

# THE CHARACTERIZATION OF PVC ADHESIVE TAPE

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Over the last decade a considerable amount of plastic adhesive tape, mainly of the polyvinyl chloride (PVC) variety, has been submitted to the Northern Ireland Forensic Science Laboratory for examination, mainly in association with improvised explosive devices. The main objectives of scientific type work are to link together a series of incidents or connect a crime strip to a recovered roll. The tape may be used to secure, wrap or insulate the explosive device or its components.

As far as the United Kingdom as a whole is concerned, limited systematic work on the examination of tape has been carried out (Curry 1979; Kee 1982; Miller *et al.* 1984). The overall aim of this report is to describe the methods evolved in the author's laboratory to examine and compare PVC tape. The work will be illustrated by the presentation of results from the examination of over 100 black PVC tapes received in the laboratory during 1980 and 1981. These tapes were selected from a large collection of casework tape ends amassed from the early stages of the present terrorist violence in Northern Ireland. The collection is primarily concerned with facilitating the comparison of tape ends from new and old explosive devices. The availability of this material has allowed the Laboratory to adopt a much more systematic approach to the collation of tape than otherwise would be possible.

The work on the characterization of tape was begun following a case several years ago involving a radio-controlled improvised explosive device. Some time after the resultant explosion, a modified transceiver was recovered from a hedge some considerable distance from the original incident. Fragments of orange and red tape recovered from the scene of the explosion were compared with similar colored tape attached to the transceiver and the linking evidence presented in court. The methods used to link the tapes are described in this report.

## THE MANUFACTURE OF PVC ADHESIVE TAPE

As far as the United Kingdom and Republic of Ireland markets are concerned, PVC adhesive tape is supplied from a number of sources including the United Kingdom, Europe and Taiwan. There are two distinct stages in its manufacture. The first is concerned with the production of PVC plasticized film, the second with coating. In the United Kingdom, where only limited manufacture of PVC ad-

hesive tape takes place, the two processes are carried out by different manufacturers. In Europe and Taiwan the two operations may be integrated. The manufacturing information in this section was partly obtained from discussions with manufacturers in the United Kingdom.

### Plastized PVC Film Production

The process of compounding and pressing plasticized PVC into a thin film is described as calendaring (Surprenant 1966) (Figure 1). The PVC polymer and various additives are thoroughly mixed together and the resultant compounded plastic transferred to the top of the calender. It is then passed through a series of nip rollers which mix it and reduce it in thickness. Further reduction in the thickness of the final backing may be produced by overdriving the take-off rollers. The film surface finish may be controlled by the finish on the calender rollers or by the application of embossing rollers following the calender. Finally the film is cooled, cut to the required width and wound into rolls for supply to the tape manufacturer.

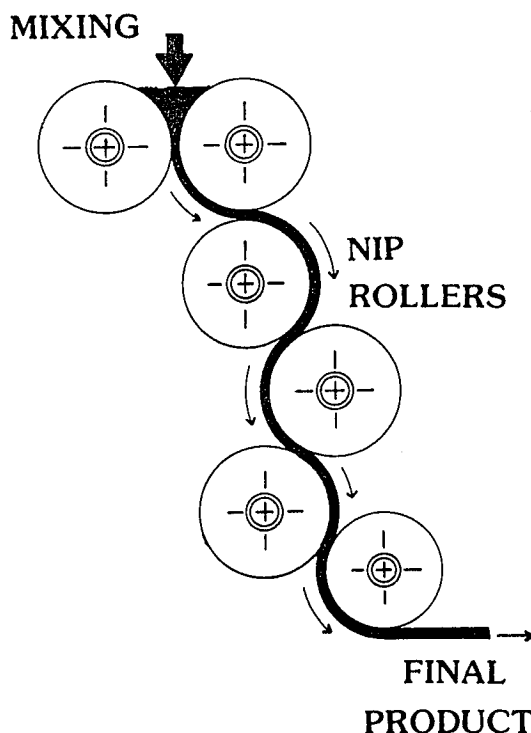


Figure 1. The calender manufacture of plasticized polyvinyl chloride film.

## Film Coating

At least two coats are applied to the plasticized PVC film: a primer or key coat before the adhesive and the adhesive coat itself. Sometimes a release coat is also applied to the top surface of the tape backing to aid unwinding. These processes are carried out as a continuous industrial operation, the film being passed through roll coaters and large ovens to remove the associated solvent (Figure 2). The technique of roll coating is based on the transference of adhesive or primer solutions from a trough by means of a pick-up roller partially immersed in it, to a contacting transfer roller. Film is continuously coated with adhesive or primer when fed between the transfer roller and a pressure roller which is adjusted to determine the coat thickness. The final product, in the form of a long roll, is sectioned into the much smaller commercial rolls.

FILM TAPE COATING

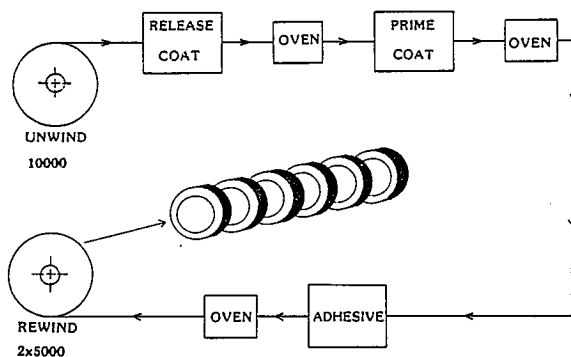


Figure 2. Coating of plasticized polyvinyl chloride film in the manufacture of adhesive tapes.

## ADDITIVES IN PVC BACKING

Untreated PVC polymer film is a rigid, unstable product, unsuitable as an electrical tape. Various materials are therefore mixed with the polymer at the compounding stage to improve the final product. These include plasticizers, stabilizers, fillers, pigments, lubricants, fire retardants and copolymers. Plasticizers, stabilizers, fillers and fire retardants are important during the chemical examination of tape.

## Plasticizers

Three classes of plasticizer are commonly added to PVC backing, namely, phthalates, sebacates and phosphates. Some types employ a single plasticizer commonly di(2-ethylhexyl) phthalate, while others use a suitable blend of various classes of plasticizer, for example, phthalic and sebacic acid esters of a mixture of heptyl, octyl and nonyl alcohols.

## Stabilizers

Stabilizers are used to prevent decomposition, if the polymer is subjected to excessive heat during processing or service life. They also help to prevent degradation by ultraviolet irradiation. A common additive is lead carbonate.

## Fillers

Fillers being cheaper than PVC polymer are added to reduce overall manufacturing costs. Common additives are whiting (calcium carbonate) and clay (silicates).

## Fire Retardants

Although PVC polymer is itself self-extinguishing, the heavy loading of plasticizers (between 20-60 percent of total weight) may sustain burning. Tapes manufactured in the United Kingdom, therefore, incorporate fire retardants such as antimony oxide or chlorinated hydrocarbons.

## COATING MATERIALS

A common primer coat consists of a mixture of natural rubber and methyl methacrylate applied in a toluene/ethanol solvent system. In the United Kingdom adhesives are normally a blend of rubber and synthetic resins, while in the rest of Europe, acrylic adhesives are popular.

## METHODS USED IN THE CHARACTERIZATION OF PVC TAPES

The preceding two sections have shown that a number of processes and materials are involved in the manufacture of PVC adhesive tapes. The aim of this section is to capitalize upon this variety, and indicate methods and measurements which may characterize individual PVC adhesive tapes.

## PHYSICAL METHODS

### Color and Gloss

Adhesive tapes are available in a wide range of colors and the initial classification is normally on the basis of color. Some tapes, such as those colored red or blue, consist of a band of similar colors with a few additional distinctive hues. Other colors show little variety. The finish on the surface of the tape may vary from very dull matt to distinctly

glossy. This is an important parameter when black tapes are examined. Both instrumental and non-instrumental techniques may be used to measure these variables.

### Dimensions

Although a wide range of widths are available, most tapes are close to 19 mm in width. There is also a variation in the thickness of the backing, the manufacturing tendency being towards thinner backings.

### Surface Features

#### Top Surface

Viewed using a scanning electron microscope, the top surface of the backing can vary considerably from tape to tape. The features observed include ridges (Figure 3), irregular grooves (Figure 4) and small oval pits (Figure 5). The different surfaces are the result of the PVC film being imprinted by the various calender or embossing rollers. Sometimes broad parallel impressions on the tape are also observed by the naked eye under oblique light.



Figure 3. Magnified view of tape surface, photographed using a scanning electron microscope (carbon coating; tape ex 2490/81).

#### Under Surface (Adhesive Side)

If a piece of tape is immersed in hexane until the adhesive can be easily removed, sometimes distinctive wavy markings are noticed as the tape dries. This effect would appear to be due to a hexane insoluble primer coating. The pattern is produced by the transfer roller during coating. The pattern, if present, may also assist the comparison of tape ends where these have been damaged or lack cut features (Figure 6).

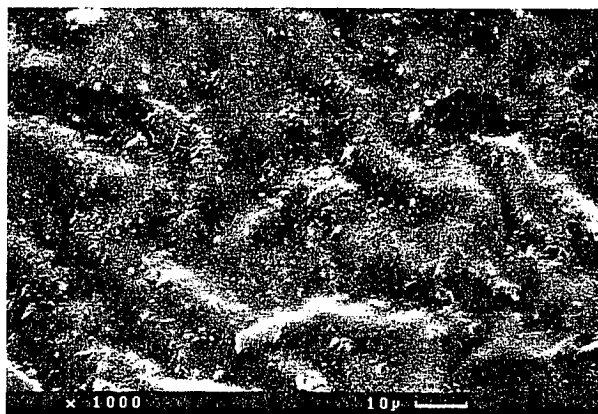


Figure 4. Magnified view of tape surface, photographed using a scanning electron microscope (carbon coating; tape ex 353/81).

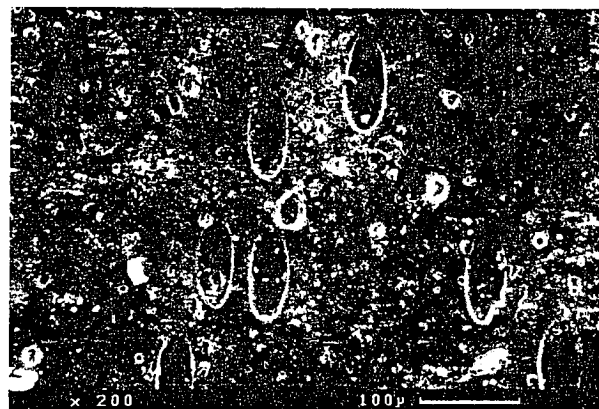


Figure 5. Magnified view of tape surface, photographed using a scanning electron microscope (carbon coating; tape ex 2800/81).

#### Edge

The initial long PVC type roll produced by the coating manufacturer is sectioned into the smaller commercial rolls by a stationary knife (and revolving roll) or a circular rotating blade. As a result, the overall shape of the edge can also vary from tape to tape (examples are shown in Figures 7 and 8).

### CHEMICAL METHODS OF COMPARISON

Although the physical comparison of tape may be highly discriminating, there are advantages in a wider analytical approach. A tape may be damaged or stretched if involved in an explosion or roughly treated. Furthermore, the use of gentian violet to

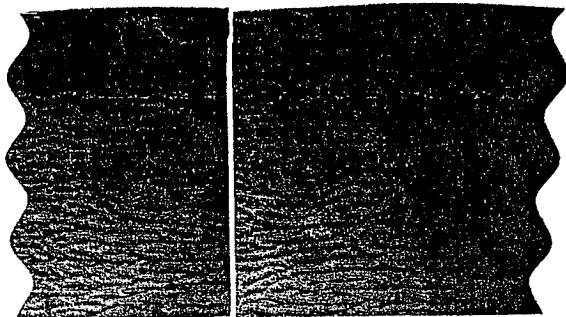


Figure 6. Photograph of visualized primer pattern on the underside of tape backing.

detect fingerprints complicates color comparisons - the dye is sometimes hard to remove completely, particularly in the case of white or light colored tapes with a high loading of titanium dioxide. Because of these possible problems and in order to increase the ability to discriminate, tapes are also subjected to a chemical examination. In fact, chemical information plays a key role in the classification of black tape. A similar dual approach is also employed during the forensic examination of glass with refractive index measurements being supported by chemical results.

X-ray fluorescence spectrometry (XRF) (Bertin 1975) and infrared (IR) spectroscopy using a multiple internal reflectance (MIR) accessory (Wilks 1972) have been found to be excellent complementary techniques for the fast, non-destructive, chemical examination of small tape samples. X-ray fluorescence spectrometry provides rapid, reproducible information about inorganic additives such as fillers, stabilizers and fire retardants. Infrared multiple internal reflectance spectroscopy (IR/MIR) provides information about organic additives primarily plasticizers. Tape being a relatively soft material is an ideal subject for this technique. Using both techniques, the homogeneity of four different rolls of purchased tape was confirmed.

Infrared multiple internal reflectance examination of either the backing or adhesives side of a typical tape with a single phthalate plasticizer (for example, di(2-ethyl-hexyl) phthalate identified by extraction and gas spectrometry/mass spectrometry) produces a spectrum which closely resembles that of a typical di-alkyl phthalate. A relatively small contribution to the spectrum is made by either the PVC or adhesive (Figure 9). On the backing side this may be due to enhanced liquid contact. On the ad-

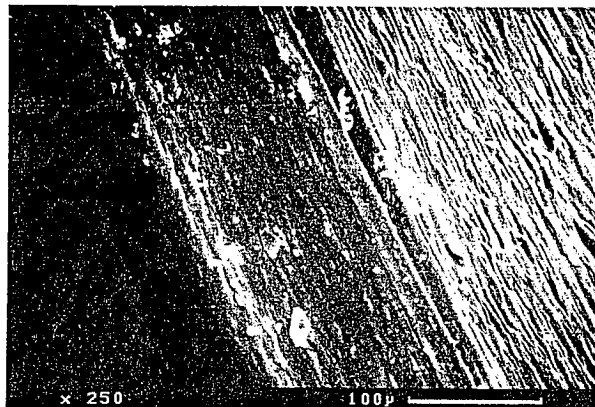


Figure 7. Magnified view of tape edge, photographed using a scanning electron microscope (carbon coating; ADAstra Electronics Ltd. brand).

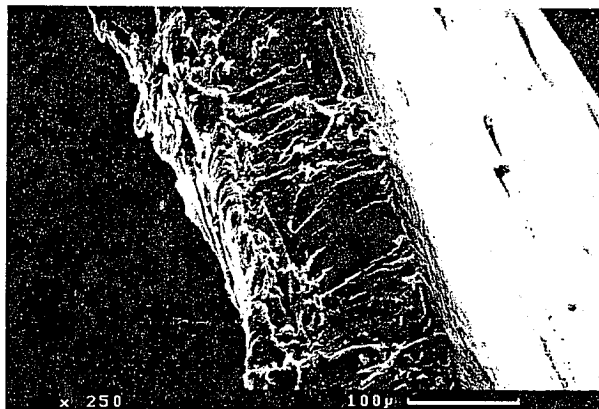


Figure 8. Magnified view of tape edge, photographed using a scanning electron microscope (carbon coating; tape ex 3012/80).

hesive side, leaching by the adhesive solvent system during the coating process, deliberate introduction of plasticizer or plasticizer migration may be responsible. In view of the limited additional information obtained by examination of the adhesive side of single phthalate plasticizer backings and the possibility of earlier external contamination of the adhesive, MIR analysis, generally, is only carried out on the top surface.

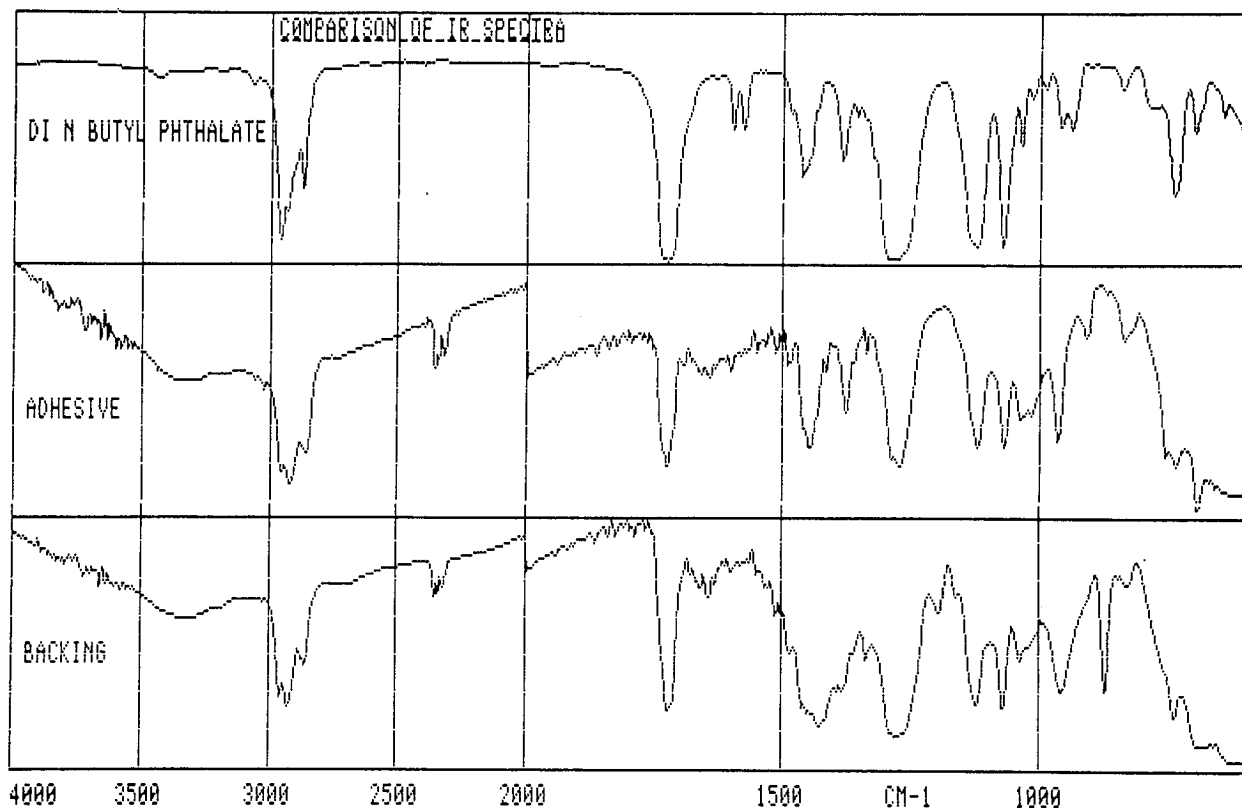


Figure 9. Comparison of infrared spectra of (a) n-butyl phthalate (NaCl discs) and (b) backing and adhesive coating (multiple internal reflectance spectrometry) from a tape sample (1125/81).

**EXPERIMENTAL**

**X-ray Fluorescence**

A Spectrace 420 X-ray fluorescence spectrometer with a Link 290 multi-channel analyzer was used throughout the work under the following instrumental conditions:

- X-ray source: Rhodium Tube, unfiltered radiation
- Accelerating voltage: 35 kV
- Beam current: (i) qualitative work, 0.05 mA  
(ii) discrimination study, 0.07 mA
- Collimator: 1 mm
- Preset count time: 200 seconds
- Chamber environment: All samples were run in vacuo
- Window setting for discrimination study: Calcium 3.500 to 3.800 KeV  
Lead 10.280 to 10.780 KeV

**Infrared Multiple Internal Reflectance Spectroscopy**

A Perkin Elmer 983 dispersion IR spectrometer (Perkin Elmer, Ltd., Buckinghamshire, England) with a micro MIR accessory and a 3600 Data Station was used throughout the work under the following instrumental conditions:

- Scan range: 4000-600 cm<sup>-1</sup>
- Scan time: 2.5 minutes
- Scan mode 3, noise filter 1 (nominal resolution 5 cm<sup>-1</sup>)
- Crystal transmission: 15-20 percent at 4000 cm<sup>-1</sup>
- Procedure: Digitized signal averaged over 16 consecutive runs resultant spectrum expanded (ABEX), flattened and smoothed using the Data Station software.

Sample preparation: Top surface of backing was lightly wiped with hexane. For XRF analysis, a 1 cm long piece of tape was attached externally to MYLAR film (E. I. duPont de Nemours & Co., Inc., Wilmington, DE) held on a plastic sample cup. For IR analysis, two strips of tape, each 4 mm x 8 mm, were lightly clamped to a micro KRS-5 crystal (Perkin-Elmer, Part No. 0186-2357). The top surface only was analyzed.

**CLASSIFICATION OF BLACK PVC ADHESIVE TAPES FROM CASES RECEIVED IN THE NORTHERN IRELAND FORENSIC SCIENCE LABORATORY DURING 1980 AND 1981**

The procedures described in the previous section have been applied to the examination of black plastic adhesive tape samples from casework received in the laboratory during 1980 and 1981. Black tape was selected because of common usage and the lack of color variation. Some variety in the surface finish was present, however.

The classification method adopted relies on grouping and additional subgrouping according to XRF results. Multiple internal reflectance spectrometry results and physical characteristics are then compared in an attempt to further divide the subgroups. The initial use of XRF spectra for classification has been found to be an effective overall approach.

Using the criterion of absence or presence of lead and calcium, the tapes examined were spread over the four possible elemental combinations:

- Class 1: Lead present, calcium absent (30.5 percent)
- Class 2: Lead and calcium absent (5.3 percent)
- Class 3: Lead absent, calcium present (6.1 percent)
- Class 4: Lead and calcium present (58.1 percent)

The use of lead and calcium as prime discriminating elements is in line with PVC additives usage. Lead carbonate is a commonly used stabilizer while calcium carbonate is a commonly used

filler. As might be expected, Class 4 with both calcium and lead present forms the largest group.

Each class is then further subdivided according to the presence, absence or relative amounts of additional elements. The full results are set out in Appendix I. A total of 15 subclasses are created, with the two largest subclasses containing 22 tapes each.

It is worthwhile to look at a class in further detail, for example, Class 1 with four subclasses:

- 1A Lead only dominant: 14 tapes (Figure 10).
- 1B (i) Lead and phosphorous: 2 tapes (Figure 11).
- 1B (ii) Lead and antimony: 22 tapes (Figure 12).
- 1B (iii) Lead and silicon: 2 tapes (Figure 13).

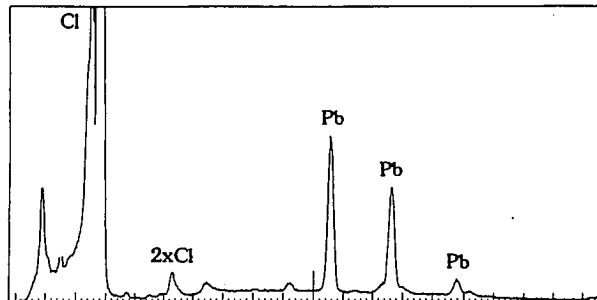


Figure 10. X-ray fluorescence spectrometry spectrum of a typical member of Class 1A (lead only).

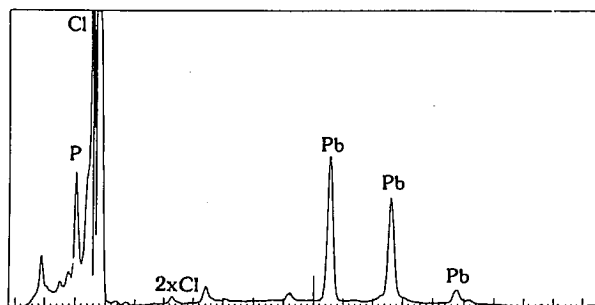


Figure 11. X-ray fluorescence spectrometry spectrum of a typical member of Class 1B (i) (lead and phosphorous).

The detection of phosphorous in Subclass 1B (i) may be due to a phosphate plasticizer or a phosphorous fire retardant. The detection of antimony in Subclass 1B (ii) is due to antimony oxide. The detection of silicon in Subclass 1B (iii) is possibly due to silicate filler.

The individual members of a subgroup are then compared using the IR/MIR results and physical characteristics. This is particularly important where large subgroups are involved. For example, if Sub-class 1B (ii) (lead and antimony: 22 tapes) is investigated more closely the tapes separate out into two distinct types. The IR/MIR spectra of both types are shown in Figure 14. One type is additionally characterized by an irregular surface pattern (Figure 4) and primer visualization with hexane. The other type is further characterized by a ripple pattern on the surface (Figure 3) and a black adhesive coating.

that the distribution pattern is dominated by a limited number of major products. Similar patterns have also been shown by red, blue (Kee 1982) and white tape (author's unpublished results). No attempt has been made in this work to correlate specific types of tape with named products.

### ADDITIONAL DISCRIMINATION

Although quite a high degree of discrimination is achieved by the above procedures, millions of tape rolls may be associated with a single product. In addition, two products may only be slightly different. Some work has therefore been carried out to determine if further discrimination is possible on casework tapes not distinguished by the above qualitative work. No attempt has been made to distinguish batches of tape from any manufacturer.

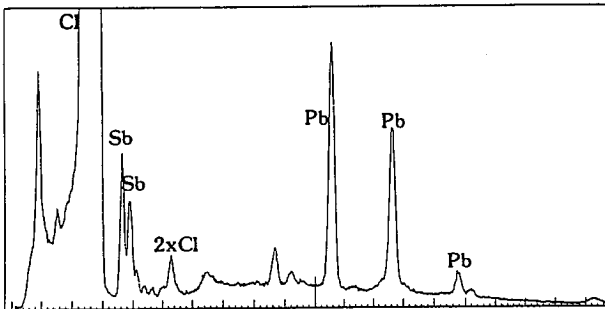


Figure 12. X-ray fluorescence spectrometry spectrum of a typical member of Class 1B(ii) (lead and antimony).

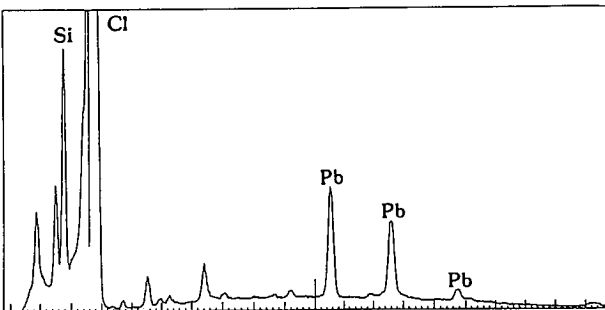


Figure 13. X-ray fluorescence spectrometry spectrum of a typical member of Class 1B(iii) (lead and silicon).

Similar results are obtained for other large subclasses within the overall classification scheme. Each major subclass splits at most into two distinct tape types (Appendix II). A few irregular tapes may also be associated with the major subclasses, for example, a few matt tapes with a gloss group.

Although this survey is fairly limited in terms of numbers and time span, it appears that black PVC tape exhibits a great deal of overall variety and

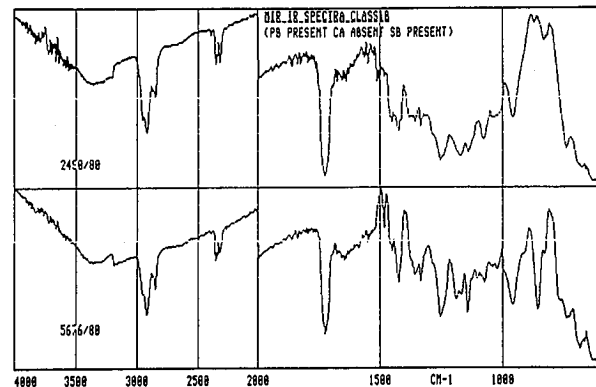


Figure 14. Infrared multiple internal reflectance spectrometry spectra of typical members of Subgroup 1B(ii) (lead and antimony).

### Relative amounts of PVC additives

Subclass 4C (i) (calcium and lead dominant - titanium absent) consists of some matt and a majority of gloss tapes. The gloss tapes are characterized by a pitted surface and a typical phthalate plasticizer IR/MIR spectrum. These were re-examined quantitatively using a XRF technique. The nett calcium K ( $\alpha$ ) peak area, ratioed to the nett lead L ( $\alpha$ ) peak area, was determined for six separate pieces of tape all from the one roll and a population range devised (four standard deviations; Table 1). Using the same experimental conditions, peak ratios for individual pieces from nine tapes in the same gloss group were obtained and compared with the initial range. Four were found to fall well outside this range and were discriminated. Two of these four tapes could not be distinguished by the physical and chemical techniques discussed earlier (the remaining two differed originally in MIR spectrum and more elongated ovals, respectively).

Table 1. DISCRIMINATION OF GLOSS TAPES FROM SUBCLASS 4C (i)

Results from the calcium to lead ratio of six pieces of tape from 1125/81:

Mean = 65.27  
 Standard deviation = 2.12  
 Range (4 SDs) = 56.79 to 73.85

Source Case Number	Calcium to Lead Ratio
925/80	56.93
2070/80	67.75
3339/81	80.11
3012/81	54.12
51/80	61.48
1004/80	63.08
277/80	51.06
2202/80	67.13
2800/81	52.87

### Variation in Surface Features

Some preliminary work has also been carried out on the number of ovals per unit area on randomly selected pitted gloss tapes (tape surface and grid photographed in a scanning electron microscope at low magnification). A wide range of results was obtained. Although the exact cause of this feature is uncertain, its being associated with imported film, this work look promising.

It thus appears that additional quantitative work either of a physical or chemical nature may lead to greater discrimination. The actual technique used will depend on the characteristics of the tape under comparison.

### CONCLUSION

Fast, non-destructive techniques for the examination of PVC electrical tapes have been described and applied to the classification of black tape. The work provides a framework for the routine comparison of casework tape samples and underlines the value of a background tape collection. In addition, the usefulness of XRF analysis is highlighted.

The variety of products associated with even a single tape color suggests that tape comparison work is potentially a very fruitful activity and should not be neglected. Furthermore, at a more general level, these examination techniques may also be applied to other PVC-based materials. To date within the Northern Ireland Forensic Science Laboratory, wire sheathing and conduit have been compared with some success.

### ACKNOWLEDGMENT

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### Appendix I

#### X-RAY FLUORESCENCE SPECTROMETRY CLASSIFICATION OF BLACK POLYVINYL CHLORIDE TAPE

- CLASS 1: Lead present, calcium absent (40 tapes; 30.5 percent)**
  - 1A Lead only (14 tapes)
  - 1B (i) Lead and phosphorous (2 tapes)
  - 1B (ii) Lead and antimony (22 tapes)
  - 1B (iii) Lead and silicon (2 tapes)
- CLASS 2: Lead and calcium absent (7 tapes; 5.3 percent)**
  - 2A Antimony present
  - 2B Sulphur present
  - 2C Blank tape
- CLASS 3: Lead absent, calcium present (8 tapes; 6.1 percent)**
- CLASS 4: Lead and calcium present (76 tapes; 58.1 percent)**
  - 4A Silicon present
    - 4A (i) Silicon dominant (22 tapes)
    - 4A (ii) Calcium dominant (6 tapes)
    - 4A (iii) Titanium dominant over calcium (1 tape)
  - 4B Phosphorous present
    - 4B (i) Phosphorous large relative to calcium (8 tapes)
    - 4B (ii) Phosphorous small relative to calcium (12 tapes)
  - 4C Calcium and lead dominant
    - 4C (i) Titanium absent (17 tapes)



4C (ii) Titanium present (9 tapes)

Appendix II

SUBDIVISION OF MAJOR X-RAY FLUORESCENCE SPECTROMETRY SUBGROUPS USING INFRARED MULTIPLE INTERNAL REFLECTANCE SPECTROSCOPY AND PHYSICAL CHARACTERISTICS.

- Subgroup 1A Lead only (14 tapes): one group
- Subgroup 1B (ii) Lead and antimony (22 tapes): two groups
- Subgroup 4A (i) Silicon dominant (22 tapes): two groups
- Subgroup 4B (ii) Phosphorous small relative to calcium (12 tapes): one group
- Subgroup 4C (i)-Calcium and lead dominant - titanium absent (17 tapes): one group.

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DISCUSSION

*King:* Have you done any work trying to extract and identify the pigments that are used for your different colors?

*Kee:* No, we deliberately shied away from any processes that slowed down our analysis. What we were aiming towards was trying to build up fast population information.

*King:* Have you considered using X-ray diffraction as well as X-ray fluorescence?

*Kee:* We do not have X-ray diffraction. I should say that it is my overall opinion that I do not know if I would get a lot more class information. I think I really would be down to looking at very small or minute differences within the material. I am not sufficiently expert in X-ray diffraction to say that would give me that sort of additional information.

*Munson:* We are just finishing a small project looking at PVC black tapes with pyrolysis capillary. We have looked at 30 tapes and got 26 profiles that are very easily discriminated from each other. It looks promising. We also looked at some fragments recovered from exploded devices. Some of those match back very nicely, the ones that weren't so terribly dirty.

*Kee:* Well, that is the only problem with bomb fragments particularly, but I can see your point. There is no reason that you should not clean up the tapes and pyrolyze them. You may be getting a lot of useful information that way on copolymers and additional organic constituents. I am not getting information about them and it may be very useful in that respect.