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The Identification of Polyester Fibers in Forensic Science

A polyester fiber is by definition one composed of linear macromolecules comprising at least 85% (by mass) of the chain of an ester of a diol and terephthalic acid [1]. In 1941 it was discovered in the laboratories of the Calico Printers Association in Lancashire, England that fibers could be spun from polyethylene terephthalate (PET). I.C.I. Ltd. began production in 1948 under the name "Terylene," and production was expanded to a large scale in 1955. DuPont began to produce a polyester known as Fiber V in the U.S.A. in 1950. This fiber subsequently became known as Dacron[®] and was produced in quantity from 1953 onwards [2].

Polyethylene terephthalate is made by condensation of terephthalic acid or dimethyl-terephthalate with ethylene glycol and such fibers are produced in at least 29 countries. Some of the more well-known examples are as follows:

- United States—Blue C[®] (Monsanto); Dacron[®] (DuPont); Encron[®] (American Enka); Fortrel[®] (Celanese); Kodel[®] (Eastman-Kodak); and Vycron[®] (Beaunit)
- W. Germany—"Diolen" (Glanzstoff AG); "Trevira" (Hoechst A.G.)
- England—"Terylene" (I.C.I.); "Lirelle" (Courtaulds)
- Netherlands—"Terlenka" (AKU)
- Japan—"Tetoron" (Teijin)

In 1958 Eastman-Kodak produced a new type of polyester fiber spun from the polymer made by condensation of terephthalic acid with 1,4 cyclohexane-dimethanol to give poly (1-4 cyclohexylene dimethylene terephthalate), otherwise known as PCDT. The fiber is marketed under the name Kodel 211[®]. More detailed information is provided by Cook [2].

For many years PET and PCDT were the only types of polyester fibers on the market, the latter being only occasionally found in the forensic science laboratory as it was used primarily for carpets and rugs.

Because of their widespread use today in the manufacture of both men's and women's clothing, polyester fibers are one of the most commonly encountered fiber types in forensic casework, at least one example being present in nearly every fiber transfer case. Besides being found alone or in conjunction with other fiber types (particularly cotton or viscose rayon) in underwear, shirts, casual trousers and jeans, suiting, jersey shirts, blouses, skirts, and dresses, they are also frequently found in nightdresses, housecoats, bedsheets, and other household fabrics. It is therefore extremely important for the forensic scientist to be able to recognize these fibers and correctly identify them for comparison purposes.

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In their original form, exemplified by "Terylene," PET fibers are regular unstriated fibers normally round in cross section which may be found as filament or staple in varying degrees of tenacity and with different degrees of luster. Polyester fibers are easily recognizable because their birefringence under polarized light is higher than that of any other man-made fiber [3,4]. When the multiple entry card-index system of Culliford [5] is used, they can be differentiated by this characteristic alone.

The physical properties of Kodel 211 allow it to be differentiated from PET fibers by its lower density (1.23 g/cm^3 compared with 1.38 g/cm^3 for PET), higher melting point (290°C against 250 to 260°C) [6], and lower birefringence. The latter is an unreliable distinguishing test as birefringence varies in polyester fibers according to the degree of tenacity of the fiber. Because of the greater degree of orientation of the crystallites in a high-tenacity fiber, a higher birefringence value will be obtained. More accurate birefringence measurements may be made by examining the diagonally cut end of the fiber under monochromatic light using a de Sénarmont compensator [7].

Polyester fibers may also occur with triangular or lobed cross sections. They are frequently found in textured varieties to give greater bulk or stretch, and the fibers often have characteristic "beaded" ends from thermal finishing processes. A Pneumacel® polyester with a cellular structure pressurized by air and Freon® is being developed by DuPont [8]. These fibers may be bonded and used as seat cushions and in mattress and carpet underlay because, as a result of diffusion processes, they re-inflate after subjection to load.

Much research on polyester fibers has been connected with improving their dyeing characteristics. Initially, attempts were made by adding active groups into the molecule to attract dyestuffs, as PET and PCDT are themselves chemically inactive [2]. Another modification was the introduction of a small amount of another component into the polymerization mixture; this led to the appearance of polyester-polyether co-polymers. ("Grilene," which Cook [2] describes as a co-polymer of terephthalic acid, ethylene glycol, and *p*-hydroxybenzoic acid, is said by the manufacturers to be a normal polyester fiber [9] and gave an infrared spectrum consistent with being so.)

Braun et al [10] describe recent studies on chemically modified, carrier-free, dyeable polyester fibers in which the properties of three types are evaluated and discussed in relation to their end uses.

The need to be able to identify and separate these new forms of polyester fiber is of prime importance to the forensic scientist. The easiest and most reliable method of identifying small quantities of fiber appeared to be infrared spectroscopy, and the project was carried out as described below.

Method

Standard samples of polyester fiber were received from various manufacturers throughout the world, and their infrared spectra were recorded with a Perkin-Elmer 621 instrument with 1.5-mm diameter KBr microdisks prepared by the method of Grieve and Kearns [11]. The samples were prepared by dissolving the fiber in a phenol/chloroform mixture (10% w:v) in a heated spot plate well and adding a small amount of KBr. This method is applicable to single fiber quantities. A length of 15 to 20 mm of fiber was used in each case. During recording of the spectra and from information received with the samples, it became apparent that other types of polyester fiber exist apart from PET and PCDT and that some of them can be differentiated by spectral differences.

The melting point of polyesters varies according to their chemical composition. These are easily determined by using a hot-stage microscope (for example, a Reichert Thermo-pan) or, as in this case, by using a Büchi melting point apparatus (Schmelzpunktbestimmungs Apparat "Tottoli," W. Büchi Glasapparatefabrik, Flawil, Schweiz). The sample

is placed in a sealed capillary tube and enclosed in a heating jacket containing silicone oil which is mechanically agitated to provide even heating. The capillary can be observed through a magnifying eyepiece, and the melting temperature can be recorded on a thermometer which is also immersed in the oil bath. Melting points vary slightly according to the method of measurement and should not be used alone as a conclusive basis for identification, but they are useful in conjunction with infrared spectra. Slight density variations also occur with chemical modifications, but they are not great enough to be of any practical value for identification. Melting points were recorded for all types known to be chemically modified. The values listed in Table 1 are average values from a minimum of three separate determinations.

Results and Discussion

It is beyond the scope of this paper to provide definitive chemical interpretations of the spectra recorded; rather, the intent is to familiarize those concerned with forensic identification of polyester fibers with the fact that different varieties exist.

The compositions of different types of polyester encountered in this study are believed to be as follows:

- Type 1—polyethylene terephthalate (known as PET);
- Type 2—poly 1:4 bis (hydroxymethyl) cyclohexylterephthalate;
- Type 3—PET/hydroxyethoxybenzoate/diethylene glycol;
- Type 4—PET/alkoxybenzoate;
- Type 5—poly (tetramethylene) terephthalate/isophthalate co-polymer (polyester-elastomer);
- Type 6—poly (tetramethylene) terephthalate (known as 4GT);
- Type 7—PET/neopentyl glycol;
- Type 8—PET/polyethylene oxide block co-polymer;
- Type 9—PET modified with a dioic acid; and
- Type 10—polybutylene terephthalate.

Type 5 has only been examined as raw polymer material, but the diversity of its end uses is such that it might be encountered in a forensic examination; its inclusion was therefore thought to be justified.

Type 1 represents most samples and gives an already well-documented spectrum [12, 13] (Fig. 1) with major absorption points at 1720, 1410, 1340, 1250, 1100, 1020, and 730 cm^{-1} . The melting point is in the region of 250 to 255°C.

Type 2 is represented by Kodel 211 manufactured by Eastman-Kodak and has a spectrum (Fig. 2) very similar to Type 1, but there is no absorption point at 1340 cm^{-1} . The melting point ranges from 286 to 291°C.

Type 3 is represented by a sample supplied as Teijin Teteron 38 manufactured by Teijin Ltd. in Japan. The fiber appears to be hollow, and the spectrum (Fig. 3) indicates it to be a PET/hydroxyethoxybenzoate co-polymer. An absorption point is present at 1340 cm^{-1} , and it differs from Type 1 by the presence of additional points at 1600, 1170, 930 (small), and 765 cm^{-1} . It has a melting point of 220 to 223°C.

Types 4, 5, and 6 are all characterized by the lack of an absorption point at 1340 cm^{-1} . Type 4 (Fig. 4) gives a spectrum similar to Type 3 with points at 1600, 1500, and 1170 cm^{-1} , but apart from the difference at 1340 cm^{-1} it is further differentiated from Type 3 by points at 930, 845, 765, and 690 cm^{-1} . In Type 3, the points at 930, 845, and 765 cm^{-1} are present but are much smaller and additional small ones occur at 870 and 790 cm^{-1} . The spectrum of Type 4 was recorded from a sample of "A-Tell" manufactured by Unitika in Japan and supplied by the Metropolitan Police Laboratory, London. The melting point is also similar to Type 3, being 221 to 223°C.

Type 5 is exemplified by a sample of polymer received from I.C.I. Ltd., Harrogate, England, supplied by DuPont under the name Hytrel[®], and described in a sales leaflet as a poly (tetramethylene) terephthalate/isophthalate co-polymer. Poly (tetramethylene) terephthalate is also known as 4GT. The spectrum (Fig. 6) differs from Types 1, 3, and 7 in the absence of a point at 1340 cm^{-1} ; it also lacks the points at 1600 and 1170 cm^{-1} which occur in Type 4. A sample of Hytrel 5555 was also received directly from DuPont and is described [14] as a polyester-elastomer. Both samples gave identical spectra. It is marketed as a raw material to the rubber and plastics industries throughout the world and end uses are quoted [14] as being hydraulic hose, air and water hose, chemical and fuel hose and tubing, segmented belting for snowmobiles and larger endless-track vehicles, solid and low-pressure tires, fuel cells and other small tanks, specialty belting, wire and cable jacketing, film and sheeting, powder coatings and binders, seals, gaskets, and numerous molded mechanical parts. No melting point determinations were made.

Type 6 is represented by two samples supplied as Trevira 4GT and Trevira 4100 from Hoechst AG and reported by Rhodes² to be poly (tetramethylene) terephthalate which gave identical spectra (Fig. 5). Rhodes also reported that the spectra of 4GT and a 4GT/isophthalate co-polymer are indistinguishable but that they are readily distinguishable by nuclear magnetic resonance studies. However, the spectra did appear to show small (but consistent) differences, particularly around 2900 cm^{-1} and in the small absorption point at 1350 cm^{-1} present in 4GT and the double point at 1370 to 1380 cm^{-1} in Hytrel. These spectra can be distinguished from Kodel 211 by detailed comparison of the region between 1000 and 700 cm^{-1} and of the point between 3000 and 2800 cm^{-1} .

Two samples of carrier-free, deep-dyeable Trevira with type numbers 810 and 813 were received from Hoechst AG and gave spectra identical to the Type 6 spectra recorded from Trevira 4GT and Trevira 4100. All four of these fiber types had very close melting points within 217 to 222°C.

Type 7 samples supplied as Trevira 320 (Hoechst AG) and Nippon Heterofil (Nippon Ester Co.) gave spectra identical to Type 1 (Fig. 7) but were reported by Rhodes to be PET/neopentyl glycol co-polymer samples. He stated that gas-liquid chromatography indicated a significant level of neopentyl glycol not detectable by infrared. R. Alan Jones³ reported that it should be possible to distinguish between the spectra of the pure compounds between 1300 and 1400 cm^{-1} where neopentyl glycol should show two comparatively strong bands between 1350 and 1380 cm^{-1} because of deformation modes of the methyl groups, which will be absent in the ethylene glycol compound. The problem is complicated by the presence of the aromatic system which has medium-strong bands in the same region resulting from in-plane ring deformation modes. The neopentyl system should also possess C-C skeletal vibrations near 1150 cm^{-1} , but these would be difficult to detect because of the strong absorptions of the -CO-O groups of the ester linkages. He concluded that it would not be possible to identify neopentyl glycol as a low concentration component of a PET/neopentyl glycol co-polymer by infrared spectroscopy. The manufacturers of Trevira 320 state, however, that none of their polyester fibers are modified with neopentyl glycol, and the melting points of these two fibers varied considerably from 224 to 227°C (Trevira 320) and from 247 to 250°C for Nippon Heterofil. The melting point of Trevira 320 would actually be more consistent with it being of Type 10.

The fibers used by Braun et al [10] for their studies on carrier-free dyeable polyesters were made from a polyethylene terephthalate/polyethylene oxide block co-polymer (Type 8), polyethylene terephthalate modified with a dioic acid (Type 9), and polybutylene terephthalate (Type 10). The melting point and density for Type 8 are quoted as

²M. D. Rhodes, personal communication, 1975.

³R. Alan Jones, personal communication, 1976.

TABLE 1—Data on polyester fibers examined.

Trade Name	Manufacturer	Type	Melting Point, °C	Remarks
Avlin	FMC American Viscose	normal PET
Avitron	Phrix-Werke AG	normal PET
Blue C	Monsanto	normal PET
Dacron 35	DuPont	normal PET
Dacron 54	DuPont	normal PET
Dacron 64	DuPont	normal PET
Dacron 65	DuPont	normal PET
Diolen	Glanzstoff AG	normal PET
Enka polyester	American Enka	normal PET
Encron	American Enka	normal PET
Grilene	Grilon S.A.	normal PET
Kodel 411	Eastman-Kodak	normal PET
Kodel 421	Eastman-Kodak	normal PET
Lirelle	Courtaulds	normal PET
Teijin Teteron	Teijin	normal PET
Tergal	Rhodiaceta S.A.	normal PET
Teron	Rumania	normal PET
Terylene	I.C.I.	normal PET
Toray Teteron	Toyo Rayon	normal PET
Trevira 120	Hoechst AG	normal PET	251-255	contains optical brightener
Trevira 130 ^a	Hoechst AG	normal PET
Trevira 132 ^a	Hoechst AG	normal PET
Trevira 160 ^a	Hoechst AG	normal PET
Trevira 220	Hoechst AG	normal PET	250-253	...
Trevira 520 ^a	Hoechst AG	normal PET
Trevira 610	Hoechst AG	normal PET	251-253	...
Trevira 820 ^a	Hoechst AG	normal PET	...	trilobal section
Trevira 823 ^a	Hoechst AG	normal PET
Trevira 860 ^a	Hoechst AG	normal PET	...	trilobal section
Trevira 863 ^a	Hoechst AG	normal PET	...	trilobal section
Wistel	Snia Viscosa	normal PET
Kodel 211	Eastman-Kodak	2	286-291	...
Teijin Teteron 38	Teijin	3	220-223	hollow filament

A-Tell	Unitika, Japan	4	221-223	...	polyester-elastomer
Hytrel ^b	DuPont	5	polyester-elastomer
Hytrel 5555 ^b	DuPont	5	carrier-free deep dyeable type
Trevira 810	Hoechst AG	6	219-222	...	carrier-free deep dyeable type; trilobal section
Trevira 813	Hoechst AG	6	217-220	...	
Trevira 4100	Hoechst AG	6	220-222	...	
Trevira 4GT	Hoechst AG	6	219-222	...	
Nippon Heterofil	Nippon	7	247-250	...	gives normal PET IR spectrum
Trevira 320	Hoechst AG	7 (or possibly 10)	224-227	...	gives normal PET IR spectrum
Trevira 550	Hoechst AG	modified-possibly 10	223-225	...	high shrink type; gives normal PET IR spectrum
Trevira 630	Hoechst AG	modified-possibly 9	236-238	...	deep dyeable type
Trevira 640	Hoechst AG	modified-possibly 9	237-238	...	cationic dyeable type
Trevira 350	Hoechst AG	chemically modified; unknown	250-252	...	low-pilling type; gives normal PET IR spectrum
Trevira 352 ^a	Hoechst AG	chemically modified; unknown	trilobal cross section
Trevira 353 ^a	Hoechst AG	chemically modified; unknown	experimental carrier-free deep dyeable variety
Trevira 210 ^a	Hoechst AG	chemically modified; unknown	

^aNo samples available; included to give a more complete record from data provided by the manufacturer.

^bRaw polyester sample.

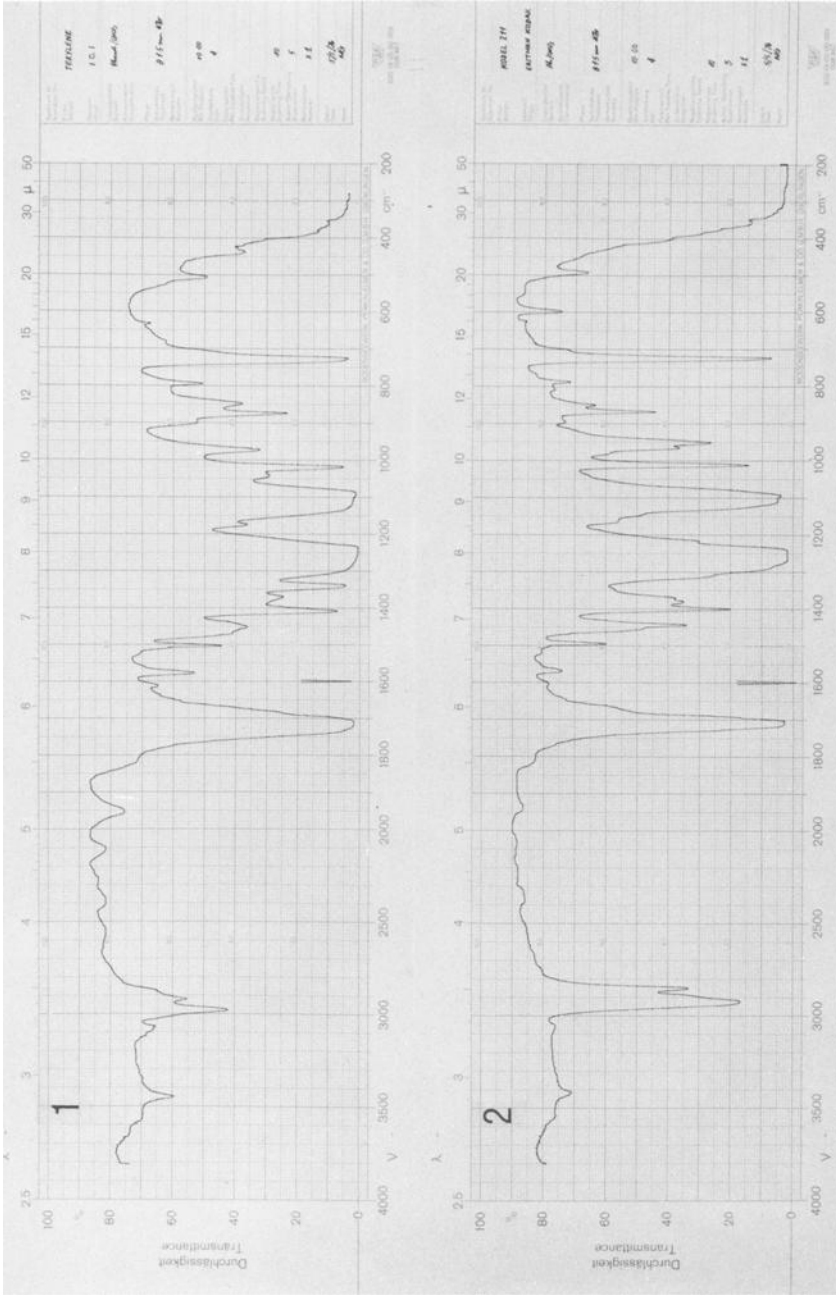


FIG. 1—Infrared spectrum of Terylene, manufactured by I.C.I. Ltd., typical of Type 1 polyesters.
 FIG. 2—Infrared spectrum of Kodal 211, manufactured by Eastman-Kodak, typical of Type 2 polyesters.

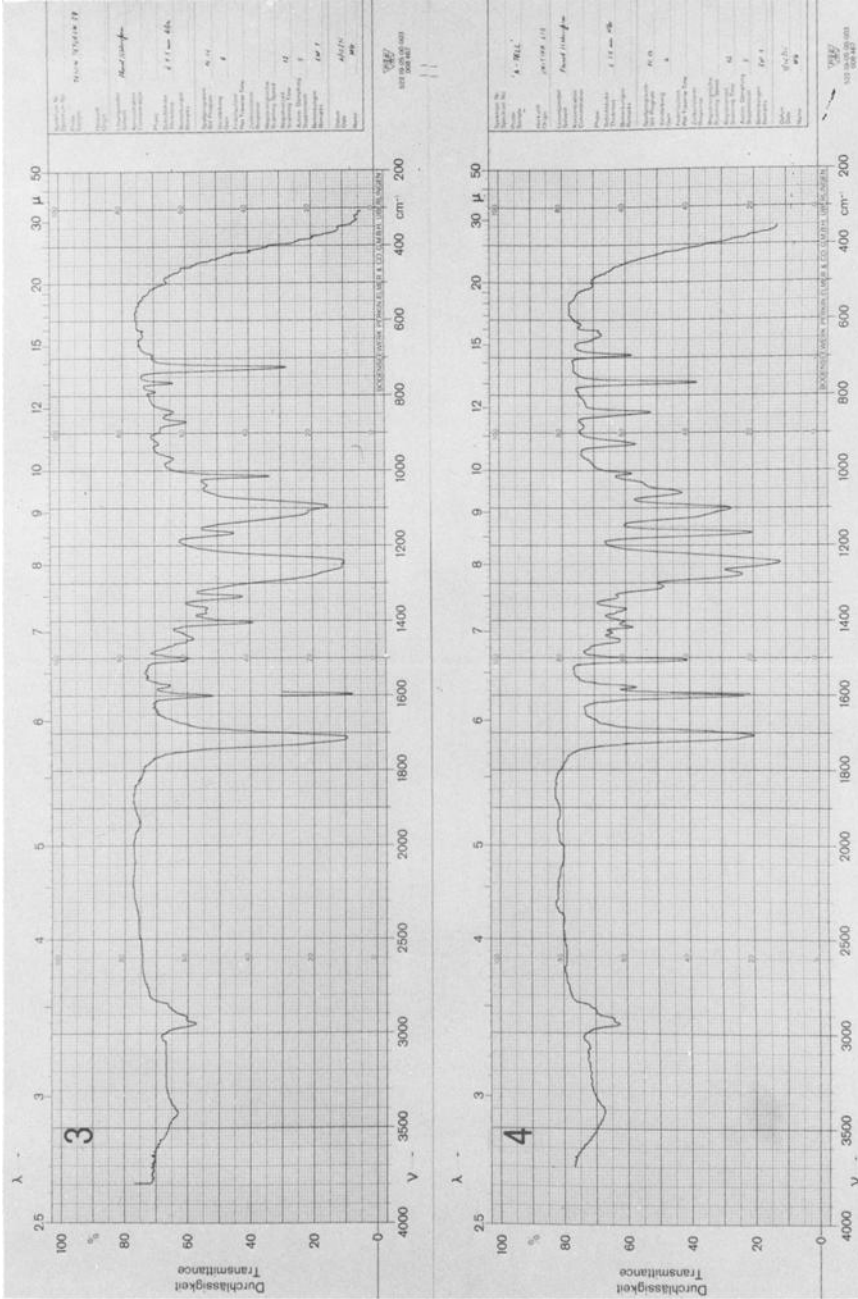


FIG. 3—Infrared spectrum of Teijin Teterson 38, manufactured by Teijin Ltd., typical of Type 3 polyesters.
 FIG. 4—Infrared spectrum of A-Tell, manufactured by Unitika Ltd., typical Type 4 polyesters.

being practically the same as normal polyethylene terephthalate fibers. In contrast, Type 9, which has been known for a longer time and is normally used in conjunction with regular PET fibers to produce differential dye effects in carpets, is reported to have a lower melting point (240°C) and slightly lower density (1.35 g/cm³). Type 10, which is also used in carpets, has an even lower melting point of 224°C and a density of 1.35 g/cm³.

Unfortunately, no known samples of these fibers were available for comparison of their infrared spectra. According to Hoechst AG Trevira Types 210, 350, 352, 353, and 550 are all chemically modified varieties, but the nature of the modifications was concealed for patent reasons. Trevira 630 and 640 are also believed to be modified. Spectra were recorded from samples of Trevira Types 350, 550, 630, and 640 (Fig. 8 gives the spectrum for Trevira 640), but they were no different from those given by a normal PET fiber. The samples of Trevira 320 and 550 had melting points between 223 and 227°C (as Type 10). Trevira 350 appeared to be anomalous in having a melting point similar to normal PET fibers of 250 to 252°C, while both Trevira 630 and 640 produced for special dyeing processes had melting points between 236 and 238°C, which is perhaps indicative of the chemical modifications being as described by Braun et al [10] for Type 9. Trevira 210 is a purely experimental fiber not in commercial production. The need for recording infrared spectra while making identifications of polyester fibers in the forensic science laboratory is self-evident. However, literature reviews reveal the number of chemically modified types to be increasing; recent references cite examples of poly (trimethylene terephthalate) (3GT) [15] and a block copolyesterether of poly (hexamethylene terephthalate) (6GT) with poly (oxyethylene) terephthalate (POET) [16] which are not covered by this paper. It is disturbing that this method does not always allow distinction between PET and other varieties with unknown modifications (see Table 1), which could lead to false identification and comparisons. For patent reasons manufacturers are not always willing to divulge the exact nature of their products. It seems possible that nuclear magnetic resonance spectroscopy may provide a method of distinction, but as usual forensic scientists are faced with the handicap of normally having to work with only a very minute quantity of material.

Summary

The forensic identification of polyester fibers is discussed. Infrared spectroscopy allowed differentiation of various modified types. Melting points were also recorded. Analysts should be aware of possible confusion arising over the identity of fibers which cannot be conclusively differentiated by this method. The need for further study, possibly by nuclear magnetic resonance, is indicated. Table 1 summarizes information on the polyester fibers examined in this study which are grouped together according to chemical type and melting point.

Acknowledgments

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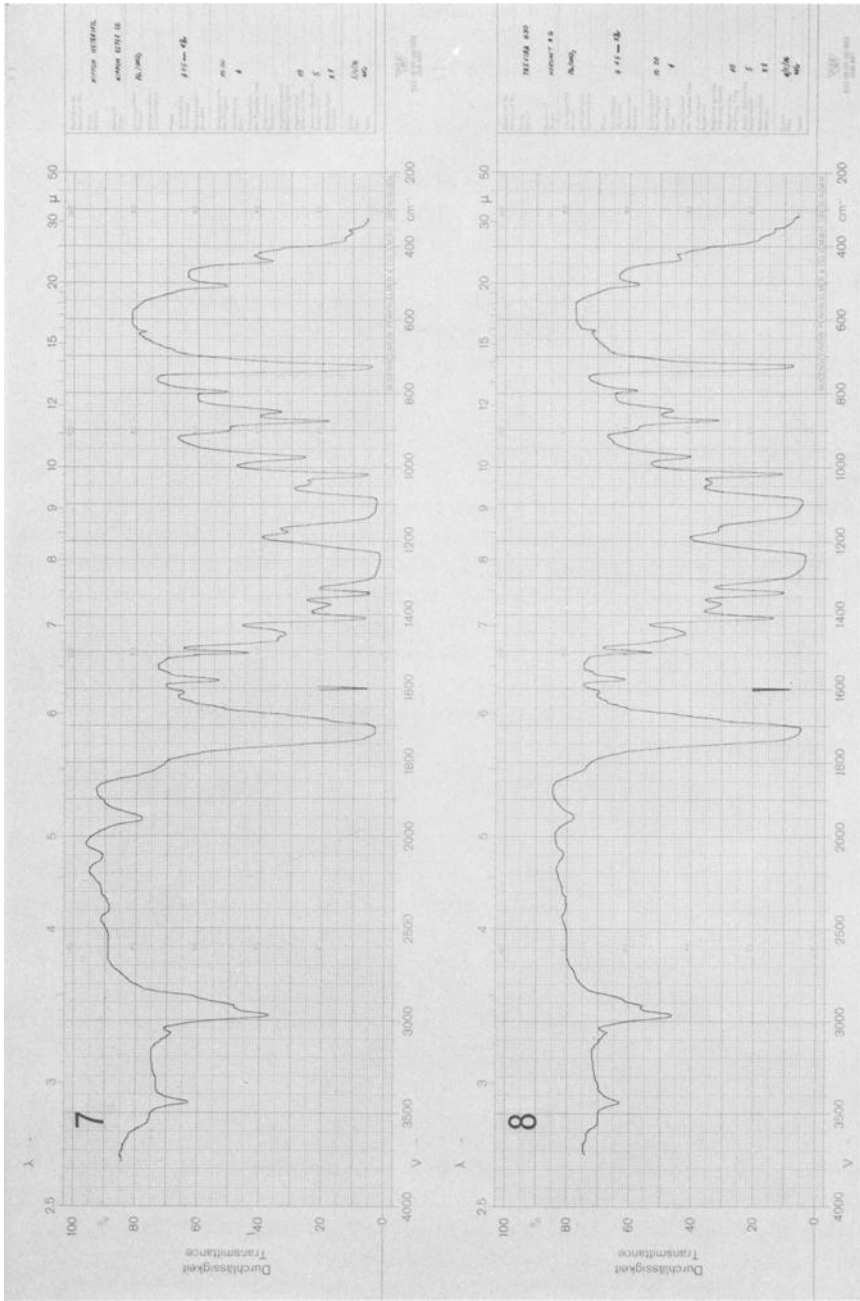


FIG. 7—Infrared spectrum of Nippon Heterofil, manufactured by Nippon Ester Ltd., typical of Type 7 polyesters.
 FIG. 8—Infrared spectrum of Trevira 640, manufactured by Hoechst AG, a polyester of unknown modification.

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