Investigations in the Influence of rounded Toner Particles on the Image Quality Parameters

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Abstract

The advantages and disadvantages of chemically produced toners (CPT) vs. conventionally produced toners by grinding and classifying are top of discussion. All OEM's of CPT contend that their toners are characterized by smaller particle size, tighter particle size distributions and higher consistence in particle shape. The ideal spherical or at least "potato" toner particle shape effects a higher capability of rendering better image quality.

Goal of our investigations was to improve the circularity of conventionally produced toner particles and to correlate the generated particle shape as well as the resulting imaging quality parameters. Test material was an adjusted purchasable CPT that was prepared in the conventional way.

In the first part of this presentation results of systematic investigations according to rounding conventionally produced toner particles will be presented. Extensive tests on a conventional intensive mixer Cyclomix by HOSOKAWA Micron B.V., Doetinchem/The Netherlands, and the new high-intensive mixer NOBILTA by HOSOKAWA Alpine Aktiengesellschaft, Augsburg/Germany, were conducted to evaluate optimal processing conditions.

The second part deals with the consequences of rounding on printing quality parameters like solid black density, ghosting, fixing and level of grey, the correlation of particle circularity and printing quality parameters as well as the comparison of mechanically rounded toner particles to chemically produced toner particles.

First results show that it is possible to generate the desired potato shape by intensive mixing on Cyclomix as well as on NOBILTA, both kinds of intensive solid mixer. The printing tests gave fully satisfying results in almost all criteria and are comparable to CPTs. In order to utilize all benefits of rounded toner quality the entire toner production process must be taken in consideration, i.e. from formulation to blending.

Further investigations including trials on the Fluidics Coating Device will be conducted to optimize the rounding step and to evaluate the optimal mechanically rounding process.

Introduction

More and more chemically produced toners (CPT) replace conventionally produced toners generated by extrusion, grinding and classification (top-down-method). Different bottom-up-processes were developed during the last two decades. Nowadays Emulsion Aggregation, Suspension Polymerization, Polyester (Elongation) Polymerization and Chemical Milling can be distinguished [1].

Main arguments for CPT are a flexible polymerization process that gives tight particle size distributions of user-defined position (d_{50}) and width (d_{10}/d_{90}, d_5/d_{95}) as well nearly spherical particle shape. Further positive aspects are good fusing, good charge control, flow and transfer which are effected by the process conditions as well as the product properties. In contrast the weak points are complex processes (difficult to control), difficult cleaning, heavily patented, difficult control of aspired particles size distribution and impurity by solvent.

Advantages of the established pulverization (consisting of grinding and dedusting/classification step) are inexpensive and sophisticated technology. For advanced applications a rounding or spherodizing step is conducted subsequently to hit the idealized spherical or potato shape. This kind of processing is much cheaper than chemical. Sometimes wide resulting particle size distribution, poorer fusing and wax migration to the particle surface (gives a poorer flow) are mentioned as disadvantages.

Methodologies

Experimental set-up

Test material, equipment

For contrasting conventionally produced toner after rounding with CPT a toner recipe was developed that showed nearly identical properties concerning to solid black density, ghosting, fixing and level of grey. The model toner was grinded on a HOSKAWA Alpine 200 AFG and it was dedusted on a HOSOKAWA Alpine 200 TTSP. The main bulk solid properties are assorted in Table 1.

Table 1. Main bulk solid properties.

Property	Model toner	CPT
Bulk density ρ_B / kg/m³	531	720
Particle size d_5 / µm	5.94	5.92
Particle size d_{50} / µm	8.32	8.36
Particle size d_{95} / µm	11.67	11.08
Glass transition temperature T_g/ °C	63.06	N/A

Table 2. Printing Quality Parameters.

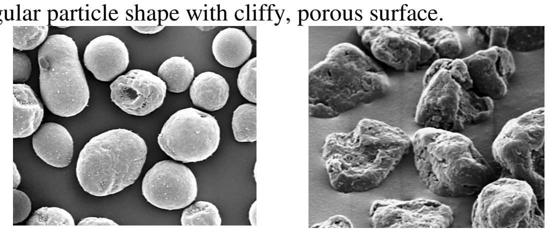
Property	Model toner	CPT
Solid black density	2	1
Ghosting	3	2
Fixing	2	2
Level of grey scale	2	1

1=excellent 2=good 3=middle 4=bad 5=very bad

Printing tests of the conventionally produced toner were conducted, valued and compared to the CPT. The main printing quality parameters are collected in Table 2.

It is obvious to see that the model toner is compatible to the CPT in almost all criteria.

SEM pictures of a CPT and a conventionally produced toner are illustrated in Figure 1. The CPT features the potato shape. Against it the conventionally produced toner is characterized by irregular particle shape with cliffy, porous surface.



CPT *Conventionally produced toner*

Figure 1. *SEM pictures of CPT and conventionally produced toner*

Investigations in rounding of the model toner particles were conducted on Cyclomix 5 by HOSOKAWA Micron B.V., Doetinchem/The Netherlands, and NOBILTA™ NOB-130 by HOSOKAWA Alpine Aktiengesellschaft, Augsburg/Germany.

Cyclomix 5 NOB-130

Figure 2. *Cyclomix 5 and NOBILTA NOB-130*

Detailed technical information is given in Table 3.

Table 3. Technical data of Cyclomix 5 and NOBILTA NOB-130 [2, 3].

Property	Cyclomix 5	NOB-130
Drive power P / kW	5.5	5.5
Tip speed max. / rpm	2,200	6,000
Volume V / l	5	0.5

As shown in Figure 3 the Cyclomix 5 is a vertical intensive mixer. Peripherical mixing blades are installed on the vertical, centric shaft. The gap between the mixing blades and the conical, double walled casing is 3 mm. In contrast the NOBILTA NOB-130 is a horizontal high intensive mixer characterized by a horizontal shaft with under a certain setting angle adjusted mixing blades. The gap between blades and casing can be changed stepwise from 1.5 up to 5.0 mm.

Agglomeration of softened toner particles was avoided by utilization of silica. To evaluate the main drivers on rounding 1 wt.-% of conventional Aerosil 150 (by Degussa) was added in preliminary tests. In the main experiment high disperse silica type HDK H-20TX by Wacker Chemie was applied.

The rounding procedure differed in both intensive solid mixers. The Cyclomix 5 was heated by an external heating loop and charged with 990g of conventionally prepared model toner. 10g of high disperse silica were added to avoid clocking inside the mixing chamber and to improve the flowability. This mixture was slowly heated up to 5°C below the glass transition temperature T_g. Afterwards the heating rate had been reduced to 1°C per 5 minutes, samples were taken every 5 minutes. The rounding procedure was stopped 5°C above the glass transition temperature. The toner was cooled down to 32°C and discharged.

The NOBILTA NOB-130 was run under permanent water cooling to avoid melting of the toner. The batch size was 268g what corresponded to 500 ccm. The rounding procedure took only 6 minutes and the test material was immediately discharged and sampled.

Evaluation of Printing Quality

80g of the prepared toner was filled in a properly cleaned OEM printer cartridge and the print tests were carried out whereas internal standard test sheets were used.

The regular print volume was 1,000 pages per tested sample. The test sheets were visually observed and assessed based on a criteria list. The following parameters were included in this evaluation:

- Solid black density: 100% full printed page having the highest possible deposition of toner particles.
- Ghosting: It means in this case the effect of loss in density by printing a 100% black page.
- Fixing: A standard rubber test with a paper towel.
- Grey scale: The test sheet contains a grey scale in form of printed squares from 5 to 100%. The criteria were the uniformity and visibility of the printed squares.

Results and Discussion

Particle Size Distribution and Particle Shape

Substantial criteria for the rounding step are unmodified particle size distribution and qualitative as well as quantitative scale of spherodization. The particle size distribution was detected by a Multisizer 3™ Coulter Counter 3®. The change in course of the particle size distributions after rounding on HOSOKAWA Micron's Cyclomix 5 is shown in Figure 3.

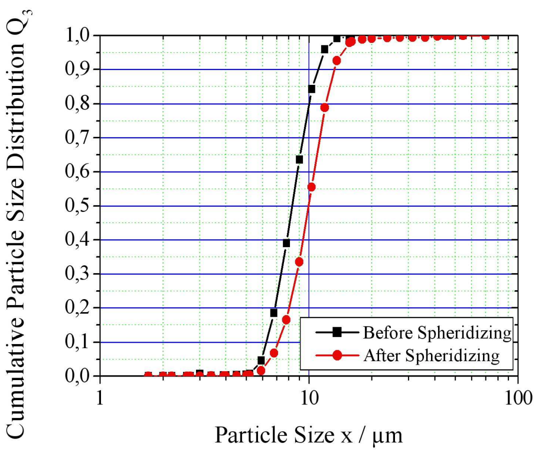
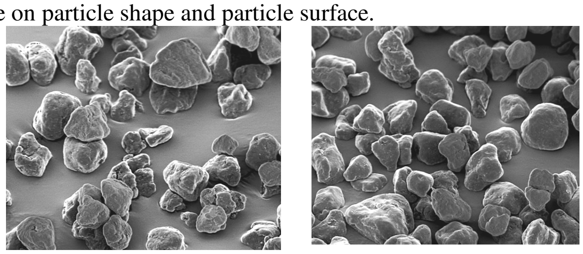


Figure 3. *Change in course of particle size distribution before and after rounding.*

In Figure 3 the cumulative, volumetric distribution Q_3 is plotted against the particle size x. The plot demonstrates that the particle size distribution is shifted into the coarser range. The median value is shifted from $x_{50} = 8.32$ µm to $x_{50} = 9.98$ µm.

The qualitative scale of spheronisation was determined by taking SEM pictures of small processed toner samples.

Figure 4 illustrates the effect of temperature and rounding time on particle shape and particle surface.



Spheridized toner at 65°C after 30 minutes

Spheridized toner at 68°C after 75 minutes

Figure 4. *Influence of processing temperature and processing duration on toner particle shape.*

In Figure 4 on the left hand side rounded toner particles are pictured for processing temperature of T = 65°C and processing time of t = 30 minutes. It's obvious to see that the particle shape has become rounder and the particles surface has been smoothed a little bit. Some bigger pores can be detected which were caused by the degassing step during the extrusion.

The picture on the right hand side shows particles at the rounding temperature of T = 68°C after 75 minutes of processing. Almost all particles are rounding and featured the desired potato-like particle shape. The pores are nearly closed and the particle surface has been smoothed completely.

Figure 5 shows SEM pictures of toner particles rounded on NOBILTA NOB-130 by HOSOKAWA Alpine Hosokawa AG, Augsburg.

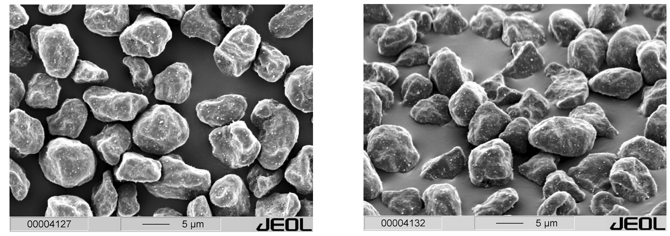


Figure 5. *Toner particles rounded by NOBILTA NOB-130.*

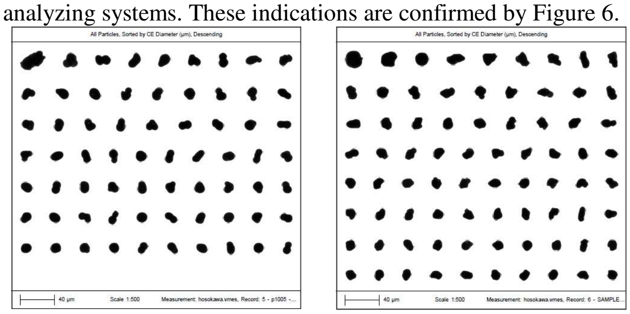
It's obvious to see from Figure 5 that toner particles can be rounded and smoothed by NOBILTA NOB-130, too. Many particles conform to the idealized potato shape. In comparison to Figure 1 the particle surface has become much smoother.

Table 4. Particle size parameters and circularities.

		CPT	CLX 5	NOB-130
Sysmex FPIA-3000	d_{10}/µm	6.63	7.35	N/A
	d_{50}/µm	8.90	9.97	N/A
	d_{90}/µm	12.32	13.09	N/A
	circ. Ψ	0.979	0.948	N/A
Mor-phologi	d_{10}/µm	7.39	N/A	7.35
	d_{50}/µm	9.51	N/A	9.60
	d_{90}/µm	11.96	N/A	12.34
	circ. Ψ	0.984	N/A	0.955

In Table 4 characteristic particle size parameters as well as circularities measured by Sysmex FPIA-3000 and Malvern Morphologi G3 are collected.

The particle size parameters indicate a shift concerning to the d_{10} and d_{50} between the CPT and the model toner rounded on the Cyclomix 5 (CLX 5). This phenomenon might be caused by coalescence of particle abrasion or of finest and middle-sized toner particles. This effect doesn't appear for particles rounded on the NOBILTA NOB-130. All particle size parameters are very similar. The circularity determined for the chemically produced toner and mechanically rounded model toner differs significantly. The difference in circularity is roundabout $\Delta\Psi = 0.03$ on both particle shape analyzing systems. These indications are confirmed by Figure 6.



CPT

Model toner rounded by NOB-130

Figure 6. *Impressions of particle shape of CPT and rounded Model Toner.*

Figure 6, left and right hand side, gives an impression of the particle shape of CPT and model toner rounded on the NOBILTA NOB-130. In the first instance the pictures of the CPT (left hand side) illustrate coalescenced particles of ideal round primary particles. The mechanically rounded toner by NOBILTA consists of round as well as potato-shaped particles.

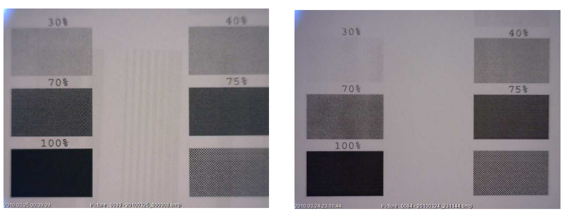
Influence on Printing Performance

Within the scope of this investigation it was studied the behavior of the aforementioned toners in the printer. For this purpose a conventional manufactured toner formulation, so called "model toner", was developed containing the components listed in Table 5.

The toner formulation before heat treatment was tested in a commercial available printer and cartridge with the determined parameters according to Table 2.

Table 5. Basic Toner Formulation.

Ingredients	% by weight
Polymer	49.00
Iron oxide pigment	44.00
Wax	3.50
CCA	1.50
External additives	2.00



CPT Model Toner

Figure 7. *Grey scale density difference between OEM and Model Toner.*

It can be seen in Figure 7 that the model toner almost achieved the quality of the CPT before heat treatment. One problem of the conventional produced toner is the fact that the bulk density tends to be lower than CPT toner due to closer packing of spheres. This leads to lower black density on printed paper.

We expected that the typical ghosting or fading effect, which occurs on a solid black printed page, could be reduced as the free flow properties might be improved by the rounding process. However, it is known that the ghosting process in mono-component development processes also depends on particle size and triboelectric charge distribution.

Furthermore the fixing or fusing properties on the paper could be influenced by the heat treatment during rounding procedure. The fine-dispersed wax component in the toner is able to migrate to the surface or even coagulate inside the particle. According to our knowledge this effects were not well analyzed so far.

Grey scale development in lower densities shows up as fairly difficult for mechanically ground toners because the transfer rate of toner particles from the OPC to the subsequent media (belt or paper) is normally lower compared to spherical CPT toners.

A target was to see which quality parameters changed after the rounding treatment. Several toners were produced under varying conditions and tested in toner cartridges. After the rounding process the toners were exactly processed like the model toner. The treated toner powders were blended by 2.0 wt.-% of surfaces additives with a mixing time of 1.5 min. and a tip speed of 3000 rpm on a laboratory mixer. Finally the products were sieved with a 63µm laboratory screen. The printing performance test showed up newly created defects as white lines or wider streaks in the direction of the paper direction which could be caused by agglomerates coming from the heating process. These agglomerates may clog the doctor blade in the development unit. All the first rounded samples revealed unevenness in grey printed areas.

Table 6 shows a comparison of the first manufactured rounded toner sample A compared to the CPT

Table 6. Print Test Sample A

Property	CPT	Sample A
Solid black density	1	3
Ghosting	2	3
Fixing	2	3
Level of grey scale	1	4

1=excellent 2=good 3=middle 4=bad 5=very bad

It is obvious to see in Table 6 that the first test toner was remarkable worsening of the print results. All toner samples A to D were prepared by the addition of the Silica Aerosil 150 during the rounding process. These series presented the pronounced defects of the stripes and the inhomogeneity of the printed grey areas. Obviously the surface additive used in the first step of surface treatment needs to be carefully selected.

Sample E and were added by Wacker's HDK H-20TX and leads to the following outcomes. Table 7 doesn't show a substantial improvement of the performance. The black density even decreased during by using the other silica. However, the building of stripes was completely disappeared. The grey printed areas were much more homogenous compared to the toner samples A to D.

Table 7. Print Test Sample E and F

Property	CPT	Sample E	Sample F
Solid black density	1	4	4
Ghosting	2	3	3
Fixing	2	2	2
Level of grey scale	1	3	3

1=excellent 2=good 3=middle 4=bad 5=very bad

In the next step the amount of post additives after the heat treatment was reduced and tested in the printer. Instead of 2 wt.-% silica the addition was set to 1.2 wt.-% total admixture.

Table 8. Print Test Sample F-1

Property	CPT	Sample F1
Solid black density	1	2
Ghosting	2	2
Fixing	2	2
Level of grey scale	1	3

1=excellent 2=good 3=middle 4=bad 5=very bad

The last toner shows now a clear improvement of the print results. The black density and ghosting are much enhanced and achieve the level of the CPT as demonstrated in Table 8. In terms of ghosting it seems that the spherical toner particle could help to avoid this defect.

Conclusion

1. The study shows that mechanical intensive solid mixers in conjunction with heat treatment are able to round the toner particles.

2. The mixers need some addition of external additives as silica to avoid toner lumps and agglomerates. The additives for the thermal process have to select with care.

3. The total amount of external additives and the type of additive is as important as without having a rounding step.

4. With a few trials it was demonstrated that a reasonable print quality can be achieved by using this equipment. However, the additional process unit for rounding the toner shape leads to the consequence that the total process of toner manufacturing is supposed to integrate into the toner development process. The raw materials could play a key roll of success.

References

[1] N.N., Color Toner – Conventional or Chemical, The practical issue, www.delacamp.com.

[2) N.N., HOSOKAWA CYCLOMIX, product flyer HOSOKAWA Micron B.V., Doetinchem, Holland (1997).

[3] N.N., Particle Design, product flyer HOSOKAWA Micron Corp., Osaka, Japan (2006).

[4] C. Yamaguchi, M. Takeuchi, J. Imaging. Sci. and Technol., 40, 436 (1996).

Author Biography

Ralf Habermann, born in Hanover/Germany in 1966, studied Chemical Engineering at the Technical University of Clausthal. In 2005 he received his doctoral degree in Process Engineering for his thesis about "Connection of Residence Time Distribution and Mixing Quality in a continuous operating Ploughshare Mixer" from the University of Paderborn. Since July 2006 he is Product Manager for the New Material Business and R&D Engineer at HOSOKAWA Alpine Aktiengesellschaft in Augsburg.

Beat Zobrist is Owner of the company Zobrist Engineering and Consulting (ZEAC). The Swiss company develops and manufactures new functional toners as well as consults companies in toner matters. He received his B.Sc. in Chemistry from the Zurich University of Applied Science. In 1993 he joined the Elfotec AG, 1998 he was Head R&D. From 2001 until 2004 he worked as Technical Director of the toner division at the company Huber Group in Munich, Germany.