

Hydrophobicity and Elemental Composition of Laser-Printed Toner Films

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ABSTRACT

Laser-printed toner films on a polymer support were treated with alkaline (NaOH) aqueous solutions at elevated temperature (80-85° C). These toner films were examined with a sessile-drop contact-angle measurement technique in order to establish the hydrophobicity of the toner surface. Also, X-ray photoelectron spectroscopy (XPS) was used to analyze changes in elemental composition of the toner surface.

The surface of laser-printed toner film was found to be hydrophobic. Although the toner used is mainly composed of styrene-acrylate copolymer and styrene polymer, it was found that Si-containing organic compounds play an important role in establishing the wetting characteristics of toner surfaces. The advancing contact angle for water drops at the surfaces of untreated toner films was found to be from 105 to 115 degrees. The receding water contact angle was 57 to 67 degrees. The treatment of toner films at elevated temperature (80-85° C) using water or aqueous alkaline solutions led to a reduced hydrophobicity of the toner surface. Sodium hydroxide solutions were found to be more aggressive than pure water. The advancing contact angle was reduced to a value of less than 90 degrees and the receding contact angle dropped to a near zero value when the toner film was contacted for 2 min with hot alkaline solution. XPS analysis of the toner film showed that Si-containing organic compounds having a decreased C/O ratio as compared to the original toner composition were extracted from the surface region.

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KEYWORDS

Contact angle, Deinking Flotation, Hydrophobicity, Ink, Recovered fibers, Toners, Waste papers, Wettability.

INTRODUCTION

Deinking of recovered paper is, in general, a two-step process consisting of pulping and washing/flotation operations during which organic ink (or toner) and mineral fillers are separated from cellulose fibers (1,2). Commonly, in the pulping stage, recovered paper is pulped at elevated temperature in an alkaline (NaOH) aqueous solution in order to separate ink (toner) and mineral filler from fibers, and eventually, to digest ink (toner) aggregates into small particles. Dispersants (surfactants) and mechanical energy facilitate the release of ink (toner) and filler particles from fiber surfaces. In the subsequent step(s), dispersed ink (toner) and mineral particles are separated from the pulp by washing and/or flotation.

A current research program in our group is concerned with surface chemistry phenomena involved in wastepaper deinking flotation because of a need to improve the efficiency of secondary fiber recovery from wastepaper pulp by surface chemistry controlled air-sparged hydrocyclone (ASH) flotation technology. This new technology is based on flotation in a centrifugal field and was originally developed at the University of Utah. It has been successfully adopted by the pulp and paper industry (3-6).

Both conventional and advanced deinking processes of washing and flotation are not very effective at reclaiming toner-free cellulose fibers from photocopied and laser-printed wastepaper. The reason for these difficulties is not well established in the technical literature. The problem is complex, and it is likely that poor flotation deinking performance is

caused by a combination of several factors including:

- (a) the presence of relatively large toner particles ($>20\ \mu\text{m}$) in the wastepaper suspension after pulping (7,8),
- (b) the flat plate-like shape of toner particles (6, 9),
- (c) the lack of appropriate solution chemistry (pH, collector) conditions (2,10),
- (d) the fusion of toner into the cellulose fiber matrix (11,12), and
- (e) the oxidation of the toner surface during the copying process (12).

In this combination of factors, another, which may contribute to the inefficient flotation deinking of laser-printed wastepaper, has been identified. Specifically, the destructive effect of the pulping solution on the hydrophobicity of a laser-printed toner surface has been observed. It was found from X-ray photoelectron spectroscopy (XPS) measurements of toner film that silicon (Si)-containing organic compounds are extracted from the surface region of laser-printed toner film by alkaline solutions (NaOH, $\text{Na}_5\text{P}_3\text{O}_{10}$) at elevated temperature (80-85° C). The extraction of these compounds from the toner surface region leads to a reduced hydrophobicity of the toner surface.

EXPERIMENTAL

Materials and Methods

The main composition of laser-printed toner (EP-S Cartridge) used in this study was 30-40 wt.% styrene-acrylate copolymer, 20-30 wt.% styrene polymer, and 30-40 wt.% iron oxide, as specified by Canon Inc. Reagents used in the experiments included distilled water with pH 5.8 ± 0.1 , analytical grade sodium hydroxide (NaOH; EM Science), technical grade sodium tripolyphosphate (TSPP) ($\text{Na}_5\text{P}_3\text{O}_{10}$; GFS Chemicals), and spectrograde toluene ($\text{C}_6\text{H}_5\text{CH}_3$; EM Science).

Toner Film Preparation

A thin film of toner was printed on an overhead transparency using a Hewlett Packard LaserJet III printer. The printing was repeated at the same surface area to increase the amount and quality of the thin film and assure complete coverage of the trans-

parency by the toner. The toner film on the polymer support was next immersed for 1 to 10 min into the hot (80-85° C) water or hot alkaline solutions of NaOH and $\text{Na}_5\text{P}_3\text{O}_{10}$. This treatment, it is believed, simulates the deinking pulping conditions found in some facilities. The sample was washed with distilled water, dried in a vacuum oven at 60-70° C, and finally, cooled down to a room temperature (21-22° C). The treated toner films were subsequently characterized by contact-angle measurements, and in this way, the hydrophobicity of the toner surface was determined. The X-ray photoelectron spectroscopy (XPS) technique was used for determining the elemental composition of the toner surface region.

Contact Angle Measurements

The hydrophobicity of toner film surfaces, freshly prepared and treated with hot alkaline solutions, was determined by contact angle measurements using the sessile-drop technique (13-16). A sample of toner film on the polymer support was placed in a glass chamber which was partially filled with water in order to minimize water evaporation from the drop and saturate the surrounding environment with water vapor. A drop of distilled water was introduced onto the toner film surface through a microsyringe and the needle remained in contact with the drop as the contact angle was measured. The drop base was made to advance or retreat by adding or withdrawing a small volume of water and the advancing and receding contact angles, respectively, were measured after 20-40 sec using an NRL goniometer (Ramè-Hart, Inc.). The contact angles were measured with an accuracy of 1-2 degrees for varying drop size. The supporting stage of the instrument is movable and calibrated in 0.02 mm divisions. This feature of the instrument allowed for accurate measurements of the drop base diameter. The contact angles were measured at both sides of each drop size and the average values are reported.

XPS Analysis

The surfaces of selected toner films, untreated and treated, were analyzed for chemical differences by XPS using a Hewlett Packard 5950B ESCA Spectrophotometer with a monochromatized Al $K\alpha$ radiation source.

In selected experiments, fresh toner particles were digested in a 0.06 M NaOH solution at 80° C for 10 min. Toner particles were filtered out using a filter paper. After cooling, the aqueous phase was extracted with toluene. The toluene extract was

Table 1. Advancing (Q_a) and Receding (Q_r) Contact Angle Data for Water Drops at Toner Films Treated With Hot Water and Aqueous Alkaline Solutions ($T= 80-85^\circ \text{ C.}$) for Specified Times (t).

t [min]:	Contact Angle [deg]				
	0	1	2	5	10
Toner film treated with water					
Q_a :	108-112	—	100-106	92-97	88-92
Q_r :	59-65	—	20-28	12-18	9-14
Toner film treated with 0.06 M NaOH					
Q_a :	107-112	—	84-90	80-85	76-80
Q_r :	62-66	—	<5	<5	<5
Toner film treated with 0.06 M NaOH + 0.06 M $\text{Na}_5\text{P}_3\text{O}_{10}$					
Q_a :	110-115	100-106	—	88-92	74-80
Q_r :	60-64	10-15	—	<5	<5

spread on aluminum foil and the solvent was allowed to evaporate at room temperature. The remaining film consisting of nonvolatile compounds was examined by XPS.

RESULTS AND DISCUSSION

Hydrophobicity of Laser-Printed Toner

The advancing and receding contact angles for water drops placed on freshly prepared laser-printed toner films are presented in Fig. 1. The contact angle measurements were repeated for three different samples. The advancing water contact angle was found to vary from 105 to 115 degrees. The receding water contact angle varied in a range of 57 to 67 degrees. Thus, the contact angle hysteresis (the difference between advancing and receding contact angle) was about 50 degrees for the toner films examined. Both the scatter in contact angle data and the large value of the contact angle hysteresis reflect the quality of the toner film. During preparation of the toner film, toner particles are deposited on the polymer transparency resulting in toner films with a rough surface (Fig. 2 and 3). In this regard, the advancing and receding contact angles represent not only the intrinsic hydrophobicity of the toner film surface, but also its roughness. In general, the advancing contact angle is larger for a rough surface than for a smooth surface of the same hydrophobic material. Conversely, the receding contact angle of a rough surface is smaller than that which would be obtained for a smooth surface, as is well documented in the literature (13,15-18). Al-

though our toner films had a rough surface, this does not discount the results presented in the next part of the paper.

The relatively large values of the advancing contact angles for toner films (Fig. 1) support the expectation that laser-printed toners should be very hydrophobic because the toner used in this study is mainly composed of styrene polymer and styrene-acrylate copolymer. The advancing water contact angle at a smooth surface of these polymers is reported in the literature to be from 80 to 91 degrees (18). The values for the advancing contact angle shown in Fig. 1 exceed the literature values for styrene and acrylate polymers. These results cannot, however, be attributed solely to the roughness effect of the samples examined. As will be shown in the following section, other components of the toner, the Si-containing organic compounds, which are not specified in the material safety data sheet (MSDS), contribute strongly to the hydrophobicity of the toner film surface.

The Effect of Pulping on the Hydrophobicity of the Toner Film

The toner films were treated with hot aqueous solutions of NaOH and $\text{Na}_5\text{P}_3\text{O}_{10}$ (80-85°C) and their wetting characteristics were examined by contact-angle measurements. The temperature and solution chemistry for these experiments were similar to those used in recovered paper pulping.

The advancing and receding contact angles for water drops placed on the treated toner films are

shown in Figs. 4-9. It is evident that the hydrophobicity of the toner films, as established from the contact-angle measurements, decreased significantly after contact of the toner film with hot water. The observed changes depend on the time of treatment and the aqueous phase composition. Even treatment of the toner film with hot water changed the hydrophobicity of the toner surface (Fig. 4 and Table 1). The advancing contact angle decreased by about 20 degrees (from 108-112 degrees to 88-92 degrees for this particular sample, refer to Table 1) after 10 min of film treatment with hot distilled water. The changes in the receding contact angle were much more pronounced. A decrease of about 50 degrees was observed (from 59-65 degrees to 9-14 degrees). The destructive effect of pulping conditions on the hydrophobicity of toner films increased when alkaline solutions were used (Figs. 6-9 and Table 1). The advancing contact angle decreased by as much as 30 degrees during 10 min treatment of the toner film with alkaline solutions. The receding contact angle dropped to a value of zero after only 2 min of digestion (Fig. 6 and Table 1).

Although a high temperature during digestion (80-85° C) slightly decreased the roughness of the toner film, (results not shown here) these effects were too small to explain the contact angle variations in Figs. 4-9. It was found that the hydrophobicity of the toner film was also reduced when the sample was treated with alkaline solution at room temperature (results not included) but the rate of change was much slower.

The results presented in Figs. 4-9 and Table 1 show that the elevated temperature and alkaline conditions of pulping significantly change the wetting characteristics of toner films. The use of the dispersing agent ($\text{Na}_5\text{P}_3\text{O}_{10}$) did not cause any additional effect on the surface of the toner sample (compare Fig. 6 with Fig. 8).

As might be expected, there is some scatter of the advancing contact angle data for toner films (Figs. 4-9). The variation of both advancing and receding contact angles increased for those toner films which were treated with hot aqueous solutions, indicating that the heterogeneity of the toner film increased during the pulping process (see Lit. Cited (15,16,19,20) for more information on the contact angle/drop size relationships for smooth and rough, homogeneous and heterogeneous solid surfaces). Residual inorganic salts remaining on the toner surface after digestion/extraction experiments, as indicated by the presence of Na (see next section

Figure 1: Advancing and receding contact angles for water drops on laser-printed toner film.

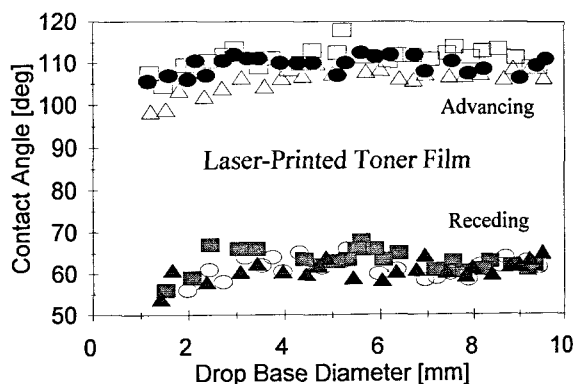


Figure 2: Scanning electron micrograph of laser-printed toner film observed from the top, 90° from the plane of surface.

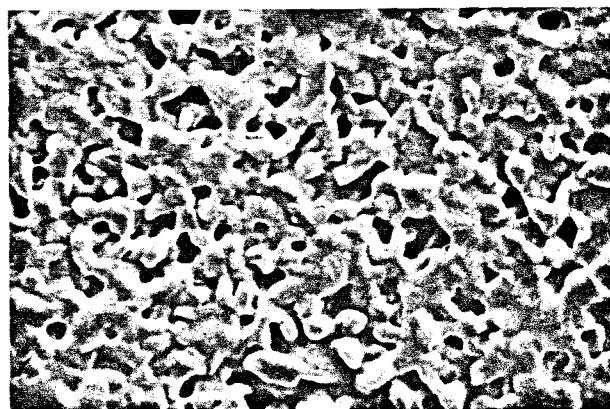


Figure 3: Scanning electron micrograph of laser-printed toner film observed from about 25° from the plane of the surface.

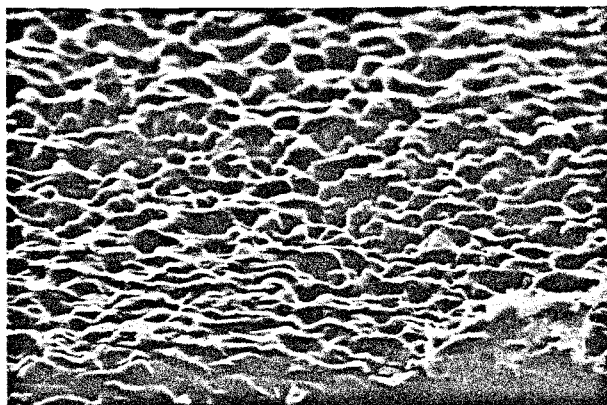


Figure 4: The changes in advancing contact angles of laser-printed toner films treated with hot (80-85°C) water for the treatment times indicated.

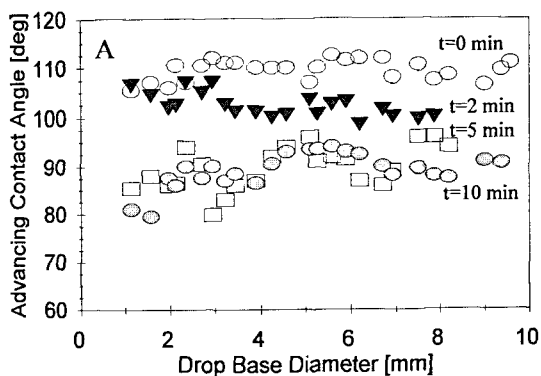


Figure 5: The changes in receding contact angles of laser-printed toner films treated with hot (80-85°C) water for the treatment times indicated.

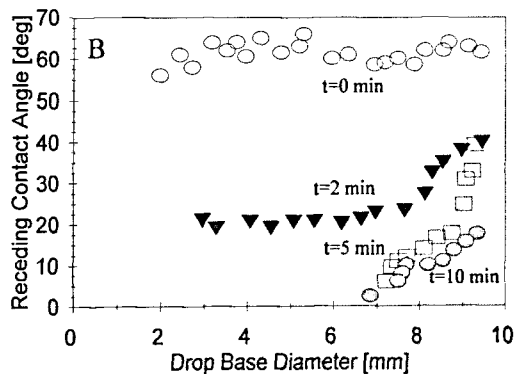


Figure 6: The changes in advancing contact angles of laser-printed toner films treated with hot (80-85°C) 0.06 M NaOH solution for the treatment times indicated.

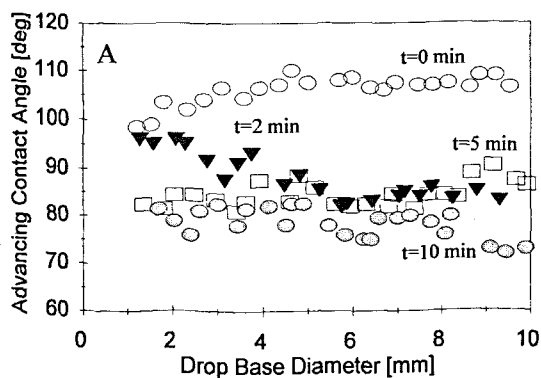


Figure 7: The changes in receding contact angles of laser-printed toner films treated with hot (80-85°C) 0.06 M NaOH solution for the treatment times indicated.

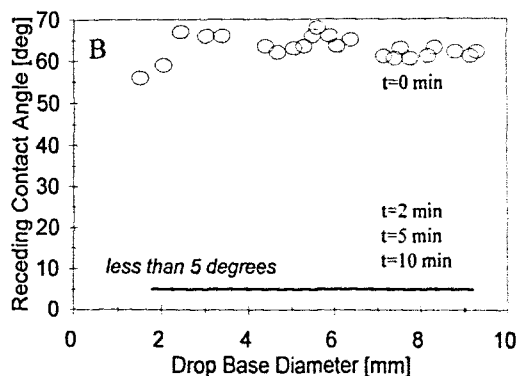


Figure 8: The changes in advancing contact angles of laser-printed toner films treated with hot (80-85°C) 0.06 M NaOH and 0.06 M $\text{Na}_3\text{P}_3\text{O}_{10}$ solution for the treatment times indicated.

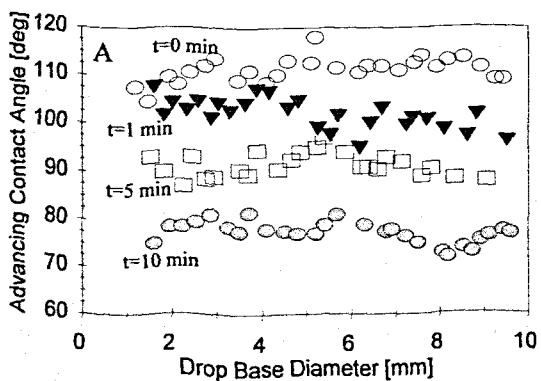


Figure 9: The changes in receding contact angles of laser-printed toner films treated with hot (80-85°C) 0.06 M NaOH and 0.06 M $\text{Na}_3\text{P}_3\text{O}_{10}$ solution for the treatment times indicated.

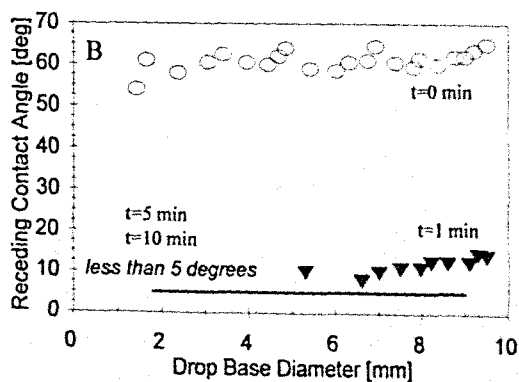
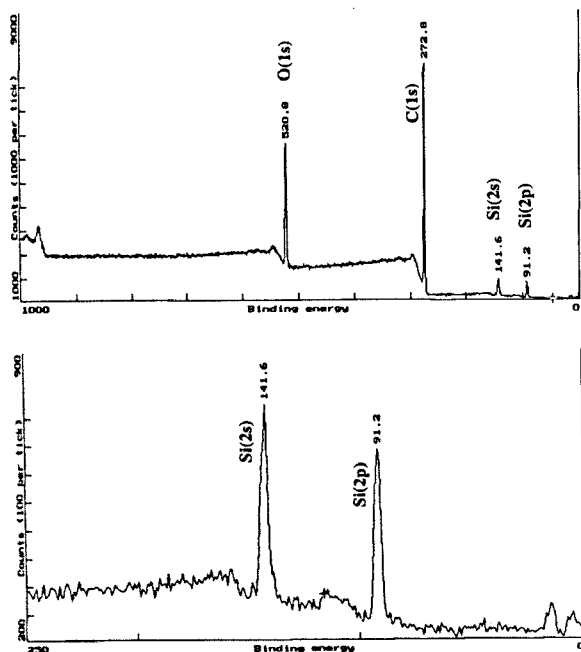


Figure 10: XPS spectrum for untreated laser-printed toner film.



on XPS analysis and Figs. 10 and 11), could create hydrophilic spots on the hydrophobic toner surface. There are two possible reasons for the decrease in hydrophobicity of the toner film in alkaline solutions:

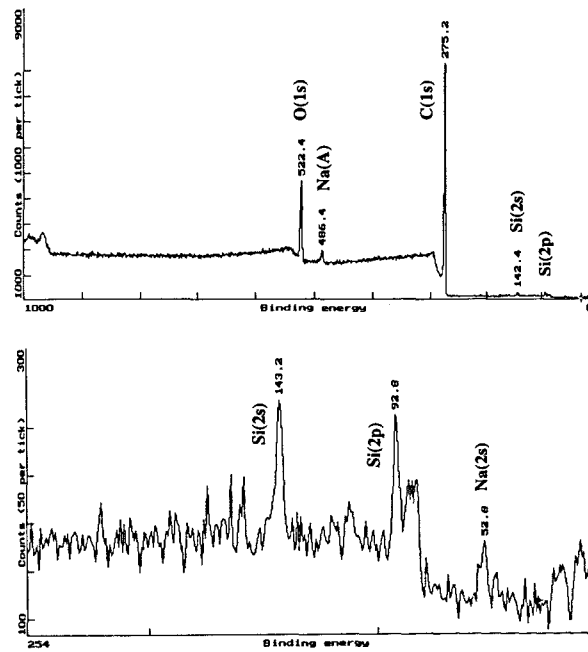
- migration, generation, and/or reorientation of polar components and/or groups at the surface of the toner film; and
- a release of hydrophobic components from the toner surface to the aqueous solutions at elevated temperature.

Which of these mechanisms is dominant can not be resolved based on contact angle measurements. For this reason, the XPS analysis of toner film surfaces was undertaken. Results of the chemical analyses are presented in the next section.

XPS Analysis of Toner Films

The XPS analysis was conducted on freshly prepared toner film and films which were treated with pulping solutions. Scans were taken from the surfaces of several samples and examples are presented in Figs. 10 and 11. From the XPS scans it is evident that there is a major difference in the Si content and in the C/O ratio between untreated and treated toner films. Elemental compositions of the surface regions estimated from the XPS scans are given in Table 2. Table 2 also presents the elemental com-

Figure 11: XPS spectrum for treated (0.06 M NaOH and 0.06 M $\text{Na}_5\text{P}_3\text{O}_{10}$ 80-85°C, 10 min) laser-printed toner film.



position of compounds extracted from the toner by the alkaline solution.

Based on binding energy considerations, it is likely that the Si would be present as a siloxane. For inorganic Si-containing compounds the binding energy is usually lower than that observed, and as an example: the 2s energy for Si in silica is 103.4 eV. Thus, we assume that Si-containing compounds are of organic nature. Such a component of the toner is not specified in the material safety data sheet provided by the producer. Nevertheless, the literature indicates that silicon oils are frequently added to toners as surface flow and cleaning additives (21). This allows us to conclude that although Si-containing organic compounds are minor components of the toners, they have a significant impact on the hydrophobicity of toner surfaces.

Table 2 shows that untreated films have a C/O ratio about 10% less than that of treated films but most of that difference is due to the siloxane's oxygen. Generally, one would expect a small C/O ratio to imply a more hydrophilic surface for the treated surfaces if polar components/groups migrate or reorient at the toner surface during the pulping process. In this view, it seems logical to assume that the difference in wetting properties between untreated and treated toner film is due predominantly to the presence or absence of the Si-containing compound(s).

Table 2. Surface Elemental Composition as Estimated From the XPS Scan Data and Expressed as Atom Percent for the Elements Detected.

Element:	Si%	Na%	C%	O%	C/O
Untreated Toner Film					
	7.0	—	77	16	7.0
	5.7	—	79	15	7.3
Treated Toner Film (0.06 M NaOH + 0.06 M Na ₅ P ₃ O ₁₀ ; t=10 min)					
	1.5	1.4 ^a	85	12	7.8
	1.4	1.5 ^a	84	12	7.7
Nonvolatile Compounds Extracted by Alkaline Solution					
	7.6	—	63	22	3.3

^a Presence of sodium on the surface of treated toner films is due to incomplete surface washing after pulping experiments with NaOH solutions

The extracted Si-containing compounds have a reduced C/O ratio as indicated in Table 2. This explains an important feature of the system. The chemically heterogeneous groups incorporating oxygen atoms are probably responsible for the hydration of Si-containing organic compounds and their tendency to be released into the aqueous phase during pulping (treatment).

CONCLUSIONS

The surface of laser-printed toner film was found to be strongly hydrophobic. The advancing water contact angle was determined to be from 105 to 115 degrees. The receding water contact angle was 57 to 67 degrees. It must be recognized, however, that these values also reflect the roughness of these laser printed films.

The pulping of toner films at elevated temperature (80-85° C) using water or alkaline solutions leads to reduced hydrophobicity of the toner surface. As might be expected, NaOH solutions are more aggressive at the toner surface than pure water. The advancing contact angle for a water drop at a toner film surface, which was treated for 10 min by hot 0.06 M NaOH solution, was reduced to 75 to 80 degrees. It should be noted that after only 2 min of

treatment the receding contact angle was reduced to a value of zero.

X-ray photoelectron spectroscopic analysis of toner films showed that hot water and hot alkaline solutions (80-85°C) extract Si-containing organic compounds from the toner film surface. The experimental data indicate that these Si-containing organic compounds play an important role in establishing the wetting characteristics of toner surfaces.

The results presented in this contribution clearly indicate that the surface characteristics of laser-printed toner change during treatment with hot alkaline solution (similar to conditions during wastepaper pulping). In this regard, the results from flotation experiments with fresh toner particles (as reported in the literature) must be reviewed with caution. The surface chemistry conditions of such model experiments may have no correlation with the conditions of full scale deinking flotation during recovered paper recycling. Digestion of toner particles may change their wetting properties and thus, will probably affect the kinetics of flotation.

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