Gelatine and Dye Fixation

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Abstract

The design of a receptive coating for ink jet printing is highly demanding. Many parameters concerning quality of the print, dry time of the ink and light stability have to be taken into account. Most of the parameters are not independent, but influence each other. One of these important factors is dye fixation. Ingredients, which improve dye fixation often affect light stability and image quality as well. The dye fixation of pure gelatine coatings for ink jet purposes has been investigated. We measured dye fixation of different gelatine types. Acid processed and alkaline processed as well as a chemically modified type have been compared in a standard test. Remarkable differences have been observed. Dye fixation for the acid processed type is much better than for the two other gelatine types, which we have investigated. We also detected a dependence of dye fixation on the pH of the coating solution. Regarding this parameter dye fixation is better for pH 5 than for pH 8. These results have been assigned to the different IEP of the various types. The dye fixation has been compared to a commercially available, high quality, non gelatine ink jet paper. It was found that dye fixing ability of the acid processed type is in the same range than for the commercial paper.

Introduction

The market for ink jet applications is rapidly developing. Several applications do exist with very diverse demands on the performance of the paper. There are office applications, where the paper is used for standard print outs or drafts. A higher quality is requested for presentations of data on a hard copy. For all these applications a good quality print out with instant drying of the inks is most important. The market for photo glossy papers is somewhat different. In that segment conventional photos are the benchmark. The consumer wants to have the photo feel, when he touches the paper, high resolution and lively colors with high color density are a must. For photos the durability of the pictures is very important.

For photo applications two systems are competing. One is a porous type with silica (nano) particles and only a small amount of binder e.g. polyvinyl alcohol. The major advantage of these systems is an instantly dry print out.

Alternatively pure binder systems are used. The uptake of water by these systems is based on swelling. For these papers gelatine is predominantly used. The results are long lasting, brilliant colors with a high gloss.

Dye Fixation and Water Resistance

For both media types water resistance is a major challenge. Pictures should be stable when touched with wet fingers or got wet by drops of rain or even when water is spilled over the image. These problems are commonly overcome by addition of small quantities of quaternary amines (poly-DADMAC).[1] The mechanism behind this is ionic interaction of the positively charged poly-DADMAC and the anionic charged side groups of the dye molecules. This fixes the dyes very well, but unfortunately these compounds are affecting light stability of the print. We suppose that the amines are susceptible to oxidation by oxygen and therefore act as a catalyst for oxidative damage of the dyes. Gelatine itself is in contrast to polyvinyl alcohol a polyelectrolyte. This makes dye fixation easier than for porous systems, which are often anionic as negatively charged silica is used. Gelatine as a protein does bear differently charged amino acids. Lysine and Arginine carry positively charged side groups, where as the amount of negative charges (carboxylates) differs very much dependent on the production process, i.e. acidic or alkaline treatment of the raw material. The net charge of the protein strands can be deduced from their IEP.[2] Proteins are positively charged in an aqueous media with a pH below their IEP and have an anionic character in water with a pH higher than their IEP. Taking this into account, we wanted to check to which extent it is possible to influence dye fixing ability of the coating by choosing different gelatine types with different IEP and different pH of the medium.

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. The solid content of the coating solution was about 15%. Drying was performed at about T = 80°C and 50% rel. humidity (climatic test chamber).

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.

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.

Isoelectric focusing was performed by a Multiphor II System (Amersham Biosciences) on a Mini Clean Gel IEF (ETC).

Results and Discussion

To check the validity of our assumptions three very different types of gelatine have be chosen with different isoelectric points. GELITA® Imagel BP 150, a low Bloom bone gelatine, basic processed, GELITA® Imagel AP, a high Bloom pig skin gelatine, acid processed and GELITA® Imagel MS, a chemically modified gelatine. All three types are frequently used ink jet types. We first checked the isoelectric point of these gelatines by isoelectric focusing. The results of the experiment are shown in Figure 1.

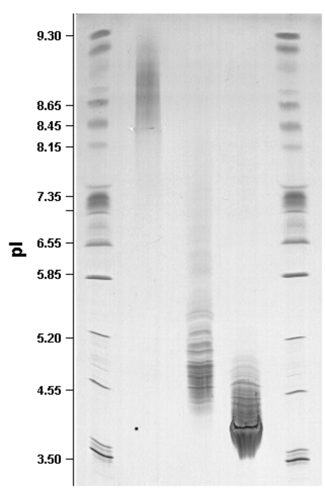

Figure 1. IEF gel of the three chosen gelatines: lane1 and 5 are marker proteins; lane 2 GELITA® Imagel AP; lane 3 GELITA® Imagel BP 150; lane 4 GELITA® Imagel MS.

Lane 1 and 5 show marker proteins, which indicate the pI at that position. In correspondence to the manufacturing process the IEP of GELITA® Imagel AP is around 8 and the IEP of GELITA® Imagel BP 150 is about 5. The IEP of GELITA® Imagel MS is even lower as this gelatine bears much more carboxylic groups and less amino groups according to the chemical modification it went through. As stated above these gelatines have different behavior dependent on the pH value of the environment and also should have different dye fixing ability. To proof this pure GELITA® Imagel AP, GELITA® Imagel BP 150 and GELITA® Imagel MS were coated on polyethylene paper with the coating solution having a pH of 5 or 8. The coated papers were checked for their dye fixation on three different office printers in the testing procedure described above. The results of the experiments are shown in Figure 2 a, b and c.

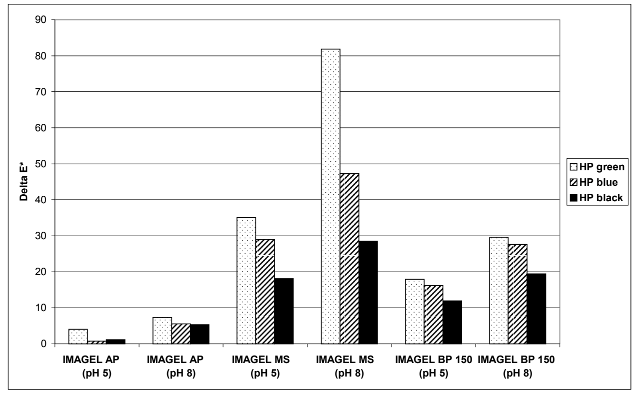

Figure 2a. ΔE values for various gelatines and HP dyes.*

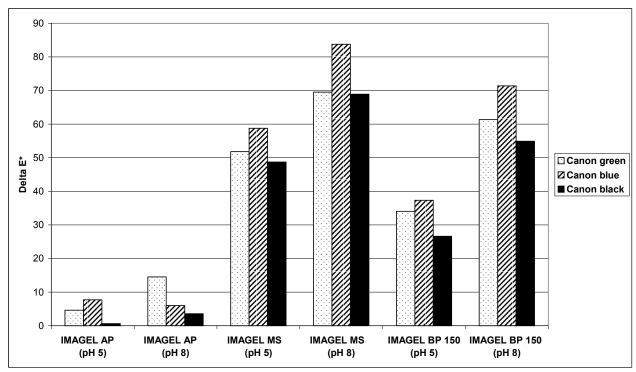

Figure 2b. ΔE values for various gelatines and Canon dyes.*

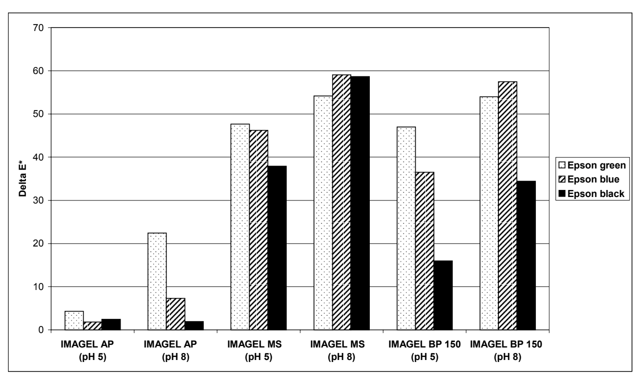

Figure 2c. ΔE values for various gelatines and Epson dyes.*

Regarding the pH dependence we see the same trend for all three printers. Dye fixation at pH 8 is worse than for pH 5. Although we have to keep in mind that for GELITA® Imagel AP the "starting position" is completely different compared to the other two types. For GELITA® Imagel MS and BP 150 pH of 8 results in a negative charge on the protein GELITA® Imagel AP does carry almost no net charge at that pH, but is cationic at pH 5, where the two others are nearly neutral.

Differences between the two different pH levels of the same gelatine are small, but the differences in the type of gelatine used are remarkable. Dye fixation of GELITA® Imagel BP 150 is better than for GELITA® Imagel MS. By far the best results were obtained from GELITA® Imagel AP.

Encouraged by these results we compared the GELITA® Imagel AP coating with a high quality, non gelatine, commercial ink jet paper. The ΔE* values for all three test printers are of the same magnitude. For the HP printer ΔE* values are even better for the pure gelatine coating than for the optimized commercial paper. See Figure 3.

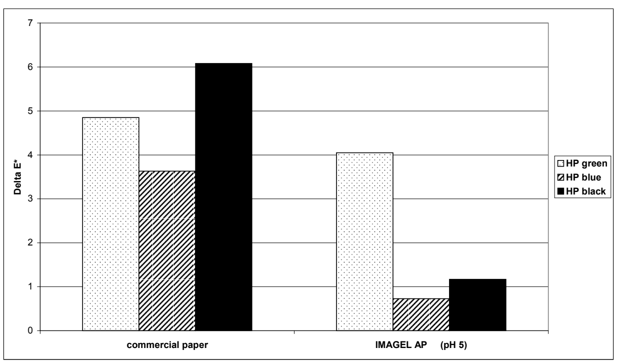

Figure 3. Comparison of ΔE values for GELITA® Imagel AP coating and a high quality commercial paper.*

Conclusion

We found great differences between certain gelatines depending on their IEP. GELITA® Imagel AP the gelatine with the highest IEP gave the best dye fixation. Dye fixation by GELITA® Imagel BP 150 is better than for GELITA® Imagel MS. This can also be explained by differences in IEP. The assumed pH dependence of the dye fixation could be detected, but the influence of this effect is not as strong as the one of the differences in the IEP of the chosen gelatine types themselves. We assigned this to the great difference in the number of binding sites (for the dyes) of the different gelatine types. The influence of the molecular weight of the different gelatines and the viscosity on dye fixation is not yet clear and is currently under investigation. Nevertheless it is remarkable that a pure gelatine coating, with high light stability can reach the same high dye fixation as a high quality commercial ink jet paper.

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References

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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 GELITA Europe in Eberbach, Germany. His main research interests at GELITA are ink jet applications and chemical modification of gelatine.

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