

# Nano-scale composition of commercial white powders for development of latent fingerprints on adhesives

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## Abstract.

Titanium dioxide based powders are regularly used in the development of latent fingerprints on dark surfaces. For analysis of prints on adhesive tapes, the titanium dioxide can be suspended in a surfactant and used in the form of a powder suspension. Commercially available products, whilst having nominally similar composition, show varying levels of effectiveness of print development, with some powders adhering to the background as well as the print.

X-ray fluorescence (XRF), analytical transmission electron microscopy (TEM), X ray photoelectron spectroscopy (XPS) and laser particle sizing of the fingerprint powders show TiO<sub>2</sub> particles with a surrounding coating, tens of nanometres thick, consisting of Al and Si rich material, with traces of sodium and sulphur. Such aluminosilicates are commonly used as anti-caking agents and to aid adhesion or functionality of some fingerprint powders; however, the morphology, thickness, coverage and composition of the aluminosilicates are the primary differences between the white powder formulations and could be related to variation in the efficacy of print development.

**Keywords:** latent fingerprints; powder suspensions; electron microscopy; adhesive tape; titanium dioxide

## 1. Introduction

The importance of fingerprints deposited at the scene of a crime has been recognised for over a century [1], and the use of fine, dry powders to develop latent fingerprints left after criminal activity has been well established for many years. However, various types of surfaces, such as rough materials, fabrics, wetted materials and adhesives have limited suitability with this type of technique. Other techniques are available, such as vacuum metal deposition (VMD), gentian violet and cyanoacrylate (superglue fuming), and recent developments in nanotechnology allow the formulation of nanoparticles (<100nm) and nanostructured particles – aggregates of smaller particles, or particles with nano-sized features - to enhance latent fingerprint detection. Titanium dioxide particles have been widely used in both powder and particle suspension form [2-12] and demonstrate effectiveness for development of latent prints in a range of media on various surfaces, including developing prints in blood [4] and on wetted surfaces [5,6]. Recent adaptations of the technique include nano-structuring TiO<sub>2</sub> with the application of a fluorescent dye [7]. The use of TiO<sub>2</sub> powders in suspension has been shown to produce reliable results when studying latent prints on the adhesive side of tapes, especially when the pre- and post-deposition history of the surface is unclear [2, 8-10]. A variety of commercial products are available for this technique; however, a number of researchers [10-12], show variations in effectiveness of white powder suspensions available from different companies, which can relate to both effectiveness of adhesion of the powder to latent print and levels of background staining – the powder adhering to areas where there is no print. This is further complicated by the range of adhesive

tapes available; composition varies with manufacturer, brand and batch, for example glues used in adhesive tapes may be based on acrylate or natural or synthetic rubber. Tapes of different sources can be distinguished by laboratory methods such as Fourier-transform infra-red analysis (FTIR) [11, 13]. Development success rates and comparative effectiveness of print development from different formulations do vary with type of adhesive tape studied, as shown by both Brzozowski [10] and Richardson [11], in their comprehensive studies of development efficacy of various power suspensions in depletion series on commercial tapes.

This work uses electron microscopy and X-ray analysis techniques to investigate the differences in structure and chemical composition of the nominally similar commercial powders, to elucidate the mechanisms behind differences in formulation effectiveness.

## 2. Analysis

This work compares four powder suspension systems, commercially available for developing latent prints on the adhesive side of adhesive tapes, including:

- TiO<sub>2</sub> grade RG-15 by Stan-Chem International Ltd
- Wet Powder™ white by Kjell Carlsson Innovation Sweden
- Wetwop™ white #1-0078 by Armor Forensics
- Adhesive-side Powder light Cat No. ASP50L by Sirchie Fingerprint Laboratories

Stan Chem International, recommended by HOSDB [14], and Sirchie Fingerprint Laboratories' powder were supplied as dry powders for mixing to powder suspensions with appropriate surfactant-carrier; "wet wop" and "wet powder white" are ready-made white powder suspensions. Where nominal composition information is available, ingredients are listed as some or all of: titanium dioxide, water and anionic surfactants [15, 16]. For demonstration purposes we show effectiveness on one type of tape studied by Richardson [11], however, we must stress that effectiveness of a particular powder on this tape does not necessarily equate to universal effectiveness. This paper concentrates on the reasons behind differences in effectiveness of nominally similar preparations, rather than recommending a particular product.

### 2.1 Developed fingerprints

Fingerprints were deposited on the adhesive side of proprietary black insulating tape by a range of donors. Latent prints were developed with one of a range of powder suspensions. A proportion of the prints were first sectioned and each side developed with a different powder suspension, to negate differences in print deposition and biochemistry in comparison of techniques. Representative photographic images are shown. The resulting developed prints representing the first depletion of a series of latent images were mounted onto adhesive carbon tape and examined utilising a Zeiss Supra 35VP field emission scanning electron microscope (FE-SEM), operating in variable pressure (VP) mode. Though this mode does not necessarily provide the best quality images, the samples can be examined without the addition of a conducting layer, an advantage that ensures no artefacts are introduced due to the coating process. Although VP mode provides the best visualisation of the surface, the electron beam does cause damage to the adhesive structure and to mitigate this in the images presented, the beam is focussed on one area and moved to an adjacent area for image recording.

### 2.2 Powder and suspension analysis

Powders were examined within an Oxford Instruments X-ray fluorescence (XRF) spectrometer operated with an X-ray beam energy of 20kV to excite any elements present within the elemental range of sodium to uranium (Z=11-92). X-ray spectra were acquired from each powder sample and the characteristic peaks identified. For particle size analysis, each powder was suspended in deionised

water and examined using a CILAS laser diffraction particle size analyser, allowing a particle size distribution to be obtained for each sample.

For X-ray photoelectron spectroscopy (XPS) measurements, an aliquot of each dry powder sample was mounted on to carbon-loaded pressure sensitive adhesive, attached to polished copper, and any excess powder removed. Mounted samples were examined within an Escalab VG X-ray photoelectron spectrometer, utilising aluminium and magnesium anodes and variable iris and detector apertures to examine different size areas on the surface; a small area size was selected to reduce the background signal. The use of a dual anode system assists with the identification of Auger and XPS lines. The XPS technique gathers compositional data from the sample surface with an analysis depth of less than 10nm; the detection limit is approximately 0.5 at. % in this region. XPS spectra were collected in the energy range 1350-0 eV with a step size of 1eV. Increased resolution was used over areas of interest, dictated by the elemental peak positions, and used for concentration quantification and identification of bonding configuration [17, 18].

For analytical transmission electron microscopy (TEM) examination, dilute suspensions of each sample were prepared in distilled water and ultrasonically mixed for two minutes. One drop of each suspension was dispersed onto carbon-coated copper transmission microscope grids. The samples were examined within a JEOL 2000FX transmission electron microscope equipped with an Oxford Instruments INCA energy dispersive X-ray analyser. Representative micrographs were recorded and X-ray spectra acquired to show the morphology and elemental composition of the particles and any coatings.

### 3. Results and Discussion

#### 3.1 Developed fingerprints

Figure 1 shows a latent print deposited on adhesive tape, sectioned and developed utilising different powder suspension formulations for each half of the print. These images, representative of a much larger analysis set that is detailed by Richardson [11], indicate the variation in effectiveness between the powders.

SEM results, figure 2, show latent fingerprints deposited on the adhesive side of adhesive tape developed with different powders. Figure 2a shows almost uniform background staining over fingerprint ridges and bare adhesive, as well as aggregates of development particle, possibly related to skin cells. Other powders, as shown in figure 2b, show the same aggregations, but also show a staining of the ridge area away from these aggregates, and lower background staining, providing greater ridge contrast in the developed image. Figure 3 shows higher magnification SEM images of development of latent prints deposited on a non-adhesive surface, which allows images to be collected at higher magnification without beam-induced distortion. Here two different development formulations are applied to latent prints from the same donor; the SEM micrographs are collected from an area of developed fingerprint ridge, in this instance, particulate coverage increases from approximately 33% to 62% with use of different powder formulation.

#### 3.2 Fingerprint powders

Particle size data, table 1, shows median particle sizes for Wet Wop, Sirchie and StanChem powders in the range 450-550 nm; Wet Powder White has a slightly smaller median particle size of 330 nm. The straddle of particle sizes about the median is also indicated and shows considerable overlap of the particle size profile of the different formulations.

The XRF technique examines the bulk sample, and spectra show the predominant presence of titanium confirming the powders consist largely of titanium oxide. In addition, the powders show traces of aluminium and silicon. Postulating that these trace elements could be contaminants or a coating on the

TiO<sub>2</sub> particles, the surface of each sample was examined with X-ray photoelectron spectroscopy (XPS), which provides data on the composition of the top few nanometres of the sample.

Figure 4a shows an XPS survey spectrum of the StanChem sample, covering energy range 1350-0eV and shows XPS and Auger lines from carbon, oxygen and titanium. An expansion of the region 300-0eV, with increased energy-resolution, Figure 4b, shows XPS lines from silicon and aluminium, in addition to previously observed carbon and titanium. The position of the lines in this spectrum (with reference to the carbon 1s peak) indicates, as expected, the oxidation state of titanium is TiO<sub>2</sub> and is consistent with aluminium in the Al<sup>3+</sup> state.

Similar XPS measurements were conducted on the remaining three powders; the quantification of elemental composition is shown in table 2. Spectra from Wet Wop and Wet Powder White samples show reduction in the silicon and aluminium content and additional XPS and Auger peaks from sodium and sulphur, which may be related to anionic surfactants. The shift in binding energy of the sulphur XPS lines suggests the presence of sulphites or sulphates. XPS spectra from the Sirchie sample highlight the presence of sodium, aluminium and silicon. The silicon XPS lines have shifted with respect to their positions in analysis of the StanChem sample, indicating a difference in the oxidation state.

The compositional data from the XPS spectra, as shown in table 2, indicates the presence of aluminium and silicon in all samples, and sulphur and sodium in the cases of Wet Wop and Wet Powder White. Low levels of titanium detected with this technique suggest that the TiO<sub>2</sub> powders are partially coated in a material rich in aluminium and silicon. The composition and chemical bonding of this coating varies between powders, as highlighted in table 2. The high carbon content can be assigned to the mounting material and adventitious contamination from atmosphere, the latter may also be the origin of a proportion of the oxygen content. The difference in levels of titanium observed suggest differences in the thickness or integrity of the coating.

Figure 5 shows representative transmission electron micrographs of the powders, showing the typical morphology of titanium dioxide. The micrographs also show that the powders have a coating of a diffuse nano-structured nature, the thickness and elemental composition varying between the powders. X-ray analysis of the coatings, figure 6, shows silicon, aluminium, and in some cases sodium and sulphur, consistent with the XPS results of the particle surface, table 2. The coating is in some instances disassociated from the TiO<sub>2</sub> particles, and the thickness, integrity and adherence of this coating varies substantially between the samples studied, as indicated in figure 4. Sirchie powder shows the thickest coating of a loosely spaced material, whereas in StanChem the coating material forms a denser thinner layer.

Aluminosilicates and variations such as sodium aluminium silicates are commonly used as anti-caking agents in a range of products to ensure smooth flow of fine powder [19-21]. The different crystal structures, chemistries, ordering and size distributions strongly affect the technological properties of the material and the addition of these components to the TiO<sub>2</sub> powders will affect the oleophobicity and hydrophobicity of the formulations [21, 22]; indeed kaolin, alumina or silica are added to some fingerprint development powders to aid adhesion or to act to encapsulate nano-structured particles [23-25]. Variation of morphology and chemical composition of the coating, as well as coverage of the aluminosilicates over TiO<sub>2</sub> particles are the principle differences among the powder formulations studied, this will affect the interaction of the composite particles with the components of the latent prints, and may also assist in explaining the differences in background staining between different adhesive types.

#### 4. Conclusions

Fingerprint powders examined gave differing performance when developing latent prints on black adhesive tape, highlighted here and in greater detail in earlier works [10,11]. X-ray fluorescence, laser

particle sizing and analytical transmission electron microscopy of the powders confirm primary constituents of TiO<sub>2</sub> particles with diameter in the range 200-500nm, and particle size distribution does not significantly vary among the formulations. Scanning electron microscopy of developed prints shows there is no preferential deposition of a particular particle size that contributes to background staining. X-ray photoelectron spectroscopy and TEM indicate the TiO<sub>2</sub> particles have a coating rich in aluminium and silicon. The coating varies in morphology among the different formulations and can be loosely packed, and thickly coating the TiO<sub>2</sub> particles, as in the Sirchie powder studied, or be manifested as a denser, thinner coating that irregularly covers the TiO<sub>2</sub> particles, as in StanChem. The chemistry of the coating, relative concentrations of silicon, aluminium, sulphur and sodium vary between powder formulations. Earlier work [10-12] shows no powder formulation has highest effectiveness on all adhesives and prints, and there is significant variation of effectiveness of different powder suspensions dependent on the structure of the adhesive. The detected aluminosilicate coating alters the surface properties of the composite particles. The variation in coating composition and adherence to the TiO<sub>2</sub> particles is likely to be the cause of the varying performance of the powders in fingerprint development.

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	Particle Sizes / nm			
	StanChem	Wet Wop	Wet Powder White	Sirchie
<b>Diameter 10%</b>	330	240	180	280
<b>Diameter 50%</b>	550	450	330	550
<b>Diameter 90%</b>	890	760	610	960

**Table 1.** Particle size data: median diameter with upper and lower size limits

	Atomic %			
	StanChem	Wet Wop	Wet Powder White	Sirchie
<b>O</b>	48.6	28.9	26.1	37.8
<b>Ti</b>	8.1	2.5	<i>Trace</i>	<i>Trace</i>
<b>C</b>	22.3	53.5	63.2	32.5
<b>Al</b>	17.6	7.8	3.9	11.4
<b>Si</b>	2.7	<i>Trace</i>	<i>Trace</i>	16.7
<b>S</b>	<i>n/d</i>	3.9	3.5	<i>n/d</i>
<b>Na</b>	<i>n/d</i>	3.4	2.6	<i>Trace</i>

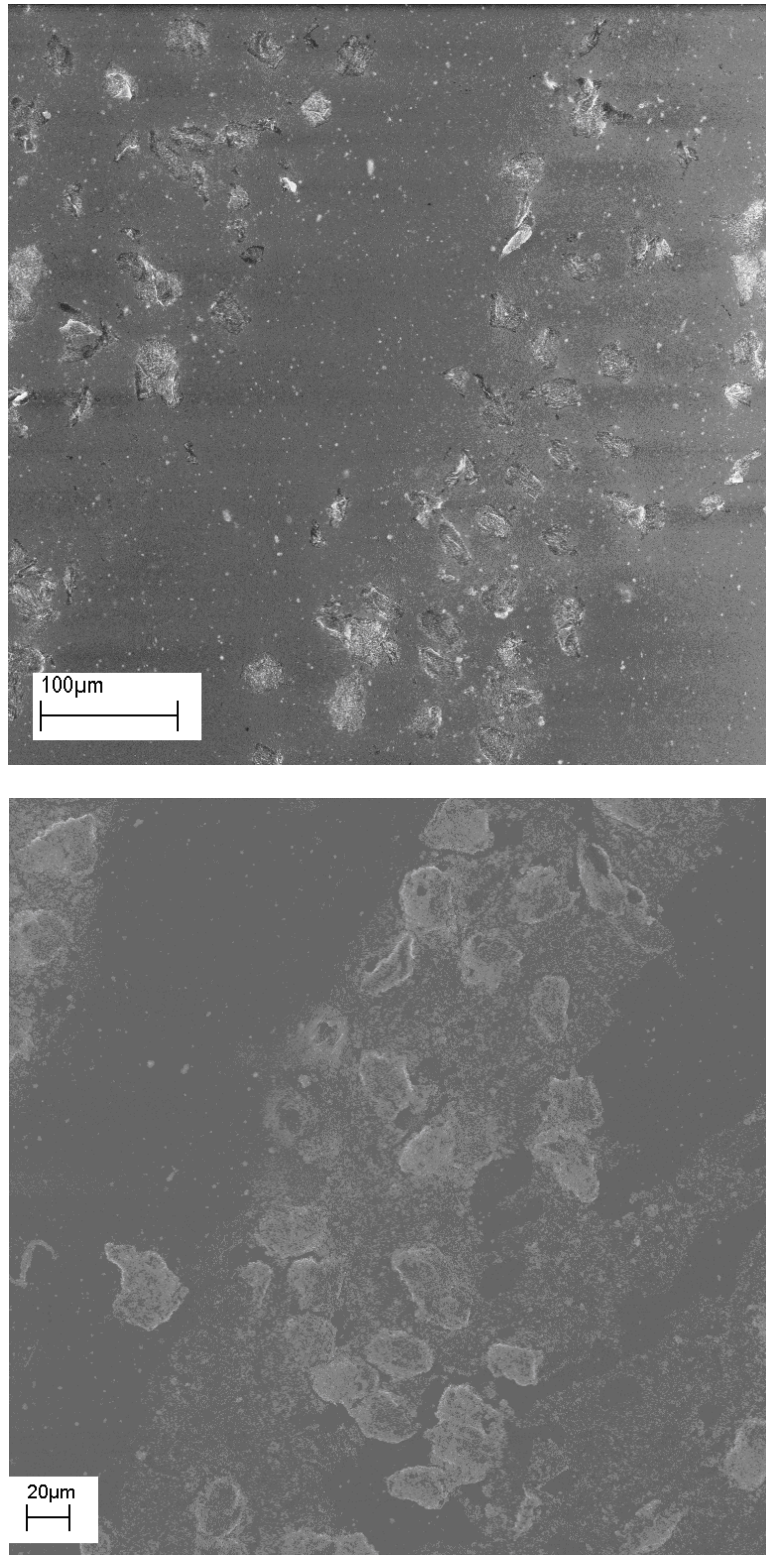
*n/d* : not detected

**Table 2.** Comparative content of powder surfaces, calculated from analysis of XPS spectra

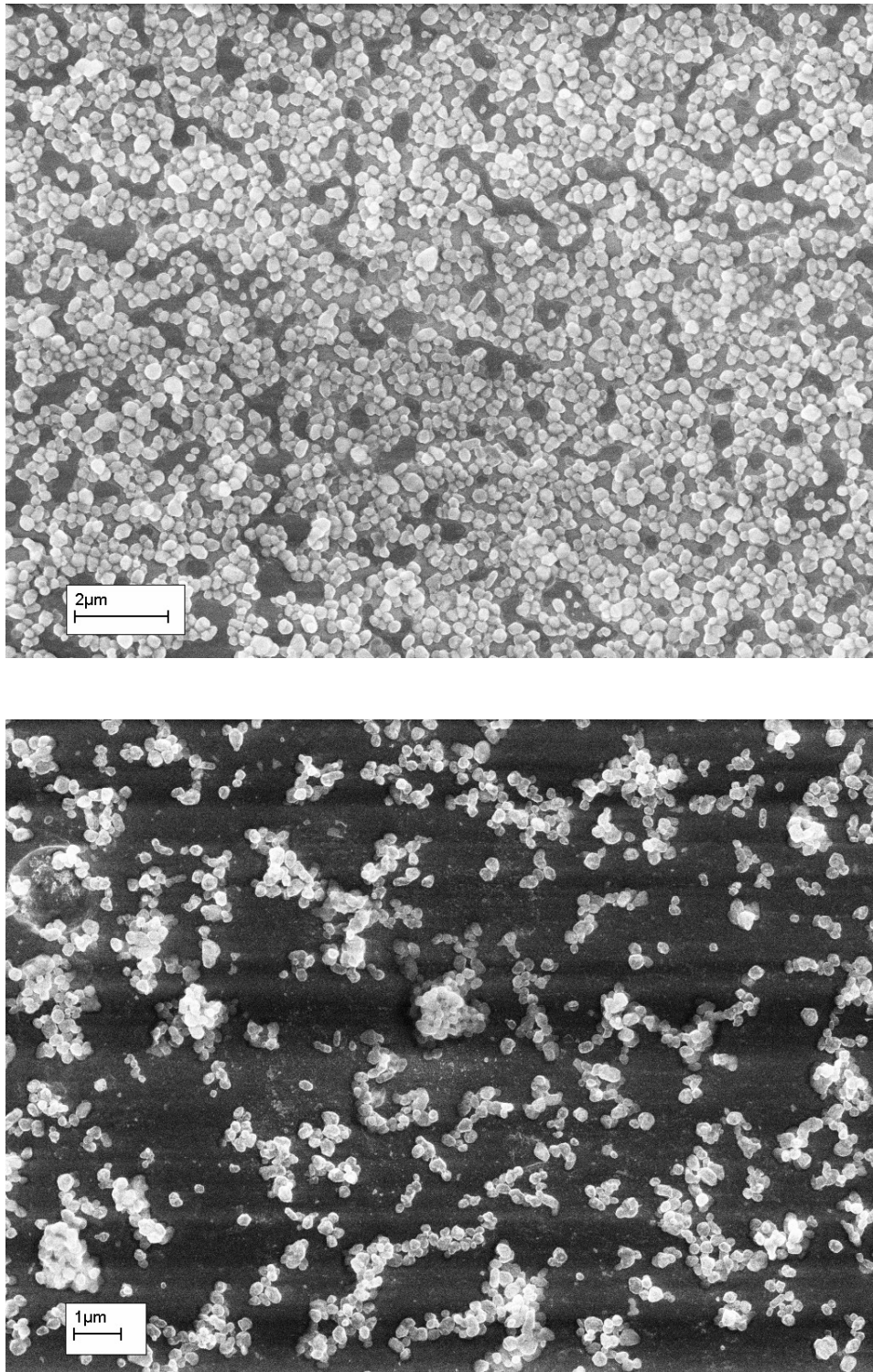


**Figure 1.** Photograph of single print with different development method utilised for each half, indicating differing levels of background staining between the development formulations

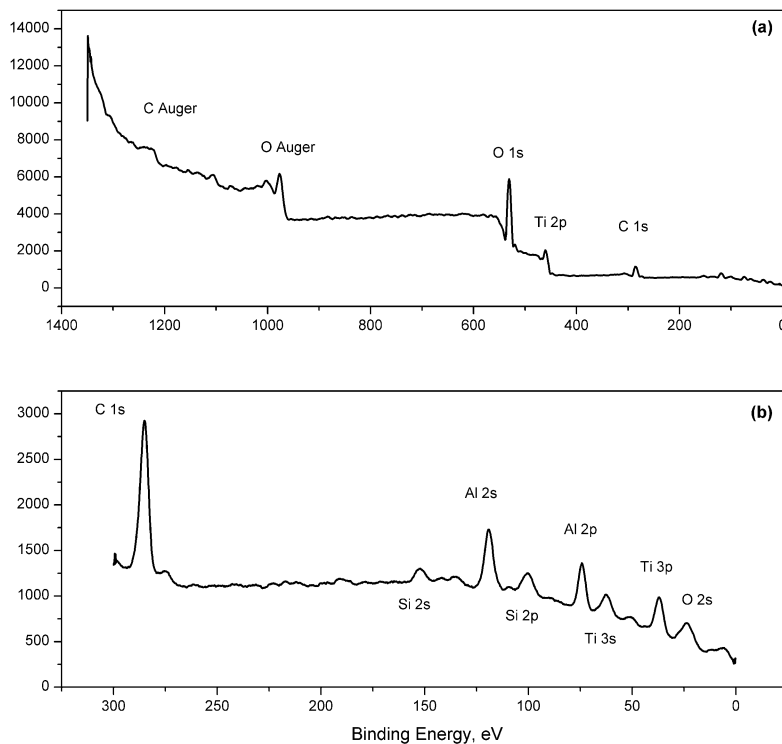




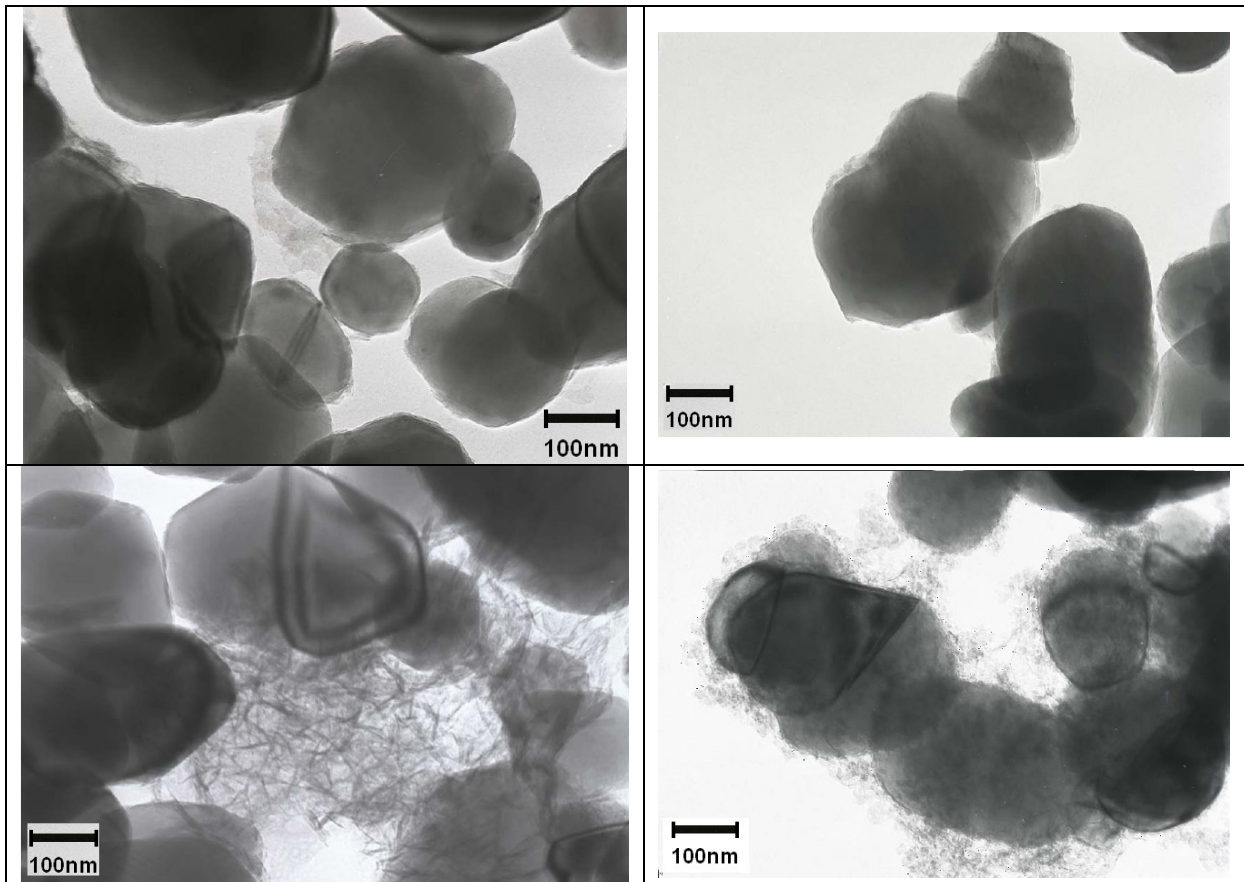
**Figure 2.** SEM images of developed prints from one donor on single tape showing differing levels of background staining when developed by different commercial powder suspension formulations



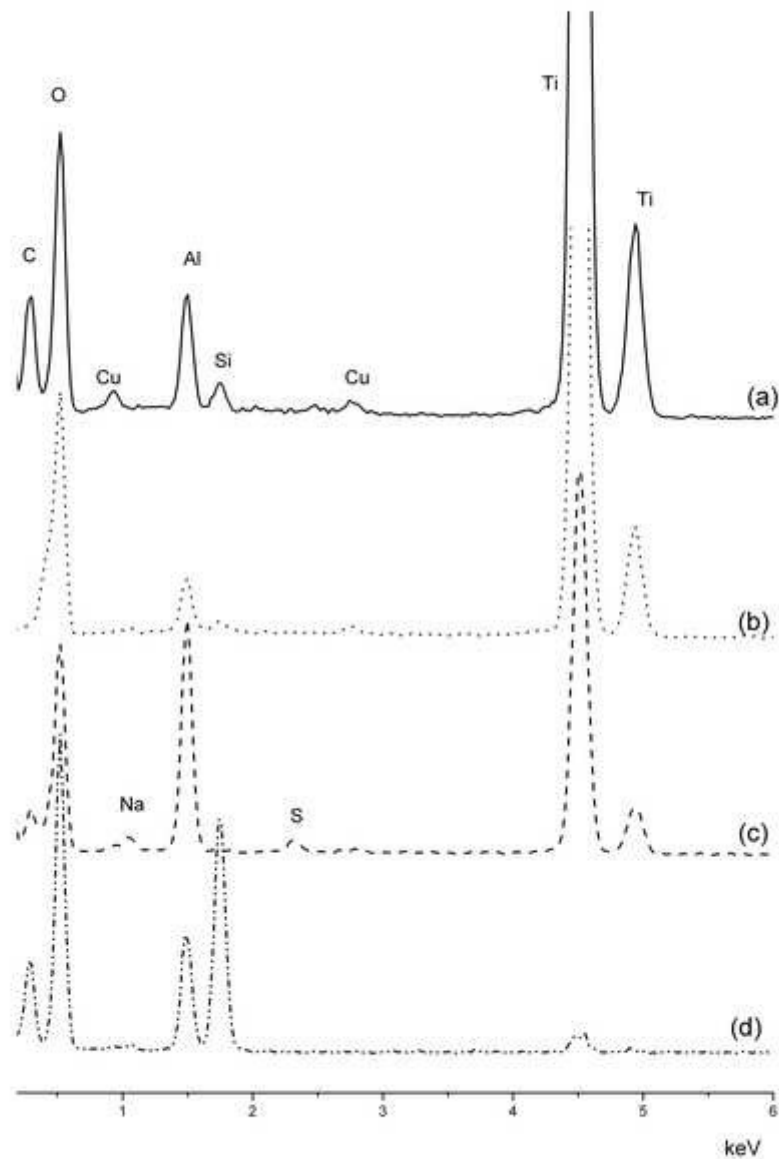
**Figure 3.** SEM images of developed latent print ridge from one donor on single surface showing differing levels of density of coverage when developed by different commercial powder suspension formulations



**Figure 4** XPS spectra of the StanChem powder, covering energy range 1350-0eV (a) indicating presence of carbon, oxygen and titanium. An expansion of the region 300-0eV, with increased energy-resolution (b) shows additional XPS lines from silicon and aluminium.



**Figure 5.** TEM images of fingerprint development powders, (a) Wet Powder White (b) StanChem (c) Wet Wop and (d) Sirchie. Images show titanium dioxide particles and coating of various forms and constituents, prevalence and coverage of coating over  $\text{TiO}_2$ .



**Figure 6.** EDX spectra of surface coating of fingerprint development powders, (a) StanChem (b) Wet Powder White (c) Wet Wop and (d) Sirchie. Spectra show differing Si / Al ratios and presence of Na and S in some formulations. Titanium signals are from the TiO<sub>2</sub> particles, intensity of which relates to thickness and disassociation of coatings. Cu signal is related to the mounting medium.