Effect of Paper Properties on Fusing Fix

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The term "fusing fix" denotes the degree of permanence of an electrophotographic toner image that has been thermally attached to a paper substrate by a hot roll fuser. The widespread change from acid to alkaline papermaking for commercial copy papers was accompanied in many cases by a reduction in fusing fix. To study this problem, a set of 25 model papers was produced with three different types of internal size, three types of inorganic filler, and three types of surface treatment. The papers were extensively characterized for their chemical and physical properties, sample sets were printed in three different high-speed copiers, and the fusing fix of the resulting images was quantified by the crease test. Out of 47 measured parameters, the crease width had a significant correlation only with the dispersive component of the surface energies of the papers. A hypothesis was constructed to explain how changes in the paper constituents affect both the surface energy and fix of the papers.

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Introduction

In an electrophotographic copier or laser printer, the final step in making a permanent copy is to fix the thermoplastic toner particles to the paper substrate, usually with a hot roll fuser. In general the degree of permanence, or fusing fix, of the copy is determined by the properties of the fuser system, the toner, and the paper. Copy papers, like other fine papers, consist of bleached paper fibers along with inorganic fillers and an internal sizing material that gives the paper enough wet strength so that a surface application of starch and other additives can be applied in a conventional size press. Traditional paper sizing chemistry was based on the rosin–alum system, in which the paper fibers are made slightly hydrophobic by a light deposit, in an acidic pH environment, of a rosin material produced from the resinous substances found in softwoods. Under acid papermaking conditions, kaolin-based clay fillers are added to improve paper opacity and whiteness. Because almost all copy papers were produced in this way, early studies of fusing fix tended to focus on the rheological properties of the toner and considered only physical variables of the paper, such as roughness.[1–4] In the 1970s, to take advantage of low-cost, high-whiteness calcium carbonate fillers, a number of synthetic sizing chemicals that could make paper fibers hydrophobic under neutral or alkaline conditions were developed. These materials, such as alkyl ketene dimer (AKD), or alkenyl succinic acid (ASA), form chemical bonds with hydroxyl groups on the surfaces of cellulose fibers. The change from acid to alkaline papermaking was accompanied by an increased variability in fusing fix, which in a number of studies[5–9] was related to variations in the surface energy of the paper substrate. It is difficult to establish a quantitative relationship between fusing fix and paper chemistry using sets of commercial copy papers, because correlations may be confounded by variations in the physical properties of the papers or by the use of a wide variety of unknown surface additives. Therefore, in the present study, a set of laboratory-produced model papers was used to study the effect of paper properties on fusing fix.

Model Papers

Production. Using the principles of experimental design, a set of 25 model papers was constructed, as shown in Table I, to contain most of the constituents that would be found in commercial acid or alkaline copy papers. The initial set was designed as a screening experiment; therefore

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TABLE I. Experimental Design for Model Papers

Pulp	Internal Size	Filler
(1) Pulp only	(2) P + Rosin	(5) P + Rosin + Clay
	(3) P + AKD	(6) P + AKD + Clay
		(7) P + AKD + $CaCO_3$
	(4) P + ASA	(8) P + ASA + Clay
		(9) P + ASA + $CaCO_3$

Surface Size 1	Surface Size 2
(10) P + Rosin + Starch	(18) P + Rosin + Starch + SMA
(11) P + Rosin + Clay + S	(19) P + Rosin + Clay + S + SMA
(12) P + AKD + Starch	(20) P + AKD + Starch + SMA
(13) P + AKD + Clay + S	(21) P + AKD + Clay + S + SMA
(14) P + AKD + $CaCO_3$ + S	(22) P + AKD + $CaCO_3$ + S + SMA
(15) P + ASA + Starch	(23) P + ASA + Starch + SMA
(16) P + ASA + Clay + S	(24) P + ASA + Clay + S + SMA
(17) P + ASA + $CaCO_3$ + S	(25) P + ASA + $CaCO_3$ + S + SMA

Table II. Characterization of Model Papers

Composition	Physical
% Moisture	Basis Weight
% Filler	Caliper
Sizing: Size press pickup	Roughness: Sheffield
Hercules size test	Parker Print Surf
AKD extraction	MicroTopograph
Surface Energy: Zisman	
Disp. & Polar	Bending: Taber stiffness
	Sonic tests
Surface Composition:	XPS Static Charge
Drifts	Formation

Responses	
Transfer:	Toner mass/area (TMA)
Fusing fix:	Crease test, Copier 1 (135 cpm) Crease test, Copier 2 (90 cpm) Crease test, Copier 3 (50 cpm)
Friction:	Static Kinetic

each constituent was added at only one level. Pulp batches were prepared with only wood pulp (75% hardwood, 25% softwood), or pulp plus conventional acid rosin internal size (0.5% by weight Pexol-200 from Hercules, Inc.), or pulp plus one of two types of alkaline internal size: AKD (0.2% Hercon 70 from Hercules, Inc.) or ASA (2% Nalsize 7540 from Nalco, Inc.). In each case, pulp batches were prepared with no inorganic filler or with the addition of 15% clay or 15% ground calcium carbonate (with the exception that $CaCO_3$ cannot be added to acid-sized pulp).

Model paper sheets were produced on an Allimand Formette Dynamique centrifugal former for each of the pulp batches corresponding to papers (1) to (9) in Table I. The internally sized base sheets, (2) to (9), were each divided into three sets. One set was left with no surface treatment; another set was surface sized in a KRK Laboratory Size Press with a 10% starch solution, resulting in a 5 wt% starch pickup on each sheet; and the third set was surface sized with a starch solution containing 3% (by weight of starch) of a styrene–maleic anhydride (SMA) copolymer (Scripset 740 from Hercules, Inc.), which has become popular in the paper industry as a surface additive for alkaline papers. After surface treatment, the model paper sheets were calendered to improve the surface smoothness. Between 21 and 24 8.5 × 11-in. sheets were produced for each of the 25 model papers. Twelve sheets were selected for printing in electrophotographic copiers, and the remaining sheets were used for characterization.

Characterization. After production, the model papers were stored in controlled (TAPPI) conditions of 73°F and 50% RH. The papers were extensively characterized for their physical and compositional properties, as listed in Table II. The composition of each sheet was analyzed, because it could differ from the composition of the initial pulp batch through varying retentions of each component. The surface energies of each paper (except unsized pulp) were calculated from contact angle measurements. The critical surface tension was calculated using the Zisman method[10,11] and the standard series of six homologous liquids. In addition, the dispersive and polar components of surface energy were calculated, using the method of Owens and Wendt,[12] from the contact angles of water and diiodomethane. The surface composition of each model paper was also studied with x-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

The physical properties of the model papers, such as density, roughness, stiffness, charge acceptance, and formation, were monitored to determine if they were comparable to those of commercial copy papers, thereby ensuring that the model papers could be run in high-speed copiers. In addition, these physical properties could be correlated with fusing fix. Whereas the object of the model paper study was to vary only the chemical composition of the sheets, some variation in physical properties is inevitable. For example, Fig. 1 shows the variation in porosity, as measured with the Parker PrintSurf device. Clearly, there are no significant differences in porosity due to internal size. However, the addition of fine inorganic filler particles does reduce porosity, and the platelet-shaped clay particles, with greater surface area per unit volume, are more effective than ground $CaCO_3$ in reducing porosity.

For each sample set, the progression of data points from left to right is uncoated base sheet, base sheet plus starch surface size, and base sheet plus starch plus SMA. It appears that the addition of 0.15% SMA to the sheet has almost as large an effect on porosity as does the addition of 5% starch. This result suggests that SMA is acting as a film former and is more effective than starch alone in sealing the sheet surface.

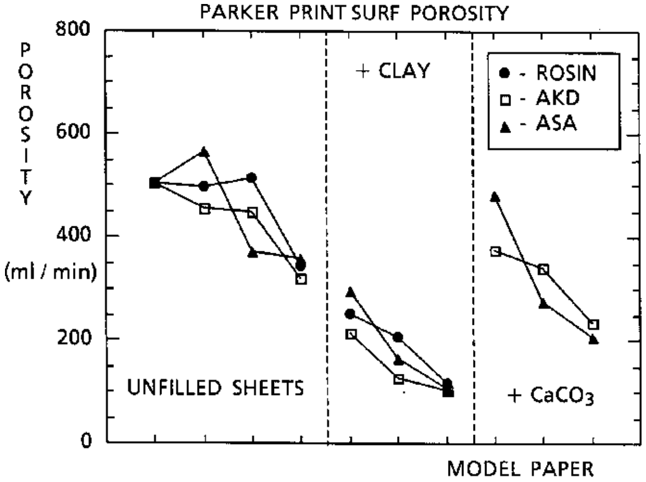

Figure 1. Porosities of the 25 model papers. For each set of samples, the progression from left to right is uncoated base sheet, base sheet plus starch suface size, and base sheet plus starch plus SMA.

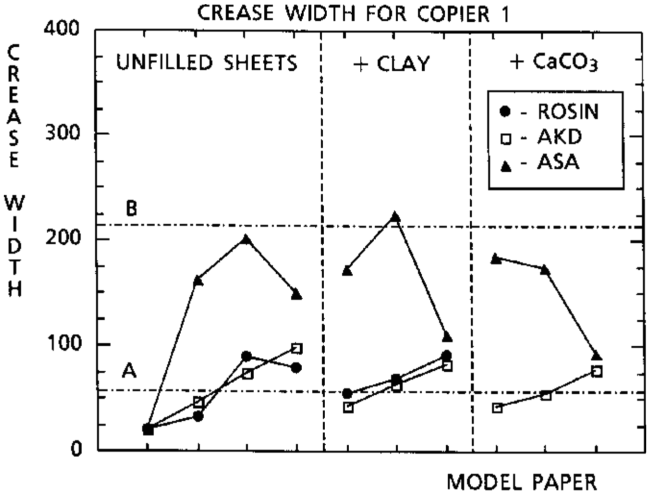

Figure 2. Crease widths of toner images printed on the model papers in Copier 1 (135 cpm). The broken lines are the crease widths on commercial alkaline copy papers A and B.

Fusing Fix

As noted in Table II, model paper sample sets were printed with a test pattern in three different high-speed electrophotographic copiers. Three sheets of each of the 25 model papers were printed in each copier. The sample sets were randomized and printed in a continuous run between large quantities of commercial copy paper. Each of the model paper sheets was conditioned to 50% RH and weighed before and after printing to monitor the transferred toner mass per unit area (TMA). There was found to be no significant variation in TMA among the model papers, which could otherwise have produced an apparent variation in fusing fix. The test pattern consisted of a number of solid areas and line copy, including three 1.5-inch-long solid areas arrayed along the axis of the hot roll fuser in each machine.

There are a number of ways of measuring the permanence of a fused electrophotographic image.[3] One such method is the crease test, in which the printed sheet is folded and creased under a known weight, with a solid area fused toner image to the inside of the fold. The sheet is then unfolded and any loose toner is wiped from the resulting image defect. An image analysis system is used to measure the average width of exposed paper along the crease. The crease width (in arbitrary units) for the 25 model papers printed in Copier 1 [135 copies per minute(cpm)] is shown in Fig. 2. Each data point is an average of nine measurements (three per sheet along the fuser roll axis and three sheets per model paper). The broken lines in Fig. 2 indicate the crease widths for two commercial alkaline copy papers, A and B, with excellent and poor fusing fixes, respectively, which were printed along with the model papers. It can be seen that the crease widths for most of the experimental papers fall within this range. In all cases, the crease width is largest (i.e., poorest fusing fix) for the papers with ASA internal size. It is apparent from the graph that inorganic filler has no significant effect on the fix. In all cases, when starch surface sizing is added to the base sheet, the crease width increases. When 3% SMA surface additive is added to the sizing, in some cases the crease becomes larger and in other cases smaller. In all cases, however, the addition of SMA reduces the variation in fix among the three types of internal size. Similar trends were noted in the fusing fix from Copiers 2 and 3.

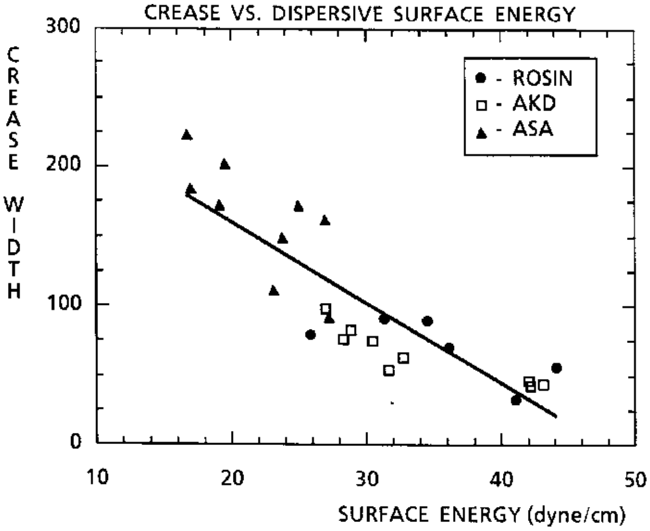

Figure 3. Correlation of crease width of toner images from Copier 1 with the dispersive component of surface energy for the model papers. Data points are distinguished by the internal size of the paper.

Surface Energy

The purpose of this study was to find the properties of paper that affect the fusing fix. To that end, RS/1 statistical analysis software was used to search for correlations between fusing fix, as measured by crease width, and 47 different physical and compositional measured parameters for each model paper, obtained from the characterization tests listed in Table II. We found that the only significant correlations were with the dispersive component of the surface energy and, to a lesser degree, the Zisman critical surface tension. This is illustrated in Fig. 3 for crease widths of toner images from Copier 1. Similar correlations were obtained for Copiers 2 and 3. It is apparent from this figure that there is no intrinsic difference in fusing fix on alkaline, as opposed to acid, sized papers, because all papers lie on the same line. The ASA-sized sheets have the lowest surface energy (and highest crease width) only because ASA was added to the model papers in higher concentrations than AKD or rosin.

The discovery of a correlation between fusing fix and paper surface energy immediately suggests that surface

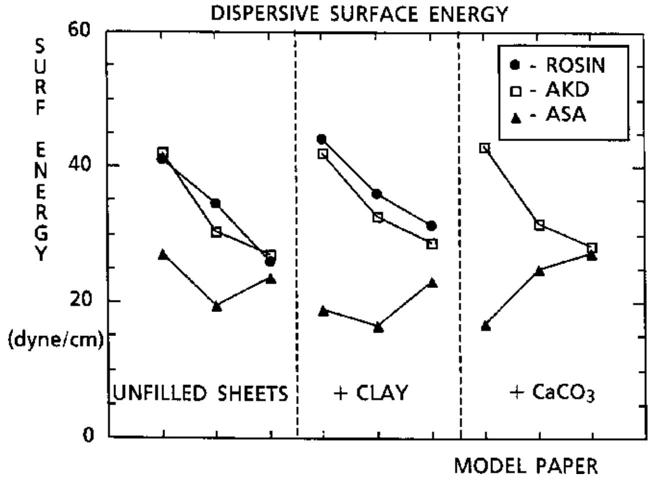

Figure 4. Dispersive component of surface energy for the model papers.

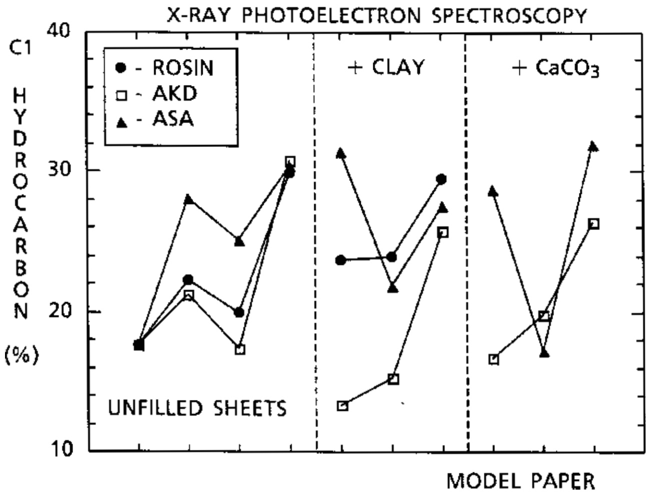

Figure 5. Percentage of carbon atoms on the surface of each model paper in the C1 (hydrocarbon) state, as measured by XPS.

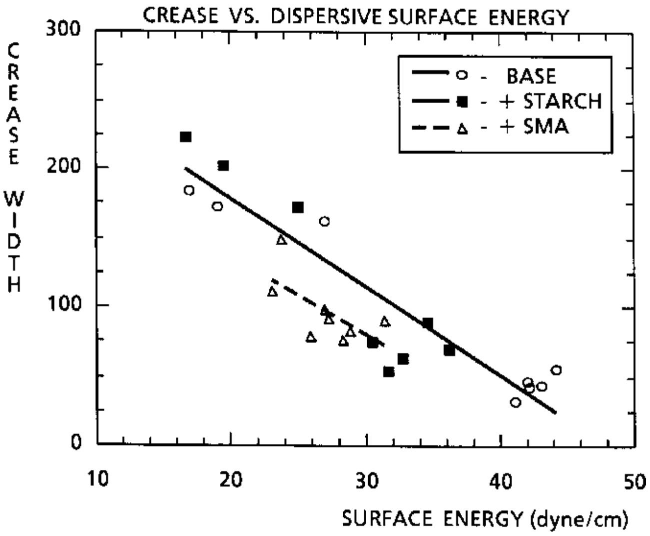

Figure 6. Correlation of crease width of toner images from Copier 1 with the dispersive component of surface energy for the model papers. Data points are distinguished by the surface treatment of the paper.

energetics are controlling the wetting and spreading of molten toner on the paper substrate. However, the macroscopic area of intimate contact between fused toner and paper fibers does not depend on paper surface energy, but is controlled by the fusing conditions of temperature and pressure and by toner melt rheology. Within this contact area, however, the surface energies of paper and toner determine the degree of microscopic wetting, the formation of a solid–liquid interface during fusing, and the strength of the intermolecular forces (presumably dispersive)[12] that produce the solid toner–paper bond after fusing. Similar results have been found in the adhesion of extruded polyethylene films to paper,[13] where the contact area between film and paper depends on the extrusion conditions, but at constant contact area the peel strength of the bond is controlled by the surface energy of the paper.

We can construct a hypothesis as to how the composition of the paper determines its surface energy, which in turn determines fusing fix. With reference to Fig. 4, it is apparent that the addition of 15% inorganic filler (clay or $CaCO_3$) has no significant effect on surface energy (or fix). The initial variation in surface energy (leftmost data points) is due to the different amounts of internal size material in the three different sheets. When starch surface size is added to the sheets, the surface energy (and the fix) is lowered further; however, in a conventional size press application, the starch does not uniformly cover the sheet surface, so internal size material in the base sheet is still exposed, and thus there are still variations in surface energy and fix among the three types of paper. When 3% SMA is added to the surface size, however, it acts as a film former and effectively masks the internal size from the molten toner. Therefore, in all cases there is little variation in surface energy (or fix) among the three types of paper. This hypothesis is supported by analysis of surface composition of the model papers by XPS.[14,15] Figure 5 shows the percentage of carbon atoms at the surface of each model paper that are in the C1 state, i.e., singly bonded to other carbon atoms or to hydrogen. In pure cellulose or starch, carbon atoms are either singly or doubly bonded to oxygen, so the C1 state can be associated with synthetic internal size or surface additives such as SMA. The effect can most easily be seen for the unfilled sheets. The sheet composed of pure pulp has the lowest C1 concentration. When internal size is added, the C1 concentration rises in all cases, with the largest increase for ASA. When starch surface size is added, some of the internal size is masked, so that the C1 concentration goes down, but there is still variation among the three papers. Finally, when SMA is added, it contributes to the surface hydrocarbons, so that the C1 content increases; however, as a film former it masks the internal size molecules from the surface, so that the C1 content is the same for all three types of paper.

Finally, Fig. 6 shows the correlation between crease width and surface energy where the data points are grouped according to surface treatment rather than internal size. Because of its film-forming behavior, the papers treated with SMA extend over a much smaller range of surface energy (and crease width) than the other papers. It was also noted that all the SMA data points fell below the linear regression line in Fig. 3 and, in fact, if the SMA- and non-SMA-treated papers were separately fitted to straight lines, the SMA-treated papers fell along a separate line with the same slope as the regression for the other papers, but were offset by a constant amount, as shown in Fig. 6. This effect is more striking in the results for the lower speed copier shown

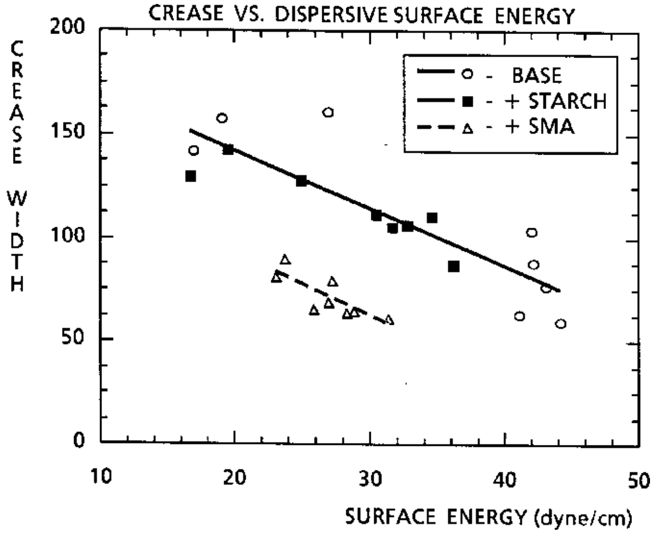

Figure 7. Correlation of creae width of toner images from Copier 3 with the dispersive component of surface energy.

in Fig. 7. Similar fits were found for data from Copier 2. These results mean that, in addition to masking internal size from the molten toner, the SMA surface additive improves the fusing fix via a specific interaction with the toner. The most likely interaction is via chemical compatibility between the SMA surface additive and the styrene-based toner resin.

Conclusions

If the physical properties of a set of papers are held constant, then the fusing fix for these papers in a high-speed electrophotographic copier is determined entirely by their surface energies. There is no inherent difference in fusing fix on alkaline-sized compared to acid-sized papers. Early alkaline papers tended to have a poor fusing fix because of higher than necessary sizing levels. The addition of inorganic fillers, either clay or $CaC0_3$, at the 15% level had no significant effect on either surface energy or fix. Whereas starch surface sizing of copy papers is required for stiffness and surface strength, it does tend to lower both surface energy and fusing fix; moreover, because a conventional size press applies starch in a discontinuous coating, fusing fix is still affected by the base sheet chemistry. When a surface additive such as styrene maleic anhydride is included in the surface size, it can improve the fusing fix in two ways. As a film former, it masks the internal size from the molten toner, and it also exhibits a specific interaction with the toner polymer, probably due to styrene–styrene chemical compatibility.

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