

Coloristic Study of Magnetic Toners and Related Print Performance

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Abstract

The first step for the development of colored magnetic toners was a coloristic model study to establish the optimum color. Red proved to be the most attractive starting point. In a next step the best pigments were established: they are a γ -Fe₂O₃ and a DPP red. The influence of opacity, color strength, pigment ratio and concentration was studied. Based on these results the formulation of the final toner was optimized. The resulting toner is suitable for standard equipment and produces an attractive highlighting red print. Further progress seems possible. A brown toner is also available. Developments of green and blue toners are in progress.

Introduction

Magnetography has been a successful high speed Non-Impact-Printing technology for many years. The magnetographic copying process is easiest characterized by the fact that the latent picture on the drum is magnetic rather than electrostatic. In commercial systems the magnetic and color forming material for black copies is the black iron oxide called magnetite. The toner consists of ~ 1/3 magnetite, the rest being resins for fixation on paper and a small percentage of additives for optimum performance.

Red Magnetographic Toner

As in any field the trend towards color is a natural one since color is a very attractive part of every day life. The big challenge here is that all magnetic materials suitable for this technology are brown or black (the color of these iron oxides originates from electronic interactions between the iron and the oxygen centers). The black magnetite can be replaced by the brown γ -iron oxide (γ -Fe₂O₃) which has all the necessary magnetic characteristics. The interesting experimental transparent iron oxide described by Ziolo et al. 2 years ago (*Science*, **257**, 219-222, 1992 and *C&E News*, 20-21, July 20, 1992) is not suitable for the present technology.

This means that for the time being a red magnetographic toner will contain a mixture of a red pigment and a brown γ -iron oxide. We will show that with this combination, attractive monochromatic highlighting colors are possible.

For an optimal red toner we have the possibility to optimize the properties of the constituents. In the following

parts the influence of the red pigment, the magnetic pigment and the composition of the toner on the print performance will be studied.

Influence of the Red Pigment

The color strength of the γ -iron oxide is very low compared with many commercially available organic red pigments. Thus a mixture of the two will look more or less red. Because of the brown component the brilliance of the color will be limited and it is hence important to choose a brilliant red pigment. The coloristic impression of this mixture can be varied considerably by choosing the best red pigment and optimizing its properties. This red pigment has to compensate for the low color strength brown color of the γ -iron oxide as much as possible. To achieve this, the pigment has to have maximum hiding power and color strength.

The hiding power of a pigment is defined as the ability to hide the color of the background (undercoat). The hiding power of a pigment is related to the scattering power of the particles, which is a function of the particle size and the particle form of a pigment (isometric particles have a larger hiding power than needles). For a given crystal form the hiding power is very low for small particles, has a maximum at a particle size of ~0.4 μ and falls again as the particle size grows.

The color strength of a pigment depends on the chemical identity of the pigment and its particle size. Inorganic pigments like the γ -iron oxides have a much lower color strength than many organic pigments (differing by approximately a factor of 10). The smaller the particle size the larger the color strength (for organic pigments this can vary by a factor of 5).

Thus choosing the best organic pigment has a large influence on the final color of the red magnetographic toner. Experiments have shown that the pigment class that fulfills best the need for a brilliant red with high opacity and color strength is the class of IRGAZIN and CHROMOPHTAL DPP reds. The following experiments have been performed with this class of pigments to optimize the performance of the red toner.

a) Influence of the Ratio γ -Fe₂O₃ to DPP Red

The first series are model experiments to optimize the coloristics of the red toner: the pigments are dispersed in PVC rather than the regular toner (the total pigment concentration is constant). The coloristic data are represented in CIE-Lab coordinates:

Table 1. Color as a Function of Pigment Ratio

ratio $\gamma\text{-Fe}_2\text{O}_3$ to DPP	L (lightness)	a (red)	b (yellow)
only $\gamma\text{-Fe}_2\text{O}_3$	49.3	19.4	28.4
5 to 3	42.5	37.0	24.0
1 to 1	42.8	39.7	24.5
3 to 5	43.1	43.1	26.5
only DPP	45.6	54.5	33.5

It is obvious that the ratio of the two pigments has a big influence on the color of the toner. For reasons discussed below, this ratio is limited by other factors and a ratio of 5 to 3 is realistic. Thus the following experiments are performed with a ratio $\gamma\text{-Fe}_2\text{O}_3$ to DPP red of 5 to 3.

b) Influence of Opacity and Color Strength

As the following table indicates, the pigmentary property of the red pigment has a large effect on the color of the toner.

Table 2. Color as a Function of Opacity and Color Strength

$\gamma\text{-Fe}_2\text{O}_3$ with	L	a	b
opaque DPP	41.8	37.0	23.0
transparent DPP	39.9	35.7	20.6
low color strength red	45.7	27.4	27.0
red dye	41.9	33.9	23.0

Visually the most attractive red combination is the first one. The second one is darker and bluer, the third one appears almost as a brown, and the fourth also appears as darker and browner.

Influence of the Iron Oxide

The second component of the toner is the iron oxide. Its influence can be visualized with the following data:

Table 3. Influence of the Iron Oxide

DPP red with iron oxide...	L	a	b
black magnetite	40.8	10.7	6.9
$\gamma\text{-Fe}_2\text{O}_3$	42.5	37.0	24.0
more transept. $\gamma\text{-Fe}_2\text{O}_3$	43.6	36.9	21.6

The obvious switch from the black magnetite to the brown γ -iron oxide has a huge influence. Because of the low color strength of the Siren oxide further optimization here has a smaller overall effect than optimization of the red pigment, despite the fact that the $\gamma\text{-Fe}_2\text{O}_3$ is the major component.

Influence of the Quantity of Pigment on the Print

The effect of the print density (the quantity of toner/pigment on the paper) can also be simulated:

Table 4. Color as Function of Print Density

rel. quantity	L	a	b	hiding
2.0	42.4	35.4	22.8	0.3
1.0	42.5	37.0	24.0	2.8
0.5	44.5	42.4	26.8	8.6
0.25	48.7	50.9	33.4	23.1

Above the relative density of 1 the color is quite stable. If the relative quantity drops below 1 the white background starts to shine through. This results in a dramatic shift of the color towards a saturated red. This effect is caused by the large difference in color strength between the $\gamma\text{-Fe}_2\text{O}_3$ and the DPP red.

This experiment would imply that for red prints a small print density would be preferable. The drawback is the large color difference caused by the inevitable small variations of the print density. For practical purposes a hiding print density is preferred, which results at the above relative quantity of 1.

Composition of the Red Toner

As mentioned the standard black toner consists of $\sim 1/3$ magnetite. This corresponds approximately to the maximum pigment concentration for a toner with optimum performance. The major role of the resin is to ensure correct fixation of the toner on the paper. For this purpose, after the transfer, the resin is molten and thus is fixed on the paper. The viscosity of this melt has to be low enough to work properly. The viscosity of the toner increases with higher pigmentation. These viscosity problems are very common in many pigment applications like paint and printing inks. The viscosity of a pigmented system in general depends on the concentration, degree of dispersion, the particle size and form. For a given product, surface treatment and use of appropriate additives result in vast variation of the properties. For standard application like paints a great deal of knowledge has been acquired. For the magnetographic toners experiments have shown that surface treatment of the red pigment has a positive effect on the melt viscosity of the toner. The use of additives has similar effects but is accompanied by negative effects on other properties of the toner. At the present time not enough know-how has been acquired in this area and further progress seems possible.

The composition of the red toner is a delicate balance between color, magnetic properties and print performance. The maximum pigmentation being limited by the melt viscosity of the toner, the amount of $\gamma\text{-Fe}_2\text{O}_3$ set by the magnetic requirements and the amount of red pigment is the difference between the $\gamma\text{-Fe}_2\text{O}_3$ loading and the maximum pigment concentration: at the present time the maximum loading of the red pigment in the toner for acceptable viscosity for fusion and fixation on the paper is approximately half the γ -iron oxide concentration.

Performance of the Red Toner

Based on the results outlined above, the target of this project was to develop an optimized toner composition to reach the following three main objectives: maximal attractiveness of the color, processing characteristics that allow use of the available printers, and results in print quality comparable to the black toner. To achieve these objectives, the following three criteria have to be met: good toning on the magnetic dots, good fusion of the toner on the paper, and good color reproducibility of the color of the print.

Toning

For a good toning in magnetographic technology we need sufficient magnetic properties of the toner. We have

shown that a saturation magnetization of 15 - 18 emu/g, a remanent magnetization of 6 - 8 emu/g and a coercive field of 280 - 300 Oe result in a toner with correct toning on the magnetic drum. We have been able to achieve these requirements with a red toner based on a DPP red and a $\gamma\text{-Fe}_2\text{O}_3$.

Fusion

The fusion of the toner is directly dependent on its capacity to absorb the energy of the heating device of the printer. Red toners have a lower absorption of this energy than black toners. Experiments have shown that 20 - 30 % more heating energy is required for red toners compared to black toners.

The fusion characteristics depend on the viscosity of the toner. The following table shows the viscosity (in Pa.s.) as a function of the temperature and ratio resin to total pigmentation (sum of magnetic and red pigment).

As discussed above, the melt viscosity depends on the ratio resin/ pigments. In this toner composition the behavior of the magnetic and the red pigment are very similar.

Color of the Print

First print trials qualitatively confirm the coloristic model experiments. The actual prints seem to vary even more with changes in parameters than the model experiments suggested and visually the color looks more attractive.

One possible cause may be the fact that only approximately 90% of the white paper is covered with toner, which had not been simulated.

Table 5. Viscosity of the Toner

toner ratio resin/pigment	110°C	125°C	140°C	150°C
67/33 black	190	85	50	40
67/33 brown	190	100	60	50
80/20 brown	90	35	15	10
60/40 red	260	200	140	125
65/35 red	215	110	60	45

Conclusions and Outlook

The optimization of the red magnetographic toner requires a compromise between conflicting trends in magnetization, fusion and color. Thanks to close technical cooperation between Nipson and Ciba it has been possible to achieve an optimal result which would not have been possible by either party alone. Thus close technical collaboration between client and supplier was the key for the success of this project.

As indicated before, also a brown toner based on γ -iron oxide alone has been achieved. Thus a red and a brown magnetographic toner are available which can be used on standard equipment without major modification. We think that we soon will also be able to develop green and blue toners based on the experience gathered so far. Producing bright yellow and thus entering the trichromic printing technology with magnetographic toners requires fundamentally new approaches or colorless magnetic materials and remains a dream in the foreseeable future.