Factors Influencing the Selection of Materials for Flash Fusing Pressure Sensitive Conductive Magnetic Monocomponent Toners

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Abstract

The factors controlling materials suitable for flash fusing pressure sensitive conductive magnetic monocom-ponent toners to meet the demands of high speed non impact printing have been studied. These toners are particularly applicable to the Delphax Imagefast range of Electron Beam high speed printers. The machines are unusual in that they combine inductive magnetic toner development with pressure transfix of the toned image to bond paper.

The requirements of the melt rheology of the materials are examined in relationship to the fusing properties of the experimental toner formulations. Scanning electron microscopy is used to examine the fused toner surfaces. This is in particular to aid understanding of surface resistance to abrasion of the toned images when subjected to the stringent demands of the latest US Postal sorting equipment.

Differential scanning calorimetry has been used to compare the raw materials. The evolution of volatiles from the low molecular weight polymers present problems when subjecting the materials to the high temperatures involved in flash fusing. Weight loss and Gas Chromatography linked to Mass Selective Detection has been used to identify the materials which contribute most to the problem.

Introduction

The utilisation of flash fusing for conductive magnetic pressure transfe/fixable toner places considerable constraints on the materials suitable for forming a pigment binder system. The requirements for rapid melting and pressure sensitivity whilst maintaining an adequate resistance to blocking must be carefully considered. Acceptable levels of volatile release are required. This is to prevent overloading of flash fuser filtration system during high volume print runs.

The resins and waxes selected to meet these conflicting properties must also exhibit compatibility to ensure pigment dispersion is satisfactory during melt blending and that the polymers do not separate when the system is molten.[†]

A number of papers in the past have dealt with non contact fusing. Lee¹ identifies 3 stages during fusing. Coalescence by sintering accompanied by shrinking, subsequent

spreading followed by penetration into the paper fibres. The following equations indicate that toner melt rheology plays a major factor in non contact fusing.

Three shift factors determined for sintering, spreading and penetration respectively are shown below.

$$\tau_{ST} = \gamma a_o / \eta$$

$$\tau_{SP} = \gamma r_o \cos \theta / \eta$$

$$\tau_P = \gamma \delta \cos \theta / \eta$$

 γ = surface tension θ = contact angle of drop α_0 = original radius

 η = viscosity

 r_o = original radius of cap

Toners today must produce prints able to withstand the demands that modern mechanisation of document handling and scanning places on them. The latest US Postal sorting equipment has been reported to produce an offsetting effect from documents generated by many of today's laser printers. Toners which must exhibit a level of pressure sensitivity such as those used in the current range of high speed Electron Beam print engines may be susceptible to this phenomenon. The US Postal effect results in a replication of the printed image on opposing faces of the document and envelope. This appears to be a surface rather than bulk effect. Microscopic examination of the final fused toner surface is pertinent.

Studies of the temperatures reached at both the toner surface and toner paper interface have been made by a number of groups including Mitsuyu², et al and Katugiri³, et al. Both reach similar conclusions that the during the milli seconds of flash fusing with a typical fuser, the peak temperatures at these points are of the order of 200°C and 120°C respectively. Thus rheological and thermal studies have been carried out within this range.

The object of this paper is to identify the properties of the raw materials most relevant to flash fusing performance via a number of experimental toner formulations.

Experimental

The Printing and Fusing System

Prints from the toner formulations were prepared by printing them in a Delphax Electron Beam printer. The re-

[†] errata paragraph submitted by author

sultant prints which were pressure transfixed within the machine were flash fused off-line using a Delphax bench top unit operating at a charging voltage of 1.7kV corresponding to a typical surface energy of 1.2 J/m2. This gives a surface energy comparable to that from the current range of Delphax Imagefast 180 EBI printers. Since the toners are conductive they develop by the induced charge mechanism. The main force opposing development is the magnetic counter force from within the toner particles. The threshold voltage for background development is highly dependent on this force. Obviously this in turn depends on the level of magnetic oxide within the toner for a fixed toner conductivity.

The magnetic oxide content of the experiment toners were set between the following limits. Minimum of 50% to maintain an adequate threshold voltage and less than 65% since above this level the melt rheology is significantly affected.

Toner Raw Material, Formulation and Preparation

Polyester resins were combined with waxes of widely differing properties. The toners were prepared by melt blending the binder polymers with magnetic oxides over the levels described above. Subsequent melt blends were milled, classified and then external carbon black added to reduce the toner resistivities to approximately 1×10⁵ ohm/cm. Table 1 summarises the major properties of the polyester resins and waxes.

The experimental toner formulations used for this study are described in Table 2.

Fusing—Assessment of Prints

A suite of tests were applied to the print samples to compare fixing/fusing of the different toners. Both pre and

post flash fusing levels were evaluated.

- (a) Tape test—180° 3M Scotch™ Magic™ Tape peel test on a checkerboard print sample.% reduction in P.D. of a solid square.
- (b) Crease test—Standard crease generated by passing a folded checkerboard area through chromed rollers. % crease determined as described by Neilson⁴.
- (c) Post Office Offset—Amount of toner transferred to clean bond paper by testing a checkerboard square in a rig simulating the Post Office effect.
- (d) Print through—P.D. change of paper when a scanning loaded needle is applied to the back a checkerboard square face down on clean paper.

Effluent

A general indication of the levels of volatiles available for release was obtained by the following method. A known weight of toner was held at 180°C for 24 hours. The percentage weight loss was measured. This test was carried out both for the toners and binder polymers. Confirmation that the majority of effluent resulted from the breakdown of wax A was obtained by Gas Chromatography linked to a Mass Ion Detector.

Hardness

To give an indication of the relative surface hardness of the toner formulations tablets of toner were produced by heating toners in a mould under a load of 16 tons at 40°C. The tablet surfaces were then tested for hardness by an established pencil hardness method.

Material	Melting Point °C	Tg °C	Molecular Wt. Mw Mn Mw/Mn			Effluent % wt	Penetration © 25°C mm	a Acid No.
Polyester P ₁	_	56		3,200		3.2	-	~ 75
Polyester P ₂	-	54	18,000	3,300	5.46	1	-	5 - 15
Wax A *	106	-	300 - 400	-	-	21.5	10	4
Wax B *	127	-	500 - 600	-	_	3.3	7	3-5
Wax C * *	107	-	700 - 900	-	-	2.5	2	0

Table 1. Polyester Resin and Wax Properties

Table 2. Experimental Toner Formulations

Material	Toner						
	1	2	3	4	3	6	/
Mag. Oxide	61.5	56	51.5	51.5	51.5	51.5	51.5
Polyester P ₁	24.5	28	31	31	31	31	-
Polyester P ₂							31
Wax A	9	10	11	17.5	-	-	11
Wax B	-	-	-	-	11	17.5	
Wax C	5	6	6.5	-	6.5	-	6.5

^{*} Wax compatible with polyester P₁ and P

^{* *} Wax incompatible with polyester P_1 and P_2

Rheology

The rheological properties of the experimental toners and polyester resins were examined using a TA Instruments CSL 500 controlled stress rheometer with a 4cm. parallel plate geometry. Creep tests were performed on the toners at 135°C. this temperature being selected as providing the most useful data from earlier MFI measurements. The steady state viscosity was calculated from these measurements.

Electron Microscopy

Print samples were examined at a magnification of X200 using a Jeol JSM 5300 scanning electron microscope.

Results and Discussions

The dynamic viscosities of the toners at 135°C are given in Table 3. Figure 1 shows a comparison of the viscosity against temperature profiles for the two polyester resins. The corresponding creep curves from which this data were calculated are shown in Figure 2 below.

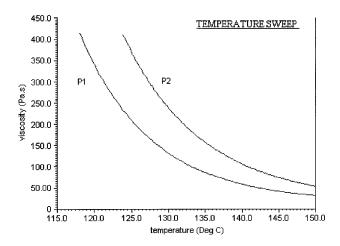


Figure 1. Viscosity v. Temperature for Polyesters P1 & P2.

The viscosities of toners 1 - 3 are as expected, the viscosity reducing as the oxide content is lowered whilst maintaining a constant ratio of 1:2.7 of wax to polyester resin. Although the viscosity of P2 is higher than P1 the resulting viscosity of toner 7 is lower than toner 3. This is surprising since the formulations are identical except for the polyester resins. This can be explained if the compatibility of P2 for the waxes is lower than for P1 giving the appearance of a higher wax content.

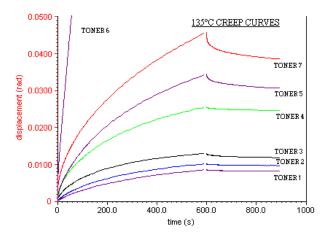


Figure 2. Creep Curves for experimental toners.

Table 3 summarizes the results of the fixing, effluent and hardness tests on the toners. Print densities both pre and post flash fusing are recorded.

US postal offset is visibly worse with increasing oxide content. Toner 4 is identical to toner 3 except its wax content consists solely of the low melting point soft wax A. General fusing is improved but at both the expense of postal offset and print through. Toners 5 and 6 correspond to toners 3 and 4 but replace the low melting point wax with a harder, higher melting point wax B. From Table 5 it can be seen that this results in a substantial lowering of the effluent(volatiles) by approximately 50%. Fixing however is reduced. Incorporation of the incompatible wax C in toners 3 and 6 is beneficial in reducing postal offset.

Table 3.	Experimenta	ıl Toner	Fusing	Resu	lts
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Toner	P.D. Pressure	P.D. + Flash	Tape % Pressure	Tape % +	Crease % +	Post Office	Print Thru	Pencil Hardness	Effluent % Wt. Loss
	Fix	Fuse	Fix	F/F	F/F	P.D.	P.D.		180°C
						F/F	F/F		
1	1.38	1.26	31.1	99.5	74.8	0.086	0.28	4B	5.5
2	1.38	1.32	30	99.3	74.4	0.082	0.33	3B	5.5
3	1.52	1.44	25	99.8	77.3	0.078	0.39	2B	6
4	1.46	1.38	28.5	99.4	74.8	0.094	0.37	4B	7.2
5	1.41	1.25	18.9	99.9	65.1	0.081	0.22	3B	1.9
6	1.42	1.34	24.2	99.4	60.8	0.088	0.28	3B	2.9
7	1.28	1.19	23.4	99.5	59.7	0.088	0.24	H.B.	4.7
H.R.	-	1.41	-	58.8	64.5	0.071	0.11	-	-

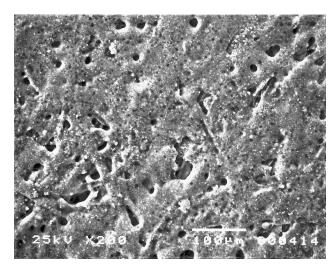


Figure 3. Toner 3 X200

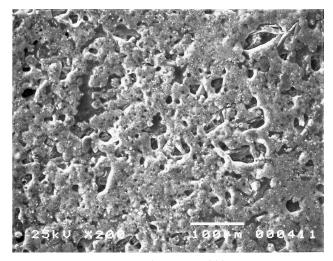


Figure 4. Toner 7 X200

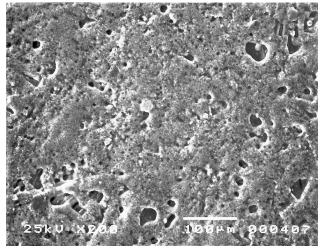


Figure 5. Toner 4 X200

Toner 7 surprisingly shows the poorest level of fixing for all toner formulations SEM micrographs below compare toners 3, 4 and 7.

Figure 3 shows a solid area of print made with toner 3. The toner is seen to have flowed and wetted the paper fibres forming a well integrated surface.

Figure 4 is from a print made with toner 7. Here the toner either has not flowed well, or has not wetted the paper fibres to the same degree. A rougher surface is evident.

Figure 5 represents a solid image made with toner 4. As can been seen the toner has again flowed well and wetted the paper fibres.

From Table 3 in terms of overall fusing toner 3 makes the best compromise in providing excellent tape and crease performance whilst also giving a significantly superior Post Office test result. It maintains a level of pressure sensitivity although slightly inferior to toners 1,2 and 4. Toner 7 produces a surprising result when compared to toner 3. The formulations differ only in the polyester and the thermal properties of P1 and P2 do not appear to differ significantly yet its flash fusing is the poorest. This suggests when reexamining Table 1 that the chemical and mechanical properties as indicated by the considerably differing acid number are more significant than the melt rheology.

Toner 4 gives again good overall flash fusing properties but vastly inferior resistance to mechanical handling. Again melt rheology is not a factor but the surface hardness is insufficient to resist abrasion. Toners 5 and 6 help address the effluent problem.

Conclusions

We have seen that combining the properties of pressure sensitivity and flash fusing lead to compromises in formulation. Low melting point soft waxes impart pressure sensitivity and are beneficial in lowering a magnetic toners melt viscosity. They however have an undesirable influence in producing unwanted effluents owing to their volatility and provide toner surfaces with insufficient mechanical resistance. The choice of the binder resin must not be ignored and chemical and mechanical properties are at least as important as rheological considerations. Surface tension and surface energy studies are needed to help define the important factors.

Acknowledgements

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