Internal Release Agents for Electrophotographic Toners

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Continuous improvements in printer resolution place greater demands on toner performance. As the pel size becomes smaller, the requirements for edge definition and the elimination of hot offset increasingly become limiting factors in determining print quality. Edge definition, resolution, and offset can be addressed to some extent by improved charge control for narrower charge distribution and elimination of wrong size toner. Another contribution to the offset lies in the adhesion of toner to the fuser roll and subsequent redeposition on the paper where it is not intended. This study evaluates wax internal release agents to determine which combinations of waxes and additives, including block copolymers and polydimethylsiloxane oils, provide the best release properties. Primarily the focus is on polyethylene and polypropylene waxes. There is little effect of polyethylene wax molecular weight on peel strength. Lowest peel strength is with polyethylene wax and polydimethylsiloxane oil. Lowest offset with little effect on tribocharging is with polypropylene wax and polydimethylsiloxane oil. Release properties are controlled by the distribution of release agent between surface and bulk as well as the dynamics of migration from the bulk to the surface. X-ray photoelectron spectroscopy is suggested as a sensitive means for further analysis of these effects.

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Introduction

The key elements of electrophotography as employed in photocopiers and printers have changed little since its inception. A photoconductor is charged by corona wire at high potential to ionize air molecules. The ions follow the electric field to the photoconductor. An image pattern in the charge is created by selective exposure to light, e.g., laser. Incident photons generate electron–hole pairs that neutralize the charge in the exposed areas. Charged toner is repelled from unexposed regions and selectively deposits on the image area. Toner is then transferred from the photoconductor to an oppositely charged paper or a transparent sheet. The thermoplastic toner is then fused onto the sheet between heated rollers. Residual toner is cleaned off the photoconductor by a brush or cleaning blade. For the process to be robust and function properly for many printing cycles, the toner must not accumulate on or contaminate the photoconductor, cleaning tool, or fuser roll. This study focuses on the release of the toner from the fuser roll.

In the past, much consideration has been given to the deformation and flow properties of the toner melt during fusing.[1] The melt rheological properties of the toner resin during fusing are now adequately controlled by lightly cross-linking toner resin below the gel point.[2] The current issue in fusing is the sticking of the melt to the fuser roll or release.[3] This shows up as unwanted smudges and hollow character defects. The fuser roll is made of a low-energy polymer such as Teflon to reduce its adhesion to the melt. Adhesion has been further reduced by applying a thin film of siloxane oil to the fuser roll. This oil provides adequate release but also presents several disadvantages. Additional hardware (i.e., expense) is needed to maintain the oil film, and the siloxane oil degrades over time with the continued exposure to high temperature. If an elastomeric fuser roll is used, the oil can swell it. The current trend is to eliminate the need for the oil on the fuser roll by incorporating an internal release agent in the toner.

The most straightforward approach to toner internal release from the fuser roll is to employ the technique already used during injection molding of thermoplastics. A mold release agent or internal lubricant is incorporated at low concentration in the thermoplastic matrix. The concentration of the release agent is kept low enough so as not to impact the mechanical or flow properties of the finished product. The release agent should have a comparable or lower melt viscosity than the matrix at the processing temperature, adhesion at the interface should be low, and the release agent should be immiscible in the matrix, so that it provides an interfacial layer and exists as finely dispersed liquid droplets within the bulk of the matrix.

As the drawbacks of a wicking oil on the fuser roll used as a surface release agent became more apparent during the past decade, toner design engineers began to incorporate the concept of internal release agent into the toner. Initially, traditional release agents such as beeswax and carnauba wax were added to the formulation.[4–8] These materials showed some modest improvement in release properties as reduced offset, but had their own shortcomings. The waxes alone tended to film (or plate out) onto the developer roll and cleaning blade, which interfered with tribocharging and gave rise to "blooming" of the print. This unwanted exudation was attributed to the low viscosity of the traditional waxes. Melt viscosity of straight-chain hydrocarbons, which increases with increasing molecular weight, led to the substitution of moderate molecular weight polyethylene (PE) and polypropylene (PP) for the wax ($1500 < Mw < 6000$),[9] although PE and PP in this molecular weight range can also be considered waxes.[10] The combination of PE or PP with or without waxes and fatty acid salts or long-chain alcohols greatly improved the release properties without the need for a lubricated fuser roll. Their use has led to a plethora of patents.[4–9,11–22] The key features of this class of wax-containing internal release agent are summarized below.

An internal release agent that is immiscible with the toner resin is schematically illustrated in Fig. 1(a). The

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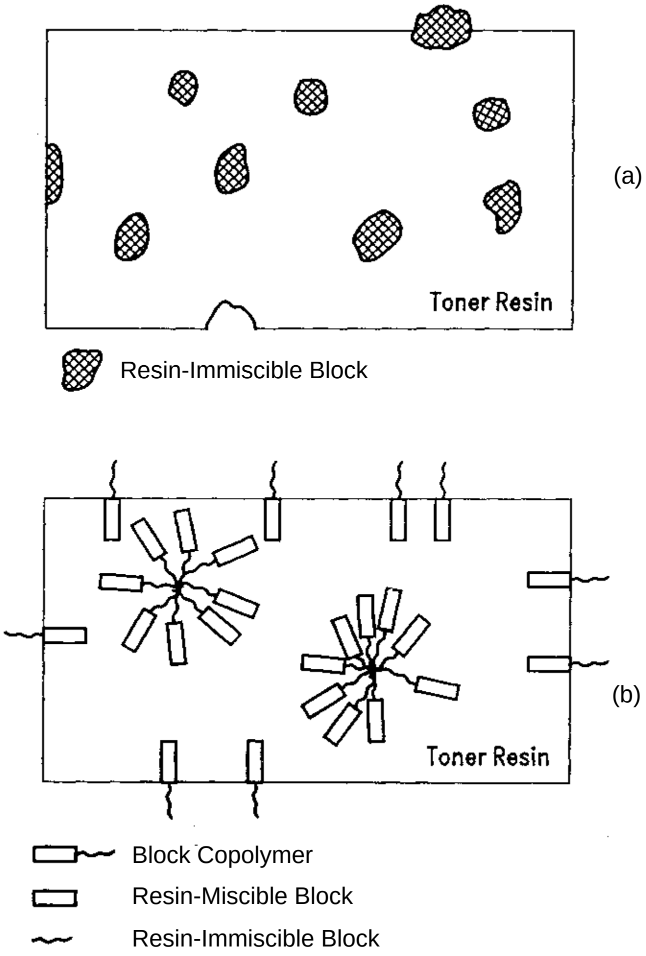


Figure 1. Schematic structure of an internal release-agent-containing toner melt showing (a) a resin-immiscible release agent and (b) a resin-miscible/resin-immiscible block copolymer.

release agent exists as domains that are smaller than the particle size of the toner. When the blend is fractured after melt mixing, some of the release agent domains may protrude from the surface, others can fracture evenly with the surface of the resin, and domains can be pulled out. Only release agent that is exposed at the toner interface is effective as a release agent, forming a film between the print and the fuser roll. Numerous combinations have been reported to control the release agent domain particle size and properties.[12] A low molecular weight wax can be used in solid solution with the PE or PP to tailor melt properties. Fatty acid salts[11] and long-chain alcohols[9] were found to act as surfactants and to improve the dispersion of release agent during melt mixing. Improved dispersion increases the effectiveness of the release agent by increasing the probability of domains being exposed on the fractured surface of the toner particle.

Another approach to the incorporation of internal release agent in the toner is the application of block copolymers. One way to improve the compatibility of the wax with the toner resin is to use a block or graft copolymer with one block having the same composition as the resin and the other block being a straight-chain hydrocarbon. Hence, one block is miscible in the resin and the other block is miscible only with itself (forming micelles) and is also miscible in any wax homopolymer. A commercially available block copolymer of styrene/butylmethacrylate and wax was found to improve release properties,[23] and others were found to improve the dispersion of wax.[24]

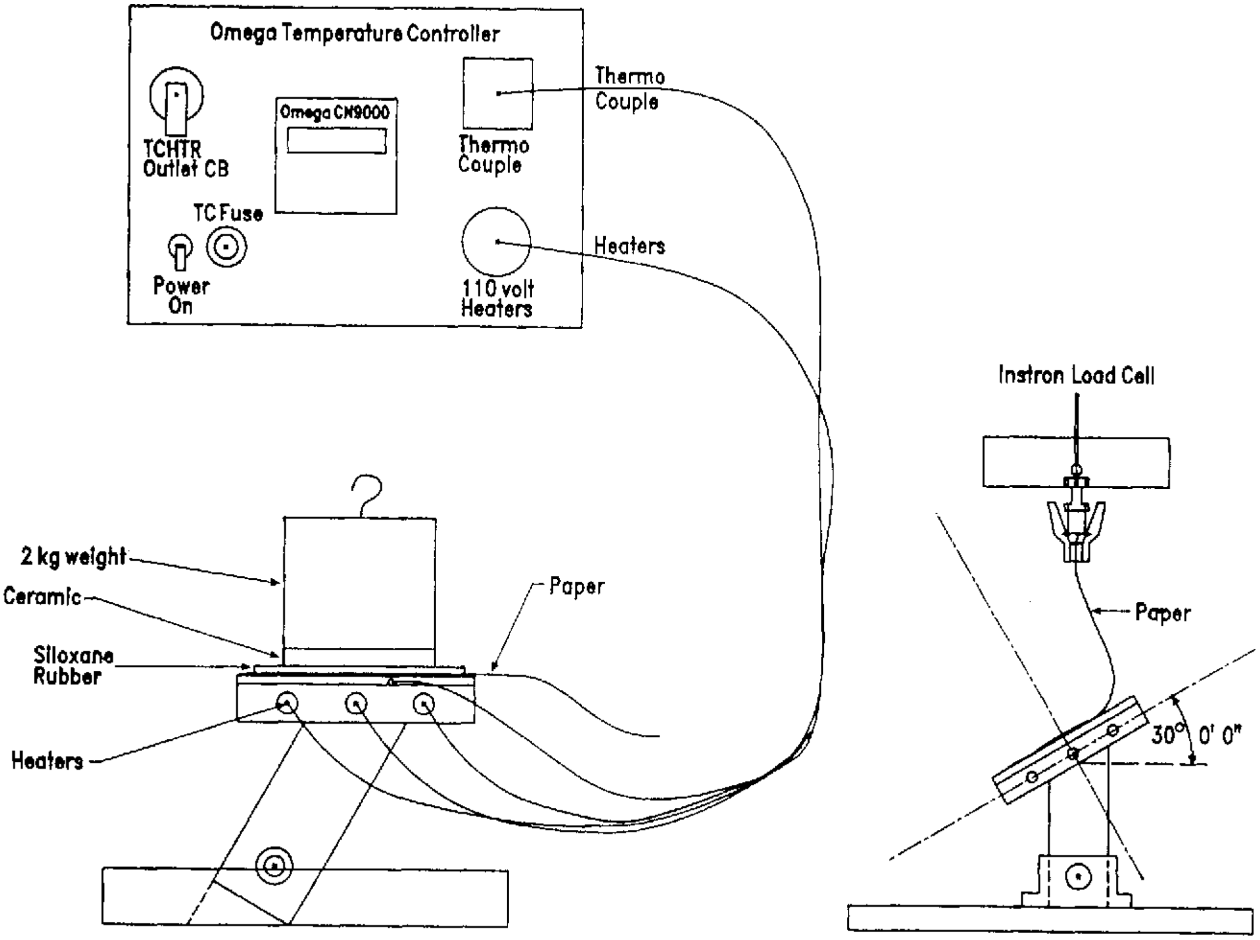
The fact that polymers other than wax could present a low-energy surface to the fuser roll was also considered. Because polydimethyl siloxane (PDMS) oil had been applied to the fuser roll previously for improved release and reduced hollow character defects, toner scientists included siloxane oil in the toner formulation. Use of the PDMS alone as an internal release agent produced filming of the photoconductor, adversely affected tribocharging, and PDMS exuded from the toner, causing agglomeration. These problems were overcome by incorporating an organosiloxane block copolymer in the toner.[25] This resulted in an internal release agent structure shown schematically in Fig. 1(b). An organic block is designed to be miscible with the resin and the siloxane block is immiscible with the resin. At a sufficient concentration, micellar domains form, and block copolymer tends to exude onto the exposed surface. This is a general phenomenon that occurs for organosiloxane block copolymers blended with a polymer matrix.[26] A similar type of block copolymer using a fluorocarbon polymer block rather than a siloxane block has also been reported.[27]

In summary of the patent literature, there are two classes of internal release agents. One is an immiscible blend of intermediate molecular weight straight-chain hydrocarbons along with surfactants or compatibilizers. The PP release agents show less filming than do the PE-based systems.[11,12] Another class is that of block copolymer additives. One block is miscible in the toner resin and the other block is immiscible in the toner resin. The immiscible block is surface active and provides the improved release properties.

Although there is extensive patent literature on the subject of internal release agents for electrophotographic toners, there is no methodical study available in the open literature. The patents are limited to demonstrating the application. Typically only generic results are given, which makes physical interpretation of the results difficult to ascertain. The goal of this work was to initiate a fundamental study of the toner internal release mechanism. The release agents and formulations employed were based on those reported in the patent literature for immiscible waxes. A uniform toner melt blending procedure was adopted along with a commercial resin and carbon black. PE, PP, and a number of commercial additives were selected for study. The PE was obtained over a wide range of molecular weight to evaluate the effects of melting temperature and viscosity on release. Silicone oil and surfactants were incorporated to study their synergistic effects on release. A peel-test apparatus was constructed and employed to measure the peel strength of the toner formulations over a wide range of temperatures. Annealing was carried out to examine the effects of surface migration on peel strength. The most effective release agent combinations were evaluated by functional tests in an experimental printer robot apparatus.

Experiment

Toner Preparation. Test samples were prepared as 55- to 60-g dry blends containing 89.5 wt% toner resin (random copolymer of styrene/butlyacrylate/divinylbenzene, 68/30/2), 8 wt% carbon black (Raven 1020), 2.5 wt% charge control agent [zinc bis(di-*t*-butyl salicylate)], and release additives as specified. The dry blend was compounded in a Haake Buchler HBI System 90 with a Rheomix Model 600 batch mixer for 15 min. During this time, the temperature was increased linearly from 150 to 180°C, and the rotation rate was increased linearly from 50 to 100 rpm. The composite was then coarse ground to pass through a 1-mm screen and jet milled in a 4-inch-diameter Jet Pulverizer mill. Particle classification was completed on an MZR100 Alpine Air Classifier running lab ambient air.



(a) **(b)**

Figure 2. Schematic of the peel test apparatus showing (a) the preheat stage and (b) the peel test stage for the Instron.

Peel Test Apparatus. A peel-test fixture was designed and constructed. The dependent variable in the peel test is the peak force required for separating a 1- × 4-in. solid fill area of the toner printed on paper from a heated Teflon surface. The solid fill areas were transferred and fused in a modified 4019 fuser from the Lexmark laser printer with the oil cleaner removed from the fuser. The 4-in. length was in the process direction. The page was then cut into a 1- × 14-in. strip containing the 4-in. solid fill area near the center. The filled area was placed toner side down on the 1.5- × 4-in. Teflon surface mounted on an aluminum heater block, as shown in Fig. 2(a). The heater block contained three heater elements, which were regulated by an Omega temperature controller. Temperature could be maintained between 40 and 220°C within ± 2°C. The heated platen was mounted on an insulating post, which served as a mounting handle and for placing the sample into the Instron tensile tester stage. The solid fill area was pressed onto the heated surface by a 2-kg weight with a siloxane rubber and a ceramic insulator strip between the weight and the paper [Fig. 2(a)]. The weight remained on the sample for a period of time referred to as the *bonding time*, which is discussed later.

After the bonding time, the 2-kg weight was removed, leaving the solid fill area bonded to the Teflon surface. The test stage was then clipped to the Instron load cell (1- to 5-N transducer range), as shown in Fig. 2(b). The stage held the plane of the Teflon stage at a 30° angle. The peel strength of the toner formulation was defined as the maximum force from the Instron load cell divided by the width of the printed area.

For the peel test to be an objective measure of a material property such as peel strength, the results should be independent of bond time and peel rate, or these independent parameters should be held constant. Figure 3(a) shows the typical peel strength as a function of bond time. After about 30 s of bonding the peel strength has become independent of bond time. This is probably due to the time required for the temperature of the solid fill area to equilibrate with that of the Teflon platen. The peel force as a function of peel rate is shown in Fig. 3(b) for 4019 toner, and for a wax-containing toner. It is difficult to distinguish between the two samples below a peel rate of 10 in./min; the largest difference was found at 50 in./min.

Materials Selection. The requirements for potential candidate release agent materials were considered. A wide scope of materials was narrowed down to several of the most promising candidates, which were then subjected to extensive testing. Initially, the literature melting points of 3-hydroxy acids, fatty acids, alkanes, diesters, alkyl amides, *n*-alcohols, and 1-alkenes were categorized as functions of the number of carbon atoms. The melting points of these materials were too low for practical application into a toner as internal release agents.

A survey of commercial internal release agents made for use in the plastics industry was carried out. These agents included PE with a wide range of molecular weights, as well as various other types of waxes. The melt–flow properties of the PE wax series were characterized by thermal analysis. A typical differential scanning calorimeter, (DSC) trace shown in Fig. 4 illustrates

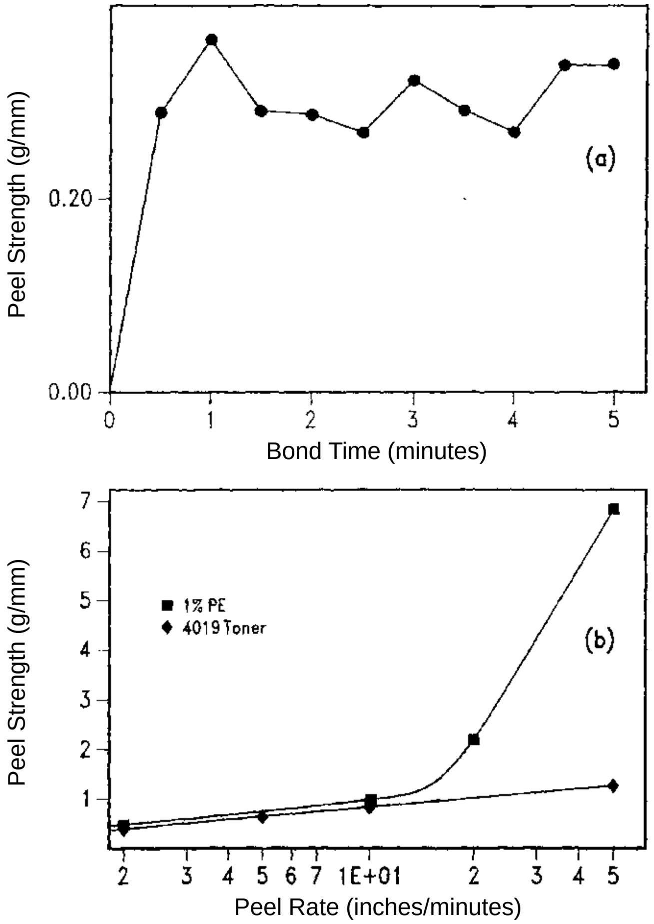


Figure 3. Peel test parameters: (a) peel strength as a function of bond time and (b) peel strength as a function of peel rate.

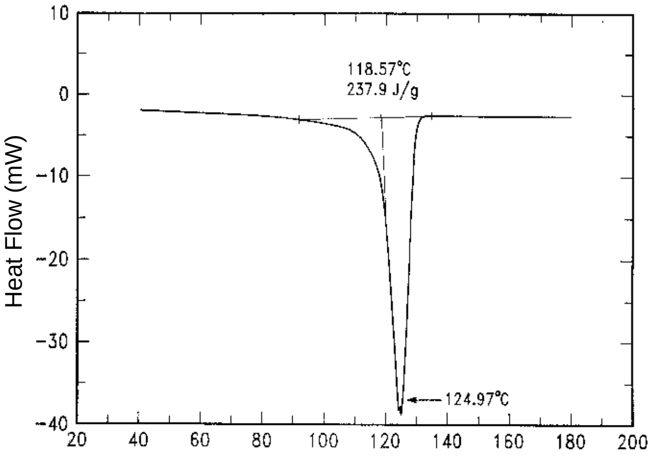


Figure 4. Differential scanning calorimeter trace showing the melting transition of a PE wax with a degree of polymerization of 142.

the general features of the PE wax series, which includes a sharp melting transition characteristic of microcrystalline waxes.

The availability of PE waxes in a wide range of molecular weights provided an opportunity to explore the effects of release agent melting temperature and viscosity on the toner release properties independently of molecular structure. The molecular weight primarily determines the melting temperature and the viscosity above the melting temperature. The melting temperature measured by DSC is shown as a function of molecular weight in Fig. 5. The melting temperature changes from about 60 to 160°C over this range of molecular weight. The viscosity for several of the PE waxes, also shown in Fig. 5, changes by more than 3 orders of magnitude. Given these dramatic variations in melting temperature and viscosity, one would expect to observe some effect of the molecular weight on the toner peel strength when this series of waxes is incorporated in toner formulations as internal release agents.

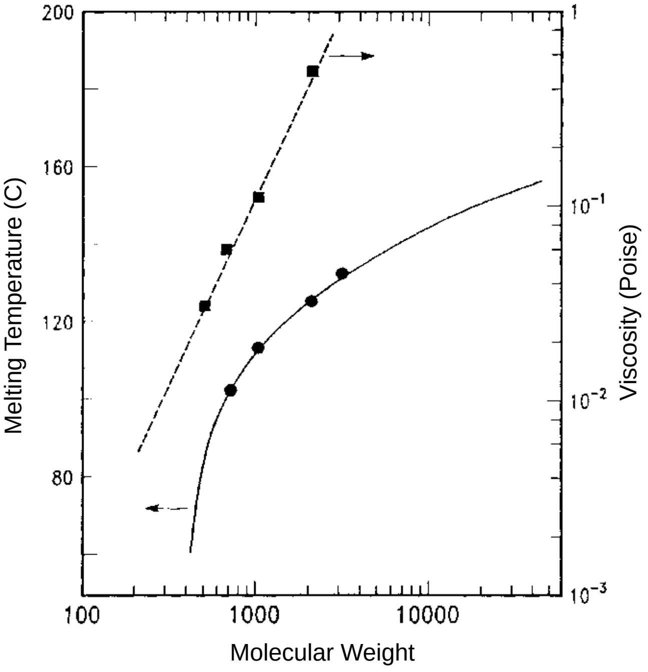


Figure 5. Melting temperature and melt viscosity of PE wax as a function of molecular weight.

The viscosity of the waxes above their melting point is orders of magnitude lower than that of the molten toner, as shown in Fig. 6, which compares the viscosity of the 4019 toner (*solid circles*) with that of the PP (*solid squares*) and the PE with molecular weight 2000 (*solid triangles*). The wax viscosity suddenly drops by orders of magnitude as the temperature is increased above the melting point. In contrast, the toner viscosity decreases only gradually over the same range of temperature. This relative viscosity property suggests that during melt mixing the wax has a viscosity much lower than the toner resin and forms a dispersion of liquid droplets throughout the melt, because the wax is completely immiscible with the toner resin. In addition, during the fusing process the melted wax internal release agent is a low-viscosity liquid that may escape from the toner to form a thin release layer on the surface.

The ultimate size of the liquid droplets of release agent formed during melt mixing depends on the applied shear field, duration of mixing, temperature of mixing, and the surface energy of the interface between the liquid droplets and the toner resin. A lower interfacial energy favors smaller droplets. Block copolymer additives were selected in an effort to reduce the wax particle size by lowering the interfacial tension and to minimize flocculation and coalescence. Qualitatively, the ideal block copolymer should be designed such that one block is miscible in the wax and the other block is miscible in the toner resin. Ideally, the block copolymer should be half identical to the toner resin and half identical to the wax structure and composition. For this study, commercially available block copolymers

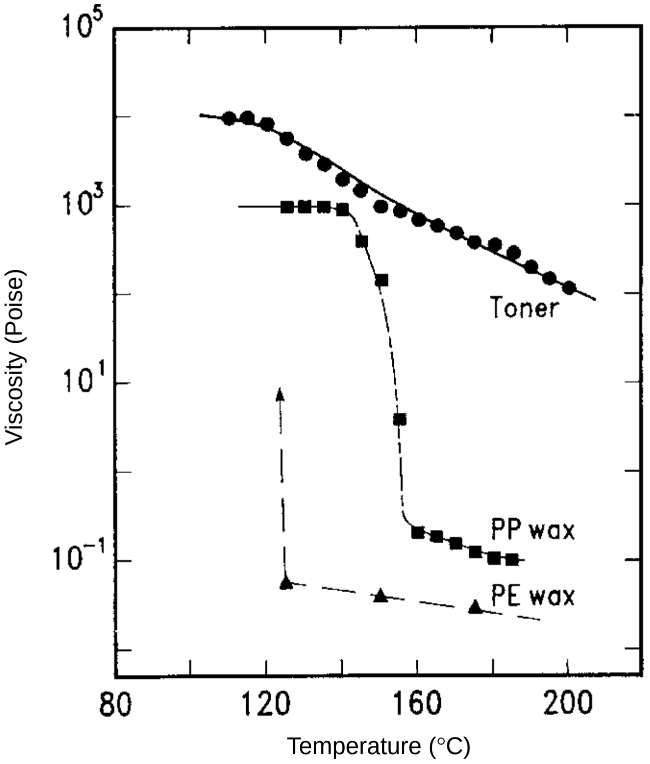


Figure 6. Viscosity of toner compared with typical PP and PE wax as a function of temperature.

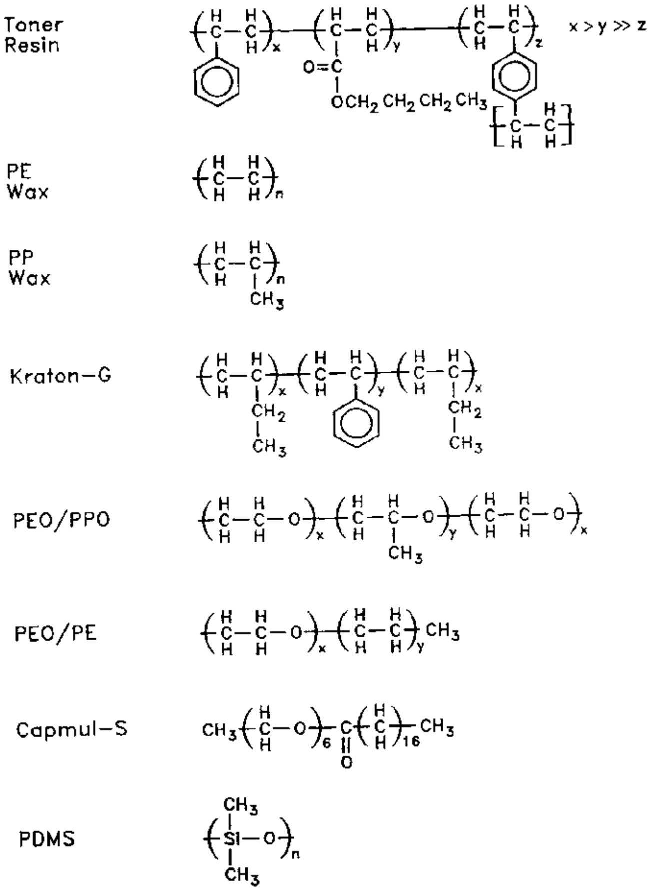


Figure 7. Molecular structures of the toner resin, wax release agents, and other additives.

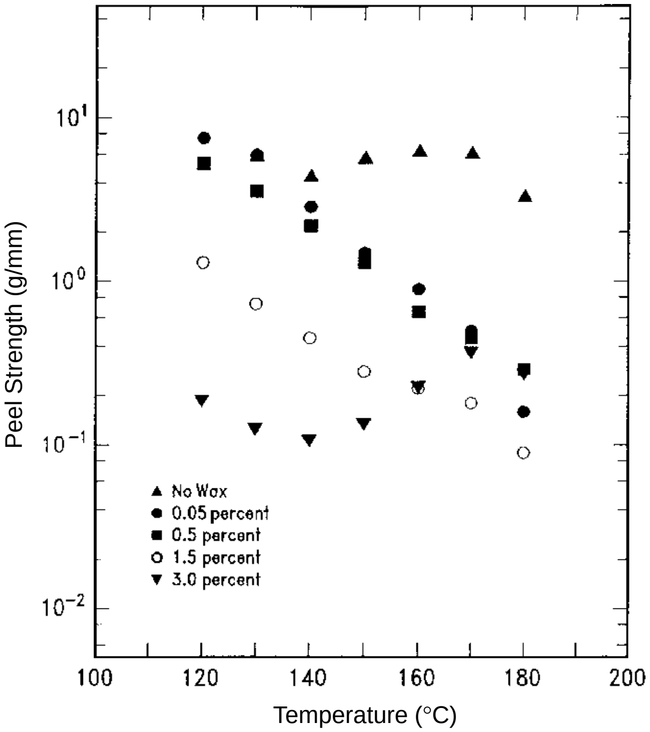


Figure 8. Peel strength as a function of temperature, showing the effect of PP wax concentration.

that closely approached the ideal requirements were selected. The structures of these polymers are illustrated along with the generic molecular structures of the toner resin and the PE and PP waxes in Fig. 7. The toner resin consists of aromatic styrene monomers and the more polar *n*-butyl acrylate, whereas the waxes are aliphatic hydrocarbons. With Kraton-G, the aromatic styrene blocks should be more compatible with the toner resin, and the aliphatic 1-butene blocks should be more compatible with the wax. The PEO/PPO should be more highly miscible with the toner resin than with the wax because of the polar oxygen linkage, whereas the PEO/PE and the Capmul-S each provide one block that is more compatible with the toner resin and one that is more compatible with the wax.

Another additive material selected for test was a PDMS silicone oil. The glass transition temperature of the oil is well below room temperature, so that it remains liquid at room temperature. The PDMS oil is used in conjunction with the wax internal release agents.

Peel-Test Results. Peel tests were carried out to study the effects of the wax release agents and additives on the peel strength. As shown above, the melting temperature and viscosity of the PE wax changed significantly over the available range of molecular weight. Peel tests on toner samples containing PE over this range of molecular weight showed no significant difference at constant temperature. In all cases, the peel strength decreased with increasing peel temperature. The independence of peel strength versus molecular weight suggests that the toner release mechanism is not controlled by the release agent viscosity or melting temperature.

A large number of additional peel tests were performed on toners containing PE, PP, carnauba, beeswax, and perfluoro wax in conjunction with the Kraton-G, PEO/PPO, PEO/PE, and Capmul-5 additives shown in Fig. 7. Although these combinations of wax and additives must have altered the wax particle domain size in the toner, the additives had minimal effect on the peel strength of the toners.

The peel strength decreased by an order of magnitude as the PP wax concentration was increased to 3%, (Fig. 8). Overall, the PP alone lowered the peel strength more than the PE alone, (Fig. 9). Peel tests were also performed on wax-containing toners incorporating 0.5% of PDMS oil. There was no significant reduction in the peel strength of the PP-containing toner on addition of the oil (open versus solid circles in Fig. 9). However, there was a dramatic reduction in peel strength with the combination of PDMS oil and the PE-containing toner, (open versus solid squares in Fig. 9). There appears to be a synergistic effect between the PDMS oil and the PE wax. PDMS oil without wax did not significantly lower the peel strength.

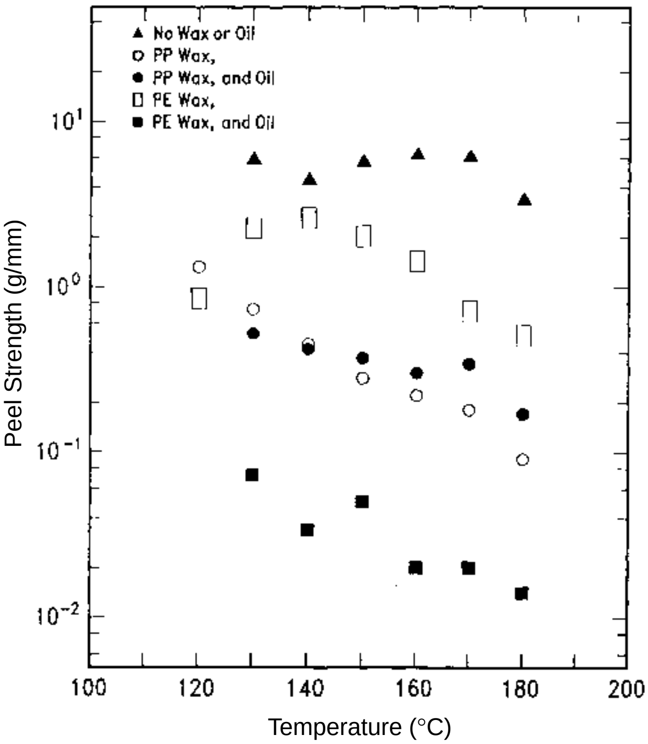
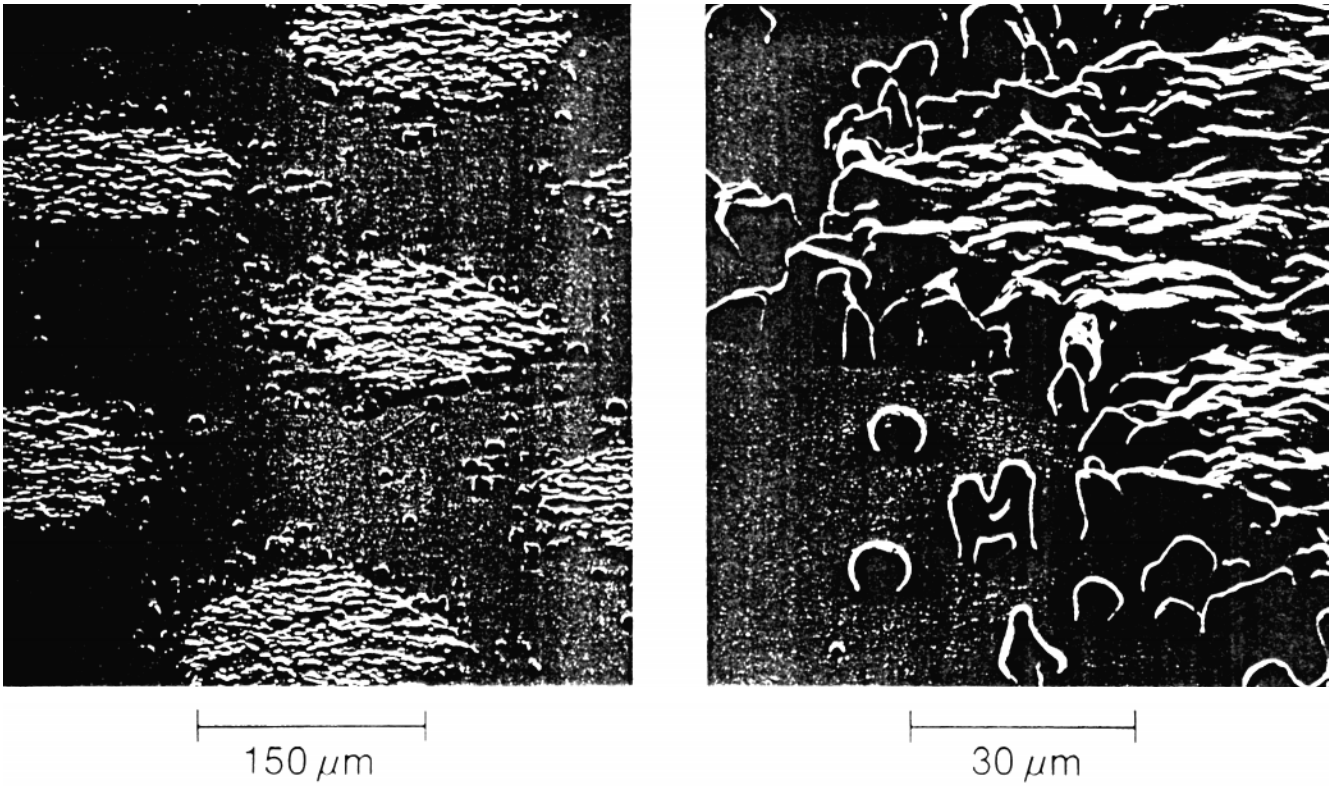


Figure 9. Peel strength as a function of temperature showing the effect of PDMS oil in conjunction with PP or PE wax.

Annealing. The importance of good toner release and low peel strength is graphically illustrated by scanning electron micrographs of 4019 toner fused on transparency film with a 4019 fuser roll. Figure 10(a) shows several pels surrounded by stray toner particles. Figure 10(b) shows a close-up near the edge of one pel. Some of the toner particles are apparently stretched up away from the film as if the melt nearly stuck to the fuser roll. Poor release causes sticking, which shows up as hot offset. Surface roughness of the fused image can thus be employed as an indirect measurement of the toner release properties or peel strength.

Reduction in peel strength by a release agent takes place at the interface between the toner melt and the fuser roll. If the release agent remains primarily in the bulk of the melt as liquid droplets, it is ineffective at the interface. Annealing of the melt may allow time for the release agent to migrate to the surface. A study was carried out to determine the effects of annealing at 180°C on the surface properties and peel strength of toners. Initial tests were done on the 1- × 4-in. solid fill area prints. The print was annealed and then subjected to the peel test. An initial test was done to find an optimum method for annealing that resulted in the lowest peel strength. The results of



(a)

(b)

Figure 10. Scanning electron micrographs of toner fused on plastic showing (a) toner scattered around pels and (b) the roughening effect of toner adhesion to the fuser roll.

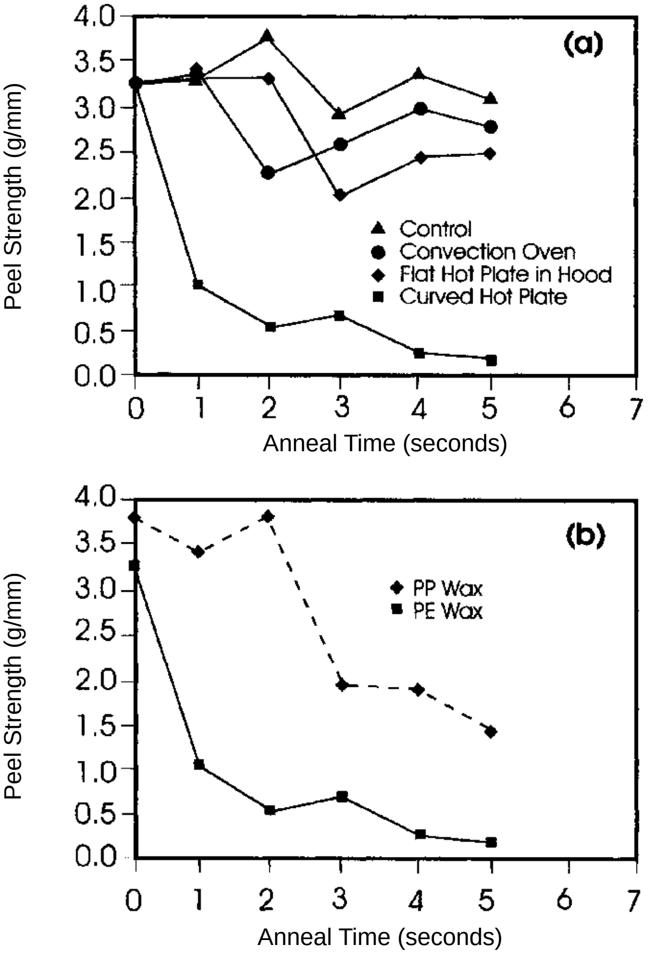


Figure 11. Peel strength as a function of annealing time showing the effect of annealing method with (a) PE wax and (b) PP versus PE wax.

the annealing method study using a control and a PE wax-containing toner are shown in Fig. 11(a). Annealing in a convection oven or on a flat hot plate in the hood somewhat lowered the peel strength. The largest reduction in peel strength was observed after annealing on a curved hot plate with the sample stretched over the curved hot surface. This result probably indicates that the heat transfer is less efficient in the convection oven or on a flat hot plate than when the paper is in uniform physical contact with the heated surface, as with the curved hot plate. The most important conclusion of this initial annealing study is that the effectiveness of the wax release agent is controlled by its distribution between the surface and the bulk of the toner melt.

The rates of migration and relative effectiveness of annealing time on reducing the peel strength were examined to compare PE- and PP-containing toners, using the curved hot plate. The results of this test are shown in Fig. 11(b). Here the lower curve for the PE-containing toner is the same as the lower curve in Fig. 11(a). The upper curve is for the PP-containing toner. Overall, the peel strength of the PP containing toner is lowered by annealing, but it remains above that of the PE-containing toner. This difference may be because the effectiveness of the PP wax at the surface is less than that of the PE wax at the surface, or it may be that the rate of migration of PP to the surface is lower than that of the PE. Disparate rates of surface migration may be due to the different structures and molecular weights in conjunction with the relative sizes of the PP and PE wax domains in the toner.

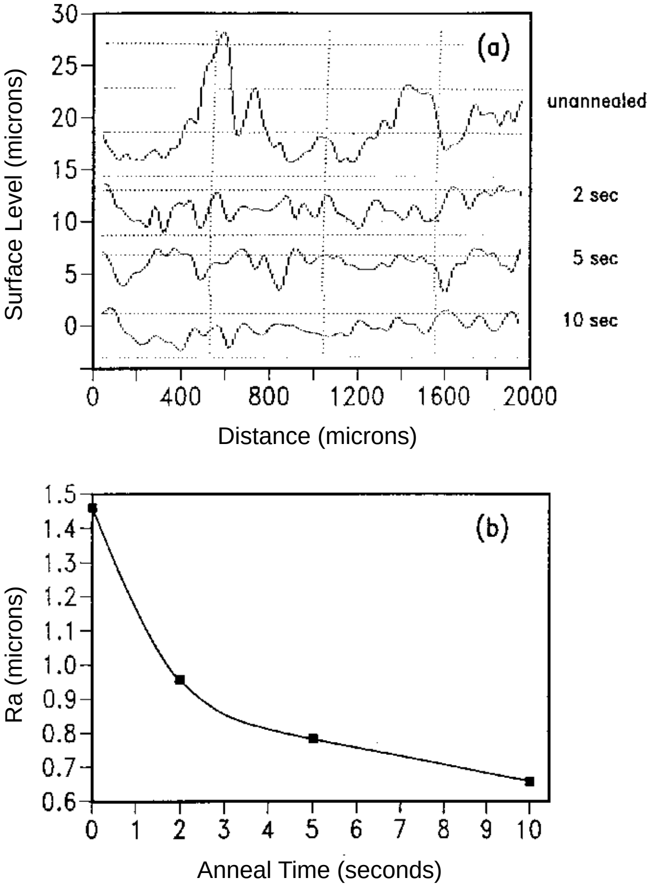


Figure 12. (a) Stylus profilometer traces after increasing anneal time and (b) surface roughness as a function of anneal time.

The annealing lowers the peel strength and also lowers the surface roughness of the print sample following the peel test. The roughness decreases, as does the tendency of the toner to stick to the Teflon surface with decreasing peel strength. Profilometer traces of the print sample following the peel test after various times of annealing at 180°C on the curved hot plate are shown in Fig. 12(a). Clearly, pre-peel annealing reduced the surface roughness following the peel test. As a quantitative measure of the surface roughness, the center line average roughness, R_a, corresponding to the surface profiles in Fig. 12(a) is shown in Fig. 12(b) as a function of annealing time. Similar annealing tests with Fluorowax-, PDMS-, and PEO-containing toners all showed comparable reduction in peel strength and roughness following annealing.

As mentioned, the reduction in peel strength following annealing is attributed to migration of the release agent from the bulk of the toner to the surface. The melt then presents a lower energy surface to the fuser roll. The hypothesis of surface migration during annealing could be tested using x-ray photoelectron spectroscopy (XPS). This technique impinges x rays on the surface at a grazing angle. The energy of the emitted photoelectrons is analyzed along with their relative intensity to obtain a measure of surface atomic composition and the atoms chemical bonding environment. An example of the XPS measurement on dry unfused 4019 toner containing a fluorinated ethylene propylene (FEP) wax release agent is given in Fig. 13. The electron binding energy is along the horizontal axis and the integrated number of electrons at each energy is along the vertical axis. The peaks corresponding to the atoms' ionized shells are identified in Fig. 13.

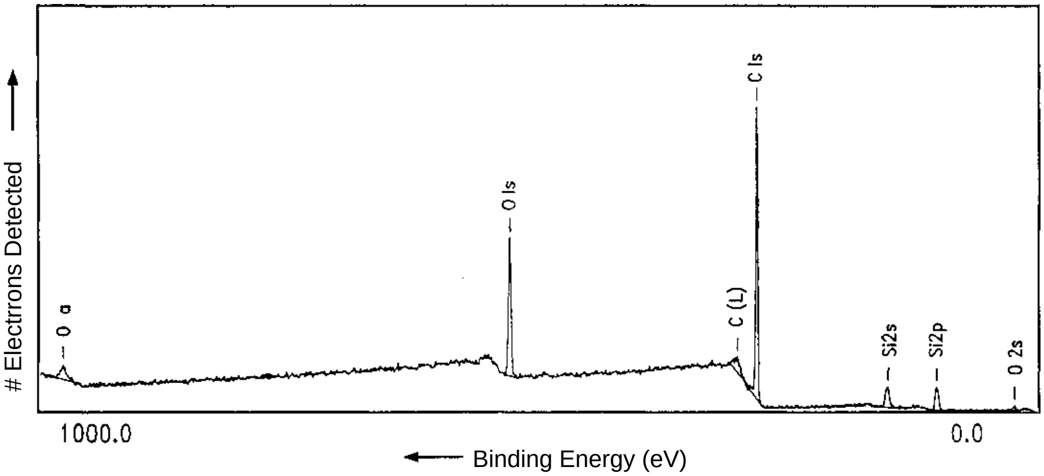


Figure 13. XPS spectrum of a typical toner surface showing the elemental composition.

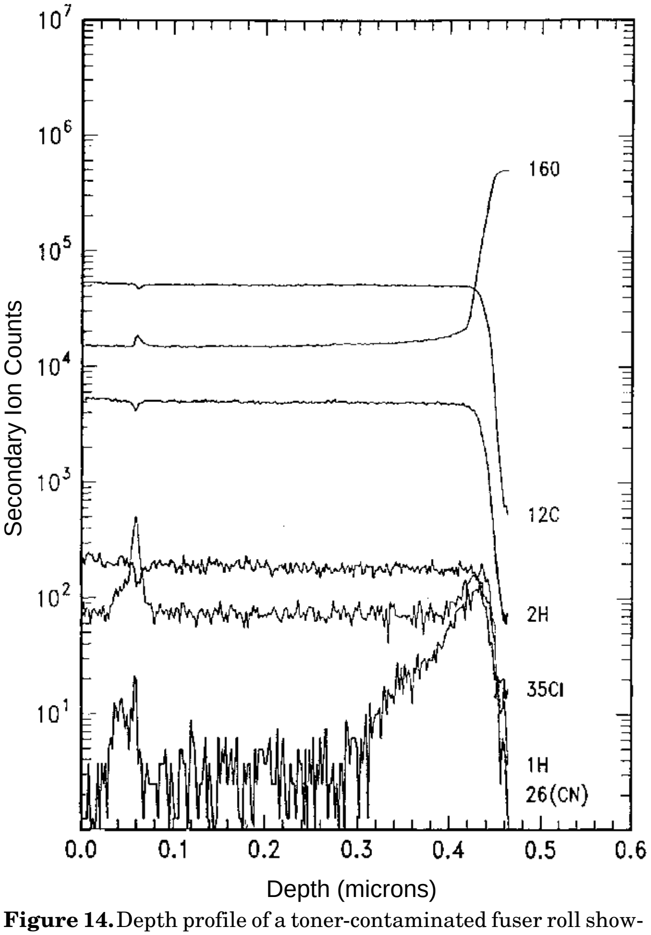


Figure 14. Depth profile of a toner-contaminated fuser roll showing the elemental composition as a function of depth.

The atomic percent of each element on the toner surface was calculated from XPS data. The surface composition is primarily that of the toner. Trace amounts of fluorine from the FEP wax (~ 0.2%) were also detected. This concentration of the FEP wax is an order of magnitude lower than that in the toner formulation. These results show that in the unfused, unannealed toner most of the wax release agent resides not on the surface, but within the bulk of the toner, and is not exposed to the fuser roll.

Another technique that may prove useful in further detailed toner surface studies is XPS with ion milling to obtain a profile of atomic composition as a function of depth near the surface. In this technique, the XPS areas corresponding to selected elements are recorded while the surface is removed at a controlled rate by ion milling. For illustration, the depth profiling measurement on a fuser roll is shown in Fig. 14. The horizontal axis is depth below the surface, and the vertical axis is proportional to the mass fraction of each element. These data indicate that there was an approximately 420-nm buildup of toner film on the fuser roll. Measurements such as the XPS, and XPS with depth profiling, in conjunction with toner preparations containing novel release agents, could improve our understanding of the release mechanism.

Functional Testing. An essential complement of the ex situ tests described above is the in situ functional performance of the toner formulation with release agents. An in-house modified 4019 printer test robot, set up as shown in Fig. 15, included the typical components and an additional station with a preheater to study the effects of annealing just prior to fusing. Some improvement was found using this method of annealing. However, the paper speed required in practice does not allow sufficient residence time in the annealing station for this technique to be of practical use.

A large number of test prints were made with the wax-containing toners. The effectiveness of the release agent was evaluated by measuring the offset, as the ratio of the optical density outside to that within a printed dark area. The offset results shown in Fig 16(a), compare the effects of various combinations of PP wax, PDMS oil, and DB additive (Krayton-G) on the offset. The best offset performance was obtained with the combination of PP, oil, and DB, with PP at 3%.

Another important consideration that must be taken into account is the effect of the release agent on the toner charging. Tribocharge as a function of PP concentration is shown in Fig. 16(b). PP concentration above 1% adversely affected the charging, with a sign reversal between 1 and 2%. Consequently, on the basis of the functional tests, the release agent composition for best release among the set of materials examined in this study is 1% PP and 0.5% PDMS oil.

Summary and Conclusions

A toner master batch was prepared by dry blending and melt mixing laboratory quantities in the usual manner. The master batch was then ground, jet milled, classified, and processed into finished toner. A peel-test apparatus capable of measuring the peel strength of solid fill areas was constructed. Wax additives and compatibilizing agents for use as potential internal release agents were obtained from commercial sources. Toners were prepared incorporating a wide range of PE wax molecular weight, types of

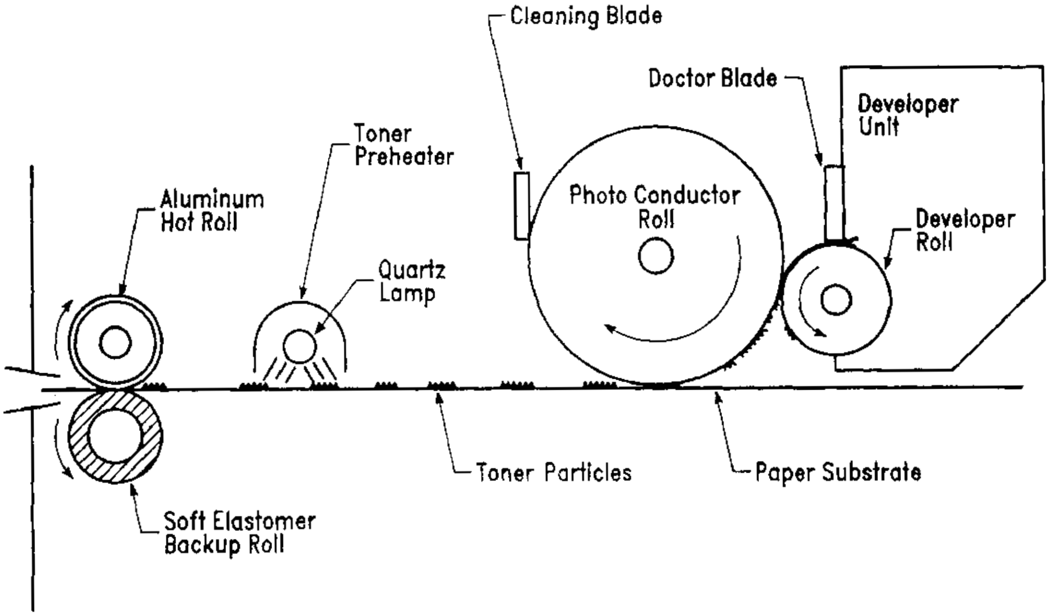


Figure 15. Schematic of the printer robot apparatus used in functional testing of the wax-containing toners.

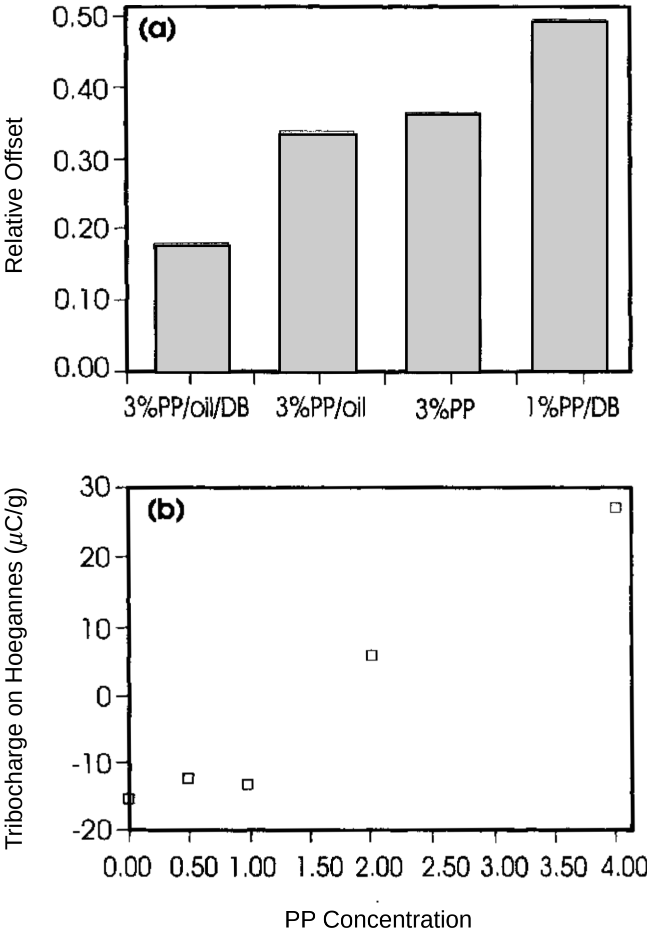


Figure 16. (a) The toner offset for various combinations of PP wax, PDMS oil, and Krayton-G (DB) and (b) the toner charge as a function of PP wax concentration.

waxes, compatibilizing agents, and PDMS oil. The peel strengths of the fused toners in solid fill areas were measured over a temperature range from 120 to 180°C. There was no effect of PE wax molecular weight on peel strength, which indicates that the peel strength is independent of the release agent viscosity. Peel strength decreased in the following rank order: no release agent > PE wax > PP wax ≈ PP wax + PDMS oil > PE wax + PDMS oil. Annealing tests illustrated that the peel strength and surface roughness after peel test decreased with increased annealing time at 180°C. From these results it seems that the peel strength is controlled by the relative distribution of the release agent between the bulk of the toner and that on the surface of the melt. Increasing the amount of release agent on the surface by annealing lowered the peel strength. Sensitive surface analysis by XPS might be useful in further characterizing the amount of release agent on the surface.

Among the combinations of release agents tested, the functional test using 3% PP wax and 0.5% PDMS oil showed the lowest offset. Tribocharging tests revealed that toner charging was adversely affected above 1% PP. Consequently, the best functional combination of release agent recommended from this study is 1% PP wax and 0.5% PDMS oil.

In the peel tests, the combination of PE wax and PDMS oil had lower peel strength than the PP wax with PDMS oil, in contrast to the functional test results. The main difference between the peel test and the functional test is the process time. In the peel tests the bond time was in excess of 1 min, whereas in the functional tests the residence time is on the order of milliseconds. Therefore, the functional performance of an internal release agent is governed by the release agent's intrinsic release qualities at the interface, as well as the dynamics of migration from the bulk to the interface on the time scale of milliseconds as the toner is fused in the nip. Further study of internal release agents should be performed with an instrumented printer engine.

The difference between the PP and PE peel versus offset characteristics may also be due in part to the crystal nucleation and growth rate being faster for PE than PP. Thus PE would tend to be crystalline, and PP amorphous, within the bulk of the toner as well as at the interface.

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