Nanoporous Photorealistic Materials for InkJet

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Abstract

Recently, microporous inkjet materials have attracted considerable interest because of image quality and instant drying features as required by modern fast inkjet printers. The technology and characterization methods behind the design of the new generation of ILFORD's nanoporous photopaper will be addressed. Proprietary patented technology of nanosized rare earth modified metal oxide particles were developed and coated into layers by photographic multilayer coating technology. Transparent layers, due to tailored oxide particles having a size distribution in the 20-nanometer range, lead to outstanding color quality and color rendition. Nanopores initiate immediate ink absorption. Excellent dye fixation is achieved thanks to controlled chemical modification of the nanopore surface charge distribution.

Evidences of the structural changes caused by the insertion of Lanthanum into Aluminium oxide/hydroxide could be proven with the most modern analytical techniques. We can conclude that La-doped Aluminium oxide/hydroxide is significantly different from the undoped Aluminium oxide/hydroxide precursor material.[1, 2]

Introduction

It has been shown[1] (Engels et al.) that certain rare-earth ions incorporated into the lattice of Al-oxides lead to a considerable increase of their specific surface area.

This increase is particularly high if ions with large ion radii as La^{3+} (0.103 nm) or Ce^{3+} (0.101 nm) are used for insertion.

In order to see whether such rare-earth doped Al-oxides lead to enhanced ink-absorptivity due their higher internal surfaces, we have synthesized and introduced them into coatings for inkjet media.[2]

Physical-chemical and structural characterization of these new compounds was carried out by different methods (table I). After coating, we have observed the following advantages of rare-earth doped Al-oxide/hydroxide vs. undoped boehmite (χ-AlOOH): nanocrystalline dispersions from powders leading to higher metal-oxide concentrations in coating solutions, better imaging quality (coalescence, dye bleed), higher light stability and water-fastness.

Experimental

Modifications of Aluminium oxide/hydroxide with one or more elements of the rare earth metal series (atomic number 57 to 71) may be prepared by a similar method as described in[1]. In another preparation method Aluminium oxide/ hydroxide is mixed in aqueous solution at 90°C with a solution of a salt of the rare earth metal, stirred for 120 minutes, filtered, washed 3 times with deionised water and dried at 110°C.

Recording sheets of the various modified powder dispersions with PVOH were coated on transparent polyester, printed with an inkjet printer Epson Stylus Color 500.

Image quality was evaluated through the visual inspection of a stepped wedge test image having 77 fields (Y, M, C, B, G, R, K, each color having 11 density fields between 5% and 100% ink loading). After printing the number of fields showing coalescence were counted on a light box. Large numbers indicate a poorer image quality, with inhomogeneous fields and poor ink absorption.

Color-to-color bleed was judged on full density boundary of blue-yellow, green-magenta and red-cyan full density patches. An arbitrary scale was applied, from 1 (extremely high color-to-color bleed) to 5 (no color-to-color dye bleeding).

Analysis Applied to Rare Earth Doped Aluminium Oxide/Hydroxide

Rietveld Analysis of XRD Data

The Rietveld method is a very powerful tool to see differences in crystal/lattice differences.

When doping aluminium oxide/hydroxide with Lanthanum, it replaces statistically aluminum sites in the crystal lattice of aluminium oxide/hydroxide, if the Lanthanum is inserted into the crystal lattice. Lanthanum with atomic number of 57 - compared with 13 of Al has a larger crystal ionic radius and contains about 4 times more electrons. The La-doped aluminium oxide/hydroxide shows an increase of the crystal unit cell compared to undoped aluminium oxide/hydroxide.

If the population parameter of the aluminum for refinement in the La-doped data is freed, the result shows, that we have better agreement between calculated and observed diffraction with higher electron density at the position of Al.

Table I: Methods of Physical-chemical and structural characterisation applied to rare- earth doped Aluminium oxide /hydroxide powder

Method of investigation	Type of information obtained
X-ray Fluorescence Spectroscopy	detection and quantification of rare-earth elements
Temperature dependence of high-resolution RAMAN peaks	Different transition temperature behaviour of doped Al-oxide
RIETVELD analysis of XRD data	Crystallographic unit cell and structure different after rare-earth doping
High-temperature XRD	different thermal stability and transition temperature into Al_2O_3
SANS (Small Angle Neutron Scattering)	Changes of Q^{-n} dependence of intensity for high momentum transfer Q for doped and undoped
Acoustophoresis	Higher zeta potential after doping
BET	Higher pore volume and specific surface after doping

Note: Due to their sensitivity most of these methods must be applied on the powder, without additives and before coating.

This gives evidence to the structural changes caused by the insertion of La into aluminium oxide/hydroxide lattice, and that it is different from non-doped material. These findings are complementing the observed changes seen with other methods like BET or SANS (see table I).

Small Angle Neutron Scattering

SANS (Small Angle Neutron Scattering) as a nondestructive method allows to investigate inhomogeneities in solids or liquids, whereas inhomogeneities can be e.g. a different phase or as a special case a pore. Porod plots (ln I (Intensity) vs. ln Q (Momentum Transfer)) classify -by shape and gradient of the curve- the investigated specimen. The shape of the plot gives information of the porous nature and dispersivity of the pores within the sample. Differences of the Q^{-n} dependance of the slope are an immediate indication to structural differences, and significant different Q^{-n} dependancies are observed for La-doped and undoped aluminium oxide/hydroxide.

Experimental Results with Different Dopings

La, Ce, Pr, Nd and Yb as trivalent rare-earth ions were tested at the same molar concentration vs. Al_2O_3 (2.2 mol%). Table II shows that the imaging quality, i.e., homogeneity (speckle, coalescence) as well as dye bleeding is improved by doping.

If other doping ions than rare earths with similar ionic radius (r) or similar charge (q) were compared at the same concentrations, the imaging quality was not improved (Table III). These ions were chosen such that the ratio q/r was varied within large limits between very low values (Cs) and high values (Sn). It is also seen that the imaging quality does not depend on the ratio q/r, as Au has almost the same value of q/r as Yb, and Mg is similar to Nd. Therefore, the incorporation of these ions does not have the same consequence for inkjet media as that of rare-earth ions.

Table II: Influence of rare-earth dopants on imaging quality

Ions	*Ionic radius (nm)*	*Charge /radius (q/nm)*	*Image Quality*	*Color Bleed*
None	---	---	14	4
La^{3+}	0.103	29.126	5	5
Ce^{3+}	0.101	29.703	8	5
Nd^{3+}	0.100	30.000	9	4
Pr^{3+}	0.101	29.703	9	4
Yb^{3+}	0.086	34.884	7	5

Table III: Comparison with other metal ions

Ions	*Ionic radius (nm)*	*Charge /radius (q/nm)*	*Image Quality*	*Color Bleed*
None	---	---	14	4
Li^{+}	0.068	14.706	19	4
Ba^{2+}	0.134	14.925	22	4
Sr^{2+}	0.112	17.857	27	3
Ti^{4+}	0.068	58.824	15	5
Sn^{4+}	0.050	80.000	14	4
Au^{3+}	0.085	35.294	39	3
Cs^{+}	0.167	5.988	39	2
Mg^{2+}	0.066	30.303	18	4

Table IV: Level of Lanthanum rare-earth dopants on imaging quality

Ions	*Counter ion*	*Level (mole %)*	*Image Quality*	*Color Bleed*
None	-	0	14	4
La^{3+}	Cl^{-}	0.21	13	4
La^{3+}	Cl^{-}	0.66	13	5
La^{3+}	Cl^{-}	1.12	5	5
La^{3+}	Cl^{-}	2.20	5	5
La^{3+}	Cl^{-}	2.66	9	4
La^{3+}	Cl^{-}	3.32	10	3
La^{3+}	NO_3^{-}	2.20	5	5

Table IV shows that the molar concentration of La^{3+} vs. Al_2O_3 is very important for the imaging quality. An optimum is found at ca. 1 - 2.5 mol%. This table also shows that the anion (chloride, nitrate) and also acetate (not shown here) is of no importance for the imaging quality.

Aliphatic Hydroxy Acids at Hydrolysis

Optimum dispersions for coating solutions for these doped Al-oxides are obtained by using aliphatic hydroxy monocarboxylic acids for surface stabilization.[4] The acid molecules are chemisorbed on the surface (shown by infrared spectroscopy and microcalorimetry), and by building up a steric barrier the particles are stabilized in such dispersions against flocculation or sedimentation. Calculations using standard DLVO-theory confirmed experimental rheological results, which show that at least a barrier thickness of 0.5 nm has to be obtained in order to receive stable dispersions [similar results on γ-Al_2O_3 see [3]]. The powder hydrolysis is made in presence of lactic acid, which has the advantage to further stabilize the surface of the nanosized particles.[4]

Conclusions

Experiments have shown that the insertion of rare-earth ions into Aluminum oxides leads to considerable improvements in the performance of inkjet media containing these new compounds as nanoparticles. The observed increase of the pore volume[5] and the specific surface area leads to better imaging quality (speckle, coalescence, dye bleeding). As discussed in another paper,[5] doped Al-oxides also show increased light stability, which may be in relation with the higher positive surface charge density[5] observed by acoustophoresis. Analytical experiments have shown that the structure of these new compounds is significantly different from that of the undoped Al-oxide precursors.

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Biography

Pierre-A. Brugger received his Ph.D. in Physical Chemistry at the Swiss Federal Institute of Technology in 1982. He joined the IBM Research San José, California, as a Postdoctoral fellow, working on optical memory. In 1984 he collaborated at the Lab of Ceramic Powder of EPFL in the field of Ti-Al oxide. He joined Ilford in 1985 as a silver halide chemist, and since 1995 he worked on polymeric, microporous or composite multilayer inkjet media design.