THE USE OF ATOMIC FORCE MICROSCOPY TO DETERMINE THE SEQUENCE OF CROSSED LINES

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ABSTRACT: The temporal order in which the lines are written can, in most cases, be established by optical and electron microscopy techniques. During the last years, new, non-destructive microscopical technologies, such as scanning probe microscopy [5], have been developed which offer new possibilities for surfaces analysis at high magnification. The aim of this study was to explore if such a technique could be used to line crossing problems. According to the nature of the ink lines, the exploration of this technique has been performed by an atomic force microscope (AFM) [1]. Only the imaging abilities of this instrument were investigated. The obtained AFM images show the same qualitative information compared to the SEM images. Consequently, the sequence of two crossed lines can be determined by this visualisation technique.

KEY WORDS: Atomic force microscopy; AFM; Paper; Ink; Line crossing; Intersection; SEM; Document examination.

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INTRODUCTION

A variety of approches have been developed to solve crossing problems [9]. Different techniques are chosen in function of the material configuration and the nature of the intersecting lines. Therefore, no technique exists which is applicable to the whole range of line crossing problems.

The most widely used sequence in the analysis of line crossings is based on optical and electron microscopy. The physical limitations of light microscopy (low resolving power, decrease of depth of focus and the low magnification range, interaction of light with the matter) are overcome by the electron microscopy [2, 6, 8, 10, 11]. Both methods are based on the surface examination of the ink deposits at the intersection area.

The recent development of new microscopical technologies offers new possibilities in the field of surface analysis. Scanning probe microscopy allows imaging of structures under ambient conditions (no need of vacuum) without sample modification (conductive coating).

These new technologies include a family of instruments used to image and measure surfaces properties, such as topography, conductivity, friction or elasticity. The main feature to all the different types of scanning probe microscopes (SPM) is that the measurements are performed with a sharp probe or tip scanning over the surface of the sample. As opposed to optical microscopes (OM) and scanning electron microscopes (SEM), neither electromagnetic radiation nor lenses generate the image. Furthermore, SPM's scan samples in all three dimensions (x, y and z). OMs and SEMs have larger fields of view, but SPMs provide the highest resolution (cf. table I). However, only SPMs work on nearly all samples with minimal sample preparation and without sample modification.

TABLE I. COMPARISON OF MEASUREMENT PARAMETERS OF DIFFERENT TYPES OF MICROSCOPES.

	Optical microscope	SEM	SPM
X, y resolution	1.0 μm	5 nm	0.1 – 3.0 nm
Z resolution	–	–	0.01 nm
Magnification range	1x – 10^3x	10x – 10^6x	10^2x – 10^8x
Sample preparation & Required sample characteristics	Little Sample not completely transparent	Coating Vaccum compatible	None Maximal sample roughness should not exceed 5-15 μm

The most versatile member of the SPMs is the atomic force microscope (AFM). The aim of this study is to establish if this new technique by the means of an AFM can be used for the examination of intersecting ink lines on paper and can be applied to rough and irregular surfaces, such as paper and different types of inks, and, therefore, different thicknesses or heights of ink layers.

INSTRUMENTATION AND MATERIALS

Atomic force microscope: principle and functioning

Like all other scanning probe microscopes, the AFM utilises a sharp tip (radius of curvature ≈ 20 nm) moving over the surface of a sample in a raster scan [7]. The tip is mounted on the end of a 100–200 μm long cantilever which bends or deflects in response to the sample topography (cf. Figure 1).

Fig. 1. Illustration depicting the working principle of the atomic force microscope.

This deformation is detected by reflecting a laser beam off the back of the cantilever onto a two (or sometimes four) segment photodiode. The cantilever deflection gives rise to a modification of the laser beam reflection angle. This change is detected by the photodiodes that are connected to a computer, which reconstructs on the monitor screen the topography of the sample. The nature of the sample has an influence on the instrument resolution: flat and hard samples can be imaged with a higher resolution than rough and soft ones. The resolution can achieve values of less than one a under ideal conditions.

A conventional optical microscope is optionally mounted on the top of the AFM so that the tip above the area to be explored can be precisely positioned.

The imaging of topography can be achieved in many ways (contact, tapping mode, etc.). Additionally, the AFM offers several different operating

modes, such as friction [4], force volume [3] or phase. These modes give complementary information about the physico-chemical properties of sample surfaces.

For this first exploring step of this microscopic technique, only the imaging abilities of the AFM were investigated. This work has been performed by operating the AFM in the tapping mode.

In this mode, the cantilever is oscillated near its resonant frequency as it is scanned over the sample surface. The tip is brought closer to the sample surface until it begins to intermittently contact (tap) the surface. This contact with the surface causes the oscillation amplitude to be reduced. This characteristic is used to follow the surface topography. Because the contact with the sample is intermittent, the tip exerts negligible frictional force on the sample, thus, leading to an increase in resolution for the instrument and a high quality image of soft samples, such as ink layers.

Sampling and instrumentation

For this first approach, heterogenous line crossings were produced on two different qualities of plain papers and the following writing media were chosen: dot matrix fabric ribbons (new and worn out), typewriter carbon film ribbon, toner (laser printer), ball-point pens, floating ball pens and fibre-tip pens. The color of all media was black.

The crossing samples were cut and mounted on 12 mm AFM sample holders using double sided carbon coated adhesive tabs. Thanks to the size compatibility, the prepared samples could be fixed without modification on SEM holders.

The results presented were obained with a Digital Instruments® (Santa Barbara, CA) AFM series Nanoscope® IIIa with a J scanner (having maximum scanning size of 120 μm) and tapping mode cantilevers (Digital Instruments® and NT-MDT®). All the images were generated in tapping mode in air at room temperature. The AFM was additionally equipped with an optical microscope mounted above the AFM base.

Some of the obtained AFM results were verified by SEM examination of the crossing samples. This control was performed by a JEOL JSM 6300 field-emission scanning electron microscope (FE-SEM) with an acceleration voltage of 5 KV and a working distance of 15 mm.

RESULTS

In order to know the structure of each ink deposit, as well as that of the supports, all of these have been checked. After that, the crossing zones of the model crossings have been examined. It appears that the characteristic

structure of each ink medium is similar to the known SEM images. Inks containing pigments can be easily distinguished from the paper, particularly if the deposits are thick. Water/aqueous based inks (i.e. fibre-tip pen inks) are more problematic, because of the aqueous nature of these ink types. The dyestuffs generally are absorbed into the cellulose fibres, therefore, they do not lay at the surface as in glycol based ball-point pen inks.

Figure 2 and Figures 4–10 present the AFM images of the crossing areas of some model crossings and show the ink deposit topography in the intersections of two lines. As mentioned, only heterogenous ink crossings were examined. In Figure 2 the ball-point pen ink deposits appear as a fluid dense and smooth layer, while the printer ribbon ink deposits exhibit a granular surface as it can be noticed on the right side of Figure 2. The paste of the ball-point pen covers the granular ribbon ink, and, therefore, the sequence is clearly recognizable. The SEM image (Figure 3) shows the same structure particularities as visualised in Figure 2. The ball-point pen ink (above) is situated on the ribbon deposit (below).

Figures 4–6 show the case of crossing between a floating ball pen line and a toner line. The visualisation of the floating ball pen ink is less easily detectable on paper. The layer is often less compact. However, both layers could be distinguished by their surface appearance. One has a granular aspect (Figure 4), while the toner has a smooth and homogeneous surface (Figure 5). The transition zone depicted in Figure 6 shows the ink layer which covers the toner surface. The opposite case (toner on the top of the ink deposit) is more difficult to visualise because of the capability limits of the AFM used. The height variation between both layers in the transition zone exceeds the z-axis freedom of motion of the instrument used.

Figures 7 and 8 concern the crossing configuration between a carbon film ribbon deposit and a floating ball pen stroke. Compared with the toner layer, the ribbon deposit is less smooth, but still compact with a slightly granular surface (Figure 7). As shown before, the floating ball pen ink is granular, but the constituent particles are finer than the ribbon particles. Consequently, the sequence can be distinguished as shown in Figure 8. The ink stroke lies on the ribbon pigments.

The visualisation of the fibre-tip pen ink is very difficult on a paper surface because of its penetration into the paper substrate. In order to know the morphological structure of this kind of ink, some ink lines were drawn on polycarbonate filters (one side is polyvinylpyrolidone coated, Millipore®). In this way, it was possible to visualise some of the non-absorbed ink droplets (Figure 9). Figure 10 depicts the 3D representation of Figure 9.

All these images represent only a view of selected zones, the determination of the line crossing sequence is based on the observation of the whole crossing area.

Fig. 2. Transition zone between ribbon dye on the right side and ball-point ink on the left side. The ball-point ink deposit lies on top of the grains of the ribbon dye.

Fig. 3. Same crossing as shown in Fig. 2. Similar ink aspects are encountered by SEM examination (ball-point pen ink at the top of the ribbon deposit).

Fig. 4. AFM image of the floating ball pen ink structure.

Fig. 5. AFM image of the toner deposit (compact smooth layer) outside the crossing.

Fig. 6. Crossing zone between the floating ball pen ink (left side) and the toner deposit (right side). The latter is covered by the floating ball pen ink.

Fig. 7. AFM image of carbon film ribbon deposit (compact slightly granular layer) outside the crossing.

Fig. 8. Crossing area between floating ball pen ink and ribbon layer. The floating ball pen ink pigment particles are on the ribbon dye. Consequently, the letter has been printed before the writing.

Fig. 9. Fibre-tip pen ink on a Millipore® filter (scale: μm). The white spots represent the non-absorbed ink droplets.

Fig. 10. Same image as Fig. 9 in 3D representation (image rotation: 120°).

DISCUSSION

The examined samples have shown that reliable and conclusive results can be obtained with the AFM. The visualisation of ink deposits and their differentiation according to their origin are possible, and, therefore, the determination of the sequence in which the lines cross. The topography imaging was performed at medium magnification and acquired under ambient conditions. The surface is neither altered by conductive coating (SEM) nor by tip contact. Consequently, the AFM technique can be a part of the microscopical examination sequence for line crossings. The technique is non-destructive. However, the samples had to be reduced to the stage size of our instrument (below 2 cm^2). This limitation is related to the instrument used and can be overcome by using an other type of AFM.

In this work, not the whole range of writing media was examined, but the verified samples of different ink nature allow one to conclude that the limitation is given by the ink absorption into the cellulose fibre of the support. In the case of the fibre-tip pen ink, it was not possible to distinguish the deposit on the paper fibres, but the thin ink layer could be detected on a less

absorbant support (Millipore® filter). Another problem was the variations in height between two ink deposits. In these cases, it was not possible to image the transition zone of toner deposit laying on the ink. The difference in height that exceeds the z-range capacity of our instrument (restricted to 5 μm). In this case, only a higher magnification and, consequently, a smaller field of view can overcome this limitation, as well as, a translation into the crossing area of both media. This restriction is also due to the instrument used and can be eliminated by using a different instrument model (Bioscope®).

CONCLUSIONS

For this exploring approach, only a few different inks have been studied. On this basis, the obtained results indicate that this microscopical technique could be a powerful alternative to the SEM. The absence of sample modification gives the possibility to include this method in an examination sequence (OMÕ AFMÕ SEM). However, these first encouraging results do not allow one to conclude that all possible configurations could be solved by the AFM. Limitations are likely given by the absorption of the ink layer into the paper fibres. Only one operating mode has been used for imaging the topography of ink deposits. It is possible that other modes can give reliable and conclusive results to the line crossing problem. Further studies are necessary in this sense to achieve an overall evaluation of the method.

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