THE EFFECT OF INK TYPES AND PRINTING PROCESSES ON FLOTATION DEINKING

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ABSTRACT

Examination of ink types reveals that newsprint oil-based offset-cold and offset-heat inks contain substantial oil (45 to 60%) and resin (5 to 35%), water-based ink contains water (40%) and resin (polystyrene, 30%). These inks are liquids with densities around 1 g/cm^3, having various viscosities which range from 10 to 35 Pa s at 25 °C. On the other hand, photocopy and laser-print toners are solid powders with particle diameters of about 20 μm, densities of 1 to 1.5 g/cm^3, and a composition which consists primarily of styrene-acrylate copolymers (60 to 90%). Except water-based ink, which is water soluble, all inks in their initial state tend to be hydrophobic. As such it should be possible to separate them from hydrophilic cellulose fibers by flotation. During the printing process, however, changes in ink properties occur. Newsprint oil-based offset-cold ink is simply absorbed by pores in the paper; water-based ink and oil-based offset-heat ink are physically dried by evaporation at a temperature less than 60 °C. For these inks there is little change in the surface chemical properties and so their hydrophobic character is retained. On the other hand, photocopy and laser-print toner ink particles are thermally/photothermally fused and bonded to the cellulose fiber during the printing process. Due to exposure to heat, light, and oxygen (air), the toner particles undergo polymerization (fusion) and oxidation with the subsequent formation of peroxide bonds. The fusion due to polymerization causes bonding to the paper fibers and the creation of larger toner particle sizes. The oxidation creates a greater polarity at the toner particle surface. These effects account for the poor efficiency in the flotation deinking of office waste. It is evident that ink types and printing methods can have a significant effect on the efficiency of flotation deinking operations.

KEYWORDS

Cellulose, Toners, Inks, Photocopying, Laser printing, Flotation, Deinking, Recycling, Office waste, hydrophobicity.

INTRODUCTION

In the USA approximately 50% of municipal-solid-waste is made up of paper and related fiber products, which has a great impact on environmental, economic and energy issues.[1-8] Therefore, legislation in many states has focused on recycling.[1] Wastepaper recycling is now being practiced in many urban areas and is becoming an increasingly important industry.[1-4,9] Worldwide, recovered paper comprised 37% of the raw material supply in 1991.[10] The American forest and Paper Association (AF&PA) has projected that overall waste paper recovery in the USA will rise from approximately 40% in 1993 to 50% or more by 2001.[11] Profitable conversion of this relatively abundant and inexpensive raw material into quality products demands the development of effective and efficient means for removing contaminants, with ink removal being one critical problem. Currently, 145 deinking facilities are operating, under construction or announced for construction in the USA.[12] According to a Jaakko Poyry study, worldwide deinking capacity will rise to 31 million tons by 2001.[13] Meeting these expectations will require significant investment in research for the development of improved deinking processes because of the importance of deinking and cleaning cellulose fiber in wastepaper recycle.[14] Generally, deinking has been accomplished by washing and/or flotation, but recently, it has been shown that magnetic separation can be used effectively in some cases.[15]

Paper is a felted sheet of cellulose fibers formed during the papermaking process. The cellulose fibers have the basic structure of cellulose (poly(1-4)-β-D-glucopyranose) and the conformation of the glucopyranose ring is in the characteristic chair form.[16] Because of its large content of oxygen-functional groups (mostly -OH and -O- linkages) cellulose exhibits a distinct hydrophilic character.

On the other hand, the surface characteristics of ink depend on their composition and the nature of their reaction with the cellulose fibers to form print and images. Inks consist of four major compounds: pigments (color dye or carbon black or iron oxide), binders (polymers or oil), carriers, and small amounts of additives,[17] and basically tend to be hydrophobic. Therefore, the separation of ink particles from wastepaper pulp by froth flotation should be a reasonable processing strategy.[16,18] Air and chemicals are added to the suspension, ink particles attach to the air bubbles, collect in a froth, and hence are separated from the hydrophilic cellulose fiber.[19,20]

Many research efforts (mostly in Germany and Japan) have been made during the last decade to improve flotation deinking for wastepaper recycle and some significant progress has been made,[1,18,21-27] so much so that flotation has become the predominant process for deinking of wastepaper in Europe and Japan.[16] U.S. flotation deinking technology has lagged behind that of Japan and Europe until recently.[1,9,14,28,29] For example, efficient flotation deinking of newsprint wastes has been achieved at the University of Utah using the high specific capacity air sparged hydrocyclone (ASH).[16,21,22, 30-36] Under appropriate control, a clean fiber product with about 7 points brightness gain can be obtained at a yield of greater than 92% by single-stage ASH flotation of a waste newspaper stock.[18,21]

In the case of photocopied and laser-printed office waste, where the ink particles are thermally fused and bonded to the cellulose fibers, flotation deinking has been much less successful when compared to the flotation deinking of waste newsprint.[37-40] Further fundamental studies are needed for a better understanding of the surface chemical reactions in photocopy and laser-print inks during the printing processes so as to optimize the flotation deinking process for efficient recycle of this material.

EXPERIMENTAL

Materials

Flexographic water-based ink (Table 1), offset-heat deodorized oil-based ink, and offset-cold- web soy oil-based ink were obtained from Flink Ink Corporation (manufacturer) and *Salt Lake Tribune* Newspaper Agency Corporation (user). Fresh (unused) newsprint paper was obtained from *Salt Lake Tribune* Newspaper Agency Corporation.

Printed material included both Newspaper (*Salt Lake Tribune*) and Magazines (*Time*, *Windows* and *TAPPI*).

Photocopy toner (Xerox dry ink plus 5052/1050, Xerox Corporation) and laser-print toner (EP-S Cartridge, R64-0001, Canon Inc.) were used and their composition is given in Table 2. White photocopy paper (Xerox 4200, Xerox Corporation) was also used.

Photocopied wastes were made by using a Xerox 5052 (series 15P355826, Xerox Corporation) copy machine and the *discarded* toner was the toner collected from the machine's discard waste bottle. Laser-printed wastes were made by using an HP Laser Jet-III printer.

Methods

The thermogravimetry/mass spectrometry (TG/MS) system used for this study, consisting of a Perkin-Elmer TFS-2 microbalance (sensitivity 0.1 μg, accuracy 0.1%) and a Perkin-Elmer 7 series high temperature furnace was developed at the University of Utah,[40-42] and operated at the heating rate of 25 °C/min up to a temperature of 800 °C. An Extrel EL 1000 quadrupole mass filter operating at 12 eV electron energy and a Teknivent Vector 2.2 interface combined with a PC based data system was operated at scanning rates of 2.5 spectra/scan covering the 10-600 amu range. A 50 mg aliquot of sample (paper-and-ink) was loaded into a regular platinum crucible, and placed in the TG furnace where pyrolysis was performed in helium at atmospheric pressure. The gas, 100 ml/min of helium, was introduced through the top (95%) and bottom (5%) of the TG furnace. Between the TG and MS a special interface consisting of concentric outer (15 mm i.d.) and inner (3 mm i.d.) quartz tubes was used to reduce the pressure and transfer the vapor products. A countercurrent helium flow acts to direct the evolved gas and descend flows toward the 80 μm dia orifices of the quartz tubes. All of the sample vapors are drawn through the outer orifice and about 5% of the sample vapor is drawn through the inner orifice into the MS ion source region (10^{-6} torr). The short distances between sample holder and vapor sampling inlet (< 2 cm) and between inlet and MS ion source (< 15 cm) ensure vapor product response times < 2 seconds,[40] which minimizes secondary reactions.

Scanning electron microscopy (SEM) experiments were carried out with a Cambridge Stereoscan 240 (Cambridge Instruments, Inc.) in 10^{-6} torr of an argon vacuum. X-ray photoelectron spectroscopy (XPS) analyses were done by Fisons Instruments 220i-XL in 10^{-7} torr of a helium vacuum. Atomic force microscopy (AFM) measurements were conducted using a Nanoscope E (Digital Instruments, Inc.) in the ambient atmosphere.

Zeta potential measurements were conducted with the ZETASIZER 3 (Malvern Instrument Ltd.). Suspension about 0.02% by weight were used and the ionic strength was maintained at 10^{-3} mol/L with KCL.

The water contact angles were measured on a paper sheet and an ink pellet with a Rame-Hart contact angle goniometer using a captive-bubble method, in which the water-ink or water-paper interface was replaced by the air-ink or air-fiber interface. A smooth ink pellet was prepared by carefully pressing ink at 20,000 psi with Carver Laboratory Press (Fred S. Inc.). The paper sheet was taped to an aluminum plate prior to the contact angle measurement. After preparation of ink and newspaper samples, the contact angles for ink and newspaper were measured in aqueous solution at neutral pH. All measurements were done at room temperature. Several small air bubbles, about 2 mm in diameter, were introduced at the water-ink and water-paper interface after the surface was immersed in aqueous solution. In each case, the average values of contact angles were obtained from ten measurements.

Other analyses were performed in a Perkin-Elmer 7 Differential Scanning Calorimeter under a nitrogen atmosphere at a flow rate of 20 ml/min and a heating rate of 20 °C/min. In each case, 10 mg of sample was used.

Surface areas were measured by a SA3100 (COULTER Corporation) instrument.

RESULTS AND DISCUSSION

Hydrophilic Characteristics of Paper

Paper consists mainly of cellulose fibers. Cellulose has the basic structure of poly(1-4)-β-D-glucopyranose and the conformation of the glucopyranose ring is in the characteristic chair form. According to the application, the paper can vary in composition with different types and amounts of inorganic mineral fillers, such as kaolin, talc, titanium dioxide, etc. Because of the effect of these fillers and other additives, paper will exhibit some physical and chemical differences.

The specific surface areas of photocopy and newsprint papers were measured to be 1.36 and 1.45 m^2/g, respectively, which were smaller than the surface area of pure cellulose with an average size of 100 μm (the surface area measured was 1.79 m^2/g). The surface area of a magazine, *TAPPI*, was found to be 1.92 m^2/g, which is larger than that of 100 μm cellulose but smaller than that of 20 μm cellulose (2.29 m^2/g). Thermogravimetric profiles show that about 20% by weight residue remained from paper decomposition compared to almost no residue being left from the treatment of pure cellulose (Fig. 1). Low quality paper, such as newsprint paper, contains more impurities and cheaper fillers, so it has a darker color and wider thermal decomposition profile compared to high quality paper, such as photocopy paper, for which the decomposition profile is closer to that of the cellulose (Fig. 2). Correspondingly, in ambient pressure helium, after a big weight loss caused by fiber decomposition at a temperature of around 400 °C, newsprint paper continuously lost it weight to 800 °C compared to cellulose and photocopy paper which actually stopped their weight loss at 400 °C (Fig. 1). The mass spectrometry spectra in Fig.3 show that the main thermal decomposition products of high quality papers, i.e., photocopy paper (Fig. 3b) and magazine paper (*Time* and *Windows*, Figs. 3c and 3d) were similar to those of cellulose (Fig. 3a), which were found to be dianhydro-α-D-glucopyranose (m/z 144), 5-hydroxy-methylfurfural and laevoglucosenone (m/z 126), furfurylalcohol (m/z 98), propionic acid (m/z 73), methylvinylketone (m/z 70), acetic acid (m/z 60), acetone and glyoxal (m/z 57), acetaldehyde (m/z 43) and formaldehyde (m/z 31), except for a little more of water (m/z 18), oxygen (m/z 32) and acetaldehyde (m/z 43) were determined. In comparison, besides containing much more water, oxygen and acetaldehyde (m/z 18, 32, 43), low quality paper, newsprint paper has a lot of alkenyl quaiacol group substances (m/z 124, 138, 150, 164, 178 etc.), (Fig.5e), which are typically from the thermal decomposition of hardwoods or their lignin components.[43,44]

However, despite the variation in the decomposition products from different paper types, all the decomposition product compounds contain =O, -O-, and/or OH functional groups, and it is these oxygen groups which account for the fibers extensive hydration and the lack of a contact angle (Table 3). Combined with their typical close-to-water densities, which were measured as 1.48, 1.56 and 1.56 g/cm^3 for pure cellulose, photocopy and newsprint papers, respectively, the hydrophilic character explains why paper fibers generally remain dispersed in suspension during flotation.

Hydrophobic Characteristics of Inks

According to the requirement of different printing processes, inks must have various physical properties and consequently various chemical compositions. Of course, this results in various thermal decomposition profiles and products.

Water-based ink is a water soluble liquid with a density of 0.96 ~ 1.0 g/cm^3, a viscosity of 15 Pa s (after diluted for printing) and a boiling point of 100 ~ 110 °C. Water-based ink demonstrates three decomposition weight loss stages (Fig. 4). From 100 to 150 °C, 30 ~ 40% of the weight loss was measured. On-line MS measurements show that the weight loss was primarily caused from the evaporation of unbonded water (Figs. 5 and 6a). In the 400 ~ 500 °C interval, about 32 wt% of the ink was decomposed (Fig. 4), for which the decomposition product (Fig. 6a) was found to be polystyrene (resin) by comparing these results to the spectrum of pure polystyrene (Fig. 7). Because of the properties of polystyrene, the residue left on the paper from printing and drying of water-based ink is hydrophobic. Within the temperature range of 690 and 760 °C, about 15 wt% of the phosphotungstic molybdate pigment (blue color) was evolved (Fig. 4). In order to determine the pigment□s effect on the ink's properties, two different colors (blue and red) were used and these inks were found to have similar decomposition products.

Oil-based offset-cold and offset-heat inks contain similar chemical compositions, vegetable or mineral oil, pigments, and resin. At room temperature, both are liquid with densities of 0.96 ~ 1.1 g/cm^3 and viscosities of 15 ~ 25 Pa s. However, because they contain different types and amounts of oils, such as 60% vegetable (soy) oil in offset-cold and 35 ~ 45% mineral deodorized middle distillate petroleum oil in offset-heat, they have different thermal properties. For example, offset-heat inks have a wider boiling-point temperature range of 230 ~ 370 °C compared to 270 ~ 315°C for offset-cold ink. In ambient helium, from 80 to 320 °C, 18 wt% of the complementary substances (wax and drying oils) in the offset-cold ink was slowly evaporated (Fig. 4) with the formation of the main decomposition products of saturated hydrocarbons (Figs. 5 and 8a); from 320 to 500 °C, the vehicle vegetable oil in the ink quickly evolved, 60 % of the weight (Figs. 4, 5 and 8b); and from 550 to 600 °C, 5 wt% of the binder resin in the ink was further decomposed (Fig.4). The offset-heat ink contains much more low-boiling-point saturated oil (45 wt%) which decomposed in the temperature range from 60 to 260 °C with the formation of saturated hydrocarbons (Figs. 4, 5 and 9a). From 350 to 500 °C, 35 wt% of the hard resin in the ink was further decomposed (Fig. 9b).

Magazines use different printing processes and different types of inks according to the requirements of the printing process. The *Time* magazine uses a heat curing ink-setting method for its high-gloss protective coating varnishes. The mass spectra of its ink decomposition products are basically hydrocarbons and resin (Fig.10), which is similar to that of oil-based offset-heat ink. On the other hand, the *Windows* magazine uses the rotogravure print process, of which the mass spectrum of the decomposition products of the ink is the same as that of water-based ink, with styrene being the main product (Fig. 11).

Photocopy and laser-print toners are dry black powders with densities of 1.21 and 1.48 g/cm^3 and average particle sizes of about 15 and 25 μm (Fig. 12), respectively. They have similar chemical compositions, which is 60 ~ 90 wt% of styrene-acrylate copolymer as binder. The main difference between them is that laser-print toner contains ~35 wt% of iron oxide as pigment while the photocopy toner contains ~12 wt% of carbon black as pigment (Table 2). (Some photocopy toners also use iron oxide as pigment.) Since both carbon black and iron oxide do not decompose during thermogravimetry, the decomposition profiles of photocopy and laser-print toners are quite similar. Both have only a single decomposition peak in the temperature range of 350 ~ 460 °C (Fig. 12) with identical decomposition products, which are styrene (m/z 104), α-methylstyrene (m/z 118), toluene (m/z 92), methylacrylate (m/z 87), benzene (m/z 78), acrylic aldehyde (m/z 56) and dimer and trimer styrenes and acrylates (Fig. 14). The laser-print toner has about 20 wt% more residue left after decomposition (Fig. 4). It should be noted that the decomposition temperature of photocopy and laser-print toners is lower than the decomposition temperatures for both pure polystyrene and polyacrylate (Fig. 13). This is probably caused by the impurities (pigment and metallic additives) in the toners and/or the possibility that a styrene-acrylate copolymer has a lower decomposition temperature than its solo polymer. The metallic impurities in the toner act as catalysts for the toner thermal decomposition reaction, and probably also contribute to the toner oxidation during the printing process.

Although there are many types of inks, it has been found that all the main decomposition products of inks are non-polar compounds, such as hydrocarbons. So the inks are originally hydrophobic with large contact angles (>80 degrees) with water (Table 3) and under theses circumstances should be easily separated from hydrophilic cellulose fibers by means of froth flotation.

Effect of Printing Processes on Ink Characteristics and Flotation

One obvious requirement of a printing ink is that it should satisfy the demands of the printing method. For different printing techniques, inks are attached to the fiber in different ways and undergo different changes in their physical and chemical properties. Such changes in ink characteristics can have a direct bearing on the efficiency of flotation deinking.

According to the ink-setting mechanisms, print processes can be divided into two main groups. One is the printing processes which use absorption and evaporation for ink attachment. In this case, the inks are liquids with different viscosities for different printing requirements. These processes include lithography, letterpress, flexography and rotogravure.

The lithography printing process is based on the principle that oil and water are immiscible. The image areas on the printing plate are made receptive to oil-based inks but not water. Lithographic inks, usually called offset oil-based inks, are based on water-resistant vehicles and pigments that do not bleed in water or alcohol. This method is used to print newspaper, glossy magazines, books and photographic reproductions. In this method, offset-cold oil-based ink is simply absorbed by pores of the paper at room temperature, leaving the pigment behind on the paper surface without drying.[37,45] The ink structure is obtained mainly by penetration of liquid components into the substrate leaving a dry-to-handle ink on the surface. All inks will have an absorption mechanism when applied to an absorptive substrate, even if attachment occurs by drying or chemical reaction. Therefore, in the case of offset-cold oil-based ink, the ink properties apparently do not change during the printing process.

Letterpress and its modification, flexography are the printing methods used where inks are applied to the raised surfaces on a printing plate. When the plate is pressed against the web, the ink on the raised surfaces of the plate is transferred to the paper. The inks for letterpress are of moderate or low viscosity and rapid-drying, such as oil-based and water-based inks. These methods are typically used for printing newspapers and magazines, such as *Windows*. Rotogravure uses recessed areas in the plate to form the image. The plate with the area forming recessed image is immersed in an ink bath. The paper is pressed into contact with the ink-filled recesses by an impression cylinder covered with a resilient rubber covering. Rotogravure is typically used to print color newspapers and magazines, such as *Time*. In the processes of letterpress and rotogravure, water-based ink and oil-based offset-heat ink are physically dried by evaporating the volatile solvent (water or low-boiling-point organic solvent, such as aromatic hydrocarbon or ester) at around 60 °C, and leaving resins and other material to bind the pigments to the paper.[37,45] Because no chemical reaction happens during the printing, oil-based offset-heat ink and dried water-based ink keep their original hydrophobic characteristics after the printing process.

The other major printing process is indirect printing which uses a relatively high temperature for the ink attachment to the fibers. When the inks are fine solid powders, these processes are recognized to include photocopy and laser-print.

For the photocopy process, a latent image is formed on a charged photoconductive surface and transferred to the paper. The charged surface receives light reflected off the document to be copied. The light reflected from the nonprinted areas causes the surface charge to dissipate, while other areas in the absence of light retain their charge. The surface is then exposed to toner particles of opposite charge, which adhere to the charged area, forming a visible image. Finally, the image is transferred to the paper and the toner particles are heated to about 200 °C to fuse the styrene-acrylate and to bond the toner particles to the paper.[37,45] Therefore, during the photocopy process, thousands of small photocopy toner particles with diameters of several micrometers are melted, fused and bonded to the paper fiber to form the image consisting of larger polymerized particles with diameters of millimeters. These particle size changes can be clearly seen by the results from scanning electronic microscopy (SEM) and optical microscopy (Figs. 15 and 16). Also the fused boundary of the original small particles can be easily seen from the results of atomic force microscopy (AFM) (Fig. 17). Due to this fusion and polymerization, the melting points of discarded and printed toners shift to a higher temperature or even disappear as the degrees of polymerization and oxidation increase (Fig. 18).[40] Correspondingly, the decomposition profile of the discarded and printed toner particles shift to a higher temperature range (Fig. 19a), and their decomposition activation energies increase from 38.9 to 53.9 kcal/mol (Fig. 19b). Even with the short time of exposure to heat (fusion), light, and oxygen (air), the styrene groups, especially the styrene groups at the particle surface, undergo oxidation and polymerization with the formation of peroxides.[46-49] Oxygen concentrations at the ink surface were found by X-ray photoelectron spectroscopy (XPS) to be almost doubled (Fig.20), changing from 9.8% to 12.4% to 18.0% as the degree of oxidation increased from fresh toner to discarded toner to photocopied toner. The captive-bubble contact angles of toner with water changed from 93 degrees to 68.5 degrees from fresh toner to the discarded toner, see Table 3. In general, the smaller the contact angle the greater the hydrophilicity. In other words, the ink should be more difficult to float from the fiber suspension. Finally, the zeta potentials of the discarded toner particles shift to a more negative value (Fig. 21).

As the name implies, laser-print forms an image with the aid of a laser beam. The printing principle is similar to that of photocopy. A laser beam forms a latent image on a charged drum by neutralizing the charge on the non-image areas. Toner particles applied to the drum adhere to the charged image areas and form a visible image. The image is then transferred to the paper, where the toner particeps are fused to its surface. Since, as mentioned before, the composition of laser-print toner is similar to that of photocopy toner, the laser-print toner particles undergo similar physical and chemical changes during the printing process. The particle size of laser-print toner changes from about 20 μm to several millimeters after printing (Fig. 22). The decomposition temperature of the printed toner particles shifts by an increase of 20 degrees compared to the decomposition temperature for fresh toner (Fig. 23a), and the corresponding decomposition activation energy of the printed toner increased from 47.9 to 73.6 kcal/mol (Fig. 23b).

The polymerization of toners during the printing process results in the formation of larger particles,[50,51] which makes paper cellulose fibers chemically bonded to and physically trapped in, the toner ink particles. Of course, the oxidation creates a greater polarity at ink surface and makes flotation more difficult, see Table 3.[40] Even if the ink can be separated from paper fiber in the flotation pulp, there are still some cellulose fibers bonded to the ink particles.[52] Both effects make the toner ink particle more hydrophilic, and account for the poor efficiency in the flotation deinking of office waste. The need for the design of improved deinking process, such as might be achieved by the appropriate design of toner particles for recycle and the promise of magnetic separation,[15] is evident.

SUMMARY AND CONCLUSION

Basically, newsprint oil-based (offset-cold-web/offset-heat) inks contain 45 to 60 wt% oil and 5 to 35 wt% resin, water-based ink contains 40 wt%

water and 30 wt% resin (polystyrene), and laser-print and photocopy toners contain 60 to 90 wt% styrene-acrylate copolymer. Except water-based ink which is soluble in water (but its dried residue is hydrophobic), the other inks (including dried water-based ink) are originally hydrophobic so that separation of ink can be achieved by froth flotation from the cellulose fiber, which is hydrophilic with its basic poly(1→4)-β-d-glucopyranose structure.

Because of the different printing processes, inks undergo different physical and chemical surface property changes during the printing process. Newsprint oil-based offset-cold ink is simply absorbed by pores in the paper, and water-based ink and oil-based offset-heat ink are physically dried (evaporated) at a temperature below 60 °C. Therefore, these inks have no significant change in their chemical properties, specifically their hydrophobic characteristics, which makes them easily separated from cellulose fibers by flotation. On the other hand, during the printing process, the photocopy and laser-print toner particles are thermally/photothermally fused and bonded to cellulose fibers. Due to exposure to heat (up to 200 °C), light and oxygen (air), the toner particles undergo polymerization and oxidation with subsequent formation of peroxides bonds. The polymerization causes a strong chemical and physical bonding with cellulose fibers and creates larger particle sizes. The oxidation creates a greater polarity at the toner particle surface, which account for the poor efficiency in the flotation deinking. It is evident from the results presented that the printing processes play an important role in the surface chemical and physical properties of printed ink and this can have a critical effect on the efficiency of flotation deinking. In order to improve the efficiency of deinking flotation of laser-print and photocopy waste, these factors must be taken into consideration. Improvements may be possible both by the design of new toner particles and modification of the surface properties of the printed toner particles.

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Table 1. Composition of Flexographic Water-Based Ink [53]

COMPONENT	COMPOSITION (wt%)
Water	40 ~ 60
Polymer Resins	15 ~ 30
Pigments	10 ~ 25
Amine Compound	< 5
Glycol Ethers	4 ~ 8

Table 2. Compositions of Photocopy & Laser-print Inks*

COMPONENT	COMPOSITION (wt%)	
	PHOTOCOPY [54]	LASER-PRINT [55]
Styrene Acrylate	85 ~ 90	50 ~ 70
Carbon Black	10 ~ 15	--
Iron Oxide	--	30 ~ 40
Amorphous Silica	< 1	--
Zinc Stearate	< 1	--

* The photocopy toner used was Xerox dry plus 5052/1050, Xerox Corporation and the laser-print toner used was EP-S Cartridge, R64-0001, Canon Inc..

Table 3. Contact Angles for Different Materials

SAMPLE	CONTACT ANGLE (captive bubble)
Blank Newspaper	0.0°
Oil-base Black Ink	81.2°
Fresh Xerox Ink	93.0°
Discraded Xerox Ink	68.5°
Fresh Laser Ink	91.5°

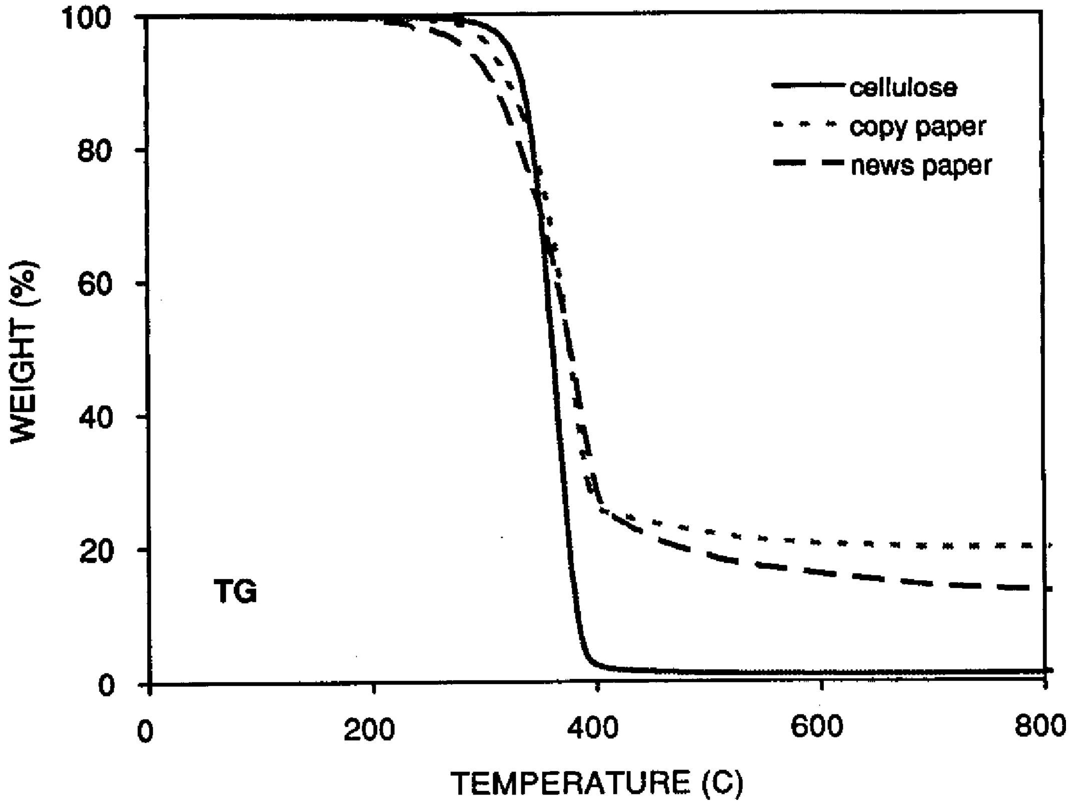


Fig. 1 Thermogravimetric (TG) profiles of cellulose fiber, office paper and newsprint paper

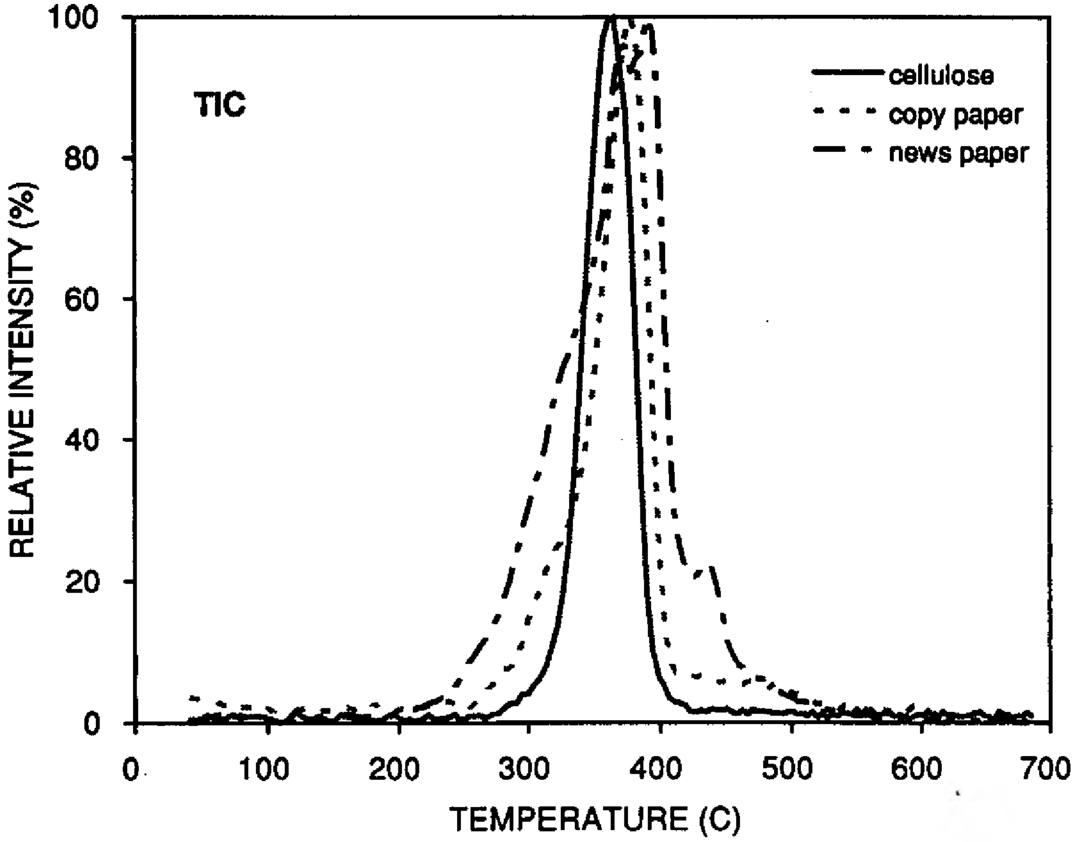


Fig. 2 Mass spectrometric (MS) total ion chromatogram (TIC) spectra of cellulose fiber, office paper and newsprint paper.

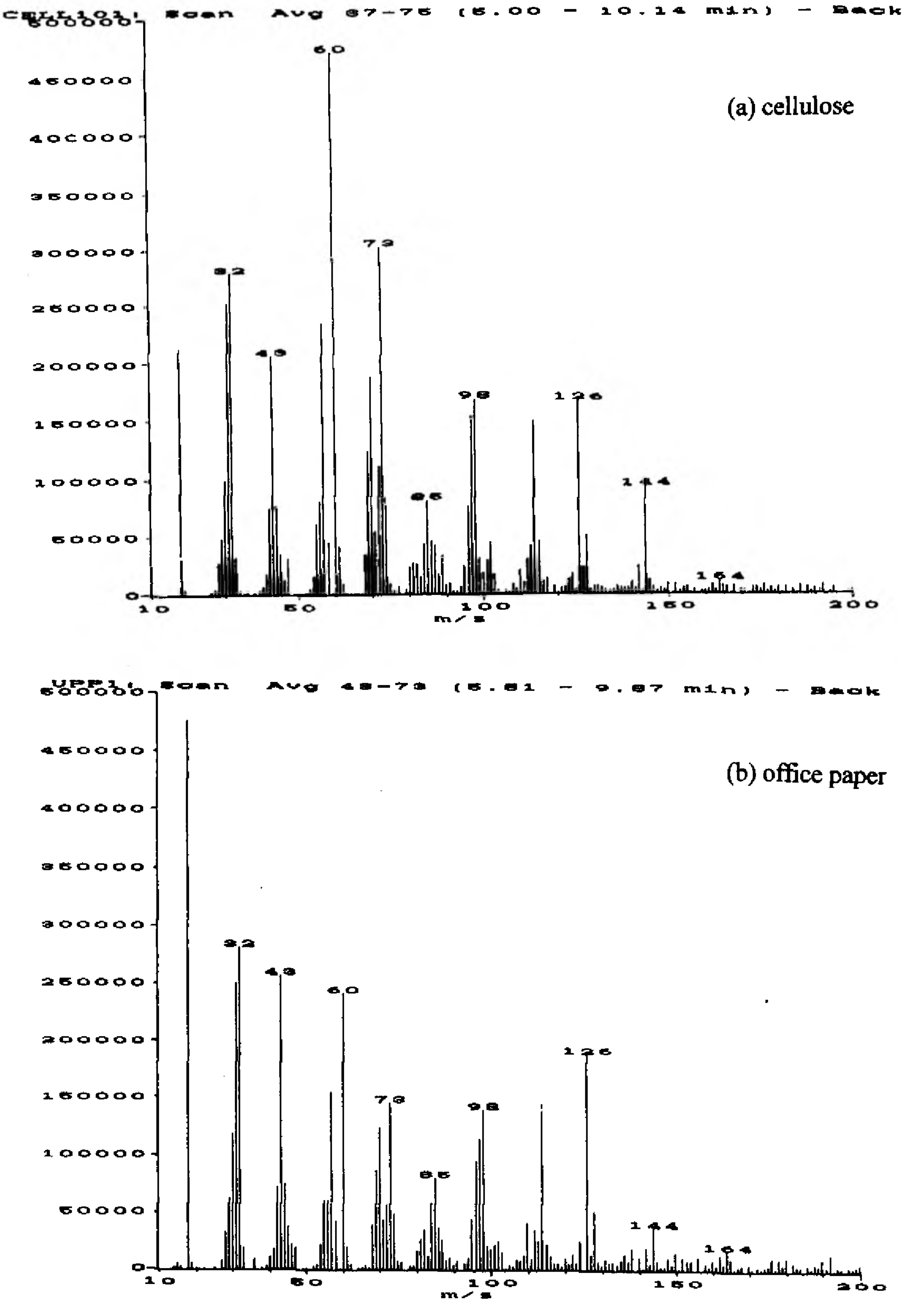
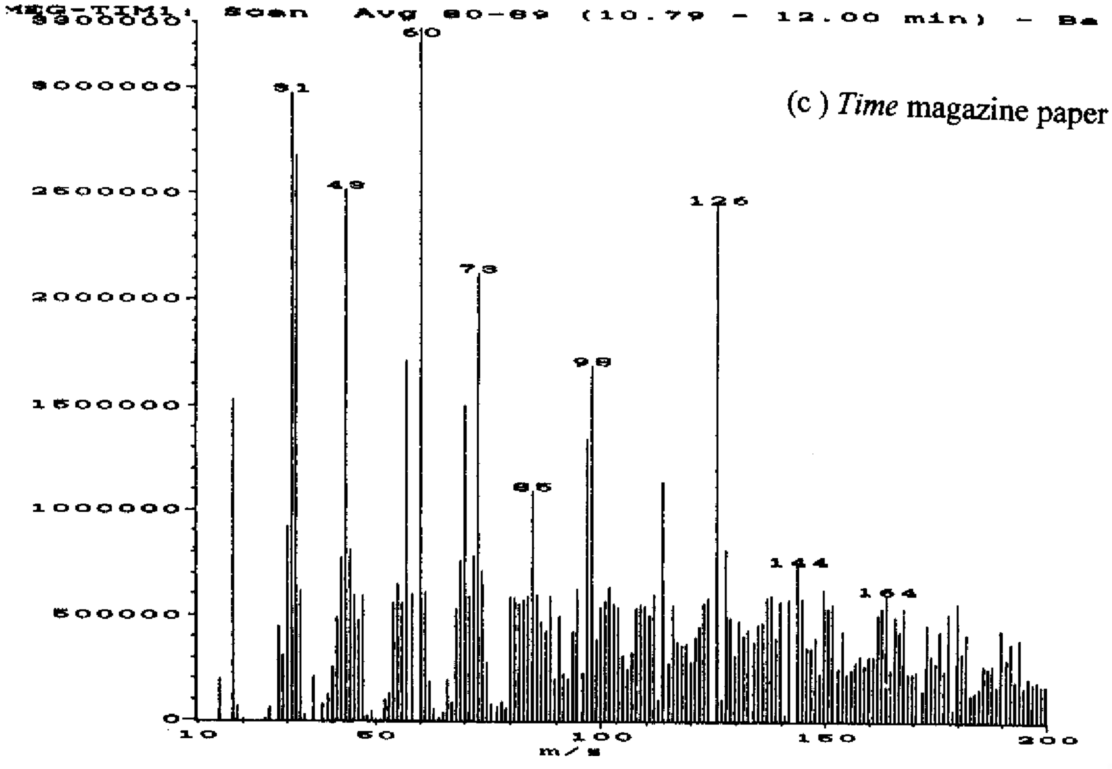


Fig. 3 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for (a) cellulose, (b) office paper, (c) *Time* magazine paper, (d) *Windows* magazine paper, and (e) newsprint paper.



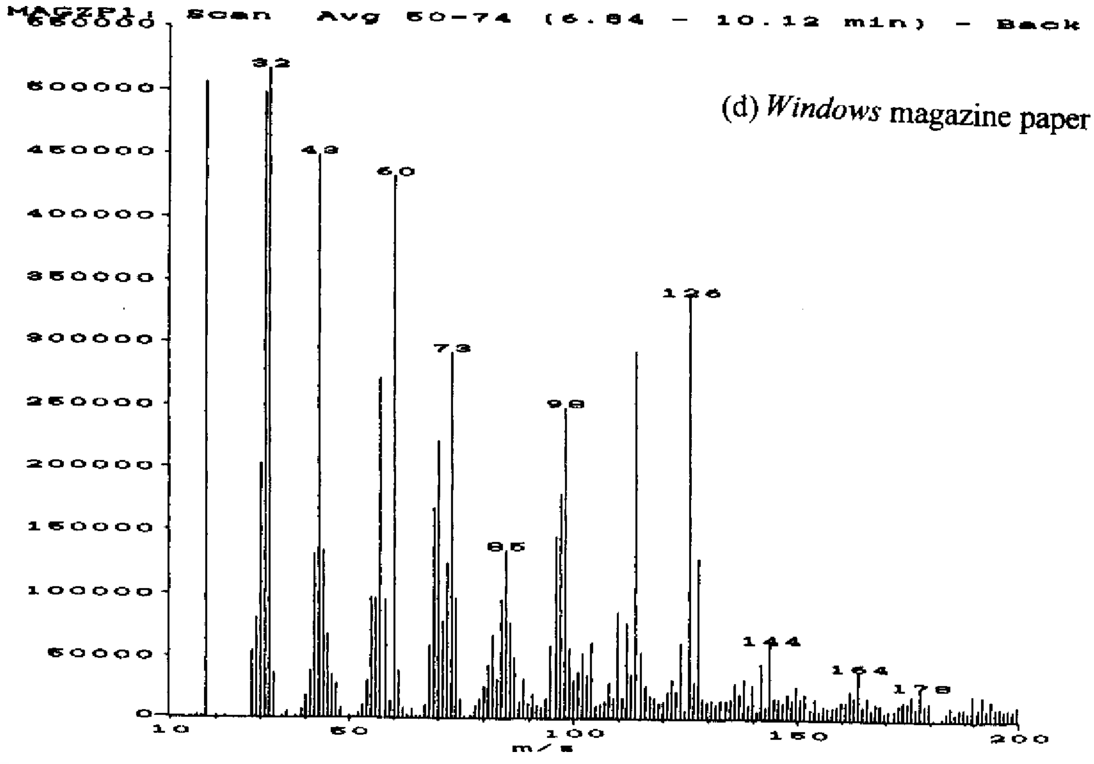


Fig. 3 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for (a) cellulose, (b) office paper, (c) *Time* magazine paper, (d) *Windows* magazine paper, and (e) newsprint paper.

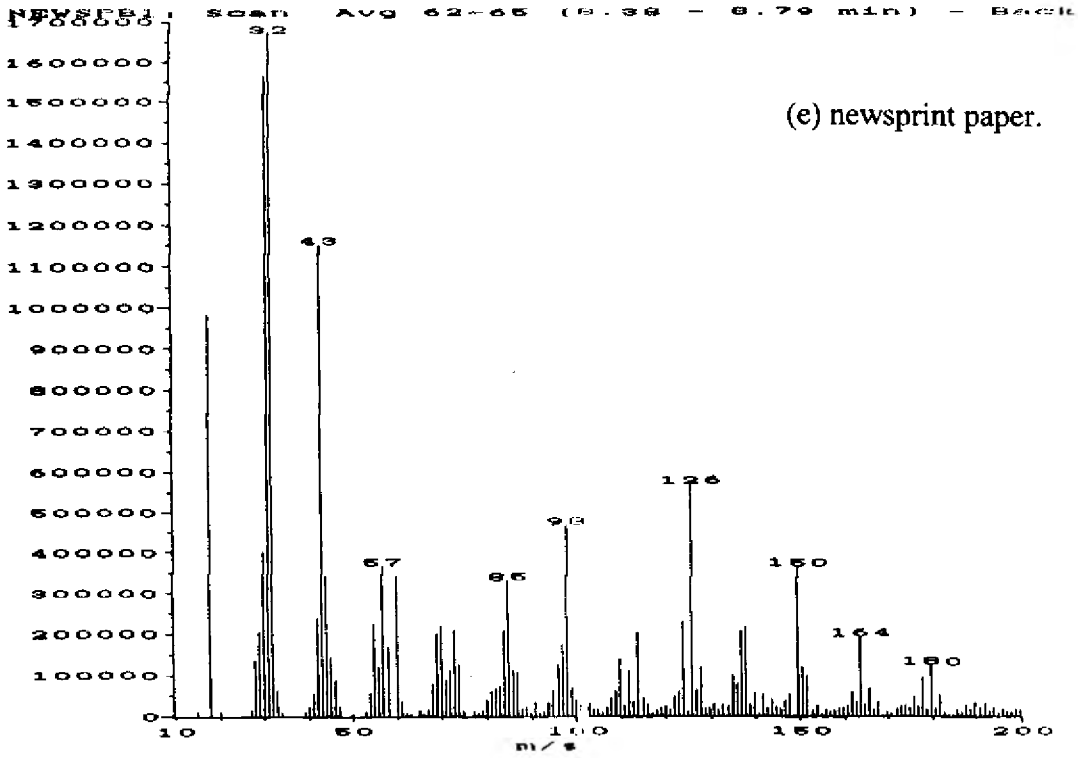


Fig. 3 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for (a) cellulose, (b) office paper, (c) *Time* magazine paper, (d) *Windows* magazine paper, and (e) newsprint paper.

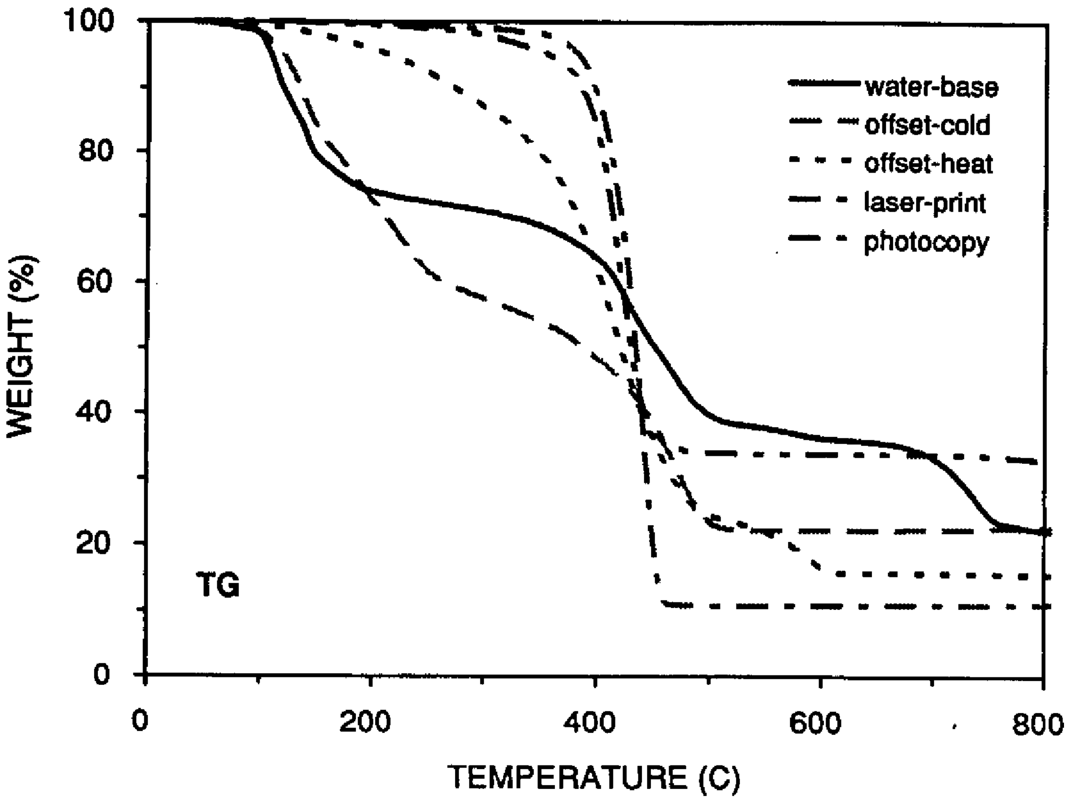


Fig. 4 TG profiles of water-based, oil-based offset-cold, oil-based offset-heat, laser-print, and photocopy inks.

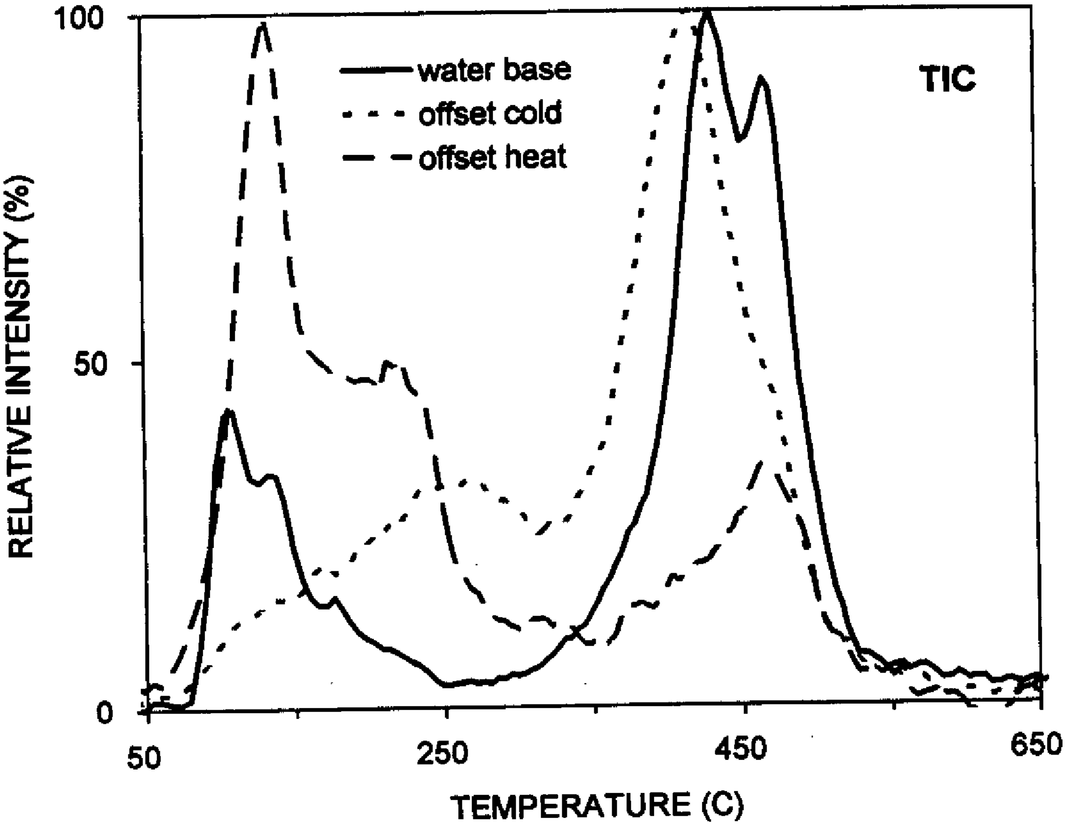


Fig. 5 MS TIC spectra of water-based, oil-based offset cold and oil-based offset-heat inks.

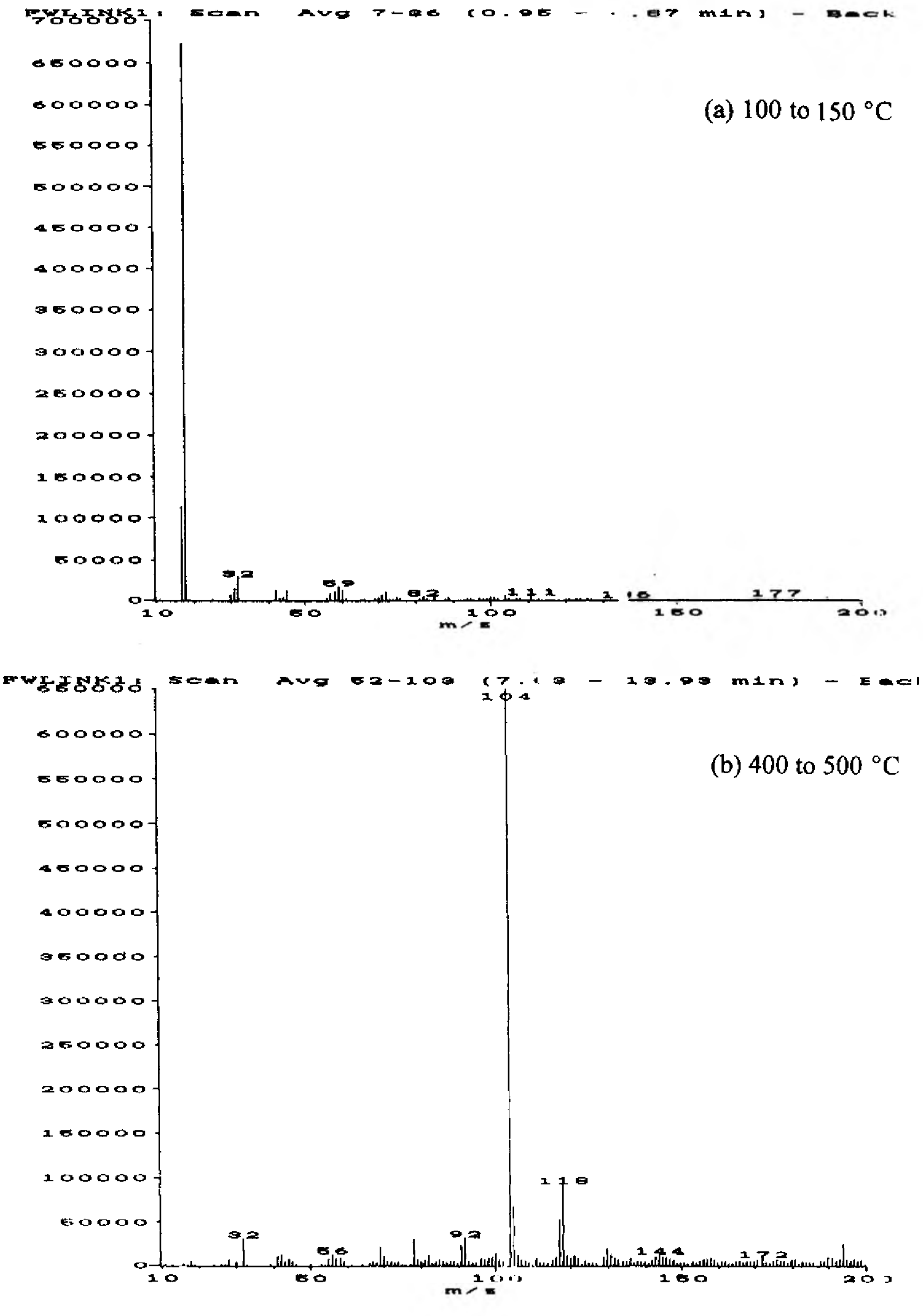


Fig. 6 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for blue water-based ink for temperature ranges of (a) 100 to 150 °C and (b) 400 to 500 °C.

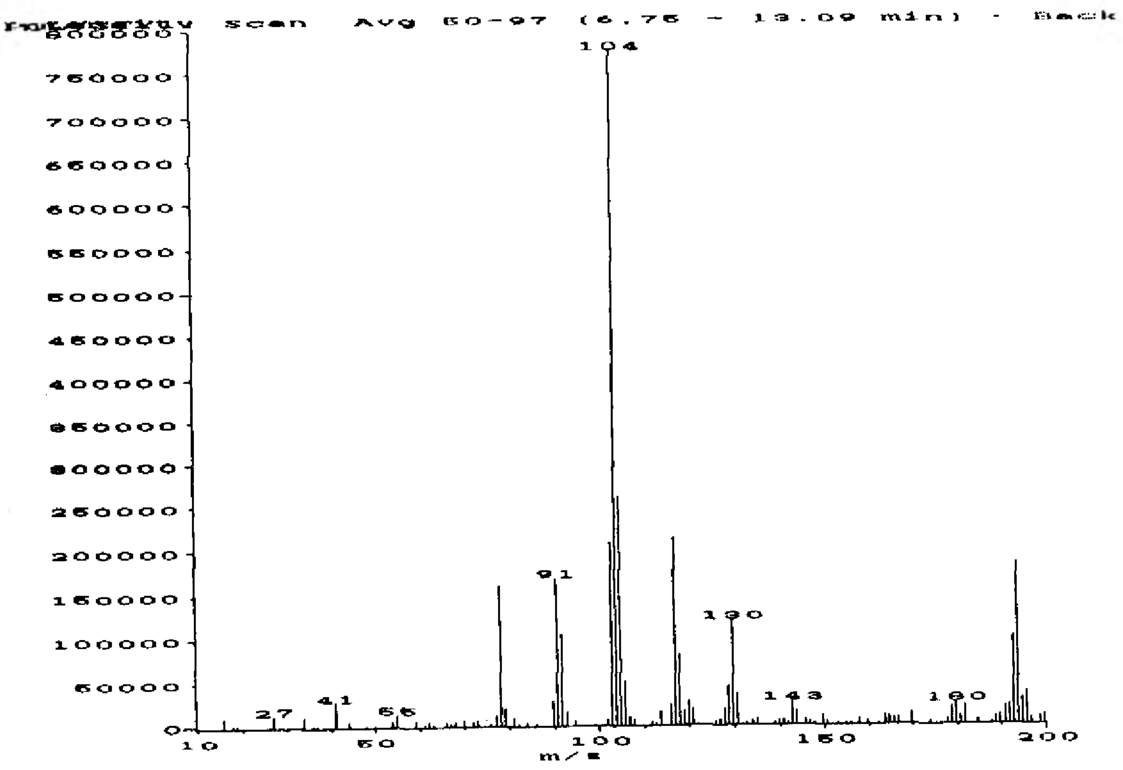


Fig. 7 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for polystyrene.

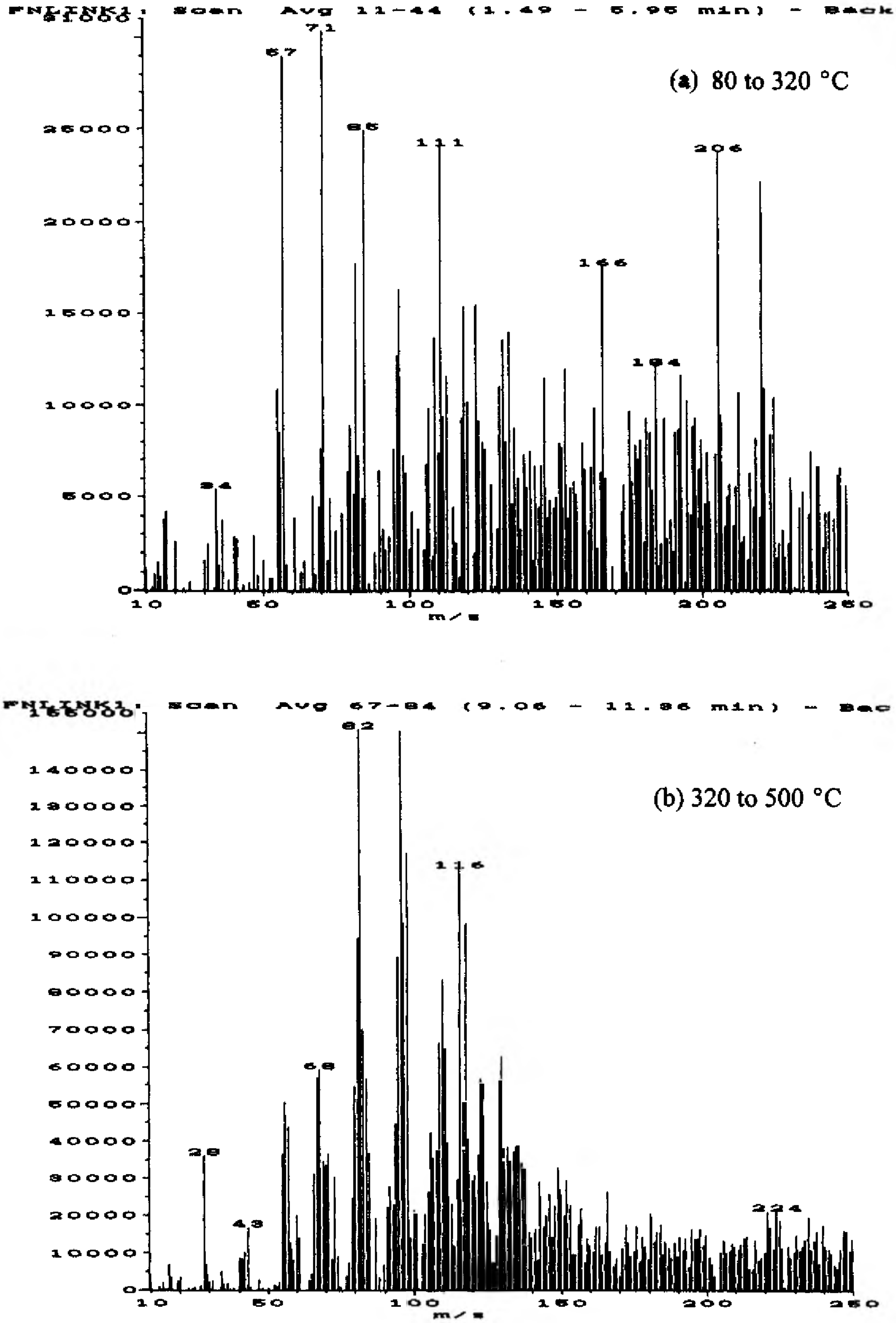


Fig. 8 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for blue oil-based offset-cold ink for temperature ranges of (a) 80 to 320 °C and (b) 320 to 500 °C.

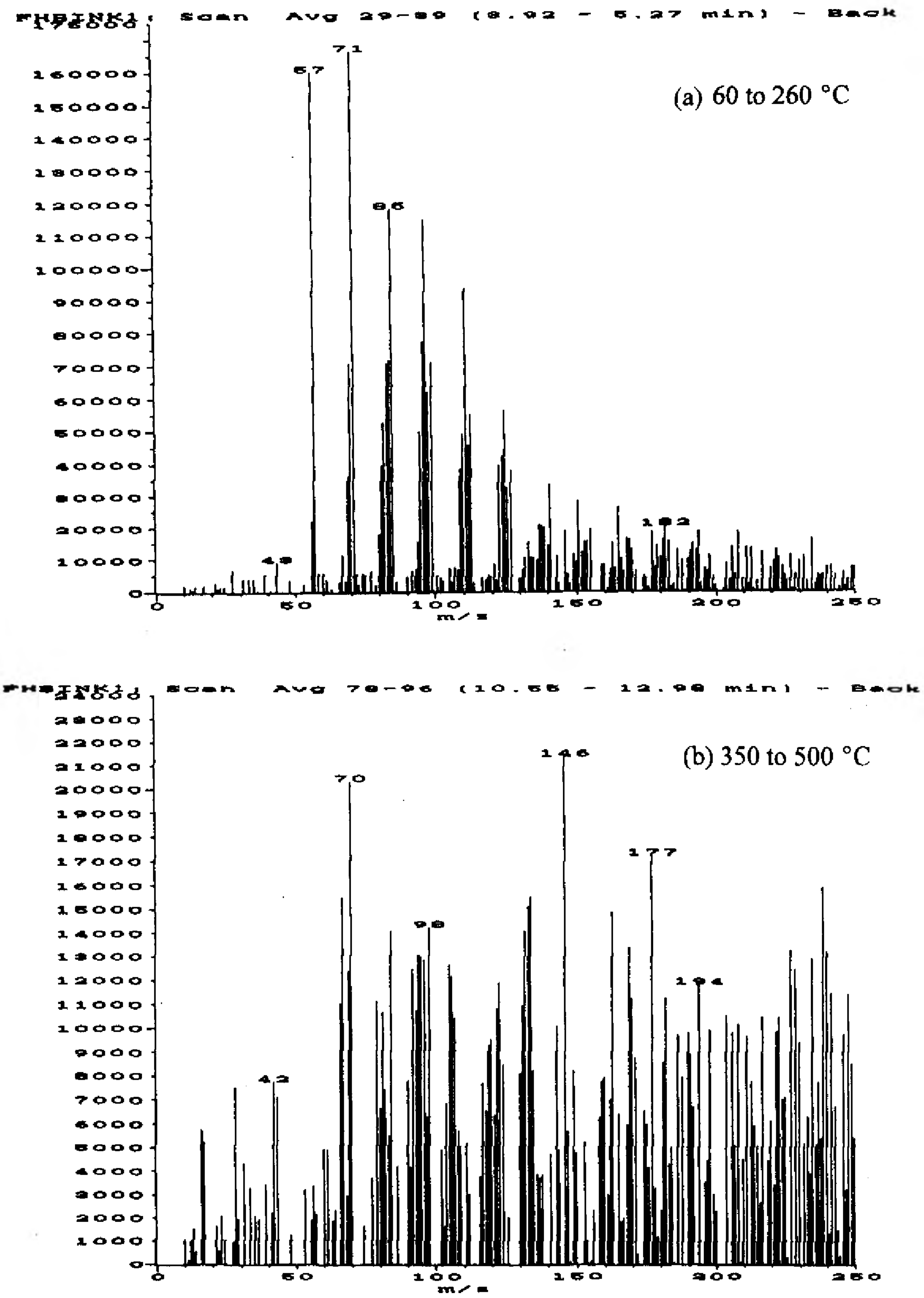


Fig. 9 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for blue oil-based offset-heat ink for temperature ranges of (a) 60 to 260 °C and (b) 350 to 500 °C.

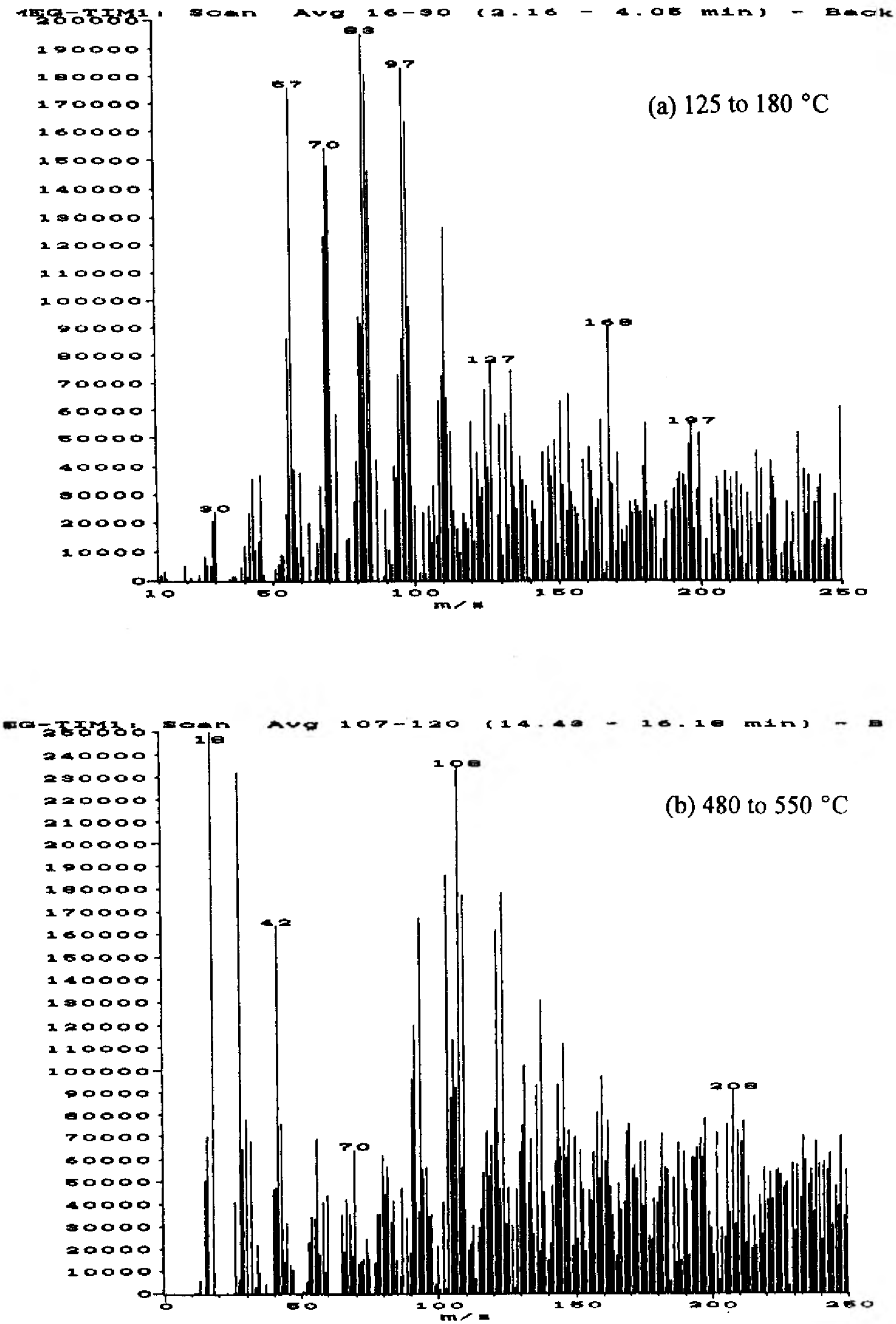


Fig.10 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for the *Time*-magazine ink for temperature ranges of (a) 125 to 180 °C and (b) 480 to 550 °C.

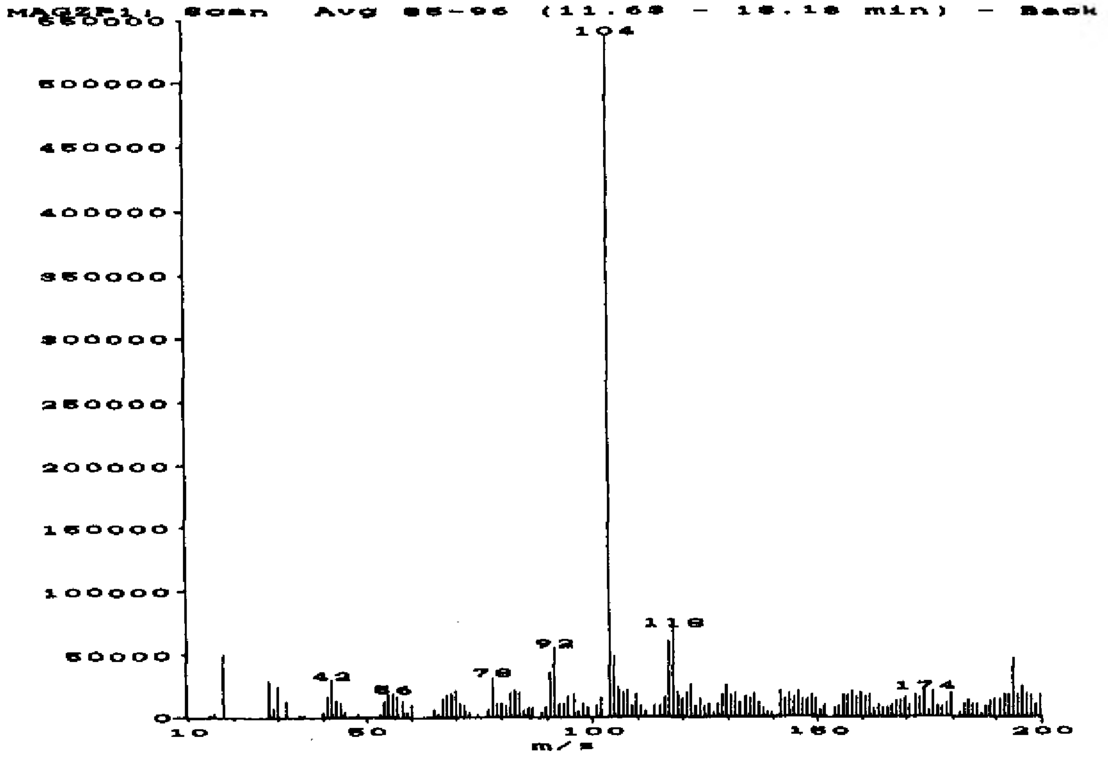


Fig.11 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for the *Windows*-magazine ink for temperature ranges of 400 to 460 °C.

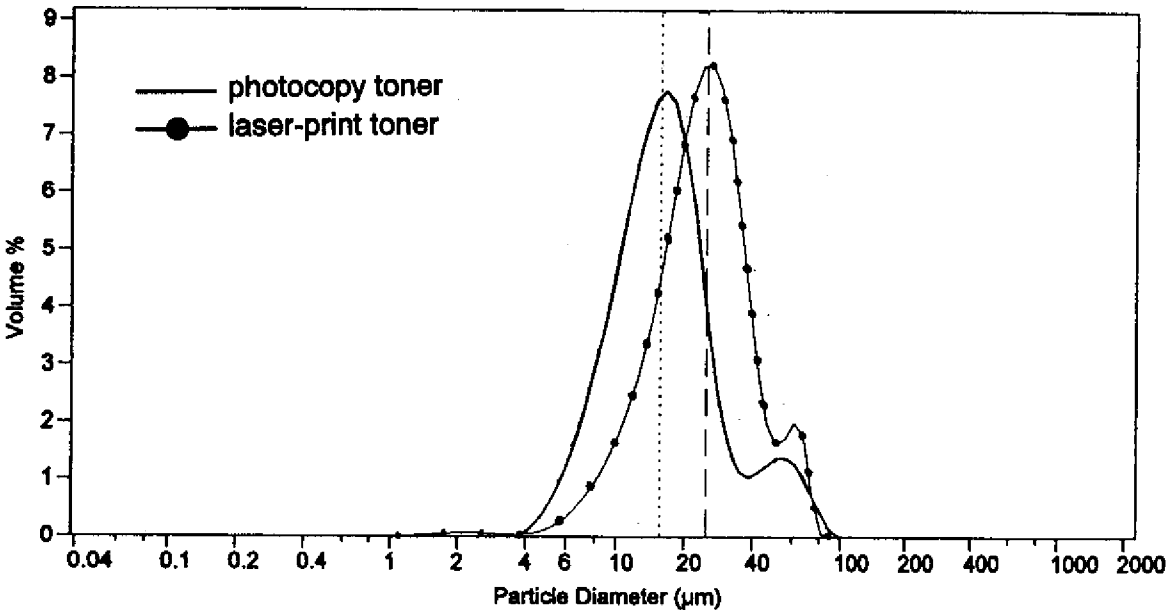


Fig. 12 The particle size distributions of fresh photocopy and laser-print toners measured by the SA-3100LS Particle Size Analyzer (Coulter Co.).

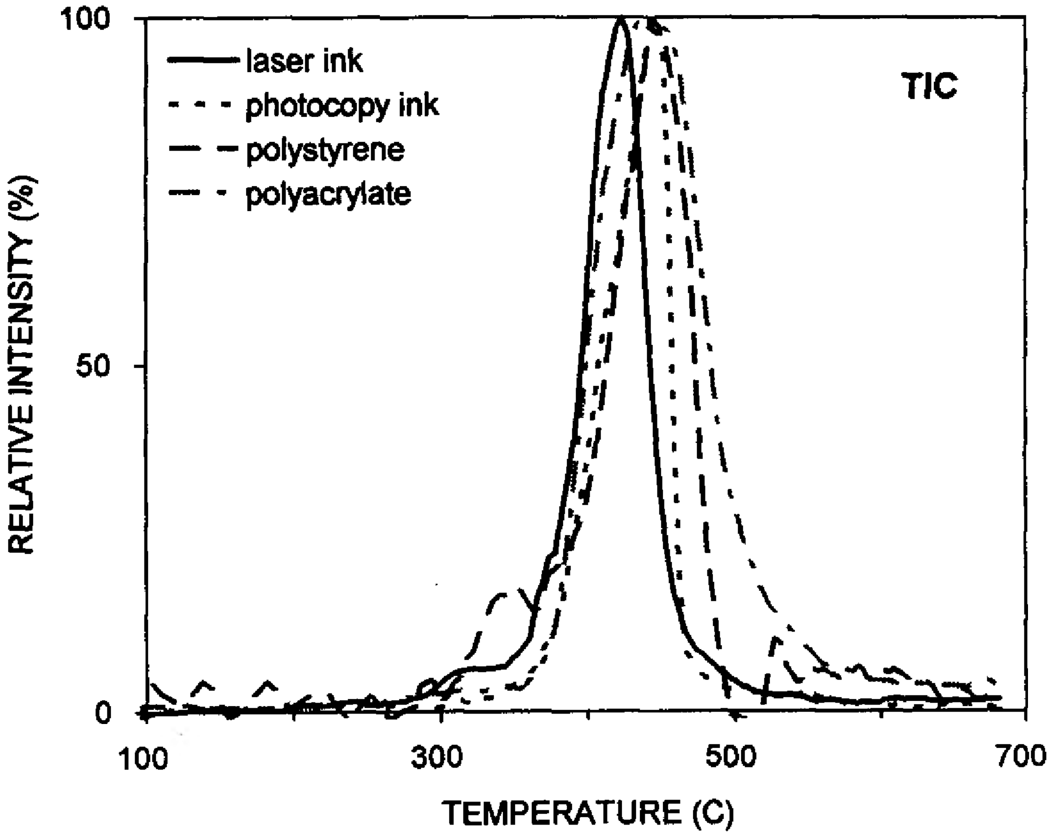


Fig.13 MS TIC spectra of laser-print toner, photocopy toner, polystyrene and polyacrylate.

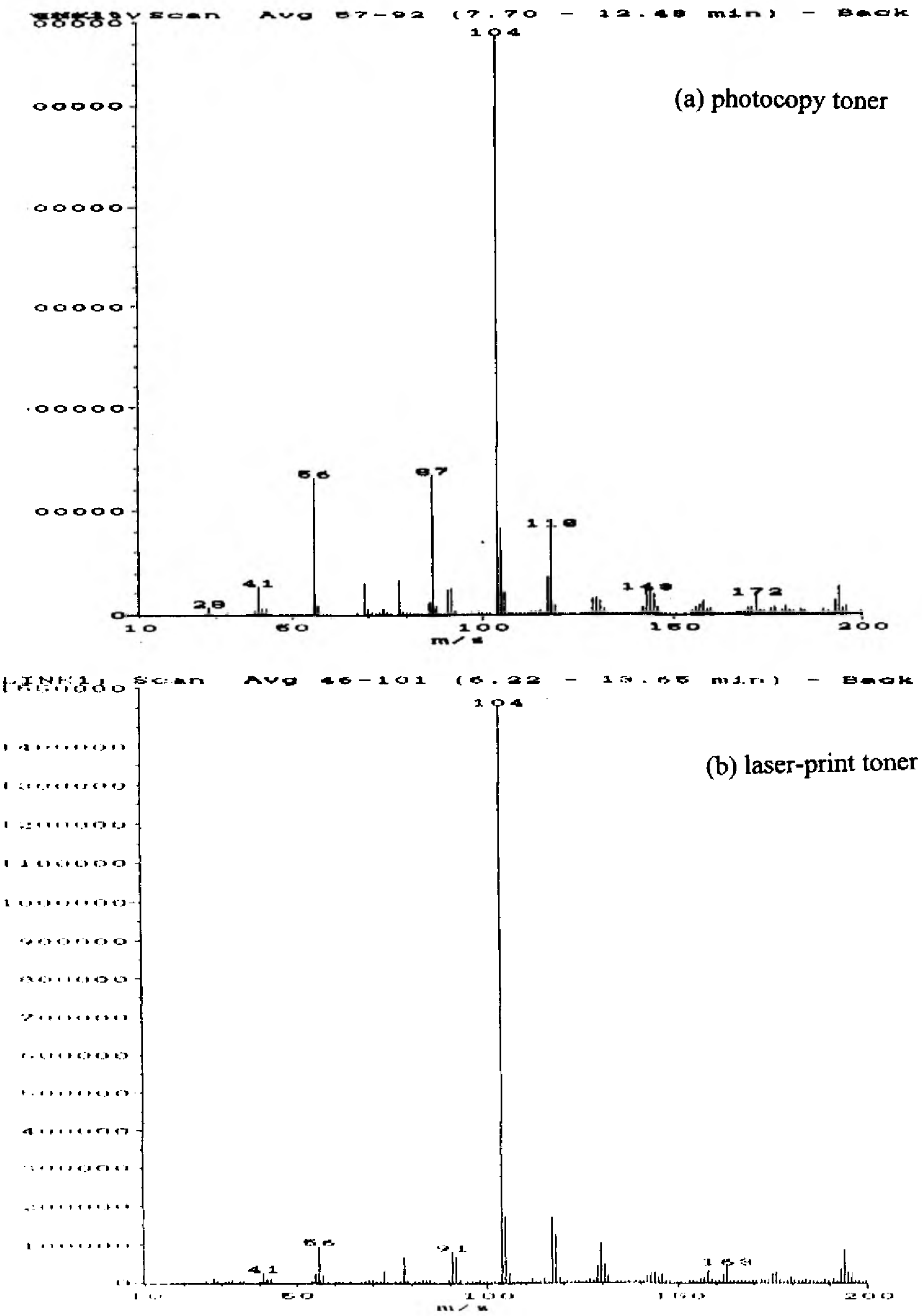


Fig.14 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for (a) photocopy toner and (b) laser-print toner.

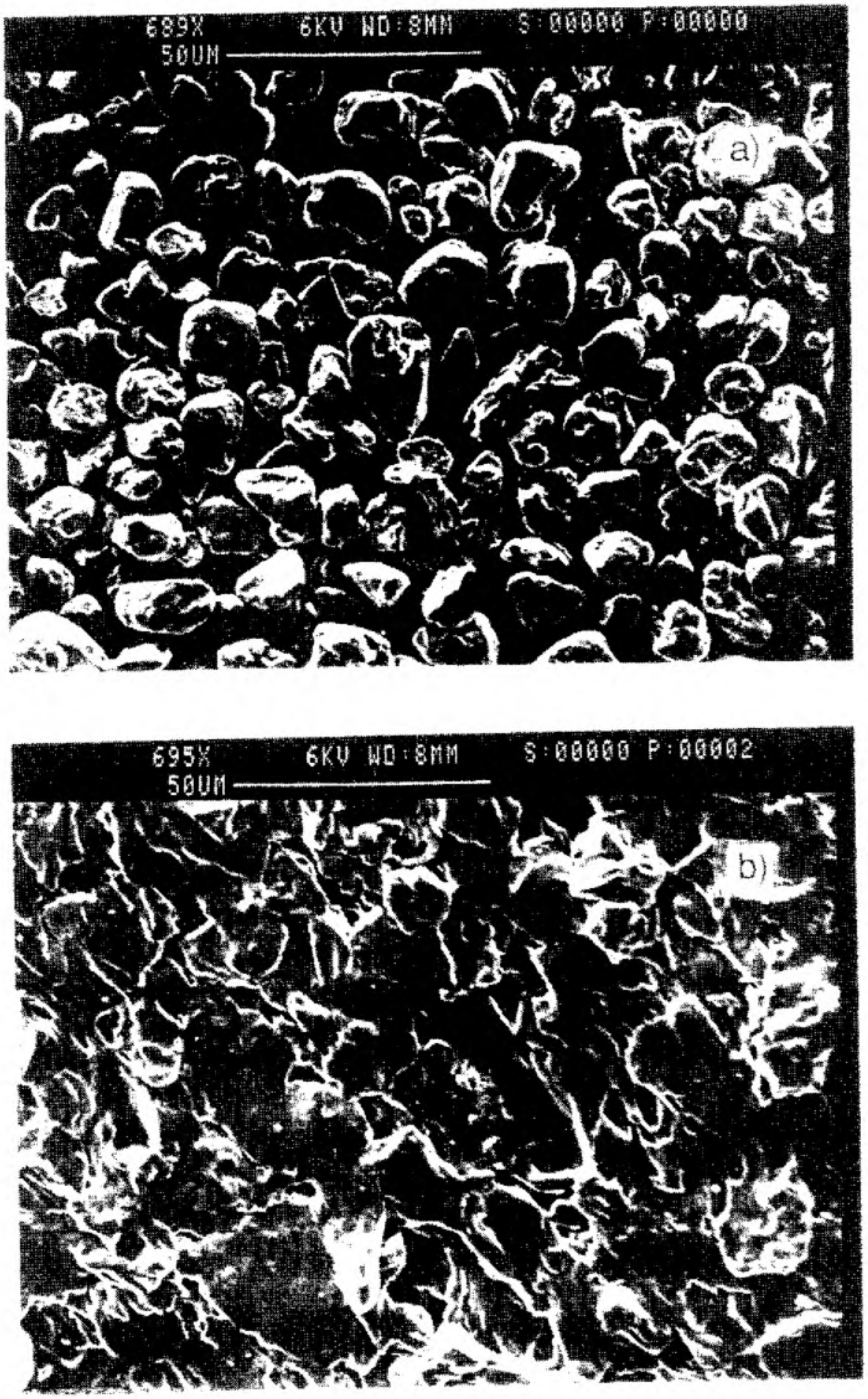


Fig.15 SEM photographs of (a) fresh photocopy toner and (b) printed photocopy toner.

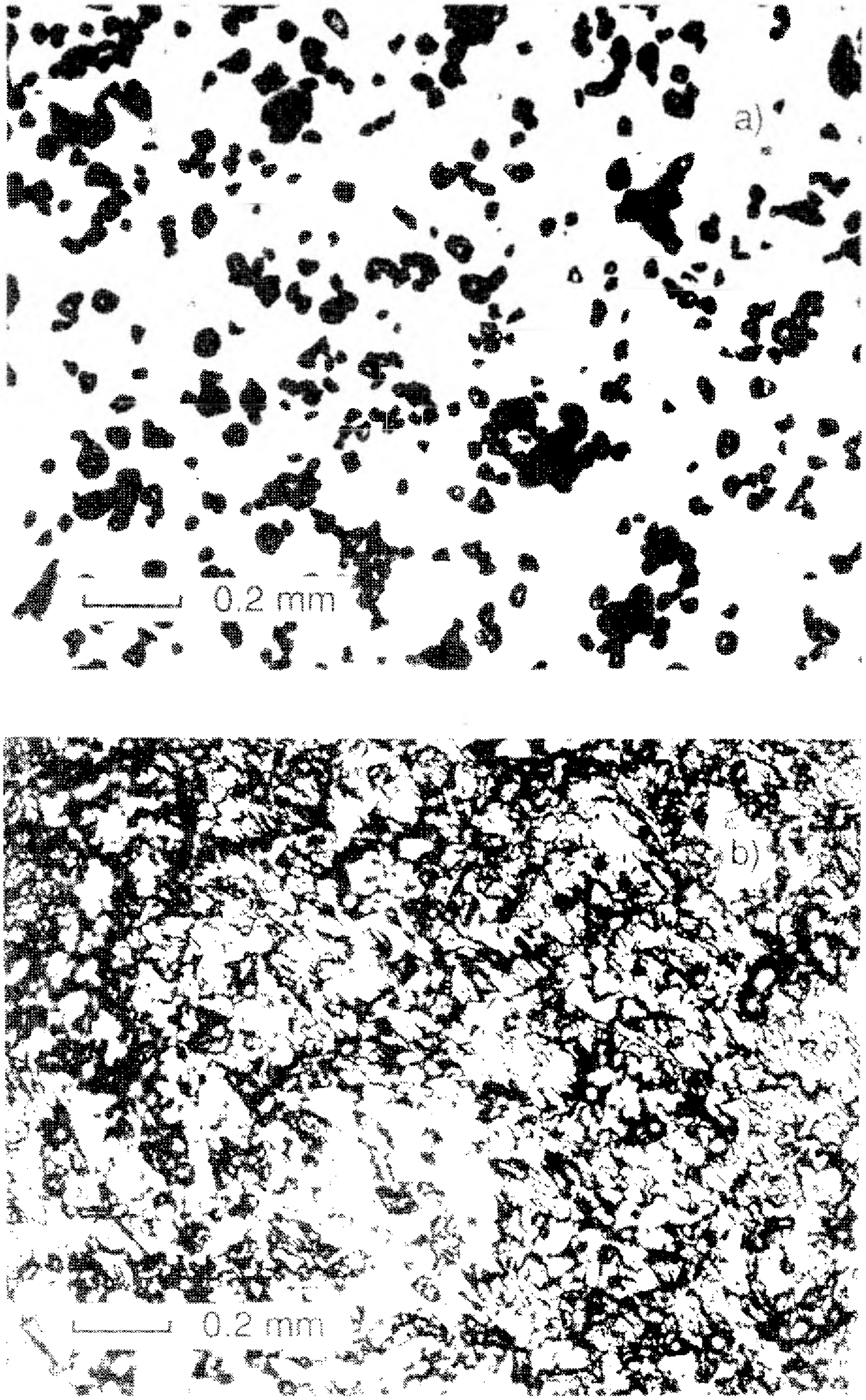


Fig.16 Microscopic photographs of (a) fresh photocopy toner and (b) printed photocopy toner.

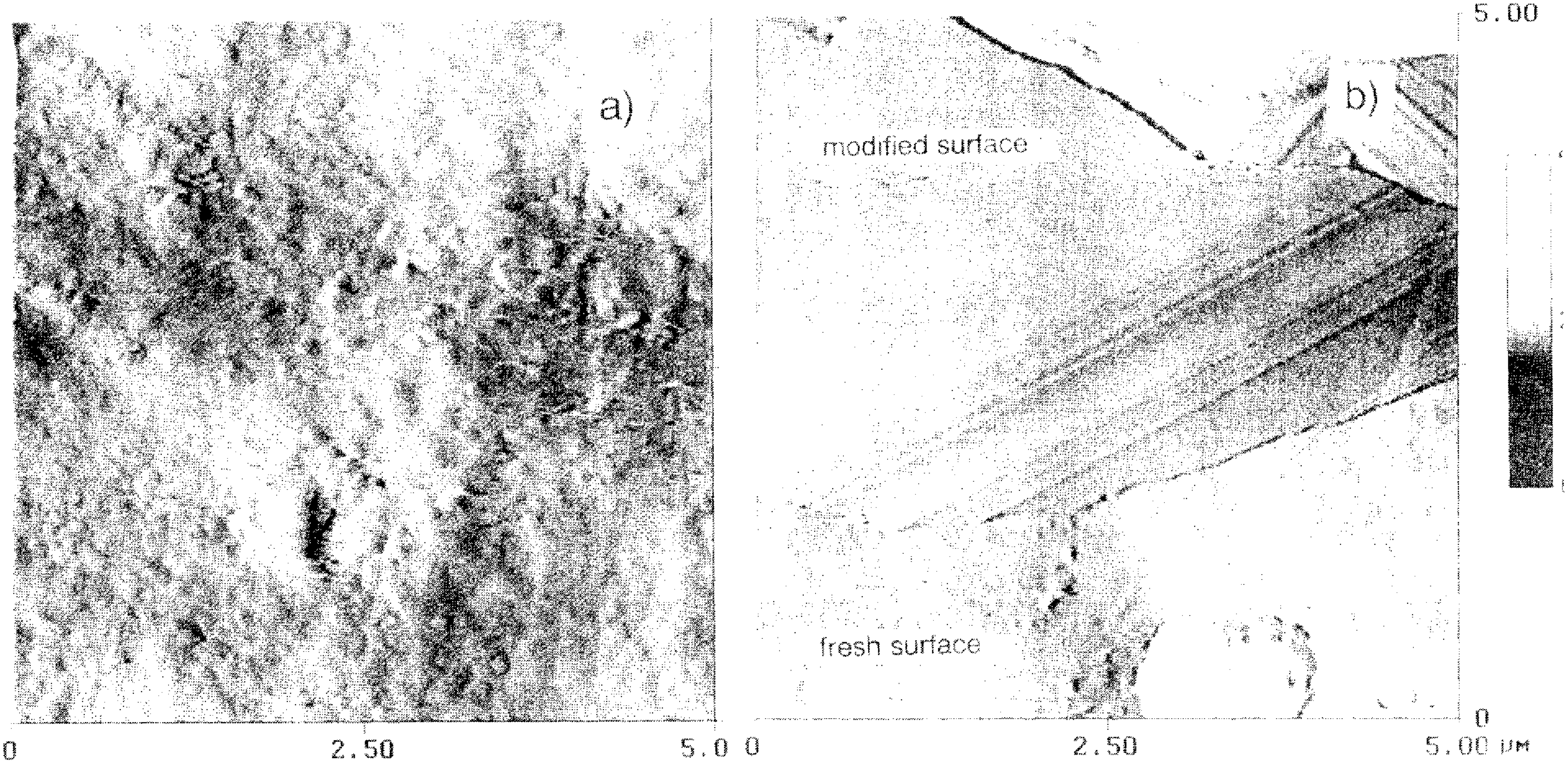


Fig.17 Atomic force microscopy (AFM) images for (a) fresh photocopy toner and (b) printed photocopy toner.

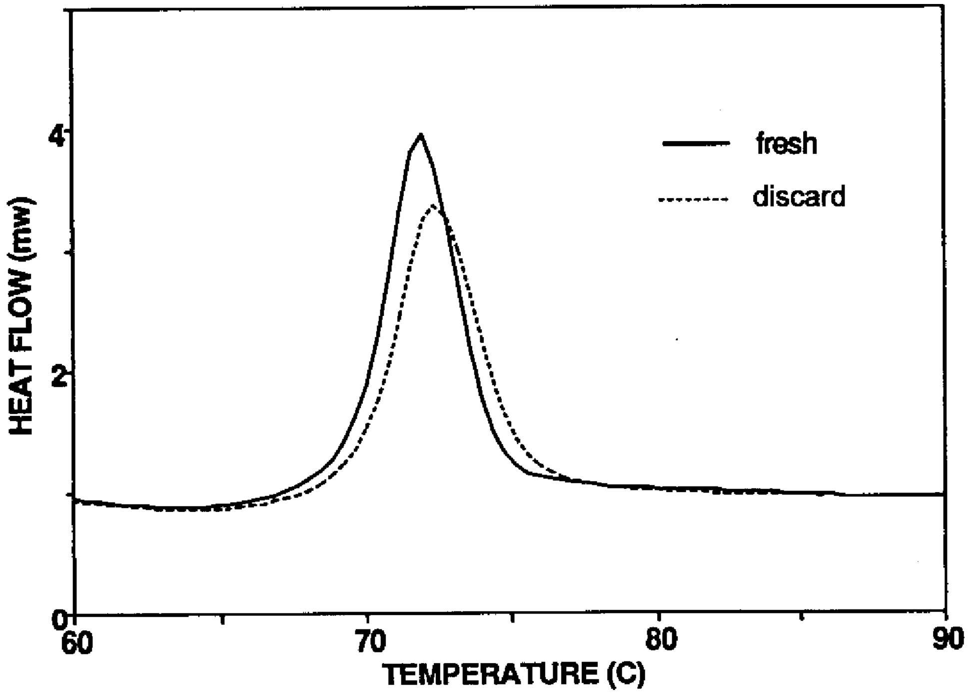


Fig.18 DSC profiles of fresh toner and discarded toner collected from the photocopy machine's waste bottle.

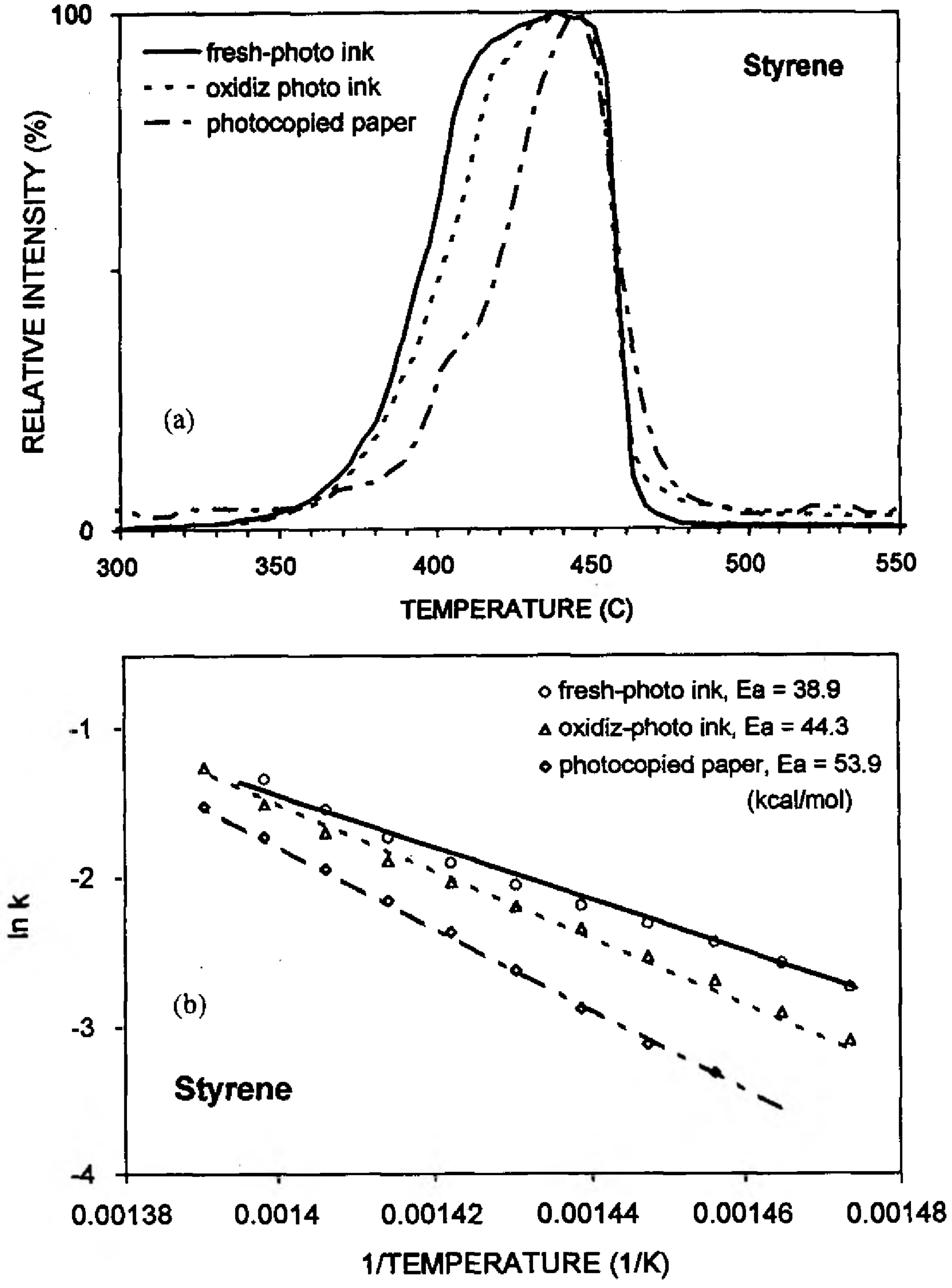


Fig.19 (a) MS selected ion chromatogram (SIC) spectra of styrene (m/z 104) from the thermal decompositions of fresh, discarded and printed photocopy toners, (b) activation energy plot of the rate constants calculated from the MS SIC of styrene (m/z 104) of photocopy toner versus reciprocal temperature.

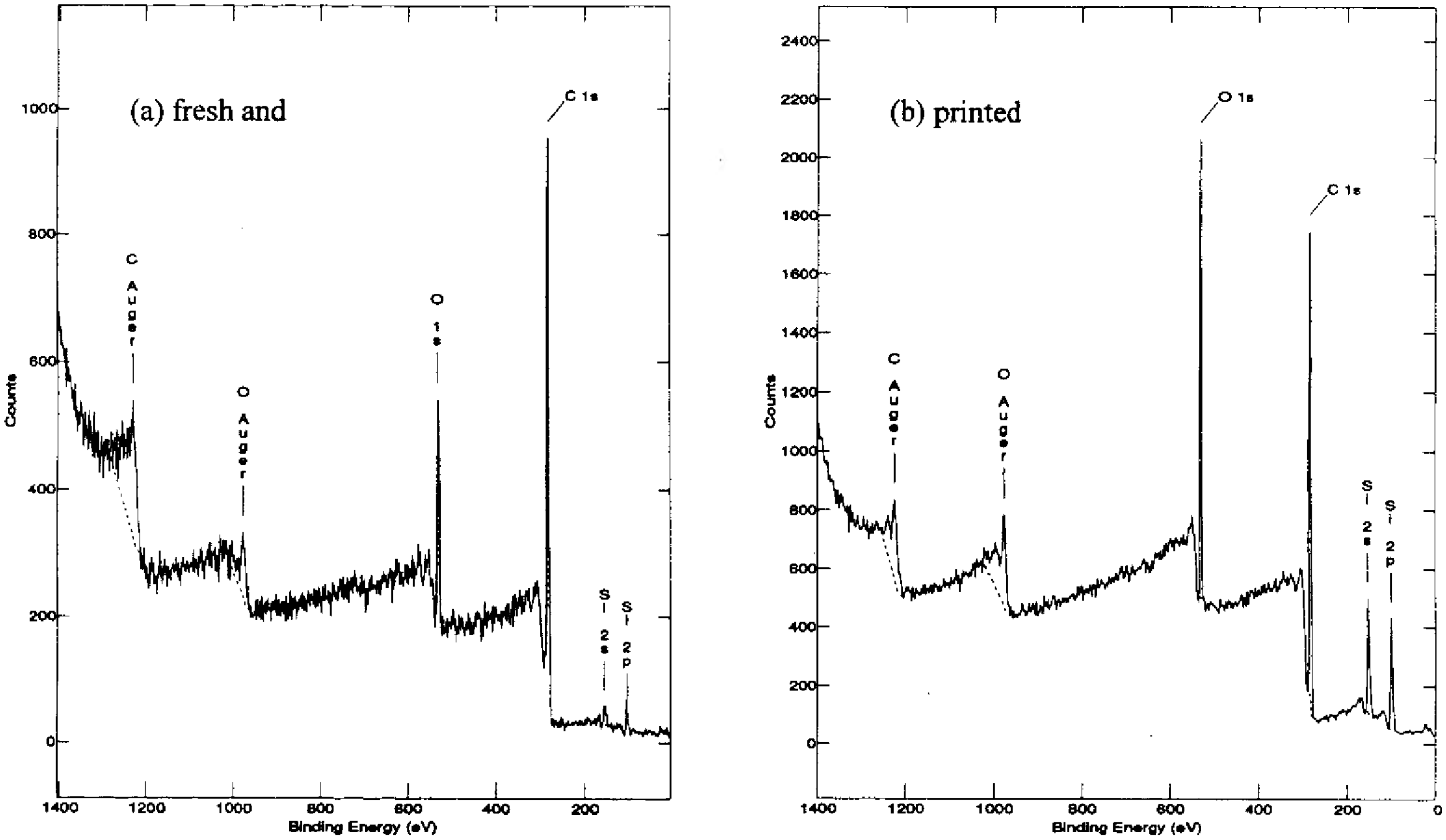


Fig.20 X-ray photoelectron spectroscopy (XPS) spectra of (a) fresh and (b) printed photocopy toners.

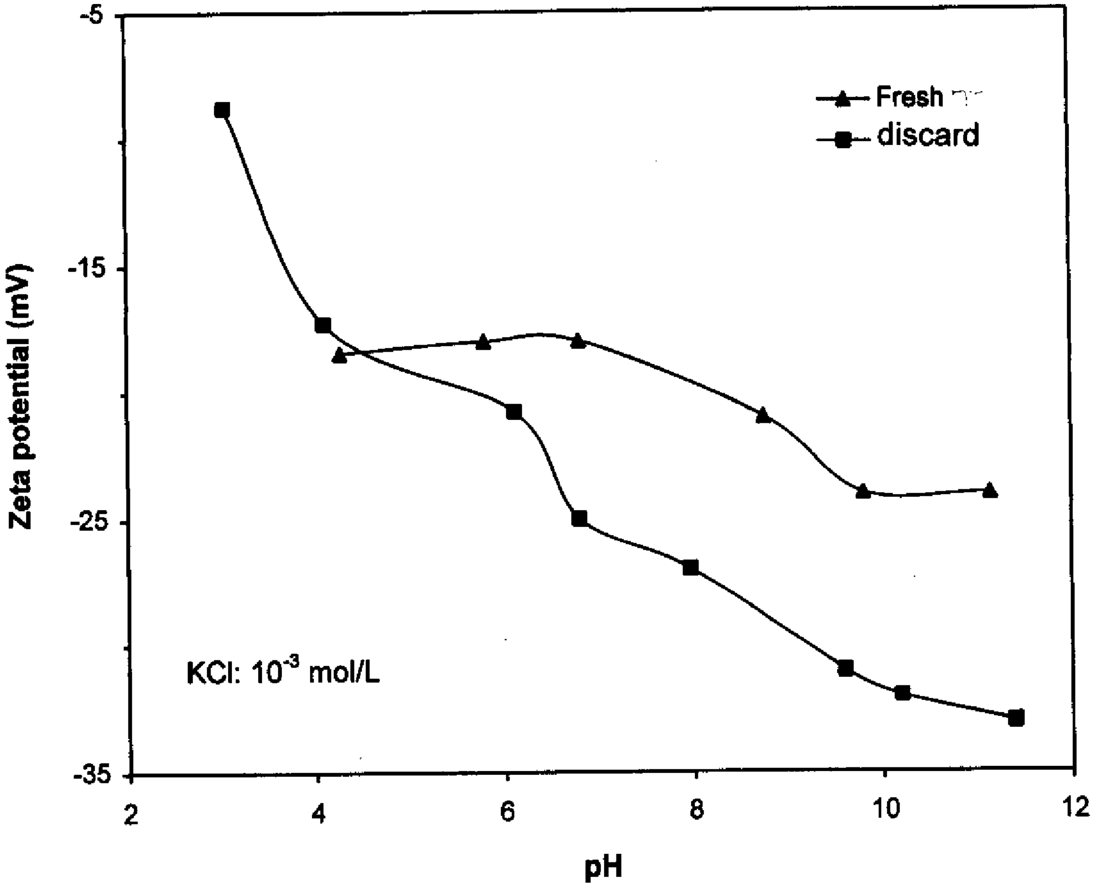


Fig.21 Zeta potentials of fresh and discarded toners as a function of suspension pH.

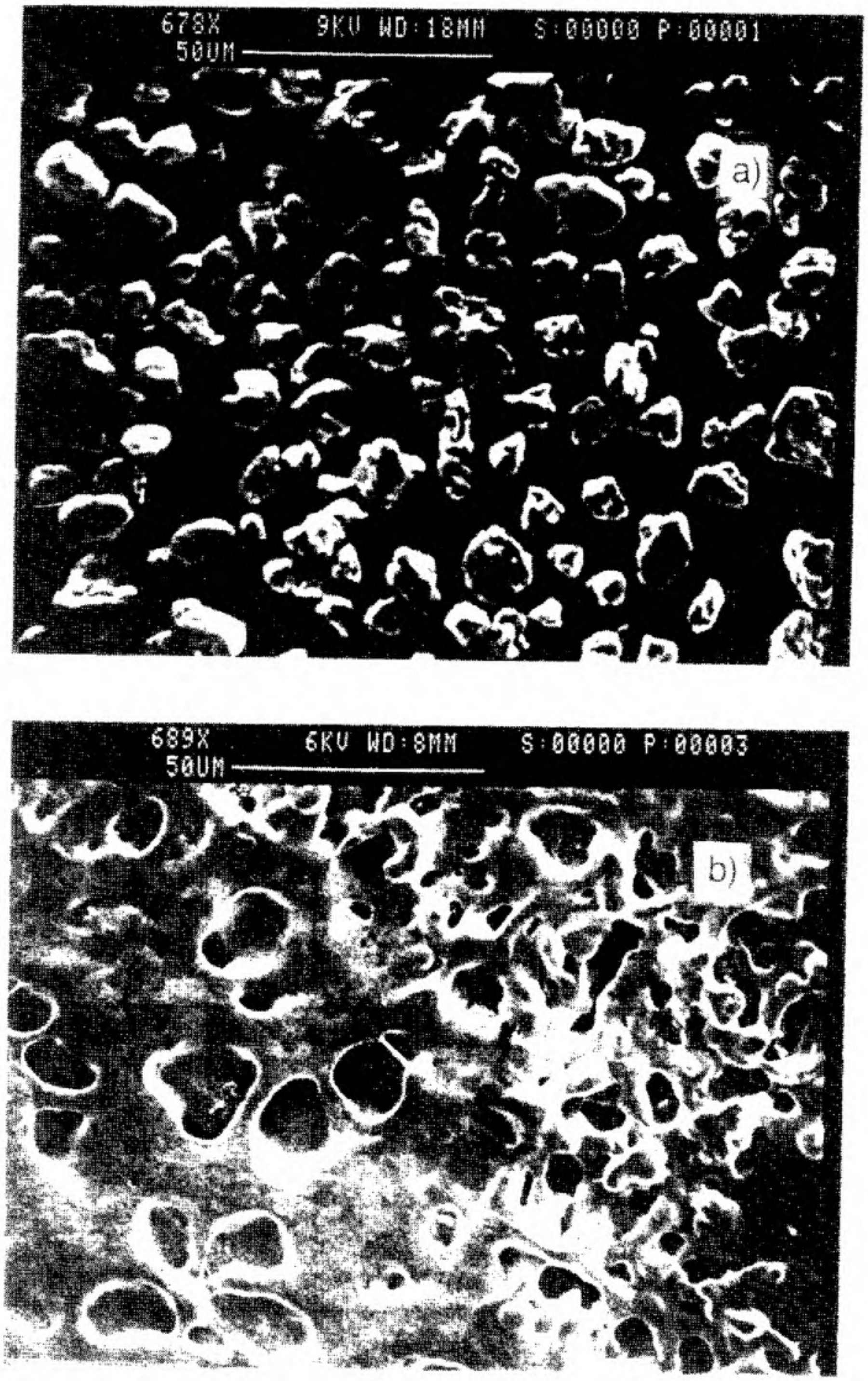


Fig.22 SEM photographs of (a) fresh and (b) printed laser-print toners.

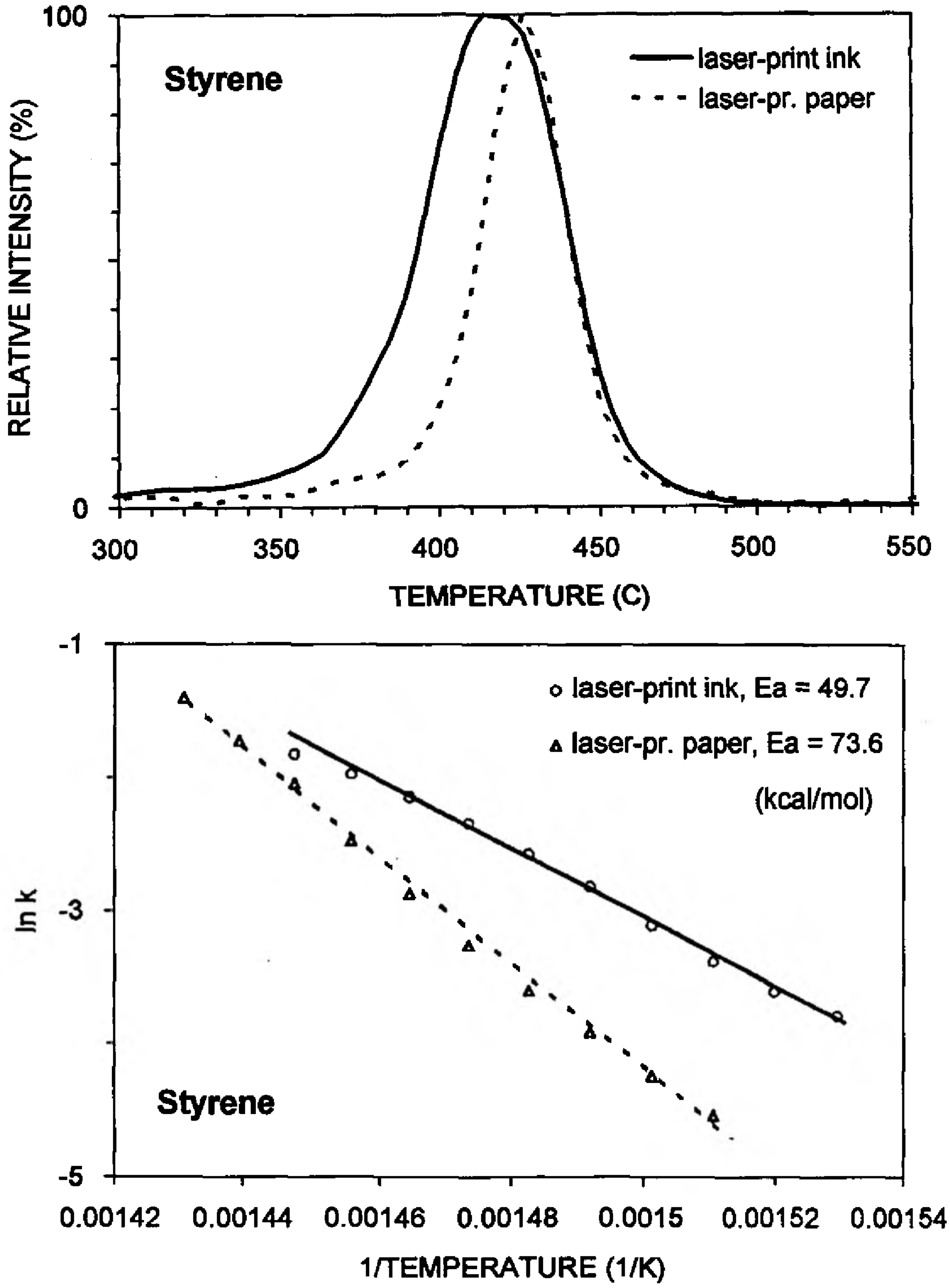


Fig.23 (a) MS SIC spectra of styrene (m/z 104) from the thermal decompositions of fresh and printed laser-print toners, (b) activation energy plot of the rate constants calculated from the MS SIC of styrene for fresh and printed laser-print toners versus reciprocal temperature.