Chitosan for Dye Fixation of Highly Lightfast Gelatine Coatings

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Abstract

Fixation of the ink is one of the important factors determining the quality of inkjet media for photo glossy applications as well as for mat inkjet paper. In our previous paper, presented at the NIP 19, we have shown that depending on the IEP (number of acidic and basic groups) of gelatine and the pH of the coating formulation, some dye fixation can be achieved by gelatine itself. To further improve dye fixation quaternary amines, like poly-DADMACs, are very often used. Unfortunately, besides affecting the image quality, these compounds reduce the lightfastness of the prints. GELITA has now tested various chitosan types as dye fixing agents. We tested the compatibility of these compounds to different gelatine types. These mixtures show substantial differences in viscosity. Some low viscosity formulations, which are suitable for coating, have been identified. Coatings on polyethylene base paper have been prepared with these gelatine/chitosan mixtures. The coatings show excellent dye fixation and give good image qualities and dry time. We tested the lightfastness of these papers and compared them to gelatine coated papers containing other dye fixing agents. Here we found a much better stabilization of the dyes by the gelatine/chitosan formulations. Therefore chitosan as an additive for gelatine coatings improves dye fixation of the coating and keeps the lightfastness of the image at the high level observed for pure gelatine coatings. A patent application about these findings has been recently filed.

Introduction

Gelatine is indispensable for photos based on AgX technology. The quality of these 'classical' photos and their lightfastness are the benchmark for digital photos printed by inkjet technology. To obtain high quality print outs with an inkjet printer the performance of the printer as well as the media have to be excellent and well adjusted. If we look at the interaction between media and ink many different parameters have to be considered. Dry time of the ink on the media has to be fast: Prints should be dry, when coming out of the printer. Intensive colors with high color density are requested, resulting in brilliant and lively pictures. The prints have to show a high resolution of the detailed structures. From classical photos the customers appreciate as well a certain photo feel and of course the high gloss of the photo.

In the course of time lightfastness of the prints gained more and more importance. This is understandable as photos should not last only a few months and then fade away. The customer wants to preserve the pictures and expects to see the same brilliant colors, from the time the photo was printed, after years.

Dye fixation has become another major topic and is discussed extensively in the moment.[1,2] Drops of rain or spillage of water should not immediately result in blurring of the colors and destruction of the image. Good dye fixation will also prevent migration of the dyes under conditions of high humidity.

Swellable versus Porous Media

To solve these problems two systems compete. Porous media with a high pigment to binder ratio take up the ink by capillary action. Sophisticated systems with highly porous silica and high coating weights have been set up. These systems take up the ink very fast, but often show less gloss and poor color density. Gelatine coatings, as the most prominent representative for swellable media, take up the fluid by swelling, which is not as fast as capillary action. Gelatine coatings provide a highly glossy surface and a very high color density. One of the major advantages of gelatine is the high lightfastness of images printed on these papers. As in classical photography gelatine is the benchmark for high lightfastness of inkjet prints nowadays. As gelatine is a polyelectrolyte the cationic charged groups are able to fix the anionic dyes of the ink to some extent. This dye fixation can be improved by preparing the coating at low pH. Data on these investigations were presented at NIP 19 last year.[3] Nevertheless to further improve the dye fixation polycationic substances like poly-DADMACs are very often added to the coating solution. Unfortunately these additives, which mostly are polyamines have a negative effect on light stability of the dyes. The amine structure probably acts as a catalyst for oxidative damage of the organic dyes.

For porous media lightfastness is a very big problem in general. This is due to the highly open pore structure, which makes a much better access of air (oxygen and pollutants) possible. The dyes of the ink can be easily attacked and destroyed. Poly-DADMACs make these problems even worse.

Chitosan a Natural Polymer

To improve the performance of gelatine coatings we were looking for a substance, which is able to improve the dye fixation of gelatine coatings without affecting the high lightfastness of prints on gelatine coatings. One of the substances we tested in our lab was chitosan.

Chitosan is a biopolymer derived from chitin, the major component of the exoskeleton of insects. It is generally obtained from crustaceans e.g. crab. By treatment with NaOH chitin is deacetylated to chitosan. See Figure 1. By this procedure different types of chitosan with different viscosity and varying degree of deacetylation can be obtained.[4]

Chemically spoken chitosan is a poly-(β-(1,4)-D-glucosamine). The deacetylated chitin has improved solubility in water. Solubility is good at pH ≤ 5. This is due to the high number of amino functions, which are protonated at low pH-values.

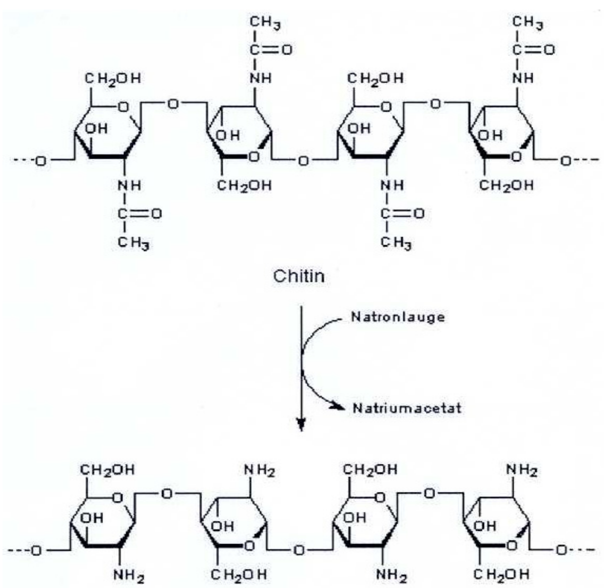

Figure 1. Deacetylation of chitin to chitosan by treatment with NaOH.

Chitosan for Dye Fixation

We expected that, due to the high number of cationic groups, chitosan is an excellent material for dye fixation. Therefore the compatibility of different chitosan types to various gelatines has been investigated.[5] Finally, a few types of gelatine and chitosan have been identified, which have a viscosity suitable for coating on paper. In this paper we focus on a special gelatine type and a chitosan type which show good compatibility and we found suitable for inkjet applications. Mixtures of these two polymer types were coated on paper. The performance of the paper, the quality of the print outs on various office printers and the fixation of the dyes have been checked. We also tested the lightfastness of the prints.

Experimental

For the coatings we prepared in the laboratory we used polyethylene paper as a base. The paper was coated with an Erichsen Coatmaster MC-III with a 120 µm rod. Drying was performed at about T = 80°C.

For the light stability tests a SUNTEST XLS+ apparatus (ATLAS) was used. Due to the fact that with this instrument the humidity and the temperature cannot be controlled, only relative tests, comparing prints, which were tested in the apparatus at the same time, were performed.

For the irradiation experiments areas (4 cm x 2,5 cm) of cyan, magenta, yellow and black were printed on the papers to be tested. As printers HP DeskJet 970Cxi, CANON S800 and EPSON STYLUS PHOTO 870 (office printers) were used. The inks we used were the ones recommended by the printer manufacturers. Half of every printed area was covered and then placed in the SUNTEST XLS+. The prints were exposed to filtered Xenon light simulating conditions behind 3 mm window glass with an constant irradiance of 710 W/m^2. The differences between covered areas and those exposed to the light source were evaluated by measuring ΔE* values of the primary colors with a MINOLTA CHROMA-METER CR 300.

Dye Fixation was determined in the following way: Three stripes in green, blue and black (15 mm x 48 mm each) were printed by the above mentioned office printers. The prints were left for drying under ambient conditions for 24 h and then half of each stripe was immersed in water at room temperature for 10 minutes. Afterwards the stripes were dried. The difference between the two parts of each stripe was evaluated by measuring ΔE* values of the colors with a MINOLTA CHROMA-METER CR 300.

Image quality was tested by printing out a test image on the coated papers with the three office printers mentioned above. Tackiness, bleeding, beading, banding, bronzing wicking and feathering of the print were evaluated.

Results and Discussion

We have checked various gelatine/chitosan mixtures. Coatings in the range of 1% to 20% (w/w) chitosan have been prepared. The total concentration of solids of the aqueous coating solutions was about 16% (w/w). As benchmark EPSON Premium Photo Glossy Paper (indicated as Coating EP) and a gelatine paper containing Certrex, which is a commercially available poly-DADMAC (indicated as Coating DAD) were used.

Four different coatings with increasing amount of chitosan have been prepared:

Coating 1: gelatine containing 2% (w/w) of chitosan
Coating 2: gelatine containing 3% (w/w) of chitosan
Coating 3: gelatine containing 6% (w/w) of chitosan
Coating 4: gelatine containing 17% (w/w) of chitosan
Coating DAD: gelatine containing 17% (w/w) of Certrex

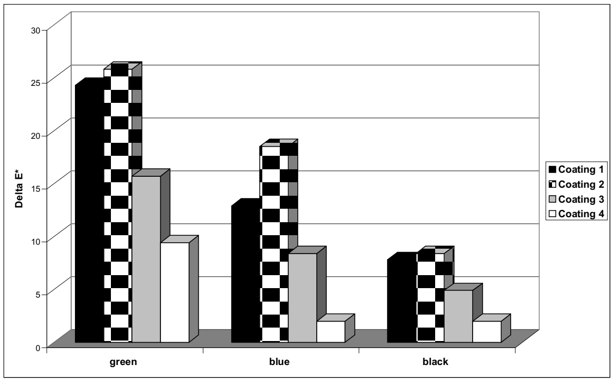

Figure 2a. ΔE values of the dye fixation test for HP inks.*

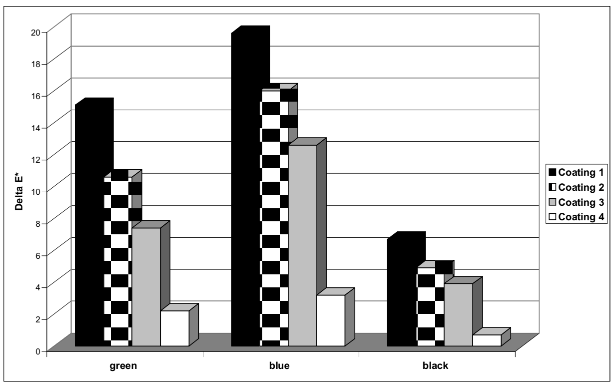

Figure 2b. ΔE values of the dye fixation test for Canon inks.*

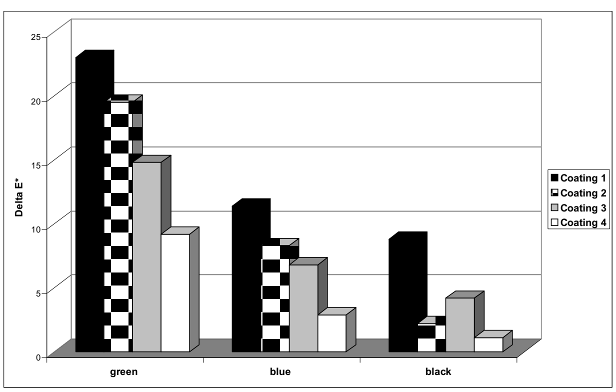

Figure 2c. ΔE values of the dye fixation test for Epson inks.*

The results of the dye fixation test for three office printers are shown in Figures 2a to 2c.

If we compare these results, it is obvious that as expected dye fixation is improved with increasing concentration of chitosan.

In the next step we checked the print quality and the dry time of the prints. For Coatings 1 - 3 virtually no difference in dry time and image quality could be observed compared to the high quality print outs on a pure gelatine coating. For coating 4 stronger beading, resulting in a decrease in image quality, was observed. Dry time of the inks was longer.

We therefore focussed on coating 3 with a chitosan content of 6% by weight.

A comparison of the dye fixation of this coating with a commercial Epson paper and a gelatine paper with high amount of poly-DADMAC (Certrex) revealed, that the chitosan paper nearly does reach the dye fixation of the Epson paper and mostly shows a better performance than the poly-DADMAC paper. See Figures 3a to 3c.

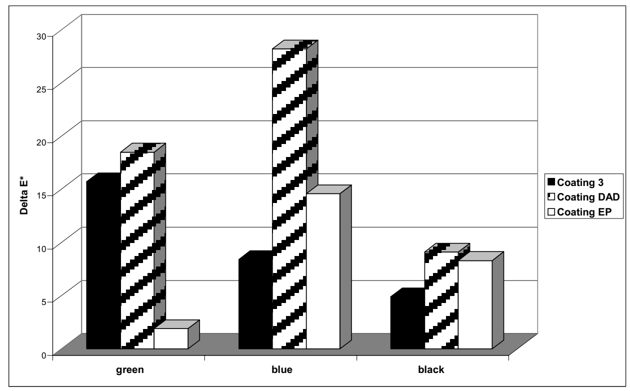

Figure 3a. ΔE values of benchmarking of dye fixation for HP inks.*

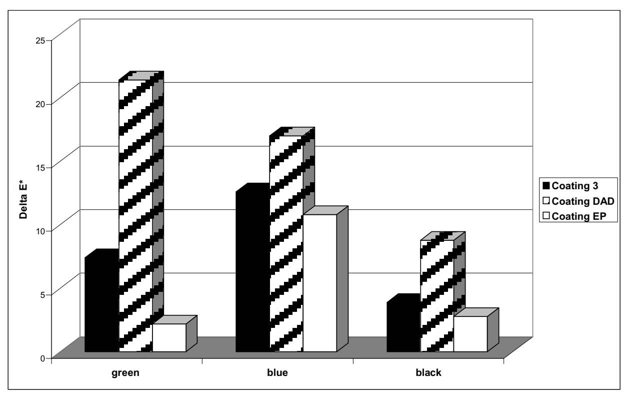

Figure 3b. ΔE values of benchmarking of dye fixation for Canon inks.*

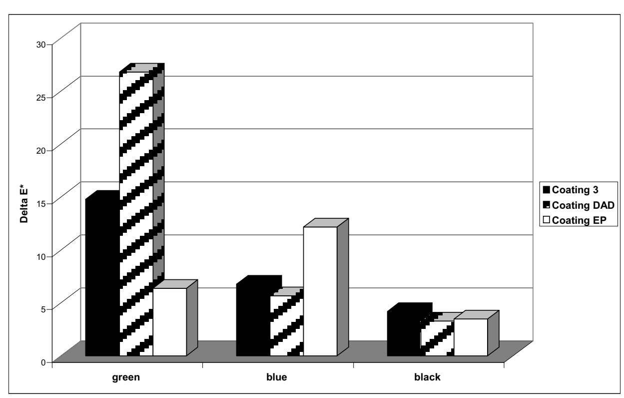

Figure 3c. ΔE values of benchmarking of dye fixation for Epson inks.*

From these results it can be concluded, that papers containing a concentration of 6% chitosan or more have the same or better dye fixation than the benchmark papers.

We have also conducted light stability tests with these papers. To our surprise the light stability of the chitosan paper was much better than for the papers we tested as benchmark for dye fixation (Coating EP and DAD). ΔE* values are comparable to a pure gelatine coating we prepared (indicated as GEL Coating).

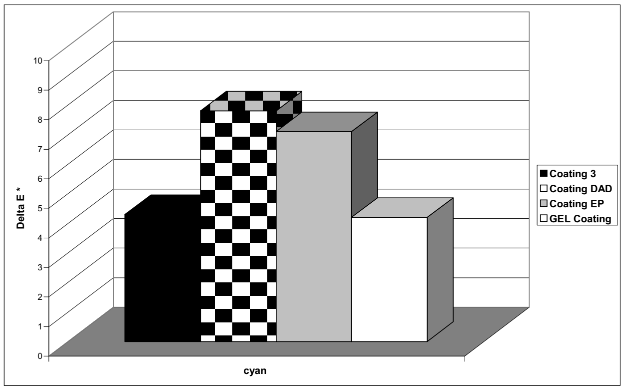

Figure 4a. ΔE values of light stability test of cyan ink for various coatings.*

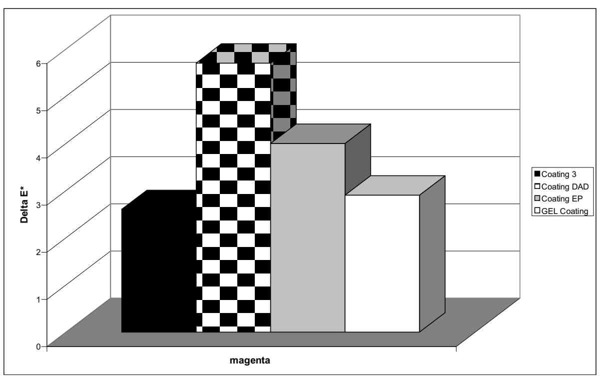

Figure 4b. ΔE values of light stability test of magenta ink for various coatings.*

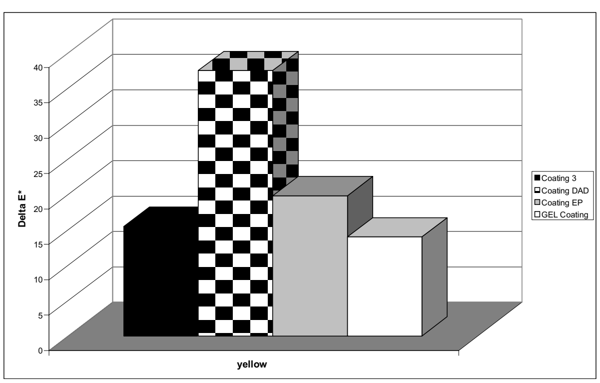

Figure 4c. ΔE values of light stability test of yellow ink for various coatings.*

Figures 4a to 4c show the results of the light stability tests for Canon inks after 24 hours of irradiation. The ΔE* values for the black ink of the various coatings are only small and no major differences could be observed between the coatings we compared. Therefore no diagram of the light stability test is presented for that color in this paper.

We also performed light stability tests for the inks of the two other office printers. The same general trend was observed. Light stability of Coating 3 is better than for the Epson paper and Coating DAD. The values are in the range of a pure gelatine coating as well.

Conclusion

We have tested gelatine coatings on polyethylene base paper containing increasing amounts of chitosan. A clear dependence of chitosan concentration and dye fixation could be detected for all ink types tested. The higher the amount of chitosan used, the better the dye fixation.

Image quality and dry time was not effected by chitosan addition up to a concentration of 6% by weight. At this concentration the dye fixation was comparable to a commercial high end porous paper and better than a gelatine coating containing 17% poly-DADMAC. Light stability tests revealed, that with a concentration of 6% chitosan in the gelatine coating the high preservation of the dyes by gelatin is not affected.

Therefore chitosan as an additive for glossy gelatine coatings can be used to improve the dye fixation without affecting the lightfastness of the dyes. The lightfastness is kept at the same high level, which we know from pure gelatine coatings. As this is a major step forward to improve the performance of gelatine coatings, all these findings have been covered by a patent application.

We assume, that the reason for this unexpected behavior of the coating formulations is related to the film forming properties of chitosan; but so far we have no evidence to proof this.

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Biography

Berthold Köhler studied Chemistry at the University of Karlsruhe (Germany). He received his PhD in Chemistry at Prof. János Rétey, Chair of Biochemistry, Department of Organic Chemistry, University of Karlsruhe in 1997. Since October 1999 he is member of the R & D Department of DGF STOESS AG in Eberbach, Germany. His main research interests are ink jet applications, chemical and enzymatic modification of gelatine. e-mail: berthold.koehler@ dgfstoess.com