

# Allessan<sup>®</sup> APT – A versatile additive for paper treatment

Tanja Schaffer, Peter Koch (AllessaChemie GmbH, Frankfurt am Main, Germany)

## Abstract

*The usage of specifically coated paper can overcome some limitations of the common inkjet technology. However, even these special papers could not improve the limited water resistance of the inkjet images, so inkjet images still show disadvantages which limit their usage in the high-performance fields of application.*

*The special polymer “Allessan<sup>®</sup> APT” which is commercially available in large scale for the production of highly sophisticated inkjet paper can overcome these limitations.*

*Allessan<sup>®</sup> APT, the new additive for paper treatment can be applied on paper via a separate coating step or can be added directly in the size-press. Allessan<sup>®</sup> APT is an easy to handle aqueous solution.*

*The compound has the effect that the color is retained near the surface and the liquid ink carrier is bound on the paper, preventing colors from streaking or fading during the printing process, and even when exposed to water. The material can decrease the ink-drying times and increase the color density to obtain brighter, more vibrant colors.*

*The combination of special papers treated with Allessan<sup>®</sup> APT and the inkjet technology based on water-soluble printing inks can lead to new opportunities and new application fields of inkjet application and can increase the future potential of the inkjet technology.*

## Introduction

### *The potential of inkjet technology*

Inkjet printers are the most common type of printing devices which are used in home environments, and they are also widely used as printers in offices. The main advantage of this kind of printing is the good ratio between image quality and purchase price of the devices. Today's inkjet printers show a very impressive image quality that equals or even exceeds the traditional photographic film. Best results can be obtained when tailor-made systems of printing devices and special inkjet media are used. The market for inkjet printers has grown at a tremendous rate in the last few years, which means that the market for inkjet materials also increased quite strongly.

### *Limitations of inkjet technology*

Inkjet is a dot-matrix printing technology in which droplets of ink are jetted from a small aperture directly onto a specified position on a media (in most cases paper) to create an image. The printing resolution is mainly determined by the geometry of the printing head and the volume of the ejected ink drops. The most common inkjet devices are running with water-based inks. The ejection of water-based ink is controlled at the nozzle by the

growth and collapse of a water vapor bubble on the top surface of a small heater located near the nozzle. With a current heating pulse of less than a few microseconds, heat is transferred from the surface of the heater to the ink. The ink becomes superheated to the critical temperature for bubble nucleation, which is around 300°C. When the nucleation occurs, a water vapor bubble instantaneously expands to force the ink out of the nozzle. The bubble collapses; the droplet breaks off and excels towards the paper. This is a very efficient and reliable method to control the volume of drops derived from water-based inks. The physical properties of the ink like viscosity and particle content have to be controlled carefully to ensure an ejection of uniform small ink droplets and to optimize the resolution of the printing device.

In general, the viscosity of water-based inks ranges from 2 to 8 cps to ensure a proper drop ejection. But this typically shows some unwanted effects on the used media. As soon as the liquid ink droplet contacts the rough surface of paper, it tends to spread along the paper fiber lines as well as penetrates into paper sizing and voids. Some evaporation of water is taking place, but this drying mechanism is often very slow. The spreading of the ink droplets is often too excessive and too irregular to maintain the expected resolution. The drying and penetration of ink into the paper is often not fast enough to fix multiple ink drops on the same spot within very short time intervals. This result in ink spreading, intercolor bleeding and limits the image quality. The penetration into the paper reduces the color density and therefore the colors brightness of the image. All these mentioned effects limit the technical performance of standard inkjet printing devices.

By logic, major improvements of the quality of inkjet images can not be reached just by further improvements of the printing devices itself, but can be obtained by using optimized systems of the printer in combination with dedicated inkjet media, e.g. special inkjet papers. The surface of these special papers requires a specific surface treatment to overcome the mentioned limitations. This treatment must balance between many design parameters such as drop volume, evaporation rate, penetration rate, and porosity of the media. A special coating of the paper surface can limit the effects of spreading and absorption, to obtain more brilliant colors and to increase the resolution the printer could achieve. Even other disadvantages like long drying times can be improved by using specially coated inkjet papers.

Another disadvantage of inkjet images which previously could not be solved via conventional coatings is the limited resistance against water. The ink is not strongly bound on the paper and can be re-dissolved quite easily by moisture. It will also be dissolved and smeared by working with a standard highlighter on inkjet printouts. Both effects still limit the usage of the inkjet technology for many high-performance applications.

## The development of Allessan<sup>®</sup> APT

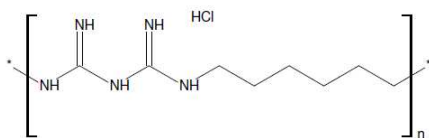
The usage of specifically coated paper can overcome some limitations of the common inkjet technology. However, even these special papers could not improve the limited water resistance of the inkjet images, so inkjet images still show disadvantages which limit their usage in the high-performance fields of application.

Therefore numerous chemical substances were tested for their performance in coatings for paper to optimize the quality and to build a basis for a further extension of the application fields of inkjet technology.

Some years ago, polymeric biguanides were identified as promising lead structures [1] which could be used in coatings for paper, resulting in improved color brightness, faster ink-drying times and improved water fastness. These compounds have long been known and used as disinfectants [2, 3, 4] and dyeing auxiliaries [5, 6]. Enhancement of the fastness to water of dyeings on textiles has been achieved with these compounds, especially with natural fibers. Obviously the polymeric biguanide is fixed to the fibers by hydrogen bonding, and the dye molecule, which contains anionic parts (e. g. sulfonic acid or similar functional groups), interacts with the cationic parts of the polymer. Since natural textile fibers are structurally similar to cellulosic fibers in paper, it is not surprising that polymeric biguanides are suitable as additives enhancing the water fastness of printings with aqueous inks on paper as well.

From the range of polymeric biguanides one compound known as "Polyhexamethylenebiguanide" (PHMB, Polyhexanide) was chosen as most promising candidate (Figure 1).

### Allessan<sup>®</sup> APT – Product Description



• **Active:** (C<sub>8</sub>H<sub>18</sub>ClN<sub>5</sub>)<sub>n</sub>      **Poly(iminoimidocarbonylimino-imidocarbonylimino-hexamethylene) hydrochloride**

• **CAS-No.:**                      **27083-27-8**

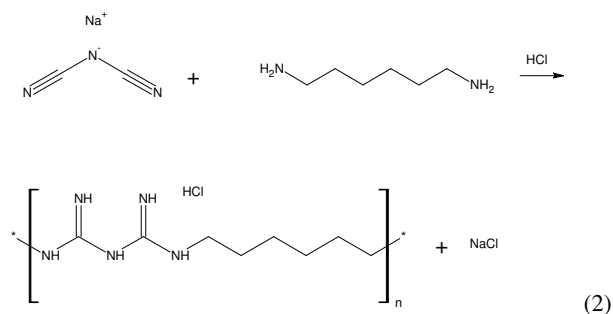
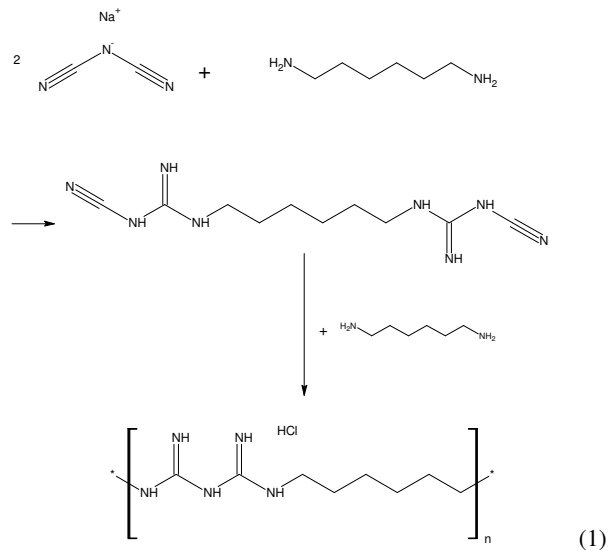
Figure 1. Chemical structure of the active ingredient in Allessan<sup>®</sup> APT.

### Synthesis and Properties of Allessan<sup>®</sup> APT

PHMB can be prepared in a two step synthesis by addition of two equivalents of sodium dicyanoamide to hexamethylenediamine, resulting in hexamethylenediamine-bis-dicyandiamide, which is isolated. Reaction of this intermediate with another equivalent of hexamethylenediamine yields the desired product [2] (Equation 1).

It is as well possible to combine both steps in a one pot reaction [7] by mixing sodium dicyanoamide and hexamethylenediamine and treating the mixture with one equivalent of hydrochloric acid (Equation 2). Heating and distilling off water up

to 150°C yields the desired resin together with sodium chloride. The salt is removed by dissolving the resin in methanol, filtering the undissolved salt and distilling off the methanol from the resin solution. The final resin is dissolved in water and, if necessary, the pH is adjusted to neutral by adding aqueous hydrochloric acid.



As both published procedures result in formation of large amounts of inorganic salts which have to be separated from the resin and disposed of, it was desirable to find a salt free process.

AllessaChemie has developed and successfully scaled up a modified polymerization process which avoids the formation of an inorganic salt as byproduct. The molecular weight of the polymer as well as the nature of the end groups can be controlled by the stoichiometry of the monomeric raw materials. Both parameters affect the solubility of the resin in water, the stability of the formulation, and the performance.

The development was accomplished in close partnership with Hewlett Packard (HP). HP is one of the companies working on paper additives, which can improve the image quality to realize the maximum performance offered by the current inkjet technology. The close collaboration of both companies and the combination of application competence (HP) with optimization and production know-how (AllessaChemie) resulted in the development of the paper additive Allessan<sup>®</sup> APT which is now commercially available in large scale for the production of highly sophisticated inkjet paper.

The professional interaction between the two companies has been the crucial factor for the project's success. In view of the different time zones covered, a proper project management and clear communication were indispensable factors to success. Taking into account that AllessaChemie provided the chemical know-how and HP the application expertise, the teams had to cooperate closely to combine chemistry and application technology across the two companies. This was a fairly new approach in the field of industrial chemistry.

The product obtained with the new process shows the desired performance (see next chapter).

Allessan® APT is applicable to different types of papers:

- Uncoated free sheet papers
- Heavy weight / cardboard papers
- Digital fine arts papers
- Thermal mechanical papers
- High end newsprint
- and much more...

Allessan® APT significantly reduces smearing when highlighting or touching fresh printouts. It improves color brightness; 15-20% increased color space can be achieved.

Allessan® APT is delivered as an easy to handle 20-25% aqueous solution [8].

### Application and test conditions for Allessan® APT

Allessan® APT, the new additive for paper treatment, can be applied on paper via a separate coating step or can be added directly in the size-press.

### Interaction of Allessan® APT with water soluble inkjet dyes

The interaction of Allessan® APT with dyes in water soluble inks leads to the formation of a stable insoluble salt. The ink is precipitated in this case and will not re-dissolve when added to water. Thus Allessan® APT can as well be used for de-inking processes and waste water treatment.

### Treatment of paper with Allessan® APT – Handling Example

Prepare a 5% solution, i.e. dilution of 1:3 of 20% Allessan® APT.

Calculate the required amount of solution with the recommendation of 0.5 – 1 g active per m<sup>2</sup> of uncoated free paper.

The solution is homogeneously dispersed on the paper.

Dry the treated paper at 100°C for 60 sec. or under pressure of 60-70 bars at 55°C for 60 sec.

### Drip Test

Prints with an inkjet printer are performed on uncoated free paper and paper treated with Allessan® APT as described above. After drying the printed papers are treated with water as depicted in figures 2 and 3.

It can be seen that Allessan® APT performs as desired. The ink on the paper treated with Allessan® APT is not re-dissolved with water (Figure 3), whereas the ink of untreated paper shows significant bleeding with water (Figure 2).

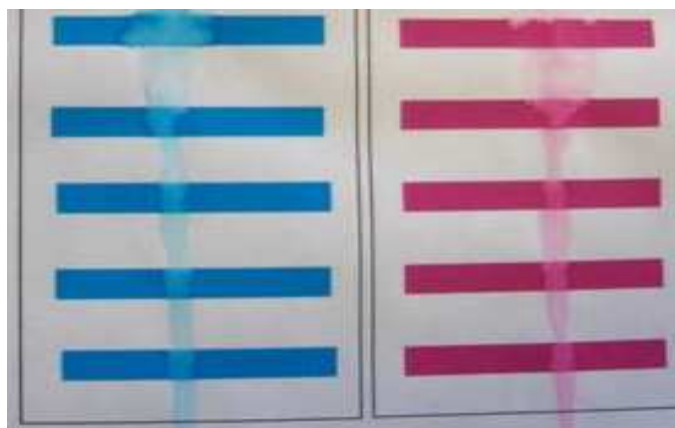


Figure 2. Drip test on uncoated paper.

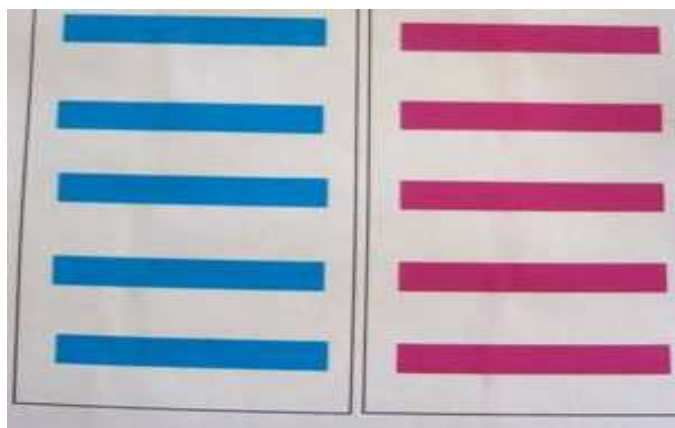


Figure 3. Drip Test on paper treated with Allessan® APT:

## Summary

The new paper additive Allessan<sup>®</sup> APT has been developed in a close partnership between HP and AllessaChemie and can be used to produce special inkjet papers that overcome most limitations of the traditional inkjet technology. This material now enables the development and production of improved types of inkjet media which are broadly available.

Applications in de-inking processes and waste water treatment are possible as well.

## References

- [1] US Patent US6485139, "Ink-jet printing process using polymeric biguanides" (1998).
- [2] British Patent GB702268, "Polymeric diguanides" (1949).
- [3] British Patent GB2182245, "Disinfectant composition" (1985).
- [4] US Patent US6316669, "Bis-amido polybiguanides and the use thereof to disinfect contact lenses and preserve pharmaceutical compositions" (1998).

- [5] European Patent EP0692511, "Method of fabrication of a dying aid" (1994).
- [6] British Patent GB522539, "Improved process for enhancing the fastness to water of dyeings on textiles" (1938).
- [7] US Patent US3428576, "Manufacture of polymeric diguanides" (1965).
- [8] Technical Information, "Allessan<sup>®</sup> APT – Bringing Color to Life"; [http://www.allessa.de/fileadmin/user\\_upload/PDF/Marketing/AllessanAPT2009\\_en.pdf](http://www.allessa.de/fileadmin/user_upload/PDF/Marketing/AllessanAPT2009_en.pdf)

## Author Biography

*Tanja Schaffer holds a PhD degree in Physical Chemistry from the University of Regensburg, Germany. She started her career in R&D before she became active in the field of Business Development. She is currently working as a Director of Marketing and Business Development, Line Products at AllessaChemie in Frankfurt.*

*She is a member of the board of the German Chemical Society (GDCh).*