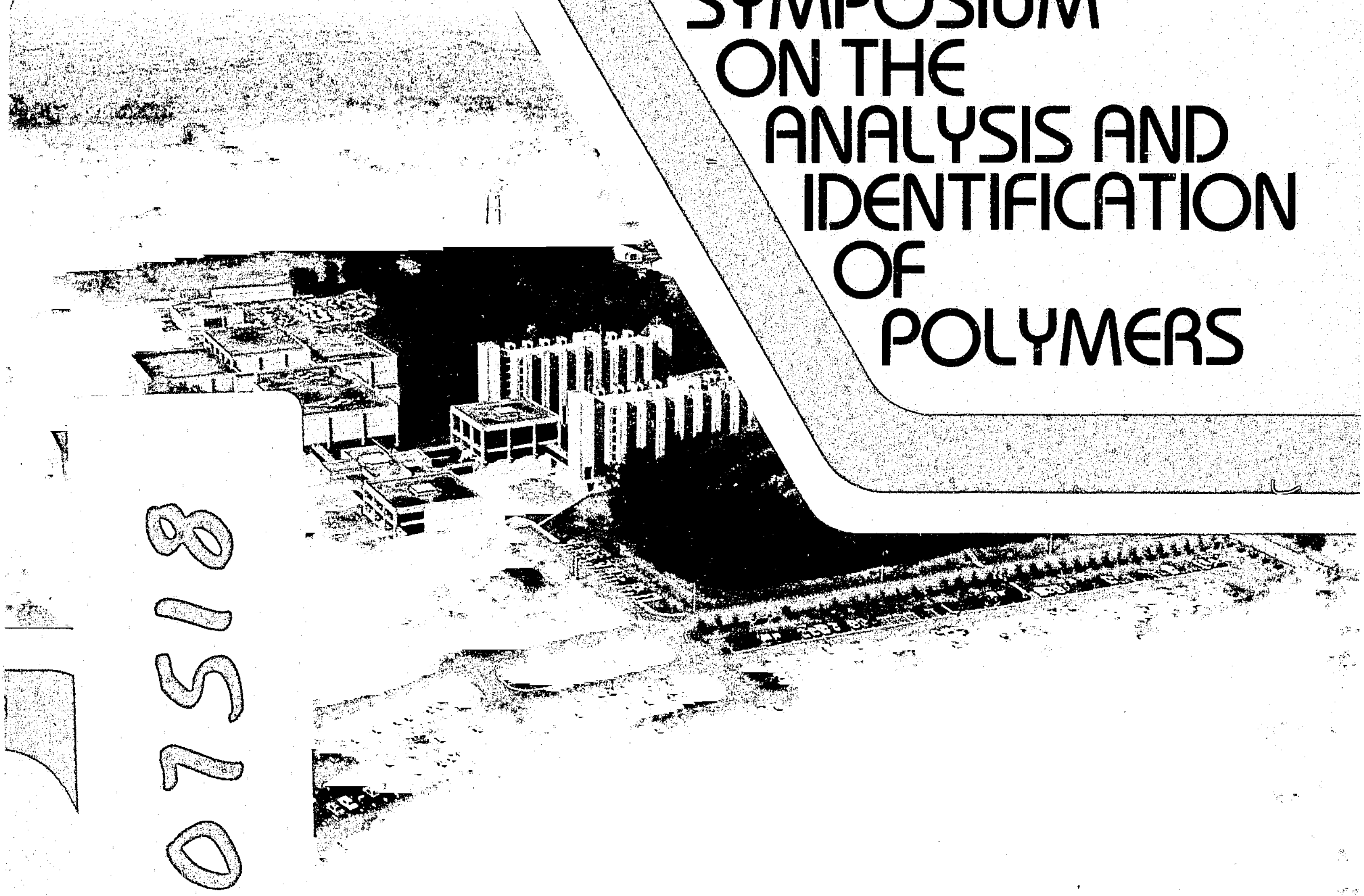
U.S. Department of Justice
Federal Bureau of Investigation

# PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON THE ANALYSIS AND IDENTIFICATION OF POLYMERS



FBI ACADEMY
QUANTICO, VIRGINIA
JULY 31-
AUGUST 2, 1984

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# Proceedings of the International Symposium on the Analysis and Identification of Polymers

Host
Laboratory Division
Federal Bureau of Investigation

July 31 - August 2, 1984

Forensic Science Research and Training Center
FBI Academy
Quantico, Virginia

## NOTICE

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# FOREWORD

On July 31 - August 2, 1984, the FBI Laboratory hosted the "International Symposium on the Analysis and Identification of Polymers" at the Forensic Science Research and Training Center, Quantico, Virginia. There were 113 individuals from industry, government and university laboratories from the United States, Canada, Germany, Great Britain and Switzerland.

Prominent scientists made presentations on topics such as the formulation and synthesis of coatings and polymers, as well as analytical techniques used in discriminating these materials. Additional presentations were made on polymer products with fabrication or manufacturing marks and methods developed that are pertinent to forensic analysis of polymers.

It is hoped that the exchange of ideas communicated at the symposium will further generate research into the forensic application of polymer analysis. I believe the overall objective of the symposium - to gather scientists to discuss polymer analysis - was met with much success. I thank all those who participated.

WILLIAM H. WEBSTER
*Director*

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| | |
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# Contents

SECTION I LECTURES

SECTION II - EXTENDED ABSTRACTS

SECTION III - SHORT ABSTRACTS

SECTION IV - PANEL DISCUSSION

# SECTION I
# LECTURES

# FINISHING OF GENERAL MOTORS VEHICLES

*Donald R. Hays*

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The finishing of passenger cars and trucks is a complex process using many different materials. While the materials may vary somewhat from one plant to another, the processing is generally similar, but may be different in detail. The resulting finishes will all meet General Motors' high standards for durability and appearance. The coatings on automobiles and trucks are designed to provide protection from the environment from sunny, hot, humid tropics to frigid arctic climates --- some vehicles may be subject to alternating hot and cold. Protection against salt mist in coastal areas and salted winter roads provides the greatest challenge an automobile paint engineer faces.

Automobile and truck coatings must also be attractive. Joseph's coat was quite limited in its colors compared to the rainbow of colors and dazzling effects available to the automobile designer today. I might add that the use of the new clear coatings over a color coat will allow the use of exciting new pigments and appearance effects. The smoothness and high gloss of these coatings require a high degree of quality control and processing care for their successful use.

The painting of vehicles has always been a complicated process utilizing materials and application methods many times on the cutting edge of technology. Until 1922, air dry varnishes, like those used on coaches and buggies, were used to paint automobile bodies. These varnishes required as many as 20 to 30 coats with hand rubbing between coats. On higher priced vehicles, it could take as long as three weeks to finish the body. And then the varnish would last only about six months before it would become dull and crack if it were left out of doors. Hoods, fenders and a few high production bodies were coated with high bake enamels. Henry Ford's statement that "the customer can have any color as long as it is black" was based on the fact that black was the only color in which these enamels had any durability.

The introduction of nitrocellulose lacquer in 1923 broke the production bottleneck and provided a much more durable finish in a wider range of colors. The introduction of "metallic" finishes containing aluminum flake, first used in General Motors in 1936, provided a styling advantage that has continued to grow in popularity today.

Acrylic lacquers were first used on a trial basis in 1954. Several colors were introduced in 1955 which could not be used in the old nitrocellulose system. General Motors converted completely to acrylic lacquers in the 1959 model year (summer of 1958). The acrylic lacquers provided a substantial improvement in durability (resistance to dulling and fading in service). New primers, thinners and adjustments in application techniques had to be developed for the new lacquers.

To meet compliance with Federal and local regulations on solvent emissions from painting operations, General Motors' plants have made many changes in the ways in which vehicles are painted. Experimental and pilot line operations have checked out a large number of paint materials and processes for their suitability for use. Solvent-borne acrylic enamels, urethane enamels, and powder acrylic enamels were run on pilot lines in the mid-1970s. Waterborne enamels have been used at selected plants since 1974. Base coat/clear coat enamels were introduced at the Corvette plant in 1982. The Wentzville, Orion and Pontiac Fiero plants started up their operations with base coat/clear coat in the fall of 1983.

In contrast to passenger cars, trucks have used enamels through the years. Before 1956 alkyd enamels were used. From 1956 to 1969, non-drying oil melamine cross-linked alkyd enamels performed an upgrading of quality over the alkyds. Quality in terms of better durability and selection of colors was again improved with the use of acrylic enamels introduced in 1969. Solids content has been raised in acrylic enamels from approximately 17 percent to 50 percent and higher through the years to further enhance compliance with increasingly stringent Federal and local regulations.

The introduction of new materials and processes can be a complex process involving testing of paint quality, determining its application and processing characteristics, trial runs in one or more plants, and extensive interaction with the paint supplier and equipment manufacturers before it is finally put into use on a regular basis in our plants. The time from submission of a new material until its final adoption in plants can take from 2 to 4 years depending on the amount of development needed to make it work well in production and how much background we have in that specific technology. We prefer to have at least 2 years of Florida exposure data for final approval in new technologies.

Some things such as colors change on a regular basis. Until the mid-1960s each of our motor divisions had their own selection of colors. Since then, about a dozen colors which represent most of our production are shared by all divisions. Each division has a few special colors reserved for itself. Cadillac uses more special colors than the other motor divisions, especially in the high glamour metallic colors. One-third to one-half of the colors will be new each year. Most of these new colors will be in the special color categories. The corporate colors which represent most of our production change only a few colors each year. A few colors such as black, white, silver and light blue metallics may not change or may change only slightly for many years.

Let us look at the materials and processing of automobile finishing in more detail. Steel has been and continues to be the automotive substrate of choice for construction of automobiles. Even those vehicles with plastic exterior panels have a structure of steel supporting them. Lighter weight materials such as aluminum and plastic are being used more and more in order to reduce vehicle weight. The need to reduce vehicle weight as part of the industry's efforts to improve efficiency in gasoline mileage and the development of high strength low alloy steel has resulted in the selective use of thinner steel parts where performance would not be affected. Aluminum hoods and deck lids, for example, have been used on selected models.

Zinc coated steels are also being used in increasing quantities in selected areas to provide added corrosion protection. The zinc coated steels include those painted with paints containing zinc dust as well as several forms of galvanized one side, two side, minimum spangle, ultrasmooth, etc.

All painting must be done over a clean substrate if the paint is expected to be resistant to moisture and corrosion. Metals and plastics are vigorously scrubbed and/or immersed in alkaline cleaners to remove oils, lubricants, mold releases (from plastics) and dirt. After rinsing, plate-like crystals of zinc phosphate are grown on metal (steel, zinc and aluminum) surfaces. These crystalline coatings provide a tight anchor for the paint applied over them improving resistance to impact and corrosion in service. The process of cleaning and surface treatments provides a well controlled and consistent surface upon which to apply the paint. Only cleaning is required for plastics. All surfaces, whether metal or plastic, must be rinsed clean of water soluble salts before painting to eliminate the probability of blistering in humid weather.

Today electrodeposited primers are used by virtually all automobile manufacturers. General Motors has coined the acronym "ELPO" (Electrodeposition of Polymers) to describe the process. In this process, the metal part or car body is immersed in a waterborne dispersion of the primer and deposited by an electrochemical reaction. Developed in the mid-1960s, General Motors began using a black anodic amine solubilized melanized linseed oil ELPO primer on production hoods and fenders in 1967. The first ELPO primers used on bodies were modified epoxies pigmented with iron oxide so they were reddish-brown in color. Colors used varied from the reddish-brown iron oxide color to black as different plants exerted their preference for color. Potassium hydroxide solubilized modified epoxies were introduced in the 1970s to provide improved "throw" - the ability to coat into recessed and hard to reach internal body areas. These changes occurred over a period of several years as new ELPO facilities were constructed at various plants and existing ones adopted the new materials.

Cathodically deposited ELPO primers were first tested in 1974 and introduced into production in 1976. The cathodic ELPO process has provided a quantum jump in improved corrosion resistance. These epoxy resins are solubilized with an organic acid. They are deposited onto the cathode instead of the anode. They become highly cross-linked and are virtually impossible to remove when properly baked. Cathodic ELPO was first used to prime production bodies in 1978. The deposited films were black or grey, depending on the plant's particular preference in color. The original cathodic ELPO primers were 0.5 to 0.7 mils thick and were usually covered with 1.0 to 1.2 mils of a tan colored primer surfacer. Recent development of high build ELPO (called "Uniprime" by its manufacturer) will allow us to eliminate the primer surfacer and to apply enamel topcoat directly over the gray "Uniprime". Because the "Uniprime" is up to 1.8 mils thick, it can be sanded where needed to eliminate roughness and dirt. The high build "Uniprime" will allow us to simplify the processing, eliminate a source of solvent emissions and maintain quality in corrosion resistance and appearance.

Primer surfacers have been used over the years for their filling properties. They can be easily sanded to provide a smooth surface for topcoating. These surfacers have binders of epoxy or polyesters. They are usually reddish brown to a greenish gray or charcoal gray depending on the pigmentations of iron oxide, titanium oxide, carbon black, barytes (barium sulfate), talc, clays, etc. Primers and/or primer surfacers are used to fill minor substrate imperfections, to provide corrosion resistance, moisture resistance, good adhesion and a smooth substrate for the topcoat. The surfacers may be sprayed or applied by an electrodeposition process. Surfacers are sanded to remove dirt and to smooth the surface for topcoating. Sealants are applied during this stage of the processing to make seams, covered openings, etc., watertight. They are then set up and cured along with the paint in the paint ovens.

Pit fillers are much more heavily pigmented than primers. Sealants are applied to seams to make the body watertight. They are applied as a soft bead which hardens when baked. Meltable patches are laid over access and drain holes to seal them shut. These sealant materials are found in well hidden places under interior trim or have been covered by paint.

Dip and flow coat primers have been used for many years on small miscellaneous parts, hoods and fenders. They have gradually been replaced with the ELPO primers. Only a few of these systems are still in operation on small parts. They will soon be replaced with ELPO primers. Except for a few plants, all hoods and fenders are now painted along with the body. Dip and flow coat primers have thin coating on sharp edges with a thick bead of primer along what was the bottom edge when it was dipped in the primer. These primers had alkyd or epoxy binders with carbon black, barium sulfate, clays, titanium dioxide and anti-corrosion pigments.

The topcoats provide protection from sunshine and the environment. It is the topcoats which provide the color and the attractive surface that is visible to the customer.

General Motors has traditionally used lacquers as a topcoat on passenger cars. Lacquers become a serviceable film by the physical process of evaporation of solvent. Even though the solvents evaporate from an enamel, it will not be a serviceable film until the chemical process of polymerization or curing has taken place. Through the years, lacquers have produced a very smooth, attractive glossy surface. They are easy to repair and can be successfully spot repaired. Until recently, high glamour, light-colored metallic colors could be produced only in lacquers. In the early 1960s cellulose acetate butyrate was added to the acrylic polymer to allow the lacquer to reflow to a high gloss in the final topcoat bake oven after light sanding to minimize orange peel and remove minor imperfections.

In the 1970s solution lacquers began to be replaced with higher solids dispersion lacquers. The dispersion lacquers have allowed the use of higher molecular weight polymers. In addition to the acrylic polymers and pigments, plasticizers, ultraviolet screeners and other additives are used to improve the properties of the paint film and to enhance their stability to out-of-doors exposure. The dispersion lacquers have no added cellulose acetate butyrate. All of these lacquers can be dissolved with solvents such as acetone, toluene or other strong polar solvents.

In the quest to further enhance compliance with Federal and local regulations on solvent emissions from stationary sources, higher and higher solids paints have been developed and used over the last 15 years. The practical limit of 27 percent solids in lacquers has been in use since the late 1970s and is now used on most General Motors passenger cars. Enamels can be formulated to solids contents higher than 50 percent at the time of application. Because of their differences in application properties and their more difficult repair (requiring panel repair), enamels cannot be applied on the same paint line as lacquer without extensive rebuilding of spray booths, application equipment and ovens. Therefore, plants are being converted to enamel one by one as paint lines are renovated for new car lines or as new plants are built. The acrylic enamels contain acrylic polymers, melamine cross-linking agents, ultraviolet screeners and pigments. After baking, enamels cannot be dissolved with any solvents, however strong.

General Motors stands ready to help law enforcement agencies in providing information on the materials, especially paints used in the manufacture of their products. We already supply the Federal Bureau of Investigation with samples of the yearly colors and the charts of finishing systems and materials used in each plant. We are in the process of arranging to supply samples of full finishing systems on a regular basis for sample analysis.

Questions should be directed to the FBI in Washington, D.C. They are able to answer many of your questions in ways that will be most helpful to you. To answer those few questions they cannot answer, you will be referred to a General Motors representative.

## DISCUSSION

*Schneider:* Do you have the same chart system over in Europe? If you have, are these charts also available for us in Europe?

*Hays:* They may be available in Europe through the Opel organization, but we do not have them in the United States.

*Corby:* With respect to your repair systems, particularly, original equipment material in repair systems in inplant production, are they the same materials or do they vary when they go through the repair line?

*Hays:* They are basically the same materials. The final repair materials, if they are enamels, may be catalyzed so that they can be baked at a lower temperature. Catalysts are used because the tires will blow, the glass distorts, the taillights distort, and the air conditioning system blows at a surprisingly low temperature. The key here, I think, in the identification of repairs is the extra layers that show up on cross section. Generally, these same materials are used on repairs.

*Praschan:* In the case of waterborne enamels, as Mr. Hays mentioned, we presently use them in two plants. They are repaired with lacquer, acrylic solution lacquer, so they should be identifiable in a manner similar to the other solution lacquers encountered elsewhere. The only difference is they do not receive the high bake.

In the case of the present dispersion lacquers which are used in all of our plants except for the Canadian plants, we repair them with solution lacquer as well. So again, on the same vehicle, you could see both types of finish that may be distinguishable in the normal manner.

*Hays:* With the waterborne enamels, you are not going to get it dissolved with much of anything. I have never seen anything quite so insoluble as that material once it is laid down.

So as Mr. Praschan said, with enamel to lacquer repair you can pick that up with the difference in solvency, and under the microscope you can clearly pick that up.

The dispersion lacquer and the solution lacquer, I do not believe that one could really distinguish them.

*Praschan:* That last question did not seem to be answered fully. It seems to me, note I am not an analytical chemist, that if the forensic scientists have the tools to distinguish between one supplier and another of dispersion lacquer or solution lacquer, surely there are some identifiable characteristics in composition.

You may have to go in-depth to distinguish solution and dispersion lacquer, but there are some compositional characteristics that are different. Mr. Hays alluded to a cellulose acetate butyrate, that is one that would be different between the two.

*Hays:* There is no cellulose acetate butyrate in dispersion lacquers. They wish they could get it in, but they have not been able to.

*Kubic:* As far as touch ups and using lacquers to touch up go, how large of an area on an automobile may be touched up by lacquer? Also I would like to ask Dr. Nordstrom, since Ford uses mostly enamels, does Ford do their final touch ups with lacquers also, and how large of an area on an automobile may be touched up by the lacquer if Ford indeed does so?

*Nordstrom:* I am not sure I can answer the "how large" question. I suspect that depends on the extent of damage. When you say touch up, I assume you mean repair, body shop repair, once it has left the assembly line.

*Kubic:* In-plant.

*Nordstrom:* The original equipment paint is catalyzed in-plant at Ford and this is usually not within small areas. Usually it is a whole door, a whole deck lid or a whole hood.

There are different catalysts for high solids materials. A typical catalyst has monobutylmaliate and butylphosphate, sometimes in combination with the maliate as our typical catalyst to convert our regular paint to catalyzed repair.

*Question:* Do we use pertoluene sulfamic acid?

*Nordstrom:* That might be used in some of the high solids materials, it has not been used in the materials to the high solids.

*Hays:* One of the reasons General Motors has stayed with lacquer is because it enables us to do what we call "spot repair". Some spot repairs work out very well even if you have a real bull's-eye right in the middle of your door, depending, of course, on the skill of the people doing it, whether it is in-plant or outside at a repair shop.

With lacquer you can melt this with miscoat thinners that are applied just after you apply the color coat. Usually this blends in very well, therefore, repairs are very easy to make in lacquer. But with enamels, we have to do panel repair and the size of the facilities required for panel repair are one of the major requirements for rebuilding our lines for our repairs.

Of course, we try our best to do the job right the first time so that we do not have to make repairs. We are getting there. But with enamel, you repair to a break line, either a door, a fender or where there is a major change in the direction of the metal.

*Question:* In the laboratory the main purpose in a hit-and-run case, of course, is to identify the vehicle. In order to identify the vehicle, we have to have the original finish. Is it possible in General Motors' plants to have two different formulations of the same topcoat on the same automobile? Also, I have seen in some plants that there may, in fact, be two different types of primer on the same automobile. So is it possible to have, for example, an Inmont formulation of the topcoat, a PPG formulation on the topcoat and/or two different primers on the same automobile made at the same plant?

*Hays:* In the topcoat, you could have an Inmont with a PPG if it were two-tone, and that inner compatability we do require. We would rather not do it this way, but it could happen, yes.

As far as different primers on the same body are concerned, today this is less likely to occur, but we do have a few plants where the body is finished in one plant and the hoods, fenders and sheet metal in another plant. This happens with automobiles that are built at the Buick home plant, at the Oldsmobile home plant in Lansing, and the Cadillac home plant in Detroit. The Seville is built in Linden, New Jersey, and the El Dorado, I believe, is built there too, therefore, they have the same systems on the hoods, fenders and body. But within the three home plants, I think they are all dip primer on the hoods and fenders, and the E-coat on the bodies. That will change as Buick City comes on-line, as

Lansing consolidates its sheet metal with the body, and with the building of the New Detroit plant, primers on these vehicles will be the same throughout.

We do try to minimize the mixing of suppliers within the plants, but once in a while the usage volume is so low for a few colors that not all three suppliers may supply a particular color.

One point that I would like to mention is that we have a number of colors which we call Fire Mist (an E. I. duPont de Nemours & Co. trade name). They have a large aluminum flake in them and they have a very high degree of sparkle to them. These colors tend to be used more on the specialty cars than on others, for example, the Cadillacs and the Riviera.

Another point I would like to mention concerns plastics. The body panels of the fenders of the Fiero are called "rim reaction injection molded" urethane parts. When viewing a cross section with transmitted light, one will see small bubbles. The bubbles are built into the plastic, if you will, to help provide flexibility. We try to have within a skin, a bubble-free skin at the surface. Sometimes this works and sometimes it does not.

Paint systems used on plastics are very complex as far as combination of materials go. You just about have to have different paints and primers for every plastic. Eventually, I think this will be simplified, but right now it is very difficult to keep track of.

*Norwicki:* You talked about coating on plastics. What about fiberglass bodies, do you need any special kind of primer for those also?

*Hays:* The fiberglass qualities have usually what is called a mold coat. What they do in the molding of the plastic is open the mold a very precise amount and inject a material, a primer-like material. There is no fiberglass in it, and is used to fill any porosity that may be left for wetting of the fiberglass, and provides a better surface for us to paint. With the fiberglass reinforced plastics, we may apply a special primer, but then it will be topcoated along with the rest of the system.

*Gordon:* How dependable are spectrophotometric curves for the identification of the colors in your finishes? That is, if you have a small flake of material and put it on a microspectrophotometer, can you depend on the spectrophotometric curve as an identifying means?

*Hays:* I do not think I can answer that question directly. The spectrophotometric curves can be difficult to handle.

Most of our work is done with colorimeters reducing them to the L, A, B or their X, Y, Z numbers. I think with some limitations, this can be pretty good. Right now we are working out how precise those numbers should be. The metallic colors are especially difficult because you can vary the color of these metallic colors enormously by just moving your gun in or out just a few inches. Anything that will affect the solvent that evaporates between the gun and the work can change the color of a metallic enormously, and you do not even need a spectrophotometer to tell that it does not match. The application of metallic colors is a very tricky business because of the small flakes. As the paint dries down, the flakes tend to orient more and more parallel to the surface and it is that parallel orientation that we depend on for the color match, not composition.

# FORENSIC ANALYTICAL PYROLYSIS

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Forensic science is a discipline concerned with the application of science to the enforcement of criminal laws. If the ultimate objective of law is justice, then forensic science aims to impartially assemble factual data to define the bounds of truth. Our practical experiences teach us that science cannot completely replace those human judgments needed for gauging guilt or innocence, truth or deception, benefit or risk. Nevertheless, the desire to maximize impartiality and to minimize error when dispensing justice have combined to enhance the role that science plays in the judicial process. This paper is devoted to discussing just one aspect of that endeavor - the application of pyrolysis technology to the characterization of crime scene or physical evidence. Physical evidence encompasses any object retrieved from a crime scene which can aid investigators in determining whether a crime has been committed or can provide a link between a crime and its victim(s) and/or perpetrator(s). The term "physical evidence" accounts for a wide variety of materials and the forensic analyst must be prepared in skill and equipment to undertake a wide range of analytical chores to accomplish their characterization.

Pyrolysis as an analytical tool became feasible when the technology emerged for separating and characterizing pyrolysates. It was the gas chromatograph that made this development possible. The combination of pyrolysis and gas chromatography (Py-GC) is a powerful and sensitive method for discriminating materials belonging to the same group or class. Pyrolysis gas chromatography's utility as a forensic technique stems from its ability to transform a nonvolatile organic material into a series of volatile compounds reflecting the chemical composition of the degraded material. Considerable credit must be given to Dr. Paul Kirk and his group of researchers at the University of California who performed most of the earlier works aimed at demonstrating Py-GC's potential usefulness for the characterization of various types of physical evidence (Kirk 1967). Kirk and his coworkers showed how pyrogram patterns were applicable for differentiating commercial plastics and paints (Nelson *et al.* 1962; Jain *et al.* 1965). They also explored the possibilities of using Py-GC for identifying assorted drugs, specifically, barbiturates (Nelson and Kirk 1962; 1964), phenothiazines (Fontan *et al.* 1964) and alkaloids (Kingston and Kirk 1965). While Kirk's efforts at applying Py-GC for drug identification purposes have not gained wide acceptance as a viable forensic science technique, Py-GC certainly has become an indispensable tool for the identification and comparison of paints, fibers, plastics and other polymeric evidence. In fact, the successful utilization of Py-GC for forensic science problems has encouraged the investigation of other forms of analytical pyrolysis to forensic analysis. What has emerged is an exciting array of pyrolysis techniques designed to discriminate and identify key items of evidence. It is the purpose of this paper to review state of the art pyrolysis procedures used in forensic science.

## PYROLYSIS GAS CHROMATOGRAPHY

### Paint Evidence

The majority of paint evidence processed in crime laboratories arises from a transfer of paint from one surface to another. Such a transfer may take place between an automobile and the garment of a hit-and-run victim, or it may occur between a painted wall molding and a tool being used to jimmy open a window. In any case, given such a set of circumstances, the forensic analyst will strive to relate the paint to its suspected origin employing a series of physical and chemical tests. How successful one is at making this association is dependent on many variables (for example, color, layer structure and chemical composition). Often, even under the best circumstances, the analyst is unable to express even in probabilistic terms the significance of a paint comparison. Less frequently, the forensic analyst will be called upon to identify the manufacturer of a paint chip. In practice, this situation usually relates to identifying the make and model of an automobile. Here the analyst will generally refer to color charts available from various paint manufacturers, refinishers and the U.S. National Bureau of Standards, in attempting to narrow the number of possible sources. Other approaches relevant to this problem have been reported, but they have not yet gained widespread popularity within the forensic science community. Deaken (1975) has described an approach for vehicle identification based on the varied primer color combinations used by automotive manufacturers. Others have proposed using an infrared (IR) spectral data base for the identification of automotive paints (Cartwright and Rodgers 1975; Percy and Audette 1980). Audette and Percy (1979; 1982) have developed a computerized data retrieval system for identifying automotive paints. Their system encompasses topcoat and primer colors, layer sequences, and data derived from the IR and elemental analyses of the paint layers.

While there has been no systematic effort at incorporating Py-GC into a forensic paint identification scheme, there is ample evidence to demonstrate its utility for classifying automotive paints. Wheals and Noble (1974) employed Py-GC for differentiating alkyd, thermoplastic acrylic and thermosetting acrylic automotive paints. The pyrograms obtained with automotive paints using a 4 m stainless steel GC column containing 15 percent Carbowax 20 M were found to be reproducible and sufficiently characteristic to frequently discriminate paints from vehicles of different manufacturers. However, as the authors appropriately pointed out, many of these paints are produced by a number of suppliers and automotive producers. Unfortunately, there exists no data base to show when a particular supplier's paint is being used. Under these conditions the contribution of Py-GC to a systematic analytical scheme for automobile identification is rather limited. Stewart (1974) also successfully employed Py-GC to distinguish many 1973 model automotive finishes. Using a combination column comprised of 3 m x 3 mm, 15 percent Carbowax 20 M and 1 m x 3 mm, 10 percent DC-200, he successfully associated a variety of acrylic enamel finishes with paint suppliers. The effectiveness of this approach is amply demonstrated in Figure 1, which shows three pyrograms of blue automotive dispersion finishes used by three different manufacturers. All three finishes can be distinguished both by peak intensity and peak location. Unfortunately, this 1974 work was not further pursued in the published literature and now can only be cited as an example of the potential applicability of Py-GC to automobile model identification. Cardosi (1982) has updated the pyrolysis conditions used in conjunction with Stewart's combination column.

In carrying out a paint comparison the discrimination power of Py-GC is markedly linked to the GC stationary phase employed. Wheals and Noble (1972), after evaluating 22 phases for differentiating alkyd paints, concluded that a 4 m, 15 percent Carbowax 20 M was best suited for differentiating alkyd paints on the basis of pyrogram patterns. The major products in alkyd paint pyrograms are acrolein, methacrolein, allyl alcohol, benzene, and a complex mixture of saturated and unsaturated hydrocarbons. However, the ratio of acrolein to methacrolein in the pyrolysate mix seems to be the most important factor for discriminating alkyd paints (Wheals 1977; Fouweather *et al.* 1973). These two products are apparently produced by the pyrolytic breakdown of glycerol and pentaerythritol in the resin mixture. Fortunately, their ratio in pyrograms of alkyd paints displays very high levels of reproducibility. The ratio of other pyrolytic products are not as reproducible, for example, the acrolein/methacrolein peak ratios display coefficients of variation ranging from 3.5 to 7.0 percent, while acrolein/benzene ratios have coefficients of variation on the order of 40 percent (Wheals 1977). Wheals (1977) also compared the relative ability of Py-GC and emission spectroscopy to discriminate 20 white household paints. Py-

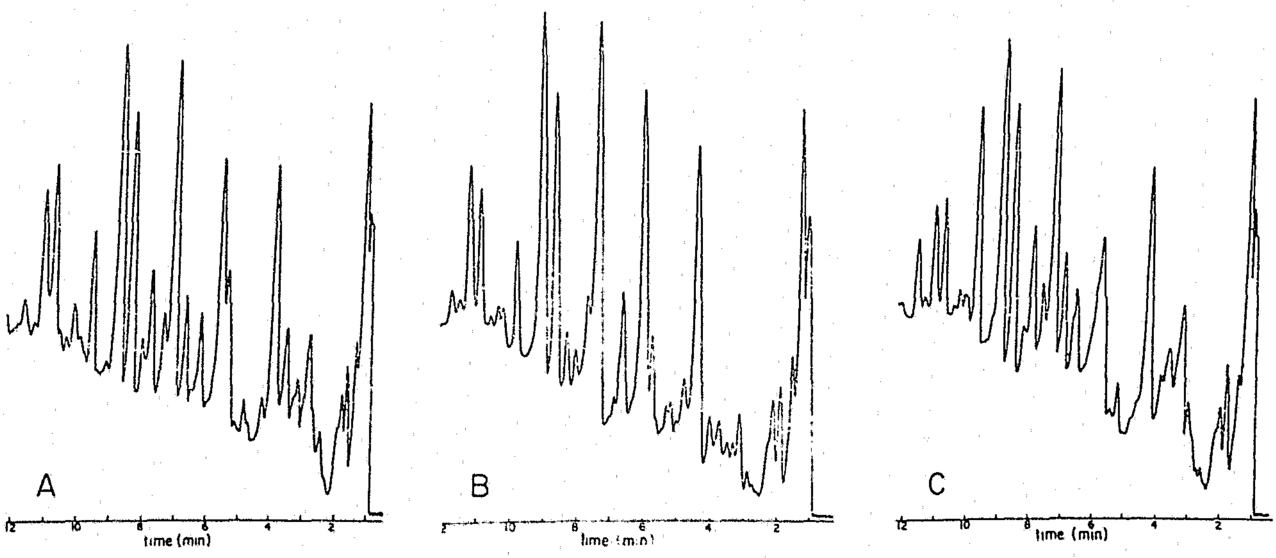

Figure 1. Comparison of similar blue metallic dispersion-type finishes, (a) Ford Motor Company, (b) Chrysler Corporation and (c) American Motors Corporation (Stewart 1974).

rolysis gas chromatography proved to be three times more effective for this purpose. Researchers at the Central Research Establishment in England have also investigated the discrimination power of a number of analytical methods, including Py-GC, for alkyd paints (May and Porter 1975). Eleven white, ten red and ten green paints were each divided into four distinct groups by Py-GC utilizing a Porapak Q column. However, in a follow-up study on the white paints, higher levels of discrimination were attained with both 4 m and 5 m, 15 percent Carbowax 20 M columns (Fouweather *et al.* 1973).

A number of investigators have used Porapak Q for discriminating automotive paints by Py-GC (Levy 1977; Gothard 1976; Ryland and Kopec 1979). Others have been critical of this column citing extremely long retention times (up to 1 hour) for common pyrolysate components (Fouweather *et al.* 1973; Dixon *et al.* 1981). In a study conducted at the New Jersey State Police Laboratory, a number of GC column packings, including Porapak Q, were evaluated to ascertain their relative effectiveness for discriminating a variety of household and automotive paints (A. Lane and N. Walsh, New Jersey State Police, personal communication). Utilizing a Chemical Data System Model 190 Pyroprobe (Chemical Data Systems, Inc., Oxford, PA), 71 white household paints of both the alkyd and acrylic types were compared by Py-GC. The columns studied achieved discrimination in the following order: 15 percent Carbowax 20 M > 10 percent SE-30 > Porapak Q. Further studies were conducted with automotive paint chips randomly sampled from 500 vehicles located in a local wreck yard. These paints were compared microscopically by color and layer structure, as well as by solvent tests and Py-GC. As shown in Table 1, an analytical scheme incorporating an SP-1000 (terephthalic acid ester of Carbowax 20 M) column provided the highest discrimination for the automotive paints.

The attainment of higher discrimination powers for paints and other related materials by Py-GC may ultimately depend on successes in gaining higher levels of GC resolution. In this regard, the potential contribution of capillary GC has not gone unnoticed by the forensic science community. De Forest (1969) viewed the approach of using a split sample injection into a capillary column as having the distinct disadvantage of requiring unrealistically large samples. Instead, he experimented with a cryogenically cooled capillary precolumn system which allowed a large volume of dilute pyrolysate to be concentrated on a precolumn prior to its chromatography. While De Forest's initial experiments with this approach were disappointing, he held out the hope that improvements could be made by eliminating excessive dead volume which he felt adversely affected GC resolution. Twibell *et al.* (1981) concerned with the significant reduction in sensitivity which accompanies a split injection system, designed a splitless inlet interface between a Curie Point pyrolyzer and a capillary GC column. Various samples were pyrolyzed at 610° C into a 50 m glass, wall-coated OV-101 column. Initial tests with low density polyethylene and nylon 6-10 gave well-resolved chromatograms. Pyrolysis of a white alkyd paint gave good resolution of all products except for phthalic anhydride. However, the authors were quick to point out that this deficiency was outweighed by the fact that phthalic anhydride would not normally elute at all from a packed column, thus denying the analyst an important piece of analytical information (Twibell *et al.* 1979).

Levy (personal communication) has reported obtaining highly resolved pyrograms of automotive paints with a 50 m, wall-coated OV-101 column at 100:1 split ratio. The required sample size was approximately 100 μg. Utilizing the conditions shown in Figure 2, three acrylic automotive paints, indistinguishable by color, were compared by capillary GC. The pyrograms of samples A and B were similar, but the pyrogram of C showed a significant difference in the relative height of two major

Table 1. MICROSCOPIC COMPARISON OF AUTOMOTIVE PAINT CHIPS

| Column | Column temperature | Pyrolysis temperature[a] | Pairs undiscriminated[b] |
|---|---|---|---|
| 2.5 m x 3 mm 10 percent SP-1000. | 60 to 160° C at 6° C/min | 550°C | 10 |
| 2.3 m x 3 mm 15 percent Carbowax 20 M. | 60 to 180° C at 10° C/min | 550° C | 11 |
| 2.0 m x 3 mm 15 percent Didecylphthalate. | 100° C | 770° C | 35 |

[a] Chemical Data Systems Pyroprobe 190

[b] Includes microscopic examination for color and layer structure as well as acetone and chloroform solvent tests.

peaks. Likewise, staff members at the Centre of Forensic Science in Toronto, Canada have equipped their pyrolysis capillary GC system with an injection splitter for the routine examination of automotive paints (Dixon *et al.* 1981). Their experiences with capillary GC have shown it to achieve sufficient baseline resolution and high reproducibility to make a quantitative comparison of pyrograms meaningful to the extent that paints of similar components could be differentiated. With packed columns such quantitative comparisons were judged to be difficult. The GC conditions employed were as follows:

| | |
|---|---|
| Column: | 25 m x 0.2 mm SP-2100 fused silica |
| Carrier: | He at 0.4 ml/min |
| Make-up gas: | He at 20 ml/min |
| Split ratio: | 275:1 |
| Inlet temperature: | 250° C |
| Detector temperature: | 300° C |
| Column Temperature: | 23° C for 3 min, 15° C/min to 240° C, hold for 5 min. |

Challinor (1983) interfaced a standard Curie Point pyrolyzer to the injection port of a capillary GC column using a hypodermic needle inserted through the port's injection septum. The pyrolysis products produced in the pyrolyzer were flushed into the inlet port of the GC by a flow of nitrogen carrier gas. Using select samples of alkyd and polyurethane paints the author showed improved discrimination with a capillary column over packed column chromatography. Peak height reproducibility with a capillary column was found to be generally comparable or superior to that obtained on Carbowax 20 M packed columns.

Audette and Percy (1978) have demonstrated the feasibility of first examining a paint chip by IR using a KBr pellet and then pyrolyzing the same pellet for GC analysis. This sequential IR/Py-GC approach offers the analyst distinctly different types of information on the same specimen with a minimum amount of sample (3 to 5 μg). Unfortunately, there is no evidence at this time to indicate that this approach is being given serious consideration by other forensic analysts.

### Fiber Evidence

When considering the applicability of Py-GC to synthetic fiber identification, one finds the forensic literature suprisingly sparce on the subject. There is ample evidence to demonstrate that Py-GC can adequately distinguish between various types of fibers - that is, polyesters, acrylics, nylons, cellulose acetates and so forth (Wheals and Noble 1972; Wheals 1977; Janiak and Damerau 1968; The Textile Institute 1975; Crighton 1972; Bortniak *et al.* 1971). However, the effectiveness of Py-GC as a technique for distinguishing the various members belonging to each fiber class is still a subject for investigation. Bortniak *et al.* (1971) examined 27 acrylics and 14 modacrylics by Py-GC. These fibers were classified into a total of 15 different groups of 12 acrylics and 3 modacrylics on the basis of pyrogram patterns. The authors also indicated that differentiation of various types of nylon fibers was feasible by Py-GC. Pyrograms readily distinguished nylon 66, 11, 610, 6 and Nomex.

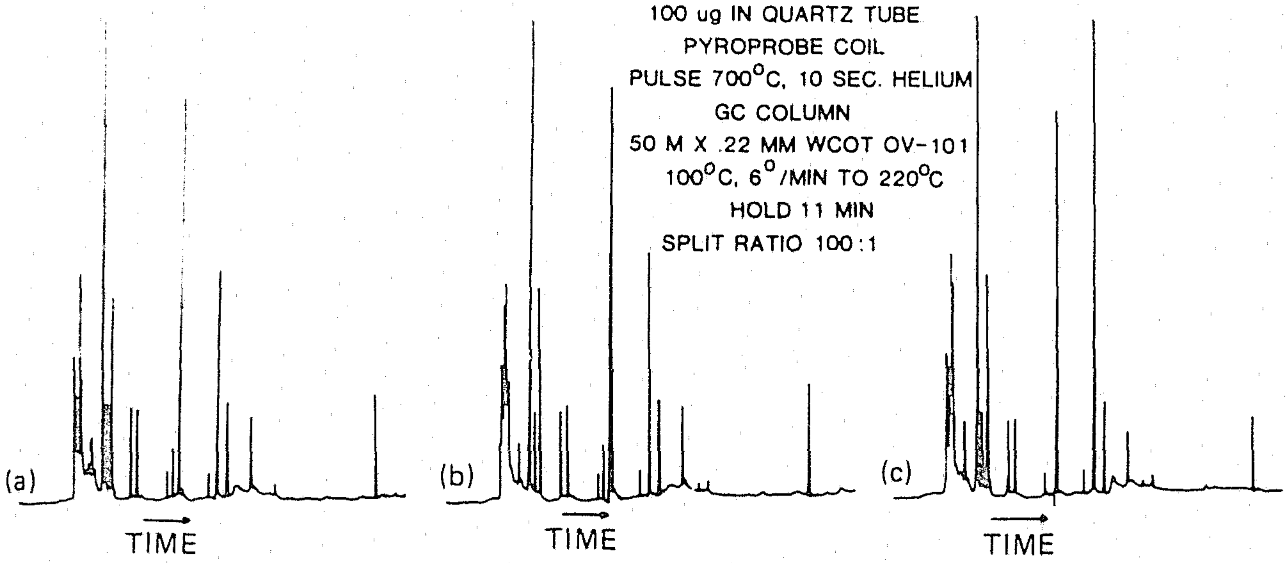

Figure 2. Pyrograms of three acrylic automotive paints (courtesy of E. J. Levy).

In a review of the subject, Wheals (1977) observed that the chromatographic system he normally used for paint analysis (15 percent Carbowax 20 M stainless steel column) was unsuitable for fibers because of the irreversible absorption of pyrolysis products. Use of short glass columns and a less reactive support material largely overcame this problem. The chromatographic system suggested was as follows:

| | |
|---|---|
| Column: | 183 cm x 6.3 mm o.d. glass packed column with 15 percent Carbowax 20 M on Gas Chrom Q (80/100 mesh). |
| Injector temperature: | 200° C |
| Detector temperature: | 220° C |
| Column temperature: | 70° C to 190° C at 20° C/min, then isothermally maintained for 20 min. |

Using those conditions it was possible to obtain useful pyrograms from less than 5 mm of single fiber. Furthermore, with the exception of the cellulose acetates and triacetates, various classes of fibers were distinguishable by Py-GC. Wheals nevertheless contended that Py-GC was "slightly less effective" than IR for discriminating fibers.

### Other Types of Trace Evidence

Beyond paint and fibers, Py-GC has been applied to the characterization of a number of different types of polymeric and biological materials frequently received by forensic science laboratories as criminal evidence. In one of the early publications relating to Py-GC, Nelson *et al.* (1962) demonstrated how various types of synthetic plastics could be readily identified and differentiated by Py-GC. Further evidence of the applicability of Py-GC for plastic identification in forensic situations was offered by Wheals and Noble (1972). May *et al.* (1977) published a pyrogram library of various plastics using a Porapak Q column. Home *et al.* (1980) applied Py-GC to the characterization of motor vehicle body fillers utilizing a 15 percent Carbowax 20 M GC column. The discrimination power of Py-GC for body fillers was estimated to be 0.83. A computer-based system was developed for comparison of the pyrograms and the authors suggested that a similar approach could be used for the evaluation of pyrograms from a wide variety of other materials.

The utility of Py-GC for the characterization of adhesives has been described by Wheals and Noble (1972) and Noble *et al.* (1974). Tests examined 179 different adhesives by both Py-GC (using a 4 m, 15 percent Carbowax 20 M column) and IR. The combination of techniques enabled each of the adhesives to be distinguished. Even those adhesives belonging to the same chemical class exhibited sufficient differences in their pyrograms and/or IR spectra to be differentiated (Noble *et al.* 1974). Blackledge (1981) used Py-GC to compare a rubber bumper guard removed from a suspect car to one recovered at a hit-and-run scene. Prior to the pyrolysis procedure, the rubber materials were first heated by the injection port of the GC to produce a chromatogram of the rubber's volatile components. This approach, also reported by Chih-An Hu (1977;1981), has the potential of further differentiating similarly constituted polymer materials. Another interesting forensic application of Py-GC was reported by Lloyd and Roberts (1973). They used Py-GC to narrow the origin of cooking fat extracted from the stomach contents of a murder victim. The fats were first hydrolyzed and then characterized by their oleate/palmitate peak height ratios. Another homicide provided the opportunity to apply Py-GC in a rather unique fashion. Pyrograms were successfully used to compare chewing gums found on the throat of a deceased child to gum recovered from material found at the site where the murder was thought to have been committed and to gum found on the suspect (Lloyd *et al.* 1974).

Newlon and Booker (1979) studied the identification and characterization of smokeless powders by Py-GC. A 1.8 m, 0.4 percent Carbowax 1500 on 60/80 mesh Carbopak A column was used to examine 40 different powders. The pyrogram resulting from each powder was distinguished from the others. Furthermore, a comparison of the chromatograms of partially burned powder granules to those of unaltered powdered granules from the same lot showed no detectable changes in their chromatographic patterns.

A Py-GC method has been reported for the differentiation of adult and fetal bloodstains (Clausen and Rowe 1980). This distinction is based on the peak height ratio of two long retention time peaks. A 3.5 percent Carbowax 20 M column was used to separate the pyrolysates. In a blind-coded study, adult and fetal bloodstains were identified with 100 percent accuracy by the Py-GC technique. The application of Py-GC for the analysis of hair has also been investigated (De Forest and Kirk 1973; Porter and Fouweather 1975). However, the results are not promising. The pyrograms of all individuals studied were essentially identical and any small differences detected between individuals were within the normal range of variation expected of hairs.

## PYROLYSIS MASS SPECTROMETRY

The combination of pyrolysis and mass spectrometry (Py-MS) is a logical extension of current efforts at applying pyrolysis to the characterization of forensic evidence. The idea of linking a pyrolyzer directly to a mass spectrometer is neither new nor novel. This approach has been successfully applied to the characterization of mircroorganisms and polymers (Risby and Yergey 1978; Windig *et al.* 1982; Franklin 1979; Shimizu and Munson 1979). The appeal of Py-MS to forensic scientists rests with its ability to generate data that can be stored, manipulated and retrieved by a computer. Furthermore, determinations performed by Py-MS are rapid; they can be performed in less than 5 minutes, a significant reduction in analysis time when compared to Py-GC.

The application of Py-MS to forensic problems in a meaningful and practical manner is still not a reality. Whether Py-MS actually represents an improvement over Py-GC in terms of reproducibility and discrimination are key questions yet to be fully addressed. How best to interface the pyrolyzer to the mass spectrometer and the type of ionization techniques best applied, that is, electron impact (EI) or chemical ionization (CI), are other issues still ripe for exploration. Hickman and Jane (1979) have published a detailed comparison of the effectiveness of interfacing three different types of pyrolyzers to a mass spectrometer. An empty GC column served to link either a Curie Point pyrolyzer or a resistively heated coil filament type pyrolyzer (Chemical Data Systems Pyroprobe) to the spectrometer's source. Also, a direct insertion probe was modified to deliver pyrolysates directly into the spectrometer's ionization chamber. In each case, an EI ionization source was employed. Typical mass pyrograms for acrylic paint and alkyd paint samples on the three Py-MS systems are given in Figures 3 and 4. Of particular interest to these investigators was the reproducibility of the spectra generated by the paint samples. In general, better short-term and long-term spectra reproducibility were obtained with acrylic paint than with alkyd paint. The latter gave a more complex mass pyrogram than did the acrylic paint. Additionally, it was observed that some ions in the alkyd paint spectra were formed more reproducibily than others. In particular, ions associated with benzene, phthalic anhydride and benzoic acid showed poor reproducibility. Overall, the best experimental results with respect to reproducibility were obtained with either the Chemical Data Systems Pyroprobe connected to the source via a glass column or with a direct insertion probe.

As a result of work carried out at the Metropolitan Police Laboratory, London, England, it was noted that optimum discrimination of alkyd paints by Py-MS was attained by comparing only those mass pyrogram ions displaying the largest variations between samples (Wheals 1981). If one was to give equal weight to each ion in the mass pyrogram, differences in significant ions would tend to be submerged in the detail accumulated from all the ions present in the spectrum and would result in a lower discrimination power for the technique. A careful study of alkyd paint mass pyrograms reduced the most discriminatory and reproducible ions to the following:

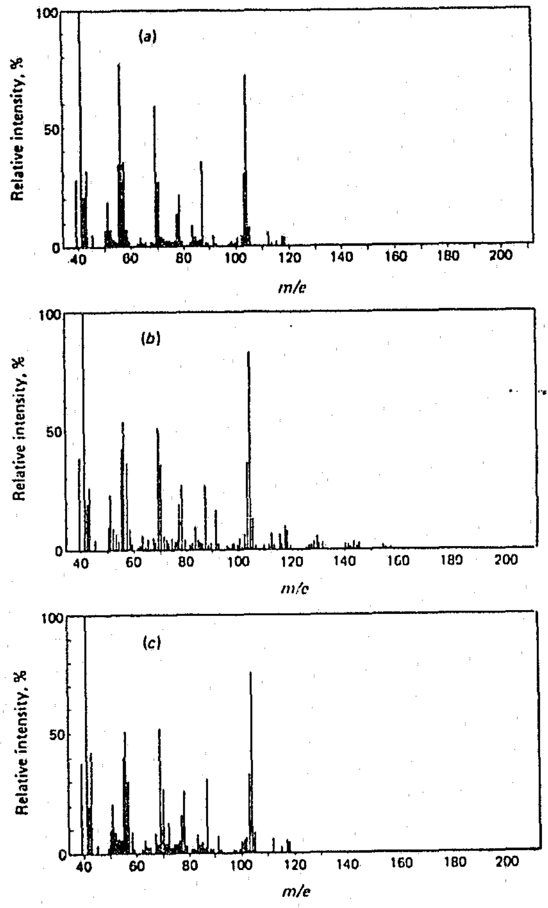

Figure 3. Mass pyrograms for yellow acrylic paint, (a) Curie Point pyrolysis into an empty glass gas chromatography column, (b) Chemical Data Systems Pyrobrobe into a glass column and (c) direct insertion pyrolysis probe. (Hickman and Jane 1979).

| *m/z* | *Derived from* |
|---|---|
| 174 | Toluene diisocyanate |
| 118 | Vinyl toluene |
| 105 | Benzoic acid |
| 104 | Phthalic anhydride |
| 77 | Unknown |

Using these five ions for discrimination, a blind trial involving eight paints was conducted. All eight paints were correctly matched with their corresponding control. However, the differences between pyrograms for some of the samples examined were not great. It would appear to be likely

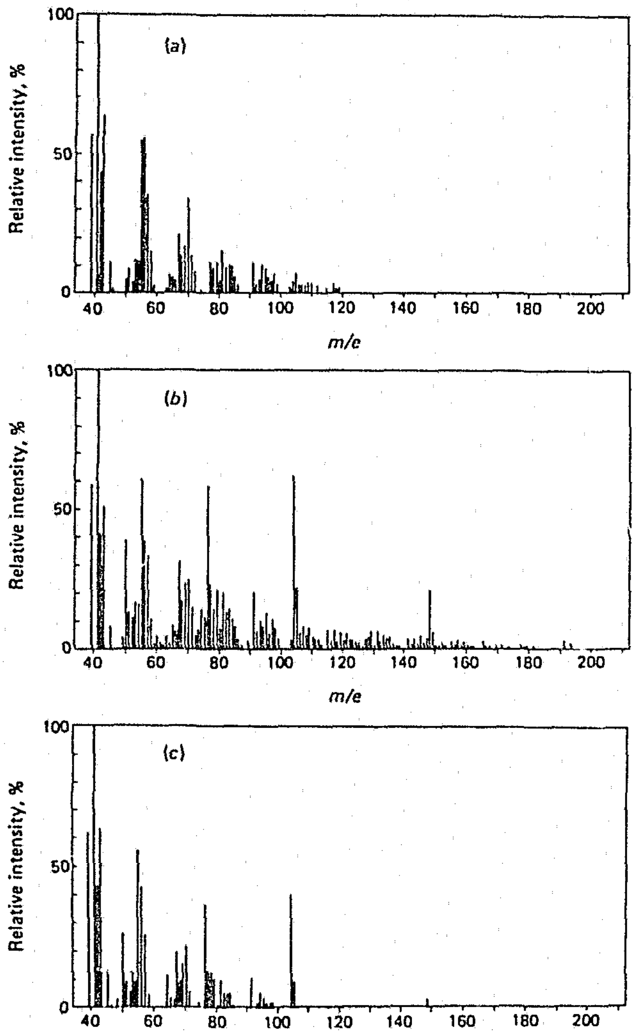

Figure 4. Mass pyrograms for white alkyd paint, (a) Curie Point pyrolysis into an empty glass column, (b) Chemical Data Systems Pyroprobe into a glass column and (c) direct insertion pyrolysis probe. (Hickman and Jane 1979).

that a much lower level of success in discrimination would be achieved if samples were compared against control data that had been acquired many months before. Various natural and synthetic fibers were also examined by Py-MS in studies conducted by Hughes *et al.* (1977; 1978). The discrimination power of Py-MS varied with the fiber class; however, in general, IR was found to be superior to Py-MS for discriminating synthetic fibers. Nevertheless, in a blind trial conducted mainly with nylon fibers, Py-MS identified every fiber correctly; whereas, IR analysis led to only two correct assignments (Hickman and Jane 1979). Interestingly, in a later publication, Wheals (1981) suggested that by adopting the same selective ion approach previously described above for comparing alkyd paints, one may be able to improve the discrimination power of Py-MS for synthetic fibers.

The feasibility of characterizing pyrolysates by CI mass spectrometry has also been explored. The CI process basically involves the reaction in the ion source of a mass spectrometer of an ionized reagent gas with sample molecules. The major advantage of this approach is the ability it gives the examiner to control the complexity of the spectrum's fragmentation pattern. For example, when isobutane reagent gas is ionized by 70 eV electrons, its principal product is the tert-butyl ion. Another useful reagent gas is methane. The major ions generated from methane's ionization are $CH_5^+$ and $C_2H_5^+$. These ions can readily transfer a proton to a sample molecule. Such a reaction creates an $MH^+$ ion which will either be stable or will further decompose into fragment ions. The amount of energy imparted to the $MH^+$ ion is directly proportional to the exothermicity of the proton-transfer reaction. Since $t\text{-}C_4H_9^+$ is lower in acid strength than either $CH_5^+$ or $C_2H_5^+$ it is to be expected that $MH^+$ ions generated in isobutane would be more stable than those formed in methane. As a result, pyrolysis conducted in an isobutane CI source should yield a simpler spectrum when compared to methane CI.

Saferstein and Manura (1977) have utilized a CI source for analyzing the pyrolysates of various paints and fibers. The pyrolysates were first passed into an evacuated sample chamber before they were allowed to enter isobutane CI source. A simple fragmentation ion pattern was formed in which a large number of the ions created were associated with the expected thermal degradation products of the polymers examined. Importantly, the resultant mass spectra were used to discriminate a number of acrylic paints as well as acrylic fibers.

## SUMMARY

For sound and logical reasons Py-GC has taken its place alongside other analytical techniques as a vital tool of the forensic scientist. Few analytical methods possess its combination of attributes: cost-effectiveness, sensitivity in the microgram range, reproducibility and facility for revealing subtle differences in the compositional character of polymers. On the other hand, the appearance of a pyrogram will depend on the composition, construction and condition of the GC column. Unfortunately, these factors combine to make interlaboratory and long-term comparisons of materials by Py-GC an uncertain excerise at best, thus restricting Py-GC's forensic utility to short-term intralaboratory comparisons. Furthermore, the failure of the forensic science community to develop uniform chromatographic and pyrolysis parameters has hampered efforts at formulating and implementing quality control standards. This situation has discouraged the creation of pyrogram libraries which could be useful for characterizing and identifying polymeric physical evidence. However, as discussed in the Pyrolysis Gas Chromatography section, round robin tests and standardization methods, such as the "molecular thermometer" should aid those in the Py-GC field to meet these needs. Having the discrimination of evidence as their primary objective, forensic scientists are certain to pay greater heed to the enhanced resolution power afforded by capillary GC. The concept of linking a pyrolysis unit to a capillary column has yet to be the subject of intense investigation by forensic scientists, although limited research has shown that this combination affords added success to the Py-GC process. Also worthy of continued investigation is the combination of pyrolysis and MS. Pyrolysis mass spectrometry when utilized with computerized data-handling facilities promises to significantly reduce analysis time and provide for a means of collecting, storing and diseminating pyrolysis data.

The content of this paper attests to the vitality of analytical pyrolysis in forensic science. Its future looks equally as bright, as forensic scientists seek to capitalize on new facets of pyrolysis technology to further refine the chemical characterization of criminal evidence.

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## DISCUSSION

*King:* When you were doing your solid probe mass spectrometer analysis on paints and polymers, did you perceive this as being a quick enough method enabling you to use it on a routine basis or is cleanup time excessive if this method is done on a routine basis?

*Saferstein:* We have abandoned this approach, mainly because we did not have the equipment to follow through on the initial work that we had performed. Our unit is not interfaced to a computer and it was not feasible for us to continue on, at least with the work that we performed.

However, it is my understanding, based on discussions with Brian Wheals and my reading publications of the Metropolitan Police Forensic Science Laboratory that they are routinely utilizing this approach in examining synthetic polymers. It is very feasible. I am sure Brian Wheals will be talking about this technology in his talk during this symposium.

*Tracy:* Several years ago I had the opportunity to attend a school on capillary GC. In that class, we discussed the reversal of peaks and the instructor was of the opinion that peak reversal was not uncommon and should not be given that much priority as to discrimination of one or the other. My personal experience has been that when you run the same sample you can get the peak reversal, depending on the size of the sample you inject. I am not disagreeing with you; I just wanted to point that out.

*Saferstein:* I would tend to agree with you. I certainly would not want to say that two pyrograms are different based on one peak reversal, peak reversal between one pair of peaks. What I was attempting to illustrate, however, was the fact that apparently that type of situation is more reliable when one is dealing with capillary GC as opposed to packed column GC. One can assign more weight to peak reversal obtained on a capillary column as opposed to a packed column.

*King:* I have also seen that reversals usually come with two peaks that are very close together or maybe on a shoulder. You get peaks that are separated by several centimeters in reverse, then they are more distinguishable there.

*Kubic:* Apparently you have done a considerable amount of work with both SP-1000 capillary columns and Carbowax 20 M. Would you comment on the stability of SP-1000 as compared to Carbowax 20 M. Even though it appears that the 20 M will give you a little better discrimination, would you also comment on which one you would rather use as far as stability is concerned?

*Saferstein:* Most of our work with one exception, has been done with packed column, not capillary column SP-1000 versus Carbowax 20 M. One of the reasons that we began to look at SP-1000 was that we felt the 20 M column was somewhat unstable at the higher temperatures. When we were temperature programming we would get it up to about the 160, 170, or 180 range and then the baseline would start to climb rapidly.

We did not find this to be the case when we used the SP-1000. When we looked at the discrimination power of the SP-1000 versus the 20 M, we found that the SP-1000 was slightly superior to the 20 M. So that was a bonus. Our original inclination was to use the SP-1000 because it seemed to provide a steadier baseline at the higher temperatures.

*Kubic:* Besides baseline, would you comment on what your experience has been on long-term stability of the column. How long could you use it before you had to discard the column and restandardize, etc.?

*Saferstein:* I think that is a difficult question to answer because a lot depends on usage. Quite honestly, our columns could perhaps stand for 1, 2 or 3 weeks without being used. Perhaps no cases would come in that would relate to that type of application.

But quite honestly, for the most part, our SP-1000 columns last quite a long time, I would say at least a year, if not longer.

*Kee:* What do you think are the main reasons for the lack of long-term reproducibility? What factors are really at the heart of this lack of long-term reproducibility?

*Saferstein:* I would suggest that one can achieve long-term reproducibility if one was working with a single gas chromatograph, a single system in a single laboratory.

The problem is that you probably would not accomplish much as far as the forensic science community is concerned. If we are to begin to think in terms of generating pyrogram libraries for domestic distribution and even for international distribution, we need to get everybody on line; laboratories in California, New York, New Jersey and North Carolina should all run in the same fashion, and generate the same data over a prolonged period of time.

The fact of the matter is that based on the data I have shown you, the crime laboratories in this country cannot even agree on the type of columns that are best utilized for Py-GC. In fact, some of us now are probably thinking about using capillary GC, while others are not prepared to make that jump. That further complicates the situation. In terms of long-term reproducibility within one laboratory using one particular GC, I think that is achievable with some effort. So I am a little more concerned about pulling all the crime laboratories together.

*Kee:* We are dealing with investigating the production of radicals and should we not be thinking in terms, as it were, of clamping down and stabilizing the conditions?

*Saferstein:* We can think along these lines. I tend to be a little more practical. I think at this point I would rather take the time and effort that would be involved in generating a national library of plastics and paint, and invest that time and effort into generating infrared spectra and distributing that type of information.

I think perhaps a long-term effort will maybe pay off with respect to coming up with a reproducible pyrogram or pyrolysis system. But I think that is a long way off and I do not think the forensic community at this time has the resources to make that sort of a commitment.

We all recognize the need for generating standard libraries with respect to plastics and paints for identification purposes, so let us focus on infrared technology.

*Wheals:* I would like to follow up the last question with a point on long-term reproducibility.

We at the Metropolitan Police Forensic Science Laboratory have been involved in part of this technique since the mid-60s and by the mid-70s we were convinced the major reason for the lack of long-term reproducibility lay almost exclusively in the chromatographic stage of the process.

The more I have worked in this area, the more I have become convinced that this is true because of the nature of the pyrolysis products that are being produced. If one takes alkyd paints as an example, on the Carbowax 20 M systems, which is one of the best GC systems that we have come up with, one finds that things like benzoic acid and phathalic anhydride, which are major pyrolysis products, do not even elute from the column.

This must mean that these things are building up on the columns so there is constant chemical change taking place on the chromatographic column. Given that this is the situation, there does not seem to be any way to get around it. This is really our reason for moving away from the chromatographic stage and over to a direct mass spectrometry approach.

I would add that the use of quartz capillary columns have changed the situation considerably in that you can now elute from these columns quite polar materials, including the anhydrides, the acids and so on. But even those we found showed slight chromatographic variation with time. So it seems to me that the chromatography rather than the pyrolysis is the underlying weakness of all these pyrolysis methods.

*Haroldson:* What do you believe are the chances for the realization of a pyrogram library across the United States, and are you now trying to pursue this endeavor?

*Saferstein:* I do not believe that is a practical goal at this point. I believe that the diversity which exists at the present time within the United States forensic science community would not allow for the creation of pyrogram libraries that would be utilized by the vast majority of crime laboratories. For that reason, I would like to see us move in the direction of generating infrared libraries for those types of problems.

On the other hand, I do want to emphasize that I feel very strongly about utilizing pyrolysis for short-term comparisons. I think that is an excellent technique. It is superior, in my opinion, to infrared, particularly when you are dealing with paints.

*Morgan:* With regard to long-term and short-term reproducibility, I think the problem in my experience has been that it is not only a combination of chromatographic and pyrolysis variables, but other things as well, for example, sample preparation.

With regard to the statement about flexible fused silica columns, we have been using cross-link stationary phases with flexible fused silica columns for over a year and a half, coated with cross-linked SE-54 and cross-linked OV-1701. We found these columns to be very stable and resistant to change.

One thing that is necessary is to apply a little common sense in terms of quality control and to continually monitor the performance of chromatographic columns in use with a test sample. For example, a polarity test sample to continually check for column activity because these columns will change.

The advantage of a cross-link stationary phase is that when you detect a column change you can often either, particularly with a fused silica column, just break off the end of the column or, in fact, rinse the column, which is coated inside with a polymer, to clear up contamination problems.

With regard to sample preparation, we have often found that simple variations in sample preparation can make dramatic differences in pyrograms. Different ways of treating the pyroprobe to clean it, for example, to change the activity of the probe itself and change a pyrolysate distribution.

The sample matrix itself can have a dramatic effect on the pyrogram even though you have the same basic substance that you are looking at in the sample. The background that the sample exists in can have a tremendous effect.

Of course, all these variables need to be standardized and controlled to achieve reproducibility.

*Levy:* We have been involved through the American Society of Testing Materials (ASTM) on an inter-laboratory standardization round robin program for standardizing pyrolysis GC results. This has gone on for a period of years.

The sequence is as follows: the first step that was needed was simply to tune the gas chromatograph. This meant sending out a number of compounds and making sure that everyone injecting these compounds could get the same gas chromatogram.

Once one got that, and that took quite a while to get, the next step was to tune the pyrolyzer, and again, tune it with a standard material, a material that was very sensitive to changes in pyrolysis condition.

Once one had tuned both, then there was a chance for improvement in reproducibility. The limitation when one has tuned both of these, is the data interpretation. With packed columns the peaks add to one another when there is not complete separation of the peaks, so reproducibility is not as good as it should be.

With capillary columns, this problem was mitigated because in many cases you had almost baseline resolution and it is possible, with test samples, to get reproducibility with Py-GC to a quarter and half, a percent relative deviation, which offers some hope that a library is possible.

The frustration of trying to establish a library, particularly in the forensic field, is that there are working laboratories that have independently selected their columns and generally will not change from these.

But in the general field of Py-GC, under ASTM, it is possible to recommend a column. There will be a fifth round robin that all of you are invited to participate in, and generally the feeling is now that it should be done with the capillary column which has the best chance of higher reproducibility and I suspect after the fith, there will be a sixth with a packaged data interpretation - a standard canned package.

When those two standard reproducibility round robin samples are run, then I think we perhaps can take another look at whether it is feasible.

# FUTURE TRENDS IN GENERAL MOTORS' FINISHES

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The automotive industry is an extremely competitive worldwide arena. As a result, it thrives on change -- continually working on new models, shaping different styles, introducing new features and developing products with improved performance. Design objectives may address safety, environmental and efficiency issues, or just generate excitement and appeal. Of course, these efforts are motivated by the desire to offer the customer greater variety and value at a price that will generate prosperity for the company. All of this must be accomplished while obtaining better fuel economy, reducing emissions and providing a safer vehicle. Overall, we must satisfy an increasingly more sophisticated and value-conscious consumer.

Just as these factors have led to many improvements in cars and trucks over the past years, they continue to have a strong influence on trends in the technology of the finishes used on these vehicles. While in the past, changes in paint systems have been implemented according to development and maturing of new research and technology, we are now pushing the technology to accomplish specific objectives in a prescribed time frame. This concentrated effort is driven by the desire to remain competitive on a worldwide basis for finishing quality and cost while meeting government regulations for reducing solvent emissions from painting processes.

## PAINT TECHNOLOGY DIRECTION

Thus, at General Motors (GM), we are presently in the process of making extensive changes in paint materials, equipment and facilities; in fact, revolutionizing the way we paint vehicles. In 1980, we decided that the best way to meet all of the objectives was to adopt the following finishing concepts for future direction:

1. Electrodeposition primer on the entire metal body.
2. High solids primer-surfacer where required on exterior surfaces.
3. Use of anti-chip coatings in severe stone-damage areas.
4. High solids thermoset enamel topcoat colors utilizing the Basecoat/Clearcoat concept.

This decision was based on evidence that our paint and equipment suppliers were making satisfactory progress on development of new technology for these paint materials along with effective equipment and processes for applying them to automotive products. In most cases, these changes require extensive revisions in the painting facilities or complete new paint shops.

## PRIMERS

We are already well underway with these conversions. Virtually all of our assembly plants now have the cathodic type electrodeposition primer. The entire body and some of the attached parts are immersed in a tank of this water-based material for at least 2 minutes to cover all surfaces inside and out. This provides an excellent base for the paint system and overall protection against corrosion and chipping. Chemistry modifications of this primer are being introduced that produce increased film thickness on the exterior body surfaces. This improves quality while affording the possibility of reducing or eliminating the subsequent coats of primer-surfacer on the exterior. We expect this general pattern to continue. The color of these electrodeposition primers range from black to light gray.

For those situations requiring the use of a second primer or primer-surfacer, we will continue in the direction of high-solids type materials. The chemical composition and color will vary depending on how the paint is to be formulated to meet cost and quality goals.

## TOPCOATS

The topcoat finishes are undergoing the most radical changes as we move toward high solids thermoset enamel technology, with Basecoat/Clearcoat colors. For the most part, these changes are planned to coincide with the introduction of new model vehicles because of the extended downtime required to accomplish major modifications in the facilities. This particularly is the case with the passenger car systems, most of which have been using lacquers that require somewhat different processing for application, baking and repair. Acrylic lacquers will continue to be used until replaced by the new paint systems.

Since our paint specifications are primarily oriented to performance objectives rather than composition, the suppliers may utilize somewhat different resin chemistries and additives in formulating products to meet our requirements. We have specified that, for our vehicles that are designed with flexible fascia parts, the basecoat should have sufficient flexibility so that it can be used on the fascia as well as on the rigid body components. Urethane, polyester and acrylic basecoats are available. Even though different clearcoats are used because of the flexibility requirements, use of the common basecoat color provides the best color match for those parts with critical appearance match-ups.

Of course, the ultimate system would be a common basecoat and clearcoat, which could be considered a "universal" system. Materials based on urethane chemistry appear to hold the greatest opportunity of meeting the required appearance, flexibility and durability properties for use on all body components, both rigid and flexible. In addition, urethanes offer low temperature cure potential, which lends itself to use on a variety of plastic substrates. We already have candidate materials in for laboratory testing. Operator work environment protection is part and parcel of moving in this direction. Fully automatic paint application using sophisticated turbine wheel dispensing devices, rather than spray guns mounted on machines, will open up new ground for exploration in the decade ahead.

Development work continues on other topcoat technologies that may hold promise for future use, particularly a waterborne basecoat with a high solids clearcoat now under study which seems to have a number of interesting properties. Another new technology being explored involves a paint stream treated with amine gas that causes the paint to cure almost instantly. New ideas and combinations continue to emerge from paint research efforts throughout the world, so we can expect continuing changes in the chemistry of GM paint systems.

## SUBSTRATES

With vehicles ranging from sleek sports cars to family sedans, utility vehicles and luxury cars, GM body designs include a considerable variety of materials. We can expect to see increasing use of different types of plastic parts and coated steels in selected areas of the body, for reasons of corrosion, design flexibility and weight savings. The coated steels include one-side and two-side galvanized and Zincrometal.

Plastic parts may be divided into two categories -- flexible and rigid. Flexible fascia front and rear panels are primarily made of urethane Reaction Injection Molded (RIM) with or without fiberglass reinforcement; thermoplastic urethane (TPU) and polyolefins (TPO) are also used. Chemistry modifications and other types of flexible materials are continually under study and development for specific situations. For these applications, we use flexible primers and topcoats.

In the last 2 years, there has been increasing use of semi-rigid parts made of reinforced RIM or polycarbonate/acrylonitrile - butadiene - stryene (ABS) blends. A new competitor in this area is amorphous nylon, which is expected to be used in a production application later this year.

Although polyesters (SMC or BMC) are used for the majority of rigid type plastic panels (such as header panels, extensions, hoods, tailgates, etc.), there are parts in current use or under study involving polycarbonate, nylon, polyethers and blends of materials. Many of these plastic materials require specific types of primer formulations to provide the required adhesion and appearance of the paint system.

## CONCLUSIONS

As mentioned previously, GM uses several different paint suppliers who develop their own unique formulations to meet our product and process requirements. In a given assembly plant, we generally use most of the paint material from one supplier. There are occasions where suppliers cross-license specific paint materials for business or economic reasons. These patterns affect the chemical distinction between the various models and producing plants. In many cases the differences are so small that sophisticated analytical equipment is required to distinguish between them.

Overall, it is apparent that GM paint systems will continue to show some situations where distinct chemical differences can be identified by laboratory analysis, while in other cases, distinguishing identification may be difficult. In spite of GM's decision to convert to enamel topcoats, common basecoats and similar technologies, unique chemical characteristics remain that will provide a basis for identification with appropriate analytical techniques.

Varied usage of different substrate materials -- both coated steels and plastic parts -- will provide additional distinguishing compositions on individual car models. We will continue to provide to the FBI the technical information necessary for use by forensic scientists and laboratory examiners in identifying GM cars from analysis of the paint films.

## DISCUSSION

*King:* In regards to plastic pin striping, plastic decals, Firebird emblems, etc., what are they comprised of and how are they applied?

*Praschan:* The various divisions of the corporation specify some of those things themselves, and some of it is specified by the Fisher Body engineers. I am sure that the information is available. I know a lot of them are supplied by the 3M Company, for example. Most are adhesive applied. In some cases, special preparation on the part of the paint surface is necessary before application, either heating, special treatment and/or cleaning.

One has to look at each individual case. One should not assume that a Firebird emblem and a Camaro emblem necessarily have the same composition. They may be altogether different.

*Corby:* So in effect, what you are saying is that if you have one of these, it may be only one or two of its kind out there provided for a certain application.

*Praschan:* No, I mean that, for example, for the Chevrolet Z-28 emblem within a given model year, a particular type of emblem, probably from the same manufacturer would be applied in the same way. But a similar emblem on a different model, for example, a Pontiac Firebird, would not necessarily be the same type of emblem at all.

*Ryland:* Would you elaborate on where we might expect to see sandings stria on paint chips that we recover off of a vehicle that has original finish on it, that is, sandings stria on the bottom of the primers. Where is the sheet metal sanded, and is sanding done in repair refinishing?

*Praschan:* Repair may occur during the in-line repair step, where before it leaves the paint shop it has an opportunity for sanding and repair of defect. How that is handled may differ from one facility to another, but the point is that before it gets the final bake there is an opportunity for an in-line repair. In some cases that repair could go all the way through to the bare metal. In fact, in that local area you might be destroying a small area where the zinc phosphate would be applied on the metal surface. There is really no opportunity to reapply that zinc phosphate coating so you have to build in some protection through the repair primer in those cases where you have gone all the way through.

I wonder if maybe what you are seeing in some instances is that type of situation. It would generally be very local in nature. For example, you would not see that type of situation on an entire hood, but you might see a spot where they have sanded through. No zinc phosphate is present. You would see the sanding perhaps, on the back side of the primer film. And the primer used in that case would be different from the electrodeposition primer on the major portion of the vehicle.

Then, of course, the other opportunity for that would be the final line repair, which is a low-bake system. Again, the opportunity to sand through to the bare metal exists. We do not like to do this but when we do we generally confine that to very small areas. Again, the primer would be different and the topcoat, in a typical case, would be either laquer or a catalyzed version of the basic topcoat enamel, depending on the original paint.

*Burr:* The rigid plastic parts are each of a different type of plastic. In regards to the difference in the specific primer required, will it show up in the color or will it be strictly a chemical formula difference?

*Praschan:* It could show up in the color but not necessarily. I think the major distinction would be the chemistry of the product because where possible, we like to use the same color primers on a given vehicle. In fact, in the case of the Pontiac Fiero, we apply a coat of the same primer over all of those parts before the color coat is applied.

The incoming parts may have different color primers on them. They come in from the source with a primer already applied. The primer may be light grey on one part and a little darker on the other, this being rather coincidental.

The main thing that we like to see, if at all possible, is at the time we are putting the color on, we would like to have the same primer color over the entire vehicle. So for that, as well as other quality reasons, we do apply, in the case of the Pontiac Fiero, a uniforming primer over the entire vehicle before color.

# FUNDAMENTALS OF THE POLYMER CHEMISTRY OF ACRYLICS AND VINYLS

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## BACKGROUND AND DEFINITIONS

Polymers and polymeric materials are becoming increasingly important in modern society. Traditional common applications include coatings, paint, elastomers, films, wrapping material, clothing and foam rubber. New uses are so widespread that a listing would continue for pages. An illustration of how polymers can be used for both positive and negative change is in the area of bulletproof vests. The advent of aramids provided police officers with lightweight and high-performance vests. DuPont's star in this field is Kevlar® (E.I. duPont de Nemours & Co., Inc., Wilmington, DE), a material so strong and lightweight that the routine wearing of protective vests was feasible for the first time. Unfortunately, the "problem" of impenetrability of these vests was soon solved, again with the use of polymers. Specifically, it was discovered that bullets which had been coated with Teflon® (duPont) (polytetrafluoroethylene) would penetrate the new vests easily. Thus, while polymers provided the answer to a long standing problem, they also provided a way of circumventing this answer.

My task in this paper is to provide a short summary of the chemistry of typical polymers. Emphasis will be on acrylics and vinyl polymers, mainly because of their application in so many areas that impact forensic science. Automotive uses include coatings, signal light covers, car body parts, panels, bumpers, safety glass and interiors. Other areas impacted include tapes, sealants, textiles, fibers, superglue, household appliance casings and a host of thin-film materials. I will not discuss the natural polymers nor the extensive field including insoluble, step-growth polymers, although these are also increasing dramatically in importance.

Let us first review some basic concepts and definitions regarding polymers. The fundamental property of any polymer that gives it its unique properties is high molecular weight (MW). This is manifest mainly as length; that is, polymers are enormously greater in one dimension than in the other two. For example, a typical molecule of polyethylene may have a MW of 560,000 daltons. This corresponds to 40,000 $CH_2$ repeat units. If we imagine that each of these small units is 1 cm in length and diameter, this typical polymer chain would have a length of 1/2 km. This would correspond to a bicycle chain five football fields long. Of course, like a bicycle chain, polymers tend to be highly coiled and entangled in an unstreched state. If one imagines a football stadium filled with bicycles chains of this typical length that had been haphazardly thrown in, the amount of interaction and entanglement of the ensemble is easily visualized.

A further example of the change in properties of a molecule with increasing length is presented by the homologous series of alkanes. Methane with one carbon is a gas. Hexane has six carbons and is a free-flowing liquid and commonly used solvent. Petroleum jelly possesses approximately 20 carbon atoms in a linear arrangement and has a viscous, gelled consistency. Wax has still longer carbon chains with about 25 to 30 $CH_2$'s in a linear arrangement. Carrying the series one step further, typical polyethylene possesses approximately 40,000 of the same methylene groups in a reasonably linear chain. Despite similar chemical composition, it is clear that increasing the number of repeat units can drastically modify properties.

The basic driving force for polymer formation is illustrated in Table 1. Conversion of ethylene to polyethylene involves repetitive chain growth of long molecules with the same structural repeat unit over and over. This conversion of $sp^2$ carbons to $sp^3$ species takes place through a fundamental electronic reorganization. The chemical bond strengths for the monomer and polymer are calculated for ethylene as 163 kcal/M versus 176 kcal/M, or an overall change in the bond strength of approximately 13 kcal/M. The entropy of the polymerization must also be considered, however, and is normally not favored by polymer formation. The two competing forces of enthalpy and entropy are balanced in favor of polymer formation at normal temperatures. High temperature can, however, increase the importance of the entropy term and drive the polymerization back towards monomer. This is the reason many polymers depolymerize at high temperatures. Both styrene and polymethyl methacrylate (PMMA) will thermally degrade back to monomer with high efficiency. Other polymers, of course, may degrade through mechanisms other than depolymerization, and the range of products observed can provide a basis for characterization and identification. This is the reason for such widespread use currently of pyrolysis-gas chromatography-mass spectroscopy (Py-GC/MS).

Table 2 lists several terms with definitions that are fundamental to polymer chemistry. While I will be discussing some of these in more detail later, let me point out that branching, cross-linking, and crystallinity all take on unique meanings for poly-

**Table 1. ENERGETICS OF POLYMERIZATION: WHY DO POLYMERS FORM ANYWAY?**

$$\begin{array}{l} CH_2{=}CH_2 \\ \quad + \longrightarrow \text{active chain end} \longrightarrow -(CH_2-CH_2)_n- \\ \text{initiator} \end{array}$$

$sp^2$ carbons ⟶ $sp^3$ carbons

$1\ \sigma + 1\ \pi$ bond ⟶ $2\ \sigma$ bonds

163 kcal/M ⟶ 176 kcal/M

$PE \approx 7-10$
$PSt \approx 9-10$
$PMMA \approx 4-6$

**Table 2. BASIC DEFINITIONS OF POLYMER SCIENCE**

| | |
|---|---|
| MONOMER: | SINGLE UNIT |
| OLIGOMER: | SEVERAL UNITS |
| POLYMER: | MANY UNITS |
| HOMOPOLYMER: | IDENTICAL REPEAT UNITS |
| COPOLYMER: | DIFFERENT REPEAT UNITS |
| BRANCHING: | POLYMER BACKBONES BRANCH |
| CROSS-LINKING: | BACKBONES JOINED IN THREE-DIMENSIONAL ARRAY |
| CRYSTALLINE: | FOR POLYMERS, MEANS SOME REGIONS OF CRYSTALLINITY: PROCESSING & HISTORY DEPENDENT |

mers depending on the system being discussed. That is, there is a range of types and degrees of each that is very different than that observed for small molecules. For example, cross-linking encompasses a range of cross-link density and length that has enormous impact on the polymer properties observed, and such variation is only possible with polymeric materials.

A final distinction is necessary between two fundamental types of polymer-forming reactions. In the past, polymer textbooks have referred to condensation and addition polymerizations as the two main types of polymerization processes. Condensation polymerization involves loss of a small by-product molecule, while addition polymerization involves simple adding-on of each monomer repeat unit to the polymer. The former results in a change in chemical composition while the latter does not. The new terms now being used to describe polymerizations deal more specifically with the mechanism of polymerization rather than the overall chemical composition. The terms *step-growth* and *chain-growth* refer to how the individual chains are formed. The former process involves a sequence of slow and distinct steps that very gradually lead to polymer formation. Inherent in this process is the fact that high MW chains are not obtained until the last 1 percent of reaction. In chain-growth polymerization, on the other hand, each chain forms rapidly as a result of a chain reaction of steps and results in high MW polymer chains forming right from the beginning of the reaction. In general, step-growth reactions include most condensation polymerizations while chain-growth processes include most addition reactions.

While there are important differences between "normal" chemistry and polymer science, they are more imaginary than real. The attitude inherent in schools and universities in America is generally not favorable to the study and understanding of polymers, and this despite their enormous importance. In fact, understanding polymer chemistry simply requires an extension of understanding the chemistry of small molecules. Several textbooks will be referred to later that are excellent reference and study guides for polymer chemistry. The one by Stevens (1975) provides a fine introduction to the basic difference between step-growth and chain-growth polymerizations. The other textbooks available also discuss this topic and others efficiently and concisely.

## CHEMISTRY AND PROPERTIES

The chemistry of vinyl and acrylic polymers is basically the chemistry of polymerization of carbon-carbon double bonds. Thus, typical monomers for these polymers include reactive compounds containing one or two double bonds. Tables 3 through 5 list a number of commercially important monomers along with their common names. Many of these may be familiar either by

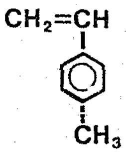
Table 3. COMMON VINYL MONOMERS
$CH_2=CHX$

| X | POLYMER | ABBREVIATION |
|---|---|---|
| H | polyethylene | PE |
| $CH_3$ | polypropylene | PP |
|  | polystyrene | PSt |
| Cl | poly(vinyl chloride) | PVC |
| CN | polyacrylonitrile | PAN |
| $\overset{O}{\overset{\|}{C}}-O-CH_3$ | poly(methy acrylate) | PMA |
| $O-\overset{O}{\overset{\|}{C}}-CH_3$ | poly(vinyl acetate) | PVAc |

Table 4. COMMON VINYLIDINE MONOMERS
$CH_2=CXY$

| X | Y | POLYMER | ABBREVIATION |
|---|---|---|---|
| $CH_3$ | $CH_3$ | polyisobutylene | PIB |
| Cl | Cl | poly(vinylidine chloride) | PVDC |
| F | F | poly(vinylidine fluoride) | PVDF |
|  | $CH_3$ | poly(α-methyl styrene) | - |
| $CH_3$ | $\overset{O}{\overset{\|}{C}}-O-CH_3$ | poly(methyl methacrylate) | PMMA |
| CN | $\overset{O}{\overset{\|}{C}}-O-R$ | poly(alkyl α-cyanoacrylate) | - |

Table 5. MISCELLANEOUS MONOMERS

| MONOMER | POLYMER | ABBREVIATION |
|---|---|---|
| $CF_2=CF_2$ | polytetrafluoroethylene | PTFE |
| $CF_2=CFCl$ | polychlorotrifluoroethylene | PCTFE |
| $CH_2=CH-CH=CH_2$ | polybutadiene | PBD |
| $CH_2=\overset{CH_3}{\overset{\|}{C}}-CH=CH_2$ | polyisoprene | – |
| $CH_2=\overset{Cl}{\overset{\|}{C}}-CH=CH_2$ | polychloroprene | – |
|  | poly(p-methylstyrene) | PPMSt |

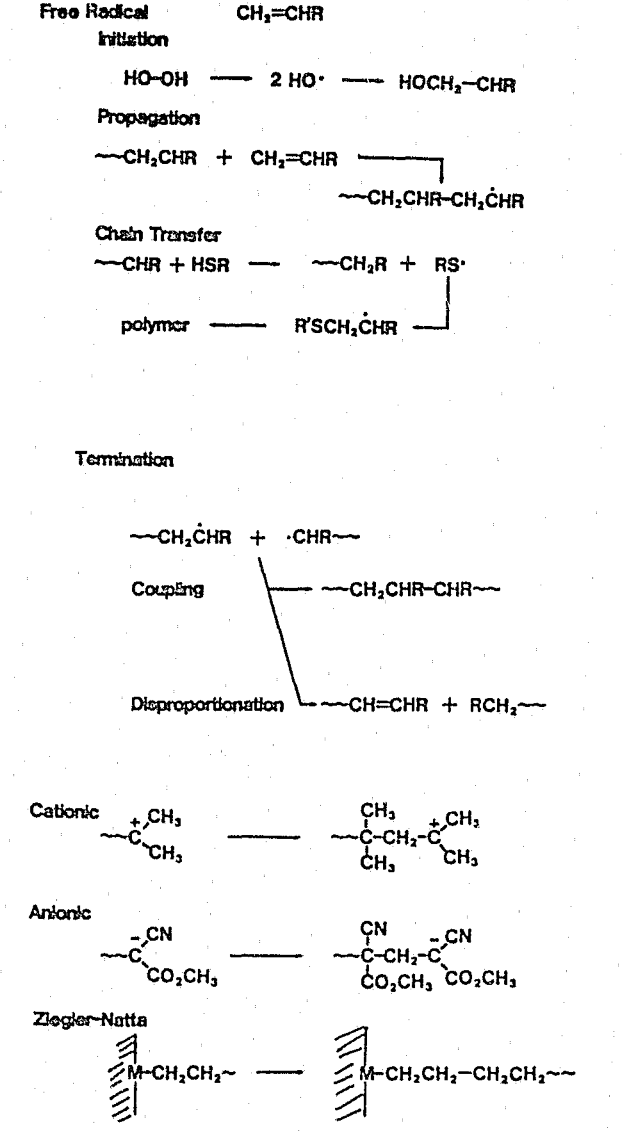
their name or abbreviation. Most people are aware, for example, of the use of polyvinyl chloride (PVC) in pipes and plumbing applications. In general, however, many of the polymer structures and names will not be familiar to the general population. Rather than spend time discussing the enormous number of applications of these typical polymers, I refer the reader to the textbook by Seymour and Carraher (1981). This book has an excellent description of many of the commercial uses and trade names associated with these polymers.

It should be clear to a practicing analytical chemist or forensic scientist that the properties of the polymers obtained from these monomers are intrinsically related to their chemical composition. More importantly, the characterization and identification of the polymers requires and is also facilitated by their chemistry. There are thus two main requirements for accurate identification of a given polymer sample. These are identification of the monomer or monomers present and determination of how these monomers are incorporated into the polymer. Understanding the typical polymerization mechanisms used today will assist in evaluating such factors as polymer configuration, copolymer structure and composition, MW and molecular weight distribution (MWD).

### Polymerization Mechanisms

There are four fundamentally different mechanisms of polymerizations available today. Table 6 characterizes these mechanisms in terms of general behavior. Free-radical polymerization involves several different steps. The initiation and propagation steps are reactions involving the initiator molecule or reactive chain-end radical with new monomer molecules. The high reactivity of the radical plus the overall driving force of double bond conversion to two single bonds result in very rapid chain growth. Competing processes, however, are termination and chain transfer.

**Table 6. BASIC POLYMERIZATION MECHANISMS**



Termination may be of two types, involving two radicals coupling or undergoing disproportionation. These two processes lead to small amounts of chemically distinguishable functionality in the polymers. Thus, depending on the exact conditions employed in polymer synthesis, the presence and concentration of these terminating groups may be used for polymer identification.

Chain transfer is a process involving termination of a growing chain through a transfer process leading to initiation of a different polymer chain. In addition to spontaneous processes observed for many systems, deliberately added transfer agents (such as mercaptans) are employed commercially to control the MW of the final polymer obtained. Again, the presence of these chain transfer moieties can be used for polymer identification.

Cationic polymerization is rare in commercial polymers. One of the few examples involves conversion of isobutylene to polymers that are used as adhesives, innertubes, and the inner lining of tubeless tires. The specific initiator molecule used for the synthesis of these polymers may provide a clue to manufacturer identification, as can the overall MW and MWD.

Anionic polymerization is becoming more popular for the synthesis of polymers with unique properties. One of the most unusual applications of anionic polymerization is in the alpha-cyanoacrylates, or super glues. This is one of the few examples in adhesive chemistry in which polymers are not formed before application to the bonding surfaces. With the alpha-cyanoacrylates, liquid monomer is applied to surfaces which normally contain small amounts of absorbed water. Under pressure, anionic polymerization is initiated by surface imperfections and water leading to the polymer that actually forms the adhesive bond.

Transition metal catalyzed polymerizations, commonly called Ziegler-Natta processes, employ a metal complex as the polymerizing site. The mechanism involves a monomer insertion process between the bound polymer chain end and the metal cluster. This interaction results in a degree of control over the polymerization process not possible by other mechanisms. Specifically, monomers such as ethylene and propylene can be homopolymerized and copolymerized to give products not available through other procedures. In addition, a diverse range of stereocontrol of the polymer configuration is possible that is unique to this mechanism. With modern high-efficiency catalysts, the transition metal cluster is often not removed from the final polymer and may therefore be used as an identifying characteristic through techniques such as X-ray activation analysis.

Table 7 summarizes the characteristics of the polymerization processes and polymer properties for radical, anionic and Ziegler-Natta mechanisms while Table 8 lists the relative ability of the common monomers to polymerize by each of these three mechanisms. Of the three, radical polymerizations are by far the most common, although increasing demand for high-performance materials is making anionic and Ziegler-Natta polymers more attractive.

Table 7. MECHANISTIC CONSEQUENCES

**Radical**
- **Easy, Fast, Efficient**
- **High MW, Broad MWD**
- **Atactic to Syndiotactic**
- **Range of Copolymers**
- **Noncrystalline, Disordered**

**Anionic**
- **Difficult, Expensive**
- **High MW, Narrow MWD**
- **Stereoregular**
- **Block Copolymers**
- **Functional Polymers**

**Ziegler–Natta**
- **Fast, Efficient**
- **HMW, MWD varies**
- **High Stereoregularity**
- **High Density PE**
- **Alkene Polymers, Copolymers**

Table 8. MONOMER REACTIVITY

| MONOMER | RADICAL | ANIONIC | ZIEGLER-NATTA |
|---|---|---|---|
| ETHYLENE | + | + | + |
| α-OLEFINS | – | – | + |
| 1,3-DIENES | + | + | + |
| STYRENE | + | + | + |
| HALO OLEFINS | + | – | – |
| ACRYLATES | + | + | – |
| ACRYLONITRILE | + | + | – |
| VINYL ACETATE | + | – | – |

## Homopolymer Tacticity

A further very important consequence of the particular polymerization mechanism employed for vinyl polymer synthesis is the configuration of the repeat units along the polymer chain. Typical vinyl monomers and many of the vinylidine monomers have two different functional groups on the same carbon atom. These groups may be incorporated into the polymer chains with characteristic stereochemistry (called tacticity) that depends on the mechanism and specific reaction conditions employed.

Three major types of tacticity are possible, as illustrated in Figure 1. The structures are drawn in the extended zig-zag conformation in which the carbon atoms of the polymer backbone are constrained to lie in the plane of the paper at the characteristic angle of 109°. It is easy to visualize the relationship of pendent groups with this convention. Syndiotactic and isotactic configurations possess, respectively, alternating and same-side arrangements of substituents along the polymer backbone. Atactic is used to describe a polymer which has no overall order of side group configuration. The term is, in fact, a misnomer since adjacent pairs or groups of three may in fact have syndiotactic or isotactic configurations.

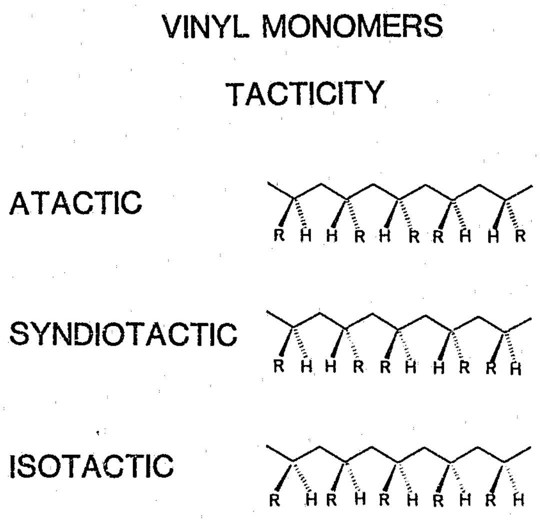


Figure 1. Vinyl polymer tacticity.

The important consequence of stereoregularity in the form of tacticity is how it affects final polymer properties. These are related to the ability of the polymer chain to interact and pack in crystalline domains. Thus, syndiotactic and isotactic polymers have very different properties from atactic properties since their regularity allows good packing and interaction in the solid state.

Figure 2 illustrates the fact that for vinylidine monomers in which the two substituents are identical, stereoregularity is inherent. Thus, polyvinylidine chloride is a highly ordered and crystalline material despite the fact that the same type of radical polymerization process used for this monomer leads to an atactic product for vinyl chloride. Also drawn is an example of syndiotactic PMMA, a vinylidine polymer which may display tacticity because the two substituents are different. In actual fact, PMMA is formed with highly syndiotactic structure despite the fact that free radical initiation is used that normally leads to atactic structures. This is due to the steric interaction of the ester side-groups which promotes the alternating arrangement of these large units along the polymer backbone.

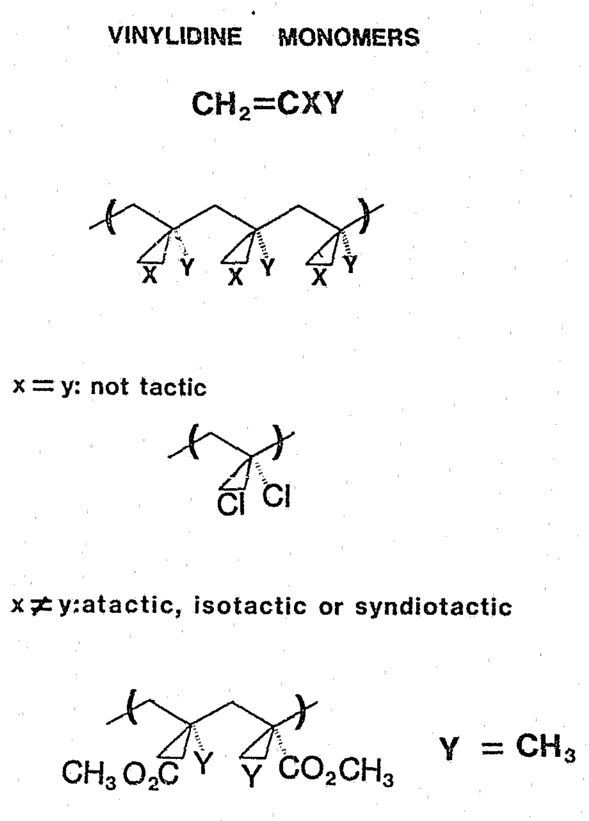


Figure 2. Stereochemistry of vinylidine polymers.

Figure 3 illustrates further consequences of polymer mechanism and free radical polymerization specifically. For all mechanisms listed in Table 6, it is assumed that the normal mode of addition is head-to-tail. This is a consequence of the forces stabilizing the active intermediate species, whether it is a radical, an anion, or a metal-bound chain end. Occasionally, however, a head-to-head addition occurs during propagation. The coupling mode of termination for radical polymerization also leads to a head-to-head grouping of adjacent repeat units. It is possible to identify and quantitate these unusual repeat structures in many polymers using sensitive Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectrometers. Not only are these moieties sensitive to the mechanism of polymerization, but they vary with specific reaction conditions such as temperature and concentration and may therefore provide a means of accurate identification.

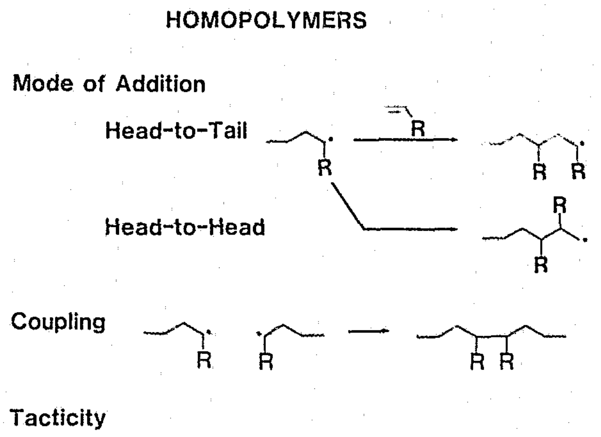


Figure 3. Other structural features of homopolymers.

The butadiene monomers in Table 5 play an extremely important role in homopolymers and copolymers in modern society. They are used in synthetic elastomers, such as in tire tread, as well as in copolymers employed as impact resistant and high performance molding material, such as in small appliance housings. Figure 4 summarizes the three main configurational structures possible. The two 1,4-structures are geometrical isomers that may interconvert thermally to some extent, although the trans arrangement is the more stable. The 1,2-structure is chemically unique, however. It not only offers the possibility of cross-linking through the pendent vinyl group, but the backbone may display tacticity similar to that for typical vinyl monomers. The synthetic procedure used for obtaining butadiene polymers controls the relative amounts of these structures. Thus, free radical polymerization leads to the presence of all three randomly distributed along the polymer backbone. Various anionic mechanisms, as well as a large number of Ziegler-Natta procedures, make available each of the three structures drawn as pure homopolymers. In addition, the 1,2-structure may be obtained with various degrees of tacticity ranging from highly isotactic to highly syndiotactic. Ready spectral identification of the presence and amount of each of these structures in a polymer can provide specific identification and some indication of past history.

### Copolymer Structure

One of the most important ways of modifying the structure and properties of polymeric materials is by incorporation of a comonomer. There are four basic types of copolymer structures as depicted in Figure 5. Random, alternating, and block copolymers all possess backbone sequences of two or more comonomer repeat units. Graft copolymers,

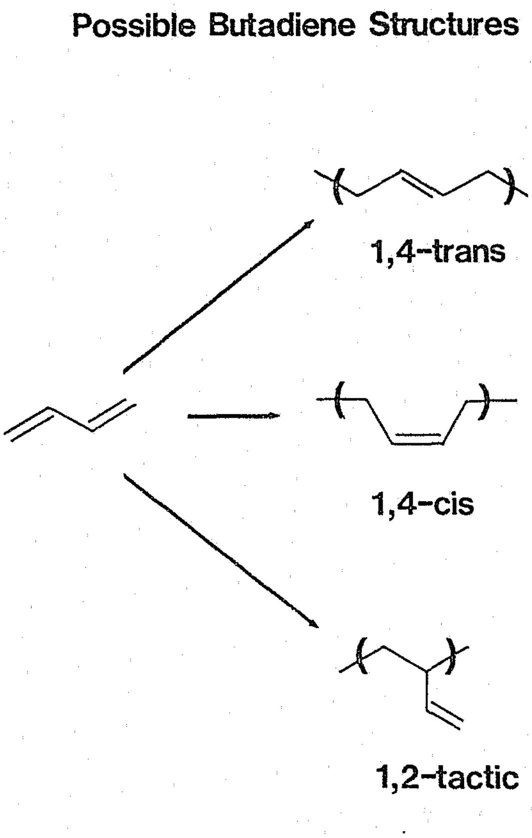


Figure 4. Possible butadiene structures.

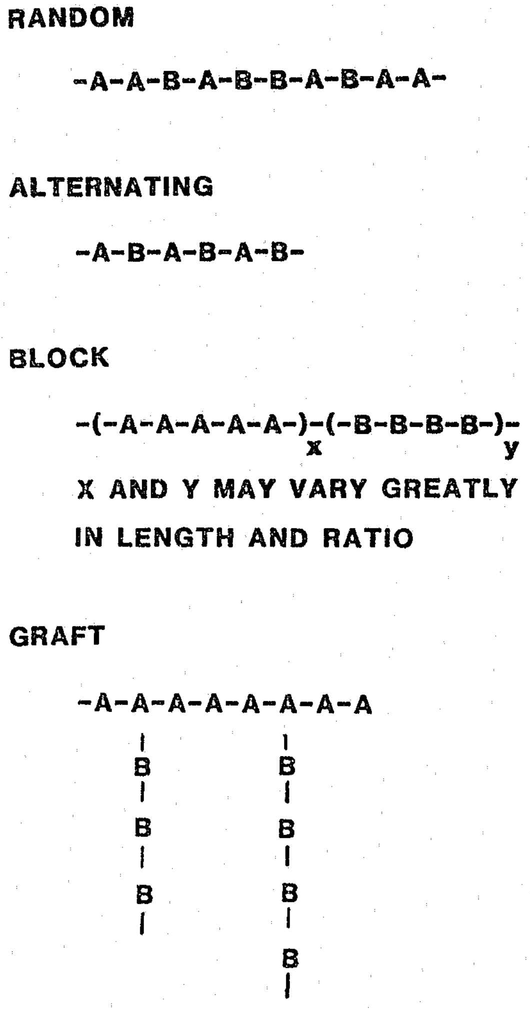


Figure 5. Possible copolymer structures.

on the other hand, are obtained by first synthesizing a homopolymer such as poly-A, and then grafting a second monomer B from this polymer backbone. Alternatively, a preformed poly-B may be reacted with poly-A to generate a grafted structure.

Table 9 summarizes the relationship between polymerization mechanism and the type of copolymer possible. The most widely used copolymerization procedure involves free radical propagation. Depending on the relative reactivity of the comonomers, random, alternating and block structures may be obtained. It is difficult, however, to force a type of structure that the comonomers are unwilling to adopt. That is, a given pair of comonomers will tend to form only one type of copolymer structure.

Anionic polymerization is especially suited for formation of block copolymers. Careful control of reaction conditions, monomer purity and sequence of monomer addition can lead to block structures with very precisely controlled block lengths. It is even possible to form structures with more than two blocks of the same or different comonomers.

Ziegler-Natta type polymerization systems are the only methods available to obtain copolymers of alpha-olefins. While any number of comonomers can be incorporated into essentially random structures, the most common commercial polymers contain ethylene and propylene. By varying the monomer ratio and catalyst, it is possible to obtain polymers with a wide range of properties. Thus, with the same inexpensive monomers, easily processed thermoplastic polymers may be synthesized with properties ranging from hard to flexible to elastomeric.

Table 10 summarizes some of the effects of polymerization conditions on copolymer composition. It is important to emphasize that for a given reac-

**Table 9. SYNTHETIC METHOD EFFECTS**

**Copolymer Type**

**Radical:**
- Random
- Alternating
- Block
- Hard to control, maintain

**Anionic:**
- Block Easy
- Multiblock Possible

**Graft:**
- Two steps involved
- Make polymer A, Initiate B
- or React polymer B

**Table 10. REACTION CONSEQUENCES ON COPOLYMER COMPOSITION**

**TIME DEPENDENT:**

ONE MONOMER MORE REACTIVE,
USED UP FASTER, CHANGES MONOMER RATIO,
CHANGES POLYMER COMPOSITION

**AZEOTROPIC:**

REACTIVITY RATIOS AND FEED SUCH THAT
COMPOSITION DOES NOT CHANGE

**CONSTANT FEED:**

ADD ONE MONOMER CONTINUOUSLY
TO MAINTAIN COMPOSITION

tion containing a specific ratio of comonomers, one monomer will be more reactive, and therefore used up more rapidly. This results in a change in the monomer composition present during the course of the polymerization. Consequently, the polymer composition will change throughout the reaction. However, for some comonomer systems, it is possible to find a given feed ratio that leads to an azeotropic polymerizatiton. This is one in which the composition of the feed and the copolymer remains constant throughout the polymerization.

One of the most important techniques for controlling copolymer composition in systems employing free radical propagation is constant addition of monomers. By continually adding both of the two comonomers at the same rate at which they are consumed in the polymerization, it is possible to maintain a constant copolymer composition throughout the reaction. This concept, in fact, forms the basis for many commercial copolymerizations. However, it does not provide a universal method of obtaining any copolymer composition desired because the comonomer reactivities will limit the extent to which the feed ratio can be varied.

Table 11 gives several examples of commercially important copolymers. Most of these are systems involving only two comonomers with the single terpolymer example of acrylonitrile-butadiene-styrene (ABS). The structures drawn oversimplify the copolymer compostions that are possible and actually produced commercially. By varying the reaction conditions and monomer concentrations, it is possible to synthesize a wide range of structures from the same basic comonomers. In addition, the polymerization mechanism that is employed may also effect the structure of the copolymer obtained. For example, with styrene-butadiene, both free radical and anionic mechanisms may be employed. The former will lead to a fairly uniform random copolymer with a 50:50 starting ratio of monomers. The latter, however, can be applied with a sequential addition of monomers to give a block copolymer. The physical properties of these idealized copolymers will be very different despite similar chemical compositions.

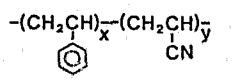
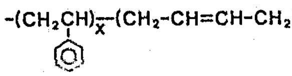
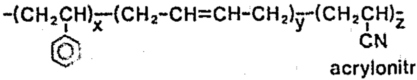
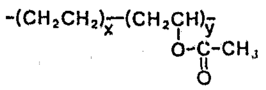
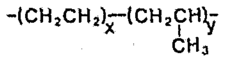
### Molecular Weight and Molecular Weight Distribution

As mentioned in the introduction, the MW or length of a polymer chain is its most unique characteristic. The exceptional properties displayed by polymeric materials are inherently related to the fact that the polymer chains are very long and can engage in strong intermolecular interactions and entanglements.

For most polymers, physical properties increase almost linearly with MW up to a limiting value. Beyond this value, little further change is observed. The amount of change and the limiting value itself are dependent on the polymer chemical structure, configuration, cross-linking and processing. In fact, the need to be able to process the polymer inherently limits the maximum MW desired.

There are four basic types of MWs measured. These are the number average value ($M_n$), the viscosity value ($M_v$), the weight average molecular weight ($M_w$) and the z-average value ($M_z$). The

**Table 11. COMMON COPOLYMERS**

| Structure | Monomer | Abbreviation |
|---|---|---|
|  | styrene-acrylonitrile | SAN |
|  | styrene-butadiene | SB rubber |
|  | acrylonitrile-butadiene-styrene | ABS |
|  $-(CH_2CH_2)_x-(CH_2\underset{\substack{\vert\\ O-\underset{\substack{\Vert\\ O}}{C}-CH_3}}{CH})_y-$ | ethylene-vinyl acetate | EVA |
|  $-(CH_2CH_2)_x-(CH_2\underset{\substack{\vert\\ CH_3}}{CH})_y-$ | ethylene-propylene | EP elastomer |

first three of these are measured by a variety of different techniques which are described in available textbooks such as that by Seymour and Carraher (1981).

Because of the inherent randomness of most polymerization reactions, a single uniform MW is not obtained. Thus, a distribution of MWs is observed for all commercial polymers. Figure 6 illustrates how the two main types of free radical termination can affect the MWD. As an idealized example, consider 10,000 monomer units of structure A. Assuming simultaneous initiation with 20 initiator fragments and uniform chain growth with no termination, 20 polymer fragments with active terminal ends will result. If it is now assumed that equal amounts of coupling and disproportionation occur, 15 polymer molecules will form. Five will have MWs of 1,000 daltons and 10 will have MWs of 500 daltons. Whatever MW technique is employed to evaluate this sample, the measured value will be some average of these two values which is not representative of the actual polymer composition.

In a typical radical polymerization, initiation and termination occur throughout the polymerization. This entails a distribution of probabilities for termination of growing polymer chains. What results, then, is a wide range of MWs. This range may be characterized by using two or more different MW measurements to indicate how much variation exists. Normally, the ratio of weight average and number average is used, with the former measured by osmometry and the latter obtained with light scattering, for example.

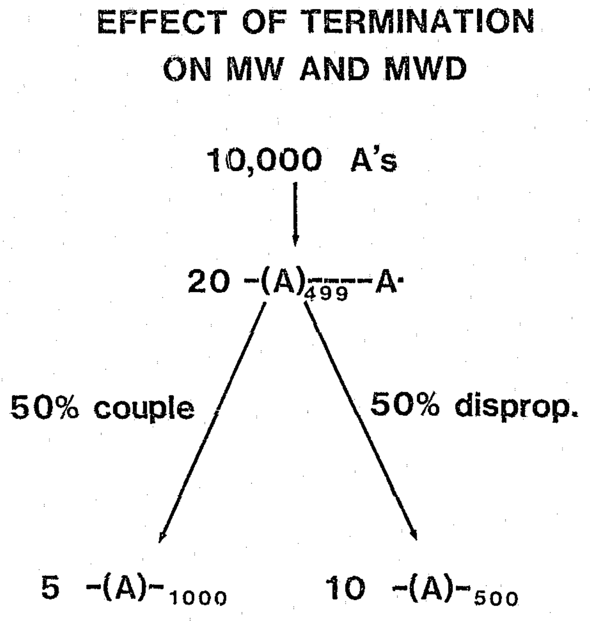


Figure 6. Effect of termination on molecular weight and molecular weight distribution.

Even with the use of more than one MW measurement technique, an accurate picture of the MWD is not obtained. It is possible to imagine a number of different distributions of MWs that would lead to similar values of the ratio $M_w/M_n$. It would be highly desirable, then, to have a complete picture of the concentrations of each MW fraction in a given sample. This is possible through the use of a chromatographic technique called size exclusion chromatography (SEC). This technique involves the use of porous column packing material in which the pores are of comparable size to polymer molecular dimensions. Size separation can then occur by passing a polymer sample down an appropriately packed column with a difference in time required for different size molecules to penetrate the packing pores. An excellent reference book by Yau *et al.* (1979) describes the theoretical background and application of SEC to polymer analysis. Since the MWD of a polymer is very sensitive to both polymer synthesis and processing conditions, SEC provides a very accurate tool for identification of commercial materials.

## Morphology

Table 12 summarizes some of the important morphological properties of polymeric materials. Unlike most low MW chemicals, polymers may be either crystalline or amorphous in overall behavior. However, even the most highly crystalline polymer will have MW dispersity and imperfections that lead to the presence of amorphous phases. In addition, the amount of crystallinity present can depend dramatically on processing conditions.

**Table 12. MORPHOLOGY: STRUCTURE OF SOLID POLYMERS**

**CRYSTALLINITY**

- KINETIC vs EQUILIBRIUM
- TYPE OF CRYSTALLINITY
- DEGREE OF CRYSTALLINITY

**AMORPHOUS BEHAVIOR**

- ABOVE, BELOW $T_g$
- ORIENTATION
- STRAIN

**CROSS-LINKING**

- PHYSICAL, CHEMICAL
- DEGREE
- LENGTH OF TIE SEGMENTS

Branching from the polymer backbone has a large effect on the ability of a polymer to pack in a crystalline array. Figure 7 describes the three major types of polyethylene (PE) obtained commercially. The amount of branching for a given system depends on the type of polymerization procedure employed. High density PE (HDPE),which is fairly linear, is obtained with Ziegler-Natta initiation. The low density material is highly branched and amorphous and is synthesized using high pressure, free radical initiation. A newcomer on the commercial scene is the linear low density PE (LLDPE). This polymer has much less branching than that of the normal free radical material, although the linearity is not as high as the Ziegler-Natta product. However, because LLDPE is more easily produced than HDPE and has much better properties than the LDPE, it is becoming accepted in a wide range of applications.

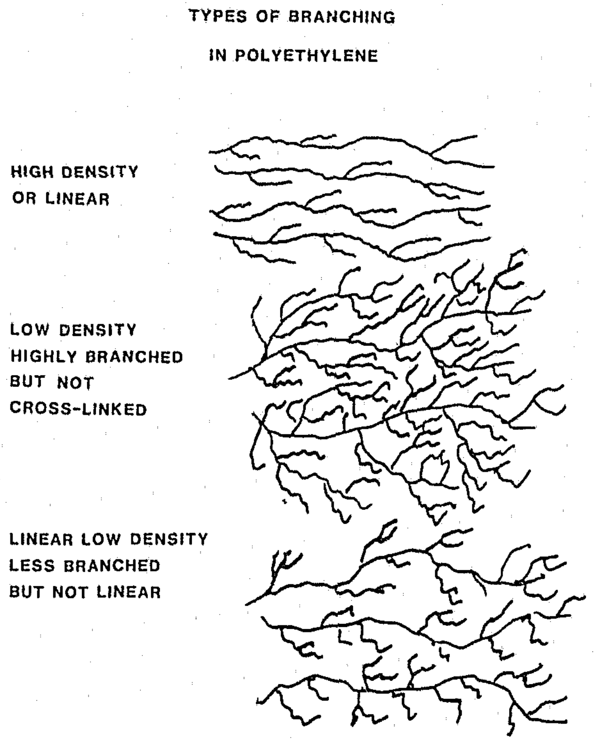


Figure 7. Types of branching in polyethylene.

Table 13 summarizes available techniques for obtaining quantitative data on the amount of branching of PE and other polymers as well. These include traditional techniques such as infared (IR) spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction. New IR techniques such as attenuated total reflectance (ATR), multiple internal reflectance (MIR) and diffuse reflectance (DR) spectroscopy are becoming more widely employed, especially when it is desired that the polymer not be transformed or destroyed during analysis or when surface effects are under examination.

Dichoric IR is a technique that has been available for many years but is now seeing new application in polymer characterization. This technique is useful in the transmission mode for thin films, although application with ATR is becoming more routine with the advent of FTIR and computer-assisted data acquisition and handling.

High resolution $^{13}C$ NMR of a variety of polymers, such as PE dissolved in xylene at 125° C, can provide detailed qualitative and quantitative information on chain branching. In addition, recent advances in solid state carbon NMR have made possi-

Table 13. BRANCHING QUANTITATION

| | |
|---|---|
| IR | TRANSMISSION OF THIN FILM<br>ATR MIR DR<br>DICHROIC IR<br>AS OBTAINED AND STRETCHED<br>TRANSMISSION AND REFLECTED |
| 13C NMR | SOLUTION ( EG, XYLENE, 125 o C )<br>SOLID STATE ( SEMI-QUANTITATIVE ) |
| DSC AND X-RAY (INDIRECT) | DEGREE OF CRYSTALLINITY<br>ANNEAL AND REEVALUATE - |

ble semi-quantitative determination of polymers without sample transformation or destruction. Solid state NMR is one of the most powerful new tools for polymer identification available today.

Table 14 summarizes the characteristics of several important characterization techniques. In addition to those discussed above, polarizing microscopy and Raman spectroscopy are becoming more widely applicable. The latter has been slow to develop because of the requirements for high-power irradiation. With recent advances in laser technology, this technique is rapidly developing and becoming routine. However, it has the limiting requirement that the samples be noncolored, and this severely inhibits use of this technique in many situations.

Table 14. METHODS OF MORPHOLOGY EVALUATION

| ORIENTATION | CRYSTALLINITY |
|---|---|
| POLARIZING MICROSCOPY<br>OFTEN NON-TRANSFORMING<br>QUANTITATIVE<br>FAST, EASY | X-RAY DIFFRACTION<br>NON-TRANSFORMING<br>QUANTITATIVE<br>SLOW BUT EASY |
| DICHROIC INFRARED<br>NON-TRANSFORMING<br>QUANTITATIVE<br>TRANSMISSION and SURFACE<br>FAST, EASY | DIFFERENTIAL SCANNING CALORIMETRY<br>TRANSFORMING<br>MOSTLY QUALITATIVE<br>FAST, EASY |
| RAMAN<br>NON-TRANSFORMING<br>SLOW, DIFFICULUT | SOLID STATE NUCLEAR MAGNETIC RESONANCE, INFRARED<br>GENERALLY NON-TRANSFORMING<br>QUALITATIVE<br>SLOW-TO-FAST, DIFFICULT |

The final topic to be discussed in this section is that of polymer cross-linking. Figure 8 depicts three states of polymer interaction and bonding. Soluble polymers possess varying degrees of intermolecular interaction depending on the basic composition and MW of the polymer chains. Light cross-linking may be obtained through chemical reaction during or after synthesis and results in flexible materials that form swollen gels with solvent. Rubber tires are a good example of this type of structure. More highly cross-linked materials are rigid and hard, are not easily swollen and are difficult to characterize by most available techniques. Again, solid state NMR offers one of the most valuable methods of analyzing insoluble polymeric materials.

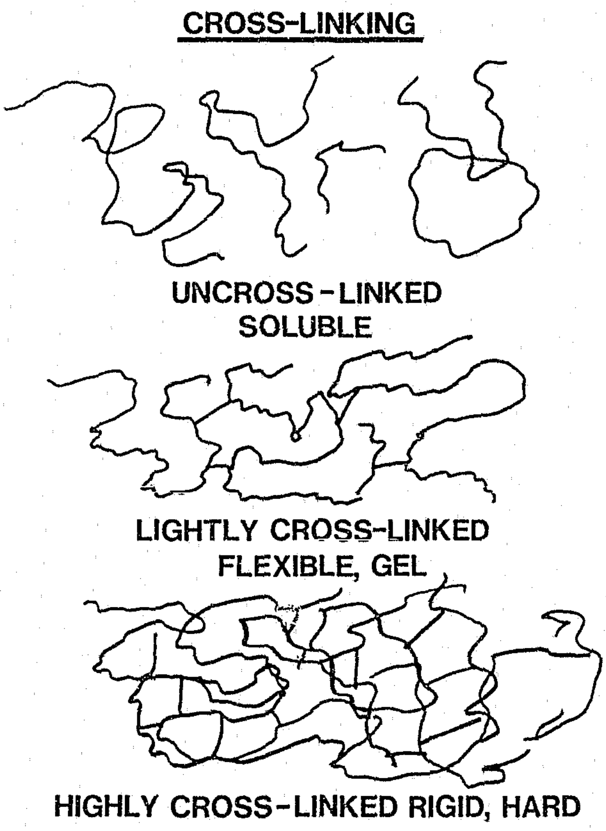


Figure 8. Cross-linking effects.

### Reactions of Polymers

There are two basic types of reactions that take place on polymer systems. The first includes those reactions which are done deliberately to modify the properties of the material, while the second involves those natural or induced decomposition and degradation reactions which result from normal service life. Figure 9 depicts two typical reactions used to modify commercial polymers. The first involves complete or partial hydrolysis of poly(vinyl acetate) (PVA) to give either a copolymer containing pendent hydroxy groups or the homopolymer, poly(vinyl alcohol) (PVA). The second reaction shown, between PVA and the four-carbon aldehyde butyral, is used to give poly(vinyl butyral) (PVB). Because the reaction requires adjacent hydroxy groups, it is only possible to obtain partially substituted copolymer. The obtained PVB is used in safety glass as a tough, flexible interface that prohibits glass shattering during accidents. The structure and composition of PVB varies depending on reaction conditions and age of the glass. Careful evaluation of the amount of reaction on a polymer can provide a means of identification and age determination.

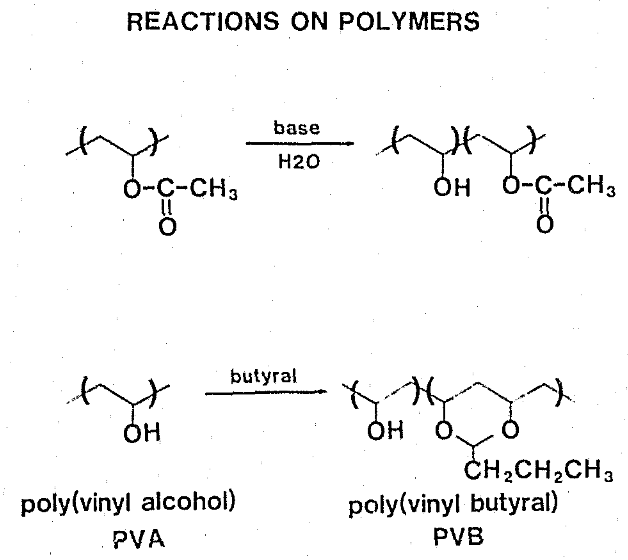
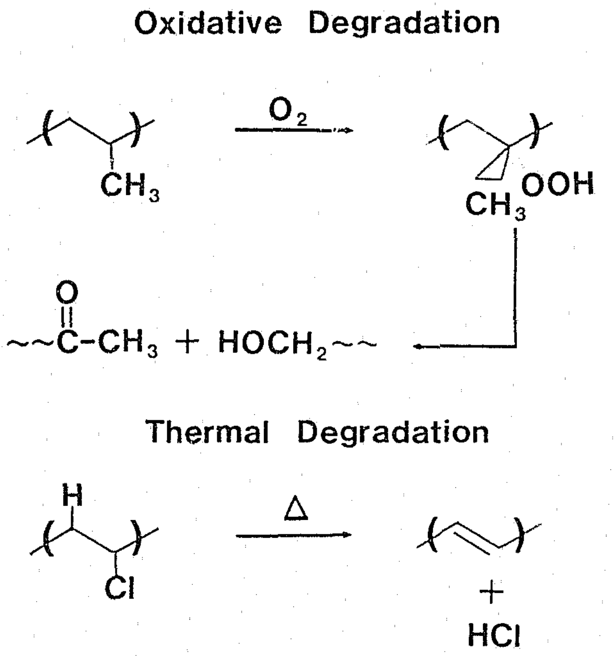

REACTIONS ON POLYMERS

Figure 9. Reactions on polymers.

Polymer degradation can occur through a number of mechanisms. Figure 10 shows two examples of oxidative and thermal reactions. The ubiquitous nature of oxygen and its high reactivity, especially in the presence of sunlight, leads to widespread and common degradation of the type indicated. Thermal degradation, on the other hand, is fairly specific for certain classes of polymers. Thus, PVC is especially susceptible to loss of HCl molecules resulting in formation of colored fragments in the polymer backbone.

Photodegradation and thermodepolymerization at high temperature are two other commonly observed reactions of polymers. The former occurs most often with materials exposed to sunlight for prolonged periods of time. Detailed mechanisms of photodegradation depend on the polymer structure, processing conditions, and the presence of additives or inhibitors. The amount and type of reaction that takes place can be very characteristic for a specific sample. Depolymerization, on the other hand, normally takes place at elevated temperature such as that found in burning buildings and automobiles and has limited forensic value. However, analytical applications of thermodegradation and depolymerization involve the use of pyrolysis-GC/MS. This technique requires very little sample and can give extremely detailed data that may be used to accurately characterize the polymer composition, structure, history and age.


Oxidative Degradation

Thermal Degradation

Figure 10. Oxidative and thermal degradation.

Additional time-dependent changes in polymer structure and properties are summarized in Table 15. This is, of course, an incomplete list of all possible reactions and processes which can take place during a polymer's usable lifetime. It is also important to remember that any time-dependent process is also temperature dependent, and the specific thermal environment that a given sample experiences will accelerate or retard any or all of these processes. A large range of physical and spectroscopic characterization techniques are required to evaluate completely most or all of these polymer properties.

### Additives, Fillers and Fibers

Almost all commercial polymer samples contain one or more additives or reinforcing agents. These compounds are present to retard or modify the time-dependent changes which can take place in polymer samples, or are present to improve the processing and physical properties of the final products. The presence of these additives is both a blessing and a curse. They greatly complicate the characterization of the sample because of the complexity and variety of the type of additives employed. Thus, for a given type of typical polymer a large number of different additives may be used to achieve essentially the same product performance. In addition, these additives also experience age-dependent changes which can complicate further the characterization and identification of a given polymer sample.

The presence of these additives can be helpful in providing a degree of complexity that allows "fingerprinting" of a specific polymer sample. That is, the combination of polymer plus additives is often unique with respect to manufacturer, application and time of processing. Thus, if samples are available for comparison, it is often possible to conclusively identify a given product through the combination of additives and degradative changes observed in the sample.

**Table 15. GENERAL TIME-DEPENDENT CHANGES OF POLYMERS**

- CHEMICAL REACTION
- PHOTODEGRADATION
- OXIDATION
- THERMAL DEGRATION
- IMPACT MODIFICATION
- PLASTICIZER LOSS
- CRYSTALLIZATION

EXAMPLES

- CRAZING OF PMMA BY GAS FUMES
- LOSS OF FLEXIBILITY IN PVC SHEET AND PIPE

## CHARACTERIZATION TECHNIQUES

Table 16 summarizes the structural complexity of polymers as described in this article. Evaluation of this complexity involves a wide range of chemical and physical techniques. Dozens of reference books and textbooks are available detailing past and present procedures for carrying out these analyses. The reader is referred to the collection of recent reference works by Craver (1983), Klopffer (1984), Krause *et al.* (1983), Randall (1984), and Siesler and Holland-Moritz (1980). The first three provide the most comprehensive discussion and background descriptions available in three reference works today. The book by Krause *et al.* (1983) is particularly unique in that it summarizes an enormous number of wet chemical procedures for qualitative and quantitative polymer characterization. The books by Randall (1984) and Siesler and Holland-Moritz (1980) describe two of the most generally valuable spectroscopic techniques now available, those of NMR and IR. With the technique descriptions, leading references, and detailed procedures described in these five books, the structural characteristics included in Table 16 should be amenable to evaluation for most commercially available polymers. Of course, limitations of sample size may require judicious selection of techniques and order of application to maximize information and improve the accuracy of identification. Years of experience and dedicated continuing education are needed to maintain current awareness of available procedures. But then, the successes resulting from such dedication make the effort worthwhile and rewarding.

**Table 16. STRUCTURAL COMPLEXITY OF POLYMERS**

- HOMOPOLYMERS
  - HEAD-TO-HEAD UNITS
  - TACTICITY
  - BRANCHING
- COPOLYMERS
  - IDENTITY AND NUMBER COMONOMERS
  - RATIO OF COMONOMERS
  - MICROCOMPOSITION
    - AVERAGE
    - INDIVIDUAL CHAIN
- MOLECULAR WEIGHT
  - $M_n$ $M_w$ $M_z$ $M_v$
- MWD (NARROW, BROAD, BIMODAL)
- CROSS-LINKING
  - NUMBER AND LENGTH
- MORPHOLOGY (CRYSTALLINITY, ORIENTATION)
- REACTION AND DEGRADATION
- IMPURITIES (CATALYST, Rxn VESSEL)
- ADDITIVES

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## DISCUSSION

*Suzuki:* In the nuclear magnetic resonance (NMR) work that you are doing for the solids, is that magic angle spinning?

*Mathias:* Yes, there are two different ways of doing solids NMR. There is magic angle spinning and there is non-spinning spectroscopy. The non-spinning spectroscopy is becoming more important but it is not nearly as sensitive as magic angle spinning. Most all of the analytical techniques that are useful to forensic scientists would involve magic angle spinning, yes.

*Suzuki:* Don't you lose resolution if you do not spin it?

*Mathias:* Yes, but there are ways of overcoming that. There are pulse sequences that can be used to increase resolution in non-spinning samples. But those are only available on non-routine instruments right now so they are not readily available.

# CHARACTERIZATION OF POLYMERS BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

*Kenji Kawaoka*

Eastman Kodak Company
Rochester, New York

With current technology, the combination of pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) is a powerful and convenient analytical method for the characterization of polymers. In addition to the identity of the repeating molecular units, it can provide information about additives, impurities, residuals and even microstructure. Furthermore, the chromatogram of the pyrolysis products, the pyrogram, can serve as a "fingerprint" of a polymeric sample. Much of this information can be obtained on small amounts (.1 mg or less) of sample and often in a single experiment with a minimum of sample preparation and handling. With the aim of determining how much detail can be obtained from polymer pyrolysis products, we have applied Py-GC/MS to a variety of polymeric samples. I report here the results of this study. I will first briefly review the development of this method of analysis.

## BRIEF HISTORY

Characterization of a polymer by examining its pyrolysis products was practiced more than a century ago by Williams (1862). He deduced the nature of a rubber, polyisoprene, by destructive distillation, separation of the degradation products by fractional distillation, and identification of these products by classical chemical methods. This laborious and time-consuming process was not greatly improved for almost a hundred years. Improvement in the identification technique came when Madorsky and Straus (1948), Wall (1948) and Zemany (1952) used mass spectrometry (MS) to examine polymer pyrolysis products. Shortly thereafter, Bradt *et al.* (1953) used the combined pyrolysis-mass spectrometry technique (Py-MS) to analyze polymers. Improvements in the separation technique came after the introduction of gas chromatography (GC) by James and Martin (1952) when Davison *et al.* (1954) used GC to characterize polymer pyrolysis products. Several workers, Martin (1959), Radell and Strutz (1959), and Lehrle and Robb (1959), subsequently introduced combined pyrolysis-GC (Py-GC) to examine polymers. The combination technique Py-GC/MS required the direct coupling of a gas chromatograph and a mass spectrometer. This was first accomplished by Holmes and Morrell (1957), and Gohlke (1962) interfaced a capillary column to a mass spectrometer. Gibson (1964) was apparently the first to apply Py-GC/MS to polymers.

Today all of the necessary equipment for Py-GC/MS is commercially available. An examination of current literature suggests the following. The most frequently used pyrolyzer units appear to be a Curie Point type, first introduced by Giacobbo and Simon (1964), and the pulsed filament type such as the one produced by Chemical Data Systems, Inc. (CDS, Oxford, PA). Fused silica capillary columns are popular, as are fast-scanning quadrupole mass spectrometers with dedicated data systems.

## EXPERIMENTAL

The apparatus for the Py-GC/MS experiments is shown schematically in Figure 1. The pyrolysis unit was a CDS Pyroprobe 120 solids pyrolyzer with a flat ribbon probe and a temperature-controlled interface. The GC/MS was an RTE-6 upgraded HP5985B with an HP5840 GC and an HP18835C capillary inlet system (Hewlett Packard, Palo Alto, CA). The capillary column was a J & W 15 m x 0.25 mm DB-1 (0.25 $\mu$m film thickness) fused silica column (J & W Scientific, Inc., Rancho Cordova, CA). Helium was used as the carrier gas, and the exit end of the column was placed directly in the source of the mass spectrometer. Samples were, with few exceptions, pyrolyzed at 610° C for 10 seconds. The following programming was typical for the chromatographic separation: 30° C (isothermal for 3 minutes) and heating to 300° C at 10° C/min. Mass spectra were continuously acquired and stored on a dedicated data system at a rate of about one spectrum (20-500 amu) every 2 seconds. Samples were usually stuck to the ribbon probe with a drop of solvent such as dichloromethane, which was carefully evaporated away by heating to approximately 50° C.

With two exceptions, all the polymers examined were prepared at the Kodak Research Laboratories (Rochester, NY). Atactic perdeuteropoly(methyl methacrylate) (PMMAd) was prepared by Dr. Leslie Stanford of duPont via free-radical polymerization. O'Reilly *et al.* (1981) gave the characterization data for this polymer. Atactic poly(methyl methacrylate) (PMMA) was prepared in the same manner as PMMAd. A PMMAd/PMMA blend (20 weight percent PMMAd) was also prepared. Low molecular weight (MW) PMMA was prepared by

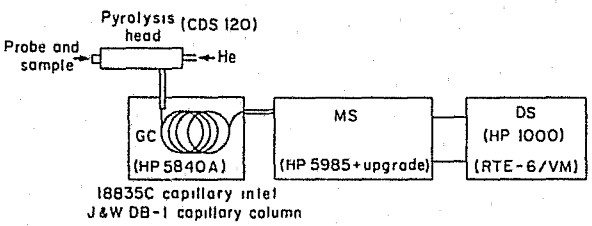

Figure 1. Schematic for the pyrolysis-gas chromatography-mass spectrometry apparatus.

free-radical polymerization, with 2.2 weight percent of 2,2′-azo-bis-(2-methylpropionitrile) (AIBN) in methanol. The styrene equivalent MW of this polymer, as determined by gel permeation chromatography, was 2.8 x $10^4$. Atactic polystyrene (PS) and perdeuteropolystyrene (PSd) were synthesized by anionic polymerization. Isotactic PS was a Dow Chemical product (Midland, MI), Lot II-40161. The percent isotacticity based on triads, as determined by nuclear magnetic resonance (NMR), was greater than 80. Polystyrene-co-*n*-butyl acrylate (PS/PBA), 75/25 by weight, and polystyrene-co-*n*-butyl acrylate-co-divinylbenzene (PS/PBA/DVB), 75/25/0.58 by weight, were prepared by free-radical polymerization. Poly(4-vinylpyridine) (PVP) was prepared by free-radical polymerization. Poly(vinylidene chloride) (PVDC) was prepared by free-radical emulsion polymerization, with Rohm and Haas Triton 770 (Philadelphia, PA) as the surfactant. Polyacrylonitrile (PAN) was synthesized by free-radical emulsion polymerization, with AIBN as the initiator. Poly(2-hydroxyethyl methacrylate) (PHEMA) was derivatized by dissolving the polymer in a mixture of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and acetone. A 40/60 monomer ratio blend of PVDC/PAN was prepared by ball-milling the appropriate amounts of the homopolymers.

## RESULTS AND DISCUSSION

### Poly(methyl methacrylate) (PMMA) and Blend with Perdeuteropoly(methyl methacrylate) (PMMAd)

The 80/20 blend of PMMA/PMMAd will illustrate some of the features of PY-GC/MS. The reconstructed total ion pyrogram (Figure 2) has only one strong feature. The mass spectrum at the leading edge of this band is consistent with perdeuteromethyl methacrylate and that at the trailing edge with methyl methacrylate (Figure 3). Although these compounds were not cleanly separated chromatographically, they were separated and identified by their mass spectra. Poly(methyl methacrylate) is an example of a polymer whose thermal degradation is dominated by chain depolymerization or unzipping (Irwin 1979), where the propagation step can be represented by

$$\cdots(CH_2\text{-}CRR')_n\text{-}CH_2\text{-}CRR'\bullet \rightarrow \cdots(CH_2\text{-}CRR')_n\bullet + CH_2{=}CRR'$$

and leads exclusively to monomers. This produces a simple pyrogram, which reveals little more than the identity of the basic molecular unit. In the present case, the absence of other volatile products suggests, however, that deuteration does not noticeably alter the unzipping process nor does the blending of these two homopolymers. Not all PMMA's simply unzip.

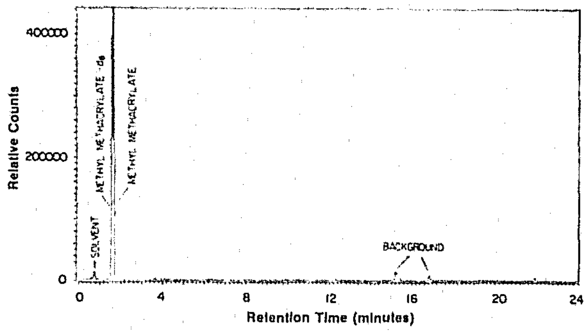

Figure 2. Reconstructed total ion chromatogram for the 610° C pyrolysis of the 80/20 blend of poly(methyl methacrylate) and perdeuteropoly(methyl methacrylate).

Figure 4 shows the pyrogram of a low MW (2.8 x $10^4$) PMMA, which was synthesized with the free-radical initiator AIBN. Although the major product is still the monomer, the other products indicate that more than unzipping has occurred. The products of interest are at retention times of 6.67, 9.03, 9.52, 10.92 and 17.90 minutes. The mass spectra and retention time corresponding to the first of these match those of tetramethylsuccinonitrile (TMSN), which is a recombination product of the free radical from AIBN. The mass spectra at 9.03 and 9.52 minutes are consistent with 2,2-dimethyl-4-carbomethoxypentanitrile and 2,2-dimethyl-4-carbomethoxy-4-pentenitrile, respectively, as illustrated in Figure 5. These two products could arise from the initiator-capped end of a PMMA chain and are observable because the chains are relatively short. The mass spectra at 10.92 and 17.90 minutes are consistent with a dimer and a trimer of methyl methacrylate, respectively, as shown in Figure 6.

The dimer and trimer could arise from an intramolecular hydrogen abstraction represented by

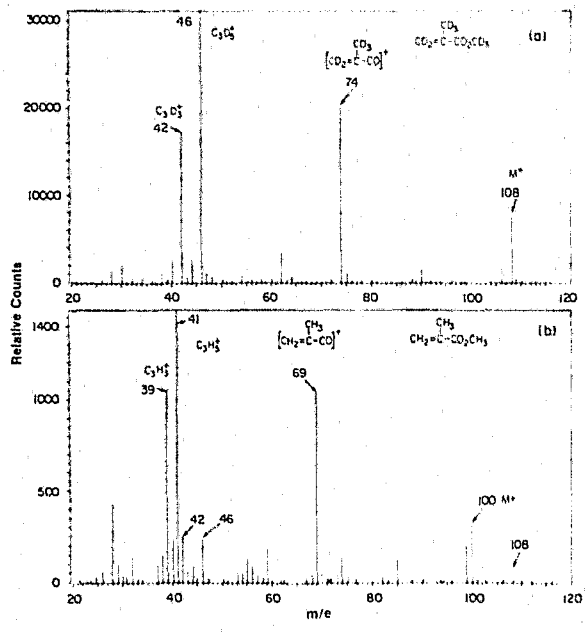

Figure 3. Mass spectra for the pyrolysis products of the blend of poly(methyl methacrylate) and perdeuteropoly(methyl methacrylate). (A) Retention time = 1.55 minutes. (B) Retention time = 1.68 minutes.

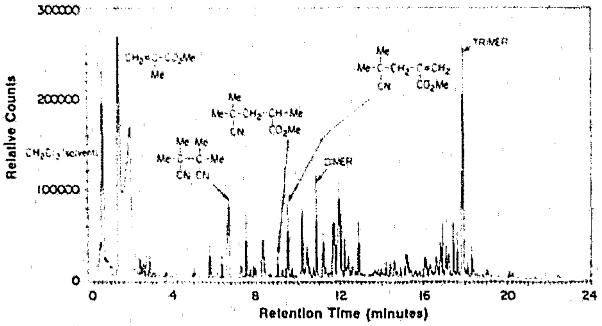

Figure 4. Reconstructed total ion chromatogram for low molecular weight (2.8 x $10^4$) poly(methyl methacrylate) pyrolyzed at 610° C.

$$\cdots CRR'\text{-}CH_2\text{-}CRR'\text{-}CH_2\text{-}(CRR'\text{-}CH_2)_n\text{-}CRR'\text{-}CH_2\bullet \rightarrow$$
$$\cdots CRR'\text{-}CH_2\bullet + CRR'{=}CH\text{-}(CRR'\text{-}CH_2)_n\text{-}CRR'\text{-}CH_3$$

where n = 0, 1 ... . This transfer presumably occurs during the chain depolymerization. The remaining products appear to arise from random cleavages. The increased participation of these latter two processes, hydrogen abstraction and random cleavage, compared to their occurrence with high MW (greater than 100,000) PMMA may be a consequence of the increased importance of

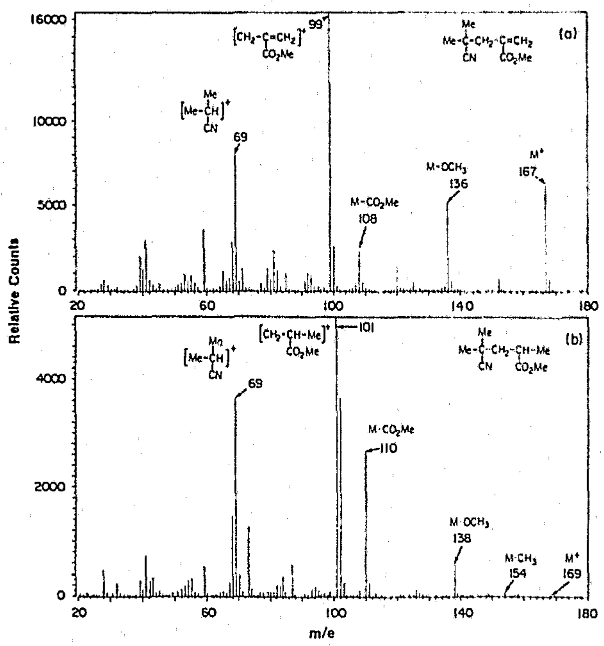

Figure 5. Mass spectra of the pyrolysis products of low molecular weight poly(methyl methacrylate). (A) Retention time = 9.52 minutes. (B) Retention time = 9.03 minutes.

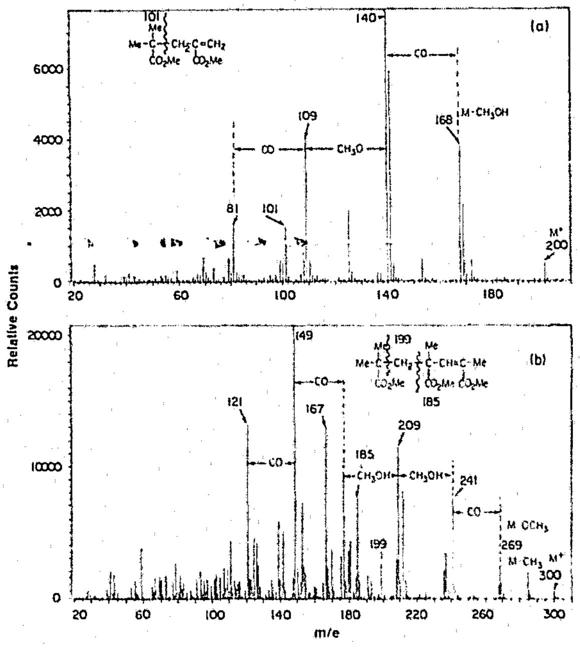

Figure 6. Mass spectra of the pyrolysis products of low molecular weight poly(methyl methacrylate). (A) Retention time = 10.92 minutes. (B) Retention time = 17.90 minutes.

the ends of the chain in the degradation of short polymers. Except for methyl methacrylate, only TMSN is detected when the sample is flash heated to 250° C, showing that only TMSN of the unexpected pyrolysates is a residual of the polymer synthesis (Figure 7). The pyrolysis products observed here appear to reflect that this PMMA was synthesized with AIBN as the initiator and that the MW is relatively low. The observation of compounds that could be polymer end segments suggests the possibility of probing polymer end-groups by Py-GC/MS, providing, of course, that the polymers are low enough in MW.

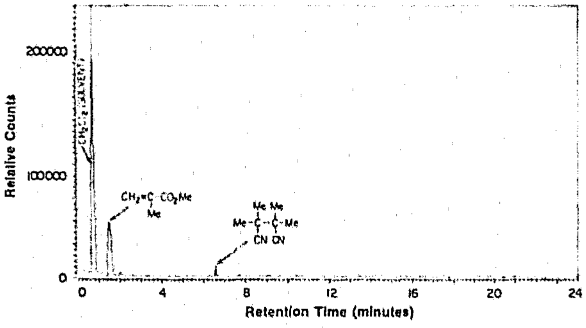

Figure 7. Reconstructed total ion chromatogram for the 250° C flash heating of low molecular weight poly(methyl methacrylate).

## Polystyrene (PS)

Polystyrene is an example of a polymer that thermally degrades by unzipping with a substantial amount of intramolecular hydrogen abstraction (David 1975). Figure 8 shows the total ion pyrograms for PS and perdeuteropolystyrene (PSd); they are remarkably similar. In fact, for every compound observed for PS there is an analogous compound for PSd, which suggests that there is little or no qualitative difference in the mechanism for thermal degradation for these two polymers. The structures of the pyrolysis products of PS were assigned by Sugimura *et al.* (1981). The assignments for PSd were made by analogy with these. The mass spectra of the dimers and trimers of PS are compared with those of PSd in Figures 9 and 10, respectively. The major products, monomer, dimer, and trimer, are consistent with the proposed mechanism. These particular dimers and trimers are consistent with head-to-tail PS (Sugimura *et al.* 1981). The 1,2-diphenylethane is not and suggests the presence of a few head-to-head linkages. Many other minor products, including toluene and 2-phenylpropene, suggest some participation of random cleavage. As Sugimura *et al.* (1981) illustrated for PS, the pyrolysis products can provide sequencing information. We observe here that the sequencing for PSd appears to be very similar to that for PS.

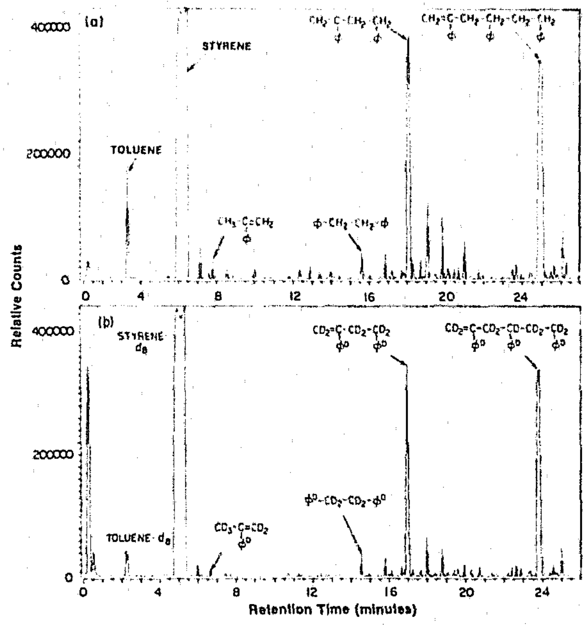

Figure 8. Reconstructed total ion chromatogram for the 610° C pyrolysis of (a) polystyrene and (b) perdeuteropolystyrene. $\phi^D$ represents perdeuterophenyl.

To go one step further, we now compare the pyrolyses of atactic and isotactic PS (Figure 11). The difference in the pyrolysis products lies not in the presence or absence of a given component, but rather in the relative abundance of some of the products. The most striking is the reduced yield of the styrene trimer in isotactic PS. We can rationalize this if we consider the conformation of isotactic PS and the mechanism for the generation of the trimer. Isotactic polystyrene has the $3_1$ helical conformation in the crystalline state (Natta 1960). Wall *et al.* (1955) attributed the formation of the styrene trimer to intramolecular hydrogen abstraction:

$$\cdots CH_2\text{-}CHR\text{-}CH_2\text{-}CHR\text{-}CH_2\text{-}CHR\text{-}CH_2\text{-}CHR^{\bullet}\longrightarrow$$
$$\cdots CH_2\text{-}CHR^{\bullet} + CH_2{=}CHR\text{-}CH_2\text{-}CHR\text{-}CH_2\text{-}CH_2R$$

The helical conformation illustrated in Figure 12 shows that the proton on the 5-carbon is poorly placed for abstraction by the free radical at the end of the chain. This could certainly affect the probability of trimer formation and consequently its relative yield.

## Poly(4-vinylpyridine) (PVP)

Having investigated polystyrene in some detail, it would be of interest to examine poly(vinylpyridine)

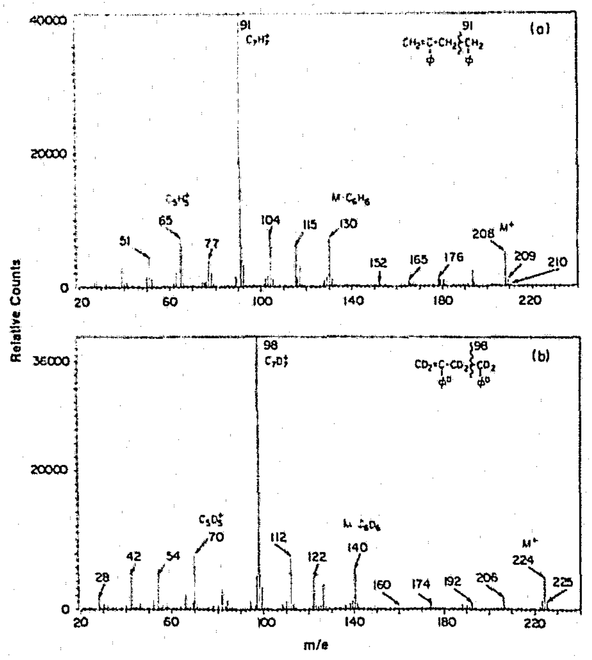

Figure 9. Mass spectrum of the pyrolysis product of (a) polystyrene, retention time = 17.02 minutes and (b) perdeuteropolystyrene, retention time = 16.93 minutes. $\phi^D$ represents perdeuterophenyl.

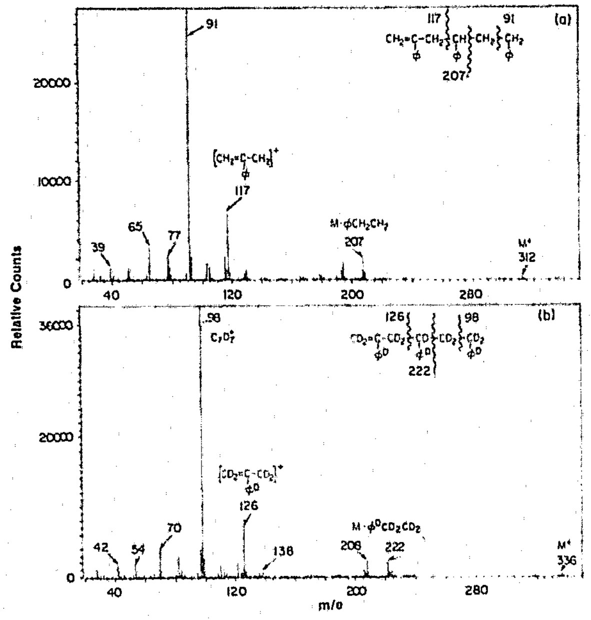

Figure 10. Mass spectrum of the pyrolysis product of (a) polystyrene, retention time = 23.80 minutes and (b) perdueteropolystyrene, retention time = 23.70 minutes. $\phi^D$ represents perdeuterophenyl.

to see if these two polymers behave similarly. The pyrogram for PVP is shown in Figure 13 along with some of the structure assignments, which are based on their respective mass spectra. The major products are similar to those observed for PS. The high yield of the monomer suggests that PVP unzips, and the presence of a dimer and a trimer suggests the participation of intramolecular hydrogen abstraction. The evolution of methylated pyridine and vinylpyridines suggests some random chain cleavage. The structure of the dimer and trimer deduced from their mass spectra suggests a preponderance of head-to-tail linkages, but there is ample evidence for the presence of some head-to-head linkages, for example, 1,2-dipyridylethane (Figure 14). Qualitatively, PVP appears to behave very similarly to PS upon pyrolysis.

## Polystyrene-co-*n*-butyl acrylate (PS/PBA)

It is reasonable to assume that the pyrolysis of copolymers should yield more than simply the sum of the individual monomers. This appears to be the case for the pyrolysis of PS/PBA (Figure 15). The PS contributions appear to be styrene monomer, dimer and trimer, and the PBA contributions appear to be butene, butanol, and butyl acrylate monomer and dimer. In addition, there are what appear to be two hybrid dimers, 2-carbobutoxy-4-phenylbutene and 2-phenyl-4-carbobutoxybutene, and at least two hybrid trimers, one containing one styrene unit and the other containing two styrene units. The mass spectra and tentative structures of the hybrids are shown in Figures 16 and 17. These hybrids suggest that the arrangement of styrene and butyl acrylate is random. Since this copolymer was synthesized with a 3:1 ratio of styrene to butyl acrylate, we would expect more styrene dyads than butyl acrylate dyads in the pyrolysis products. This appears to be the case. Thus, the pyrolysis products have given us information about the monomer sequencing in this copolymer. These results are analogous to those of Tsuge *et al.* (1975) on polystyrene-co-methyl acrylate.

## Polystyrene-co-*n*-butyl acrylate-co-divinylbenzene (PS/PBA/DVB)

Cross-linking agents, when used in small amounts, are difficult to detect in polymers. The pyrogram for PS/PBA/DVB is similar to that of PS/PBA in its major features. The only recognizable difference occurs in the retention time region of 9-10 minutes (Figure 18). The four peaks that

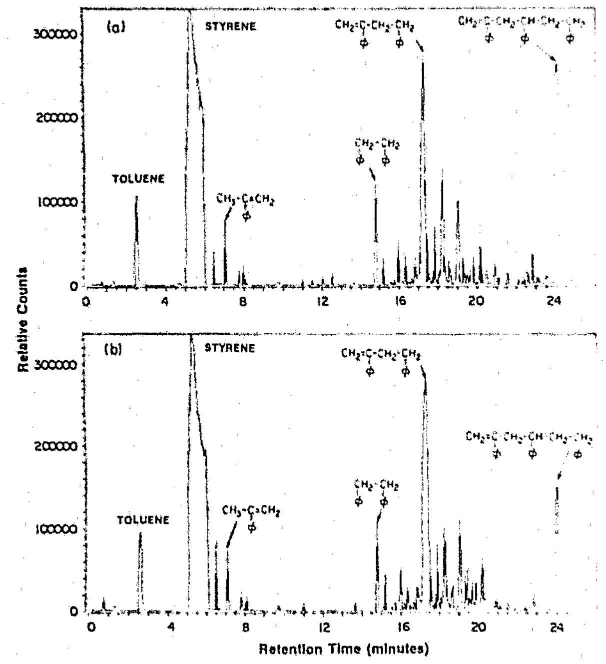

Figure 11. Reconstructed total ion chromatogram for the 610° C pyrolysis of (a) atactic polystyrene and (b) isotactic polystyrene.

occur for the copolymer with the cross-linking agent have been identified as *m*- and *p*-ethylstyrene and *m*- and *p*-divinylbenzene. All four of these are observed in the commercial DVB used to synthesize this copolymer in approximately the same relative ratios observed here. These compounds are not observed in the pyrolysates of the PS/PBA without DVB. These four compounds can thus serve as an indicator for DVB. This particular polymer was formulated with 0.58 weight percent of the mixture, and we have easily detected it at the 0.10 weight percent level.

### Poly(vinylidene chloride) (PVDC), Polyacrylonitrile (PAN), Blend and Copolymer

Poly(vinylidene chloride) is an example of a polymer that thermally decomposes via two competing processes. One is unzipping, which generates monomer, and the other is a sequential process in which a neutral molecule, HCl in this case, is eliminated, followed by cyclization to form substituted benzene (Tsuge *et al.* 1969). The pyrogram for PVDC is shown in Figure 19. Vinylidene chloride, HCl and 1,3,5-trichlorobenzene are the expected products. The other chlorinated aromatic hydrocarbons are, by extension, the end result of HCl elimination and cyclization. The other chlorinated benzenes suggest that there are some head-to-

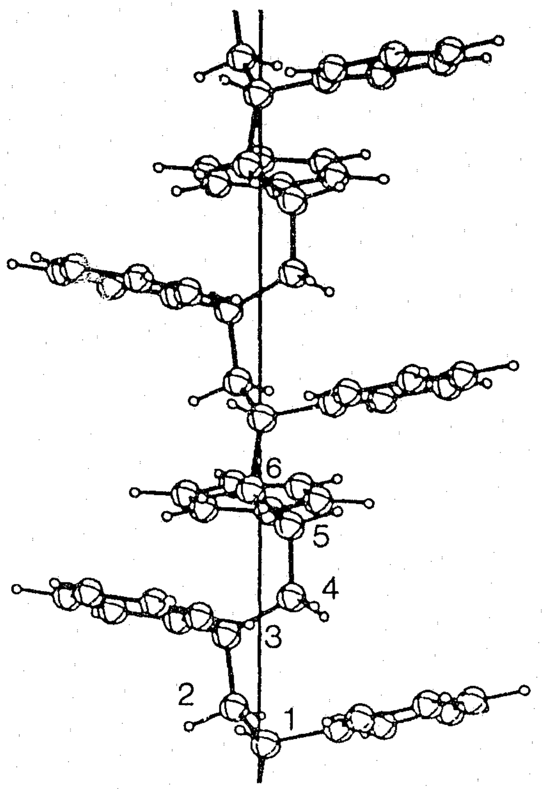

Figure 12. Representation of the $3_1$ helical conformation of isotactic polystyrene.

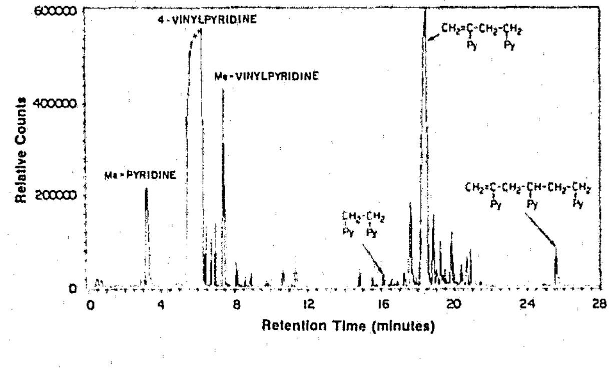

Figure 13. Reconstructed total ion chromatogram for the 610° C pyrolysis of poly(4-vinylpyridine). Py denotes 4-pyridyl.

head and tail-to-tail sequences in this PVDC. The homologous series of compounds starting with octylphenol are residues of a commonly used surfactant, Triton 770, which was used in the emulsion polymerization of this polymer. It is clear that re-

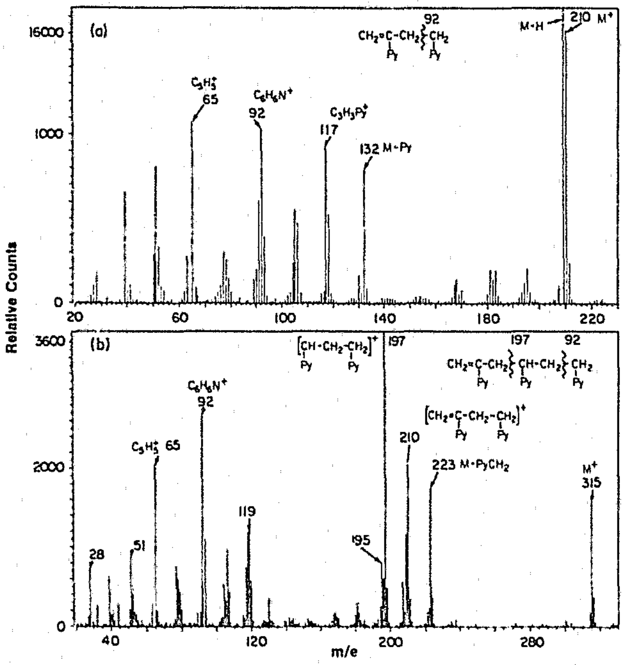

Figure 14. Mass spectra of the pyrolysis products of poly(4-vinylpyridine). (A) Retention time = 18.25 minutes. (B) Retention time = 25.65 minutes. Py represents 4-pyridyl.

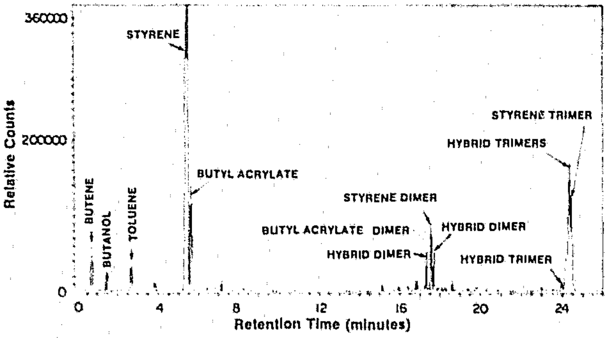

Figure 15. Reconstructed total ion chromatogram for the 610° C pyrolysis of polystyrene-co-*n*-butyl acrylate.

siduals like these can give information about how an unknown polymer was synthesized.

The pyrolysis of PAN yields a pyrogram with very broad bands (Figure 20). The mass spectra corresponding to these bands show that they are composed of several overlapping peaks. Unfortunately, only a few of these compounds have been identified. The presence of the monomer, dimer and trimer of acrylonitrile suggests that unzipping and intramolecular hydrogen abstraction occur. Although HCN is a neutral elimination product, we

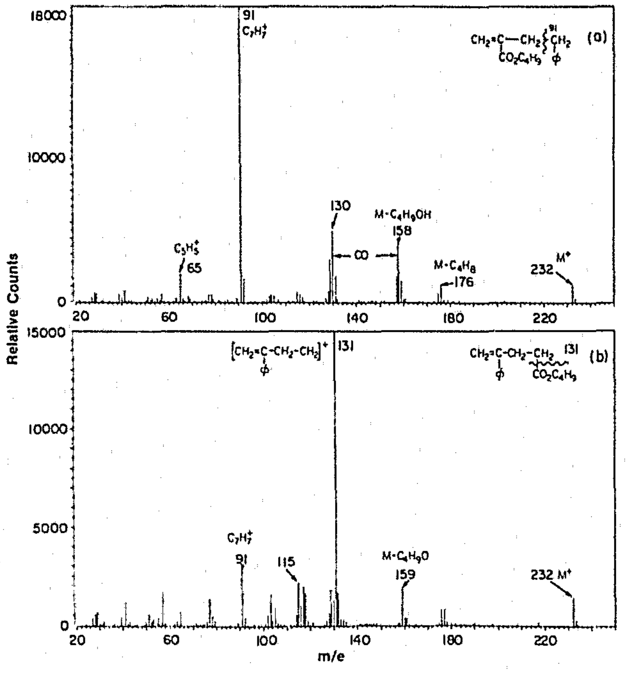

Figure 16. Mass spectra of the pyrolysis products of polystyrene-co-*n*-butyl acrylate. (A) Retention time = 17.31 minutes. (B) Retention time = 17.69 minutes.

find no recognizable evidence for cyclization, that is, aromatic compounds. Acetonitrile is probably a random cleavage product. The broad bands may be due to a multitude of random cleavage products as well as to poor chromatography. Once again we observe TMSN, which suggests that this polymer was free-radical initiated with AIBN.

The pyrogram of the 40/60 blend of PVDC/PAN is, for the most part, the sum of the individual pyrograms (Figure 21). Although all the major products of PVDC and PAN are present, there are several new products, which are unidentified and unexplained at this time. The important point is that there is no recognizable evidence for compounds containing both chlorine and nitrogen.

The pyrogram for the 40/60 copolymer PVDC/PAN is different in character from that for the blend (Figure 22). Noticeably absent are the broad bands. Present are HCN and the monomer, dimer and trimer of acrylonitrile previously observed for PAN. Also present are HCl and vinylidene chloride previously observed for PVDC. There is no recognizable evidence for any compounds containing three or more chlorines, which suggests that the number of vinylidene chloride triads is low. The presence of several products with both chlo-

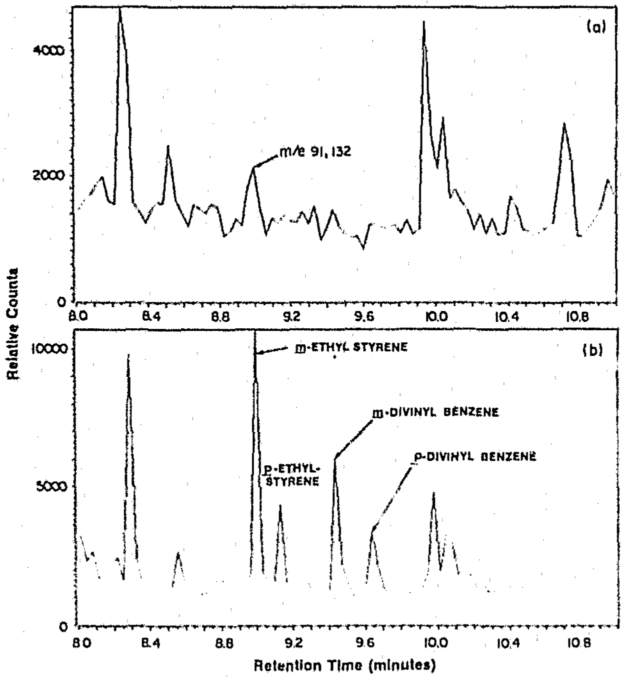

Figure 17. Mass spectra of the pyrolysis products of polystyrene-co-*n*-butyl acrylate. (A) Retention time = 23.98 minutes. (B) Retention time = 24.22 minutes.

rine and nitrile substitution suggests that this polymer is random and not blocked. The mass spectrum and a possible structure for one of the prominent chromatographic peaks are presented in Figure 23. Further details about the microstructure of this polymer are probably hidden in the uninterpreted features of the pyrogram. The acquisition of this information rests, of course, on the identification of numerous compounds for which we have mass spectra and retention data but have not deciphered.

## Poly(2-hydroxyethyl methacrylate) (PHEMA) and Its Trimethylsilyl (TMS) Derivative

Derivatization of pyrolysis products is useful not only for identification but also for simplification of a pyrogram. For example, Sugimura *et al.* (1981) successfully used on-line pyrolysis/hydrogenation to characterize head-to-head polystyrene. We present here another technique that is useful for polymers that contain free acid or alcohol functional groups. Figure 24 shows pyrograms for PHEMA before and after silylation. The polymer was derivatized with *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) before pyrolysis. The pyrogram for the TMS derivative is much improved in quality, and the oxygen silicon bond survived the pyrolysis.

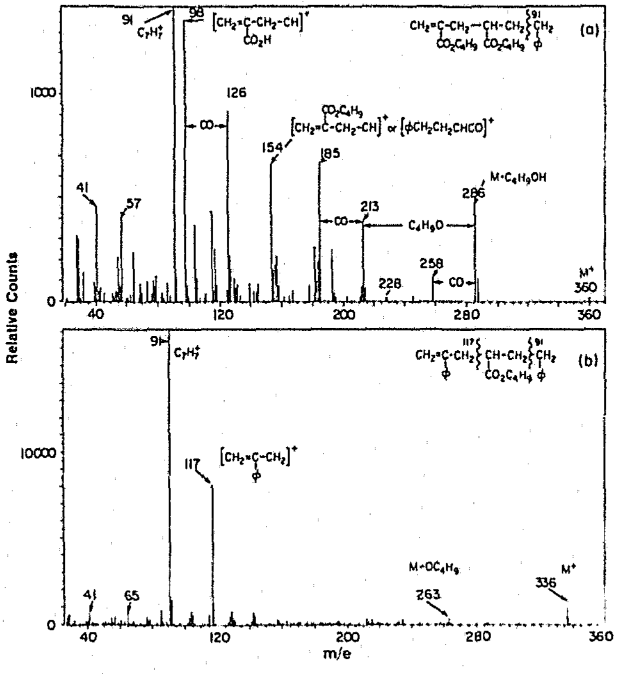

Figure 18. Reconstructed total ion chromatogram for the 610° C pyrolysis of (a) polystyrene-co-*n*-butyl acrylate and (b) polystyrene-co-*n*-butyl acrylate-co-divinylbenzene.

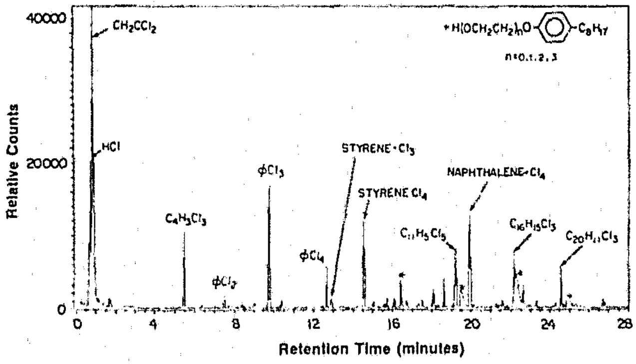

Figure 19. Reconstructed total ion chromatogram for the 610° C pyrolysis of poly(vinylidene chloride).

## CONCLUSIONS

We have applied Py-GC/MS to a variety of vinyl polymers, copolymers and blends. Examining the details of a pyrogram can reveal a great deal about the microstructure (monomer linkages and sequencing) of a polymer sample and, in some cases where residuals can be identified, can reveal the method of synthesis. Furthermore, the pyro-

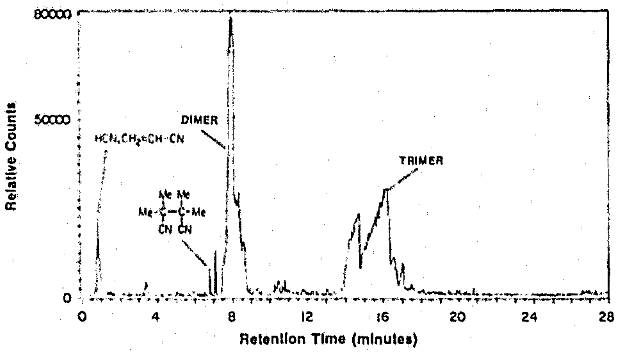

Figure 20. Reconstructed total ion chromatogram for the 610° C pyrolysis of polyacrylonitrile.

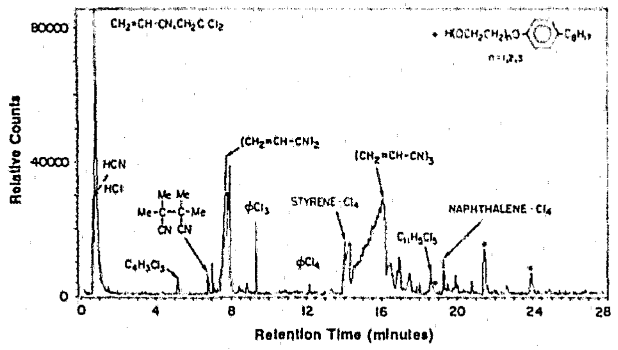

Figure 21. Reconstructed total ion chromatogram for the 610° C pyrolysis of the 40/60 blend of poly(vinylidene chloride) and polyacrylonitrile.

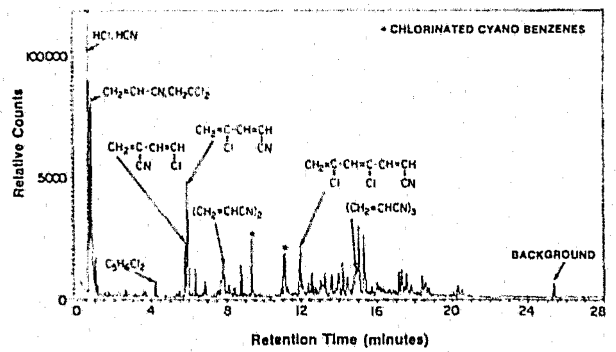

Figure 22. Reconstructed total ion chromatogram for the 610° C pyrolysis of the 40/60 blend of poly(vinylidene chloride)-co-acrylonitrile.

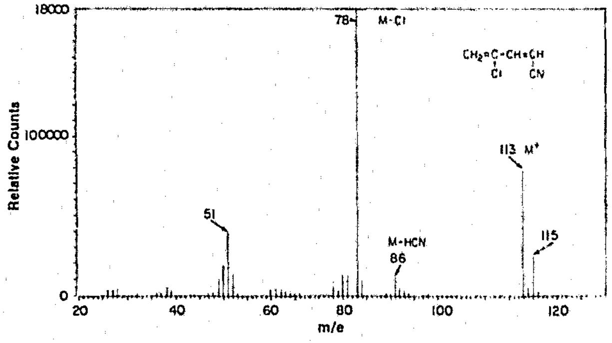

Figure 23. Mass spectrum for the pyrolysis product of poly(vinylidene chloride)-co-acrylonitrile with a retention time of 5.93 minutes.

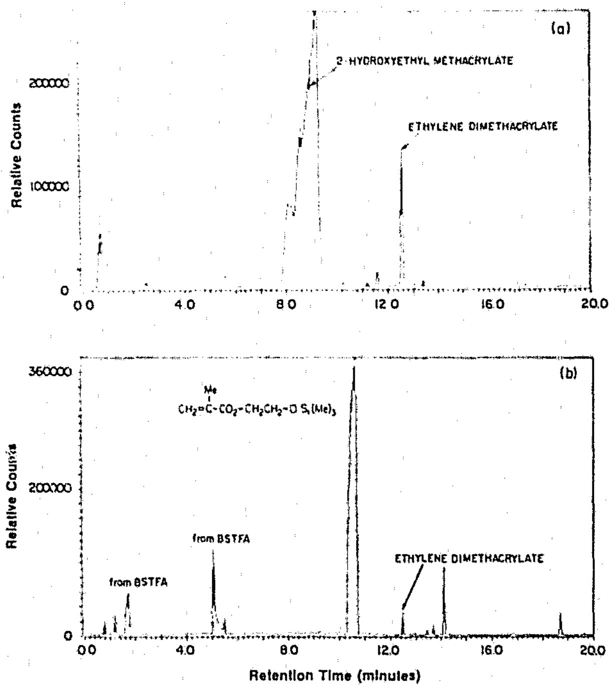

Figure 24. Reconstructed total ion chromatogram for the 610° C pyrolysis of (a) poly(2-hydroxyethyl methacrylate) and (b) its trimethylsilyl derivative.

gram was sensitive to the tacticity of polystyrene and to the MW of PMMA, where we were able to detect and identify polymer end segments. We also demonstrated the ability to detect small amounts of the cross-linking agent, divinylbenzene. Finally, we demonstrated the use of TMS derivatization of poly(2-hydroxyethyl methacrylate) to improve the chromatography of its pyrolysis products.

## ACKNOWLEDGMENT

I gratefully acknowledge R. A. Guistina, Dr. J. M. O'Reilly, L. J. Sorrierro, R. C. Sutton, Dr. R. L. Whitlock and Dr. N. Zumbulyadis for the various polymer samples, Dr. A. Leslie Stanford of duPont for samples of PMMAd, F. M. Michaels for NMR measurements on isotactic polystyrene, and M. T. Thomas for the determination of the molecular size distribution of PMMA. I also thank R. A. Guistina, R. C. Sutton, Dr. R. L. Whitlock, Dr. G. A. Russell, and J. M. O'Reilly for helpful discussions. A special thanks is in order for T. C. Brown, who performed almost all of the Py-GC/MS experiments.

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## DISCUSSION

*Question:* You indicated the importance of the small components to be able to get some clues to the microstructure of the polymer. What suggestions would you have to enhance the ability to identify the materials and to enhance their increased concentration?

*Kawaoka:* There are a variety of things that can be done. Of course, the first thing is incorporation of the usage of complementary techniques, such things as pyrolysis-gas chromatography-infrared, which we have started to do. With the advent of macrobore capillary columns, that becomes quite a feasible experiment.

That is one of the areas we have been exploring. There are a number of other instrumental techniques that can be employed. The main problem is, of course, if we have a mass spectrum we have to sit there and try to identify from the fragmentation pattern what that particular sample is.

There are numerous mass spectra techniques that can be employed to help you do that. Among them is chemical ionization. If one knows what most of the fragments of interest are, one can do a whole polymer pyrolysis in the cell of a Fourier transform mass spectrometer. Essentially one does an ion separation and then MS-MS experiments on that particular ion to help identify the compounds.

What we found actually works the best is, of course, just a matter of experience. Given time, we can work out the structure of most of the compounds and gradually build up a library for these polymers, a mass spectra library, that is. We have a compilation of mass spectra and a compilation of pyrograms. What we are trying to do at the present time is to put all of these onto a single data system and integrate the whole system so that we can do linked searches of those materials.

*Ryland:* Are you aware of any detectable parameters that you see change with crystallinity changes or molecular weight changes in polymers, based upon Py-GC?

*Kawqoka:* Yes, for molecular weight changes, to a certain extent. The first example, one of the dramatic examples of that, is poly(methy acrylate), which has been studied extensively, and that particular polymer we know gives almost quantitative yield under certain conditions of the monomer.

What we found was that by reducing the molecular weight, we got different products, and presumably that was just the influence of the initiator itself.

In terms of crystallinity, in my experience, we have not seen anything that would tell us anything about cyrstallinity.

*Munson:* You mentioned the various clues that you see in the data that can give you information about the synthesis process. I know you look at other manufacturers' products. Would you comment on how useful those clues are in being able to distinguish one batch of polymers from another when it is obstensibly the same material but maybe from a different manufacturer?

*Kawaoka:* I do not have a great deal of experience in looking at the same polymers from different manufacturers. What we have had experience in is looking at polymers which presumably go through the same synthetic process, but for some reason end up being different.

The pyrograms in those cases are distinctly different. You can tell the difference from lot to lot, and what we usually trace that to is not so much the process, but that the starting materials were altered. For example, different lots of initiators will have different compositions and they affect the polymerization process. We can at times actually see something that is not supposed to be there. Most of the time what we see are just changes in relative intensities of the various pyrolysis products; that is, the yield of products changes. But those kinds of things are indeed detectable or distinguishable.

*Fetterolf:* Have you looked at the effect of weathering on the pyrograms of polymers after they have been exposed to the sun and rain and such? How does that change the pyrograms?

*Kawaoka:* No, we have not looked at the effects of weathering. I suspect that those really should be distinguishable because for one, we know that weathering, photochemical changes, for example, changes the structure of the materials and we also can get introduction of oxygen into the polymers. Those kinds of things should be detectable.

# FORENSIC ANALYSIS OF POLYMERS AT THE METROPOLITAN POLICE FORENSIC SCIENCE LABORATORY

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London, England

Prior to the 1960s forensic contact trace analysis of polymeric materials primarily utilized microscopy but the limitations of visual examination, particularly in the field of single layer paint comparisons, led to the widespread use of emission spectrography as a complementary technique. Despite the gains made by including trace metal screening in the analytical scheme, the failure to obtain information about the organic constituents was a cause for concern. The first commercial gas chromatographs became available in the early 1950s but initially they had little impact in the forensic world, despite the fact that workers in the polymer field rapidly anticipated the scope of combining pyrolysis with the new separative method (Davison *et al.* 1954). In the next 10 years the pioneering workers in the field of pyrolysis gas chromatography (Py-GC) brought the method to a state where it could be considered routine and the forensic potential for polymer analysis was increasingly appreciated (Jain *et al.* 1964). Thereafter, Py-GC attained broad acceptance in forensic laboratories and the progress made has been reviewed by Wheals (1981) and Irwin (1982). Initially, Py-GC was used almost exclusively as a "fingerprinting" technique, but studies made by linking the apparatus to a mass spectrometer, that is, pyrolysis gas chromatography mass spectrometry (Py-GC/MS), enabled many common pyrolysis products to be identified (May *et al.* 1973; Noble *et al.* 1974), thereby placing the method on a more sound scientific basis. Before the mid 1970s few forensic laboratories had their own mass spectrometer but since then the use of GC/MS has become an accepted way of characterizing drugs and the presence of such equipment opened up new opportunities for researchers wishing to evaluate pyrolysis mass spectrometry (Py-MS) as a technique. In 1977, the forensic application of Py-MS was first reported (Saferstein 1977; Hughes *et al.* 1977), but very few forensic laboratories have subsequently exploited the procedure. The Metropolitan Police Forensic Science Laboratory (MPFSL) is an exception to this generalization. This report describes our experience of operating both Py-GC and Py-MS as analytical services over a period of several years.

## Definitions of the Various Pyrolysis Methods

The growing analytical importance of pyrolysis has led to a proliferation of "hyphenated" techniques in this field and it is important to appreciate the difference between Py-GC, Py-GC/MS and Py-MS. Figure 1 illustrates the three techniques in schematic form and it will be noted that it is in the treatment of the pyrolysate that they differ. In Py-GC the pyrolysis products are separated on a gas chromatographic column and are usually detected as they elute from this with a non-selective monitoring device such as a flame ionization detector. The chromatographic trace is termed a pyrogram. Substituting a mass spectrometer for the flame ionization detector leads to Py-GC/MS. With Py-MS, however, the chromatographic separation is omitted and the pyrolysate, preferably in a homogeneous state, passes into the mass spectrometer where the mixture is fragmented with an electron beam (directly or indirectly) and the resulting positive ions which are formed are separated to produce a mass spectrum. The mixed mass spectrum is termed a mass pyrogram.

Although Py-GC/MS has proven useful in helping to characterize the identity of individual pyrolysis products it has not found routine application at the MPFSL. The other two procedures will now be considered.

## Py-GC at the MPFSL

Experiments with Py-GC commenced in about 1967 but it was not until the Curie Point pyrolyzer became commercially available in about 1970 that substantial progress was made. Paint comparison and characterization were already recognized as the major area of application. Initially experiments were concentrated on selecting gas chromatographic and pyrolysis conditions which gave paint pyrograms of maximum complexity - the assumption being that the more peaks available the more discriminatory the analysis. The results were reported by Wheals and Noble (1972), and the experimental conditions selected at that time (Table 1) are still in use today. By 1973 over a thousand samples a year were being submitted for analysis. Table 2 shows the pattern of submissions at that time. The subsequent history of Py-GC at the MPFSL has been one of declining use. In the last 5 years the decline has increased rapidly as the alternative technique of Py-MS has taken over. Table 3 shows the pattern of submissions in recent years. Despite the overall decline in the use of pyrolytic techniques, the types of samples examined has not greatly altered over the last decade as is shown in Table 4.

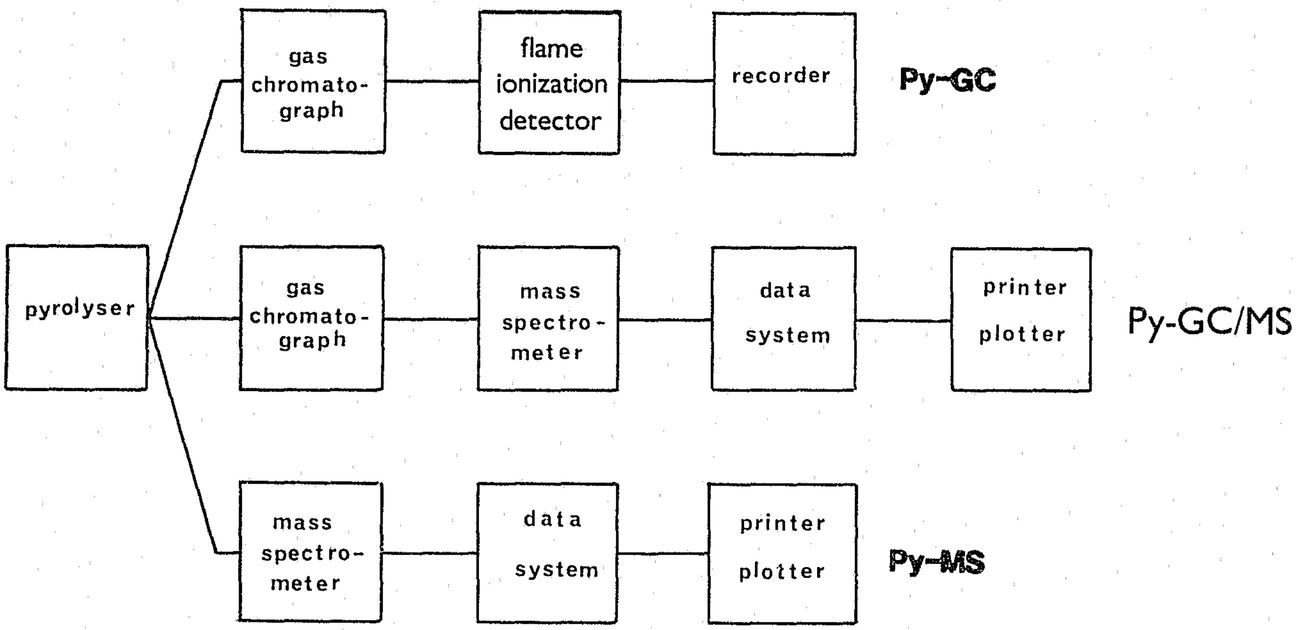

Figure 1. A schematic diagram showing the instrumental differences between Py-GC, Py-GC/MS and Py-MS.

Table 1. CONDITIONS FOR PYROLYSIS GAS CHROMATOGRAPHY AS USED AT THE METROPOLITAN POLICE LABORATORY

| | |
|---|---|
| Column: | 4 m stainless steel column of 2.2 mm i.d. containing 15 percent Carbowax 20 M on Chromosorb P (80-100) mesh |
| Carrier gas: | Nitrogen at 30 ml/min |
| Detector: | Flame ionization detector |
| Temperature: | 70 - 190° C at 10° C/min, then isothermal for 15 min |
| Pyrolysis conditions: | Curie Point Pyrolyser 10 sec burn at 610° C |
| Sample size: | 10 - 50 μg |

Part of the trend of declining use of pyrolysis methods at the MPFSL can be explained by the changing patterns of casework, with a greater emphasis now being placed on marks evidence (for example, shoe prints, tool marks, etc.) than was the case in the early 1970s. Nevertheless, the decreased use of Py-GC relative to Py-MS is attributable to quite a different set of circumstances and it is these which I hope to bring out subsequently.

Table 2. SAMPLE SUBMISSIONS FOR PYROLYSIS GAS CHROMATOGRAPHY IN 1973

| | |
|---|---|
| Vehicle paints | 35% |
| Decorative gloss paints | 33 |
| Tool paints | 4 |
| Emulsion paints | - |
| Adhesives | 7 |
| Plastics/plastic tapes | 6 |
| Bitumens | 6 |
| Rubbers/foams | 4 |
| Miscellaneous | 5 |
| Total samples | 1040 |

Table 3. SAMPLES SUBMITTED FOR ANALYSIS BY PYROLYSIS TECHNIQUES

| Technique | Number of samples submitted in year shown | | | | |
|---|---|---|---|---|---|
| | *1979* | *1980* | *1981* | *1982* | *1983* |
| Pyrolysis gas chromatography | 410 | 318 | 280 | 180 | 73 |
| Pyrolysis mass spectrometry | 80 | 86 | 160 | 406 | 407 |

Table 4. A COMPARISON OF SAMPLE TYPES, PYROLYSIS GAS CHROMATOGRAPHY IN 1973, PYROLYSIS MASS SPECTROMETRY IN 1983

| | Pyrolysis Gas Chromatography | Pyrolysis Mass Spectrometry |
|---|---|---|
| Vehicle paints | 35% | 28% |
| Decorative gloss paints | 33 | 23 |
| Tool paints | 4 | 4 |
| Emulsion paints | - | 3 |
| Adhesives | 7 | 14 |
| Plastics/plastic tapes | 6 | 15 |
| Bitumens | 6 | 2 |
| Rubber/foams | 4 | 6 |
| Miscellaneous | 5 | 5 |

The caseworker submitting samples to the analyst is invariably seeking answers to the following questions:

1. What is it?
2. Are A and B the same?
3. If they are the same, how significant is this?

Thus in the context of forensic paint analysis, it would be useful to know the resin class, and in the event of having matching pyrograms to provide some guidance on the significance of the result, for example, is the resin class unusual, have similar pyrograms been obtained before, etc. Classifying a paint into resin class proved to be quite easy, particularly with vehicle paints (Wheals and Noble 1974). It was found that three different types of resin were commonly encountered and that within-class discrimination was often high, particularly when several component peaks were present as was often found with thermosetting acrylics. Decorative gloss paints posed a more difficult problem however, for although the resin class was quite distinctive, the differences within the class were small. In the UK decorative paint is formulated from alkyd resins (polyesters produced from phthalic acid, polyols, and unsaturated fatty acids or natural drying oils). When polymerized in the paint film the alkyd forms a complex three-dimensional network structure in which appreciable cross-linking occurs between the double bonds of the fatty acid chains (Figure 2). Pyrolysis under the conditions described earlier produces a complex pyrogram from an alkyd resin. The pyrogram is dominated by three major peaks. By using Py-GC/MS we were able to charactize these products as acrolein, methacrolein and benzene, and their precursors in the resin matrix were deduced to be glycerol, pentaerythritol, and phthalic anhydride (Figure 3). It was found by replicate analysis that benzene was formed less reproducibly than the other two products. Typical data are shown in Table 5. It was subsequently found that acrolein/methacrolein ratios could be used to discriminate between alkyd resins. Table 6 illustrates the type of result that can be obtained. Unfortunately the level of discrimination afforded was inadequate to provide all that was required for this important resin class. It was then hoped to make use of minor chromatographic peaks on the pyrogram to improve the method. Unfortunately this did not provide the answer because the "fine structure" of the pyrograms was difficult to reproduce, despite a rigid standardization procedure which involved pyrolyzing a standard paint at the start of each working day and adjusting the flow rates to bring the retention times of all the major peaks within a tight "window". This procedure, although successful in relation to the major peaks, was inadequate to compensate for minor changes in the pyrograms which we attributed to column ageing and the build up of pyrolysis products on the column packing. Table 7 shows the advantages and disadvantages of Py-GC as we assessed them at that time.

Table 5. PYROLYSIS GAS CHROMATOGRAPHY OF DECORATIVE GLOSS PAINTS, VARIATION OF THE MAJOR PEAKS

| | Mean | Coefficient of variation |
|---|---|---|
| Acrolein/methacrolein | 0.15 | 6.3% |
| Benzene/methacrolein | 0.38 | 39.4% |

Twelve replicate analyses performed.

Table 6. ACROLEIN/METHACROLEIN PEAK HEIGHT RATIOS OF MONTHLY WHITE PAINT BATCHES FROM TWO DIFFERENT MANUFACTURERS

| Month | Manufacturer 1 | Manufacturer 2 |
|---|---|---|
| 1 | 0.15 | 0.81 |
| 2 | 0.15 | 0.64 |
| 3 | 0.70 | 0.97 |
| 4 | 0.15 | 0.47 |
| 5 | 0.12 | 0.81 |
| 6 | 0.12 | 0.99 |
| 7 | 0.11 | 0.92 |
| 8 | 0.13 | 0.62 |
| 9 | 0.13 | 0.82 |
| 10 | 0.14 | 0.42 |
| 11 | 0.81 | 0.54 |

Table 7. CONCLUSIONS ABOUT THE FORENSIC USES OF PYROLYSIS GAS CHROMATOGRAPHY CA 1975

| Advantages | Disadvantages |
|---|---|
| 1. Sensitive (ca 10 μg) | 1. Relatively slow (ca 30 min) |
| 2. Easy to use | 2. Some polar products not eluted |
| 3. Qualitative analysis good | 3. Inadequate discrimination of unmodified alkyds |
| 4. Some discrimination by peak ratioing | 4. Chromatographic variation creates problems for data storage and comparison |
| 5. Py-GC/MS permits the characterization of the pyrolysate | |

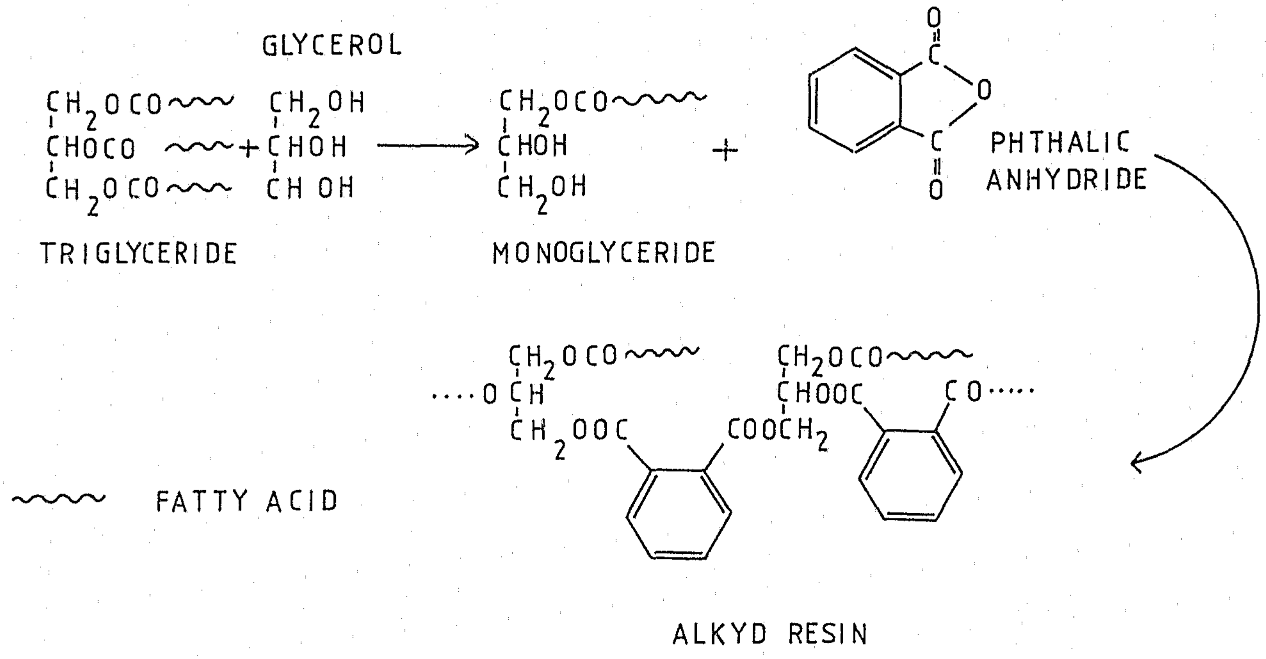

Figure 2. A simple representation of the formation of an alkyd resin.

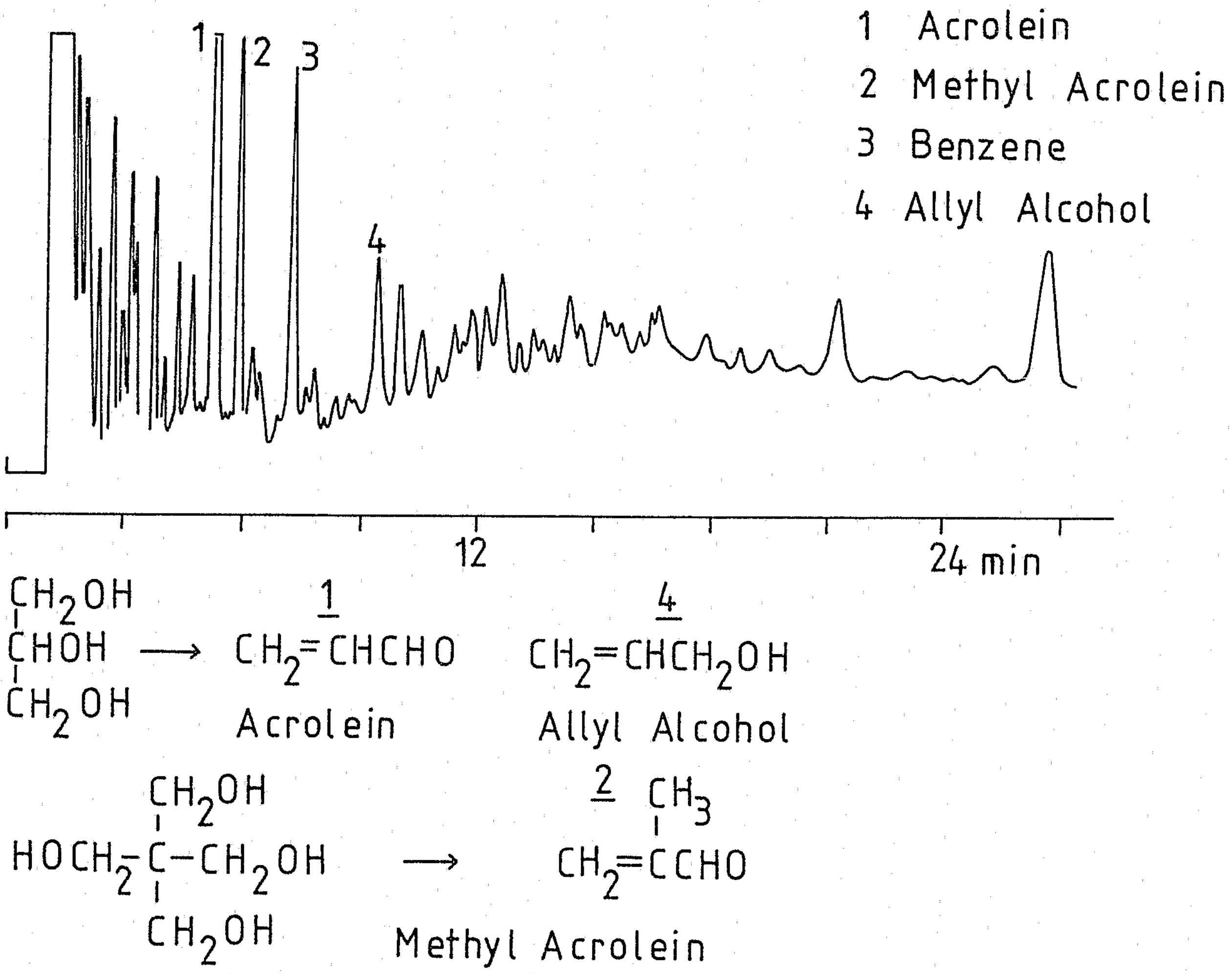

Figure 3. A pyrogram of an alkyd resin showing the major pyrolysis products and their likely precursors. The chromatographic conditions used are described in Table 1.

## Py-MS at the MPFSL

In 1974 the MPFSL purchased its first mass spectrometer but it was not until the spring of 1976 that studies were commenced on Py-MS. The way in which we decided to undertake Py-MS was considerably constrained by the need to maintain a routine GC/MS service for drug characterization. Thus we required a Py-MS system that could rapidly be switched back to GC/MS. Our solution to the problem was to introduce the pyrolysate through the same heated line and jet separator used for the GC eluate, this was reported by Hughes *et al.* (1977). At first samples were pyrolyzed with a Curie Point pyrolyzer swept by helium and then passed into an empty glass tube - 45 cm x 2 mm i.d. - which was held at 200° C in the GC oven. A make-up flow of helium was added at the end of the column to bring the combined flow rate to about 15 ml/min (optimum for the jet separator). Subsequently, a Pyroprobe filament pyrolyzer was found to be more convenient to use as it permitted the pyrolysis to be carried out well inside the oven. A wider and shorter glass expansion tube came into use also - 23 cm x 7 mm i.d., plus a 3 cm x 3 mm i.d. tube joined to it. Only about 9 cm of the first tube was, in fact, used because the Pyroprobe was inserted fully into it. In this later configuration it was also found that no additional make-up flow was required in addition to that flowing through the expansion chamber at 6 ml/min. Figure 4 shows a schematic diagram of the various phases in the development of the MPFSL Py-MS system. Figure 5 illustrates the way in which the Curie Point pyrolyzer was mounted and Figure 6 shows the arrangement used with the Pyroprobe.

The expansion chamber was an essential component in our Py-MS system as it provided a mechanism for spreading out the pyrolysate so that it entered the mass spectrometer over about a minute. This permitted multiple scanning with the magnetic sector mass spectrometer we had available. This type of mass spectrometer scans at a relatively slow rate of 1 sec/decade and then takes another second to reset. Our normal scanning range was from 250 to 25 amu. The normal operating conditions are shown in Table 8. Most of the mass pyrograms we generate are averaged from at least 6 scans and many will be based on over 12 scans, the choice lies with the analyst and varies with sample size, pyrolysate homogeneity, etc. It was sometimes found necessary to deactivate the expansion tube to prevent highly polar products from segregating in passing down the tube, but the wider diameter has also helped to reduce this problem. Tests were carried out to ensure that Py-MS was adequately reproducible, Hickman and Jane (1979), and it was concluded that:

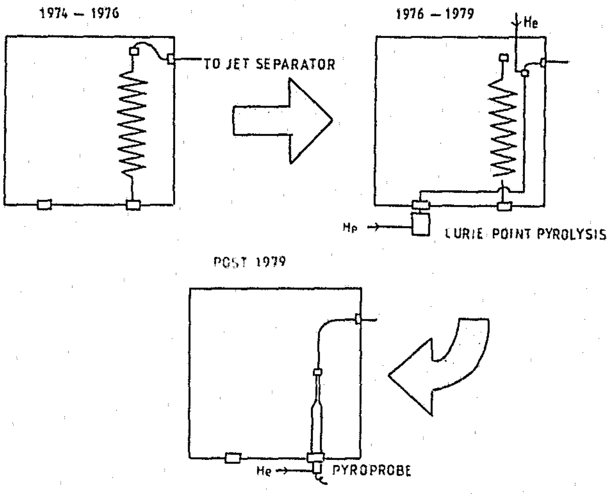

Figure 4. Schematic diagram showing the evolution of the Py-MS system at the Metropolitan Police Forensic Science Laboratory.

1. Mass pyrograms were dependent upon instrument tuning.
2. Mass pyrograms produced from multiple scans were more reproducible than those generated from a single scan.
3. Under optimum conditions Py-MS and Py-GC have a similar level of reproducibility.
4. Differences in reproducibility are found for different ions in the same mass pyrogram.
5. Py-MS had a narrower linear range than Py-GC.

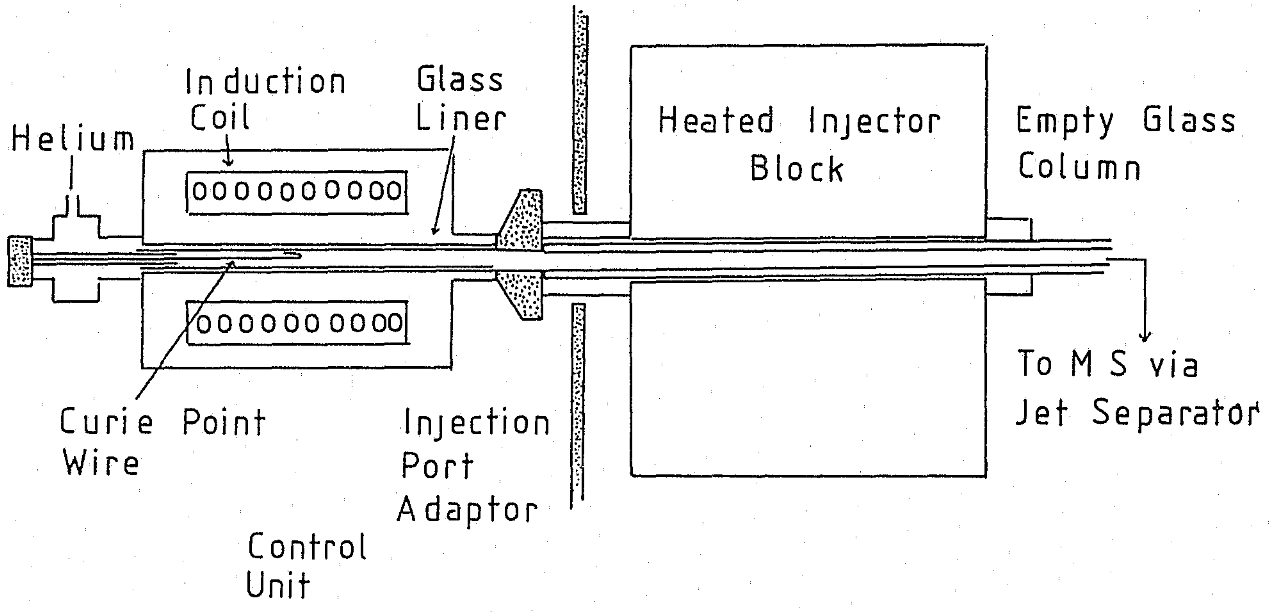

Figure 5. Diagram showing the way in which the Curie Point pyrolyzer was mounted for Py-MS.

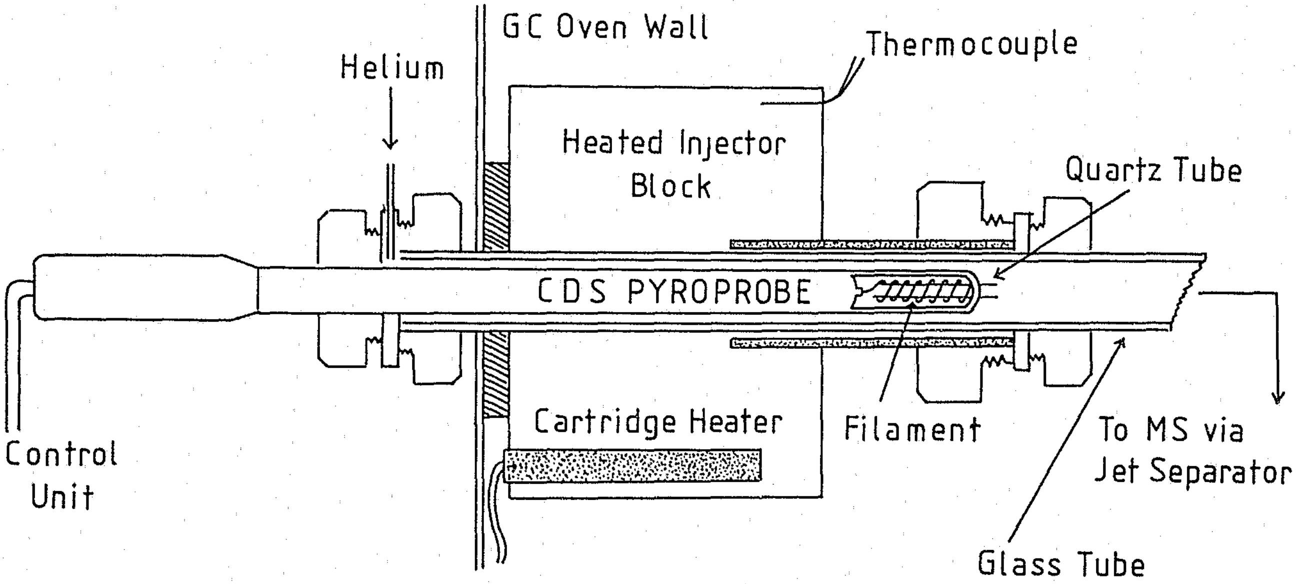

Figure 6. Diagram showing the way in which the Chemical Data System Pyroprobe pyrolyzer was mounted for Py-MS.

Table 8. PYROLYSIS MASS SPECTROMETRY OPERATING CONDITIONS

| | |
|---|---|
| PYROLYSIS | |
| Pyrolyzer | CDS Pyroprobe |
| Temperature | 700° C (nominal) |
| Time | 20 sec |
| MASS SPECTROMETRY | |
| Instrument | Single focussing magnetic sector |
| Mass range | 25 - 250 amu |
| Scan speed | 1 sec/decade<br>1 sec reset |
| Ionization mode | Electron impact 70 eV |

From 1979 onwards Py-MS has been in routine use at the MPFSL and has been applied to the analysis of a very wide range of polymeric samples. The technique has been found to be very sensitive and the minimum sample size is primarily determined by the manipulative skills of the analyst rather than instrumental parameters. An added bonus of the method is that if the sample contains volatile components, for example, residual solvents, plasticizers, etc., it is possible to produce a mass spectrum in the period before initiating pyrolysis (our usual practice is to insert the sample on the pyrolysis probe into the oven and allow it to equilibrate at about 230° C for 5 minutes before pyrolysis). It should be emphasized that Py-MS requires the facilities of a computerized data system for spectral averaging, background subtraction, the elimination of ions associated with air, library storage and comparison of the pyrograms with the reference collection. In the case of our data system the manipulations necessary to generate a pyrogram take about 15 minutes, thus computation is the time-demanding step,'with the data acquisition only requiring about 1 minute.

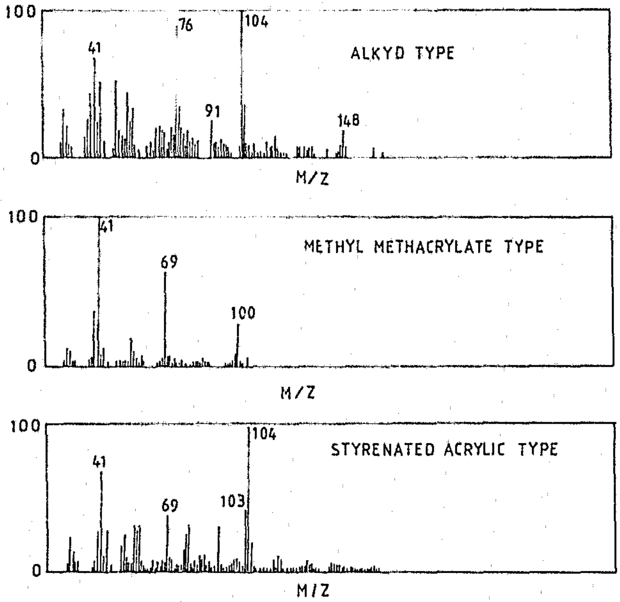

Figure 7. Mass pyrograms of vehicle paints. The conditions used were as described in Table 8.

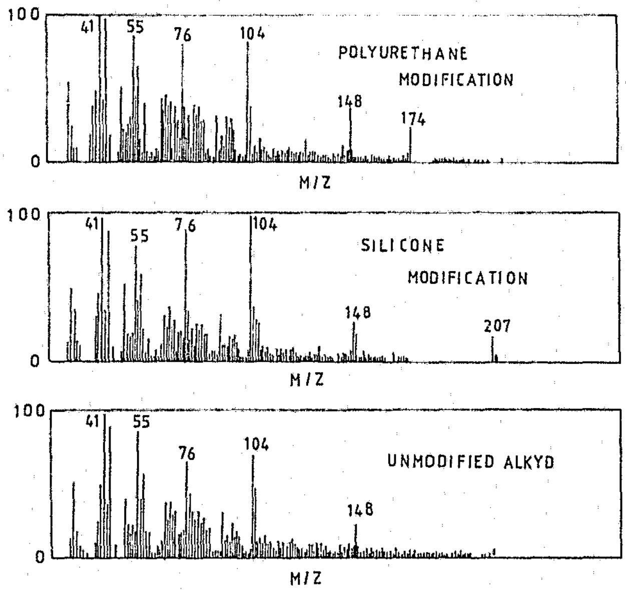

Figure 8. Mass pyrograms of alkyd paints. The conditions used were as described in Table 8.

As a fingerprint technique for characterizing paint resin systems Py-MS has proven to be very useful giving quite characteristic pyrograms for various vehicle paint systems (Figure 7). In addition a variety of modifications to the alkyds used in gloss paints are also detectable by Py-MS. It is significant that the spectra of alkyds are dominated by contributions from a variety of polar pyrolysis products, for example, phthalic anhydride, benzoic acid, etc., which were never eluted from packed GC columns. Typical paint pyrograms are shown in Figure 8. A high proportion of the alkyd paints submitted for analysis do not show features which indicate resin modification but it has been found that Py-MS provides a high level of discrimination. This is an area which we are still actively studying and a variety of different pattern recognition techniques are being tried to assess which will be the most suitable for forensic purposes. As with all instrumental methods, however, Py-MS has its failings. As far as we can see it does not permit films containing nitrocellulose to be characterized, nor is it possible to derive acrolein/methacrolein ratios from the pyrogram of an alkyd. Table 9 summarizes the current status of Py-MS and Py-GC in our hands.

Table 9. COMPARISON OF PYROLYSIS GAS CHROMATOGRAPHY AND PYROLYSIS MASS SPECTROMETRY

| Characteristic | Pyrolysis gas chromatography | Pyrolysis mass spectrometry |
|---|---|---|
| Speed | Slow | Fast |
| Cost | Low | High |
| Value as a fingerprint | High | High |
| Characterization of pyrolysate | Easy | Difficult |
| Quantitation of pyrolysate | Easy | Difficult |
| Polar compounds | Not eluted | Eluted |
| Reproducibility (long term) | Poor | Good |
| Data handling by computer | Difficult | Easy |

## Future Developments

The ease with which mass spectral data can be handled by a computer is perhaps the major reason why it has begun to play a dominant role in our arsenal of pyrolytic techniques. There seems to be every prospect of improving that aspect of the technique even further, and perhaps in the future pattern recognition techniques will permit us to detect subtle but significant differences in polymer pyrograms which will further enhance the scope of contact trace analysis. It may also be found that other types of mass spectral excitation can yield more information about specific types of polymer, than does the rather crude "sledgehammer" approach of 70 eV electron impact excitation that we use at present. On the other hand, great strides are now being made in the use of silica capillary columns for GC. There is no doubt that many of the polar products which were retained on packed columns can now be eluted. Nevertheless it is unlikely in my opinion that any GC procedure will display the long-term reproducibility that is required if significance is to be attached to pyrolytic data by comparison with a computerized data collection. The decade ahead promises to be an exciting one for those engaged in the study of pyrolytic techniques and it is hoped that in time some of the rather intractable problems of characterizing biopolymers such as hair will prove to be amenable to this type of analysis.

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## DISCUSSION

*Van Geller:* I am interested in the direct probe method of injecting paints into the mass spectrometer. Would you comment on what effect that would have on the source, on the cleaning that you would expect?

*Wheals:* I think the main need is to have a mass spectrometer that can scan rapidly. My advice would be to use a quadrupole.

I really cannot comment on the contamination problems from firsthand experience as we never routinely pyrolyze via the direct probe. High molecular weight pyrolysis products are formed with most pyrolysis systems and I assume that there is a greater prospect of contamination in the ion chamber when a probe is used than when pyrolysis products are generated elsewhere and introduced via an expansion chamber.

With the Pyroprobe we find that high molecular weight material build up on the quartz sample tubes, and these require flaming after a few runs. If such contamination takes place with direct probe pyrolysis then MS clean-ups will be needed more regularly.

*Arnold:* My question is non-chemical to you. Not being familiar with the British court system, my impression is that a chemist would come in with a sample and then would decide which of the sections to take for further analysis, is that correct?

*Wheals:* The police officer comes to the Liaison Desk in the Laboratory with the sample. The Liaison Staff acts as intermediaries between the Police and the scientists. The case material is transferred to the scientist, and if it is an exhibit involving contact traces the scientist would remove relevant samples. The scientist decides how individual samples should be examined, for example, which techniques should be applied. I am not convinced that this procedure is ideal. With paints, for example, I favor a predefined protocol of procedures, because some techniques yield more information than others. However, in our Laboratory every effort is made to allow the forensic scientists (the case officers) independence, the choice of techniques to be used is theirs.

Our approach as a service unit is to keep the scientists informed of the latest developments in Py-MS by sending out regular reports, for example, books of data, pyrograms, etc. We are trying to sell our service to the customer. Samples are not submitted if the forensic scientists do not like what we are doing.

*Arnold:* So as a final product in your court would the person who actually does the analysis, in addition to the liaison be called to testify?

*Wheals:* No, the forensic scientist who did the original searching would write the report, but the analysis would be done for the forensic scientist, in general, by an expert in the particular technique used. There is no way that we can train the 100 or so chemists in the MPFSL to perform Py-MS - it is just not feasible. We have to use specialists in certain areas. So the forensic scientist considers all the data that have been produced on a particular sample and then produces a report. The forensic scientist may then have to go to court to be examined on the findings.

The analyst may be asked to go to court; usually the analyst is not, except in less complex instances, for example, alcohol analysis, when the forensic scientist is both the reporting officer and analyst. Such an approach is not applicable when dealing with very complicated instrumental techniques.

*Fetterolf:* If you are building a library, whether it is of mass spectral data, pyrograms, or of infrared spectra, one must take the time to run a standard sample. This would be one that you are fairly confident with. Also make sure that the instrument you are using is reproducing that spectrum from day to day.

If you do not, the standards you run on Tuesday may not look the same on Friday. Thus, when you come back a year later to try to match those against the library, you are in a hopeless situation. So one must choose standards for any analytical technique and be sure that the instrument is giving the correct data.

*Wheals:* I certainly agree with that. We have Py-GC data going back 13 years on the same paint, and we have Py-MS data going back 6 years on the same paint. This enables us to accurately assess long-term reproducibility, and short-term reproducibility can always be evaluated by experiment.

Selecting the appropriate standard is not easy for one has to anticipate what the demand might be in the future - we might see a completely different type of paint system coming along in 5 years time. Alkyds have been our problem, and it looks like they will remain our problem for a long while.

In the case of paints it is not possible to apply the same long-term reproducibility to alkyds as to acrylics. Ions common to both in Py-MS may differ substantially in their long-term variation. In planning a strategy for control samples you have to try and project ahead in the knowledge that different polymer systems display different variation. A range of control samples perhaps offers the best way of building up data in anticipation of future problems.

# ANALYSIS OF POLYMERS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Infrared (IR) spectroscopy is a widely used industrial tool for the structural and compositional analysis of organic, inorganic, or polymeric samples and for quality control of raw materials and commercial products (Bates 1976; Becker and Farrar 1972; deHaseth 1982; Ferraro and Basile 1978; Grasselli and Wolfram 1978; Grasselli *et al.* 1982, 1984; Griffiths 1975, 1977, 1978; Griffiths *et al.* 1972, 1977; Kagel and King 1973; Koenig 1974, 1975; Koenig and Tabb 1974; Smith 1979). It is a relatively simple technique, non-destructive, versatile enough to handle solids, liquids and gases with a minimum of sample preparation, and accurate enough for both the qualitative identification of the structure of unknown materials and the quantitative measurement of the components in a complex mixture. An extensive body of literature on group frequency correlations exists as well as excellent spectral reference collections. Instrumentation has been reliable and low cost.

But in spite of all these benefits, IR spectroscopy has certain drawbacks which become more critical as the difficulty of the analytical problem increases. These drawbacks stem from the fact that IR is an energy-limited technique. The energy distribution of the blackbody radiation of the IR source reaches a peak in the low wavelength region of the spectrum (2-5 $\mu$m), and falls off sharply and drastically at longer wavelengths. For routine operation there is generally more than sufficient spectral energy to obtain IR spectra useful for qualitative structural characterization and for the development of quantitative methods. However, situations frequently occur where there is not enough energy to obtain useful spectra. The resulting weak bands could be due to low concentrations of the component(s) of interest, such as additives or impurities, in an absorbing matrix, or due to extremely small amounts of sample, such as trapped chromatographic fractions. They could also be bands which are naturally very weak but which must be optimized for some analysis. In addition, many IR spectrometers are not able to reliably record spectra of very thick materials, or highly absorbing, intractable materials such as polymers.

But the applications of IR spectroscopy today have experienced an explosive "transformation" with the introduction of interferometric methods of obtaining IR spectra and the subsequent mathematical processing of the interferogram via vast Fourier transform algorithms to recover the frequency spectrum. This "transformation" has given us impressive time and signal-to-noise advantages, as well as a whole new generation of instrumentation.

Table 1. SPECIAL ADVANTAGES OF FOURIER TRANSFORM INFRARED SPECTROSCOPY

- Energy-Limited Situations
    - Opaque samples less than 1 percent transmission
    - Infrared emission studies
    - Very high resolution requirements
- Time-Limited Situations
    - Kinetic studies
    - Unstable compounds
    - Reaction or catalytic intermediates
- Signal/Noise-Limited Situations
    - Trace analysis
    - Interfering absorption
    - Atmospheric sampling

Some of the special advantages of Fourier transform infrared spectroscopy (FTIR) are given in Table 1. These include energy-limited, time-limited, or signal-to-noise limited situations. Examples of each of these will be presented in the following discussion. For the spectroscopist who in the past has dealt with an analog instrument, there are aspects of the data processing in FTIR applications which must be appreciated in order to not only take full advantage of the technique, but also to understand the measurement sufficiently enough for proper data manipulation and meaningful results (Grasselli *et al.* 1984; Griffiths 1977, 1978; Griffiths *et al.* 1972, 1977; Kagel and King 1973; Koenig 1974, 1975; Koenig and Tabb 1974; Smith 1979). There are many papers and texts on FTIR spectroscopy that discuss the effects on the frequency spectrum from the mathematical operations which are carried out on the interferogram (Anderson and Griffiths 1975, 1978; Horlick 1971). Griffiths and Anderson have pointed out the effect of apodization functions on absorbance-subtraction data. Since subtraction is one of the most commonly employed types of data manipulation in FTIR, it is important that the limitations of absorbance-subtraction routines are well recognized. For the practicing spectroscopist, however, absorbance subtraction becomes a powerful tool for the identification of minor components in strongly absorbing matrices.

## APPLICATIONS TO POLYMERS

Fourier transform infrared spectroscopy has found particulary wide application in the field of polymer analysis, not only because of the ability to analyze intractable, thick, intensely absorbing materials, but also because of the ability to monitor chemical and physical changes in the polymer structure as they are occurring. Koenig and coworkers (Painter *et al.* 1982; Hart *et al.* 1977; Ishida and Koenig 1978; Koenig and Antoon 1978; Koenig and Tabb 1974) have evaluated the interaction of antioxidants in butadiene rubbers (even those with carbon black filler) and the effects of various additives on cure. They have elucidated the crystalline and amorphous components of many polymer systems.

A particularly interesting example of surface chemistry of polymers is the examination of an E-glass fiber coated with a coupling agent, vinyl trimethoxy silane (VTMS). Figure 1 (a) shows the fiber and coupling agent, and Figure 1 (b) shows the E-glass fiber alone. The difference spectrum shown in Figure 1 (c) clearly identifies the VTMS coupling agent present on the surface.

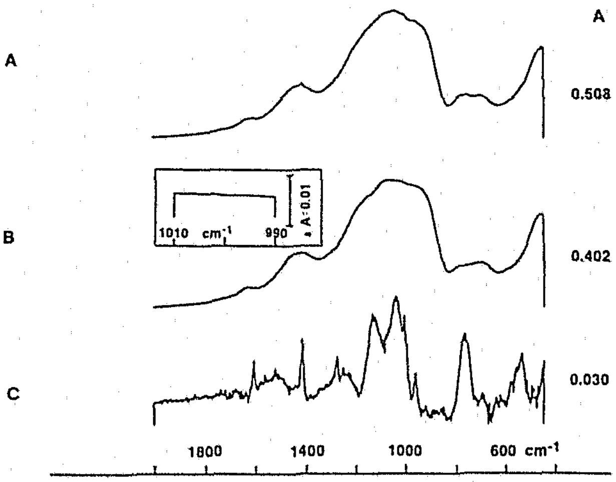

Figure 1. Fourier transform infrared spectroscopy surface analysis, (a) E-glass fiber/VTMS, (b) E-glass fiber and (c) difference spectrum showing VTMS (Ishida and Koenig 1978).

Several studies described the use of FTIR spectroscopy to measure the extent of cure in fiber-reinforced epoxy composites, and the use of FTIR to follow time-dependent intensity changes of absorption bands characteristic of reactants or products in polymerization reactions (Siesler 1980; Sprouse *et al.*; Chambles 1977). For the epoxy resins, both thin films and internal reflectance spectroscopy techniques were used. Cure was followed in a temperature-controlled cell and IR spectra were recorded at short time intervals throughout the cure cycle. The extent of cure was based on the epoxide-ring absorbance at approximately 915 wavenumbers. The authors point out that the FTIR method offers a nondestructive means for optimizing cure cycles in the laboratory and performing extent-of-cure measurements in a plant-fabrication environment.

A typical industrial application of FTIR to troubleshoot a polymer problem was described by Grasselli and Wolfram (1978). Orientation of an acrylonitrile/styrene copolymer film resulted in the development of very small spots throughout the film. The spots appeared to be chunks of gelled resin, but it was also possible that they might be due to a contaminant, a small amount of homopolymer, or even a trapped liquid or gas. Fourier transform infrared spectroscopy subtraction spectra of a pinhole aperture section of the oriented film (subtracting the clear area from the spots) gave a spectrum that was easy to identify as polyvinyl acetate, an obvious contaminant in the polymer (Figure 2). Many other examples of polymer analysis are described in the references cited in the bibliography.

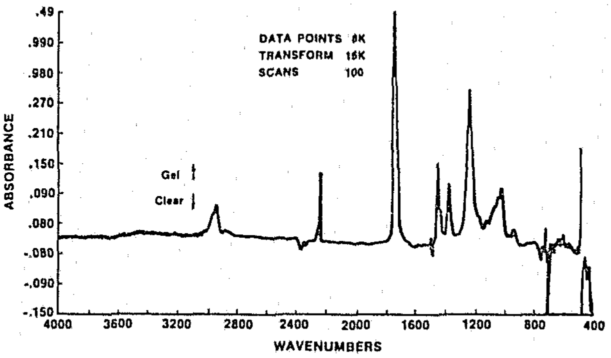

Figure 2. "Gelled" section of AN/S copolymer sheet; clear area subtracted from gel (Grasselli and Wolfram 1978).

## COMBINED TECHNIQUES

There is no question that one of the most exciting areas of application of FTIR spectroscopy has come about because of the time advantage that is gained in the interferometric method for obtaining an IR spectrum; that is, the real-time coupling of an IR spectrometer to a gas chromatograph (GC) was finally realized. Not only the packed GC column separation, but now also capillary GC separations have benefited from the identification power of the FTIR spectrometer. Erickson (1979) gives us an excellent review of GC/FTIR applications, as does the special issue of the Journal of Chromatographic Science (August, 1979). For all these applications, special attention must be paid to the configuration and dimensions of the lightpipe and the transfer lines between the chromatograph and the IR. Examples of capillary GC/FTIR are now appearing rapidly (Griffiths *et al.* 1983).

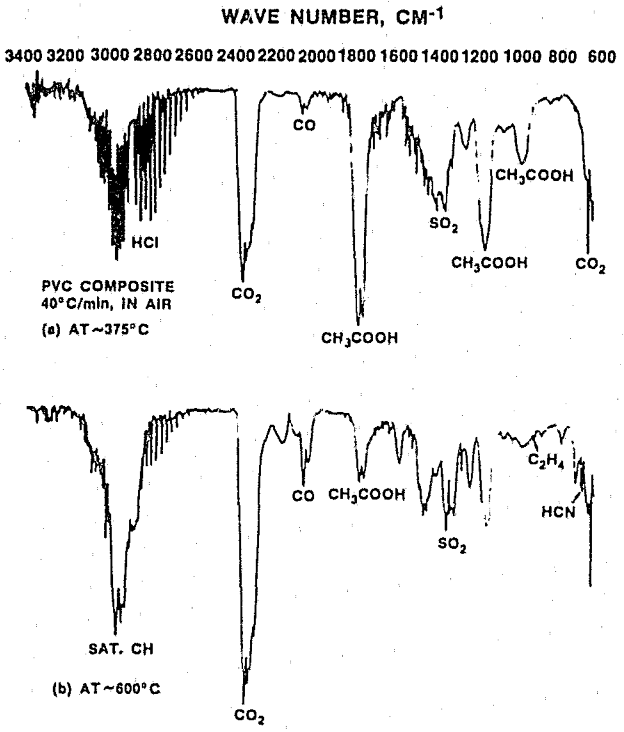

Figure 3. Fourier transform infrared spectra of products. Heat from degradation of a polyvinyl chloride composite in air, (a) at about 350° C and (b) at about 500° C (Liebman *et al.* 1976).

It is often necessary to identify polymer structure of intractable crosslinked polymer samples or other insoluble filled materials, or to follow degradation mechanisms. In recent years, techniques have been developed to observe the IR spectra of gaseous effluents during polymer degradation. The degradation products from a programmed heat treatment of a polyvinyl chloride composite in air are described by Liebman *et al.* (1976). Figures 3 (a) and (b) show the differences in the FTIR spectra of the off-gases at 350° C and at 500° C. The decrease in the amount of HCl produced at the higher temperature is especially noteworthy. Combustion products, including HCl, $SO_2$, $CO_2$, CO and $CH_3COOH$, were observed and their change in concentration was monitored as a function of decomposition temperature and time. Lephardt (1982) has elegantly coupled thermal gravimetric analysis (TGA) with FTIR and has pioneered applications of evolved gas analysis (EGA), particularly to combustion products of tobacco. The kinetics and mechanism of the combustion processes were elucidated. Compton *et al.* (1983) have coupled a low cost "portable" FTIR to a TGA to interpret differences in weight loss in polymer products, catalyst samples, coal and shale oil rock.

## SPECIAL TECHNIQUES

Griffiths and co-workers have pioneered the applications of diffuse reflectance spectroscopy using FTIR (Fuller and Griffiths 1978, 1980). An excellent recent example that illustrates the potential of diffuse reflectance as a powerful sampling technique for FTIR spectroscopy was described by Chase *et al.* (1982). They used diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) to obtain IR spectra of paints directly on paper panels. The contribution of the binder was eliminated by spectral subtraction, and the products of the photodegradation were easily identified when the samples were exposed to accelerated weathering. The analysis of fluorocarbon lubricant on magnetic-storage disks by Fourier transform infrared external reflectance spectroscopy has been described by Walder *et al.* (1984), and is an interesting application of FTIR to a particularly difficult sample.

Another promising spectroscopic method for the IR analysis of samples which do not lend themselves readily to normal preparation techniques is that of photoacoustic detection (Gardella *et al.* 1982; McClelland 1983). Examples of the application to catalyst, polymer, chromatographic sections or spots, and solid fuels such as coals, tar sands and shale oils have been discussed (Mehicic *et al.* 1981). Figure 4 shows the photoacoustic FTIR spectra of a commercial plastic of several morphologies. The spectra are all very similar, demonstrating the versatility of this technique for obtaining useful spectra of polymer samples. One of the most novel applications of infrared photoacoustic spectroscopy is that described by Riseman *et al.* (1981) on conducting polymers. Semi-conducting synthetic polymers, such as polyacetylene, produce good reflectance spectra. Photacoustic detection is a good alternative. Samples of undoped and n-doped polyacetylene were examined and spectral shifts and intensity differences were observed, which were interpreted in relation to the conducting properties.

## CONCLUSION

It is easy to see the maturity of FTIR as a powerful tool in the industrial laboratory. Many important problems in polymer characterization and analysis have been addressed, especially applications which take advantage of the enhanced signal-to-

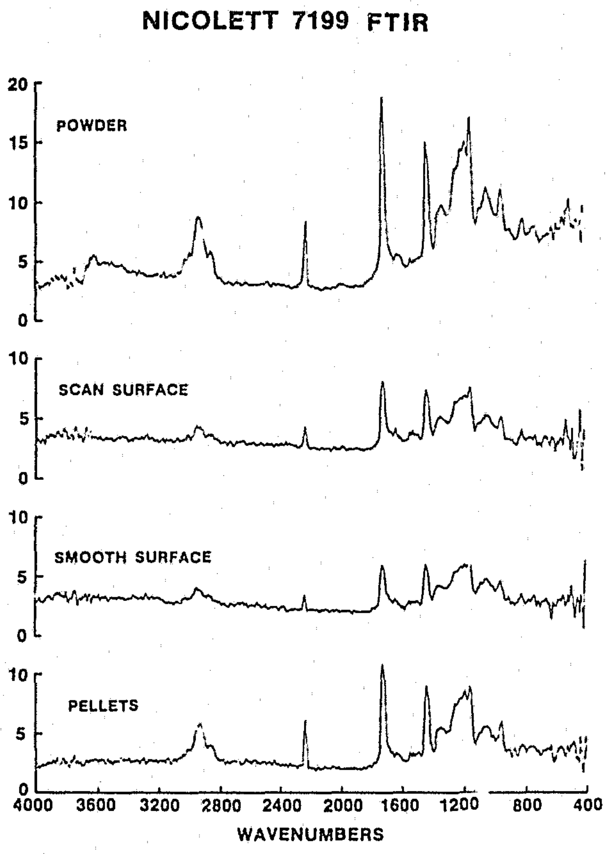

Figure 4. Photoacoustic Fourier transform infrared spectra of a commercial plastic of different morphologies (Vidrine 1980).

noise or time advantages of FTIR. But another dramatic advance in FTIR spectroscopy has come with the utilization of sophisticated mathematical techniques for the deconvolution of complex band shapes in the IR spectrum to the resolution limit of the spectrometer. This work, originating in the laboratories of the National Research Council in Canada, is described in an elegant set of papers by Kauppinen's laboratory (Cameron *et al.* 1982; Kauppinen *et al.* 1981a, 1981b, 1982). Figure 5 shows a comparison of the IR spectrum of chlorobenzene as resolved through self-deconvolution and by first, second, third and fourth derivatives. The derivative spectra are somewhat more limited by signal-to-noise than the deconvoluted results. It is certainly clear that with these powerful techniques of mathematical processing of our data, FTIR is securely in place in the industrial laboratory for both qualitative, quantitative, sophisticated structural and quality-control work.

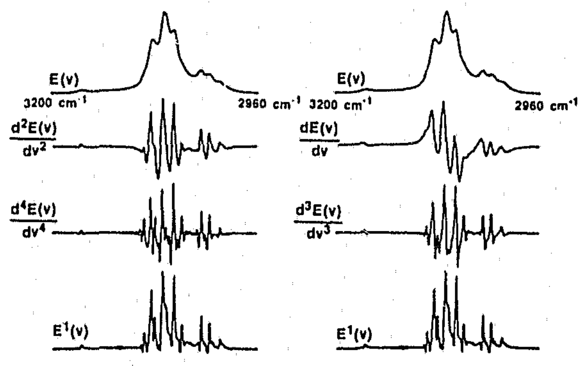

Figure 5. Comparison of the infrared spectrum $E_{(\upsilon)}$ of chlorobenzene with the self-deconvoluted spectrum $E'_{(\upsilon)}$, and with the second and fourth (column A), and the first and third (column B) derivatives (Kauppinen *et al.* 1981).

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## DISCUSSION

*Suzuki:* I noticed you wrote a book on Raman, and I was wondering if you were using the MOLE or Raman spectroscopy for some of your problem solving.

*Grasselli:* Raman spectroscopy is very powerful. Drugs, like heroin and barbiturates, can be very specifically identified by Raman in extremely small amounts, even when they are in something inert, like sucrose.

We use Raman on polymers and catalysts. It is so complementary, it gives the same molecular structure information as infrared and it is even easier in many ways to get Raman spectra now with laser.

*Suzuki:* Are you using the actual MOLE or do you have the Micromate?

*Grasselli:* We built our own microscope. Right now we have a MOLE-type accessory that is not a commercial instrument. I have a spectrophotometer with a microscope attachment, and right now we have an optical multi-channel analyzer.

*Blackledge:* With gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR), suppose you have something like eight wavenumber resolution, with high signal-to-noise ratio. Do you think you still have enough spectral detail that you can use as a "fingerprint" to positively identify?

*Grasselli:* Absolutely. I recently attended a conference where they were now down to sub-nanogram-quantity identifications specifically with GC/FTIR. This is from an Environmental Protection Agency Laboratory where you are looking at priority pollutants and the mass spectrum is not going to do very well for you on geometric isomers and infrared is going to be superb. You can do just perfect separation work using that combination.

I did indicate that in our laboratory we are using GC/FTIR/MS/NMR. We are getting all the molecular fingerprint information possible in a very short time frame. They are all matched in sensitivities. With the new pulse techniques in NMR we are down to microgram/nanogram quantities. You can interface a micro-bore liquid chromatograph to an infrared and get compatible relationships in both the time and the size of the sample.

We ought to scan other areas and see where new developments are coming up that are being published in an entirely spectroscopic journal. That is where most of these things are in analytical chemistry or applied spectroscopy. We ought to be putting some applications, perhaps into the Journal of Forensic Science or having more conferences like this where you could bring in some people with different backgrounds.

# IDENTIFICATION AND DIFFERENTIATION OF SYNTHETIC POLYMERS BY PYROLYSIS CAPILLARY GAS CHROMATOGRAPHY

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Pyrolysis has extended the use of gas chromatography (GC) as an analytical tool to samples which are neither soluble nor volatile. Thermal fragmentation of polymeric samples produces volatiles in a reproducible way which may be analyzed by packed column GC, capillary column GC, or by pyrolysis gas chromatography mass spectrometry (Py-GC/MS), as well as pyrolysis mass spectrometry (Py-MS) and pyrolysis Fourier transform infrared (FTIR) spectroscopy. Pyrolysis capillary GC has been a useful tool in the investigation of synthetic polymers both from the standpoint of degradation mechanisms and microstructural characterization. Liebman *et al.* (1984) have produced an extensive review of pyrolysis capillary GC practices in general, and Wheals (1981) has compiled a separate study of pyrolysis techniques as they pertain to the forensic sciences.

The tremendous resolution afforded by fused silica capillary columns has made possible fine distinctions between related materials, revealing differences resulting from batch variations, polymer defects, branching, etc. The characteristic "fingerprint" chromatogram generated from the pyrolysis of polymeric materials provides a wealth of information for the identification of the material, as well as for the study of the ways in which polymers behave when treated thermally. These mechanisms include random scission, zip-depolymerization, intramolecular side chain scission and cyclization to produce an enormous variety of compounds, from monomers, dimers, trimers, etc., to aromatic species and other compounds unrelated to the starting materials of the original polymer.

## Pyrolysis Gas Chromatography

In general, pyrolysis gas chromatography (Py-GC) is achieved by attaching a pyrolyzer at or before the injection part of the GC. There are several basic arrangements and types of pyrolyzers used. Modern filament pyrolyzers use a self-sensing resistively heated metal coil or ribbon to fragment the sample. The substance may be placed directly onto the surface of the metal ribbon, or held in a quartz tube which is placed inside the heating coil. Curie Point pyrolyzers are inductively heated and the final temperature of the sample is chosen by the characteristics of the alloy used in the heating wire. Microfurnaces have been installed prior to the inlet of the GC column by some analysts, including an array used by Tsuge *et al.* (1981) which employs a microfurnace and a catalytic hydrogenation arrangement.

For extended thermal treatments, or for heating in an atmosphere other than GC carrier gas, a trapping system may be used. This includes the pyrolyzer itself which is swept with a flow of gas (He, $H_2$, $O_2$, $N_2$, air, etc.) carrying the pyrolysates to a trap with either a solid sorbent used as an ambient collector or with a cryogenic arrangement. After the thermal event has been completed, the trap is desorbed by heating it and backflushing with GC carrier gas onto the GC column.

## Polymer Differentiation

Many of the various synthetic polymers available may be placed into a broad category based on the chemical type or method of synthesis of the polymer. Some examples of these categories include the polyolefins such as polyethylene and polypropylene, the polyesters, and polyamides such as the nylons.

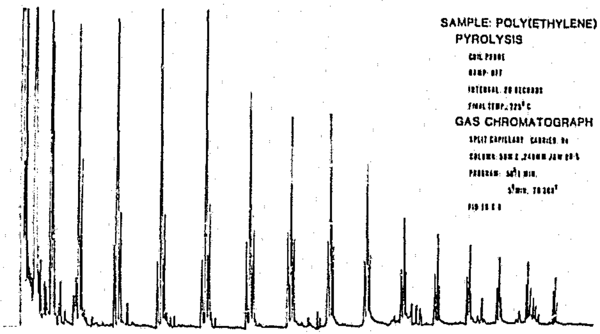

Figure 1. Polyethylene pyrolysis at 725° C for 20 seconds.

Typically, polyolefins fragment to produce a pattern of monomers, dimers, trimers, etc. A typical example of this may be seen in Figure 1, which shows the pyrolysates resulting from heating a sample of polyethylene to 725° C for 20 seconds. The overall pattern is that of a series of triplets. Each of the triplets is made up of normal hydrocarbons, specifically an alkane, a monoolefin and a diolefin with a double bond at each end of the chain. These three compounds are of the same carbon chain length. The compounds in each triplet contain one more carbon than the compounds in the triplet which eluted just before it. On an SE54 column, such as the one used here, the major peak in the center is the monoolefin, with the alkane eluting last of the three.

Polyamides like the nylons, on the other hand, produce a significantly different pyrogram. Figure 2 shows the chromatogram of the pyrolysates generated by heating Nylon 6/6 to 900° C for 20 seconds. Here, the pattern is somewhat simpler, with much of the material eluting in the early part of the chromatogram, and not as much evidence of a recurring pattern of peaks.

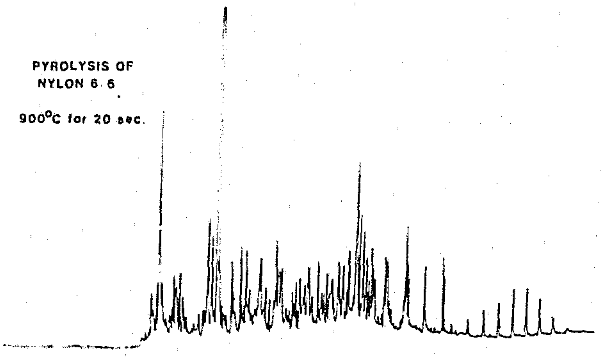

Figure 2. Nylon 6/6 pyrolysis at 900° C for 20 seconds.

### Intragroup Differentiation

The polymers within a family may be significantly different from each other, or may be similar enough to require some rather sophisticated processing to differentiate. Polyethylene, polypropylene and polyisobutylene, for example, are all polyolefins, but they may be differentiated quite readily by their pyrograms. Figure 1 shows an example of polyethylene with this recurring pattern of oligomers. Figure 3 shows a pyrolysis of polypropylene for comparison. Again, there is a pattern which arises from the generation of a series of oligomers, but the overall structure of the chromatogram makes it easy to distinguish polyethylene from polypropylene. Figure 4 shows a pyrogram of polyisobutylene. Here the extensive and fairly complex pattern of the chromatogram may be easily distinguished from the other polyolefins discussed so far.

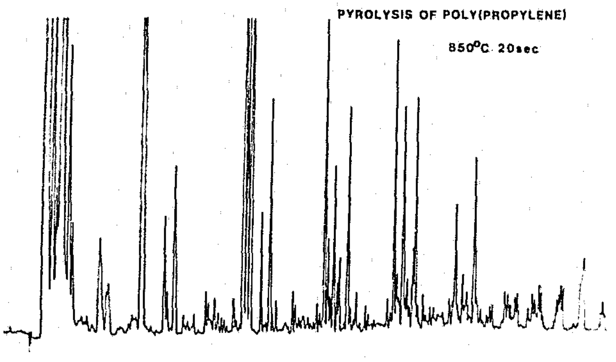

Figure 3. Polypropylene pyrolysis at 850° C for 20 seconds.

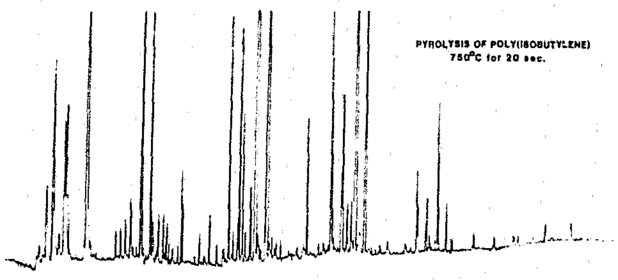

Figure 4. Polyisobutylene pyrolysis at 750° C for 20 seconds.

Within polypropylene, however, there is the opportunity for optical isomerism, yielding polymers with varying degrees of randomization in the arrangement of the methyl groups attached to the macromolecular chain. If these groups are arranged so that they are all on one side of the chain - essentially a cis arrangement - the polypropylene is called isotactic. Syndiotactic, on the other hand, has the methyl groups arranged so that they are on alternate sides of the polymer chain, in a trans configuration to each other. A random arrangement of the methyl groups throughout the polypropylene chain produces a third atactic structure. This order (or lack of it) in the arrangement of the methyl groups in polypropylene produces materials of markedly different physical properties. When pyrolyzed, the isomers of polypropylene generate volatiles significantly different from each other, and consequently the chromatograms of these pyrolysates show some interesting contrasts. Figure 3 is a chromatogram of isotatic polypropylene pyrolyzed at 850° C and shows a pattern produced by a series of oligomers. Figure 5 is a chromatogram of atactic polypropylene pyrolyzed under the same conditions. As can be seen from a comparison of the two chromatograms, there are many significant differences, especially in the groups eluting late in the program. By preparing blends of these polymers, the degree of randomness of the methyl groups in a specific sample of polypropylene may be ascertained.

Considerable attention has been paid to the microstructure of the polyolefins, specifically with regard to branching and defect structures in polyethylene, as by Liebman *et al.* (1982) and in the study of the polypropylene isomers, as in the work of Tsuge (1980).

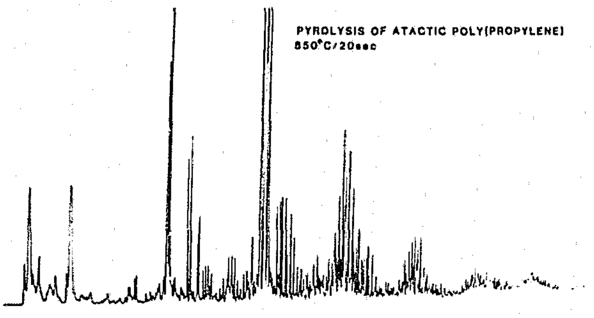

Figure 5. Atactic polypropylene pyrolysis at 850° C for 20 seconds.

The family of polyamides referred to as the nylons is an interesting study in pyrolysis. These polymers may be produced in two ways, and are designated by numbers to indicate which monomeric material was used.

If the nylon was prepared from a single monomer with a carboxylic acid group at one end and an amine group at the other end of the molecule, it is given a single number to indicate how many carbons are contained in the monomer. Nylon 6, for example, is the name given to the polyamide containing the monomeric unit:

$$\text{-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CO-}$$

Likewise, Nylon 12 would be a similar polymer from a monomeric unit containing 12 carbons, and so on. Figure 6 shows a chromatogram of Nylon 6 pyrolyzed at 900° C for 20 seconds. It is easy to distinguish this polymer from Nylon 12, which is processed in the same way (Figure 7).

Polyamides may also be produced from the polymerization of two compounds - one having an acid group at each end and the other having an amine group at each end. If the diamine has six carbons, and the diacid has nine carbons, then the resulting polyamide is called Nylon 6/9. Similarly, if the diamine contains six carbons and the diacid contains ten carbons, Nylon 6/10 is produced. In this way, the length of carbon chains between the amide linkages may be varied, and many different nylons may be produced and studied. Although it was easy to see the difference between Nylon 6 and Nylon 12, differentiation between more similar nylons can be carried out. Nylon 6/9 and Nylon 6/10, for example, differ only in the addition of one carbon in the dicarboxylic acid portion of the structure. However, pyrolyses indicate that this difference becomes a distinguishing feature in the pyrograms. Figures 8 and 9 are pyrograms of Nylons 6/9 and 6/10, respectively. A comparison of these chromatograms shows a significant peak height inversion for two major peaks, indicating the structural differences in the original macromolecules.

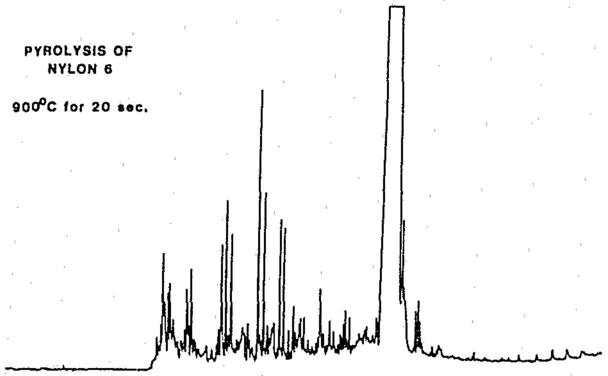

Figure 6. Nylon 6 pyrolysis at 900° C for 20 seconds.

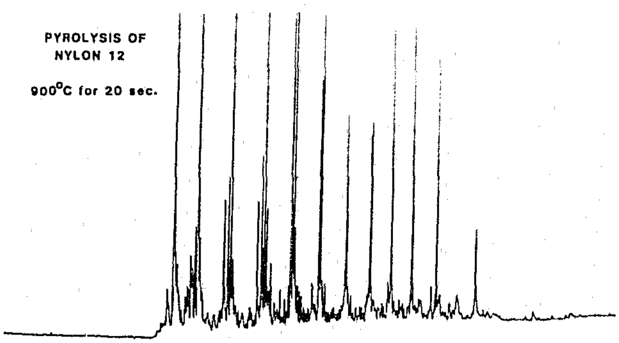

Figure 7. Nylon 12 pyrolysis at 900° C for 20 seconds.

## CONCLUSIONS

The pyrolysis of synthetic polymers may produce an enormous variety of volatile compounds. The analysis of these compounds has been greatly facilitated by the development and perfection of fused silica capillary columns. The dependence on the pyrolysis temperature of the kinds and amounts of materials produced during a pyrolysis has been demonstrated (Levy and Walker 1984), as well as the reproducibility of the pyrolysis event itself. By careful analysis of the kinds of molecules produced during a pyrolysis using the resolution af-

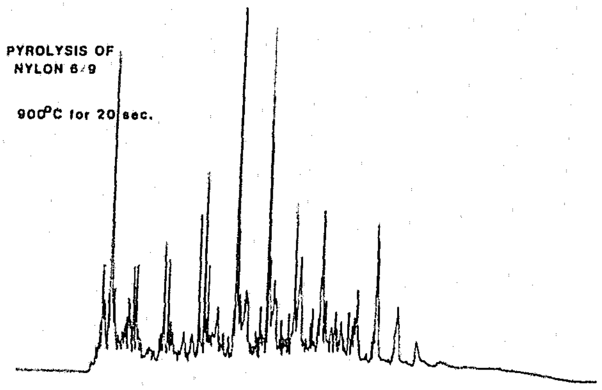

Figure 8. Nylon 6/9 pyrolysis at 900° C for 20 seconds.

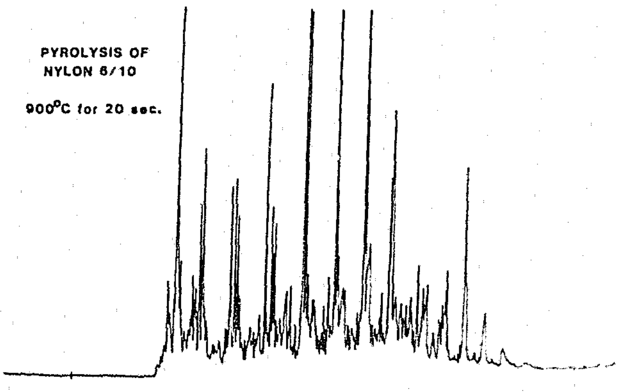

Figure 9. Nylon 6/10 pyrolysis at 900° C for 20 seconds.

forded by capillary columns, not only may polymer types be differentiated from each other, but structural differences producing isomerization within a specific polymer may be elucidated.

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## DISCUSSION

*Kee:* Would you elaborate slightly on the use of traps to capture the pyrolysis products, what you use and what the differences are in results?

*Levy:* The traps that are used are very similar to what are used for classical purge and trap, trapping concentrators. They are short lengths of eighth-inch tubing that are either packed with the materials such as Tenax, or if you are cryocooling them, they can just have materials such as quartz wool or a glass wool.

Then the material is accumulated on that trap, either at the ambient or at cryogenic temperatures. The trap is then pulse-heated and the heating rates can be as high as 600° C per minute so that you can get a pulse evolved from the trap that can go into the gas chromatograph and is indistinguishable in terms of its peak resolution and theoretical plate numbers from the best injection. That can allow you to accumulate the material from an extended heating period and put it on to the gas chromatograph as a very sharp pulse.

*Kee:* There had been some problems about collecting the polar compounds on ordinary columns. Would you comment on this problem regarding the use of Tenax?

*Levy:* Tenax is one of many trapping materials. Substances trapped on Tenax, including polar compounds, can be released if Tenax is heated properly. Tenax is particularly suitable for nitrogen containing compounds. This was one of the earliest applications of Tenax as a GC column packing. There is some difficulty, however, in releasing high molecular weight normal hydrocarbon from Tenax traps.

If you find that heating the Tenax trap to 300° C and leaving the trap, in backflush mode for several minutes, does not release the absorbed substance--then a mixed trap is needed. A small section of SE-30 on Chromosorb W at the head of the trap, followed by Tenax will extend the molecular weight range of the collection and desorption process. Or, if you want to avoid the use of any packing at all, go over to pure cryogenic collection using only a fused quartz fiber or glass wool, and you will find that you can collect and recover the material.

# THERMAL TREATMENT OF POLYMERIC SUBSTANCES WITH ANALYSIS BY DIRECT CAPILLARY GAS CHROMATOGRAPHY USING ON-COLUMN CRYOFOCUSSING

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## Pyrolysis Gas Chromatography

Pyrolysis has been employed as a means of studying solid materials by gas chromatography (GC) for decades, and has found many varied uses in fields ranging from geochemistry through biochemistry, agriculture and, of course, polymer chemistry. The application of heat in a controlled, reproducible way has promoted the study of materials such as paints, fibers, plastics, proteins, cell constituents and wood products using GC by producing from them characteristic volatile compounds. Initially, packed column GC was sufficient to distinguish between related samples, and some fine work was performed on samples such as glues, paints and papers. With the introduction of capillary GC columns, resolution of peaks in a pyrogram improved greatly, as did chromatography in general, and detailed studies of polymer microstructure became easier. The technology of capillary GC column production continues to move forward, and so does the application of capillary GC columns to pyrolysis, as reviewed by Liebman *et al.* (1984).

The introduction of instrumentation capable of long, programmed thermal treatment, in addition to pulse pyrolysis, necessitated a means of trapping or retaining the volatiles produced so that they might be analyzed by GC after the entire treatment. Generally, sorbent trapping has been used, collecting the volatiles on the surface of a material, such as activated charcoal, silica gel, Tenax, etc., then pulse heating the trap to desorb the material. During the pulse heating, thermal desorption step, the trap is backflushed with carrier gas from the GC, so that the retained pyrolysis products are transferred to the GC column, as described by Liebman and Levy ( 1983).

The ability to pyrolyze materials at slow rates, or in atmospheres other than GC carrier gas, provided some interesting insights into degradation mechanisms of polymers and the kinetics of combustion. Augmenting or replacing the solid sorbent trap with cryogenics soon became a major area of interest.

## Cryogenic Trapping

The collection of volatiles from a pyrolyzed material using a cold trap was seen as the solution to problems which arose in two areas of the analysis - sample handling and chromatography.

From the viewpoint of sample handling, cryogenic focussing would permit the analysis of extremely small samples. This benefit arises from the fact that the volatiles are focussed onto the surface of the fused silica column itself, without splitting. Since this eliminates venting most of the samples out of the splitter, the amount which is actually transferred to the GC column may be increased 100 times. This permits the same sensitivity previously acheived by split capillary chromatography, only on a sample about 1/100th as large. Additionally, samples of very low organic content may be handled by pyrolysis in a routine way because of the increase in sensitivity.

## Chromatography

The use of cryogenic means to trap volatiles prior to analysis by GC has been demonstrated by many analysts, and has been used to study samples, such as polymer volatiles (Myers 1982) and sulfur compounds (Farwell *et al.* 1979). A cold trap valving system for use with capillary columns was investigated by Jacobsson and Berg (1982). This refocussing step became especially important when it was desired to analyze pyrolysates via splitless capillary GC, using narrow bore (0.25 mm) columns. The flow through these columns is typically 1 ml/min or less. This presented a problem in the transfer of volatiles from the pyrolysis instrument to the GC. Whether one is pyrolyzing directly upstream of the GC column, or collecting first onto a primary trap, the flow through these devices would be limited to the GC carrier flow (1 ml/min. or less) when the pyrolysates are transferred to the GC. This means that the flow through the pyrolysis chamber would be very slow, producing a gradual bleeding of the pyrolysates into the GC, instead of a sharp, plug-like injection. Likewise, if a primary trap had been used, it would have been necessary to backflush it at a very low flow during the pulse heating to transfer the adsorbed material to the GC, again producing a gradual, wide evolution of the introduction, instead of a tight plug.

The solution seemed to be cryofocussing directly onto the GC column itself. In this way, it made no difference if the pyrolysates were transferred slowly into the GC column, because the actual chromatography could be delayed until after the transfer step. Once all the pyrolysates were condensed onto the inner surface of the fused silica column, they were pulse heated to vaporize the compounds, thus simulating an actual, on column injection. This arrangement permitted the analysis of the total sample, without splitting and therefore without concerns of mass discrimination. More importantly, this compensated for the transfer of materials at a slow rate, which had destroyed the resolution of peaks, particularly at the beginning of the chromatogram.

Several methods have been used to produce cryogenic refocussing of materials for GC analysis. These generally involved freezing an initial portion of the fused silica column, then heating it as the GC program was initiated. Freon spray has been used, as has the technique of holding a piece of dry ice onto the column during sample collection. Most common is probably the technique of immersing a loop of the column into a flask of liquid nitrogen, then heating the cooled area with a heat gun at the start of the GC run.

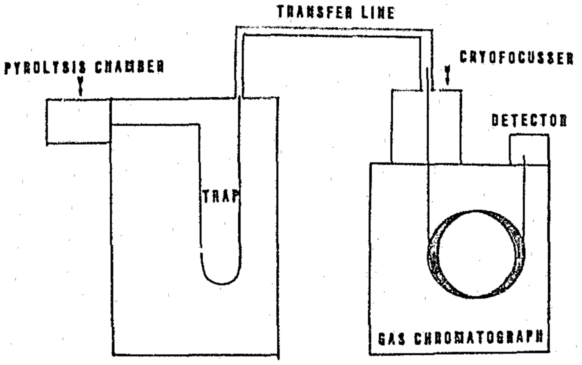

Figure 1. Diagram of pyrolysis, cryogenic refocussing systems for gas chromatography.

All of the above methods involve manual handling of the collection/desorption system, and are consequently both bothersome and prone to errors of non-reproducibility. What was desired was a system which could be programmed to perform the heating and cooling steps automatically, thus re-establishing reproducibility and freeing the hands of the analyst.

Figure 1 is a diagram of the system used to produce the chromatograms for this paper. It consisted of a pyrolysis chamber with a coil type filament pyrolyzer upstream of an ambient (Tenax filled) trap. Materials could be pyrolyzed at pulse or programmed rates, then the pyrolysates carried to the initial trap at flows from 1-100 ml/min. (30 ml/min. was typically used). The initial trap was then backflushed with GC carrier gas at 22 psi and heated to desorb the retained volatiles. These compounds were carried through a heated transfer line to the GC. A 50 m x 0.25 mm SE54 fused silica capillary column was used for the chromatography. The beginning of the column was brought up through the injection port, passed through a cryofocusser and attached directly to the end of the transfer line using a graphite ferrule. The cryofocusser contained a well for liquid nitrogen, and a heater, both of which were used to maintain setpoint temperature. During transfer of organics from the pyrolysis instrument to the cryofocusser, the GC column section was maintained at cryogenic temperature - usually -100° C. After all volatiles had been transferred from the initial trap to the cryofocusser, the GC program was initiated and the focusser was heated rapidly (10° C/sec.) to 300° C, vaporizing the condensed pyrolysates and flushing them into the GC oven proper for chromatography. Cryogenics were not used in the GC oven, which was generally programmed from 45° C to 290° C at 8° C/min.

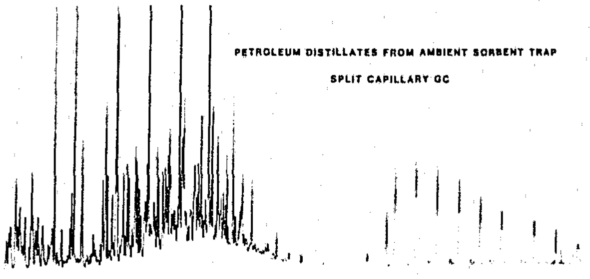

Figure 2. Petroleum distillates test mixture analyzed by split capillary gas chromatography.

A test sample containing petroleum distillates was used for the comparison of a chromatographic resolution using the direct capillary cryogenic system and a split capillary GC system. Examples of the resolution problems encountered when analyzing a sample by split capillary GC is shown in Figure 2. Notice that the early eluting peaks - the low molecular weight hydrocarbons - show considerable peak broadening and poor resolution. When one compares this to Figure 3, which is a sample of the same material analyzed using cryofocussing, the benefits of the cryofocusser become apparent.

Pyrolysis of polyethylene provides a good example of the utility of cryofocussing to these analyses. Much microstructural information is contained in the early eluting peaks and in the minor peaks found between the major triplets in a pyrogram of polyethylene. Figure 4 shows a split capillary analysis of polyethylene pyrolysates, and again, much

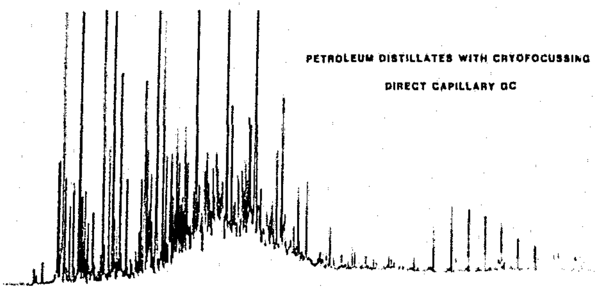

Figure 3. Petroleum distillates test mixture analyzed by splitless gas chromatography using cryogenic refocussing.

information at the beginning of the chromatogram is lost in an unresolved section of large peaks. As shown in Figure 5, cryogenic refocussing does much to untangle this area (although it will always be very complex). Just how complex this area is, and how significant the peaks between the major triplets are, may be seen by rerunning the sample at a more sensitive attenuation. Figure 6 shows that even though the major peaks are considerably off scale, the important minor peaks revealing branching are sharply resolved throughout the chromatogram.

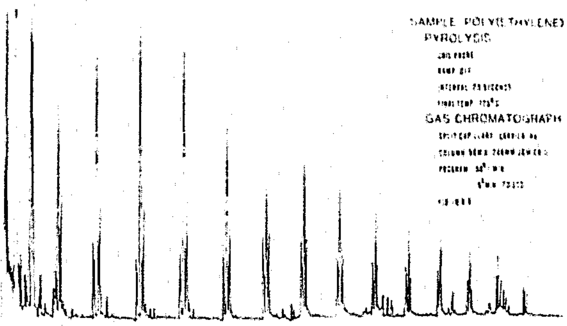

Figure 4. Split capillary gas chromatography analysis of polyethylene pyrolysates.

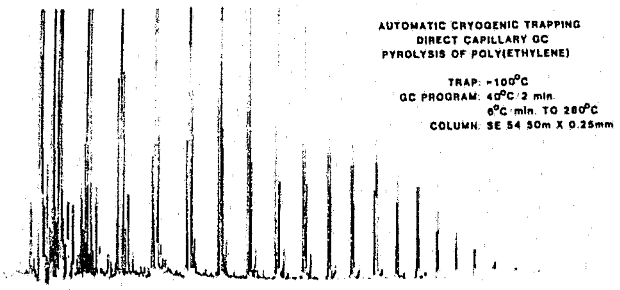

Figure 5. Splitless capillary gas chromatography analysis of polyethylene pyrolysates.

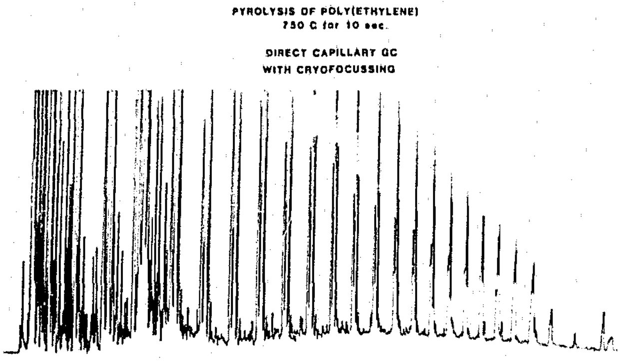

Figure 6. Splitless capillary gas chromatography analysis of polyethylene pyrolysates showing branching structure.

The ability to resolve minor peaks amid a complex pattern of major peaks in a pyrogram greatly facilitates making distinctions between closely related polymers. The two nylon products called Nylon 6/9 and Nylon 6/10, for example, are chemically and physically similar. Pyrolysis GC reveals some differences in the pyrograms of these compounds; whereas, cryofocussing shows that there are really many substantial differences. Figures 7 and 8 are direct capillary pyrograms of these nylons using cryofocussing. Here six peaks have been selected to distinguish between the two samples, although even a cursory examination reveals many others which could be used.

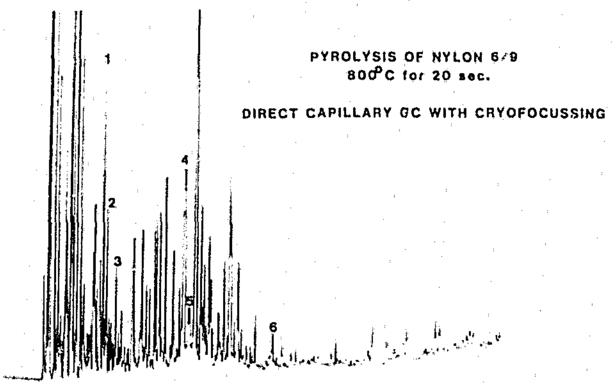

Figure 7. Pyrolysis of Nylon 6/9 with cryofocussing.

Of equal importance to some investigators is the ability to pyrolyze and analyze extremely small samples. Paint flecks, glue scrapings and cloth threads, for example, may require analysis which must be repeated and yet not deplete the valuable sample. Figure 9 is a pyrogram produced from a 2 cm length of a single human hair. The attenuation used for this chromatogram was $32 \times 10^{-11}$, which indicates how much material was produced from even such a small sample. An interesting comparison can be made between human hair and lambs wool by looking at Figure 10, which shows a strand of wool processed in the same manner as used to produce Figure 9.

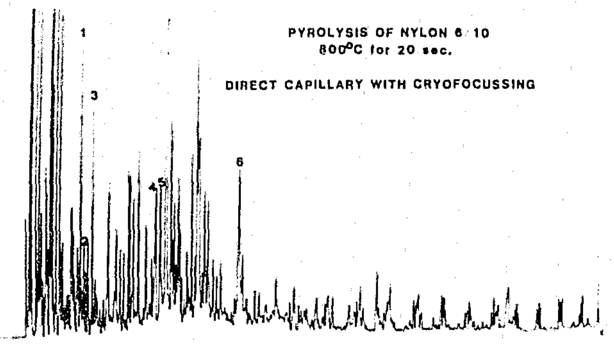

Figure 8. Pyrolysis of Nylon 6/10 with cryofocussing.

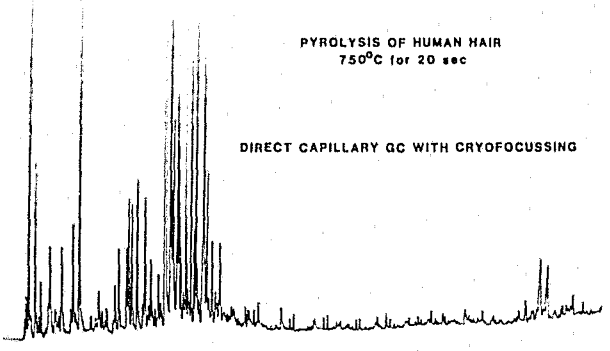

Figure 9. Pyrolysis of human hair with cryofocussing.

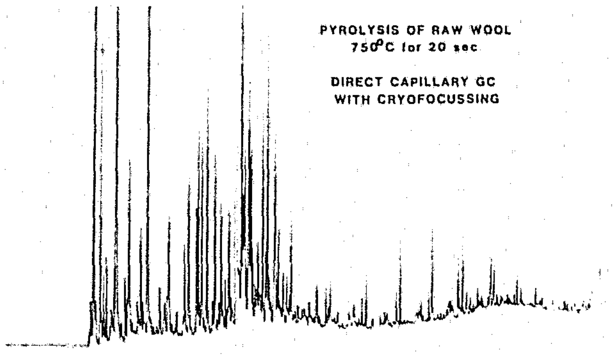

Figure 10. Pyrolysis of wool fiber with cryofocussing.

## CONCLUSIONS

Narrow bore fused silica capillary GC columns have provided exceptional resolution in the chromatography of complex samples. It is now possible to configure pyrolysis systems using cryofocussing of the pyrolysates directly onto the fused silica column, to take advantage of this resolution. In this way the ability of pyrolysis has been extended, and may also include the analysis of very small samples or samples of low organic content.

Cryofocussing involves a supply of cryogenic material, solid $CO_2$ or liquid $N_2$, for example, and generally lengthens the time required for analysis. The additional costs in time and equipment must be considered, but are frequently of secondary importance when compared to the increased sensitivity and resolution afforded by such a system.

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# 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 adhesive 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 calendering (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.

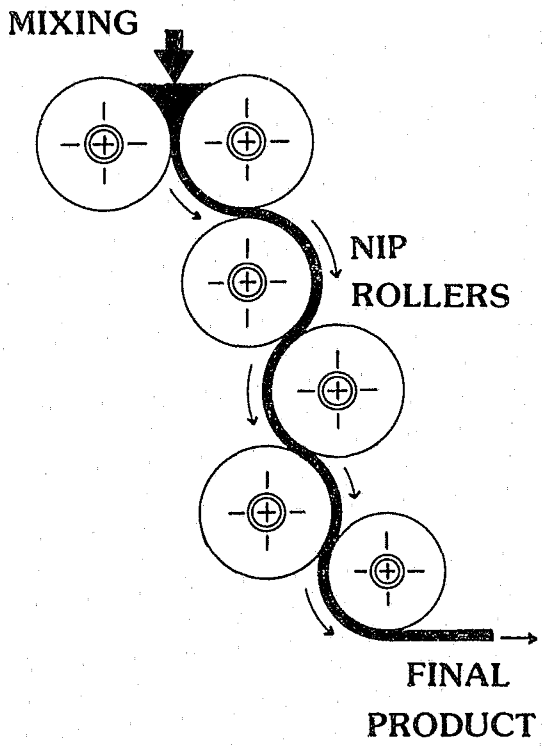

Figure 1. The calender manufacture of plasticized polyvinyl chloride film.

### 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.

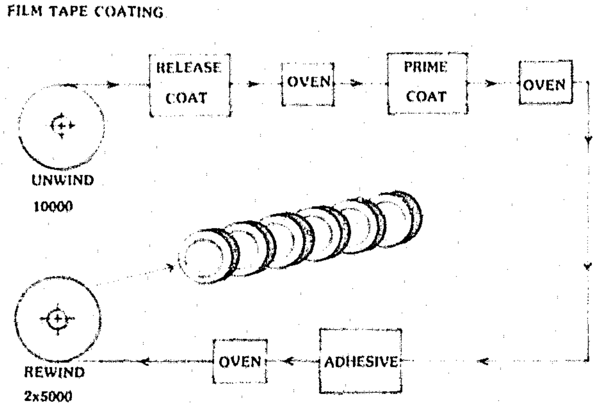

Figure 2. Coating of plasticized polyvinyl chloride film in the manufacture of adhesive tapes.

## 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.

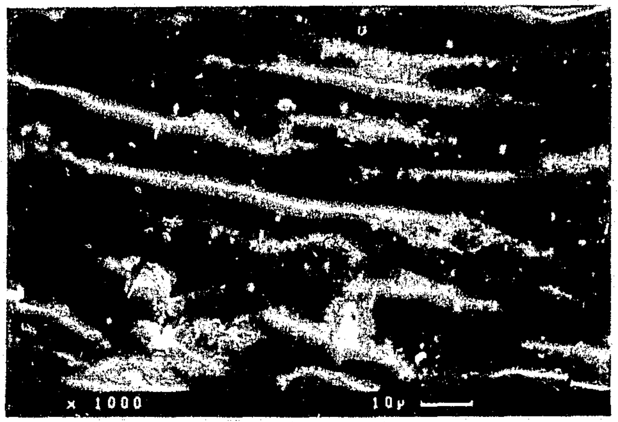

Figure 3. Magnified view of tape surface, photographed using a scanning electron microscope (carbon coating; tape ex 2490/81).

#### 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).

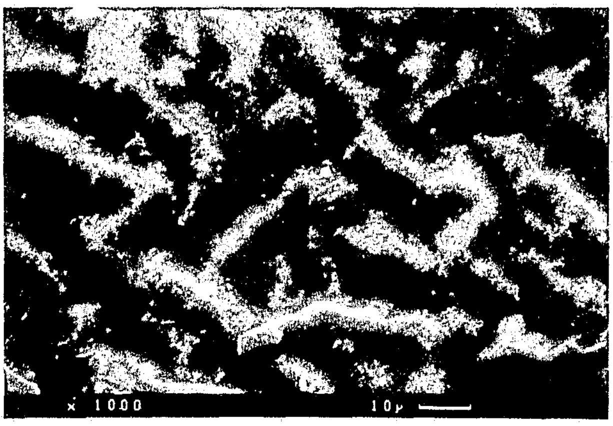

Figure 4. Magnified view of tape surface, photographed using a scanning electron microscope (carbon coating; tape ex 353/81).

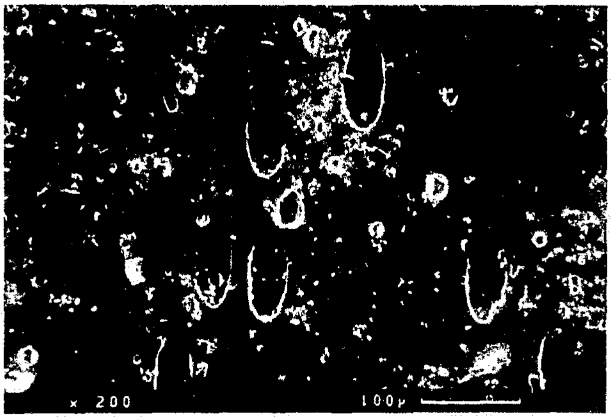

Figure 5. Magnified view of tape surface, photographed using a scanning electron microscope (carbon coating; tape ex 2800/81).

#### 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

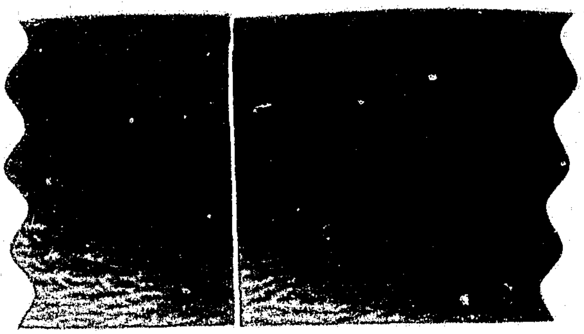

Figure 6. Photograph of visualized primer pattern on the underside of tape backing.

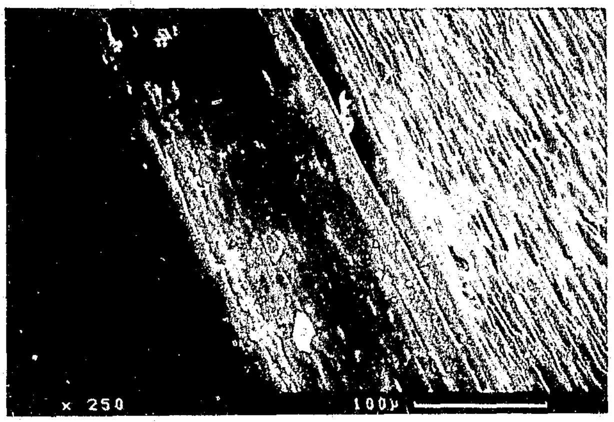

Figure 7. Magnified view of tape edge, photographed using a scanning electron microscope (carbon coating; ADASTRA Electronics Ltd. brand).

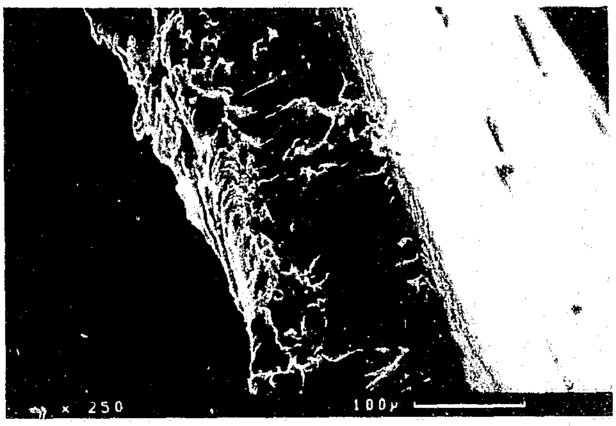

Figure 8. Magnified view of tape edge, photographed using a scanning electron microscope (carbon coating; tape ex 3012/80).

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 adhesive 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.

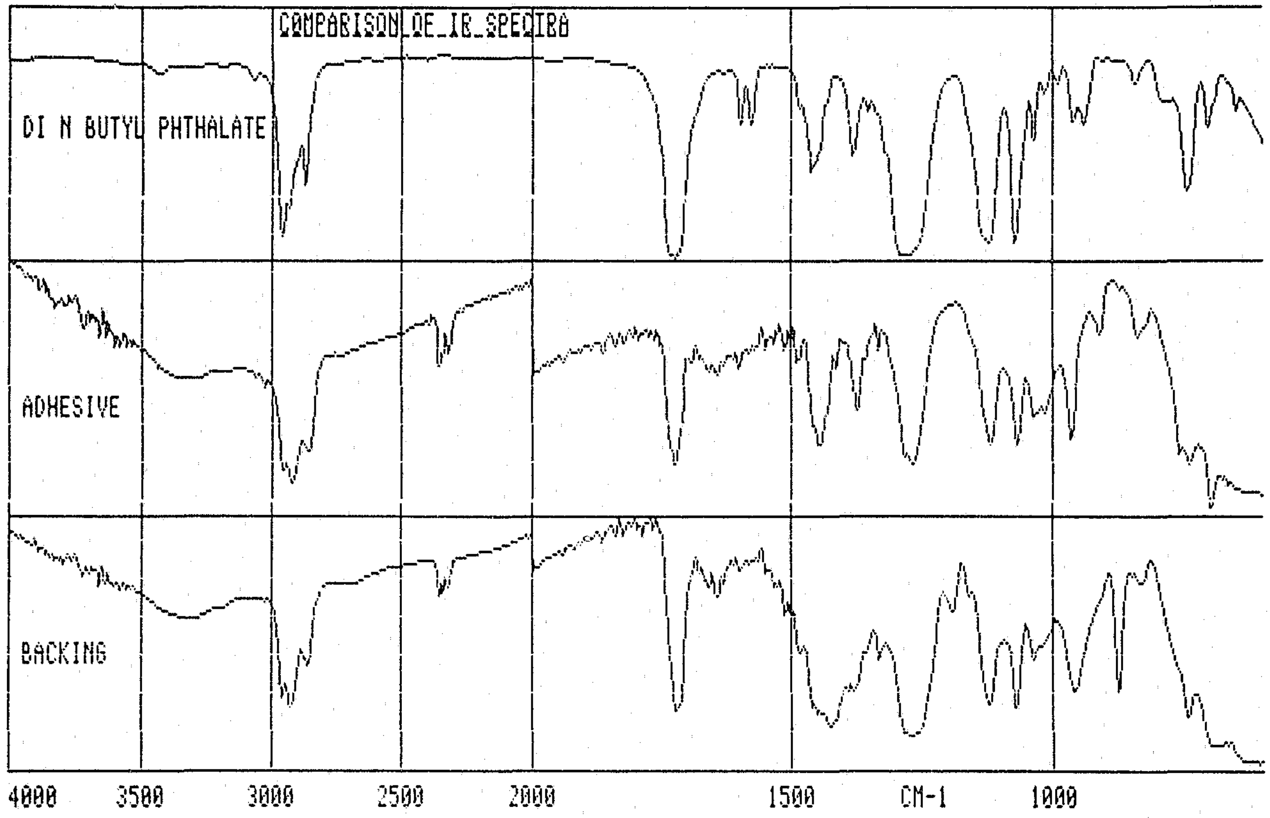

Figure 9. Comparison of infrared spectra of (a) n-butyl phthalate (NaCl discs) and (b) backing and adhesive coating (multiple internal reflectance spectrometry) from a tape sample (1125/81).

## 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<br>(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<br>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$^{-1}$ |
| Scan time: | 2.5 minutes |

Scan mode 3, noise filter 1 (nominal resolution 5 cm$^{-1}$)

| | |
|---|---|
| Crystal transmission: | 15-20 percent at 4000 cm$^{-1}$ |
| 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).

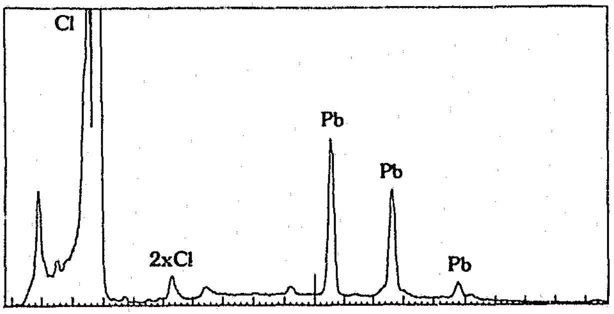

Figure 10. X-ray fluorescence spectrometry spectrum of a typical member of Class 1A (lead only).

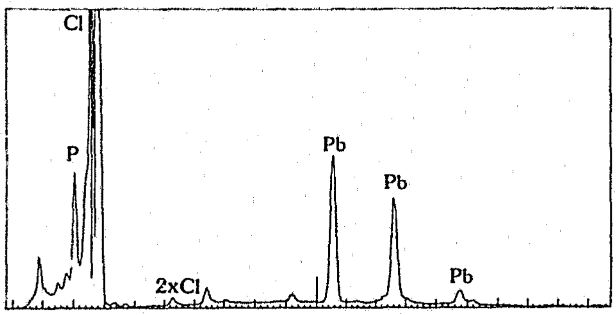

Figure 11. X-ray fluorescence spectrometry spectrum of a typical member of Class 1B (i) (lead and phosphorous).

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 Subclass 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.

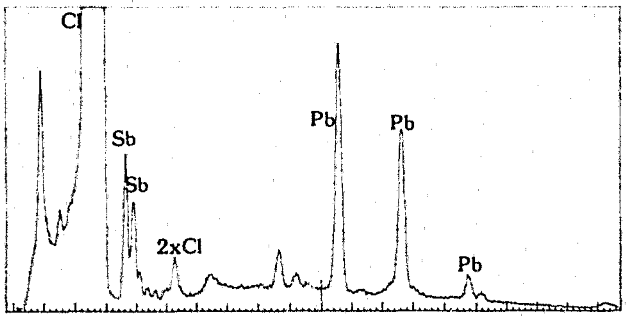

Figure 12. X-ray fluorescence spectrometry spectrum of a typical member of Class 1B(ii) (lead and antimony).

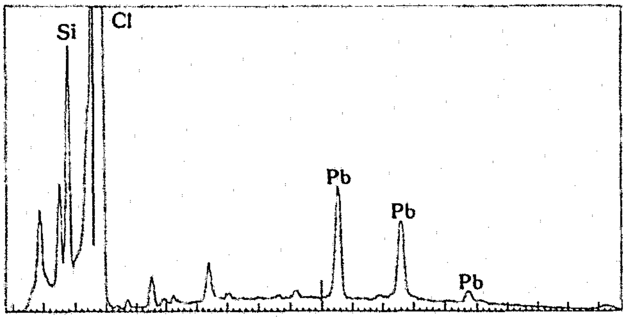

Figure 13. X-ray fluorescence spectrometry spectrum of a typical member of Class 1B (iii) (lead and silicon).

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 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.

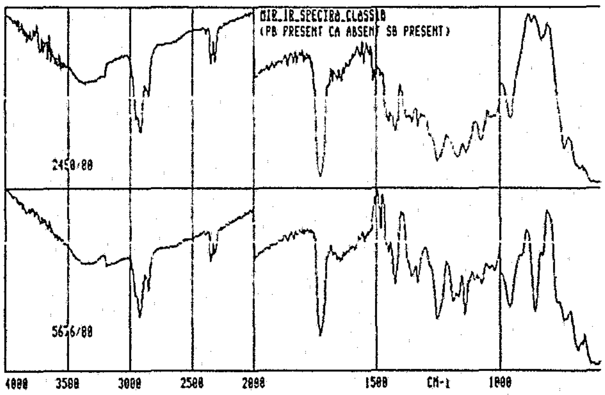

Figure 14. Infrared multiple internal reflectance spectrometry spectra of typical members of Subgroup 1B (ii) (lead and antimony).

### 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 (α) peak area, ratioed to the nett lead L (α) 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

The author wishes to thank the staff of the Instrument Section, Northern Ireland Forensic Science Laboratory, for their help in the preparation of this paper.

### 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.

# TRENDS IN POLYMER DEVELOPMENT AND ANALYTICAL TECHNIQUES

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Polymers, or plastics as they are commonly referred to, comprise a large, rapidly growing, and economically important class of materials. These materials have had a wide impact on practically all aspects of economic activity, including industry, commerce, business, technology and medicine, to name a few. The production and use of polymers is growing at an average annual rate of 8 percent, about a factor of 3 greater than other materials. As a result of this growth, the physical volume of plastics produced annually exceeds that of steel (Eby *et al.* 1984) and is attributed largely to replacement of conventional materials owing to the ability to tailor properties for specific applications at advantageous costs. Polymers have been the basis for entirely new products that rely on some special property of these diverse materials. Today, more and more products formerly made of glass, metal, ceramics, or natural products (wood, cotton, etc.) are manufactured of plastics.

In recent years, the kinds of polymeric materials used in the manufacture of plastics has undergone change. The trend has been away from synthesizing entirely new polymers for specific properties and towards combining polymers with other polymers, or with nonpolymeric materials to achieve the desired properties. Contributing to this trend are economic considerations and the technological impact of advances in polymer science and engineering. The development of new polymers is expensive and commercialization may involve large capital investments in production facilities. Advances in the knowledge of structure-properties relationships and processing of polymers have permitted extensions of useful properties and performance beyond what previously had been considered possible. Through developments in processing, polymer scientists and engineers today are able to create a variety of structures that have quite different physical properties. The newer plastics may be categorized as polymer blends or alloys, reinforced plastics and laminates.

The blending of a polymer with one or more additional polymers (polymer blends or alloys) (Paul and Newman 1978) and the combination of polymers and reinforcements (polymer matrix composites), yield a great diversity of properties and synergistic performance at competitive costs. For this reason, synthesis of new polymers has been restricted to development of polymers with higher use temperatures; a property enhancement not readily addressed by blending or reinforcing polymers. Reinforcements may be either other polymers in fiber form (polyaramids), or nonpolymeric materials such as glass and carbon fibers.

Even in markets long dominated by plastics the trend is to use polymer blends to obtain desired properties at lower costs. One such example is plastic packaging, which frequently requires high specific strength (strength/weight) and controlled permeation of atmospheric gases. By selective combinations of polymers both these properties can be provided at lower costs and in lighter weight products. The utilization trends have important consequences in the types of characterization methods that may be successfully applied to identify these materials. While the complexity of newer polymeric materials may make characterization more difficult, it may nonetheless be easier to establish the origins of the specimen under investigation.

The trend in polymer utilization towards engineered structures to achieve desired properties is particularly strong in the area of engineering plastics which are identified as those materials that serve a structural function, such as load bearing. It has been estimated that approximately 100 new engineering plastics will be introduced in 1984, and that these will be primarily polymer blends (Wood 1984a). The use of polymer blends has been growing at an annual rate of 12-14 percent and this growth rate is expected to continue over the next decade (Frados 1983).

In polymer blends, two or more polymers are combined to fill performance gaps, especially higher use temperatures, stiffness and strength, improved environmental stress crack resistance (ESCR), greater flame retardancy, better abrasion resistance, and enhanced processibility. An example is high impact polystyrene, which is a blend of the polymer and an elastomer modifier. The elastomer improves the impact properties since it is a good energy absorbing material, while the polystyrene imparts good mechanical rigidity. A similar technique is used to improve the toughness of thermosetting resins, that is, epoxies, that are used as structural adhesives. Thermosets are a class of polymeric materials formed by chemically linking low molecular weight (MW) prepolymers into a three-dimensional array during processing. These cross-linked materials are inherently brittle, insoluble, and do not melt. Figure 1 shows a scanning electron micrograph (SEM) of the fracture surface of an elastomer modified epoxy in which the elastomeric phase appears as spheres in the epoxy matrix.

This is an example of an incompatible polymer blend in that the constituent polymers separate into distinct phases. Other polymer mixtures form single phases, and are termed compatible blends. As in the case of incompatible blends, this is done to obtain synergistic effects in performance.

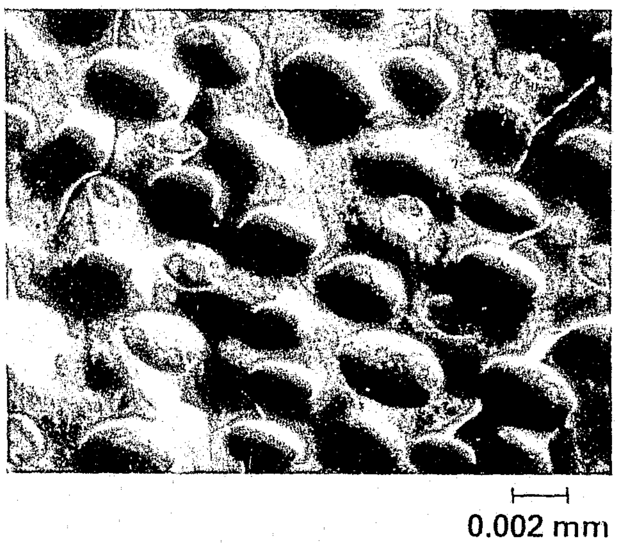

Figure 1. Scanning electron micrograph of the fracture surface of an elastomer modified epoxy. The spherical objects are the elastomeric phase.

Compatible and incompatible blends present different characterization challenges. Compatible blends are characterized by single glass transition temperatures, homogeneous morphology and structure, and molecular spectra indicative of mixing at the molecular level. Incompatible blends, on the other hand, yield special morphological features, for example, the spheres shown in Figure 1, and also yield other structures depending on the relative proportions, molecular weight, thermal and mechanical history, and solvent, if solvent cast. An example of plate-like microstructure is shown in Figure 2 for an incompatible blend of polyethylene and nylon in which the polyethylene phase is distinguished by the light regions and the nylon by the dark regions. The contrast between the two polymers in this figure has been enhanced by a staining procedure that preferentially affects the nylon. This blend uses the barrier properties of nylon to permeation hydrocarbon, thus improving polyethylene as a packaging material.

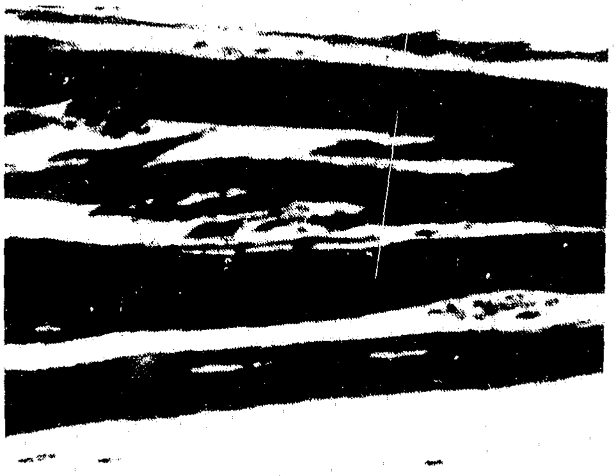

Figure 2. Micrograph of nylon (dark areas)-polyethylene (light-colored areas) blend.

The success of plastic beverage bottles is well documented (Miller 1983). A more recent exploitation of this technology is liquor bottles. With improvements in barrier properties packaging beer will be possible. The use of polymer blends has resulted in lighter weight containers. The weight factor is of particular importance to the airline industry which can realize significant savings by using plastic bottles for single drink packaging (Olcott 1984).

Blending of polymers is also done to improve processing, as in the case of polyphenylene oxide (PPO) which is blended with polystyrene. These two polymers form a compatible blend with the lower glass transition temperature compared to that of pure PPO facilitating processing.

Other chemicals are compounded with polymers to aid processing, improve handling, and enhance properties, appearance and performance (Frados 1983). These compounds are, in general, low MW compounds that may be present in varying amounts depending on the application. Mold release agents are added to reduce sticking during fabrication, antistatic agents are added to the bulk or surfaces of polymer films to reduce the tendency of electrostatic charging, and plasticizers may be added to lower the useful temperature and promote better performance. Depending on the intended application, ultraviolet (UV) stabilizers and antioxidants are used to improve performance. In addition to the general classes of additives, or compounding agents, mentioned above, inorganic fillers are frequently added to enhance mechanical properties and reduce costs. As few polymers are naturally colored, plastics are colored by compounding with colorants that may be inorganic pigments, or organic dyes. The full range of additives, modifiers, fillers, colorants and reinforcements provide the polymer technologist with the means to create new polymeric materials with tailor-made properties.

Reinforced plastics (composites) and layered structures (laminates) are other types of polymeric materials finding increased application. Reinforced plastics (Weatherhead 1980) are composed of polymeric matrix resins loaded with reinforcements that provide mechanical strength, while the function of the polymer is to spread the load. These structural materials have improved corrosion resistance in comparison to metals. The polymer matrix material may be either a thermoset, such as epoxies, or thermoplastic materials like polypropylene, nylon, etc. The reinforcements are principally glass fibers, although carbon fibers and polyaramids are used in advanced composites that are finding application in aerospace and high tech consumer products. The current trend is to combine different reinforcements to optimize properties and minimize costs.

Polymer matrix composites are growing at an annual rate of about 8 percent (Geller 1983) This growth is stimulated by wider acceptance of reinforced plastics and advances in processing. The industry is shifting away from labor intensive production and towards automated fiber layup and pultrusion methods. These materials, in a manner similar to unreinforced thermoplastics, are often compounded with a number of chemical agents to facilitate some aspect of processing, and to achieve improved properties and performance (Weatherhead 1980). The typical commercial epoxy resin is a two component system, the epoxide resin and the curing agent or hardener. Curing agents are generally primary or secondary amines. The chemical composition of the amine may vary, and this is another aspect of the chemical structure of an epoxy that can be characterized. One common feature of thermosets is that the solid state structure is formed by chemical bonds during the course of processing. The prepolymers, or monomers, are chemically reactive and as the mixture solidifies the network-forming reactions decrease significantly as reactive groups become trapped by the high viscosity. As a result, reactive chemical moieties remain subsequent to processing, and the type and concentration of these species may be specific of the starting substances, the processing conditions, and the use environment.

Reinforced plastics have been the materials of choice for marine applications for a number of years. More recently they have penetrated the construction, electrical, transportation and consumer products industries. The automotive industry is making major strides towards adopting reinforced plastics for body panels, bumpers and under-the-hood applications. It has been projected that reinforced plastics will be the successor of stamped steel in the automobile (Wood 1984b). The fiber glass body Corvette has been around for years, and more recently, the Pontiac Fiero and Honda CRX automobiles have incorporated large volumes of these materials. The body of the CRX, for example, is 40 percent polycarbonate/acrylonitrile-butadiene-stryene (ABS) based plastic (Hartley 1983). Drawbacks to more rapid introduction of composites in the automotive industry are a technology built around sheet metal, and the relatively slow processing times required. Recent advances in processing, and the potential of reinforced thermoplastics portend a greater use of these materials in the future.

An advantage of composites is the high value of mechanical properties per unit mass (specific properties). The specific modulus and strength of composites exceed those values of metals they replace by factors of up to 5 (Agarwal and Broutman 1980). A current limitation of most thermoplastics as matrix materials in automotive uses is their instability at high temperatures. Even thermoset resins are limited in this respect for many applications. Thus, technological activity has been directed towards synthesizing higher temperature thermoplastics, for example, polyetheretherketone (PEEK) and polyetherimide. Even with the current materials available, a "plastics" automotive engine has been built and is being evaluated by Ford (Keebler 1982). This engine uses reinforced plastics in practically all engine parts, with the exception of those in contact with hot surfaces (cylinder walls, piston heads, valves and exhaust manifold). The engine is about half the weight of a comparable cast iron block engine, and is 40 percent quieter.

Another growth market for composites is air transportation where use of these materials has reached 3-8 percent of the total weight of a commercial aircraft, excluding fuel. The potential for the turn-of-the-century designed aircraft is 65 percent (Geller 1983). This optimistic projection has been realized in two general aviation aircraft, the Lear Fan jet and the Raytheon-Beech Starship 1.

Plastics, including reinforced plastics, are becoming the materials of choice in the medical and dental industries which represents the fourth largest market for plastics (Gross 1984a). In many applications the superior chemical resistance of plastics, frequently brought about by blending, is a contributing factor. The resins of choice as dental restorative materials are vinyl esters that will polymerize in the oral environment. Although almost exclusively used in anterior teeth for which load bearing is not serious, the wider application of vinyl esters will rest on current efforts to improve toughness so that load bearing posterior restoratives are viable. There have been attempts to use composites as orthopedic implant materials, but currently, nearly all polymeric materials found in these devices are either ultra high MW polyethylene or polyoxymethylene.

Laminates (multilayered polymer structures) are another relatively new technology with large potential markets, particularly in food packaging (Higgin 1984; Board 1983). The advantage of laminates is that properties can be tailor-made to specific applications through incorporation of polymers that have different superior properties, that is, good mechanical properties of one polymer with good barrier properties of the other. Immediate applications are likely to be containers for drinks, condiments, and other oxygen and moisture sensitive products. One example is a six layer structure containing four different polymers that is produced by a co-extrusion process. Laminates have potential for packaging retorted food products. This type of packaging would not only permit heat processing of foods in the container, but also direct heating of the food in the container in microwave ovens prior to consumption.

Laminates are replacing other materials in applications in which a combination of properties is desired and which utilize less material. For example, the modern fan belt is made from three different polymers combined with a woven fabric to achieve a lighter weight product (about 30 percent reduction) and longer service life (from 40 to 200 percent longer) (Smith 1984). The same technology can be used to produce gas tanks, fuel cells, tubing and skis.

Metal coated plastics are another type of material experiencing rapid growth, and the projection is that their use will double in the coming decade (Gross 1984b). Expanded markets are in automotive, electrical and electronic components in which recently imposed requirements for shielding against electromagnetic interference (EMI) and radio frequency interference (RFI) is the driving force. Dominant substrates are ABS (acrylonitrile-butadiene-styrene), PPO (polyphenylene oxide)-polystyrene alloys, polyphenylene sulfide and polyethersulfone. The last two mentioned will see applications that combine reflectivity of the metal coating with high temperature use.

Advances in processing have led to new materials design. Better control of molecular orientation during processing has led to higher modulus fibers and other property improvements through biaxial molecular orientation. Alternate methods of producing cloth from fiber have also been developed. The general method of producing fabric is by weaving yarns of natural or synthetic polymer fibers. Very strong fabrics are now made by nonwoven technologies that employ chemicals, heat, solvents, or mechanical processes to link the basic elements (fibers, yarns, or filaments) together (Simon 1984). Nonwovens can be tailored to a wide variety of products ranging from tiles on the Space Shuttle to diapers, roofing materials, surgical gowns and household linens. Due to marketplace considerations it is unlikely that this technology will have a significant impact on the garment industries.

Looking to the future, developments in the processing of high modulus fibers, higher use-temperature polymers and molecular composites may lead to new commercial materials. Polymer scientists have developed processes to achieve highly oriented polymers either with flexible, or rigid rod polymer chains. Fibers of these polymers have very high tensile modulus (approaching theoretical limits) and strength in the fiber or chain direction, but very weak properties normal to the fiber or chain axis. The tendency towards imbrittlement or fribillation is diminished by surrounding the fiber with a matrix material. Molecular composites incorporate rigid rod polymer molecules as the reinforcements, rather than fibers. The matrix material in this case is a more flexible polymer which aids processing and impact properties. Rigid rod polymers have excellent longitudinal strength and modulus owing to the inflexibility of the molecular chain. However, they are difficult to process into forms other than fibers. In addition, fibrillation is of concern. The incorporation of the oriented rod molecules into a more flexible matrix material may result in a molecular composite that combines the strength and high tensile moduli of rigid rod polymers with the processibility of thermoplastics.

Recent advances have affected large volume plastics. Until recently, polyethylene was available as either high density (linear) polyethylene (HDPE) or low density (branched) PE (LDPE). The plastics industry is now supplying linear low density PE (LLDPE) which is a copolymer of ethylene and α-alkenes (Martino 1984). A wide variety of similar materials are possible given the range of α-alkenes and comonomer contents available. The LLDPE's have tailor-made properties, in particular, ESCR, that are superior to either LDPE or HDPE. The alloying of LDPE and LLDPE has been shown to further improve properties and processing.

## ADVANCES IN POLYMER CHARACTERIZATION TECHNIQUES

The overall trend in polymeric materials is towards highly engineered structures with properties tailor-made to a particular application. These specifically designed materials have complex structures that must be considered when selecting characterization methods. In addition, materials such as thermosets are intractable thus dictating the selection of techniques that require minimal specimen preparation. The complex chemical and physical structure of these materials affords opportunities for analysis from the molecular to macroscopic structural levels. For molecular structure the characterization methods are similar to those developed for homopolymers, although their application may not be as straightforward owing to a more complicated chemical composition. Analytical electron microscopic methods are becoming important probes of the intricate structures exhibited by the newer types of polymeric materials. The discussion of advances in characterization techniques begins with considerations of the diversity of chemical and physical structures exhibited by polymers.

Homopolymers can be classified by the chemical repeat unit (methylene group of polyethylene), chemical defects introduced in the polymerization process (for example, branching and tacticity), chemical species at the polymer chain terminus (end groups), MW and molecular weight distribution (MWD) in addition to additives, stabilizers and compounding agents. Copolymers formed by copolymerization of two or more monomer types are characterized by the arrangements of the different monomers in the polymer chain. This arrangement may be completely random at the one extreme (random copolymers) and complete segregation of the monomer types (block copolymers) at the other extreme. Block copolymers can be viewed as chemically linked homopolymers. Semicrystalline polymers exhibit distinctive morphologies that depend on molecular features as well as processing conditions.

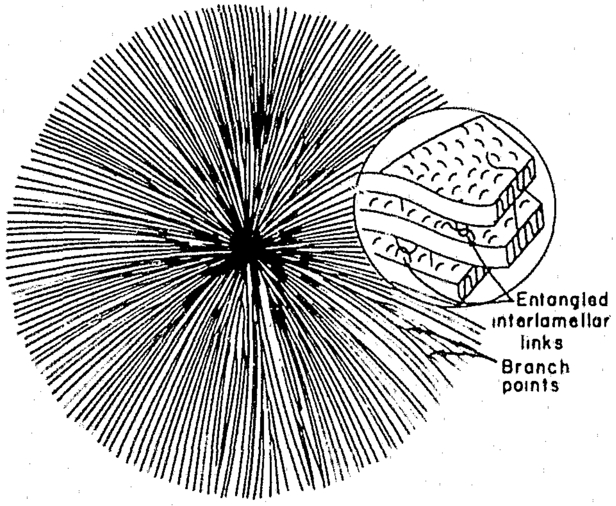

Figure 3. Model of the molecular organization and structure of melt solidified semicrystalline polymers.

An illustration of the morphologies is given in Figure 3. The crystalline portion is organized into lamellar structures in which the polymer molecules are arranged with the chain axis essentially perpendicular to the lamellar surface. Lamellae thicknesses are in the range 10-100 nm and the lateral surface dimensions are the order of micrometers. The noncrystalline material is located at the lamellar surfaces and in the interlaminar regions. The lamellae are arranged into spherulytic structures in which lamellae radiate outward from the center of the spherulite and the polymer chain axis direction is normal to the radius of the spherulite. When these chemical and physical structural features are combined with those exhibited by polymer blends, composites and laminates, it is evident that a wide range of characterization methods can be employed.

Spectroscopy has been at the forefront of methods for polymer identification. The techniques that fall under this general heading include nuclear magnetic resonance (NMR), infrared (IR) and Raman spectroscopy, atomic and molecular electronic absorption and emission, and surface and bulk methods based on X-rays and electrons. For evaluation of other aspects of structure, experimental approaches include electron and optical microscopy, differential scanning calorimetry (DSC), high performance liquid chromatography (HPLC) and X-ray and electron diffraction.

## VIBRATIONAL SPECTROSCOPIC METHODS

Infrared spectroscopy is the most commonly used method for analysis of the vibrational properties of polymers, although both inelastic neutron scattering (Logan *et al.* 1973) and Raman spectroscopy (Siesler and Holland-Moritz 1980) have advantages in some applications. In fact, IR spectroscopy is the most widely used technique of polymer identification. The advantage of IR spectroscopy relates to the availability of a large number of IR reference spectra of polymers, monomers and additives that when combined with recent advances in computer aided search routines allows for the rapid identification of unknown substances (Fanconi 1984). Low sensitivity and inflexibility in sample type have been problems with IR spectroscopy but have now been overcome with Fourier transform infrared spectroscopy (FTIR). The several hundred fold increase in signal-to-noise ratio (sensitivity) made possible with FTIR has greatly expanded the role of IR spectroscopy for microsampling and nontransmission types of sampling (Koenig 1983).

Application of vibrational spectroscopy to polymers involves identification of chemical composition and physical structure. Qualitative and quantitative information can be obtained on chemical composition of polymers, copolymers, polymer blends, composites, additives and compounding ingredients. Vibrational frequencies and band intensities may also be sensitive to chemical order, that is, tacticity, branching, end groups and degradation products. The IR spectra of solid polymers provide information on the type and amount of crystalline forms, the degree of crystallinity, orientation of macromolecules, trans-gauche bond ratios and the local environment of constituent chemical groups.

Commercially available accessories exist for specular reflection, diffuse specular reflection, diffuse reflectance sampling, photoacoustic detection, in addition to the more common technique of attenuated total reflection. Figure 4 illustrates the various sampling techniques that can be used with FTIR. A wide variety of specimen types from particulates to intractable solids can be examined by a combination of these techniques. Some of these methods probe the surface. Specular and diffuse specular reflection measure the index of refraction as a function of IR wavelength. The reflection and absorption spectra are related through the Kramers-Kronig relationship (Ditchburn 1963). Diffuse reflection (DRF) or diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) is a combination of transmission and reflection of radiation by the sample. This technique is ideally suited to microsampling with spectra obtainable from nanogram quantities of material. Reflectance techniques are sensitive to the state of the solid specimens - different sample preparations may yield spectra in which the relative band intensities vary. This spectral sensitivity, however, may afford advantages of greater specificity in identification.

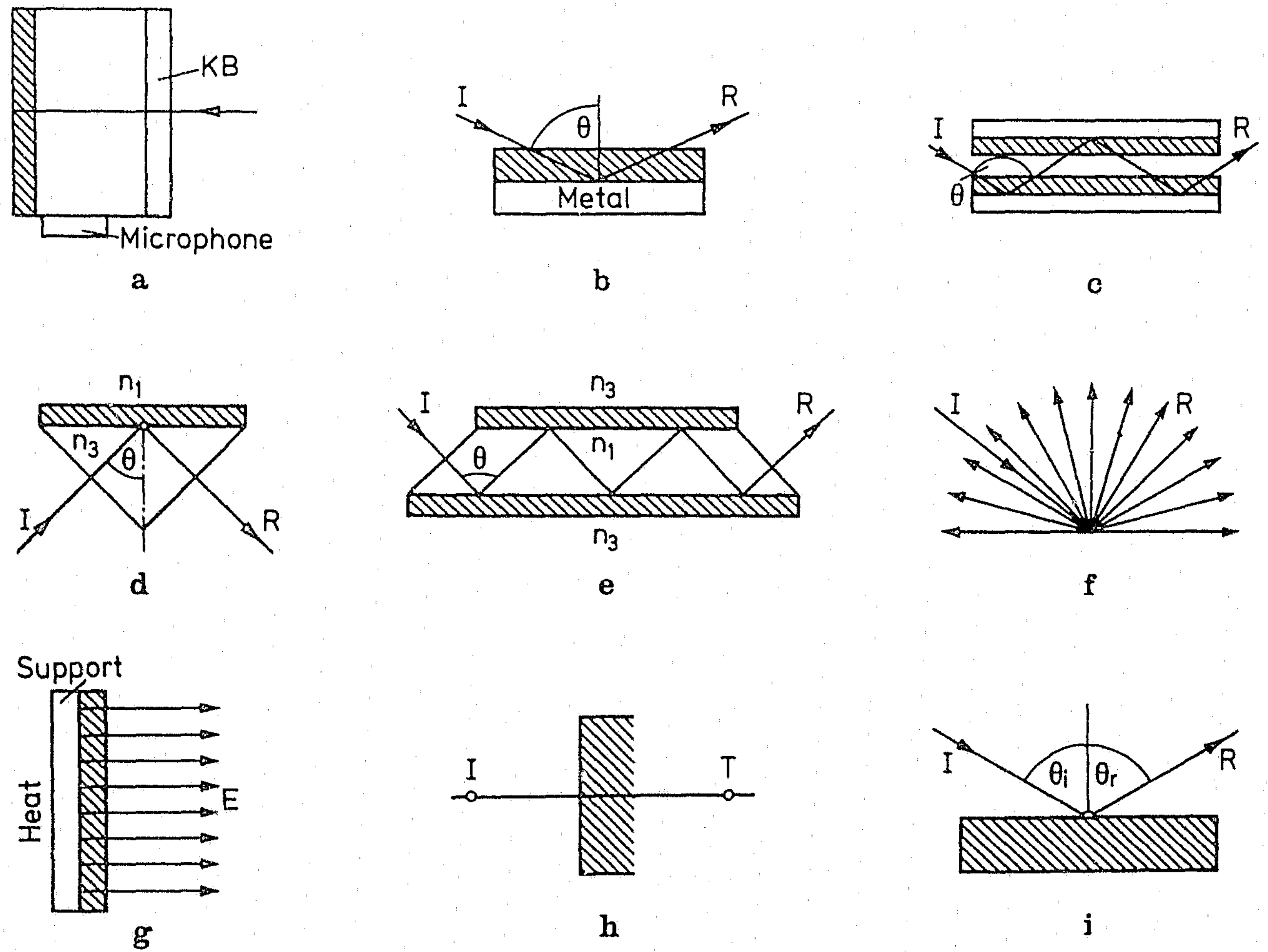

Figure 4. Sampling geometries used in Fourier transform infrared spectroscopy. (a) Photoacoustic, KB is an appropriate infrared window material. (b) Absorbance measurement combined with reflection from metallized surface (Θ should be between 70° and 89.5°). (c) Multiple pass technique based on b. (d) Single internal reflection .$\Theta > \Theta_c = \sin (n_3/n_1)$. (e) Multiple internal reflection setup. (f) Diffuse reflectance. (g) Emission of infrared radiation from heated sample. (h) Transmission. (i) Specular reflection, angle of incidence equals angle of reflection. Reprinted from Fourier Transform Infrared Spectroscopy of Polymers by J. L. Koenig in Advances in Polymer Science 54 (1983), by permission of Springer-Verlag.

Photoacoustic spectroscopy (PAS) differs from the above-mentioned sampling techniques in that IR absorption is detected by the acoustic signals produced by the heat generated through absorption of IR radiation (Vidrine and Lowry 1983). The usual feature of this detection method, in contrast to transmission approaches, is that the signal increases with absorption, rather than decreases as is the common observation. A totally absorbing material such as carbon black is used as a reference material for beam intensity. Photoacoustic detection is suitable for studying intractable solids, highly absorbing materials or specimens that cannot be prepared as thin films without destroying identification features. An example of a PAS spectrum is given in Figure 5 for the polymer polyvinylidene fluoride. The signal minima in this spectrum corresponds to absorption maxima, in this respect it takes on the appearance of a transmission spectrum.

Raman spectroscopy is a technique for determining the vibrational properties that are complimentary to IR spectroscopy. This has to do with the physical processes that are interrogated by the two methods. In Raman spectroscopy, a photon of visible light is shifted in frequency owing to the interactions between vibrational modes and electronic states (Peticolas *et al.* 1970). The frequency shifts can be either positive or negative and equal the molecular vibrational frequencies. The intensities of the frequency shifted light are proportional to the square of the derivative of polarizability with respect to the normal modes of vibration. On the other hand, IR involves the direct absorption of IR light that excites the vibrational modes to higher vibrational levels. The strengths of IR band intensities are proportional to the square of the derivative of the dipole moment with respect to the normal modes of vibration. Either method measures vibrational frequencies and intensities that are characteristic of the substance under investigation.

Raman spectroscopy has the noted advantages over IR in that the high frequency visible radiation used can be focussed to smaller areas and detectors are inherently more sensitive at higher frequencies. For these reasons the combination of laser excited Raman spectroscopy and the optical microscope yielded a micro-Raman instrument. This development was made at the National Bureau of Standards where it was used to study inorganic particles in the submicron range and polymeric particles of dimension 10 μm, or larger (Rosasco 1978). The conduction of heat generated when the focussed laser beam impinges on the polymer specimen limits the size of the sample that can be investigated. Microscopical techniques are used to position the sample in the beam.

In terms of the trend to use highly structured and complex polymeric materials, vibrational spectroscopy has distinct advantages for their characterization. A wide range of chemical and physical structure features can be identified as illustrated in part by the following examples. The IR spectra of polymer blends not only are specific of the constituent polymers, but also band frequencies and inten-

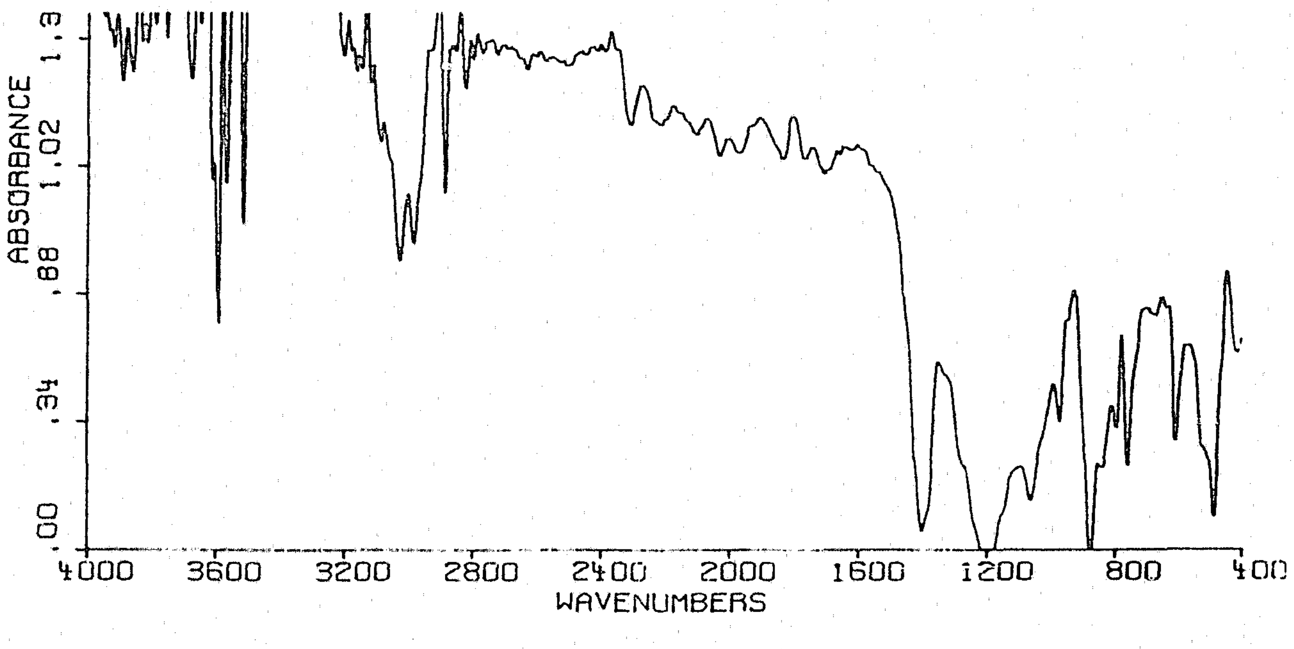

Figure 5. Photoacoustic FTIR spectrum of polyvinylidene fluoride. The minima in the PAS correspond to maxima in the absorption spectrum.

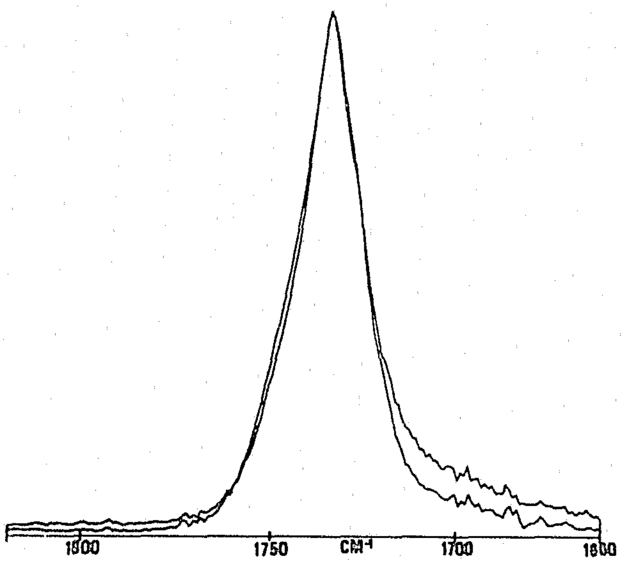

Figure 6. FTIR spectra of a *compatible* blend of polyvinyl chloride and poly(ϵ-caprotactone). The frequency shift with stoichiometry of blend is the basis for terming this a compatible blend. Coleman, M. M. and Zarian, J. (1979). J. Polym. Sci., Polym. Phys. Ed. 17:837. Copyright 1979 by John Wiley and Sons, Inc. Reprinted by permission of John Wiley and Sons, Inc., New York.

sities may be sensitive to the degree to which the polymers intermix in the blend. Figures 6 and 7 are examples of IR spectra of compatible and incompatible blends that demonstrate how band frequencies can be affected by the local environment of the vibrating chemical group. The carbonyl stretching mode band of poly(ϵ-caprolactone) (PCL) (Figure 6) exhibits a frequency shift when PCL is part of a compatible blend with polyvinyl chloride (PVC). The carbonyl vibrational mode frequency is unshifted with respect to the pure spectrum when the blend is incompatible as is the case with poly(β-propiolactone) blended with PVC (Figure 7). The frequency shifts are related to specific interactions between the carbonyl oxygen and PVC. The magnitude of the shifts depends on the stoichiometry of the compatible blends.

Thermosets are the predominant polymer matrix materials of polymer composites, and are examples of intractable solids that are not readily analyzed by solution methods or other methods of sample preparation, such as heat pressing thin films. The use of reflectance sampling in FTIR facilitates identification of composites. Central to the characterization of the composites and traceability to another piece of material, processed under identical conditions and which experienced a similar use environment, is the identification of IR bands assignable to chemical species that were either formed or depleted during polymerization (network formation). These bands can be used as indicators of the degree to which the chemical reactions that link the network were completed during and subsequent to processing. The reactions proceed at a much slower rate once solidification occurs owing to the decrease in molecular mobility. In Figure 8 a band at 1638 $cm^{-1}$ has been identified as originating from the reactive chemical moiety. This band intensity decreases in time as the specimen is exposed to a simulated use environment, as shown in Figure 8.

Polymeric materials degrade to varying degrees in the use environment. The degradation of useful properties (mechanical, electrical, optical or chemical) has associated with it changes in chemical composition or physical structure, or both. Infrared and Raman spectroscopies can be employed to quantify these changes. Generally, degradation is associated with scission of the carbon-carbon backbone bond that forms the long molecular structures of polymers. Chain scission lowers the MW and produces changes in the concentration of chemical groups at the ends of the polymer chains. Figure 9 illustrates the increase in IR bands associated with methyl, carbonyl and vinyl end groups in polyethylene as it is subjected to mechanical load and rupture. Other effects of degradation can be attributed to loss of additives, most notably low MW plasticizers, UV stabilizers and antioxidants. Under suitable conditions changes in the concentration of these substances can be detected by vibrational spectrocopic methods.

An advantage of Raman spectroscopy is its sensitivity to vibrational modes of chemical bonds forming the polymer backbone. In particular, delocalized vibrational modes that involve Cartesian displacements of many carbon atoms along the molecular chain may be Raman active. The frequencies of these modes can be measures of molecular length. An example is the ability to distinguish n-alkanes of slightly different MWs. For two high MW n-alkanes differing by one $CH_2$ group the IR spectra are virtually identical. On the other hand, in the Raman spectra there appear bands whose low frequencies are characteristic of the molecular length (Schaufele and Shimanouchi 1967). The corresponding vibrational modes have analogues in Raman spectra of semicrystalline polymers in which the frequencies are not related to the polymer chain length but to the thickness of the lamellar textured crystals (Rabolt and Fanconi 1977).

Raman spectroscopy can be combined with optical microscopy to produce an instrument capable of microanalytical quantification of polymer specimens. Another feature of a Raman spectrometer/

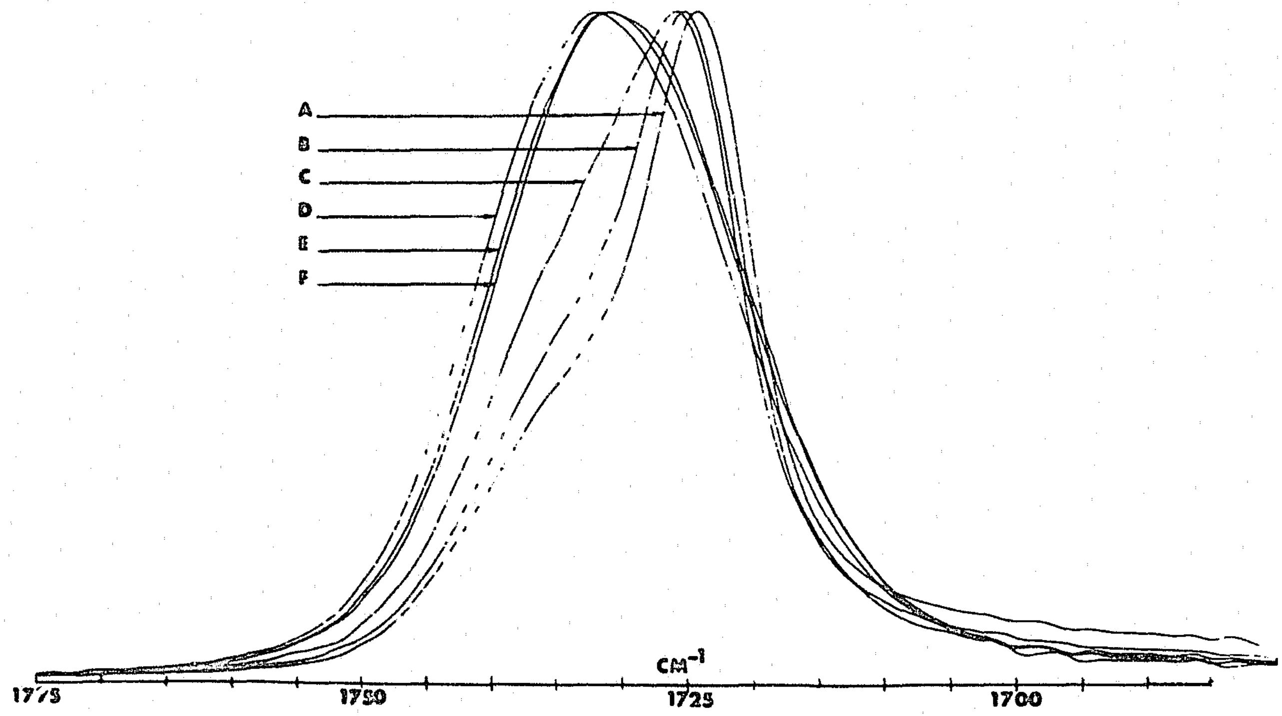

Figure 7. FTIR spectra of an *incompatible* blend of polyvinyl chloride and the lack of a frequency shift in the blend means that the two phases are separated (incompatible). Coleman, M. M. and Varnell, D. F. (1980). J. Polym. Sci., Polym. Phys. Ed. 18:1403. Copyright 1980 by John Wiley and Sons, Inc. Reprinted by permission of John Wiley and Sons, Inc., New York.

microscope (micro-Raman) system is the generation of Raman scattered light images. Consider a specimen composed of an inhomogeneous mixture of several polymers, for example an incompatible blend or laminate, in which the size of the phases are in the micrometer range, or larger. If the monochromator of a micro-Raman system is set at a frequency corresponding to a Raman band of one of the constituent polymers, then an image is produced that highlights those areas of the field of view containing that polymer. Figure 10 depicts the SEM micrograph of a polymer laminate section containing five layers of total thickness of 14 $\mu$m. By selectively scanning over these five layers and recording Raman spectra from each region it was possible to identify the laminate as polypropylene and polyethylene terephthalate (PET). An image of the PET rich areas was generated by setting the monochromator at the frequency of one of the Raman shifted bands of PET. Figure 11 shows the image produced in which the bright central portion corresponds to the PET layer.

## NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Proton nuclear magnetic resonance (NMR) spectroscopy is a powerful method for determining the structure and dynamics of organic molecules in solution (Bovey *et al.* 1983). The basis of the technique is resonant transitions between energy levels of nuclear spins in the presence of applied magnetic fields. As the energy levels are sensitive to the local electronic environment of the nucleus, detailed quantitative information is obtained from the transition frequencies (chemical shifts) and intensities. The extremely narrow NMR spectral lines (approximately a few Hz) are observed for solutions because of rapid molecular motions that average interactions. As a result of the sharp spectral bands, features attributed to sequences of chemical groups are revealed. By taking advantage of the high resolution capability of NMR solution, aspects of polymer structure, stereochemical configuration, branching, copolymer sequences and molecular dynamics have been elucidated. This method is not only restricted to protons. Fluorine NMR has been

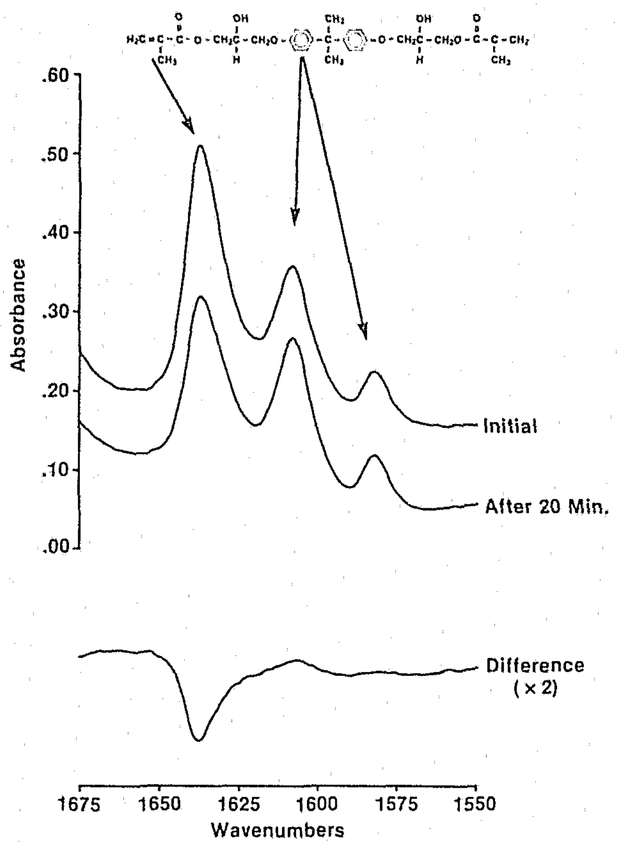

Figure 8. Portion of the infrared spectra of a bisphenol A - vinyl type polymer matrix resin: top spectrum, obtained subsequent to processing; middle spectrum, obtained after 20 minutes in simulated use environment; and bottom spectrum - the difference spectrum - obtained by subtracting top spectrum from middle spectrum. The negative peak indicates that additional cross-linking occurred after processing.

applied to fluorine containing polymers (Bovey *et al.* 1983); and with developments in fast Fourier transform spectroscopy and co-adding signals to improve sensitivity, NMR based on the carbon-13 ($^{13}C$) nucleus at natural abundance is now possible. More details concerning polymer structure are obtainable by $^{13}C$ NMR owing to the greater chemical shifts of $^{13}C$. In cases in which it is possible to solublize the polymeric material, chemical microstructure, including stereochemistry, branching and end groups may be probed by $^{13}C$ NMR. Figure 12 illustrates the power of $^{13}C$ for analyzing the stereochemistry of PVC and polyvinyl bromide. Stereochemistry refers to the specifics of the arrangements of the $-CH_2CHx-$, x=Cl or Br, groups along the chain molecules. Besides the prevalent head-to-tail arrangement ($-CH_2CHxCH_2CHx-$), head-to-head ($CH_2CHxCHxCH_2-$) and tail-to-tail ($-CHxCH_2CH_2CHx-$) configurations may occur as well. In addition, the halogen atoms can occupy positions that are meso (m) or racemic (r); these arrangements refer to the stereoregularity (isotactic, syndiotactic and atactic). Sequence lengths of up to pentamers exhibit distinct chemical shifts. The chemical shifts and intensities can be analyzed in terms of the types and amounts of the various sequences. In Figure 12 the NMR spectra are labeled by the sequences that give rise to the various peaks. The stereochemical arrangements are dictated by polymerization conditions, and therefore may be a "fingerprint" of the polymer.

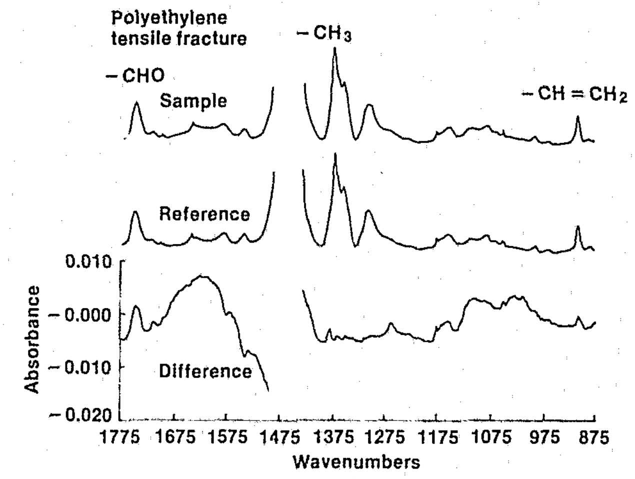

Figure 9. FTIR spectra of mechanically degraded polyethylene: top spectrum, tensile-fractured polyethylene; middle spectrum, reference material; and bottom spectrum - the difference spectrum - obtained by subtracting the middle spectrum from the top spectrum.

Another application of $^{13}C$ NMR that is of interest in the present context is the determination of branch types, distributions and concentrations. An example of the quantitative information that can be obtained is illustrated in Figure 13 for a LDPE. In this figure, the assignments of chemical shifts to the different kinds of branches is given. This example is of interest given the trend to LLDPE that are copolymers produced from ethylene and longer $\alpha$-alkenes.

Thus far, the discussion has focussed on polymers in solution, however, for various reasons it may be desirable to interrogate the material in the solid state. The solid state NMR method (Havens and Koenig 1983) has the advantage that no special sample preparations are necessary. Intractable solids may be evaluated, and any changes in the sample due to sample preparation are avoided. Generally, NMR of solids is characterized by broad distributions of resonance frequencies that obscure the small chemical shifts from which much

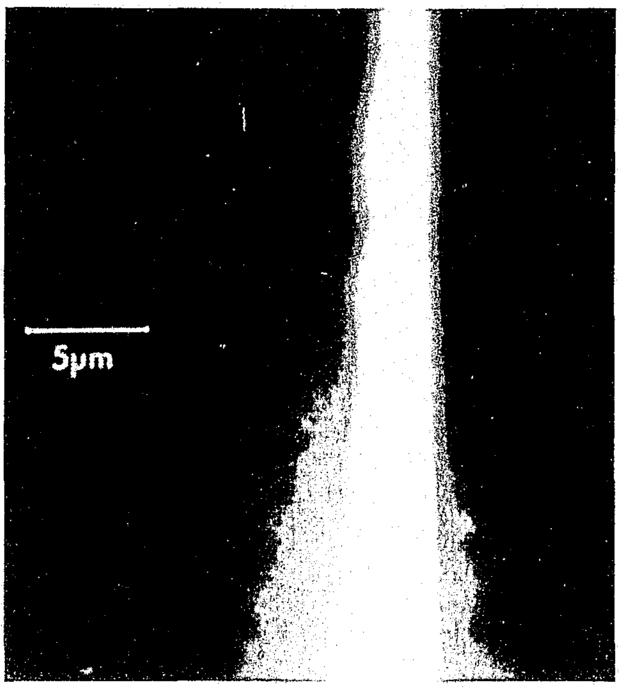

Figure 10. Scanning electron micrograph of five layer laminate of polypropylene and poly(ethyleneterephthalate). Reprinted with permission from Polymer Characterization: Spectroscopic, Chromatographic, and Physical Instrumental Techniques. Adv. Chem. Ser. 263, copyright 1983 by the American Chemical Society.

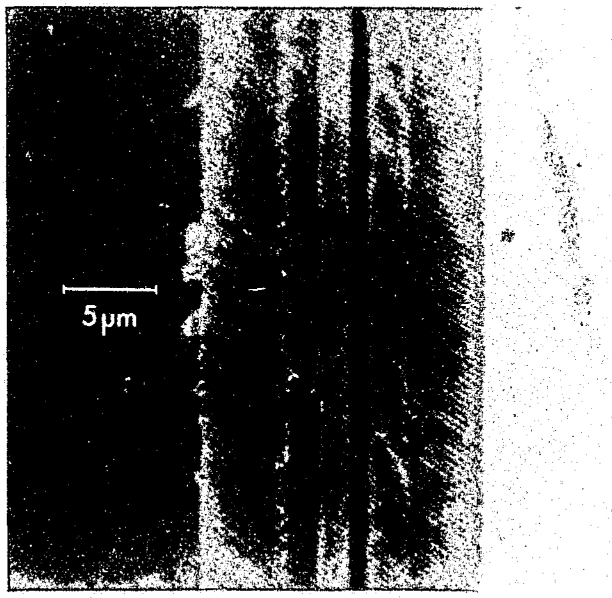

Figure 11. Raman scattered light image of the laminate shown in Figure 9. The bright region corresponds to poly(ethyleneterephthalate) (PET) since the monochromator was set to pass one of the PET Raman bands. Reprinted with permission from Polymer Characterization: Spectroscopic, Chromatographic, and Physical Instrumental Techniques. Adv. Chem. Ser. 263, copyright 1983 by the American Chemical Society.

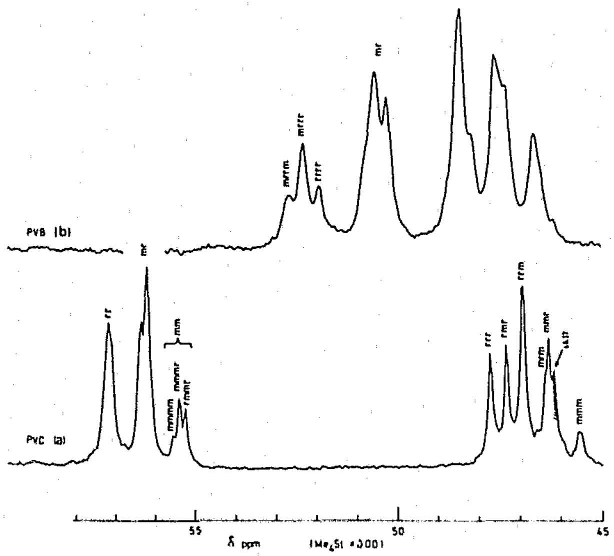

Figure 12. $^{13}C$ NMR solution spectra of polyvinyl chloride and polyvinyl bromide. The bands are labeled with the sequence (r = racemic and m = meso) to which they are attributed. Reprinted with permission from Polymer Characterization: Spectroscopic, Chromatographic, and Physical Instrumental Techniques. Adv. Chem. Ser. 263, copyright 1983 by the American Chemical Society.

information is obtained on liquid or solublized polymers. Line-widths of solid specimens recorded under conditions typical of liquid state spectra may be 20 kHz or more. The line-widths of solid specimens arise from strong dipole-dipole interactions and the absence of motional averaging in the time-frame of the NMR measurement. (Molecular motion is significantly reduced in the solid state compared to the liquid or solution states.)

High resolution techniques have been implemented to eliminate line broadening, thereby achieving $^{13}C$ spectra of solid materials whose band-width approaches that typical of the liquid state. High resolution $^{13}C$ NMR relies on high power proton coupling that practically eliminates dipolar broadening by the protons along with high speed sample spinning to average out the chemical shift anisotropy of the C-13 nucleus. The effect of these two techniques on the NMR spectrum is depicted in Figures 14 and 15. The broad band typical of solids is reduced to a complex band shape containing three distinct features arising from the chemical shift anisotropy. This idealized spectrum is for one type of carbon; if several types of carbons are present then the anisotropy may obscure features arising from different carbon types. The effect of sample spinning is illustrated in the bottom spectrum of Figure 15 for a specimen containing several carbon types. One additional technique is used, in this case to improve sensitivity. The low natural abundance of $^{13}C$ (about 1 percent) means that the NMR signals are inherently weak, and furthermore, owing to the long spin-lattice relaxation times of the $^{13}C$ nucleus, substantial improvement in sensitivity by co-adding pulses requires excessively long times.

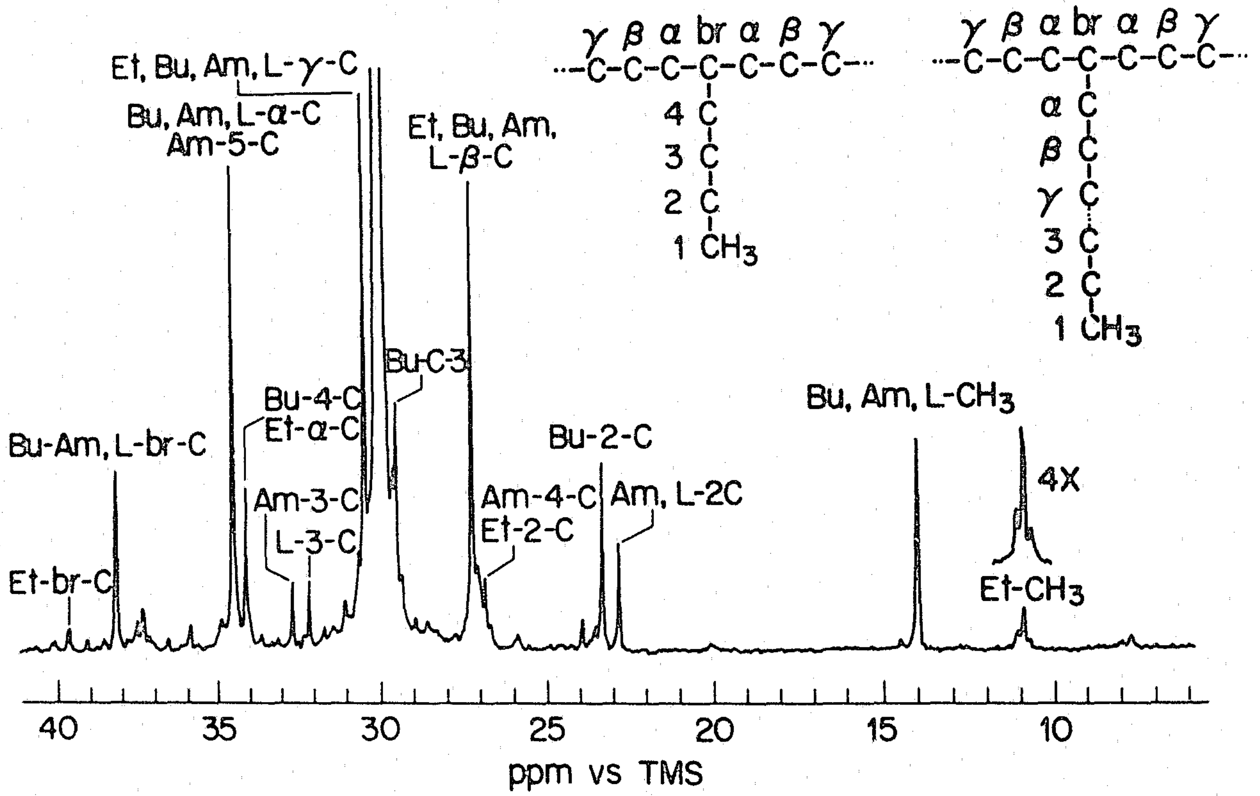

Figure 13. $^{13}C$ NMR spectrum of low density polyethylene. The NMR spectrum is labeled by the chemical groups causing the resonances. Reprinted with permission from Polymer Characterization: Spectroscopic, Chromatographic, and Physical Instrumental Techniques. Adv. Chem. Ser. 263, copyright 1983 by the American Chemical Society.

However, the time between pulses in the Fourier transform experiment can be shortened by a technique termed cross-polarization. In this method the protons are used as a source of magnetization to transfer polarization from the protons to the carbons. The greater abundance of the protons allows the system to reach equilibrium more quickly. Through incorporation of these techniques, high resolution solid state NMR has become an important tool for characterization of solid polymers. Figure 16 demonstrates the capabilities for analysis of epoxy based composites. A number of distinct lines are evident in Figure 16, including features attributed to reactive chemical species that did not react during polymerization.

The solids NMR spectrum of a PET tire cord fiber is shown in Figure 15. This spectrum contains several features that are characteristic of the structure imposed on the fiber by the processing conditions. Thus, one is able to identify not only the chemical composition of the material, but also information about how it was produced.

## CHROMATOGRAPHIC METHODS

Molecular weight and MWD are of interest in polymer identification because two polymers differing only in MW may have virtually the same IR, Raman, or NMR spectra. Molecular weight and MWD are two fundamental molecular properties of polymers that largely influence the processing abilities and mechanical properties of plastics. Polymerization processes are controlled to obtain the desired MW and MWD. A number of methods have been developed to measure these properties

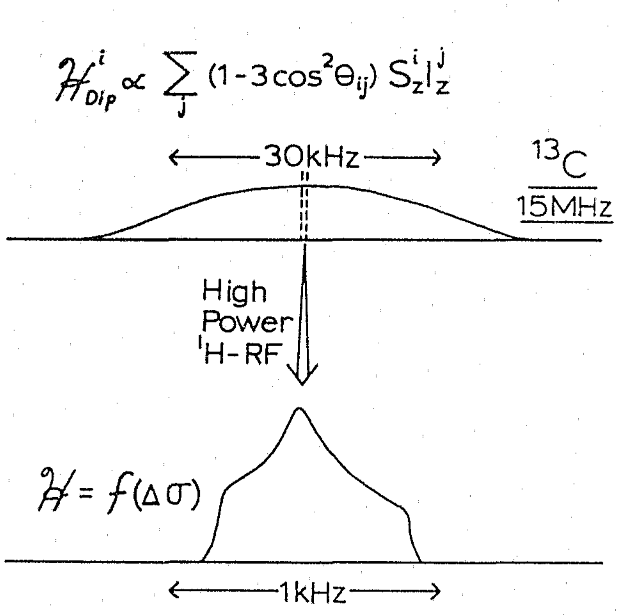

Figure 14. Line narrowing of $^{13}C$ NMR spectrum using high power proton decoupling methods. The remaining band profile is due to chemical shift anisotropy of the carbon resonance.

with chromatography having the advantage of providing measures of both quantities. Commercial chromatographic instruments are available for rapid and reliable measures of relative MWs and MWDs. Chromatograms of MWD can serve as a "fingerprint" of the polymer, and it is in this context that chromatographic methods are useful for polymer identification.

A common feature of chromatographic techniques is separation of the whole polymer (in dilute solution) into the constituent molecular sizes by various physical processes. Size exclusion chromatography, or gel permeation chromatography (GPC), is the most widely used, and in this technique separation is accomplished by the molecular size dependence of diffusion through porous media.

Recent advances in elution columns that improved separation efficiency and resolution of GPC, particularly at the low and high MWs, has led to the terminology "high performance liquid chromatography." Although these methods are only applicable to solubilizable polymers, they have the advantage of not requiring a great deal of material for identification once a suitable solvent has been selected. Typically, a few milligrams of polymer in solution is sufficient to obtain a chromatogram. As with thermal methods, chromatographic techniques are most useful once the type of polymer has been identified by molecular spectroscopy or other methods. For example, if solution NMR or IR spectroscopy were used to identify an unknown polymer, such as polyethylene, then GPC could be used to determine the MW and MWD for further characterization. A comparison of GPC chromatograms from two LDPE films is given in Figure 17. It is evident that the two films were made from different resins even though the IR spectra were virtually identical.

Gel permeation chromatography and all other chromatographic methods give relative measures of MW, and therefore the separation columns are calibrated with polymers of known MW, or as recently developed, a light scattering attachment is added for absolute calibration of the effluent. The detectors used with GPCs may be of several types that aid in the identification of constituents of polymer mixtures. Infrared and UV spectroscopy have been used in this capacity although their use is limited most notably in the case of IR by solvent absorption. The combination of GPC and UV detectors has been used for analysis of particle size, as in latex spheres.

Recent research has focussed on aqueous media chromatography and field flow fractionation methods. In the field flow methods, separation is accomplished through use of an external field, for example the different response by weight of polymer molecules in ultracentrifugation. Developments in aqueous media chromatography have been troubled by the chemical characteristics of column materials that interfere with separation processes.

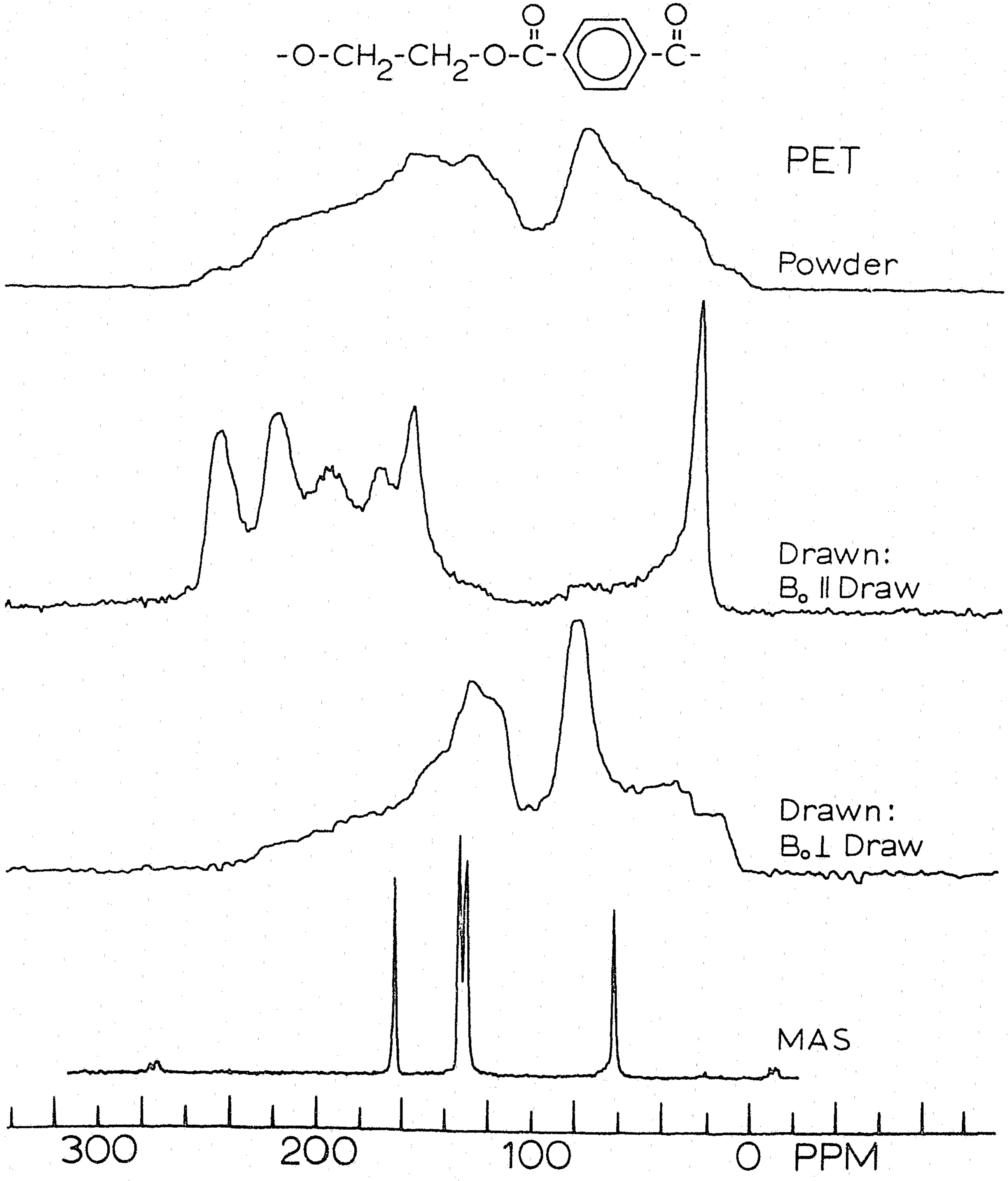

Figure 15. $^{13}C$ NMR spectra of poly(ethyleneterephthalate): top spectrum, powder orientation; middle two spectra, fiber oriented with respect to magnetic field; and bottom spectrum, powder taken with magic angle spinning.

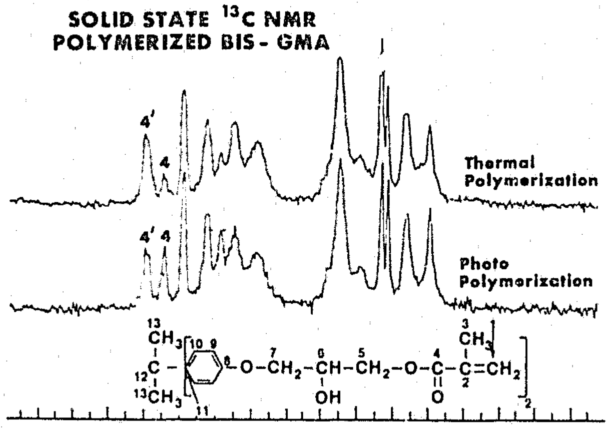

Figure 16. $^{13}$C NMR spectra of vinyl ester polymer matrix composite resin. Resonances attributed to reactive chemical species are identified.

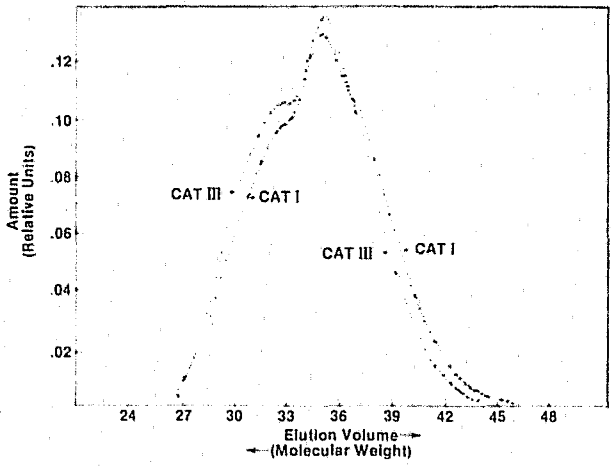

Figure 17. Gel permeation chromatograms of two low density polyethylene resins. A small difference in the proportion of the high molecular weight component is observed between the two films.

## THERMAL METHODS

Differential scanning calorimetry (DSC) is the most widely practiced technique of thermal analysis. The routine application of DSC is to studies of phase transitions (solid-liquid, solid-solid, glass transition), although heat capacity measurements are potentially of more significance to polymer characterization. Differential scanning calorimetry is not regarded as a primary polymer identification method in the sense of molecular spectroscopy. It does have utility in interrelating known and unknown polymers in terms of phase transitions and heat capacities. Heat capacity measurements are conducted at constant pressure rather than at constant volume, the latter being directly comparable to calculated values. It is possible to relate the two quantities. Limitations of DSC are the lack of perfect insulators so that some heat loss is associated with the measurement, and the lack of any direct indicator of heat. The second limitation is overcome by using electronically regulated heating of a sample and a reference standard.

An application of DSC already mentioned is to the compatibility of polymer blends. A compatible blend of two polymers displays a single glass transition temperature and an incompatible blend exhibits the two glass transitions of the constituent polymers.

The constant volume heat capacities of polymers are related to the frequencies and densities of vibrational states (Wunderlich and Gaur 1983). Vibrational frequencies are determined by molecular structure and the nature of the primary valence bonds; therefore, they are characteristic of the polymer under investigation. The calculation of heat capacities from vibrational modes involves a summation over all vibrational states; therefore, the heat capacities are not as specific to molecular structure as are the vibrational spectra themselves. The vibrational modes of linear polymers can be separated into two groups, the higher frequency localized modes and the lower frequency delocalized modes. The localized modes are only weakly dependent on the molecular conformation, or physical structure; rather they are characteristic of the types of bonds present, that is, C-H, C-0, C-N, etc. The delocalized lower frequency vibrations are sensitive to the secondary and tertiary structure of the macromolecule. These low frequency modes may be dependent through the polymer structure on the method by which the polymeric material was solidified.

Contributions to the heat capacity by a particular vibrational mode depend on the temperature, the lower frequency modes being more dominant at low temperature (below 50° K) and the higher frequency modes dominating the high temperature heat capacities. Low temperature heat capacities have been modeled in terms of one- and two-dimensional structures that have been used successfully to delineate solid state modifications of the same polymer. Most progress on modeling heat capacities has focussed on higher temperature data. The heat capacities of a homologous series such as the alpha olefins and the acrylates have been successfully modeled by considering the contributions of the pendant sidegroups as the distinguishing factors. Calculated values within 2 percent of experimental values have been reported (Wunderlich and Gaur 1983).

## MICROSCOPIC METHODS

Electron microscopy (EM) and optical microscopy are well developed techniques for polymer characterization. In combination they can be used to observe and elucidate structural features ranging in scale from fractions of a nanometer to millimeters, or larger. The power of optical microscopy and SEM for establishing the relations between two plastic pieces in terms of gross structural similarities is widely appreciated and this application holds equally for the kinds of complex polymer structures that typify recent trends in polymer usage. Clearly, with recent trends in polymer usage there are more opportunities for identification in terms of the physical structures exhibited, as for example shown in Figures 1 and 10. The laminated structures of new types of packaging materials can be examined by optical microscopy, and in combination with other methods, such as the previously discussed Raman microprobe, quantification of the various materials in the layers can be made. Incompatible polymer blends exhibit microstructural features that are amenable to study by optical microscopy and EM with most detailed structural information in the range covered by EM. Scanning electron microscopy of a blend of epoxy and elastomer is shown in Figure 1. The fiber morphology and layup of composite specimens can be identified using microscopy, and these features further serve in identification.

In addition to the gross structural features described above, information concerning crystal structure, morphology, molecular orientation, spherulitic texture, elemental composition and molecular structure can be derived from approaches that combine microscopy with other characterization techniques. The adaptation of an optical microscope to Raman spectroscopy has already been discussed, and analytical electron microscopy (AEM) methods are presented below. Molecular orientation, even in the absence of crystallinity, may give rise to birefringence effects in optical microscopy that can be analyzed in terms of the principal indices of refraction.

## ANALYTICAL ELECTRON MICROSCOPY

The ability to observe and characterize the morphology, crystallography, and elemental and molecular compositions of regions as small as 20 nm is a major breakthrough in materials identification. There are several variations of instruments that combine the high image magnification capability of EM with analytical methods based on X-rays and electrons. The arrangements of electron source, sample, emitted signals and detectors are shown in Figure 18 for SEM and transmission electron microscopy (TEM). Scanning electron microscopy is normally used to observe bulk specimens using an electron probe for sample illumination. The image is of the surface topology and is formed by detecting back-scattered primary electrons or low energy secondary electrons.

For microanalysis, the scanning electron microscope in combination with an electron probe microanalyzer permits acquisition of high magnification pictures and chemical information from micron size areas of solid samples (Hren *et al.* 1979). A most useful variation of this instrument uses an X-ray energy dispersive spectrometer (EDS) with a scanning transmission electron microscope (STEM). The main application of EDS is for the elements in which $Z > 10$. The sensitivity of EDS is related to the fluorescence yield factor for X-rays, which is near unity for heavier elements but decreases to 0.02 for magnesium. Another limitation of SEM-EDS is that although the electron probe diameter is approximately 7 to 10 nm the X-rays originate from an area 1 to 2 $\mu$m in diameter owing to electron scattering in the bulk.

Analytical electron microscopy is a fusion of SEM and TEM. In STEM a small scanning electron beam illuminates the specimen rather than the relatively large stationary beam of TEM. The advantages of STEM over TEM are that radiation sensitive materials such as polymers can be examined more easily, and simultaneous structural and chemical analysis of selected portions of the specimen on the scale of 10 nm can be made in principle. Transmission electron microscopy and STEM are used to obtain high resolution images and to establish the crystal structure of polymer microcrystals from electron diffraction data. Orientation relationships between microcrystallites may be derived from micro-diffraction patterns. Selected regions of a complex microstructure may be probed to determine the presence of crystalline or partially ordered material.

Another microanalytical technique based on analysis of the energy distribution of electrons that have interacted with a substance is electron energy loss spectroscopy (EELS). The advantage of this technique for polymer identification is its sensitivity to low Z ($Z \leq 10$) elements. The basic components of an EELS system are an electron source and a spectrometer for analyzing the energy of the scattered electrons. This type of microanalytical system is used with both conventional transmission and scanning transmission microscopes. Electron energy loss spectroscopy requires thin specimens similar to those used in transmission microscopy; the thicknesses should be comparable to the mean

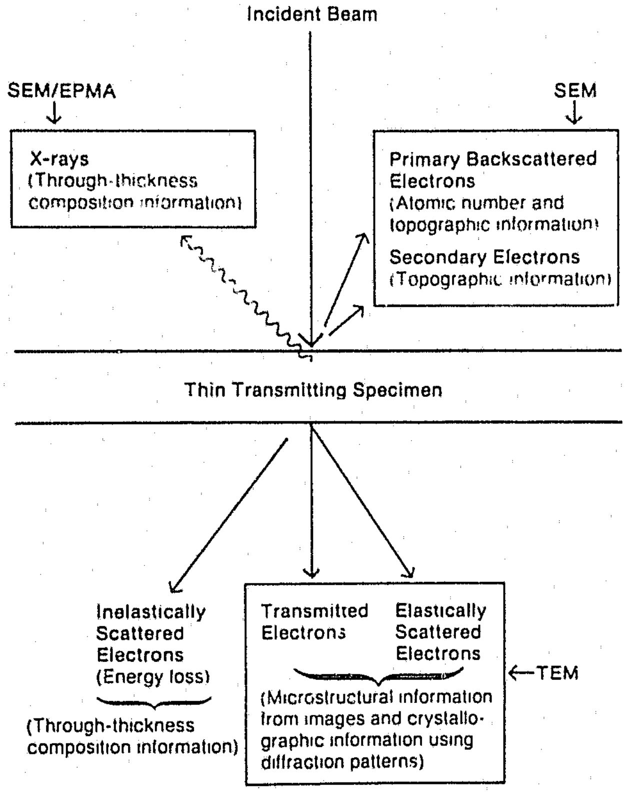

Figure 18. Scanning and transmission types of electron microscopy. Williams, D. B. and Edington, J. W. (1981). Practical electron microscopy in materials science: analytical electron microscopy, Norelco Reporter 28:2-14.

free path for scattered electrons which is about 50 nm for organic samples.

Electron energy loss spectroscopy provides information on elemental, chemical and molecular composition from spatially localized areas. Information is contained in the change in momentum and energy of electrons that are transmitted through the specimen; however, it is usually sufficient to measure only the energy loss which yields the EEL spectrum, a plot of transmitted signal intensity as a function of energy loss.

There are three distinct regions in an EEL spectrum, the zero energy loss due to electrons transmitted unscattered and elastically scattered electrons, the low loss region (0-50 eV)that arises from plasmons or molecular orbital effects, and the high energy loss associated with inner shell electrons. The most prominent feature of an EEL spectrum is the combined unscattered and elastically scattered electron peak. This peak is of little interest for chemical analysis. The inelastically scattered electron intensity diminishes rapidly with increasing energy loss and superimposed on this decreasing intensity are various features derived from specific interactions that contain the information of interest. The low energy loss region is associated with electron intereactions with valence or conduction electrons, the latter in the case of metals. For specimens in which plasmon generation is important (metals), the EEL spectrum may have multiple plasmon scattering events, and the net effect is a series of equally spaced peaks of diminishing intensity. For insulators, plasmon contributions are unimportant, and the major low loss contribution is from excitations and ionizations of electrons in molecular orbitals. This energy loss region is difficult to interpret directly but can be used as a "fingerprint," although sensitivity is limited by radiation damage to molecular groups. Higher energy loss regions contain contributions from inner shell electrons in the form of sharp absorption edges superimposed on a falling background. The energy loss at which the edge starts is the classical ionization energy of the atom and is uniquely characteristic of the element. Therefore this region is most important for microanalytical work.

A simple high energy loss measurement is sufficient to identify the elements present. In this mode the analysis is identical to EDS; in fact, the electronic processes are the first stage of events leading to generation of X-ray emission. Although the EELS cross section is smaller than the X-ray counterpart the collector efficiency factor improvement more than compensates. For studies of the lighter elements, EELS is more advantageous than EDS (Williams and Edington 1981), the break point being Z equals 10. However, higher energy losses associated with EELS of heavier elements degrades sensitivity and further ambiguities arise from overlap of K and L shells from light and heavy elements.

Fine structure features of the ionization peaks are associated with the same physical processes that give rise to extended X-ray absorption fine structure (EXAFS). For studies of spatially resolved areas, EELS should have more sensitivity than EXAFS.

The high resolution capabilities of EELS implies that not only the presence of various elements can be determined, but also the chemical bonding, although the latter realization may be limited by the severe radiation damage. Mass loss as a result of radiation damage is a limitation to the determination of relative concentrations of elements as the mass loss is element dependent, particularly for fluorine and oxygen in polymers.

Analytical electron microscopy based on X-rays is one of several methods that are particularly useful for identification of heavier atoms that may be part of the polymer molecules themselves, or part of either adventitious or intentional additives. Examples of heavier atoms that are part of the macromolecules include halogens (PVC), sulfur(polysulfone) and metal ions. The last mentioned elements are found in polymers containing ionizable groups, examples of which are copolymers of tetrafluoroethylene and perfluorinated ether side chains terminated by sulfonic acid groups. These materials are of commercial interest because of their unusual mechanical and transport properties. The metal cations associated with these materials in general are not amenable to study by molecular spectroscopic approaches. Heavier atoms may also be a constituent of additives, either as adventitious substances, such as catalysts, or intentional additives, stabilizers or compounding agents. In addition to AEM, X-ray absorption is used in the identification of heavier atoms.

Extended X-ray absorption fine structure and X-ray absorption near-edge structure (XANES) are methods of detecting the presence and local environment of heavier elements (Pan *et al.* 1983). These techniques involve the analysis of photoelectron effects on X-ray absorption profiles. Electrons are ejected from elements by high energy photons when the photon energy exceeds the electron binding energy. The photoelectron intereactions with nearby atoms perturb the absorption characteristics, and hence give information of the first few near-neighbor shells. Extended X-ray absorption fine structure data is represented in terms of Fourier transforms that produce radial structure functions (RSF). Each peak in the RSF corresponds to atoms of a certain shell at the same distance. Estimates of structural parameters are obtained from the breath position and magnitude of the RSF peak.

## SURFACE CHARACTERIZATION TECHNIQUES

Considerable recent research activity has focussed on techniques that probe the surface of materials. The chemical composition and physical structure of the surface region may differ from the bulk owing to processing conditions and/or use environment. The microstructures exhibited by polymers are sensitive to the thermal and mechanical history experienced during processing. Generally, the thermal and mechanical conditions in the interior and surface of a plastic part during manufacture differ. A lower temperature at the surface during cooling of a molded component produced from a semicrystalline polymer may bring about fractionation of MW with the higher MW components near the surfaces. Additives whose melting temperatures differ from that of the polymer may also be inhomogeneously dispersed. Other variations in chemical composition may arise from surface energy considerations. One component of an incompatible polymer blend may be preferentially located at the surface if the surface energy is more favorable than the interfacial energy between components of the blend (Clark 1976). Mechanical effects during processing influence molecular orientation, and it is not uncommon to find a different orientation at the surface compared to the bulk. In service, effects may also influence the chemical and physical aspects of the surface compared to the bulk. Wear phenomena involve orientation of macromolecules at the surface and degradation of MW. Oxygen is more readily available at the surface than in the bulk, and this can lead to enhanced degradation at the surface through oxidation.

## ESCA - ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

Electron spectroscopy for chemical analysis (ESCA) is a powerful analytical method for surface characterization (Clark 1976). Electron spectroscopy for chemical analysis involves measurement of binding energies of electrons ejected by interactions of molecules with a monoenergetic beam of soft X-rays. Electron binding energies are characteristic of the elements present and the nature of their chemical bonding. Furthermore, this information may be available as a function of depth within the sample.

Although ESCA does not compare favorably with other spectroscopic techniques in terms of sensitivity and resolution to molecular conformation it may be the tool of choice for any initial investigation of a polymer sample. Commercial instruments are available from a number of sources, and are easily used to carry out routine analysis. Other advantages include high sensitivity for elemental analysis and primary chemical bonding, requirements of about 1 mg of material, a nondestructive method for both liquids and solids (no special sampling procedures are required), straightforward theoretical interpretation of data and quantitative intensities. In addition, fundamental information is obtained about core and valence electrons.

The basis of the ESCA method is that core electrons, although not directly involved in valence bonding, do contain information about bonding through small shifts in binding energies. Removal of core electrons by high energy photons causes transitions to virtual electronic states, or loss of valence electrons which processes give rise to satellites on the low kinetic energy side of the main ionization peak. One measures the number and energies of the emitted photoelectrons. The line-widths are of the order of 1 eV and are caused by the natural line-width of the transition, instrumental broadening and line-width of source. Electron spectroscopy for chemical analysis spectra taken with excitation at two different X-ray sources are shown in Figure 19. A feature of these spectra are Auger peaks that result from de-excitation of hole states and are independent of excitation source energy.

Electron spectroscopy for chemical analysis spectra are sensitive to a depth of about 100 nm: the penetration limit of soft X-rays. A plot of escape depth versus escape energies fits a universal curve that allows differentiation between surface and subsurface contributions.

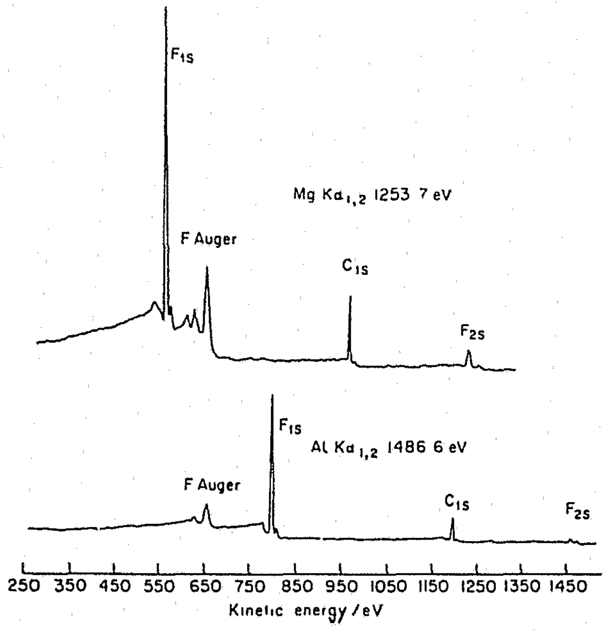

Figure 19. Wide scan ESCA spectra of polytetrafluoroethylene using two different probe sources. Reprinted from The Application of ESCA to Studies of Structure and Bonding in Polymers by Clark, D. T. in Structural Studies of Macromolecules by Spectroscopic Methods (Ivin, K. J., ed.). Copyright 1976 by John Wiley and Sons, Inc. Reprinted with permission of John Wiley and Sons, Inc., New York.

## ESCA Examples

In the preparation of ESCA samples from polymer powders, bulk specimens or thin films, care must be taken to avoid surface contamination as the main contribution to an ESCA spectrum is from the top 5 nm. The initial step to analyze a homogeneous material is to record a wide scan, low resolution spectrum to establish which elements are present and their relative abundances. Next, absolute binding energies are determined that indicate the bonding arrangements.

The application of ESCA to elemental analysis is similar to what has been discussed previously for EXAFS. Analysis of chemical bonding is the main advantage of the technique as shown in Figure 20 for PET in which the two different oxygens are distinguishable as are the three different carbon types. Even in cases where there is strong overlap of photoelectrons from C 1s, for example, in polyethylene, polypropylene and polystyrene, analysis can be made on the basis of weak transitions of valence electrons to virtual excited states. Most applications of ESCA have been on fluorocarbons because of the strong electronegative influence of F on C 1s. An example is shown in Figure 21 in which the C 1s and F 1s level spectra are shown for a series of ethylene/tetrafluoroethylene copolymers. The comonomer content deduced from these spectra are in agreement with those obtained from monomer reactivity ratios (Clark 1976).

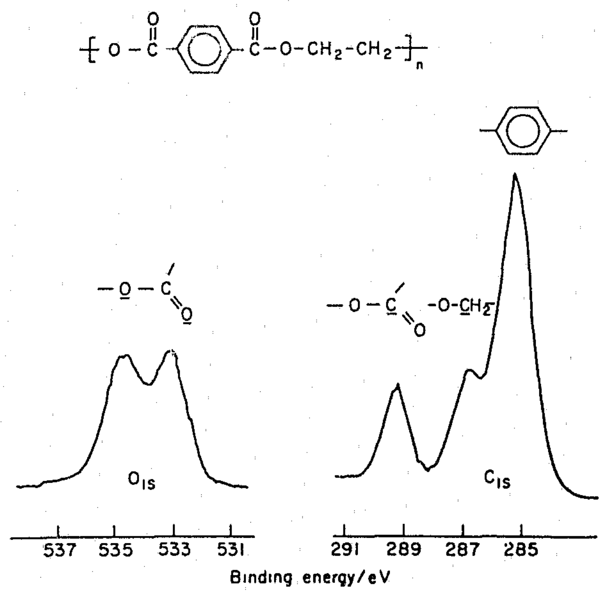

Figure 20. Electron spectroscopy for chemical analysis spectrum of poly(ethyleneterephthalate) showing distinct bands for two oxygens and three carbons. Reprinted from The Application of ESCA to Studies of Structure and Bonding in Polymers by Clark, D. T. in Structural Studies of Macromolecules by Spectroscopic Methods (Ivin, K. J. ed.). Copyright 1976 by John Wiley and Sons, Inc. Reprinted with permission of John Wiley and Sons, Inc., New York.

An application of ESCA to surface analysis is the preferential location of one of the two phases of a block copolymer at the surface. Detail morphology of the domain structure of incompatible block copolymers depends on such factors as the relative proportions, MW, thermal and mechanical history, and solvent, if prepared from solution. An example is the surface structure of AB type copolymers of polydimethylsiloxane (PDMS) and

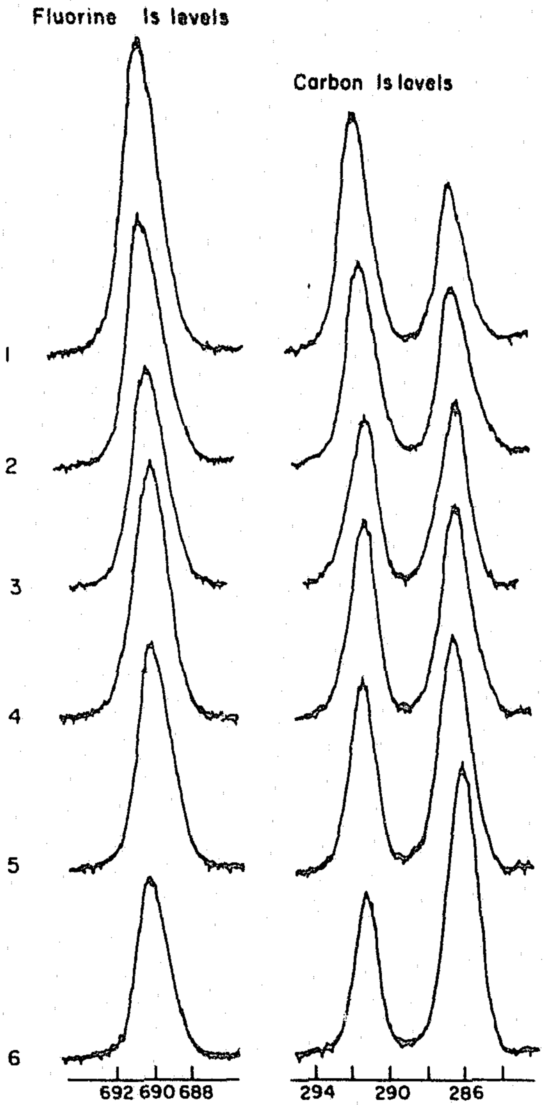

Figure 21. C1s and F1s electron spectroscopy for chemical analysis spectra of ethylene/tetrafluorethylene copolymer. Reprinted from The application of ESCA to studies of structure and bonding in polymers by Clark, D. T. in Structural Studies of Macromolecules by Spectroscopic Methods (Ivin, K. J. ed.). Copyright 1976 by John Wiley and Sons, Inc. Reprinted by permission of John Wiley and Sons, Inc., New York.

polystyrene, in which the nature and thickness of the outer layer was established (Clark 1976). Contact angle measurements indicated that outer layer was PDMS. Through analysis of ESCA spectra it was established that the layer of PDMS was about 4 nm thick. The study showed that the domain structure of the surface differed from the bulk. Another surface application is to polymer degradation. The onset of degradation by oxidation starts in the surface layer so a surface analysis is sensitive to the initial phase of degradation. Figure 22 shows the ESCA spectra of LDPE before and after desiccation indicating the presence of water. Comparisons with IR indicated that the water is preferentially located in the surface region. The ESCA spectra also indicate the presence of carbonyl oxygen, with breath of band indicating the presence of several carbonyl environments.

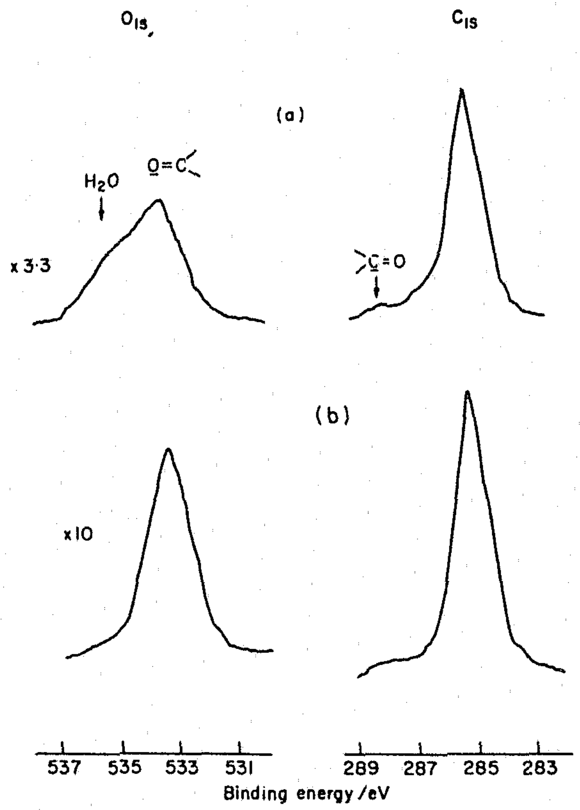

Figure 22. C1s and O1s electron spectroscopy for chemical analysis spectra for low density polyethylene (a) before desiccation and (b) after desiccation. Reprinted from The application of ESCA to studies of structure and bonding in polymers by Clark, D. T. in Structural Studies of Macromolecules by Spectroscopic Methods (Ivin, K. J. ed.). Copyright 1976 by John Wiley and Sons, Inc. Reprinted with permission of John Wiley and Sons, Inc., New York.

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# SECTION II

# EXTENDED ABSTRACTS

# THE NATIONAL AUTOMOTIVE PAINT FILE IN THE FBI LABORATORY

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The purpose of this paper is to introduce the National Automotive Paint File (NAPF) to the forensic examiner, particularly one who deals with trace evidence. This will be accomplished by discussing the components of the NAPF and briefly explaining its use in the FBI Laboratory.

The basic component of the NAPF is the collection of paint standards furnished to the FBI Laboratory by the automotive industry and by coatings suppliers to the industry. These standards represent the original finishes placed on motor vehicles at the time of their manufacture. The current size of the total collection is approximately 25,000 panels. The time frame covered by this collection is from the late 1930s to the present.

The active portion of the NAPF covers the most recent ten years of motor vehicle finishes and consists of approximately 1200 panels. At the end of this ten year time frame, a panel is removed from the active file and stored with the older panels. A review of the NAPF discloses the wide variety of sources and suppliers of these panels, including some companies that are no longer in existence.

The panels in the active portion of the NAPF are arranged in a systematic order to help the examiner most efficiently use them. The following criteria are used to arrange the panels:

1. Domestic or foreign use
2. Color
3. Metallic or non-metallic
4. Enamel or lacquer.

This arrangement has been found to be most helpful to the FBI examiner, who has usually made these determinations about a questioned specimen before going to the NAPF.

The panels in the inactive or older portion of the NAPF are stored according to vehicle manufacturer.

The NAPF has other features that have been maintained throughout the years. One such feature is a collection of repaint guides that are used in making color matches and supplying assistance to contributors, specifically in those cases where the specimens are from repainted vehicles and with no original finish. These guides, furnished by suppliers of coatings for repainting purposes, date from the late 1930s to the present, and include domestic, foreign and fleet colors. A second feature is the collection of motor vehicle brochures furnished by dealers each new model year. On occasion, these are used to aid in identifying a piece of trim, molding, facia material, or lens material and location on a vehicle.

A third feature of the NAPF is a collection of industry related publications. These include crash books, automotive publications such as *Automotive News*, and industry publications such as *Journal of Coatings Technology*. These provide useful information in maintaining a knowledge of current trends which can be of assistance to the forensic examiner.

The NAPF can be utilized to provide "lead" information to an investigating office in a hit-and-run case, to identify parts recovered from a "chop shop" operation, and to identify samples and determine the source(s) of such samples in a car ring theft case.

# PYROLYSIS GAS CHROMATOGRAPHY - REVISITED

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Although much work has been done with pyrolysis gas chromatography (Py-GC) for comparison and discrimination of paints (Cardosi 1982; Stewart 1974; Levy 1977), the technique can also be applied to fibers, greases, oils and polymer films with favorable results. As in most forensic applications, identity of a material is only part of the problem. A comparison must be done between a known control sample and an unknown question sample to establish a possibility of the samples having a common source. Pyrolysis gas chromatography is a tool that can be used for meaningful data.

## MATERIALS AND METHODS

Different polymers, greases and oils from various sources such as lubricating oils, new and used, bulk oil or grease, oil smears from the undersides of various vehicles, and household oils and greases were studied. A Varian 3700 gas chromatograph (Palo Alto, CA) with a flame ionization detector with a Chemical Data System 150 Pyroprobe (Oxford, PA) and a Varian Vista 402 Data System were used for the Py-GC. The column was 1.8 m x 2 mm i.d., packed with 80/100 Carbopack C coated with 0.1 percent SP1000. Considerable differences were seen in each group of materials analyzed depending on type of product, manufacturer and vendor.

Instrument conditions were as follows:

Injector temperature: 270° C
Detector temperature: 300° C
Attenuation: $10^{-10}$ x 32
Program: 60° C to 260° C at 10° C/min. Final hold for 15 min.
Flow rate: 20 ml/min $N_2$

Pyrolysis Unit:
Ramp: Off
Interface temperature: 150° C
Final temperature: 650° C
Burn time: 10 sec

The probe (either ribbon or quartz tube) was heated for 10 seconds at 980° C for cleaning before sample introduction. Approximately 2 mg of solid sample was placed on the probe and heated for 10 seconds at 200° C before it was introduced into the interface port.

## RESULTS AND DISCUSSION

Pyrolysis gas chromatography displayed good discrimination of the various oils, greases and polymers studied (Figures 1 - 6). Caution should be used in the interpretation of the results and it may be necessary to use another method to verify results. Case in point: An oily sludge was submitted from a tampering case (Figure 7). Standards were requested and run. Both Py-GCs were the same although their physical appearances were vastly different.

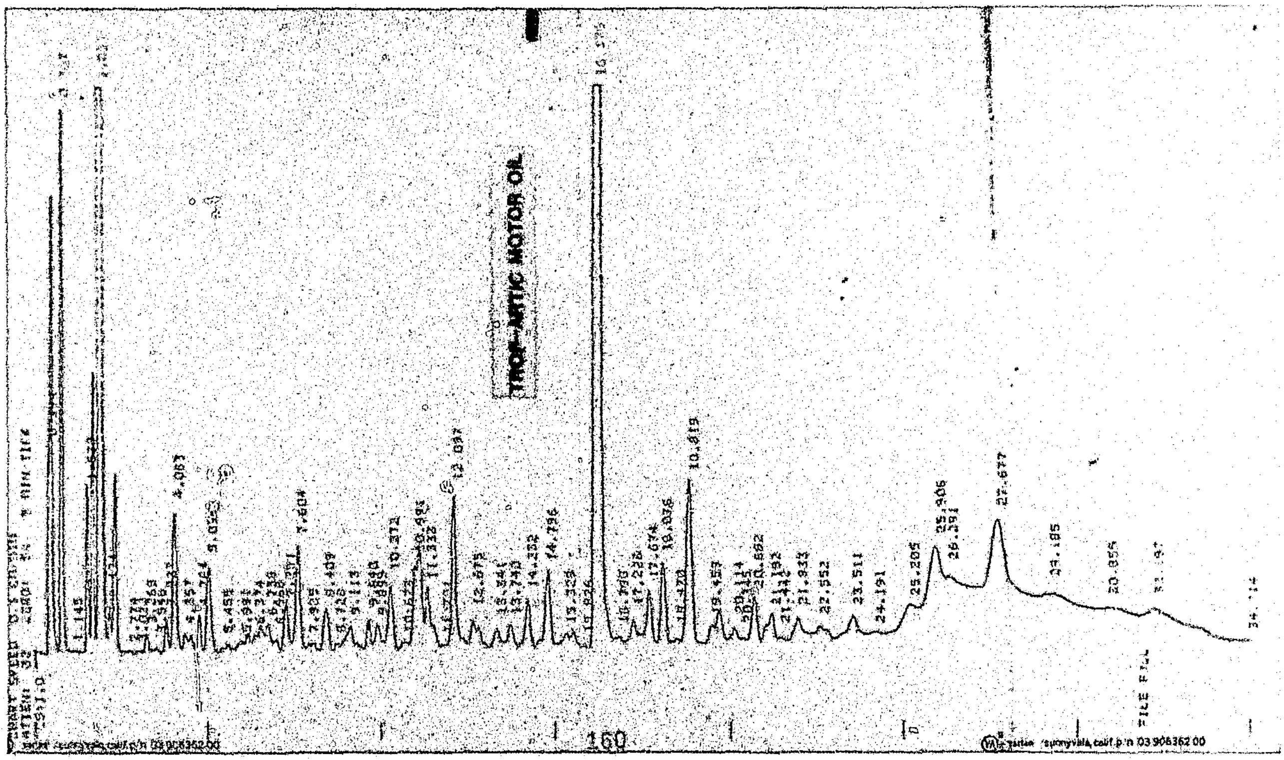

Figure 1. Pyrogram of Phillips Petroleum Trop-Artic Motor Oil.

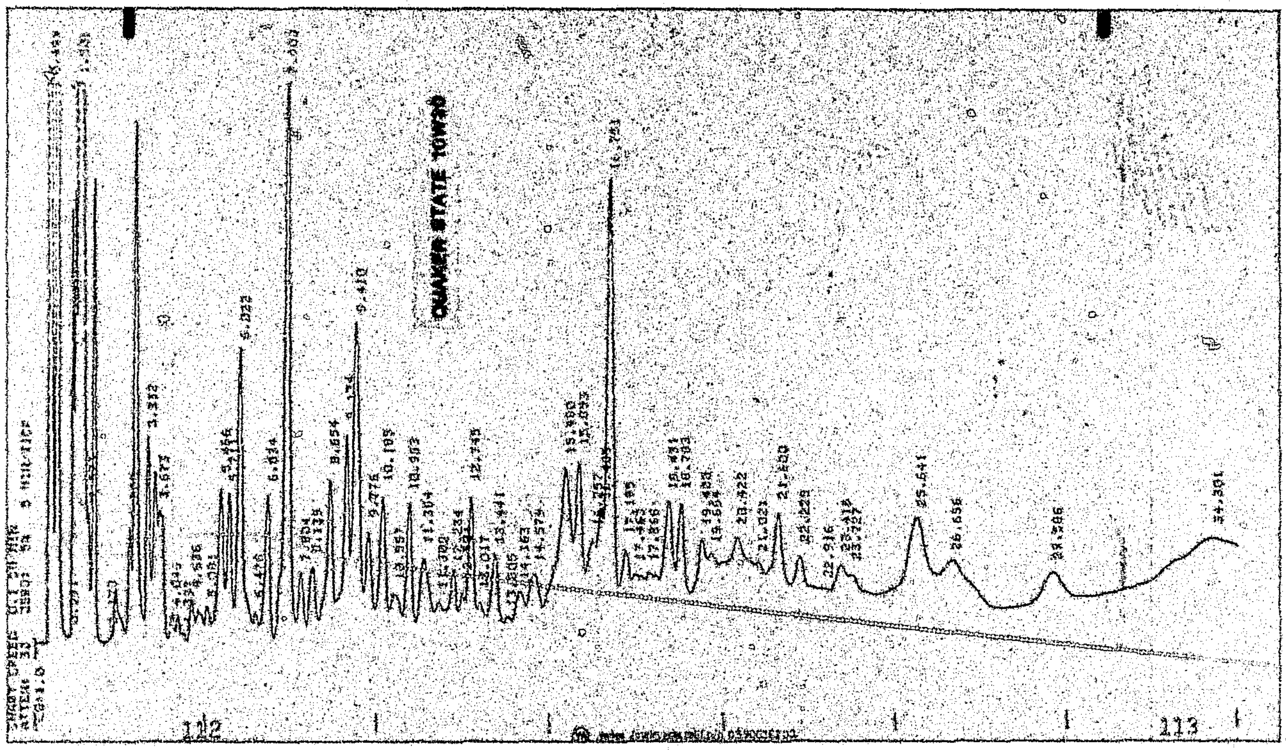

Figure 2. Pyrogram of Quacker State 10W30 Motor Oil.

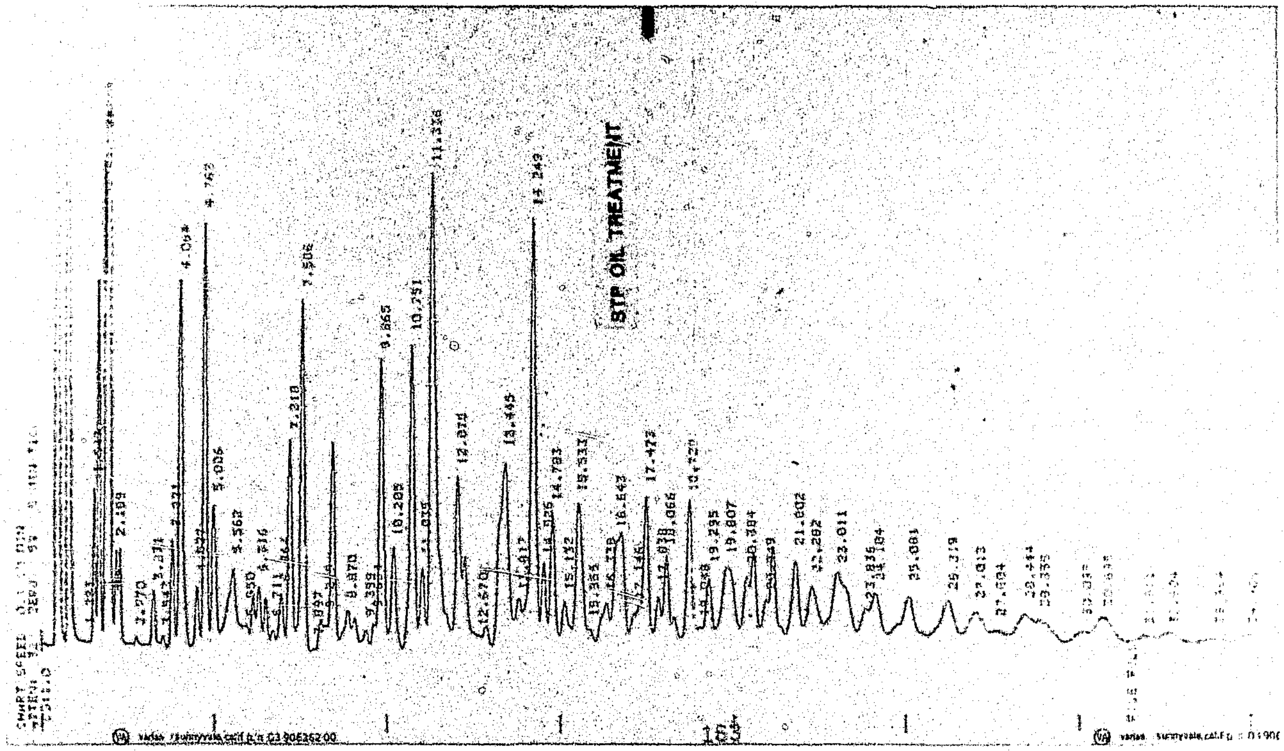

Figure 3. Pyrogram of STP Oil Treatment.

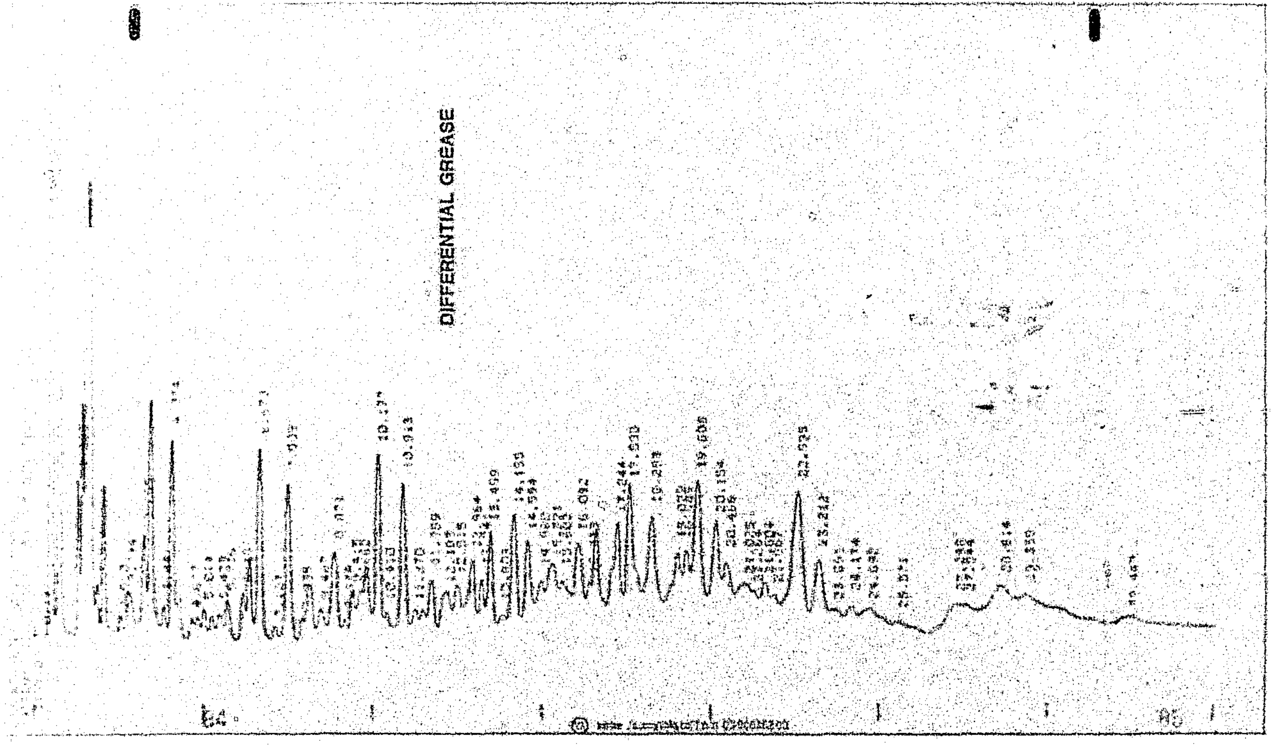

Figure 4. Pyrogram of differential grease.

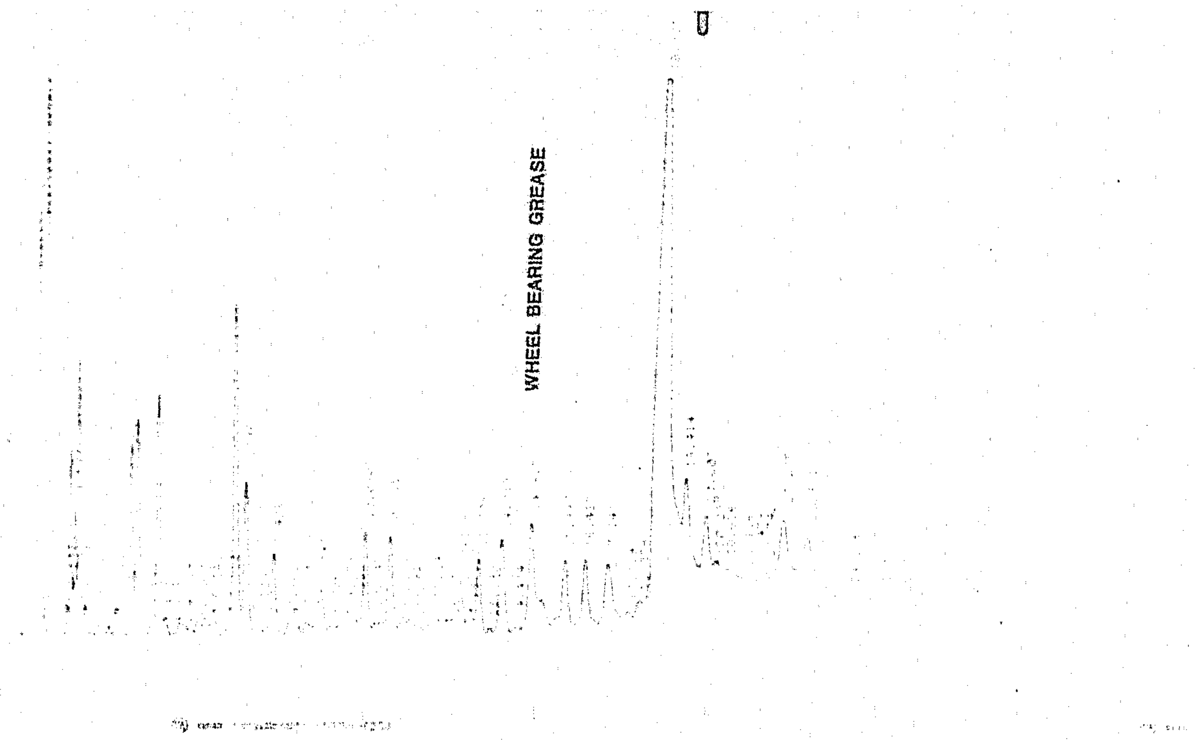

Figure 5. Pyrogram of wheel bearing grease.

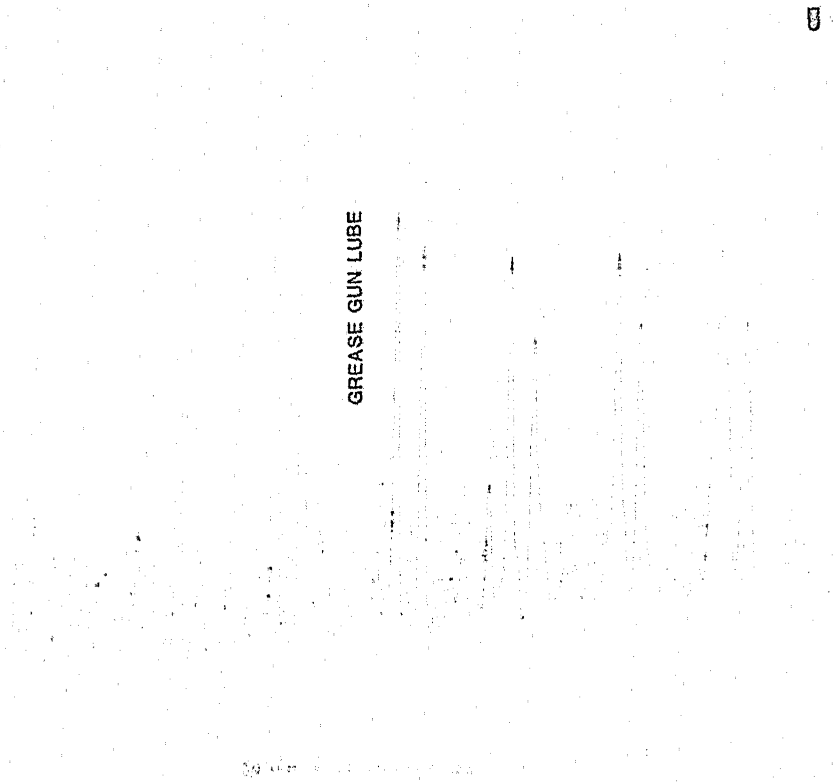

Figure 6. Pyrogram of a grease gun lubricant.

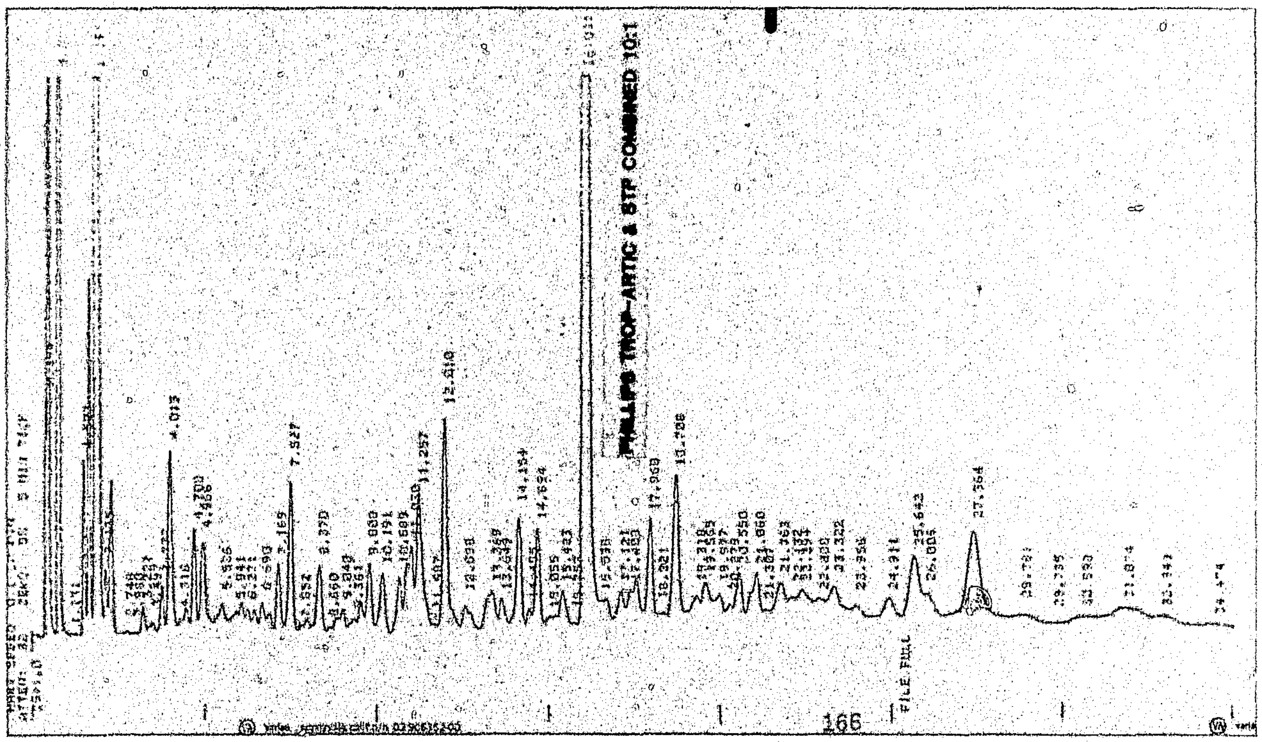

Figure 7. Pyrogram of an oily sludge consisting of Phillips Petroleum Trop-Artic Motor Oil and STP Oil Treatment, combined 10:1.

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# EXAMINATION OF AUTOMOTIVE PAINTS BY PYROLYSIS CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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A Chemical Data System Pyroprobe pyrolysis unit (Chemical Data Systems, Inc., Oxford, PA) coupled to a Finnigan 1020 gas chromatograph/mass spectrometer (GC/MS) (Finnigan MAT, San Jose, CA) was used in this study. A 30-m SE-30 fused silica capillary column (0.25 mm i.d.) was used with the following temperature ramp: 65° C for 4 minutes followed by 25° C/min. to 250° C and held for 2 minutes. The mass range 45-360 amu was scanned at 0.5 seconds per scan. The helium carrier gas flow rate for the capillary column was 0.76 ml/min. The needle assembly for the pyrolysis interface chamber was mounted directly onto the split/splitless injector of the GC. In order to get the pyrolysate components transferred onto the capillary column as narrow bands, a 20:1 split was necessary. The resulting peak heights were about the same as achieved using pyrolysis packed column GC.

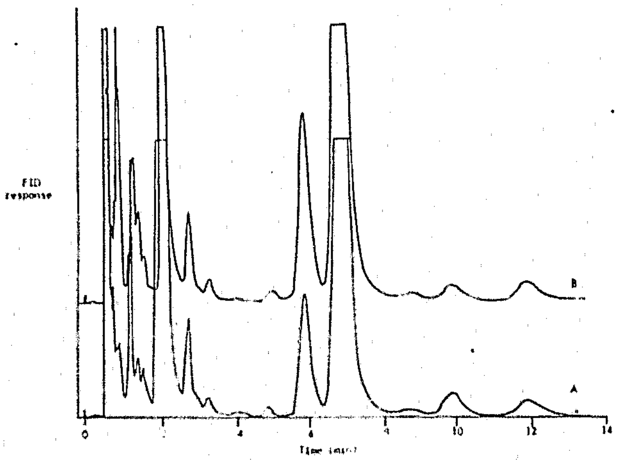


Figure 1. Pyrograms of two black paints run on a 15 percent dinonyl phthalate packed column, isothermal at 100° C.

Using this sytem, 39 paints from the FBI National Automotive Paint File (NAPF) were run. Groups of similar paints were selected for comparison, some of which were known to be difficult to distinguish using an isothermal, 15 percent dinonyl phthalate packed column. Pyrolysis capillary GC/MS was found to distinguish the paints from one another based solely upon the pattern of peaks in the capillary pyrogams (that is, not using the mass spectra). Figure 1 shows the comparison of two black paints using the packed column system, and Figure 2 shows the same two paints on the capillary system. While the paints can be distinguished from the packed column data, the differences are much more readily apparent in the capillary column data.

Using the GC/MS data system, all of the spectra from the pyrolysis capillary GC/MS run from each paint were combined into a single composite spectrum. Using the library building function of the data system, the composite spectra (one representing each paint) were used to construct a "paint library" with 39 entries. The 39 paints were then treated as "unknowns," run repetitively, and compared to the "knowns" using the library search routines. Table 1 shows the computer report for the search of blue paint (1G73BA0259) against the paint library with the nine best matches ranked by purity. A pattern recognition algorithm generates these comparison numbers: a purity of 0 indicates that the two spectra have no mass peaks in common, and a purity of 1000 indicates that the two spectra have identical mass peaks with peak intensities that are exactly proportional. The pyrogram of the correct match (ranked first) matched the sample quite closely. Figure 3 shows a comparison of the closest blue paint match (ranked fourth) to the sample. In all 102 runs of the 39 paints examined to test the library, the true identity of the paint was one of the five best matches found by the computer -- indeed, the best match in 57 cases.

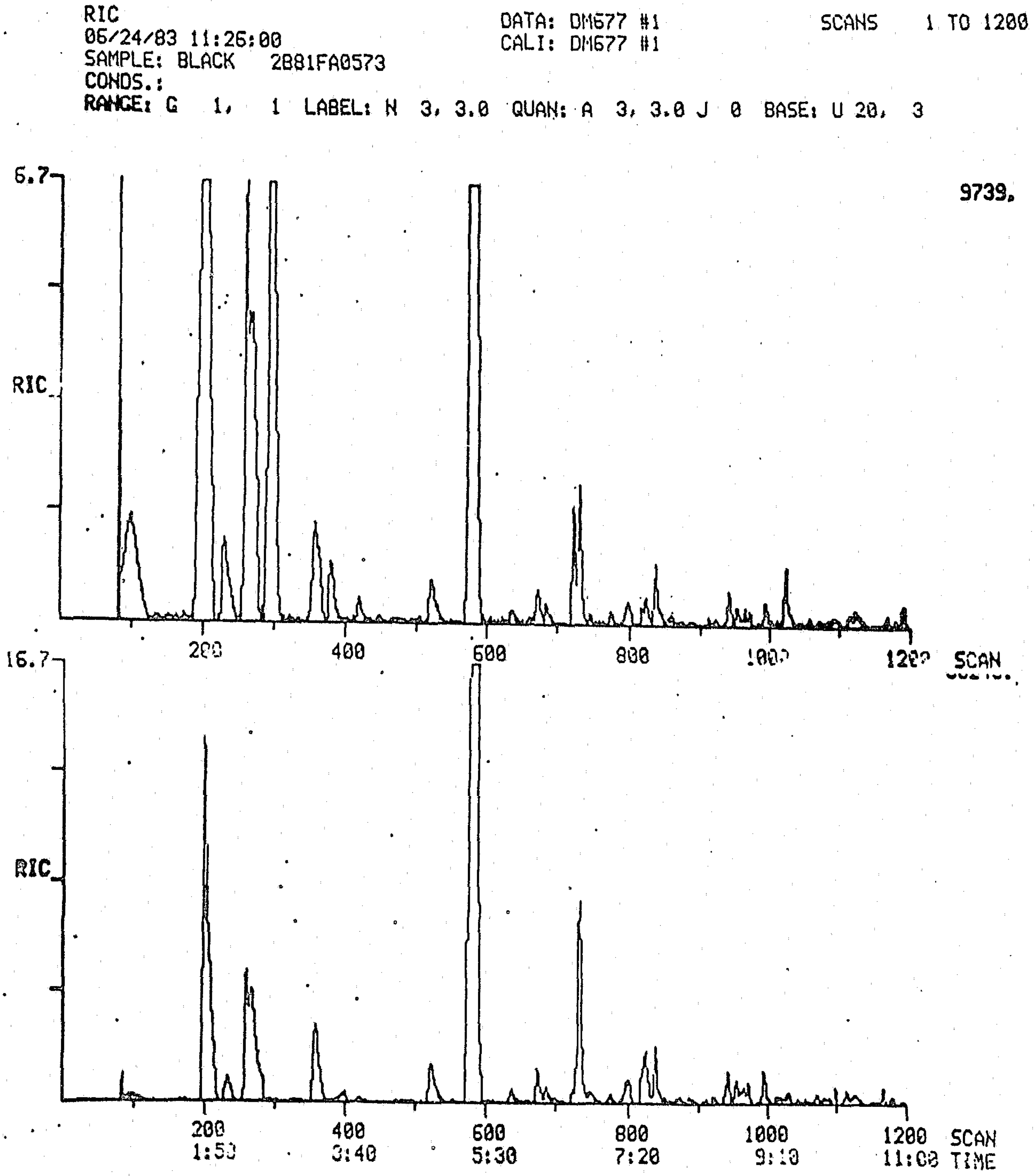
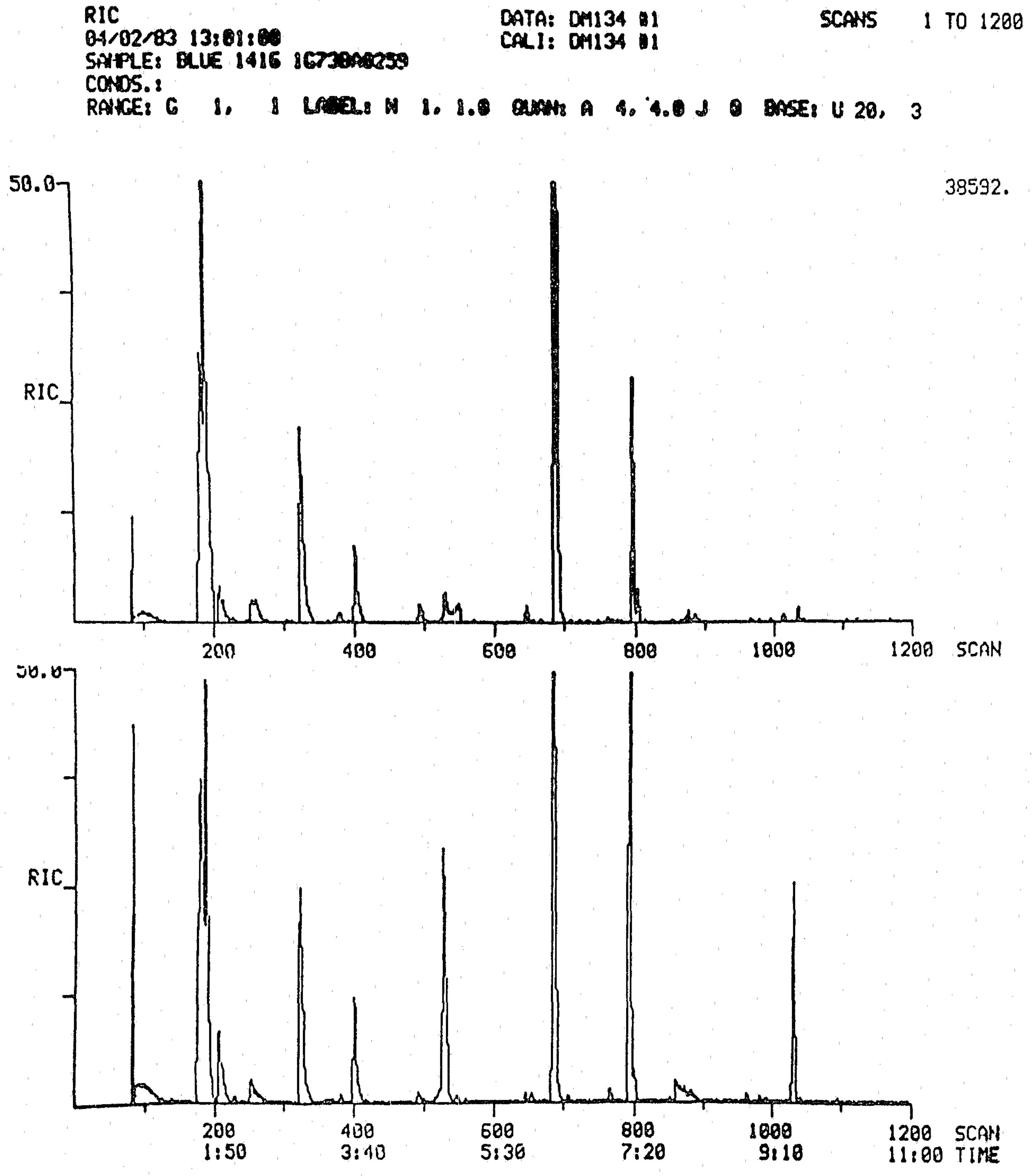


Figure 2. Pyrolysis capillary GC/MS profiles of the same two black paints shown in Figure 1 (2B81FA0573 upper as in Figure 1).



```
RIC                                          DATA: DM134 #1          SCANS    1 TO 1200
04/02/83 13:01:00                            CALI: DM134 #1
SAMPLE: BLUE 1416 1G73BA0259
CONDS.:
RANGE: G   1,   1 LABEL: N  1, 1.0  QUAN: A  4, 4.0 J  0  BASE: U 20,  3
```

Figure 3. Pyrolysis capillary column GC/MS profiles of the two blue paints from Table 1 (1G73BA0259 upper).

**Table 1. LIBRARY SEARCH USING BLUE ACRYLIC PAINT (ENTRY 1)**

Sample searched against full library

39 spectra in library PC searched for maximum purity
39 matched at least 1 of the 16 largest peaks in the unknown

| Rank[a] | In[b] | Name | | Formula[c] | Molecular Weight[d] | Base Peak[e] | Purity[f] |
|---|---|---|---|---|---|---|---|
| 1 | 1 | Blue | 1G73BA0259 | C7.0.N | 73 | 104 | 976 |
| 2 | 13 | Brown | 1E78HG0698 | C5.07.N | 78 | 104 | 962 |
| 3 | 16 | Brown | 1E78JG0698 | C5.07.N | 78 | 104 | 932 |
| 4 | 7 | Blue | 1G71GA0148 | C7.0.N | 71 | 104 | 907 |
| 5 | 26 | White | 2A76DA0172 | C.0.N2 | 76 | 104 | 904 |
| 6 | 12 | Brown | 1E78BG0698 | C5.07.N | 78 | 104 | 897 |
| 7 | 20 | White | 2A76GG0172 | C.07.N2 | 76 | 104 | 893 |
| 8 | 15 | Brown | 1E78AG0698 | C5.07.N | 78 | 104 | 892 |
| 9 | 14 | Brown | 1E78DG0698 | C5.07.N | 78 | 104 | 882 |

[a] The ranking of the matches with the highest purity ranked first.
[b] Library entry number.
[c] The C, O and N values used to code for color, paint type, and metallic or nonmetallic, respectively.
[d] Used to indicate the model year the paint was used.
[e] The most abundant ion in the composite mass spectrum.
[f] A value for how well the sample spectrum compares to the library spectrum.

Although only a small fraction of the total FBI NAPF was used in this study, the results are encouraging enough to suggest that a searchable data base might be established by utilizing the composite mass spectra as proposed here. Other information available about the sample (for example, color and model year) will allow the search to be narrowed sufficiently so that only a workable number of choices will be included. The analyst would use the computer search to select the paints to be run against the unknown for final identification.

# CAPILLARY COLUMN PYROLYSIS GAS CHROMATOGRAPHY - PROBLEMS AND PROGRESS

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Florida Department of Law Enforcement
Sanford Regional Crime Laboratory
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Several basic criteria were adopted in the conversion from a packed column pyrolysis gas chromatography (Py-GC) system to a capillary column Py-GC system. They included attainment of improved resolution and/or shorter analysis time as well as maintaining or improving the current sample size requirements. These were the ground rules for the transition.

The packed system employed a 3 m, .31 cm o.d. stainless steel column packed with 10 percent SP-1000 (Supelco, Inc., Bellefonte, PA) on 80/100 mesh Supelcoport installed in a Varian 4600 gas chromatograph (Varian Associates, Palo Alto, CA). Pyrolysis was effected via a Chemical Data System (CDS) 150 Pyroprobe (Chemical Data Systems, Inc., Oxford, PA) interfaced to the gas chromatograph's injection port with a standard temperature-controlled quartz-lined CDS interface.

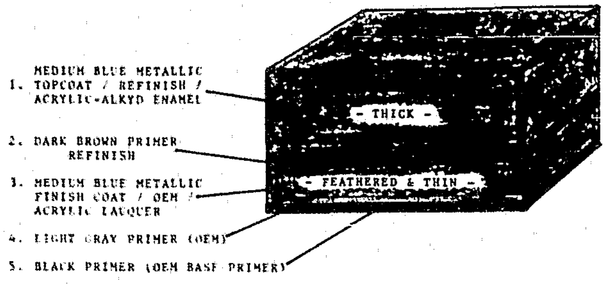

Figure 1. Layer structure of a refinish paint fragment.

The packed system did afford good sample size requirements (10 to 20 μg.) for the detection of minor pyrolysates. The small sample size is very important to us for several reasons other than the obvious limited sample case. Small sample requirements permit the pyrolysis of individual paint layers, especially finish coats, within a fragment layer structure. Making this extra effort often permits classification of the finish coats (Table 1). This can either confirm or deny previous microscopic original equipment at manufacture (OEM)/refinish classifications assigned to chips having only one finish coat. Additionally, the analysis of individual finish coats can provide improved discrimination in questioned/known comparisons of chips with layer structures similar to those in Figure 1 (where the pyrolysis characteristics of the acrylic lacquer layer number 3 are somewhat masked by those of the thick layer number 1), or more reliable comparisons between chips with layer structures similar to those in Figure 2.

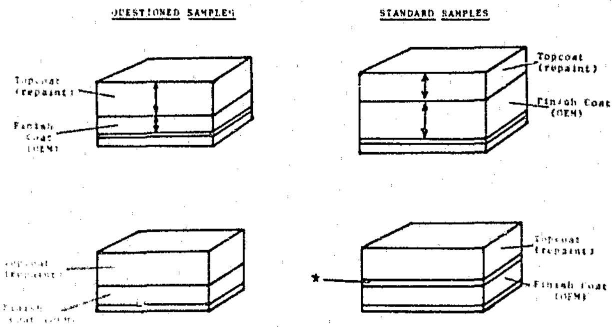

Figure 2. Typical paint layer structures presenting difficult comparisons.

**Table 1. AUTOMOTIVE BINDER TYPES CLASSIFICATIONS**

A. Acrylic lacquers
  Dispersion [original equipment at manufacture (OEM)]
  Solution (OEM and refinish)
B. Nitrocellulose lacquers (refinish and foreign OEM)
C. Acrylic-melamine enamels (OEM)
D. Alkyd-melamine enamels (foreign OEM)
E. Alkyd enamels (refinish)
F. Acrylic-alkyd enamels or acrylic-urethane enamels (refinish)
G. Polyester enamels (OEM - Ford)

Packed system problems included long run times of 60 minutes or more (including bake-out), flow equilibration upon probe removal or insertion (due to the flow controlled packed system), and poor resolution of some paint and plastic pyrolysates.

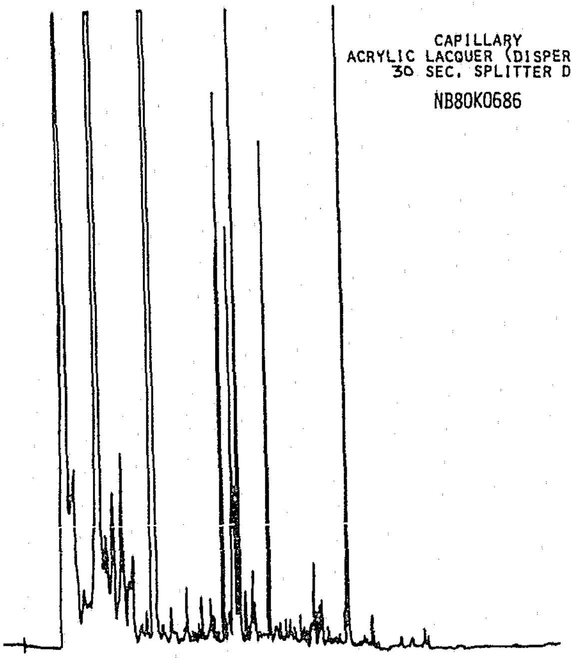

Figure 3. Pyrogram of an acrylic lacquer run on a SP-1000 capillary column using a 30 second splitter delay.

Transition to the capillary system took these previously noted problems and attributes into consideration. Choice of approach also took into consideration the nature of the sample: (1) a relatively large volume of sample vapor pouring into the injector over an extended period of time, (2) widely divergent chemical species and (3) widely divergent component concentrations.

Trials were made using a support coated open tubular column under split injection conditions. Resolution constraints suggested another approach. A wall coated open tubular (WCOT) narrow bore fused silica column coated with an FFAP phase produced excellent resolution under split injection conditions. Larger sample sizes (80 to 150 μg) were necessary for detection of the all important minor pyrolysates (less than 0.1 area percent) at flexible attenuation settings, that is, not bottomed-out. These minor fragments often permit discrimination of very similar binder formulations. Running at very low attenuations with moderate sample size produced bake-off problems.

A 25 m x 0.50 mm WCOT stainless steel column coated with OV-351 (FFAP-type polar phase) run under a splitless injection technique employing a 20 second splitter delay provided improved results compared to the packed system and the previously tried capillary systems - keeping sample size foremost in our minds. The FFAP-type column provided good separation of the major automotive paint pyrolysates - acrylates, n- butanol, and styrene. The resolution was improved further by progressing to a medium bore column, which was the most we could push the compromise of resolution versus sample size.

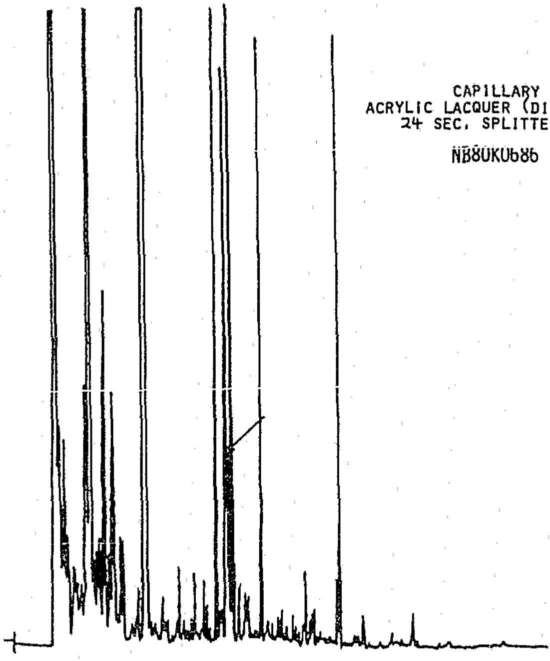

Figure 4. Pyrogram of an acrylic lacquer run on a SP-1000 capillary column using a 24 second splitter delay.

The system employed a 30 m x 0.32 mm WCOT fused silica column coated with a 1 μ thickness of SP-1000. Although decreasing resolution slightly, the thick film tempered the loss of sample capacity caused by going from the wide to the medium bore. A splitless injection was carried out using a 24 to 30 second splitter delay. Advantages of this approach are listed in Table 2. The shorter delay time provided improved resolution (especially in the first 5 minutes of the 30 minute run) at the expense of sample size (20 to 60 μg as compared to 10 to 30 μg for the 30 second delay) as illustrated in Figures 3 and 4. Nitrogen carrier was introduced through the CDS pyrolysis interface at 8 psi (u = 21 cm/sec at 170° C.). Helium carrier resulted in poorer resolution in the already troubled first 5 minutes of the run. Pyrolysis was usually carried out at 700° C (Ramp Off) for 20 seconds in the quartz tube - coil probe.

**Table 2. ADVANTAGES OF THE WIDER BORE WALL COATED OPEN TUBULAR (WCOT) COLUMN - SPLITLESS INJECTION**

A. Higher flow rate for quick sample vapor load on the head of the column.
B. Medium length to provide shorter run times.
C. WCOT liquid phase providing better resolution.
D. Wider bore providing improved sample capacity - more attuned to accommodating widely divergent fragment concentrations.
E. Pressure controlled flow - little to no column equilibration with probe removal and insertion.
F. Splitless injection to improve sample size requirements for detecting minor thermal fragmentation products.
G. Flat base lines - little bleed.

A comparison of pyrograms of one binder type run on the SP-1000 packed and capillary systems is shown in Figures 5 and 6. Chart speeds are comparable. Improved retention time and area percent precision made the conversion even more worthwhile than the shortened analysis time (30 to 45 minutes including bake-out). As shown in Figure 7, sample size has been maintained.

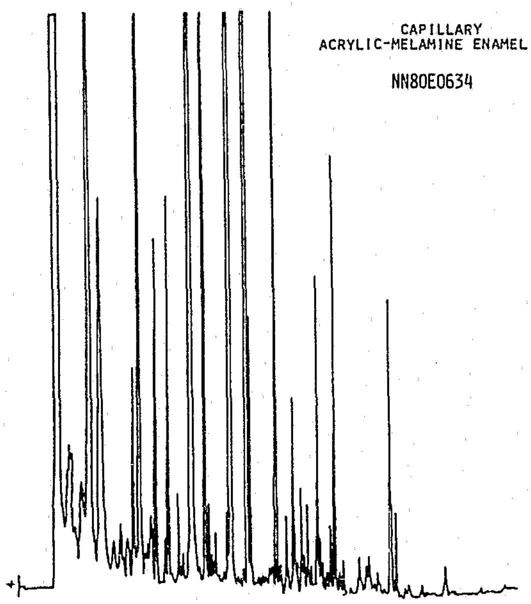

Figure 6. Pyrogram of an acrylic-melamine enamel run on a SP-1000 capillary column.

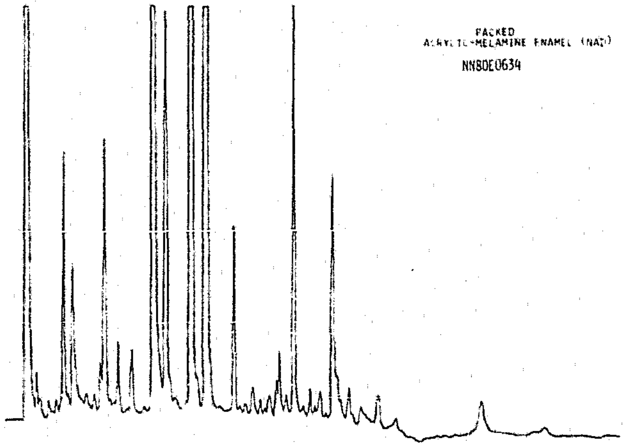

Figure 5. Pyrogram of an acrylic-melamine enamel run on a SP-1000 packed column.

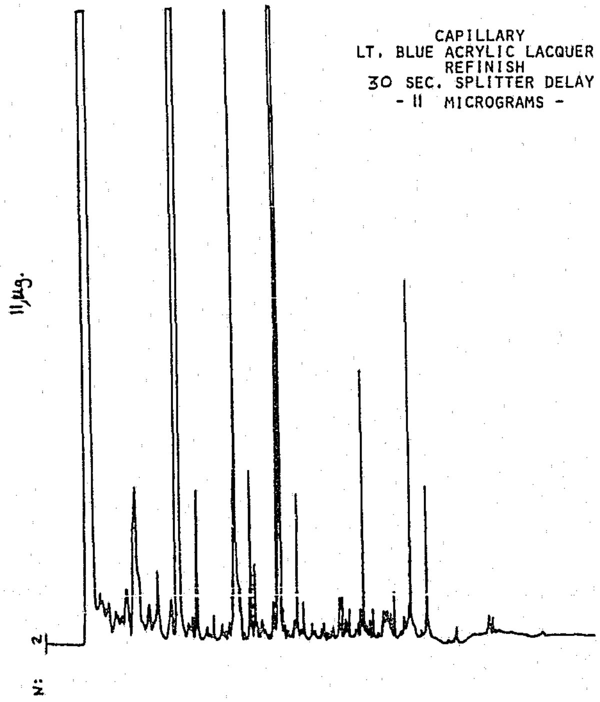

Figure 7. Pyrogram of 11 μg of an acrylic lacquer refinish run on a SP-1000 capillary column using a 30 second splitter delay.

# FORENSIC ANALYSIS OF POLYMERS USING DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY

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Diffuse reflectance has been used for several decades in the ultraviolet, visible and near-infrared regions as a special purpose sampling technique. It was only with the advent of the Fourier transform infrared spectrophotometer, however, that it became practical to perform such work on a routine basis in the mid-infrared region. Most of the early pioneering work in this area was performed by Fuller and Griffiths (1978a; 1978b; 1980; 1982) who coined the acronym DRIFTS (for diffuse reflectance infrared Fourier transform spectroscopy) to describe this new technique. Although the first paper by Fuller and Griffiths appeared in late 1978, several years lapsed before diffuse reflectance accessories became commercially available, hence DRIFTS is, practically speaking, a very recent technique.

Diffuse reflectance infrared Fourier transform spectroscopy offers several significant advantages over conventional methods of sampling such as KBr pellets, nujol or fluorocarbon mulls and cast films. Some of these include: (1) an unparalleled dynamic range (10 ng to g, or ppm to neat), (2) minimal to no sample preparation required, and (3) ability to obtain spectra of opaque or highly scattering samples. The DRIFTS technique has been applied to the analysis of a number of polymeric samples of forensic interest illustrating these advantages.

Fuller and Griffiths had previously demonstrated the feasibility of obtaining DRIFTS spectra directly on some pharmaceutical tablets. The possibility of direct sampling of other materials using DRIFTS was thus examined. In particular, many types of low density polymeric materials, such as foam insulation, foam rubber padding and packaging materials, etc., were found to be amenable to such sampling. Figures 1 and 2 show the results of direct sampling on a piece of polyurethane foam thermal insulation and a block of polyethylene foam (used as a padding for packaging), respectively. Both of these materials gave reflectances much lower than those of the powdered KBr references used, but this was compensated for by simply using higher instrument gains for the samples relative to those used for the KBr references. Conversion of reflectance data to a transmittance format involves using the Kubelka-Munk formula (Kubelka and Munk 1931), which relates the reflectance of a sample to its concentration. This formula is thus analogous to the Beers-Lambert law that applies to conventional transmittance sampling. As Figures 1c and 2c indicate, these direct DRIFTS spectra (in transmittance) agree quite well with those obtained by conventional means; only a small amount of specular reflectance distortion (an "inverse absorption" spike occurring between the two C-H stretches in Figure 2b) is evident for polyethylene. The 720 $cm^{-1}$ doublet of polyethylene (Figure 2c), on the other hand, is real but is not resolved in the diamond anvil cell (DAC) spectrum. This loss of resolution undoubtedly arises from the high pres-

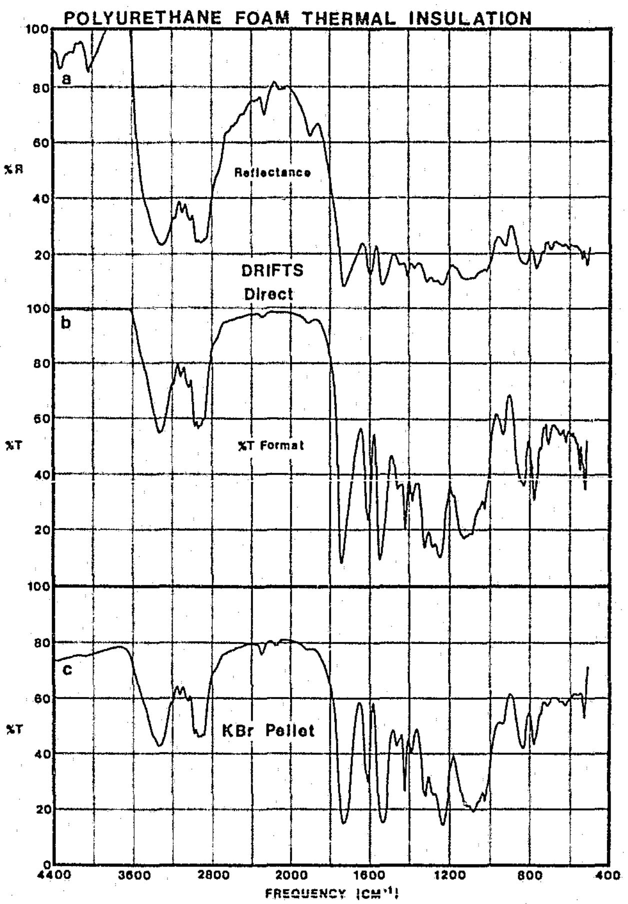

Figure 1. (a) Reflectance spectrum of a piece of polyurethane foam thermal insulation sampled directly. Reference: KBr; Gain, 4R ($R = \sqrt{2}$); Scans, 200. Sample gain 16; Sample scans, 100. (b) Reflectance spectrum "a" presented in transmittance format. (c) KBr pellet spectrum of the same polyurethane material. Sample and background gains, 1 (with an attenuator screen placed in the beam). Sample and background scans, 100 each.

sure of this technique and may reflect a pressure induced disordering.

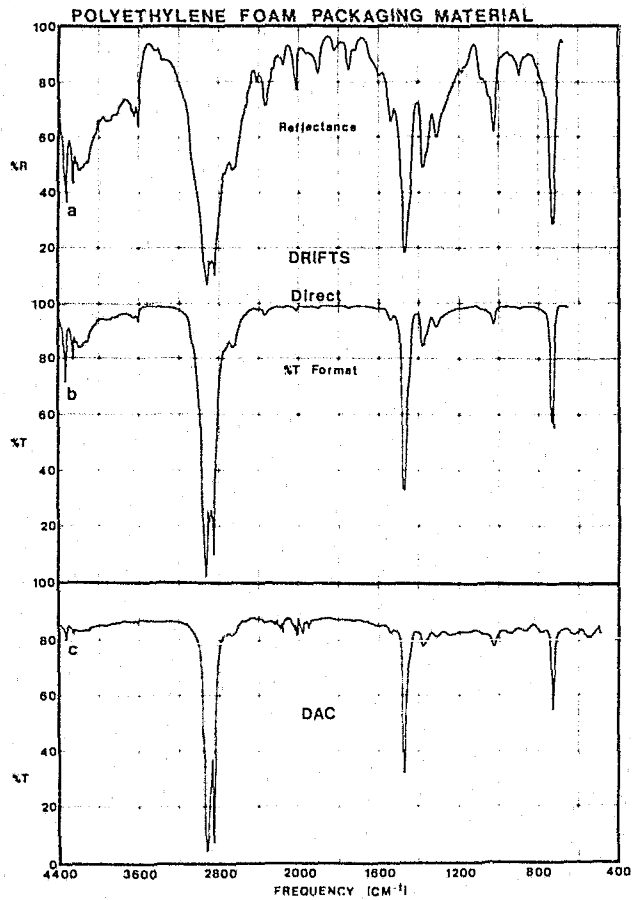

Figure 2. (a) Reflectance spectrum of a piece of polyethylene foam packaging material sampled directly. Reference: KBr; Gain, 4R; Scans, 250. Sample gain, 32; Sample scans, 250. (b) Reflectance spectrum "a" presented in transmittance format. (c) Diamond anvil cell (DAC) spectrum of the same polyethylene material. Sample and background gains, 8; Sample and background scans, 250.

Another of the materials that we examined for possible direct DRIFTS sampling was various types of paint samples. In general, most paint produced a mixture of specular and diffuse reflectance, especially if inorganic components were present. Most metallic paints, however, were found to give almost all diffuse reflectance. The reflectances from these, in fact, were always significantly greater than those of the KBr references. A mirror was thus used as a reference background for these paints. Figure 3a depicts the reflectance spectrum obtained when an intact brown metallic National Bureau of Standards (NBS) auto paint standard panel was sampled directly. The corresponding transmittance format spectrum is shown in Figure 3b. The latter agrees quite well with that taken of the finish layer of this standard (separated from the primer) run on the DAC (Figure 3c). The primer layer of this same NBS standard was also run (Figure 3d), and it is clear from a comparison of Figures 3b and 3d that DRIFTS is only sampling the metallic finish layer. Some metallic paints having lower densities of metal flakes may give spectra showing pronounced low frequency fringes, indicating a beam penetration below the finish layer.

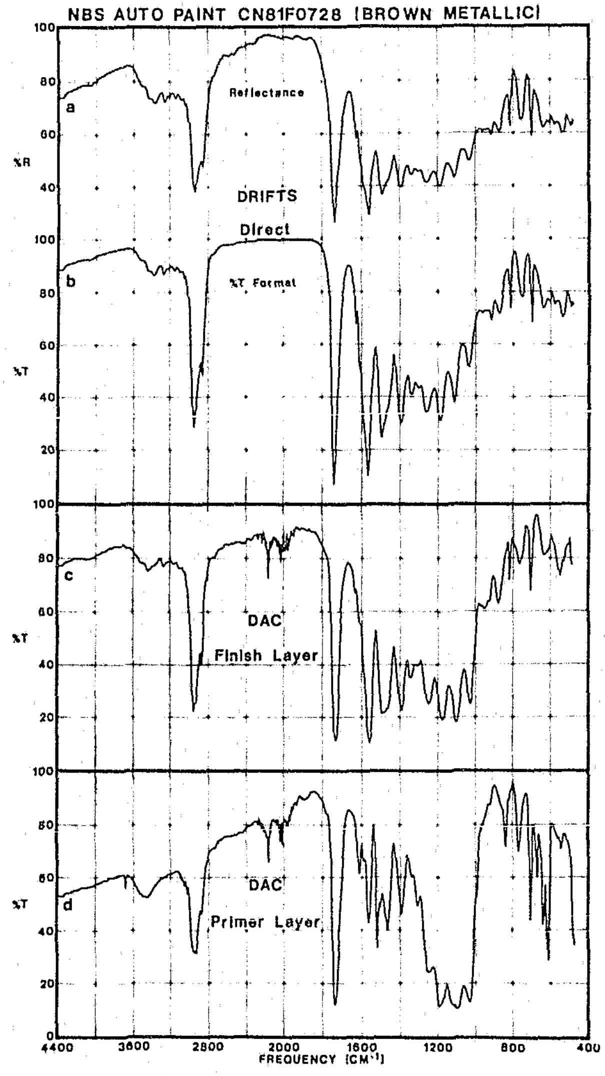

Figure 3. (a) Reflectance spectrum of a National Bureau of Standards (NBS) brown metallic auto paint standard panel sampled directly (finish side sampled). Reference: Mirror; Gain, 2 (with an attenuator screen placed in the beam); Scans, 250. Sample gain, 4R; Sample scans, 200. (b) Reflectance spectrum "a" presented in transmittance format. (c) Metallic finish layer of this NBS panel sampled in the diamond anvil cell. Sample gain, 16; Sample scans, 200. Gain of background, 8R; Background scans, 250. (d) Primer layer of this NBS panel sampled in the diamond anvil cell. Sample gain, 16; Sample scans, 200. Gain of background 8R; Background scans, 250.

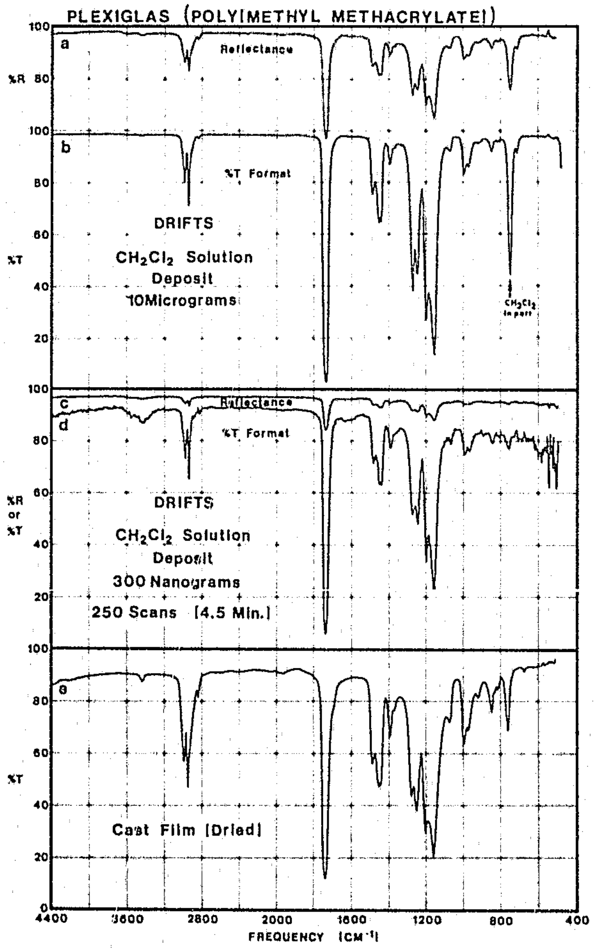

Figure 4. (a) Reflectance spectrum resulting from a deposit of 3-4 drops of a solution of Plexiglas dissolved in dichloromethane (10 μg of sample, total). Reference: KBr; Sample and background gains, 4R; Sample and background scans, 250. (b) Reflectance spectrum "a" presented in transmittance format. The sample was not dried and a small amount of residual dichloromethane is present (arrow). (c) Reflectance spectrum resulting from a deposit of 1 μl of a solution of Plexiglas dissolved in dichloromethane (300 ng). Reference: 1 μl of dichloromethane black deposited onto KBr. Sample and background gains, 4R; Sample and background scans, 250 each. (d) Reflectance spectrum "c" presented in transmittance format. (e) Residue of a solution of Plexiglas dissolved in chloroform deposited onto a KBr plate. Dried for 2 hours at 100° C to remove residual solvent. Sample and background gains, 1 with an attenuator screen placed in the beam. Sample and background scans, 100 each.

Another method of polymer analysis with DRIFTS involves deposition of a solution of the polymer in a volatile solvent. This solution is deposited directly onto KBr prepacked in a sampling cup; the solvent is allowed to evaporate leaving a residue of sample coating the KBr particles. This method is thus limited to soluble polymers; however, because of the very high sensitivity of this method, even very slightly soluble polymers can be sampled in this manner. Fuller and Griffiths in fact, demonstrated a detection level of approximately 10 ng using this procedure. A very recent comprehensive review of infrared spectroscopy states that this method is probably one of the most sensitive infrared techniques available at present, as far as routine-type methods are concerned (McDonald 1984). Figures 4a to 4d show the results of this method applied to a soluble acrylic [Plexiglas ™ or poly (methyl methacrylate)]. It is clear (Figure 4d) that with scans times longer than several minutes, spectra with reasonable signal-to-noise ratios can easily be obtained for less than 100 ng of sample.

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# SUPER GLUE ANALYSIS BY INFRARED SPECTROSCOPY AND PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Super Glue is one trade name for a family of instant adhesives based on an alkyl ester of cyanoacrylic acid. The most common esters are ethyl and methyl. Unlike solvent based adhesives, instant adhesives are applied in monomeric form and the adhesive bond is achieved through the rapid polymerization of this monomer into a high molecular weight polymer. Fixture is generally obtained within a matter of seconds and on many substrates full cure is achieved within an hour. Polymerization is brought about by moisture which is present on the surface of virtually all substrates. Cyanoacrylates are perhaps best identified as a family by infrared (IR) spectroscopy. The best technique of sample preparation for analysis of a polymerized cyanoacrylate is the KBr technique. It is impossible to press a film because of the very low ceiling temperature of these polymers which is in the vicinity of 110° C to 120° C. The most powerful solvents, such as dimethylformamide and acetonitrile, are extremely high boiling and not conducive to film casting for IR purposes.

The fact that cyanoacrylate polymers have relatively low ceiling temperatures allows one to employ a novel sample preparation technique. The polymer sample is placed in a small pan. A NaCl or KBr disk is placed over the pan and the sample heated to approximately 140° C so that when the polymer unzips (that is, reverts to monomer form) it volatilizes and condenses on the NaCl crystal where it immediately repolymerizes. This crystal is used directly for an IR spectrum.

Figure 1 shows a spectrum of methyl cyanoacrylate (bottom) and a spectrum of poly(methyl cyanoacrylate) (top). These spectra are of the same sample before and after polymerization. The sample is purposely thick so as to demonstrate what happens to the cyano absorption band when the monomer polymerizes. Figure 2 is similar to Figure 1 except that it depicts ethyl cyanoacrylate. In both cases one can see the drastic reduction in intensity of the cyano absorption band. The intensity of the cyano absorption band in a spectrum of a cyanoacrylate polymer is much less than would be expected for a molecule containing such a high concentration of cyano groups.

Cyanoacrylate monomers have a very low vapor pressure at ambient conditions, therefore, very little vapor gets into the atmosphere. However, at higher temperatures an easily detectable quantity of cyanoacrylate vapors are generated. These can become quite irritating if not exhausted. On the other hand, this can be used to advantage when analyzing cyanoacrylates. The fact that one may pyrolyze a polymer sample and deposit a solid film on a crystal, is a pretty good indication that a cyanoacrylate is involved. Also, the odor of cyanoacrylate monomers is very distinctive and leaves little doubt as to the presence of cyanoacrylate adhesives.

Nuclear magnetic resonance (NMR) spectroscopy offers an almost unmistakable means of identifying a cyanoacrylate monomer. The pendant vinyl protons of cyanoacrylates show a chemical shift on either side of 7 ppm. These same protons in an acrylate or methacrylate show a chemical shift on either side of 6 ppm. Methyl cyanoacrylate shows a singlet at about 3.9 ppm. Ethyl cyanoacrylate shows a quartet at approximately 4.3 ppm and a triplet at about 1.4 ppm. Beta ethoxy ethyl cyanoacrylate protons, which are on the carbon closest to the cyanoacrylate, show a chemical shift of 4.3 ppm. The multiple peaks in the vicinity of 3.6 ppm are due to the triplet and quartet of the ether protons as expected but are not distinguishable. The end methyl shows a triplet at 1.3 ppm.

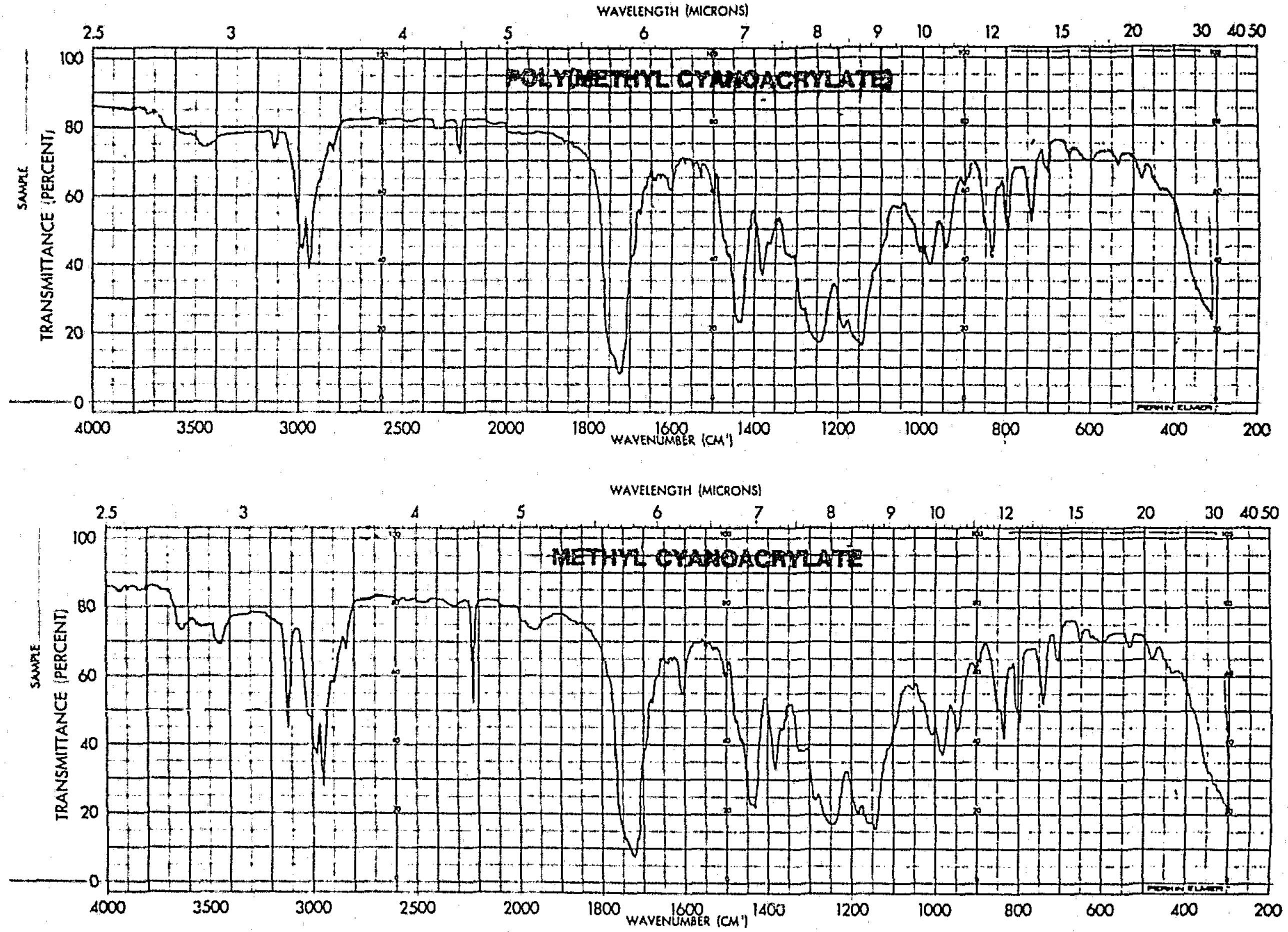

Figure 1. Infrared spectra of methyl cyanoacrylate (bottom) and poly(methyl cyanoacrylate) (top).

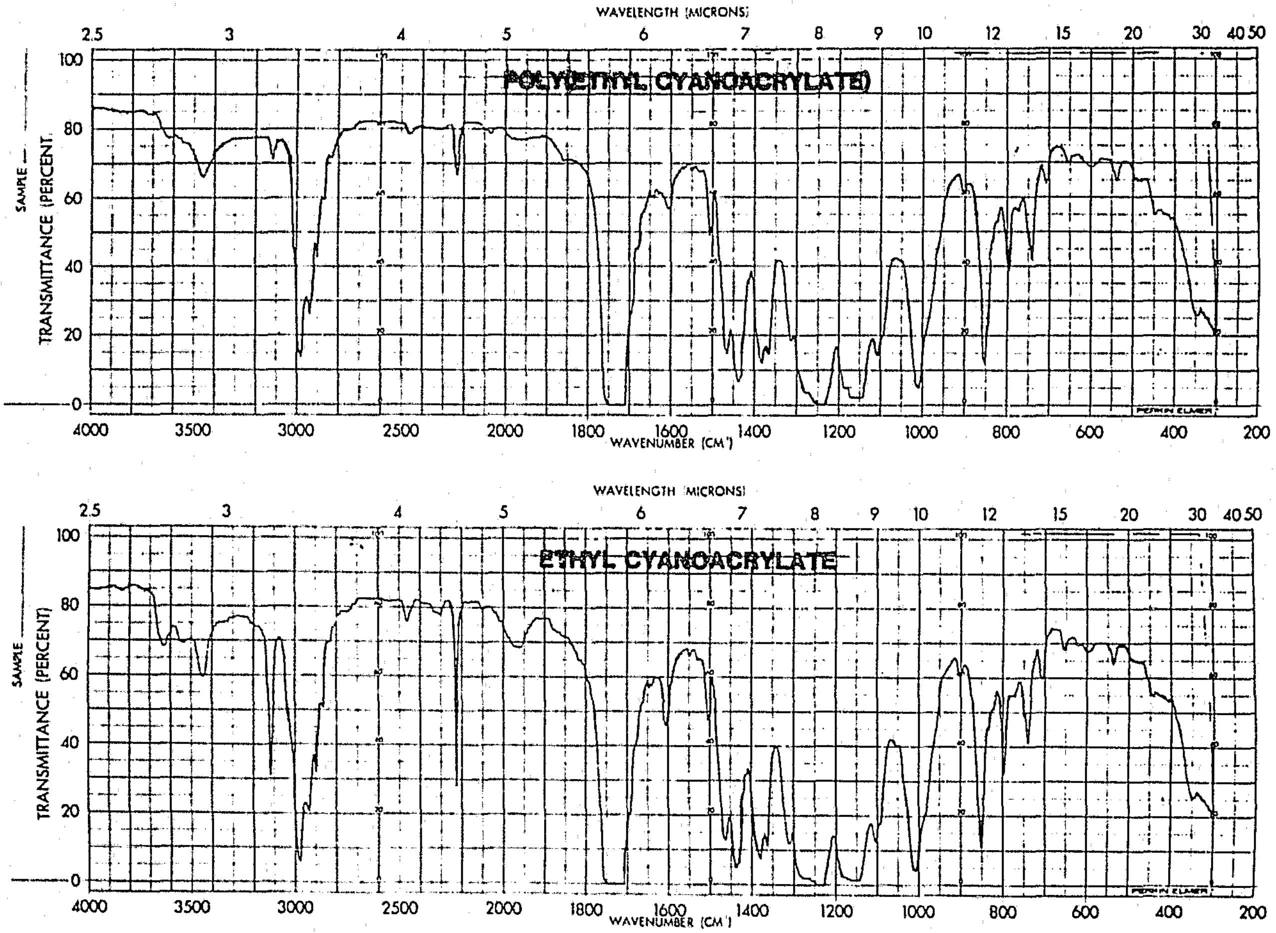

Figure 2. Infrared spectrum of ethyl cyanoacrylate.

# COMPARISON OF MASKING TAPES BY FLUORESCENCE SPECTROSCOPY

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Masking tapes as well as other tapes are frequently used in criminal activities. Such tapes may be used to bind and gag victims of kidnappings, robberies, homicides and sex crimes. In burglaries tapes may be used to prevent doors from latching, or they may be used to prevent noise from falling glass. Tapes are also frequently used in assembling explosive devices.

Ideally, latent or visible prints are found and they identify the suspect, or one end of the tape forms a physical match with the end of a roll of tape found in the possession of the suspect. But failing these possibilities, it is still worthwhile to compare the tape with any tapes that may be found in the possession of the suspect(s), or found at similar crime scenes.

Recently, the author was asked to compare small bottles containing hashish oil that had been obtained in three separate investigations. The bottles were all of the same brand and size, and all had pieces of masking tape on the outside and a price written thereon in blue ink. Comparison of the tapes, as well as the inks, indicated that all of the bottles could have originated from the same source.

Experimental results indicated that different brands of masking tapes could be distinguished by a combination of examinations including visual, infrared (IR) spectroscopy and pyrolysis gas chromatography (Py-GC). More interestingly, there were indications that fluorescence spectroscopy might be capable of distinguishing between different production runs of the same brand. The probability that two tapes might have originated from the same source would be much greater if not only different brands but also different production runs within a brand could be distinguished.

In fluorescence spectroscopy by traditional methods two spectra are produced, an emission spectrum and an excitation spectrum. Although this works well for many samples, with complex mixtures containing several fluorescent components the overlapping of the various spectra may result in a relatively featureless curve. In the examination of complex mixtures, better resolved spectra are frequently obtained by synchronously varying both the excitation and emission wavelengths. The synchronous technique (Lloyd 1971) was used exclusively in the present study, with most spectra being obtained with a fixed wavelength difference of 20 nm.

Three different brands of beige colored masking tape were examined using a Perkin-Elmer MPF-3 fluorescence spectrometer (Norwalk, CT). Instrument conditions were excitation and emission slits both set at 4 nm, sample sensitivity at 10, scan speed at 4, and chart speed at low.

First, the exterior surface of the tapes were examined using the front surface accessory. The different brands produced different spectral patterns. Although varying in fluorescence intensity, the different brands produced consistent patterns both within a tape roll and also between tape rolls from the same sample lot. Two samples that were from the same brand but different lots gave different patterns. One sample was examined both before and after dusting for prints using a Magna brush and a mixture of black powder and iron filings. After wiping the exterior surface with a laboratory tissue, the fluorescent pattern showed little change except for a reduction in fluorescence intensity.

After examining the exterior surface, small pieces of tape were soaked in dichloromethane. The solution was filtered through glass wool and then two drops were placed in a cuvette and diluted with more dichloromethane. These solutions were examined using the same instrument conditions. Again, different brands gave different fluorescence patterns, as did different lots of the same brand.

After the examination by fluorescence spectroscopy, IR spectroscopy (Noble *et al.* 1974; Pattacini 1974) and/or Py-GC (Noble *et al.* 1974) examinations may be carried out by evaporating the same solutions onto KBr disks for IR spectroscopy or onto ribbon probes for pyrolysis.

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# FORENSIC CHARACTERIZATION OF BLACK POLYVINYL CHLORIDE ELECTRICAL TAPE

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Black polyvinyl chloride (PVC) electrical tape is commonly employed in the fabrication of improvised explosive devices as a convenient means of securing components (batteries, timer, circuitry and explosive) into one package. Usually pieces of the tape survive the explosion and can be recovered for comparison with known tape found in the possession of a suspect. In this study, black PVC tapes from six manufacturers were characterized by nondestructive techniques only. These tapes represent types of PVC tapes commercially available. Two rolls from each manufacturer were studied in an effort to determine intra-roll as well as inter-roll variability.

## EXPERIMENTAL PROCEDURE

Six brands of black PVC electrical tape (3/4 inch wide by .007 inch thick) were chosen for this work: LePages, Tuck, 3M (Scotch "33"), Nashua, Vanguard and Manco. Three rolls of each brand were purchased simultaneously to ensure a high probability that at least two had come from the same batch of tape. The tapes were initially examined under a low to moderate power stereomicroscope to reveal surface features of the PVC backing (non-adhesive side). Next, non-destructive infrared spectroscopic analyses were performed on the pressure sensitive adhesive of each tape. Approximately 35-40 mm of tape was applied to one side of a 20 x 52.5 x 2 mm 45° KRS-5 internal reflectance crystal (Wilks #005-6001 or equivalent). And, finally, the elemental profiles of the tape backings were obtained with a Philips Model 9500 energy X-ray dispersive fluorescence spectrometer (Philips Electronic Instruments, Inc., Mahwah, NJ). The first revolution of tape was removed from each roll prior to analysis to eliminate any surface contamination. Ten consecutive 10-15 cm strips were cut and analyzed. The instrumental parameters are listed in Table 1. The X-ray energies used for the elemental analyses are listed in Table 2.

Table 1. CONDITIONS FOR X-RAY FLUORESCENCE ELEMENTAL ANALYSIS

| | |
|---|---|
| Instrument: | Philips Model 9500 |
| Tube: | Rhodium |
| Voltage: | 25 kV |
| Current: | Sufficient to give approximately 8000 counts per second (50-100 $\mu$A) |
| Filter: | None |
| Vacuum: | 0.5 torr or better |
| Count time: | 150 seconds |

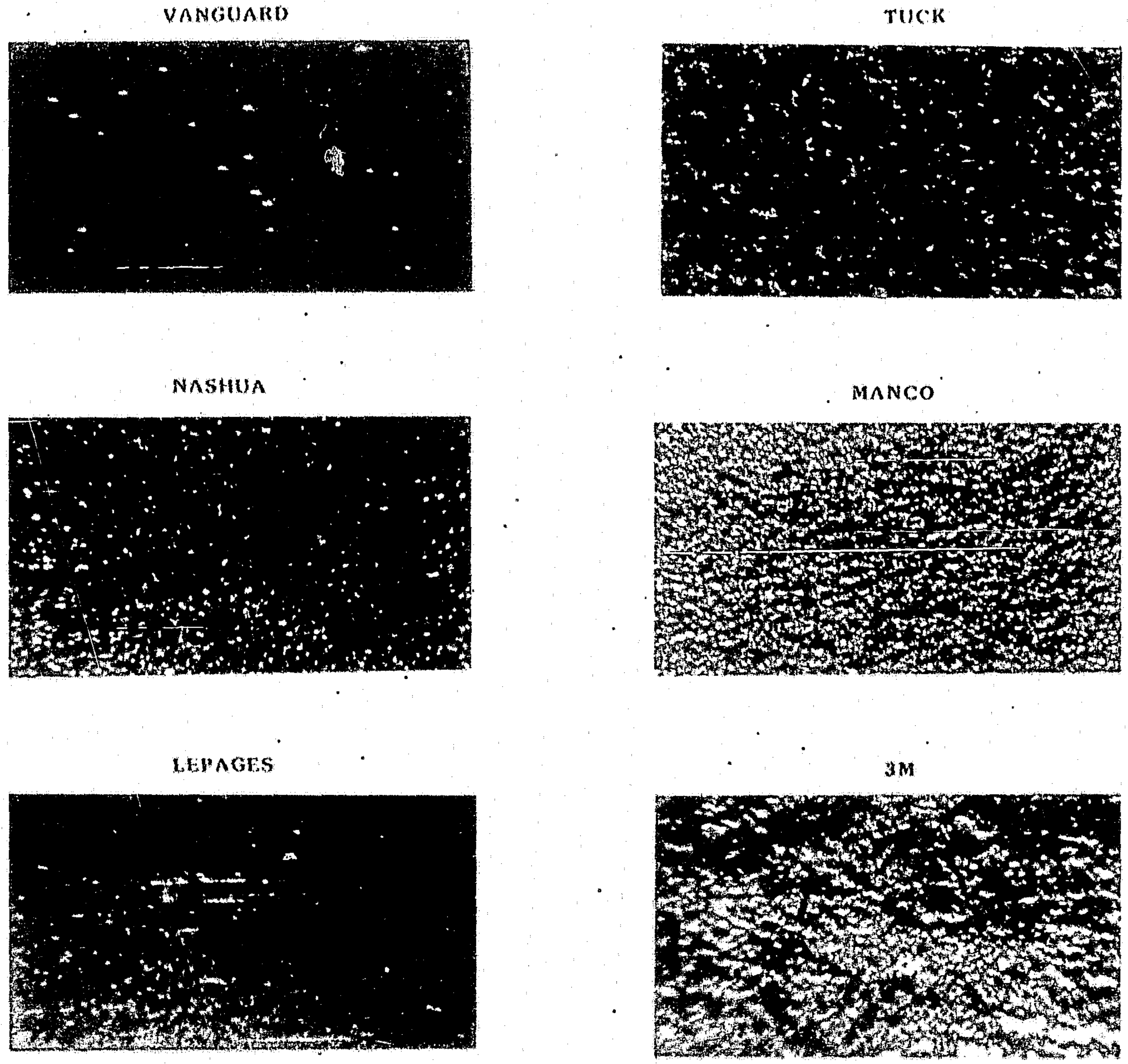
Table 2. LINES AND ENERGIES FOR 10 ELEMENTS USING X-RAY FLUORESCENCE

| Element | Line | KeV |
|---|---|---|
| Al | $K_{\alpha,\beta}$ | 1.49 |
| Si | $K_{\alpha,\beta}$ | 1.74 |
| S | $K_{\alpha,\beta}$ | 2.31 |
| Cl | $K_{\alpha}$ | 2.62 |
| | $K_{\beta}$ | 2.82 |
| Sb | $L_{\alpha}$ | 3.60 |
| | $L_{\beta 1}$ | 3.84 |
| | $L_{\beta 2}$ | 4.10 |
| Ca | $K_{\alpha}$ | 3.69 |
| | $K_{\beta}$ | 4.01 |
| Ti | $K_{\alpha}$ | 4.50 |
| | $K_{\beta}$ | 4.93 |
| Fe | $K_{\alpha}$ | 6.40 |
| | $K_{\beta}$ | 7.06 |
| Zn | $K_{\alpha}$ | 8.63 |
| | $K_{\beta}$ | 9.57 |
| Pb | $L_{\alpha}$ | 10.55 |
| | $L_{\beta}$ | 12.62 |
| | $L_{\gamma}$ | 14.76 |

## RESULTS

### Microscopic Examination

Each of the brands appeared to have distinct surface textures sufficiently unique to allow discrimination between manufacturers when examined with a stereomicroscope at an overall magnification of 25x to 50x. The Vanguard, Nashua, LePages and Tuck tapes (Figures 1 through 4) showed different forms of longitudinal stippling or striation that may or may not be visible on the photographs as printed. The origin of these marks has not been established; however, it is possible that they are associated with the equipment with which the tapes were manufactured. The 3M and Manco tapes (Figures 5 and 6) did not exhibit striations of recognizable form, but did show different forms of irregular cratering.



VANGUARD

TUCK

NASHUA

MANCO

LEPAGES

3M

Figure 1. Photomicrographs of black polyvinyl chloride electrical tapes arranged from the smoothest surface (Vanguard) to the roughest (3M), all at the same magnification (40X).

**Infrared Spectroscopy**

The spectrophotometric curves obtained (Figure 2) show that each of the adhesives could be distinguished from the others. All of the spectra contain the aliphatic C-H stretching absorption band (just below 3000 cm$^{-1}$) and the $CH_2$ and $CH_3$ bending absorptions (1460 cm$^{-1}$ and 1375 cm$^{-1}$), indicative of long chain aliphatic hydrocarbons. All spectra also contain carbonyl absorption band (1720 cm$^{-1}$ to 1740 cm$^{-1}$) typical of aliphatic or aromatic ester-type plasticizers. These two observations are consistent with ingredients known to be used in the manufacture of pressure sensitive adhesives (Satas 1982) (Table 3). No interference from PVC was observed. In the "fingerprint" regions (1700 cm$^{-1}$ to 500 cm$^{-1}$), absorption due to various adhesive substrates can be seen. A reliable identification of these substrates is difficult because of interferences from plasticizers and other compounds present. The only unencumbered bands for natural rubber are at 835 and 570 cm$^{-1}$; those for stryene/butadiene copolymer rubbers (SBR) are at 760 and 700 cm$^{-1}$; and polybutadiene rubber (PBR) bands are at 965, 910 and 775 cm$^{-1}$ (Haslam and Willis 1965). Based on these assignments, it may be inferred that the Vanguard and Manco adhesives contain SBR, while Nashua, LePages and Tuck adhesives contain both natural rubber and PBR. Phthalate plasticizers are indicated in the spectra of the Vanguard, Manco and Tuck tapes by the carbonyl band and the ester bands at 1280, 1125 and 1075 cm$^{-1}$ (Chicago Society for Paint Technology 1969). These adhesives can be distinguished from one another by the ratio of carbonyl to $CH_{2,3}$ (1730 cm$^{-1}$/1460 cm$^{-1}$). Differences can also be observed between the Vanguard and Manco adhesives in the minor peaks at 630, 710 and 885 cm$^{-1}$. The Nashua, LePages and 3M spectra all contain the ester carbonyl band, but do not contain the "fingerprint" bands for phthalate plasticizers. The Nashua and LePages spectra are easily distinguishable by differences in the unassigned bands between 700 and 760 cm$^{-1}$. The fingerprint region of the 3M spectrum is unlike any of the other five spectra and has not been further elucidated.

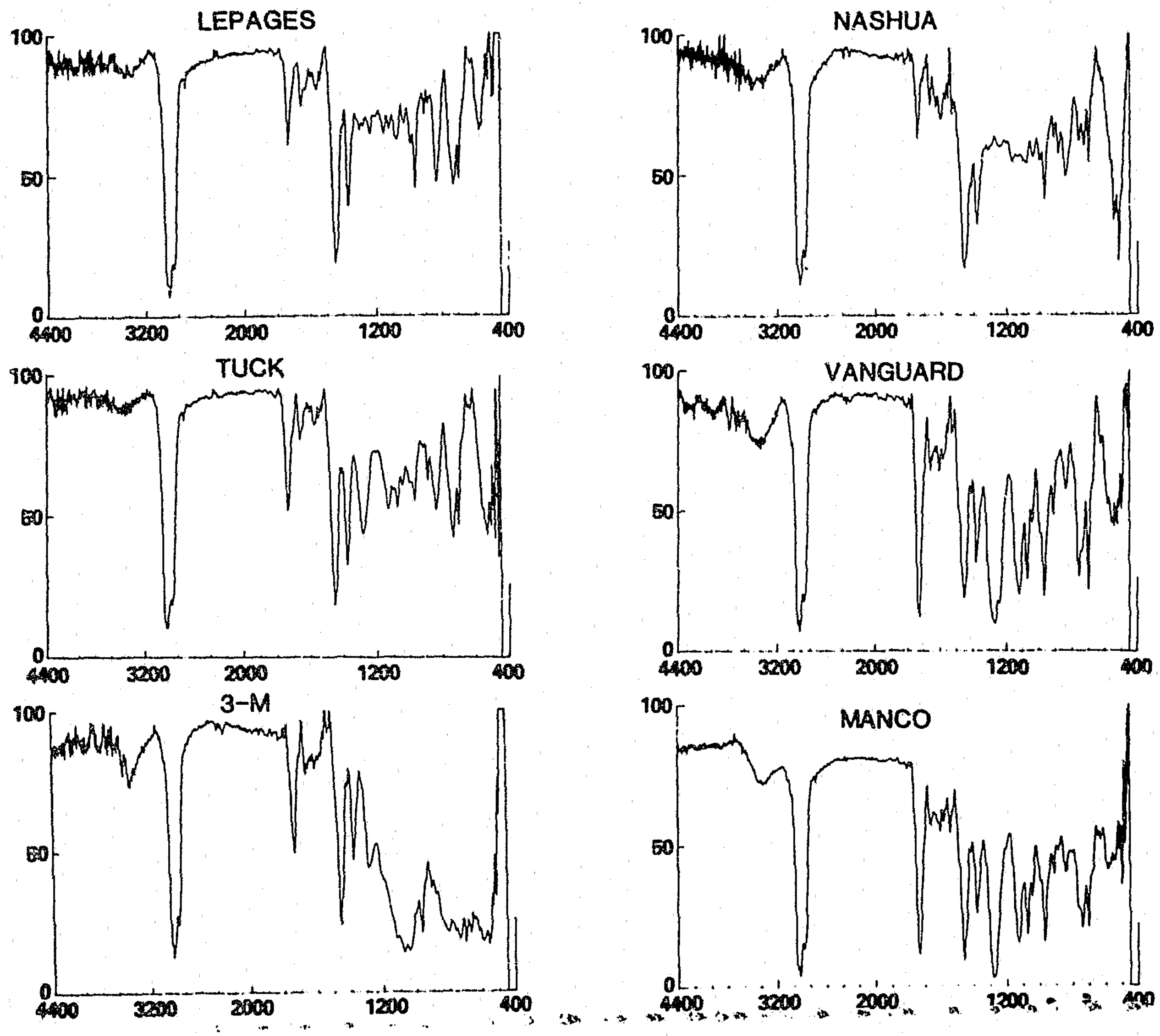


Figure 2. Internal reflectance Fourier transform infrared spectra of tape adhesives.

Table 3. THE COMPOSITION OF PRESSURE-SENSITIVE ADHESIVES

A. Polymer: natural rubber, butyl rubber, polyisobutylene, block copolymers (polystyrene/polybutadiene/polystyrene; polystryene/polyisoprene/polystyrene), acrylics, vinyl ethers, silicones

B. Rubber Tackifiers: wood rosin and rosin esters, terpene resins, terpene phenolics, phenol - formaldehyde, petroleum based resins

C. Plasticizers: mineral oil, lanolin, lecithin, phthalate esters, polybutene, petrolatum

D. Pigments/fillers: $TiO_2$, silica, $CaCO_3$, kaolin, mica, $BaSO_4$, ZnO, talc, carbon blacks

E. Antioxidants: amines, phenolics, dithiocarbamates

## Elemental Analysis

The ten elements analyzed by X-ray fluorescence spectrometry were aluminum (Al), silicon (Si), sulfur (S), chlorine (Cl), antimony (Sb), calcium (Ca), titanium (Ti), iron (Fe), zinc (Zn) and lead (Pb). The count rate data for ten elements were accumulated for two rolls of each brand and normalized by dividing the count rate for each element by the total for all ten elements and multiplying by 100. The average normalized count data and standard deviations are shown in Table 4. The count rate data do not necessarily reflect the relative abundances of the elements present. This is especially true for S, Sb and Ca. The X-ray fluorescence peak for S ($K_{\alpha,\beta}$) contains a large contribution from the M line from Pb which cannot be resolved. Likewise, a substantial overlap exists between the Sb L lines used in the analyses and the Ca $K_\alpha$ and $K_\beta$ peaks. In this situation, however, a partial resolution is achieved and the computer in the spectrometer decides how much of the area to allot to Sb on the basis of the number of counts in the channel corresponding to the strongest Sb line ($L_\alpha$). The remainder of the area is assigned to Ca. While these manupulations may not give a true representation of the elements present, they do not affect the comparison of elemental profiles from one sample to another. The elements found in the tapes are generally similar to those present in PVC fillers, stabilizers and lubricants (Satas 1982) (Table 5). Within each manufacturer, the two rolls are basically congruent, considering the standard deviations. Between manufacturers, sufficient variations exist among the ten elements to unequivocally demonstrate differences in elemental profiles. The elemental profiles for each manufacturer are shown graphically in Figure 3. The magnitude of the differences seen obviates any further tests for population overlap.

Table 4. SEMIQUANTITATIVE DETERMINATION OF TEN ELEMENTS IN ELECTRICAL TAPES

| Manufacturer | Roll | Al | Si | S | Cl | Sb' | Ca | Ti | Fe | Zn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Le Pages | A | 1.27[a](.03)[b] | 3.40(.04) | 2.29(.02) | 89.61(.14) | .70(.02) | -0- | .27(.02) | .27(.02) | -0- | 2.19(.07) |
| | B | 1.33(.04) | 3.40(.06) | 2.03(.04) | 89.60(.22) | .74(.04) | -0- | .30(.02) | .27(.02) | -0- | 2.33(.08) |
| Tuck | A | .08(.01) | 1.12(.03) | 2.40(.04) | 94.06(.09) | .15(.01) | -0- | -0- | -0- | -0- | 2.19(.06) |
| | B | .09(.02) | 1.12(.03) | 2.44(.02) | 94.04(.10) | .15(.01) | -0- | -0- | -0- | -0- | 2.15(.08) |
| 3M | A | .11(.01) | .26(.01) | 3.83(.10) | 91.49(.07) | .46(.01) | .13(.01) | -0- | -0- | .43(.01) | 3.28(.07) |
| | B | .10(.01) | .26(.02) | 3.75(.03) | 91.48(.10) | .45(.02) | .15(.01) | -0- | -0- | .44(.01) | 3.36(.10) |
| Nashua | A | -0- | .81(.02) | 2.62(.04) | 83.88(.14) | 1.05(.04) | 1.07(.02) | -0- | -0- | 7.35(.13) | 3.23(.09) |
| | B | -0- | .81(.02) | 2.62(.03) | 83.96(.18) | 1.08(.04) | 1.04(.02) | -0- | -0- | 7.14(.10) | 3.35(.11) |
| Vanguard | A | -0- | .18(.01) | 2.59(.03) | 94.45(.09) | .66(.01) | -0- | -0- | -0- | .16(.01) | 1.96(.07) |
| | B | -0- | .19(.01) | 2.61(.03) | 94.44(.09) | .66(.03) | -0- | -0- | -0- | .16(.01) | 1.95(.07) |
| Manco | A | .86(.03) | 2.18(.04) | 1.99(.02) | 90.89(.24) | 1.53(.06) | 1.14(.05) | .14(.01) | .19(.01) | -0- | 1.08(.06) |
| | B | .87(.02) | 2.20(.03) | 1.99(.04) | 90.91(.08) | 1.49(.02) | 1.17(.02) | .13(.01) | .18(.02) | -0- | 1.06(.04) |

[a] Mean, n = 10

[b] Standard deviation

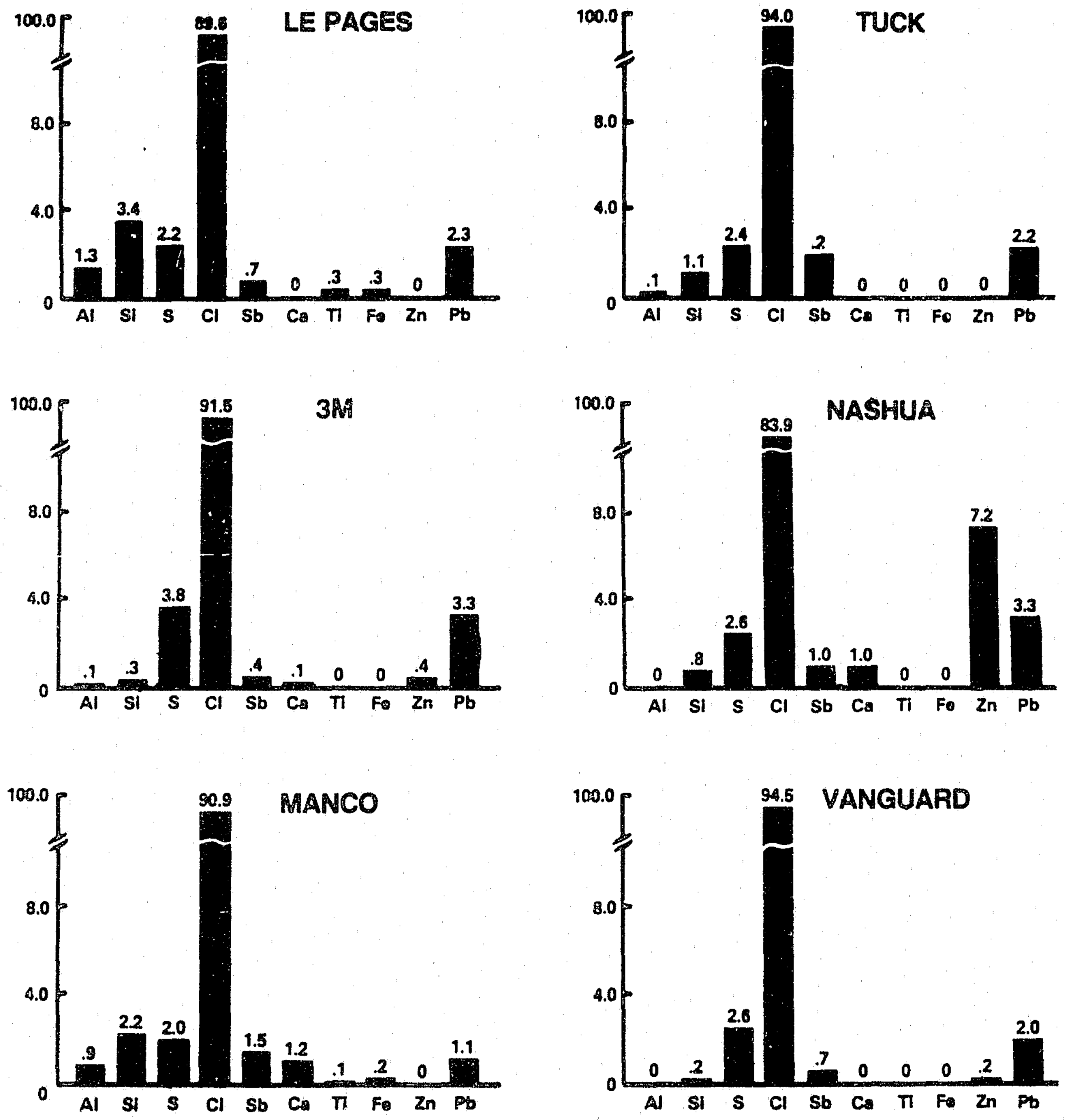


Figure 3. Relative X-ray abundances of ten elements in tape backings.

**Table 5. THE COMPOSITION OF ELECTRICAL TAPES**

A. Backing: polyvinyl chloride

B. Plasticizers: phthalate esters, aliphatic fatty acid esters, alkyl/aryl phosphates, dialkyl tin, castor oil

C. Fillers: $TiO_2$, $CaCO_3$, $BaSO_4$, kaolin, talc

D. Lubricants: calcium stearate, waxes

E. Stabilizers: basic lead carbonate, tribasic lead sulfate, Ca, Pb, Cd, Ba Stearate, dibutyl tin dilaurate, diphenyl urea

## CONCLUSIONS

All six brands of black PVC electrical tape examined possess unique characteristics which can be determined by non-destructive techniques and used to distinguish one tape from another. These characteristics consist of microscopic surface features, elemental profiles and adhesive composition. Stereomicroscopic examinations showed that all six tape backings have different and distinguishable surface textures. X-ray fluorescence showed that all six tapes have clearly different elemental profiles, while two rolls from the same manufacturer are indistinguishable. And infrared spectroscopic analyses showed that each manufacturer's adhesive is different and distinguishable from the others. Because each brand of tape can be distinguished from the other five on the basis of any one of the three techniques studied, a combination of all three techniques can lend a very high discriminating power to the examination of evidentiary black PVC tape samples.

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*Haslam, J. and Willis, H. A. (1965).* Identification and Analysis of Plastics. D. Van Nostrand Co., Inc., Princeton.

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# FORENSIC EXAMINATION OF DUCT TAPE

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Twelve samples of duct tape were examined in an effort to determine the properties which may distinguish one duct tape sample from another. Methods employed in this study included examination of the weave pattern of the reinforcing cloth; determination of the number of threads per inch in the cloth; identification of the fibers in the threads; determination of the type of twist, if any, in the threads; visual examination of the adhesive; infrared (IR) analysis of the adhesive and tape backing; determination of the solubility of the tape backing; and elemental analysis of the adhesive by emission spectroscopy.

Most of the tape samples examined were distinguished by comparison of cloth weave patterns and by thread counts. Four general types of weave patterns were observed: rectangular, rectangular irregular cross threads, distorted rectangular and parallelogram. Thread counts varied widely from sample to sample. Tape samples not readily distinguished by these methods may be distinguished by other methods explored in this study.

Infrared analysis showed that all the tape adhesives studied were polypropylene-based. Carbonate and silicate were the principle additives. In each sample the backing material, also examined by IR spectrometry, was found to be mainly polyethylene (PE). In most of the samples, the PE tape backing was soluble in hot toluene; in one sample (Tuck) the PE tape backing was insoluble in hot toluene.

The "Z" twist was the most common arrangement of the fibers in the threads. Braided threads were found in samples of two tape brands (Shurtape and Manco). Measurement of the fibers' refractive indices showed that the threads in most of the samples were cotton-polyester blends; threads in other samples were cotton-rayon blends or pure polyester.

Analysis of the tapes' adhesives by emission spectroscopy showed the presence of aluminum, silicon, iron, titanium and magnesium in all the samples examined. Calcium and zinc were detected in most, but not all, of the samples. A summary of the experimental results is given in Table 1.

Although many tape samples may be distinguished by observation of cloth weave patterns and by thread counts, other methods of analysis, such as those listed above, may be useful in differentiating between physically similar samples or in demonstrating their physical and chemical consistency.

**Table 1. SUMMARY OF EXPERIMENTAL RESULTS**

| | Brand | Weave Pattern[a] | Thread Count[b] | | Adhesive Visual Exam[c] | HCl Test[d] | Adhesive Infrared[e] | Tape Backing Infrared[f] | Solubility of Backing in Toluene[g] | Fibers[h] | Thread Type[i] | | Elemental Analysis of Adhesive[j] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | LE | CR | | | | | | | LE | CR | Ca | Al | Si | Fe | Ti | Zn | Mg |
| 1A. | Nashua | Rect. ICR | 11 | 24 | OW, R | Pos. | PP, C, LS | PE | Sol. | P, R | Z | Z | H | M | H | M | M | M | M |
| 1B. | Pay-N-Pak | Rect. ICR | 11 | 24 | OW, R | Pos | PP, C, LS | PE | Sol. | P, R | Z | Z | H | M | H | M | M | M | M |
| 2. | Shurtape | Rect. | 15.5 | 19 | OW, R | Neg. | PP, S | PE | Sol. | P | STB | ST | L | M | H | M | L | L | M |
| 3. | Shurtape | Distorted Rect. | 20 | 32 | OW, R | Neg. | PP, S | PE | Sol. | P | Z | Z | L | M | H | M | M | L | M |
| 4. | Montgomery Wards | Rect. | 32 | 19 | OW, R | Neg. | PP, S | PE | Sol. | P, C | Z | Z | None | M | H | L | L | None | M |
| 5AB. | Manco | Rect. | 15.5 | 19 | OW, R | Neg. | PP, S | PE | Sol. | P | STB | ST | L | M | H | M | M | L | M |
| 6. | Tuck | Rect. ICR | 21 | 26 | W, R | Neg. | PP, S | PE | Sol. | P, C | Z | Z | L | M | H | L | M | M | M |
| 7. | Tuck | Rect. ICR | 21 | 26 | W, R | Neg. | PP, S | PE | Insol. | P, C | Z | Z | L | M | H | M | M | M | M |
| 8. | Frost King | Parallelogram | 18 | 32 | OW, R | Neg. | PP, S, CS? | PE | Sol. | P, C | Z | Z | L | M | H | M | M | H | M |
| 9. | Anchor | Rect. | 13.5 | 30.5 | OW, R | Pos. | PP, C, LS | PE | Sol. | P, C | Z | Z | H | M | H | M | M | H | M |
| 10. | Marcy | Rect. | 19 | 31 | OW, R | Neg. | PP, S | PE | Sol. | P, C | Z | Z | L | M | H | L | M | None | M |

[a] Rect. = rectangular; ICR = irregular cross threads.
[b] Measured in threads per inch; LE = lengthwise; CR = crosswise.
[c] OW = off-white; R = rubber particles in adhesive; W = white.
[d] Pos. = positive (evolution of gas); Neg. = negative.
[e] PP = polypropylene; C = carbonate; LS = small amount of silicate; S = silicate; CS = carboxylate salt.
[f] PE = polyethylene.
[g] Solubility in toluene at 80° C; Sol. = soluble; Insol. = insoluble.
[h] P = polyester; R = rayon; C = cotton.
[i] Z = "Z" twist; STB = straight in braid; ST = straight.
[j] H = relatively high concentration; M = medium; L = low.

# ELEMENTAL EXAMINATION OF SILVER DUCT TAPE USING ENERGY DISPERSIVE X-RAY SPECTROMETRY

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Silver duct tape is commonly submitted to crime laboratories for analysis when used in such cases as homicides, kidnappings, burglaries, etc. Historically, analysis has relied on jigsaw matches and basic macroscopic, microscopic and chemical evaluations which often dismantle, alter or destroy the tape. Since a primary objective of evidence technicians and the law enforcement community is the preservation of evidence, it is recommended that a nondestructive elemental evaluation technique such as energy dispersive X-ray spectrometry (EDS) be a primary consideration in the initial analysis of duct tape.

This elemental technique can be applied to intact samples of tape. The cleanest section of tape should be examined. To ensure the cleanest section of tape, the duct tape was placed adhesive side down with Teflon-coated forceps and affixed on a section of Mylar film (E. I. duPont de Nemours & Co., Inc., Wilmington, DE). A Tracor-Northern energy dispersive X-ray spectrometer (Middleton, WI) was used. The sample was scanned for 150 seconds, at a KEV of 0.02 with an approximate dead time of 50 percent with no filtration. The X-ray tube anode current setting was at .03 with the voltage level on high. The results were plotted on a Tracor-Northern spectral plotter.

This elemental technique involved the identification of seven elements found in duct tape: titanium, calcium, zinc, iron, copper, lead and chlorine. It is important to note that not all of these elements were found in any one brand of tape. The elemental composition can vary from as few as three identified elements to a maximum of five, with the majority of samples examined (over 65) averaging four elements. The elements are routinely identified in varying concentrations.

It is the identification of these elements and the comparison of their varying concentrations that allows duct tape to be classified according to manufacturer. For example, several tape samples from different distributors (Figures 1 and 2) reveal the same elemental composition; but differences in their quantities are apparent. The quantities or ratios of all elements concerned must be considered when identifying a manufacturer. Numerous brands of duct tape contain the four most commonly identified elements: zinc, calcium, titanium and iron. These various brands can easily be distinguished by examining the varying concentrations of each element.

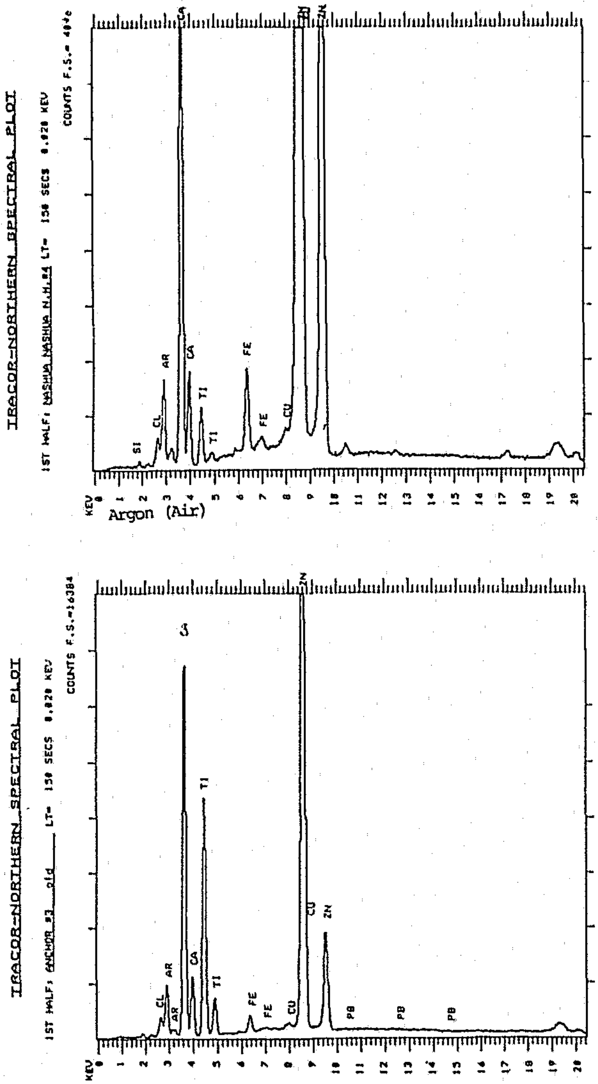

Figure 1. Energy dispersive X-ray spectra of Nashau (top) and Anchor (bottom) tapes.

To date, only three brands of duct tape (Aron, Superior and Mystik) have been found to contain titanium as the element of greatest concentration (Figures 3 and 4). In each case, titanium far overshadows the second element of lesser concentration by 3 to 1.

Chlorine has been detected as the element of greatest concentration in only two brands (Sekisui and Westape) (Figure 5). Both of these brands are manufactured in Japan; however, only one brand contains lead (Westape), creating a quick and easy method for brand identification.

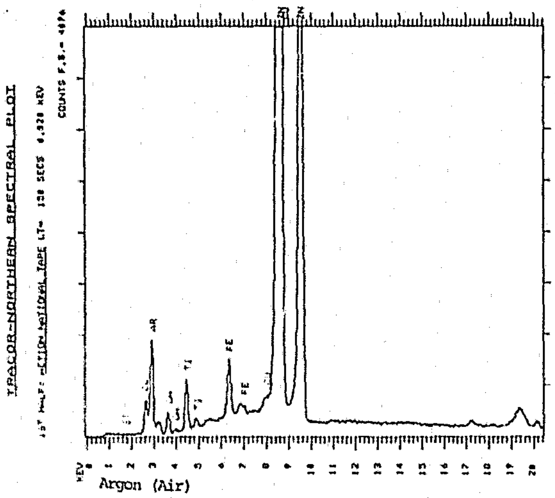

Figure 2. Energy dispersive X-ray spectrum of Action National tape.

The elements of greatest concentrations have proven to be zinc, titanium, calcium and chlorine. These elements are a direct result of fillers used in the manufacturing process. For example: $TiO_2$, $CaCO_3$ and ZnO are fillers and $Cl_2$ is used in the tape.

Elemental examination has not shown any significant differences among samples removed from the beginning, middle and end of a roll of tape, thus indicating the elements and their concentrations are homogeneous throughout the roll.

Energy dispersive X-ray spectrometry is an easy, reliable and non-destructive method of duct tape analysis. It provides vital investigative information in the identification of brands of duct tape involved in criminal cases. Its simple comparison of elemental spectra makes interpretation fast and easy, thus allowing duct tape to be classified according to manufacturer. By using this technique to determine the basic manufacturer identification, it may be possible to compile the other trace evidence techniques, such as color, texture, surface design, weave pattern, weave count, fiber identification, adhesive properties and pyrolysis to make a positive batch lot identification.

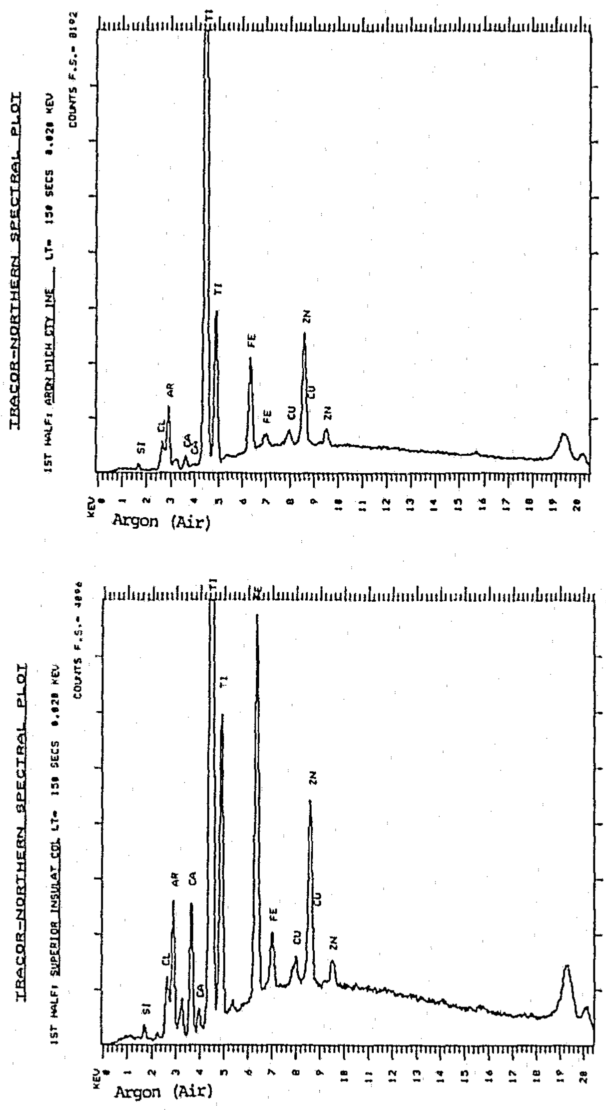

Figure 3. Energy dispersive X-ray spectra of Aron (top) and Superior (bottom) tapes.

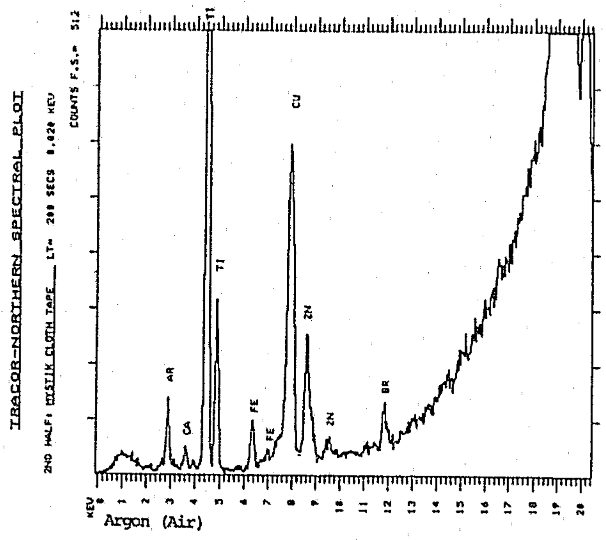

Figure 4. Energy dispersive X-ray spectrum of Mystik tape.

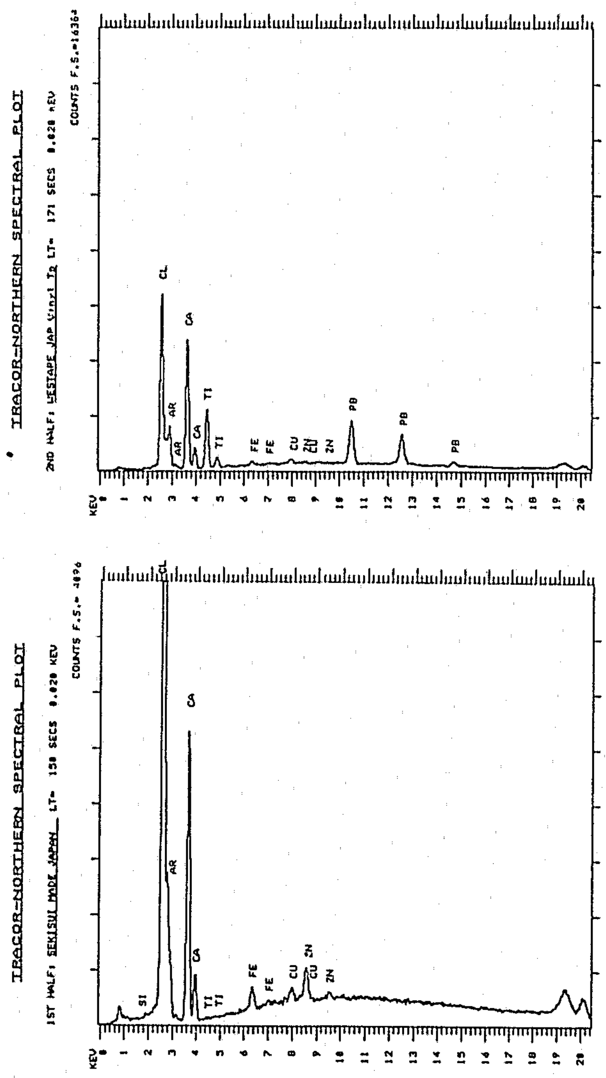

Figure 5. Energy dispersive X-ray spectra of Westape (top) and Sekisui (bottom) tape.

# EVIDENTIARY COMPARISONS OF PLASTIC MATERIALS AND PRODUCTS BASED UPON FABRICATION CHARACTERISTICS

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The usual objective of physical evidence comparisons is to determine whether or not items or materials are related as to source or origin. Positive relationships can be established if the items exhibit unique physical characteristics, such as toolmarks or fracture surfaces. When unique identifying characteristics are lacking, the evaluations are most frequently based on a comparison of class characteristics, such as composition. Associations based on class characteristics are normally not sufficiently discriminating to establish item relationship with certainty.

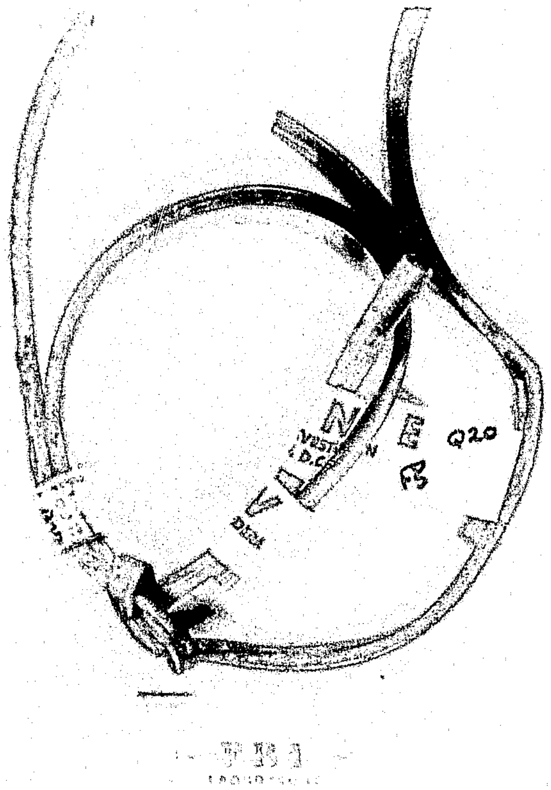

Figure 1. Tubular plastic ligature removed from neck of victim in double homicide.

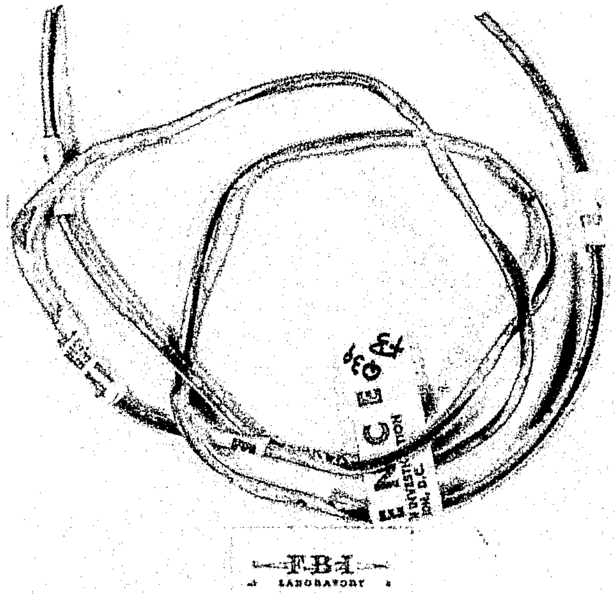

Figure 2. Split tubular plastic recovered from residence of suspect.

Another approach which can reveal uniqueness indicative of common origin is to base the comparisons on fabrication characteristics. Fabrication characteristics are those characteristics acquired by an item during the design and manufacturing process. Fabrication characteristics associated with plastic and plastic products consist principally of 1) design attributes, such as dimensions, shapes, locations of parting lines and gates and/or types of plastic used; 2) surface features attributable to processing parameters (for example, temperature, pressure and/or relative flow velocity), such as surface texture, dullness, sink marks, orange peel and/or warpage; and 3) macroscopic and microscopic surface features imparted to the plastic from forced contact with the forming tool surfaces, such as extrusion marks, mandrel striations plow marks, mold defects, parting lines, ejector pin marks and/or weld or knit lines. Fabrication characteristics in aggregate may be considered the "fingerprint" of the specific manufacturing equipment and process. Additionally, the fingerprint of the fabrication process is continually changing during the process as a result of tool surface wear, operating condition variations, part replacements, material build-up on the tool surface, refinishing of the tool, etc. If the fabrication characteristics of two items exhibit sufficient points of similarity, then it is reasonable to conclude that the items were made by the same manufacturing equipment within the same limited time frame. Thus, the limited life of the manufacturing fingerprint greatly enhances the significance of fabrication comparisons of physical evidence. In fabrication comparisons, physical measurements are made with suitable toolmaker's measuring devices and surface characteristics are directly evaluated with a comparison microscope. Faint surface features are often difficult to view and experimentation may be required to determine the appropriate type and orientation of illumination for optimum viewing. Natural lighting and fluorescent lighting are generally preferred. To facilitate examinations of curved items such as wire insulation or small diameter tubing, the plastic can be cut and secured in a flattened condition between glass slides.

The plastic tubular material depicted in Figures 1 and 2 was recovered in a double homicide investigation and was submitted to the FBI Laboratory for comparison purposes. The tubular plastic ligature depicted in Figure 1 was removed from the neck of one victim; similar tubular plastic ligature recovered from the residence of the suspect is depicted in Figure 2. Because prior toolmark examinations of the limited toolmarks on the cut surfaces and instrumental and elemental analyses, including neutron activation, revealed characteristics insufficient for positive association, the items were referred for fabrication characteristic comparisons. Fabrication and post-fabrication characteristics which were compared are shown in Table 1. Figures 3 through 6 are comparison micrographs of various surface features observed during the examinations. Based on the fabrication characteristic comparisons, the ligature and plastic material recovered from the suspect were identified as having been fabricated by the same specific manufacturing equipment within the same time frame. Because the examinations also revealed similar characteristics of post-fabrication abrasion damage and alteration, it was further concluded that the items also had a common post-fabrication source and/or history.

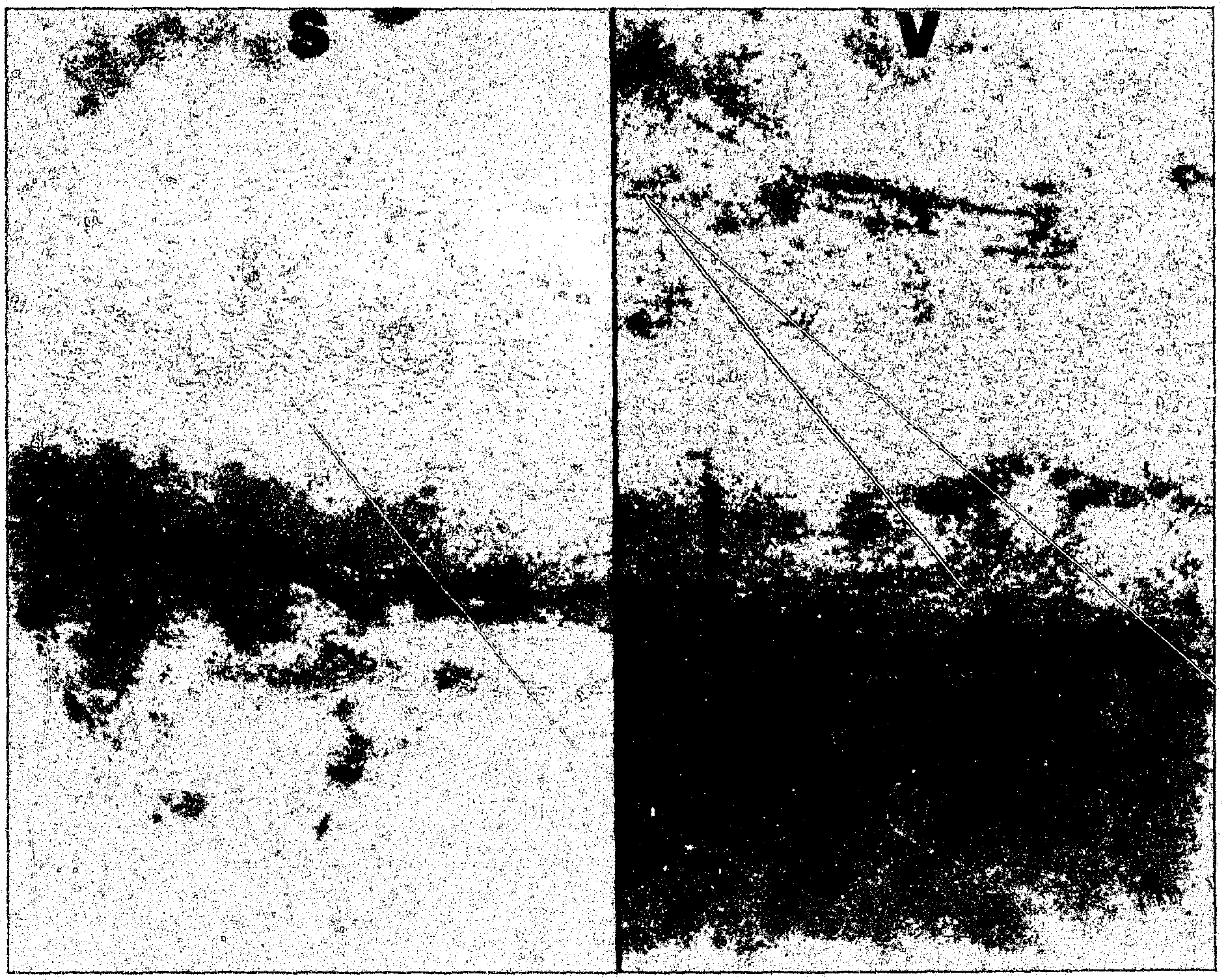

Figure 3. Comparison micrograph of the exterior surfaces of the ligature (V) and of the plastic from the suspect (S) showing a prominent extrusion die mark (a). Note similarity of surface textures as well as the nature and orientation of post-fabrication abrasion damage (b). Specimen samples were flattened and placed between glass slides for viewing. Magnification: 20X.

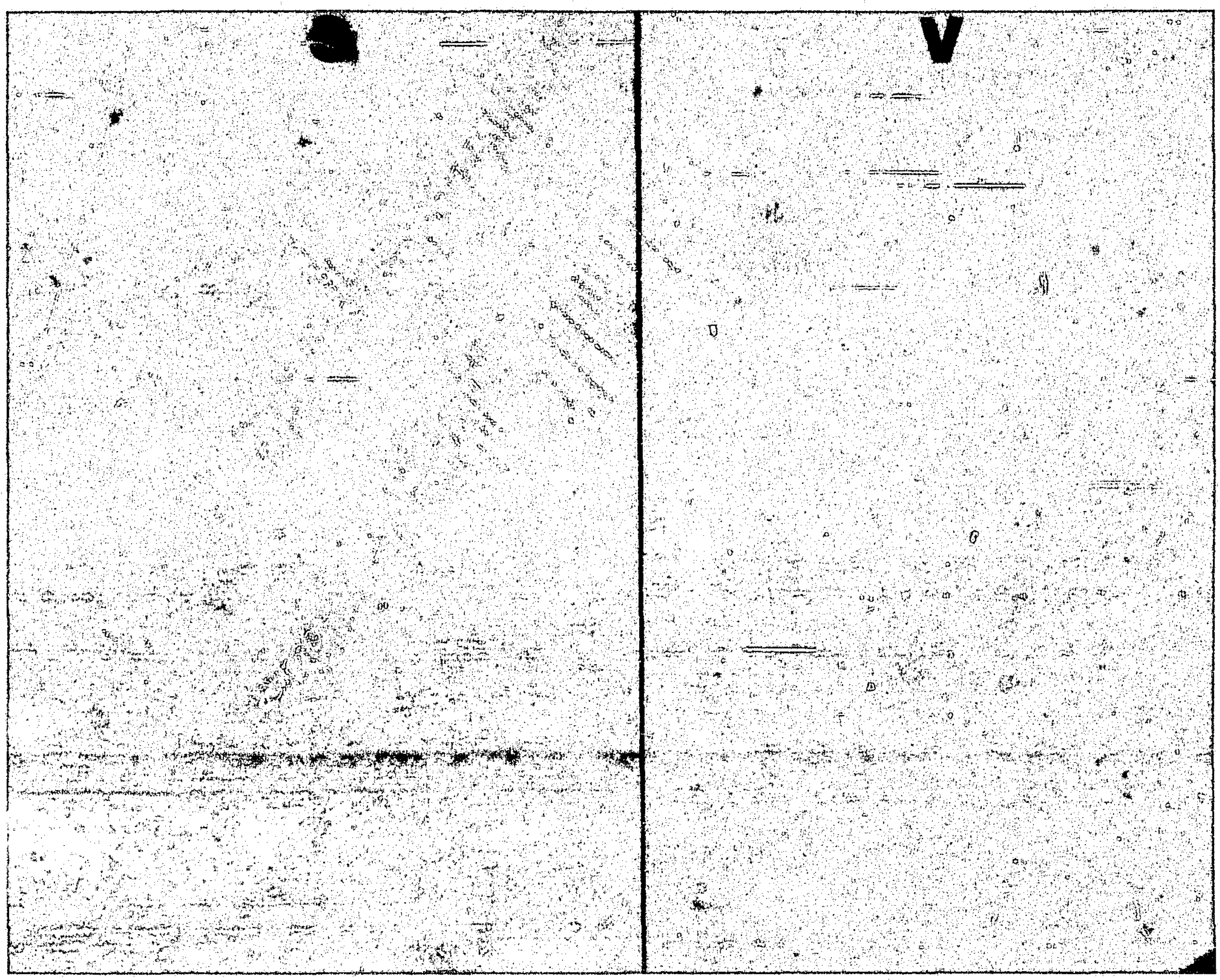

Figure 4. Comparison micrograph of mandrel striations present on the interior surfaces. Magnification: 20X.

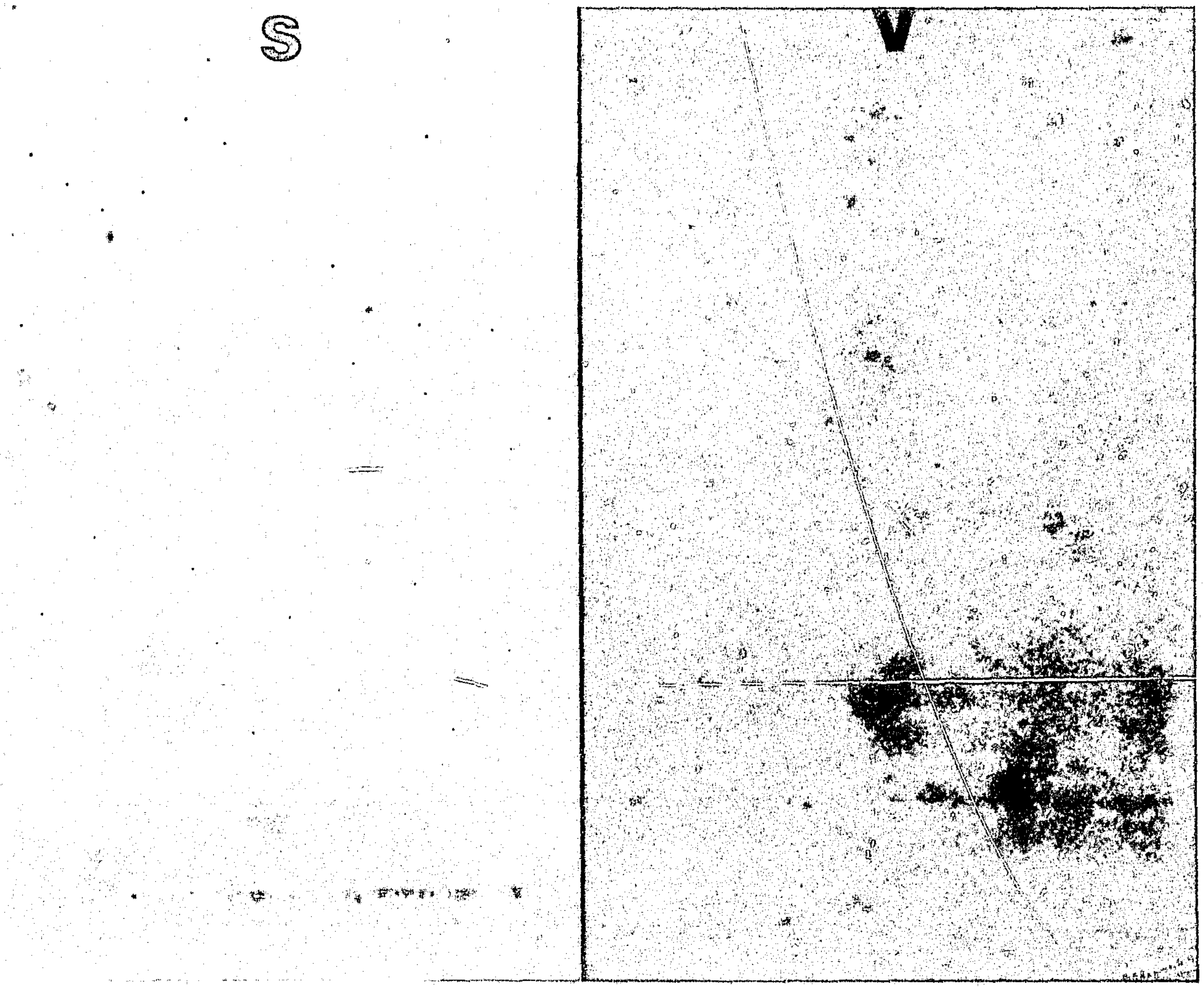

Figure 5. Same area as in Figure 4 but with different lighting. Note change in visibility of comparable striations. Magnification: 20X.

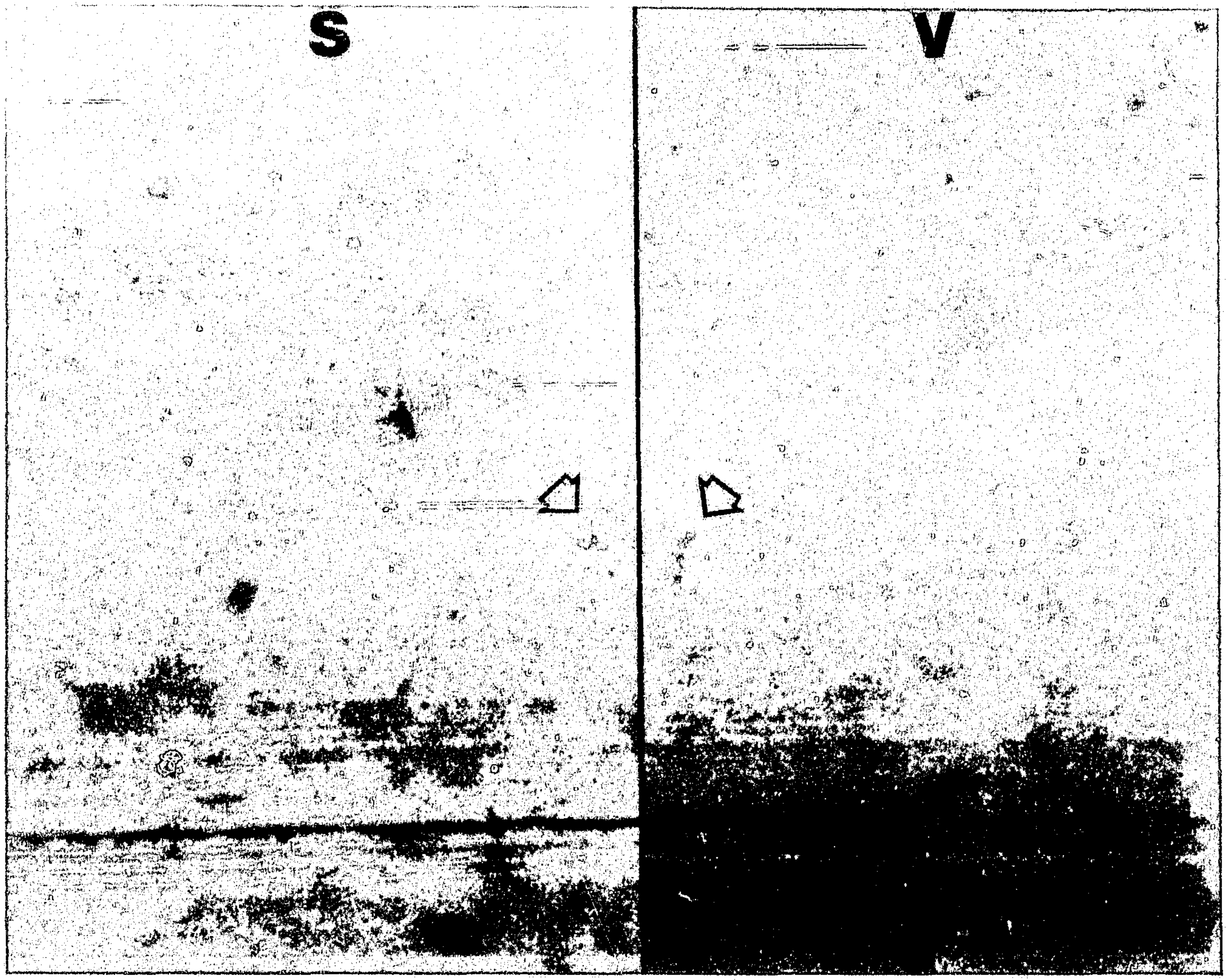

Figure 6. Comparison micrograph of the inside surfaces showing mandrel striations; wall punctures (noted) were made from the exterior side at the extrusion die marks to show the relative position of the extrusion die mark (exterior) of Figure 3 to the mandrel striations. Magnification: 20X.

Table 1. FABRICATION AND POST-FABRICATION CHARACTERISTICS COMPARED

| Characteristics Compared | Plastic Ligature From Victim | Plastic From Suspect |
|---|---|---|
| Item configuration | Length of tubular plastic: oval cross-section | Split length of tubular plastic; cross-section incomplete, but consistent with oval shape |
| Color | Yellow | Yellow |
| Fabrication method | Extrusion | Extrusion |
| Inside diameter | 5 mm x 2 mm | -- |
| Wall thickness | 0.58 mm | 0.58 mm |
| Extrusion die marks (external surface) | See Figure 3 | |
| Mandrel striation marks (internal surface) | See Figures 4 and 5 | |
| Position of extrusion die marks relative to mandrel striations | See Figure 6 | |
| Surface textures (internal and external) | See Figures 3 and 4 | |
| Post-fabrication characteristics. (abrasion marks, surface residue and alteration damage) | See Figure 3 | |

# PHYSICAL AND MICROSCOPIC IDENTIFICATION OF MOTOR VEHICLE COMPONENTS FABRICATED FROM POLYMERS

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The inherent physical properties of polymers lend themselves to be invaluable to the forensic comparative tool mark examiner. Because of the properties of polymers, this type of evidence may be submitted to the crime laboratory and is almost always suitable for comparison.

When hoses fabricated from polymers are cut with a knife type tool, the cut ends usually reproduce suitable striae for comparison. If a tool is recovered from a suspect, the tool mark examiner can tie the suspect to the stolen vehicle or its component parts. But this is normally not the case, evidence technicians usually are called upon to process the remains of a "chop shop" where there is an abundance of physical evidence left behind, the majority of which is fabricated from polymers. The valuable sheet metal having been stripped away when the vehicles were disassembled.

Because of the universal uses of polymers in the construction of a motor vehicle there are many parts that may be examined for class characteristics which may lead to a possible positive identification. This is very evident when examining air conditioning and heater hoses which have thicker walls and are more rigid than radiator hoses.

Radiator hoses have a very distinctive cut pattern, which is caused by the larger diameter of the hose and the thinner more flexible wall. But, before the physical match is made, further microscopic examination should be done. One should check for the presence of very valuable class characteristics.

1. Check that the items to be compared are of the same size, shape and color. Check for the presence of reinforcement material - are they of the same type and origin?
2. Check for the presence of similar residue on the inside wall surfaces.
3. Check for the presence of mold and/or extrusion marks on the inside wall surface.
4. Check the outside surface of the hose - the cut may pass through some manufacturer code marks, these may be in the form of printing or intentional extrusion marks.

Customarily the type of evidence submitted from a "hit-and-run" scene is also of a polymer nature. Vehicle grill work, moldings and other component vehicle parts are often recovered from the scene because they have a tendency to fracture rather than shatter when subjected to abnormal stresses. When this evidence is examined by the tool mark examiner, valuable information may be revealed to the investigator charged with the case. The fracturing usually allows the tool mark examiner to reconstruct the evidence if a suspect vehicle is recovered.

In conclusion, I have found that the "rubber" type materials are much easier to identify, because they reveal not only the marks and pattern of the cut - but may reveal mold and/or extrusion marks made in the manufacturing of the hoses and tubings as well which will aid in the identification.

# SECTION III

# SHORT ABSTRACTS

# MICRO-FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR THE FORENSIC LABORATORY

*D. C. Peters*[1], *J. C. Shearer*[2] *and T. A. Kubic*[3]

[1]Analect Instruments, Utica, New York,
[2]Rochester, New York and
[3]Greenlawn, New York.

Samples submitted to a forensic laboratory are not only quite limited in size, but must be preserved in large part as evidence. While a multidisciplinary approach is essential in the examination of these types of samples, infrared (IR) data can be crucial to achieving positive identifications. The ability to perform IR analysis on minute amounts of material (down to the nanogram level and below, Courneyer *et al.* 1977; Shearer *et al.* 1983) opens up new possibilities in forensic applications of Fourier transform infrared spectrophotometry (FTIR).

Research was initiated to apply a new FTIR microspectrophotometer to typical forensic cases, including paints, fibers and unfortunate combinations thereof. Reliability of the technique and quality of spectral results achieved with the AQS-20M were contrasted with other IR sampling techniques, such as high pressure diamond cells.

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*Shearer, J. C., Peters, D. C. and Travers Newton, G. H. (1983).* FTIR in the service of art conservation, Anal. Chem. 55:874A-880A.

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# FOURIER TRANSFORM INFRARED SPECTROSCOPY: A MODERATE COST POWERFUL TOOL FOR SOLVING OLD PROBLEMS

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Nassau County Police
Mineola, New York

*J. C. Shearer and D. C. Peters*

Analect Instruments
Utica, New York

Criminalists and forensic chemists are called upon to analyze a wide variety of different polymeric materials. Often, although the sample is microscopic in size, it is requested not only that the exhibit be identified but also that it be compared to other similar materials in an effort to establish common origin.

Historically, infrared spectroscopy coupled with microsampling techniques has been employed in attempting to accomplish the aforementioned goals.

The increased sensitivity, accuracy and speed of analysis of the Fourier transform infrared spectrometer (FTIR), in addition to the advantages of simpler sample preparation and less sample degradation, make this method highly suited for forensic applications. Advances in optical engineering and the decreased cost of computer capability have made FTIR instrumentation available to crime laboratories.

There are a number of polymeric materials readily analyzed by FTIR that are of forensic interest. These include the application of various sampling techniques such as ATR, microsampling, diffuse reflectance, infrared microspectrophotometry, and gas chromatography/Fourier transform infrared spectroscopy to inks, paints and adhesives, for example. In addition, there is the advantage of FTIR when employed with computer spectral sorting and matching of forensic samples.

## CHARACTERIZATION OF PYROLYSIS PRODUCTS FROM POLYMERS FREQUENTLY ENCOUNTERED IN DEBRIS FROM SUSPECTED ARSON CASES

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Better recovery techniques and more sophisticated analytical techniques have materially improved the analyst's ability to detect possible accelerants in debris from suspected arson cases. These same advantages have resulted in accentuation of the problem of contamination due to the presence of pyrolysis products from materials, many of them organic polymers, frequently present in a fire. The purpose of this work is to attempt to characterize the pyrolysis products obtained in order to facilitate interpretation of chromatographic results.

Samples of carpet material, as well as carpet backing and other polymeric materials, have been flame pyrolyzed without the use of accelerants and then subjected to the adsorption-elution recovery technique routinely used for arson debris. The capillary gas chromatograms of these extracts have been obtained using the program used for arson debris extracts and characterized using a quality control standard which contains n-$C_8$ through n-$C_{23}$ hydrocarbons in addition to nine other "marker" compounds.

The results to date, while not sufficient for statistical treatment, are encouraging in that they show a degree of reproducibility and consistency which will permit recognition and characterization of the pyrolysis product patterns and assist in differentiation from accelerant patterns. The techniques developed in this work also make "control" samples taken from fire scenes more meaningful. The patterns obtained from pyrolysis of control samples can be compared with those obtained from debris.

As more data is obtained the intent is to attempt to apply computerized pattern recognition techniques to this information. Work on this segment of the project has not been initiated.

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## ANALYSIS OF POYLMERS, PLASTICS, PAINTS AND COATINGS BY GEL PERMEATION CHROMATOGRAPHY

*K. E. Alden, Jr. and W. A. Dark*
Waters Associates
Milford, Massachusetts

Gel permeation chromatography (GPC) is an ideal analytical technique for the analysis and characterization of plastics, paints, polymers, coatings and adhesives. Most uncured polymers can be analyzed by this automated, instrumental technique with a minimum of operator involvement. Gel permeation chromatography is an established analytical procedure which has found wide applications in such diverse commercial products as chewing gum, coatings, paints, adhesives, plastic components, smokeless gun powders, and many rubber and petroleum products. A number of commercial products are fabricated exclusively with or contain polymers that give the product its desired physical properties. When analyzed, each product reveals characteristic information particular to that product or process used for fabrication.

The conditions for the analysis were a flow rate of 1.0 ml/min, 0.1 percent (w/v) concentration, columns - $10^6$ A, $10^5$ A, $10^3$ A, 500A, 100A ULTRASTYRAGEL® at 7 $\mu$ particle diameter, trichlorobenzene solvent at 140° C, tetrahydrofuran solvent at 45° C with a calibration curve developed based upon narrowly dispersed polystyrene standards. This set of conditions allowed the characterization of the various polymers from 10 million molecular weight (MW) to about 100 MW over a log MW range of distribution. These conditions were suitable for very large molecules, as well as small molecules that made up formulations such as paints and various polymer mixtures.

# FACILITATION OF THE COMPARISON OF TOOLMARKS AND SURFACE CHARACTERISTICS OF POLYMERS UTILIZING SURFACE REFLECTANCE ENHANCEMENT BY VACUUM EVAPORATION OF METAL

*R. W. Sibert and D. C. Ward*

FBI Laboratory
Washington, D.C.

The comparison of toolmarks and surface characteristics on polymers generally entails the utilization of standard toolmark identification techniques and equipment (simultaneous side-by-side imaging with the optical comparison microscope to determine the degree of correspondence). The ease of such comparisons is optimized when opaque materials of the same color and equal reflectance are being examined.

The transparent or translucent nature of many polymers occasions certain imaging problems which arise from inadequate surface definition due to the internal scattering of incident light. Such a condition is perceived through the microscope as a haze which masks the surface characteristics. This problem can be overcome by the application of an opaque coating. A variety of coating techniques have been utilized and evaluated. It has been found that polymers can be very effectively coated with a thin film deposition of metal by vacuum evaporation. This technique, which has been routinely used as a standard sample preparation technique for electron microscopy, is equally useful for optical comparison microscopy.

The object to be coated is placed in the chamber of a vacuum evaporator and a vacuum is drawn. In the reduced chamber pressure, a small piece of metal is melted by resistance heating. Evaporation of the metal results in the deposition of a thin, continuous metal film on the object. Iron evaporation is preferred because its reflectance is compatible with test materials used for preparing known toolmarks for comparison.

This method has been successfully used on polymers and many other transparent and translucent materials.

# SECTION IV

# PANEL DISCUSSION

# PANEL DISCUSSION
# STANDARDIZATION PROCEDURES

MODERATOR: *Eugene J. Levy*, Chemical Data Systems, Inc.

PANEL MEMBERS: *Tim Carlson*, FBI Laboratory
*Frank H. Cassidy*, California Department of Justice,
*Pat A. Harrell*, North Carolina Bureau of Criminal Investigation
*Jack Norwicki*, Illinois Department of Law Enforcement
*Brian B. Wheals*, Metropolitan Police Forensic Science Laboratory

The purpose of this panel was to em.phasize the need for standardization procedures for pyrolysis gas chromatography (Py-GC) and to promote a discussion of universally accepted procedures to follow in order to have good reproducibility among laboratories.

At its present state, Py-GC lacks outstanding reproducibility between laboratories because of small differences in chromatographic and pyrolyzer operating parameters. This lack of outstanding reproducibility was substantiated by a study conducted by the American Society of Testing and Materials (ASTM), Committee E-19. For a detailed account of this study consult the *Journal of Chromatographic Science*, Vol. 15, (July, 1977) p. 267. The testing project produced varying results on sample Py-GC runs among 25 participating laboratories that were given similar samples and column packing and specified conditions for the run.

In the first of four Py-GC correlation trials, the laboratories were given two samples, a polybutadiene and an isoprenestyrene copolymer, and a 10 percent SE-30 chromosorb W isothermal column to use for the analysis and were asked to run the sample at a temperature of 100≦ C. The pyrolysis temperature was 700≦ C for 10 seconds. Of the 22 laboratories that participated in the first trial, 12 produced "reasonably good" reproducibility, 8 "fairly good" reproducibility and 2 "not so great" reproducibility. The relative area percent was so poor in this first trial that a second trial based on the oven burn from the first trial was conducted.

This second trial was initiated in hopes of improving the results by changing some of the specified conditions and the type of column. A change in column type from the SE-30 to a 5 percent polyethylene glycol Carbowax 1500 on 80-100 mesh chromosorb G was made because the resolution from the first trial was considered poor. A new temperature of 600≦ C, 10 seconds for the pyrolyzer was recommended. Even though flow conditions, temperature and column type were set, the relative area percent amone the laboratories was still not very good. The relative retention times were reasonably good.

A third trial was conducted and major components of the styrenated alkyd paint resin were to be run. Realizing the importance of tuning the pyrolyzer, a liquid with two components, styrene and vinyl toluene, was sent to the participating laboratories to tune the GC. A suggestion was made to tune the GC so that the retention times were 7.5 minutes for styrene and 13 minutes for vinyl toluene. During this trial a 10 percent SE-30 column on 80-100 mesh chromosorb W AW and an isothermal temperature of 100≦ C were used. The results of this trial faired better than the previous two. The relative area percents were at least measurable and standard deviations ,varied from 10 percent down to 2 to 3 percent depending on the peak. Peak-height data were also reported.

Since it became evident that some laboratories did not clean their pyrolysis equipment after each run it was recommended that a clean column be used in the fourth trial that was conducted. An unclean column obviously causes cross contaminations between the current and previous runs. A recommendation to tune the pyrolyzer for accurate flow for temperature and accurate retention times with the temperature sensitive polymer provided.

Based upon the ASTM study, the following variables were suggested for good reproducibility among laboratories:

1. The sample should be within a 10 to 50 μg range, preferably 15 to 20 μg.
2. The sample should be placed in the center of the ribbon or coil. Do not spread it out.
3. The heating pulse should be as close to a square wave as possible. The rate of heating is important because if, for example, you heat at 650 slowly, the sample will decompose before this temperature is reached, therefore a fast rise time is necessary.
4. Flow rates shoud be at 20 milliliters per minute.

5. The pyrolyzer should be tuned. In this particular study, a 100 percent improvement in reproducibility resulted when the pyrolyzer was tuned. Tune the pyrolyzer for accurate flow temperature and accurate retention times with a temperature sensitive polymer such as Kraton™ (an isoprene-styrene block copolymer).

6. Clean the pyrolyzer after each run. A clean column will avoid cross contaminations.

The ability to standardize is within the realm of possiblity because of the modern equipment available today and the refined techniques we are learning through experience with Py-GC. Reproducibility among laboratories even if they are using different pyrolysis systems is also within the realm of possibility. But before any standardization procedures are established, a universal consensus on column type and viable procedures is necessary. The selection of a column, a data handling system and perhaps even an automatic data reduction system that are both viable and economically feasible for the smaller laboratories need to be examined.

Many of the state and local crime laboratories do not have the advantages of state-of-the-art equipment, access to large libraries, or continuous runs, as do independent research laboratories or'federal crime laboratories. The FBI, for example, has devised a mass spectrometer system that can call up two different stored data and display them simultaneously on the screen for comparison. This operation has been in existence for only 6 months. So far there have been no problems with maintaining reproducibility. The FBI also has access to the National Automotive Paint File which has approximately 25,000 paint standards in its collection. The fact that the FBI runs a number of paints on a daily basis, their examiners can tell when the packed column is not operating properly.

On the panel were representatives from states having more than one laboratory in their criminal justice system. They discussed how their laboratories run samples using Py-GC and the problems they encounter.

The 13 laboratories within the California system do not follow any set procedures for Py-GC. Generally, at least two samples are run to verify that the pyrolyzer is working satisfactorily, then the unknown paint sample is compared with the known paint sample. The paint sample is generally not weighed and the size is estimated. California examiners do not base their opinions solely on the pyrogram. Other tests are administered to obtain further information about the sample. If problems in running a sample arise or if a particular sample run is requested which another laboratory has had much experience in, examiners from the two laboratories might confer with one another.

North Carolina, on the other hand, has one main laboratory that analyzes all of the trace evidence collected within the state. Due to a heavy workload, the examiners do not have the luxury to closely examine each pyrogram as it is run. An emphasis is placed on micro-chemical and microscopic examination of the samples rather than pyrolysis.

Over the years, the first step in paint analysis has switched from Py-GC to micro-chemical and microscopic examination of paint samples. This approach provides valuable information before the actual Py-GC run, such as the number of layers, the thickness and the type of paint, for example, lacquer or enamel. This enables the examiner to eliminate a number of possible matches. Pyrolysis gas chromatography can be an effective and efficient comparative tool, if one can obtain as much information as possible about the sample before it is run and if one runs the sample under optimal conditions. These optimal conditions will be the standardization procedures that are established in the near future.

Another hopeful area to speculate on is a data bank, a library, that one can consult, much as one would consult the NIH mass spectrometry file or any of the other data banks that are in existence today. Creation of a data bank is a long-term goal of the ASTM. The ASTM, realizing that the difference between foreign paints and American paints is becoming less and less discriminatory, plans to include foreign paints in its data bank. This is indeed a big task for two reasons:

1. Many foreign paint manufacturers do not retain paint standards as consistently as the American paint manufacturers do. Fillers are sometimes changed within foreign paints if say, titanium dioxide versus calcium carbonate became more expedient to use.

2. One is not just dealing with a foreign company but a foreign government as well.

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# AUTHOR INDEX

# SUBJECT INDEX