet receiving layers **colloidal magenta and cyan dye particles** with a mean size of about 60 nm could be visualized by transmission electron microscopy after ink-jet printing, plasma etching, carbon replication and Cr-shadowing These dyes are about as light stable as small particles of pigmented inks in polymeric ink-jet receiving layers. About 5×10^4 dye molecules are present in one single colloidal particle of 60 nm diameter. The high light-stability of these dyes in polymer layers was shown[2] to be mainly due to the formation of large dye aggregates which can easily be formed in open polymer structures. *However*, in nanoporous metal oxides (e.g. AlOOH) with mean pore volumes of about 0.6 ml/g and mean pore diameters of about 10 nm, only about 20-60 individual dye molecules can be accomodated in one single nanopore if inks with 5% dye concentration are considered. Therefore, dye aggregates cannot contain more than about 60 dye monomers within the same pore. After surface modification of AlOOH by a stabilizing agent and dispersion into aqueous solutions containing a magenta dye with well know aggregating properties[2], diffuse reflectance spectra of the dye showed the same features as in unstabilized AlOOH (Figs. 4 and 5 in Ref. 2). From these results and from the small number of dye monomers present in a single pore of nanocrystalline metal oxides, we conclude that dye aggregation has not the same importance for the light stability of ink-jet dyes in nanoporous systems as in polymeric ink-jet receiving layers.

In order to understand which parameters influence the light stability of ink-jet dyes in **nanoporous** ink-jet receiving layers, we have coated different nanocrystalline metal oxides under pH conditions for positive surface charge on transparent polyester base and printed with an EPSON STYLUS SC 500 printer. Their light stability (ΔD, loss in optical density after exposure) is compared with that of our best experimental swelling polymer coatings in **Table I**. These results show that all studied nanoporous metal oxides except our own suffer from a considerably instability of the magenta dye after exposure to 10

MLuxhours ATLAS, although their chemistry as well as their pore characteristics are very different **(Table II)**. Only on our stabilized oxides the same light stability as in swelling polymers could be achieved **(Table I)**.

Table I

Nanoporous oxides	ΔD Cyan ± 5%	ΔD Magenta ± 5%	ΔD Yellow ± 5%
SiO_2	-17%	-47	-11
ZrO2	-22%	-66	-24
γ-AlO O H	-12%	-59	-16
γ-Al_2O_3	-8%	-71	-47
ILFORD nanoporous	-24%	-28%	-18%
Swelling polymers ILFORD	-4%	-25%	-10%

A more systematic study was carried out comparing ARCHIVA dyes, which are well known from previous physical-chemical studies,[2] with the original dyes of an EPSON 750 printer. A series of various nanoporous Al- and Si-oxides **(Table II)**, whose surface- and nanopore properties are well known,[3] was used.

These studies allowed us to investigate the influence of surface charge, pore volume, pore diameter and agglomerate size for metal oxides with different chemical compositions in coatings **(Table II)** on the light stability for concentrated and diluted (LD) dyes in inks (shown for EPSON 750, ATLAS 10 MLuxh in **Table III**).

An important conclusion was drawn from the variation of the **sign of surface charge** using two types of SiO_2 with similar porous properties, **Table II.** The sign of the surface charge and the zeta potentials were studied by **acoustophoresis. Figure 1** shows the pH-conditions under which the surface charge of SiO_2 is positively charged by surface modification with Aluminum-chlorohydrate ACH. As the isoelectric point is approximately at pH 9, the **positive** SiO_2 surface is obtained below this pH, typically at pH 4 in our experiments. **Negatively** charged SiO_2 was realized in these experiments by coating pure, surface unmodified SiO_2 (with an isoelectric point at pH 2.5) at pH 7.9.

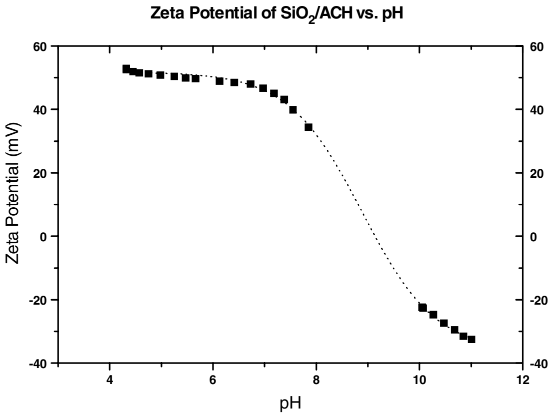

Figure 1.

Table II

Metal oxides	Surface charge (acoustophoresis)	Agglomerate size (nm) XDC, TEM, SEM, AFM	Pore volume BET (ml/g) in coatings	Mean pore diameter BET (nm) in coatings
La/X-Al-oxide (ILFORD)	POSITIVE	22.7	70	11.8
γ-AlOOH	POSITIVE	16.4	52	8.2
SiO_2	POSITIVE	45	118	26.6
SiO_2	NEGATIVE	50	135	32
γ-Al_2O_3	POSITIVE	47	84	28

The **negatively charged** SiO_2 is not water fast, although the surface charge density is similar to that of the positively charged SiO_2 under these pH-conditions. Strong dye diffusion in cyan and yellow falsifies density measurements after exposure to light. Magenta light stability in negatively charged SiO_2 is exceptionally low as compared with the positively charged SiO_2 surface **(Table III).** From spectral studies we conclude that this is mainly due the the lack of dye adsorption at negative pore walls due to the absence of COULOMB interactions between the positive surface charge and the negatively charged dyes. Dye aggregation was again shown to play no role for light stability in this case (spectra). The surface **charge density** in the case of positively charged SiO_2 and the method by which positive surface charge was brought to the SiO_2 surface (Al-chlorohydrate treatment or adsorbed cationic polymers) play both a minor role in light fastness. However, if Al- and Si-oxides with only **positive surface charge** are compared, the surface charge **density** plays an important role. This was derived from acoustophoretic measurements on our oxides and γ-AlOOH vs. pos. charged SiO_2 and γ-Al_2O_3. The highest positive surface charge density was measured on proprietary oxides which are new compounds obtained by rare earth insertion into Al-oxides,[3,6] La/X **(Table II)** being single Lanthanide ions or mixtures of them. As a consequence, dye adsorption and stabilisation at pore walls of our doped Al-oxides are optimum due to strong COULOMB interactions. Therefore, magenta light stability is higher than with any other oxide **(Tables I, III)**. It is interesting to notice that the light stability of SiO_2, which was positively charged by surface modification with Aluminum chlorohydrate, shows completely different features from AlOOH or γ-Al_2O_3 (Table III), although its surface contains Al-ions linked to oxygen atoms in the first monolayer above the SiO_2 core.

Table III

Oxides	C	C LD	M	M LD	Y	Y LD
γ-AlOOH	-47	-55	-24	-40	-3	+12
ILFORD oxides	-11	-26	-26	-28	-4	-7
SiO_2 pos	-15	-30	-43	-61	-24	-44
SiO_2 neg	Diffusion	Diffusion	-93	-74	Diffusion	Diffusion
γ-Al_2O_3	-10	-35	-20	-63	-2	0
ILFORD POLYMERS	*-20*	*-18*	*-22*	*-33*	*-11*	*-16*

Another important parameter, which is partially responsible for the higher light stability of magenta dyes in our nanoporous coatings, is the chemisorption of **reducing aliphatic hydroxi-acids** at internal surfaces,[7] leading to decreased dye oxidation. This effect is, however, only observed with γ-AlOOH and our own nanoporous oxides with much smaller pore volumes and pore diameters than SiO_2 and γ-Al_2O_3 (Table II). The larger contribution of internal pore-surfaces with smaller pore volumes favours higher surface concentrations of reducing acids at pore-walls. In the absence of these compounds, no **influence of pore-size and pore volume** on light-stability was observed with all oxides cited in Table II. This shows again that dye aggregation plays a minor role for lightfastness in nanoporous coatings, as larger aggregates would be possible in SiO_2 and γ-Al_2O_3 with higher pore volumes than γ-AlOOH and our rare-earth doped oxides (Table II). No spectral differences which could be in relation with dye aggregation were found for dyes adsorbed on these different metal oxides at the same coating pH. Another interesting subject which was studied on the oxides of Table II is the **catalytic fading** of magenta dyes,[2,8] ***triplet sensitized by cyan***. We have not observed catalytic fading in layers containing the oxides of table II, contrary to the case of the swelling polymer layers where strong catalytic fading was observed. Cyan dyes are strongly aggregated in polymers.[2] As dye aggregation decreases catalytic fading by decreasing the triplet quantum yield,[4] we cannot attribute the absence of catalytic fading in nanoporous materials to aggregation effects of the cyan dye. A possible explanation for the absence of catalytic fading in these nanoporous materials is the low probability for coadsorption of two very different dye molecules like magenta (azo dye) and cyan (Cu-phtalocyanine) within *the same nanopore with the same adsorption kinetics.* Therefore, the probability for encounter of these dyes within the same pore allowing electron transfer from excited cyan to magenta (and therefore catalytic fading) is very small. This is in agreement with the observation of some catalytic fading in Si-oxides containing very large pores and broad pore-size distributions. The influence of all discussed parameters on light stablity is very similar for EPSON 750 and for ARCHIVA inks. Experiments with a large number of different magenta dyes have shown that their light stability is much more dependent on the surface properties of nanoporous metal oxides than on the nature of the dye chromophores.

Based on spectral analysis and light stability measurements of a well known ARCHIVA magenta dye[2] on various nanoporous Al-oxides (Table II), we propose the tentative **mechanism** shown in Figure 2 for the photo-oxidation of ink-jet dyes in nanoporous Al-oxides.

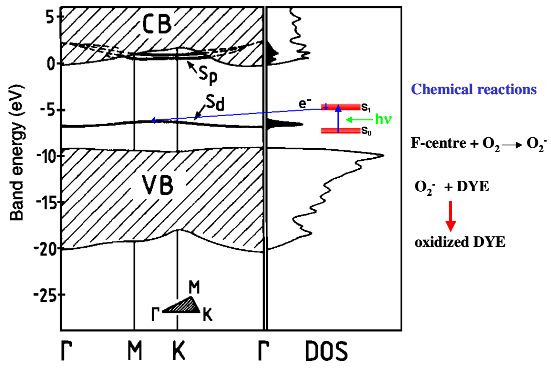
Photo-oxidation of dyes at Al-oxide surfaces

Figure 2

As the energy band structure of the ***surface*** of Al-oxides is only known[5] for γ-Al_2O_3, we base our mechanism on these data[5] assuming that AlOOH and γ-Al_2O_3 have similar surface defects (SCHOTTKY type). From MO-calculations UPS, XPS and HREELS, acceptor levels close to the valence band of γ-Al_2O_3 (Figure 2) have been identified[5] (S_d, **density of states DOS** shown on right side of band scheme). Since the action spectrum for dye photolysis was shown to correspond to the absorption spectrum of the magenta dye, our mechanism involves electron transfer from the excited dye to acceptor surface states in Al-oxides. Energy levels of azo dyes (s_0, $s_{1,}$ Figure 2) were estimated from our measurements of polarographic half-wave potentials and from absorption spectra of these dyes in the adsorbed state on AlOOH. Electron transfer probably occurs from the excited state (s_1) of the dyes to acceptor surface states (S_d) being close to the valence band. If oxygen vacancies are associated with such states as suggested[5], an F-centre (electron associated to an oxygen vacancy) is formed. From the photolysis of ZnO and TiO_2 it is known[5] that F-centres are able to produce **peroxide radicals** (**O_2^-**) by electron transfer to physisorbed oxygen at the metal oxide surface (**Figure 2**). By analogy, this strongly oxidizing peroxide radical could then also destroy the adsorbed dye at the pore surface of Al-oxides. **Figure 2** also shows that direct exposure of Al-oxides to light and subsequent electron transfer to these acceptor states (S_d) from the valence band is energetically not possible with red light near 680 nm (1.83 eV, cyan imaging dyes). As, however, cyan dyes are also photo-oxidized on Al-oxides, direct electron transfer to S_d can be excluded.

The proposed mechanism explains the **importance of chemisorbed reducing agents** being close to the reaction site between peroxide radicals and dyes, as realized in the case of hydroxy-aliphatic acids adsorbed at the pore walls of rare-earth doped Al-oxides.[7] The influence of **inserted rare-earth ions**[6] on light stability may be in relation with the higher polarisability of Lanthanide ions vs. Aluminum ions in addition to their increase of the surface charge density as discussed above. As our mechanism involves the presence of acceptor states (S_d) at the Al-oxide surface, additional space-charge effects due to Lanthanide ions could favourably influence the nature and/or the concentration of these surface states in Al oxides and therefore increase the light stability of imaging dyes in this way.

In all our experiments, photolytic effects have been observed with concentrated as well as with diluted inks. However, diluted inks were generally more strongly affected by light. This is due to decreased dye adsorption at pore walls from diluted dye solutions and not to decreased dye aggregation in nanoporous materials (spectral studies).

Gas Fading In Nanoporous Media

Four different nanoporous materials were investigated. These are based on stabilized or unstabilized rare-earth doped Al-oxides and on positively charged, stabilized or unstabilized SiO_2. Stabilization against gas-fading was obtained by adding reducing agents. An EPSON 750 printer using concentrated and diluted dyes was used for imaging.

Gas-fading experiments were carried out in a specially designed apparatus allowing for controlled environment, humidity and temperature. Humidity as a carrier of environmental gases into nanopores was shown to be important. All investigated ink-jet dyes are destroyed by ***oxidation.*** Therefore, reducing compounds added to these media were the most powerful protecting agents against gas-fading. However, these protecting agents are rapidly used up by oxidizing environmental gases being in large excess. Gas-fading always preceedes photo-oxidation and is therefore rate-determining for the overall stability of nanoporous media. No influence of exposure to light on gas-fading has been observed. Gas-fading effects were similar on unprotected SiO_2, AlOOH, our own Al-oxides and γ-Al_2O_3 . Negligible gas-fading occurs on polymeric media. Therefore, this phenomenon seems to be linked to the strong chromatographic behaviour of nanoporous metal oxide particles.

Conclusions

Our experiments have shown that ***gas-fading is rate-determining for the overall stability of ink-jet dyes in nanoporous media***. Some protection against gas-fading was observed by using certain reducing agents coated in nanoporous media. However, their protecting action is limited by the fact that they are rapidly used up due to oxidation by environmental gases which are always present in a large excess with respect to the dyes in nanopores.

The **light stability** of ARCHIVA and EPSON ink-jet dyes in our nanoporous media was shown to be as good as that in our best experimental polymer coatings ***after full protection against gas-fading.***

Acknowledgments

We thank Dr. Jean-Nicolas Aebischer for scientific support , and D.Martinez, G. Liechti, B. Wenger, R. Weber and W. Knupp for careful experimental work.

References

1. H.J. Nolte, Ph.D. Thesis, University of Marburg (Germany, 1973)
2. R. Steiger and P.A. Brugger, *Proc. of NIP 14*, Toronto (1998)
3. P.A. Brugger et al., Preprints of this Conference
4. To Ngai et al., *Langmuir* 2001, **17,** 1381
5. V.E. Henrich and P.A. Cox "The Surface Science of Metal Oxides", Cambridge University Press (1994)
6. US Patent 6,156,419
7. EU Patent 0 967 086 B1
8. M. Fryberg and R. Hofmann, *Proceedings of NIP 16*, Vancouver (2000)

Biography

Rolf Steiger received his Ph.D. in physical chemistry from the University of Neuchâtel (Switzerland). In 1967/68 he was a postdoctoral fellow in surface science at the LAWRENCE Berkeley National Laboratory. From 1968 to 1981 he worked on organized molecular systems, photochemistry and surface science applied to Photography at CIBA-Geigy Central Research Laboratories, and joined ILFORD in 1982. He teaches surface chemistry and molecular engineering as an Associate Professor at the University of Neuchâtel.