

Characterization of Photocopier Toners By X-Ray Photoelectron Spectroscopy (XPS): How They Change With Age

Review Article

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Abstract

A Past work in the examination of photocopier toners has used various infrared spectroscopic techniques and pyrolysis gas chromatography [1-7]. These approaches have been successful in differentiating between various photocopier toner “libraries”, but with some overlap among toner formulations from the same manufacturer. X-ray Photoelectron Spectroscopy is an instrumental technique that measures the surface composition of a solid sample in regards to both elemental and chemical species. Through the use of high energy x-rays, characteristic photoelectrons are generated from the uppermost 20-100 angstroms of the sample. Data are correlated with known binding energy values to identify the particular atomic species. Due to chemical shifts caused by the immediate molecular environment of the examined atoms, chemical species information is also obtained. For example, the energy of a carbon atom in graphite has a different value from carbon contained in polymeric materials. The carbon and oxygen species, as well as the ratio of carbon to oxygen, are useful for the characterization of the various toner samples. Since most xerographic toners are polymeric in nature, the carbon atoms specifically associated with alcohol, carbonyl or ether bonds yield useful information. Earlier work has shown that with age qualitative and quantitative changes occur [8-10]. This study involved the use of both heat and ultraviolet radiation to mimic the referenced changes on several different toner formulations. A variety of artificial aging conditions were evaluated and comparison with naturally aged samples categorized the parameters by which a toner samples “age” could be determined.

The characteristic surface sensitivity of XPS allowed for the direct examination of samples taken from documents without separation of paper from the toner component. The ability to remove paper, and therefore its components, from the analysis results in a clean sample absent of any contamination. This contamination can be inorganic, such as titanium or calcium from fillers or whiteners, or organic, such as carbon species from cellulose fibers or starch used as a coating.

This technique provides a methodology by which the “age” of toner containing documents can be determined. Future work will include a more comprehensive study.

Introduction

The frequency with which laboratories are receiving documents, which have been prepared by a xerographic process, is increasing as we speak. Since the mid 1980's several groups of investigators have conducted research in an attempt to characterize photocopier toner as a means of identifying the source of the toner material. [1-7]. These investigators have relied upon several different analysis methodologies, many of which included the use of

infrared spectroscopy and/or pyrolysis gas chromatography. In each of these cases a collection of toner samples was examined and compared to the other members of the collection. Groupings by similar analysis results were then made. In most cases these methodologies were able to differentiate many different sources of toner, but due to the ability of multiple machines to use similar toners a specific identification of source was not possible. These investigators did not attempt to determine any information about the age of a photocopied document.

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Background

This work is a continuation by this author concerning the use of X-ray Photoelectron Spectroscopy (XPS) as a technique for analyzing photocopier toner [8-10]. It will report on the changes that occur to toner samples when exposed to environmental conditions that have been used in other work to mimic natural aging. XPS is an atomic spectroscopy, which relies upon the ability of high energy x-rays to generate photoelectrons of characteristic binding energies from the sample. The x-rays impact upon the surface of the sample and transfer their energy, thus causing the release of photoelectrons. An important aspect of this process is that the portion of the sample from which photoelectrons are generated is limited to the very top surface, usually only the uppermost 20 to 100 angstroms. This will vary depending upon the sample material. Since the ejected photoelectrons have a characteristic energy depending upon the atomic species from which they originated, the technique can be used to identify atomic species. In addition, because each atomic photoelectron is influenced by the molecular environment from which it came, not only can you identify the atom (carbon), but the type of atomic species (carbon from an alcohol).

Experimental

Output was generated from three (3) different xerographic machines, a Xerox XD155df printer/copier, a Canon Image Runner 550(copier) and a Hewlett Packard IIP (printer). A 1cm hole punch was used to remove samples from areas of the output that were completely coated with the toner material. A total of 9 samples were removed from each output and 8 of the samples were treated with exposure to 80°C for 1 hour, 2 hours, 3 hours and 12 hours, and a mixture of short (254nm) and long (365nm) ultraviolet light for the same time periods respectively. The ninth sample was not treated. Each of these samples was analyzed within 3 days of preparation by XPS using a Perkin Elmer PHI model 5400 Spectrometer. The experimental conditions included a Mg anode at 15kV and 350ma under a pressure of 3×10^{-8} and a

hemispherical detector. The sample area was collimated to a spot 1.5mm in diameter with a stage angle of 45°, and both survey spectra from 1 to 1000ev, and multiplex spectra in the carbon (280 to 300ev) and oxygen (525 to 545ev) regions were collected. The survey spectra were analyzed to determine the presence of elemental species and the multiplex spectra was used to determine both atomic concentrations and for molecular species identification by curve fitting routines. Calculations were performed upon the data to include carbon-oxygen ratios and analysis of molecular components.

Results and Discussion

The survey spectra were found to indicate the presence of carbon, oxygen and silicon only. Oxygen appears at about 530ev, carbon at about 285ev and silicon with peaks at about 100ev and 150ev. The multiplex spectra, with subsequent curve fitting to distinguish molecular species, indicated 3 different parameters that were useful in determining the presence of change with environmental treatment. These parameters are carbon oxygen ratio (C/O), atomic percent of individual carbon species and peak energy shift as a measure of energy differential between multiple peaks in the same sample. Table 1 illustrates the trends in differences of C/O ratio, or lack thereof, between untreated samples (fresh) of the 3 toner types and samples exposed to ultraviolet radiation for varying periods of time.

A modest trend in the decrease in C/O ratio with increasing time of exposure is noted in the H-P samples. This data is not extremely convincing and would suggest that the use of ultraviolet radiation to alter toner samples with the subsequent measurement of C/O ratios is not the optimal methodology. As illustrated in Table 2, however, the use of heat to alter toner samples shows clear trends in the decrease of C/O ratio in both the Xerox and H-P samples. The trend toward a decrease in C/O ratio is expected due to the natural increase in incorporation of oxygen in the samples over time.

Table 1. C/O ratios for different toner types exposed to varying periods of ultraviolet radiation.

Sample	Xerox	Canon	Hewlett Packard (H-P)
Fresh	26.8	17.5	12.5
1 hr. UV	34.7	16.5	9.4
2 hr. UV	28.4	21.4	8.1
3 hr. UV	28.4	16.9	9.9
12 hr. UV	21.7	16.5	10.1

Table 2. C/O ratios for different toner types exposed to varying period of heat (80°C).

Sample	Xerox	Canon	Hewlett Packard (H-P)
Fresh	26.8	17.5	12.5
1 hr. heat	4.6	12.2	10.1
2 hr. heat	7.9	24.6	7.9
3 hr. heat	3.5	20.7	8.1
12 hr. heat	9.9	16.9	8.2

Table 3. Change in Atomic % and energy shift (in eV) as a result of ultraviolet radiation treatment.

Sample treatment	Atomic percent of high energy peak	Energy shift between high and low energy peaks (ev)
Fresh	11.4	3
1 hr. UV	20.9	3
2 hr. UV	6.8	3.4
3 hr. UV	6.3	3.4
12 hr. UV	6.7	3.6

Table 4. Change in Atomic % and energy shift (in eV) as a result of elevated temperature treatment.

Sample treatment	Atomic percent of high energy peak	Energy shift between low and medium energy peaks (ev)
Fresh	9.2	1.4
1 hr. heat	9.6	1.6
2 hr. heat	12.2	1.5
3 hr. heat	5	1.7
12 hr. heat	6.6	1.8

Several examples of changes in atomic percentage of molecular components were found among the toners examined. These often were found to correlate with energy shifts in peak position. Table 3 illustrates this situation with the Hewlett Packard toner when treated with ultraviolet radiation. Table 4 illustrates a similar example with the Canon toner, but with elevated temperature treatment.

Conclusion and Applications

It is clear that as with many other materials xerographic toner changes with time by the incorporation of oxygen, i.e. oxidation. The use of XPS to measure these changes has been demonstrated and provides a contamination free methodology for performing these measurements. One must clearly attend to the choice of sample to prevent the measurement of the paper substrate, but in those instances where a clear coverage of toner exists the likelihood of contamination or interference from the paper is minute. Since several measurable parameters have been identified as indicators of change in toner samples the analysis scheme should include the measurement of all these parameters.

Practical application of this methodology is similar to several techniques used in the analysis of inks for the determination of age. By comparison of untreated toner samples with environmentally treated samples of the same toner, a measurement of the identified parameters can allow for a determination of relative age. Modification of the treatment guidelines will provide for threshold values beyond which an examined toner sample can be determined to be either "old" or "new". Depending upon the circumstances surrounding the examined toner a determination of consistency with stated facts is probable. The author has noted that the changes in the measured parameters correlate with an approximate natural aging of 2 years. This will vary slightly with differing toner samples and the author is investigating this range.

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