Digital Production Printing with UV-Curable Dry Toners for Paper and Flexible Packaging

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Abstract

This paper gives some information about the use and benefits of electrophotographic printing on packaging substrates.

For packaging applications the converting process is even more important than the printing itself. To fulfill all this requirements it is very useful to have toners which can be UV-cured. This opens new possibilities for heat treatment, sealing and cooling. In combination with a high productivity web based digital press, this system allows new applications in the food, cosmetics and pharma packaging industry which have a huge market potential. The technology used (in line fusing and curing) will be discussed together with the toner composition problems which were encountered. Another benefit of the existing printing system is the fifth station, which opens the possibility to make use of white and/or spotcolor toner systems too.

Introduction

During the last years, very intense studies were carried out to evaluate the potential of using digital printing techniques for packaging applications.[1] The reasons for doing so were obvious and they still are. Having the potential of making short run for test-sales which is economically affordable is music in the ears of marketing people. Having the opportunity of printing fully variable information can be used for producing more different consumer packaging or labels in order to satisfy (and promote) the collector's mania of especially children. The problem of counterfeiting in the pharmaceutical industry will make it necessary to have a printing system that allows consumers and sellers to detect if the product is genuine. Therefore they need a variable security printing feature. For the tobacco industry it is necessary to print in each country different and changing warning sentences in different sizes. In the field of the food industry there are numerous needs for short and fast run: food packaging for ready meals, for airlines, seasonal offers,…

Market Potential

The total turnover for the global packaging market in 2000 was 500 billion US$ (with 80% printed material). The flexible packaging market had a turnover of 80 billion US$ (54% paper, 8% aluminum and 38% for plastics). The potential of digital printing in these fields is approximately 5-7% within the next 5 years. This equals a volume of 350 million square meters per year for aluminum and 1.750 million square meters per year for flexible plastic packaging.

Specifications for the Printed Matter

The only technology that can deal with the desired printing speeds and image quality is electrophotography. The toner which is used for traditional graphic arts printing or office printing exists of a resin which can melt when fusing conditions are applied (120-160°C). When the paper is cooled down to room temperature a small layer of pigmented resin is present on top of the paper. But this is a reversible process. If temperature is raised again, the resin starts remelting again. This means that a conventional toner cannot be used for these applications mentioned earlier. In table 1 there's list of the most important requirements of the toner for the use in packaging printing.

Why are these tests important? Most of all flexible packaging is heat sealed. Therefore it is essential, that the toner can withstand this sealing process because almost every product is printed in the sealing area. Some products are retorted after they are packed, for this products retort ability of the toners is essential. Some products are even cooked in the package! Every product needs abrasion resistance, it comes in moving contact with other surfaces during storage or transportation. In general we need the resistance for the use of our products to package goods! The normal toner does not withstand the above.

This means that there is the need for a toner system which should be changed after printing in such a way that the resin material becomes more resistant towards mechanical impact, temperature raises and drops and should be able to withstand an organic solvent treatment.

General Background

Toner particles are basically polymeric particles comprising a polymeric resin as a main component and various ingredients mixed with this toner resin. Apart from colorless toners, which are used e.g. for finishing function, the toner particles comprise at least one coloring substance such as black and/or other coloring substances, e.g., colored pigment.

Table 1. Most important requirements for toner for the use in packaging printing[1]

property	description
Heat seal ability	The toner has to resist a temperature of 250°C with a pressure of 80 N/cm2 and 0,6 s contact time.
Retortability	The toner has to withstand a temperature of 121°C for half an hour with 100% humidity or in a water bath (DIN 16524-5) without any changes
Legal rules for food packaging (FDA/BGA	The toner has to be licensed for indirect food (roll / roll production). A license for direct contact would also be good. (e.g. information or competitions on the inner side)
Adhesive strength	The adhesion of the toner printed on normal primers (Nitrocellulose- or Acrylic lacquers) must be strong enough that you can not pull of any toner with a scotch tape test with normal conditions.
Light fastness	The light fastness should be suitable for partial outdoor use. At least 3-4, for some applications a higher light fastness of 5-6 is needed. The price of the first toner set is also critical, economic efficiency for standard products has to be achieved. It is possible to develop a "high end" system for special applications (like retorting) later on (a higher price is feasible for special applications).
Wrinkle test	When doing the wrinkle test called "Gelboflextest" with 20 x partial flex the toner should not break away from the substrate
Water	Toner should be water resistant according to DIN 16524-1
Solvents	The toner should be solvent resistant according to DIN 16524-1. The solvents defined in the DIN are: 1. 96% Ethanol 2. Mixture of 30% vol. Ethylacetate; 60% Ethanol and 10% Metoxypropanol. The sample has to withstand a complete cover of the solvent for 15s without any changes in color or adhesion of the ink.
Rub resistance	When the customer uses the package, no toner should break of. A test device for this is a Quartant rub resistance tester. Recommended measurement conditions are: Rubbing Pressure 50 g/cm2, Rubbing Speed 0,15 m/s, 100 turns.

In the beginning color electro(photo)graphy was mostly used for producing colored images (e.g. graphic arts, presentations, colored books, dissertations). When the process speed of producing digital colored images increases, other more productive applications also became feasible (direct mailing, transactional printing, packaging, label printing, security printing). This means that after the action of being produced by electro(photo)graphy, the toner images further have to withstand some external factors applied during the subsequent treatments. The problems associated with multiple, superimposed layers of toner particles that are in one way or another fixed on a substrate are manifold, not only with respect to image quality but also with respect to image stability and with respect to mechanical issues.

An example of high mechanical impact on the toner layers is sorting of printed papers (e.g. direct mail applications). The fast turning wheels of a sorting machine can give a temperature increase above the glass transition temperature (Tg) of the resin used, which can cause contamination with pigmented toner resin on the next coming papers. Another application where the heat and mechanical resistance of the toner layer is stressed is the production of e.g. car manuals. When the temperature inside the car rises above the Tg of the toner resin (e.g. when parked in the sun), the papers in the manual can stick to each other.

In the case of printing packaging materials with the use of toner technology, increased temperatures can be dealt with in many ways. Plastics can be used as a substrate and bags made out of it with the use of a sealing apparatus. If the sealing temperature is above the Tg of the used toner resin, the toner images get disturbed or distorted.

For a lot of these applications, a toner resin with a higher Tg and Tm should be used, but then the amount of energy necessary to fuse the toner particle onto the substrate would be so high that the application is energetically not interesting anymore. Secondly a lot of substrates can't be used anymore. High Tg toners exist already, but the demand for high speed print engines increases the demand for toner particles which can be fused at lower temperatures at a very high speed.

The use of a transparent overcoat made out of radiation curable toner particles has been developed already to protect (image wise) an image produced by electrophotography to improve the weather resistance.[2-4] This is what we call spot-gloss!

A non-image wise transparent UV curable coating (applied in liquid form) is also known to give a flexible, high gloss finishing to printed papers.[5-8]

Prints obtained by means of electrophotography and by the use of thermally fixable toner are thermal stable only to approximately 100°C. Packaging materials must however partly be heated to temperatures far above 100°C during the production of sealed packaging.

The use of UV curable pigmented powders is already well known in the field of powder coatings but there are some major differences with respect to the field of toners9. The size of the particles (6-10 microns for toner versus >30 microns for powder coatings) and the particle size distribution are quite different. Also the thickness of the layers applied with powder coatings is at least a factor 3 to 4 times thicker in comparison with the toner images. The speed of fusing and curing is very low compared, for example, to the high speed printers which are now available in the field (e.g. Igen3, Xeikon DCP500D). Powder coatings are also never applied image wise. The powders are charged by some means and brought onto the surface of the material, which has to be coated. This is all quite different from toner, which is brought either directly image wise on a substrate, or via a latent image on a photoconductor to a substrate.

There is still a need to provide a toner which can be fixed at low temperatures but which is resistant to high temperatures once printed. It is the object of the study and development to provide a toner to produce images that are resistant to high temperatures, resistant to mechanical abrasion and resistant to the influence of common organic solvents.

At this moment Xeikon International is working with a polyester based resin system. We use a traditional DCP-press (simplex or duplex) where we are using the fusion system on a normal level. When the paper comes out of the machine (it is not cut) it is fed through an UV-curing with a suitable UV-source. The paper is rewinded and ready for further treatment. The speed of curing is equal to the printing speed.

If you want to apply UV curing in a production digital printing environment, then it is necessary that all colors are cured in the same extent, independent upon the layer thickness and the page coverage which is applied during image formation. This means that all colors must behave in the same manner, independent from the type of pigments and the pigment load which is used. This is the big challenge for making toner. On top of that the choice of pigments is not very huge because of the high level of light fastness we are aiming for.

Technical Description and Experiments

1. Toner Preparation

Toners were prepared by kneading the polymer together with the photo initiators and a pigment in a laboratory kneader. After the mixture has cooled down it is milled down and classified to a particle size distribution of Dv = 8 micron and Dn=6 micron. In order to improve the flow ability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

2. Test Methods

Temperature Resistance Test of Fused and Cured Toner Particles

The fused and cured samples are folded inside and put between 2 plates for 5 sec with a pressure of 6 bar. Only the upper plate is heated. The temperature at which the toner starts to stick together is determined for the uncured and corresponding cured toner sample. The temperature difference between both toner samples is a measure for the temperature resistance of the toner. The uncured toner starts to stick together between 110 and 120°C.

Images Defects After Temperature Resistance Test

After the temperature resistance test the images are visually observed and ranked on a scale: 1=excellent: no damage could be seen and 5=bad: severe damage of the toner image (by the melting of the toner during the temperature exposure).

Solvent Resistance Test of Fused and Cured Toner Particles

With a cloth soaked with MEK (methylethylketone) the fused and cured toner images are rubbed softly. One count is equal to an up and down rub. The rubs are counted till the substrate becomes visible. The number of rubs is a measure for the solvent resistance of the toner images

Abrasion Resistance of Fused and Cured Toner Particles

The toner images with an area of 16cm^2 are rubbed 50 times with a load of 600g by an abrasion paper on an abrasion tester type Prüfbau from Dr. Durner in München. The abrasion paper is a sand paper P600 which is rubbed 10 times over each other in the same apparatus

Afterwards the uncured and corresponding cured images are visually inspected and the difference between both samples is ranked as follows: 1=excellent: cured samples are much better than uncured samples- no damage of the image, only a small lowering in gloss, 3= good/acceptable: cured samples are better than uncured samples: small damage of the image and significant lowering in gloss, 5=bad: cured samples are equal to uncured samples: strong damage of the image.

Sealing Temperature

This is another method to check the temperature resistance. The printed substrate together with a silicon paper is put between 2 heated plates for 0.6 sec at a pressure of 80N/cm^2 (with a Brugger Sealing device ; see Figure 1). The temperature at which toner deposition is seen on the silicon paper is referred to as the sealing temperature.

Figure 1. Brugger test equipment for heat sealing

Tg of Toner Particles and Resin

The glass transition temperature is preferably determined in accordance with ASTM D3418-82.

3. Polymer Choice

The UV curable polymer was chosen in such a way that both an acceptable blocking resistance and a sufficient high reactivity was present in order to have the possibility to cure the toners in line with the DCP engine.

Tests were done with 2 different resins, Used resins are combinations of polyesters and epoxy resins.[10] The polyesters are obtained by polycondensation of terephthalic acid and neopentylglycol. Epoxy resins are produced by condensation of bis-phenol A and epichlorhydrine. The polyesters and the epoxy resins are functionalized with (meth)acrylic functions. The technical properties are mentioned in Table 2.

Table 2. Properties of UV curable PE resins

	Tg (°C)	AV	Mn	Eq. Wt	rubtest
polym. 1	51	< 3	3750	1100	80
polym. 2	53	< 3	3750	1400	60

From Table 2 it is clear that by increasing the number of double bonds a higher reactivity can be obtained. The equivalent weight is the amount of polymer (g) to obtain one mol of reactive groups. Further tests were done with the first polymer.

4. Photo Initiator

Based on their chemical composition 2 main types of photo initiaors can be used: BAPO i.e. bisacylphosphine and AHK i.e. alpha hydroxy ketone photo initiators (See Figure 2 for some examples).

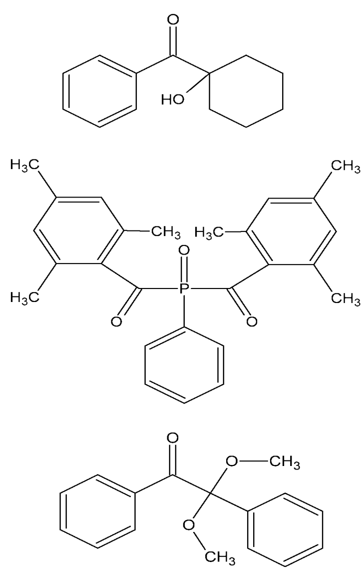

Figure 2. Typical examples of BAPO and AHK type of photo initiators

The choice is mainly determined by their reactivity, dispersibility in the polymer matrix, their effect on lowering the Tg (ie influence on the blocking resistance) and absence of forming volatiles during heating.

From the data of Table 3 (produced with a cyan toner; curing speed 12,5 cm/s, Hg bulb of 240 W/cm and a layer thickness of 10 micron) one can see that the use of a BAPO photo initiator is preferred because no drop in Tg is seen and also a better curing is obtained. By increasing the photo initiator concentration, better curing occurs resulting in higher MEK rub test and a better abrasion resistance.

Table 3. Photo initiator type and concentration effect

[AHK]	[BAPO]	MEK rub test	T resist.	abrasion resistance	Tg (DSC, 2nd run)
1,5	1,5	80	>130	2	47,6
0,75	2,25	140	>130	2	48,5
2,25	0,75	80	>130	3	45,8
2,25	2,25	200	>130	1	
0	3	200	>130	1	50,2
0	0	1	0	5	50

5. Color Dependence

Different colored toners were prepared and tested to check the dependence of the curing on the selected color.

The curing conditions used in the experiments reported in Table 4 were: 12,5 cm/s, Hg-bulb with 240 W/cm and a toner layer thickness of 10 micron. One can se that the yellow toner cures less good than magenta and cyan toner. This can be explained because a part of the UV light is absorbed by the yellow pigment. Thick UV powder coatings (e.g. 60 micron) are nearly impossible to cure!

Table 4. Differences in curing results depending upon the type of pigment

color	[BAPO]	MEK rub test	T resist °C	abrasion resistance
C	3	200	>130	1
M1	3	200	>130	1
M2	3	70	>130	3
Y	4,5	100	>130	3
K1	2	20	>130	4
K2	4	34	>130	4
K3	8	50	>130	3
K4	4	70	>130	3

The curing of black toners is also not so obvious. The curing can be improved by increasing the concentration of the photo initiator or by changing the pigment. The reason why the curing of black toner is so weak compared to other colors is not yet completely clear. A possible explanation could be that the carbon black surface catches the necessary photo initiator radicals. Incorporating amorphous polyester decreases the curing performance dramatically due to the disturbance of the cross linking reaction. This is the case in M2 where 20% of the UV curable resin as replaced by a non UV curable resin. The reference for a toner without curing is 1 for the MEK rub test. This toner has a temperature resistance of 0°C and an abrasion resistance of 5.

6. Results on Packaging Substrates

Tests were done on substrates commonly used in packaging: MIXPAP: paper laminated against a metalized PET mainly used as lid film for yoghurt cups and aluminum foil with a seal lacquer on one side which is mainly used as a push trough foil in pharmaceutical packaging.

Table 5. Curing results on packaging substrates

COLOR	MEK rub test	T resist.	MEK rub test	T resist.
C	8	110	10	120
M	10	110	14	120
Y	8	110	19	120
K	15	90	10	120

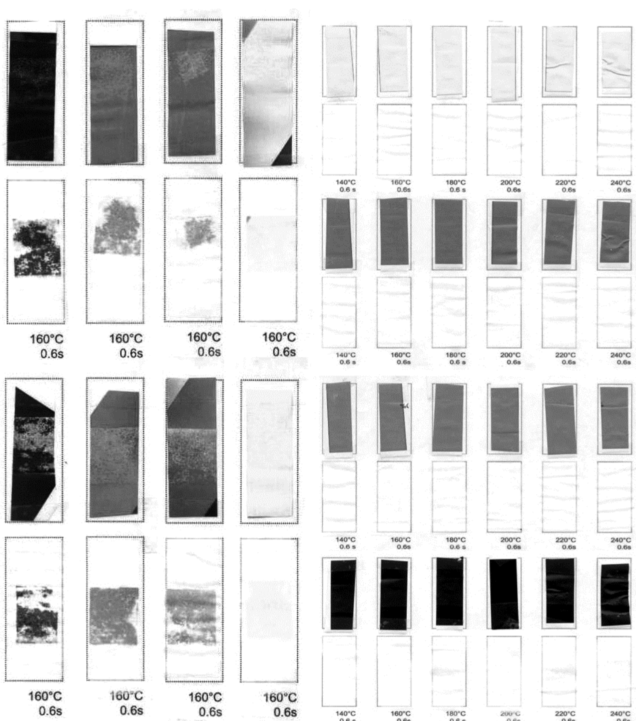

Figure 3. Heat sealability. Right is after curing when different seal temperatures are applied (140-240°C). Left: before UV curing at 160°C : upper is normal Xeikon toner, lower is Xeikon UV-toner before curing. If no toner is present on the lower piece of paper = no transfer during sealing. These tests were done with the Brugger sealing device.

The results in Table 5 show that the curing is not so good than on conventional printing paper mainly by the fact that the UV dose has to be limited due to the temperature dependence of the substrate (160 W/cm at a speed of 12,5 cm/s). Nevertheless the temperature resistance (and thus sealing temperature) is improved to a such a level that what we think is acceptable in the packaging industry (see also Figure 3). Figure 5 shows also that the mechanical resistance has been improved.

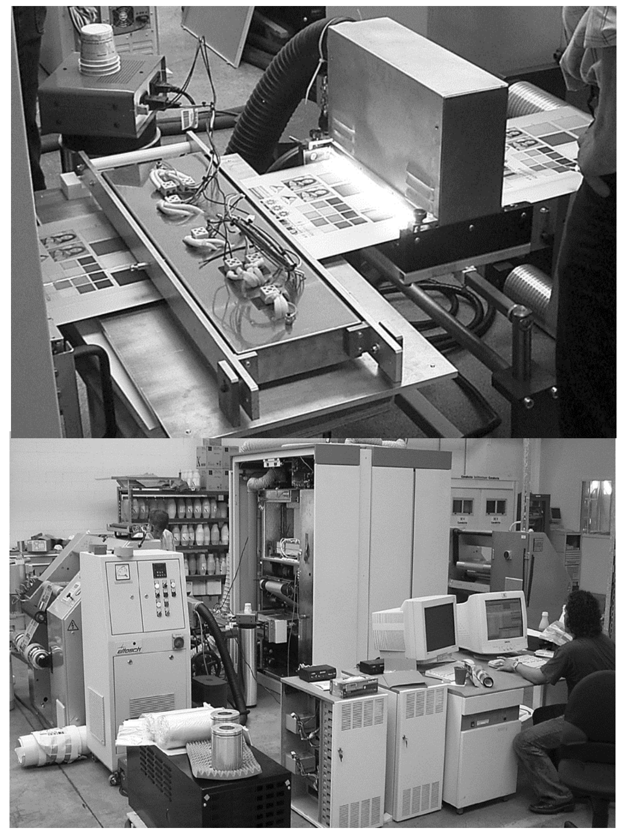

Figure 4. Complete Xeikon DCP-installation for UV curable flexible packaging printing, with in line pre heating and UV curing (upper)

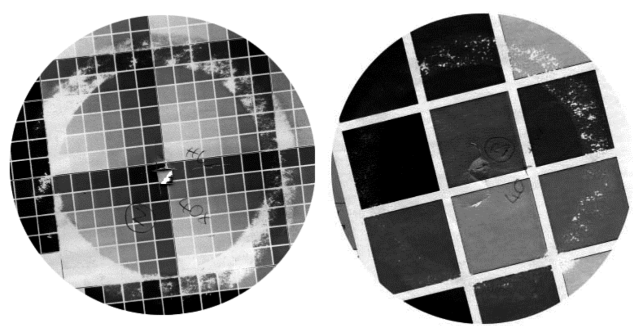

Figure 5. Taber Abraser test,(40 cycles) on packaging substrates. The right sample is UV-cured, the left is normal Xeikon toner. It is clear that UV curing leads to a much better mechanical resistance.

Conclusion

This paper clearly shows what progress has been made by changing normal graphic arts toner system to an UV curable toner system.[11-12] We have set a major step towards the use of these toners in high demanding applications where the post finishing process is as important as the printing process itself. Xeikon International continues this important development and is looking also into the development of other UV curable (spot)colors beside the CMYK toners (e.g. white and orange). The initial focus lies upon entering the packaging market with a complete system that offers the solution the printing industry is looking forward to. But it should be clear that also other applications (e.g. on paper or light cardboard), can profit from this evolution!

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Biography

Lode Deprez is Vice President Toner & Developer Group at Xeikon International. In this organization he is responsible for both R&D and toner production. He received his PhD in organic synthesis at the University of Ghent in 1990. He was active during 9 years in the R&D development department of Agfa and was specialized in silver halide based printing plates. From 1999 he joined the toner R&D department at Agfa and became responsible for this R&D group before it moved to Xeikon.