CHAPTER 9 HISTORY AND DEVELOPMENT OF EARLY PLASTICS

Introduction

The purpose of this chapter is to give an outline of the background information regarding the development of plastics including the history, structure, production method, additives, uses and tradenames. The characterization of these materials using diffuse reflectance FT-IR and a short section on the sources of degradation of the materials will be discussed in subsequent chapters.

Polymerization

The term plastic is used to describe a property of certain materials able to be moulded or deformed. Plastics has come to be known as a collective noun for semi-synthetic and synthetic materials which are capable of being moulded. However, it should be remembered that there are natural polymers that have been used to make objects by moulding under heat and pressure since antiquity. Thus, conservators and other museum staff should be aware of both natural and synthetic polymers and how to characterize the material. The diffuse reflectance FT-IR technique was thought to be very promising for the characterization of both natural and synthetic polymers and this chapter is concerned with the application of the technique to both objects and works of art made from polymers.

Polymers are long chains of repeating structural units called monomers. The chains are produced by chemical reactions which cause the monomers to join and a catalyst is frequently necessary to facilitate the reaction. Monomers must have at least two functional groups and bifunctional monomers form linear polymers. Polyfunctional monomers give branched chain and three-dimensional network systems. There are two types of polymerization reactions, condensation and addition. In condensation reactions, the monomer molecules are broken up and certain parts are joined together to form the polymer. The process produces waste products. An example is nylon which is a family of polymers which are of the polyamide type and water is produced as a by-product. In addition reactions, chemical reactions of molecules with multiple bonds are utilized. The presence of double or triple bonds or regions of unsaturation increases the reactivity of the molecule because the Pi bond is susceptible to attack (Cotterill, 1985). There are two types of catalyst for this reaction which utilize either an ionic mechanism or a free-radical mechanism. The ionic mechanism uses certain metallic or non-metallic halides

($AlCl_3$, $SnCl_4$ or BF_3) or sulphuric acid. The free-radical mechanism utilizes chain reactions and the catalyst must create free-radicals. These catalysts include organic and inorganic peroxides and the salts of peracids (benzoyl peroxide, acetyl peroxide, hydrogen peroxide and potassium perborate (Finar, 1963). The resulting polymer is made up of repeating units of the monomer and there are no by-products produced in the reaction. The presence of an electronegative group also increases the reactivity of the monomer. For example, vinyl chloride is more reactive than ethylene. Sulphur is a divalent molecule and it is used to replace hydrogen and forms sulphide bonds of the -C-S-C- and disulphide bonds of the -C-S-S-C- type. The sulphur link is very common as a cross-link in biological polymers. Cross-links or bonds that form between molecular chains cause the polymer to become rigid. Disulphide bonds are strong covalent links, but weaker hydrogen bonds which form in nylon polymers are sufficiently strong if there are large numbers of them (Cotterill, 1985).

Natural plastics

There are numerous examples of natural plastics used in antiquity and the chemistry of these materials have been discussed in earlier chapters. Materials such as bitumen, amber, shellac and albumen may be moulded into objects (Brydson, 1975). Some natural plastics are discussed in Chapter 13.

Gutta percha

Several natural polymeric materials were brought to Europe as a result of exploration of the new world and southeast Asia. John Tradescant (1608 - 1662) was an English traveller and gardener who brought gutta percha back from his travels (Brydson, 1975). The material is obtained from the bark of the palaquium tree which is grown in Malaysia and it can be manipulated after dipping in hot water. The Gutta Percha Company was formed in London in 1845 and it produced extruded mouldings which were to be imitations of those made of wood for panels and friezes. It was utilized during the second half of the nineteenth century for casting medals, decorative ornaments, buttons, clock cases and jugs. It is resistant to acids and was used for bottles for hydrofluoric acid. It was used as a substitute for papier maché, leather and wood and became a popular material for the production of golf balls (Hillman, 1986). Gutta percha was also widely used as underwater cable insulation material and was used for this purpose until 1940 (Brydson, 1975).

Natural rubber

Natural rubber was observed by sailors on Columbus' expedition to Central America where they found the natives playing with lumps of the material. The first written reference appeared around 1535. La Condamine was sent on a misson by the French government to study the shape of the earth in 1731. He obtained rubber coated cloth which was produced by the native tribes of the Amazon basin and used to make waterproof shoes and flexible bottles. Natural rubber is collected by coagulation from a latex and was at first only a novelty since it could not be shaped by moulding or extrusion. However in 1820 in England, Thomas Hancock found that the highly elastic material could be made plastic and capable of flow through shearing or mastication of the rubber. Nineteen years later in the USA, Charles Goodyear discovered that the addition of sulphur to heated rubber resulted in a product which was elastic over a wider range of temperature than untreated rubber and was more resistant to the action of solvents. Hancock also found somewhat later that masticated rubber mixed with molten sulphur produced an elastic material. Although Goodyear made the initial discovery and the work of Hancock was to a certain extent based on that of Goodyear, Hancock took out a British patent in 1843 and Goodyear did not patent his discovery in America until 1844. The process was termed vulcanization by a friend of Hancock, William Brockendon (Brydson, 1975).

The vulcanization process only required the addition of a few percent sulphur. Both Hancock and Goodyear observed that the addition of sulphur in a ratio of one part sulphur to two parts rubber resulted in a very hard product. Nelson Goodyear patented the method for making hard rubber, as the product was known, in 1851 (Brydson, 1975). It was also known as vulcanite or ebonite in England. The hard rubber or vulcanite was used to produce buttons, jewelry, combs, cutlery handles, buckets, smoking pipe mouthpieces, telephone receivers, dentures and fountain pens (Hillman, 1986). Charles Mackintosh began to produce ebonite in 1851 and several plants were in operation by 1860. This discovery is considered to be an important one in the history of rubber, but it is also very important in the history of plastics. It is the first chemical modification of a natural material to produce a thermosetting plastic (Brydson, 1975).

Twentieth century

The term plastics came into general use during the late 1920's when these new substances were being invented and utilized to make objects for a large variety of industrial, commercial and domestic uses. For example, celluloid or cellulose nitrate plastic was first exploited as a substitute for natural materials like ivory, hard rubber, amber and tortoise-shell and used to make small domestic objects which were considered to be novelties. However, plastics have come to be considered as important materials with properties which are often better than natural materials for many applications (Hillman, 1986). After the Second World War, there were large excess supplies of synthetic resins. They were used to make versions of many household objects, most of which were inexpensive and of poor quality. Thus, the term plastic has gained the reputation of being cheap, artificial and of poor quality. They are becoming increasingly necessary as natural sources are exhausted. Conveniences which have become part of recent culture such as automobiles, telephones and television would not be possible without the use of plastics (Brydson, 1975; Hillman, 1986). Plastic objects are already appearing in social history collections and in works of art and will become more prevalent in the future, especially in history of technology collections. Plastic materials are generally refered to as a group, but it important to realize that different types of plastic have unique properties and to be able to distinguish between various kinds of plastics.

Cellulose nitrate

History

Cellulose nitrate was first prepared by Braconnet in 1833 by reacting sawdust and linen with nitric acid. Shortly thereafter, Pelouze also produced cellulose nitrate by treating paper with nitric acid (Yarsley et al., 1964). In 1845, Schonbein discovered that the reaction of cotton with sulphuric and nitric acids resulted in an explosive material, cellulose trinitrate. He immediately realized the political implications of the explosive material (Kaufman, 1963). The discovery stimulated governmental interest and France, Russia, Germany and Austria set up commissions to develop the military applications of this branch of explosives chemistry (Yarsley et al., 1964). When it was found that the cellulose nitrate material was soluble in ether alcohol mixtures, cellulose nitrate could be made into films and coatings and this material was known as collodion (Yarsley et al., 1964). In the mid-nineteenth century, F. Scott Archer began to use the collodion for photographic work. The cellulose nitrate was mixed with potassium iodide and spread on a glass plate. The plate was then coated with silver nitrate then exposed while wet. The film was removed during processing and replaced on the glass after the final washing (DeMare, 1957).

Great advances in the manufacture of cellulose nitrate were made by Alexander Parkes in England. In 1852, he presented the first cellulose nitrate lacquer, pyroxylin, at the London Exposition. (Yarsley et al., 1964). The process was patented in 1856 (BP 1123/1856) (Kaufman, 1963). A mouldable, thermoplastic material produced from cellulose nitrate was shown at the universal exhibition in London (1862) which was awarded a bronze medal. In 1865, a formulation for cellulose nitrate using camphor as a plasticizer was patented by Parkes (BP 1313/1865) which was thought to have been the process utilized for the objects presented at the 1862 exhibition. He called the plastic Parkesine. This was a major breakthrough in the development of the plastic (Kaufman, 1963).

In 1866, the Parkesine Company was founded by Parkes. It was not successful and lasted only two years. The production method adopted by the company did not contain vital steps which are now known to be important in producing a stable product. Parkes was concerned with lowering the cost of his product and used cheap materials including poor quality cellulose. Also, he did not find a good solvent system for the material (Kaufman, 1963).

In the USA, the Hyatt brothers became involved with cellulose nitrate as a result of a contest to find a replacement material for ivory billiard balls. The Hyatts began to work with collodion mixtures and took out three patents on cellulose nitrate in 1869, USP88,634/1869 (for production of billiard balls), USP 89,582/1869 and USP 91,341/1869. In 1870, the Hyatts made an important discovery. They found that the use of camphor in large quantities was an effective solvent for cellulose nitrate (USP 105,338/1870). The patent suggests the use of two parts cellulose nitrate to one part camphor. The brothers used the material to produce dental plates and began the Albany Dental Plate Company. In 1872, the company name was changed to the Celluloid Manufacturing Company (Kaufman, 1963).

Cellulose nitrate production was resumed in England by Daniel Spill who had been the works manager of the ill-fated Parkesine Company. In 1869, he established the Xylonite Company on the premises of the Parkesine Company, however, this company was liquidized in 1874. Spill was perseverent and found backing for a new company which he named the Daniel Spill Company. In 1876, the British Xylonite Company was created in conjunction with L. P. Merriam with backing from three other businessmen. The new company was not immediately successful. In 1877, Spill initiated a legal suit for patent infringement against the Hyatt brothers claiming that the camphor/alcohol solvent and the bleaching processes used by them were covered by Spill's patents USP 97,454/1869 and USP 101,175/1870. After a three year legal battle, the judge decided in favor of Spill. He set up a company in the USA called the American Zylonite Company. The Hyatt brothers changed the formulation slightly and requested a new hearing. The case was reopened and in 1884, the judge reversed the earlier decision. He stated that no limitations could be put on the cellulose nitrate/camphor /alcohol formula and this allowed for competition and growth in the industry. Meanwhile, the British Xylonite Company finally achieved financial success with the manufacture of cellulose nitrate collars and cuffs in 1885 (Kaufman, 1963).

Chemical structure and nomenclature

Cellulose is a high molecular weight polymer found in nature which is made up of many anhydro-beta-glucose (Figure 9.1a) units bonded together in an extended open-chain structure. The number of glucose units in the structure (degree of polymerization) is dependent on the degradation that occurs during the purification of the cotton linters. The cellulose chains contain from 1,000 to 3,000 glucose molecules after the chemical treatment of the cotton. The six-atom ring glucose molecules are fairly rigid which are bonded by primary valence bonds or glucoside bonds through oxygen bridges in the 1:4 positions (ether linkages)(Figure 9.1b)(Yarsley et al., 1964).

Cellulose has very little internal flexibility. This is due to the limited movement at the oxygen bridges resulting from stearic hinderence from the groups in the vicinity of the bond and the rigidity of the glucose rings. The cellulose chains are aligned approximately parallel to each other in the direction of the fibre axis. The chains are held together by hydrogen bonds which form between the hydroxyl groups in the glucose molecules. The bonds which hold the chains together are strong enough to resist mechanical deformation of the fibres and thus no permanent alteration results from the temperature and pressure used for moulding plastics. Thus, cellulose cannot be processed as other plastics. Also, cellulose cannot be plasticized because it is soluble only in very strongly acidic or basic solvents. Plasticizers act by separating the chains and may be considered as high boiling point solvents which remain incorporated in the structure of the plastic (Yarsley et al., 1964).

The treatment of the cellulose with nitric and sulphuric acids results in a change in the chemical nature of the material which allows it to be manipulated as a plastic. The reaction is often refered to as a nitration, but this term is misleading. The chemical process is an esterification. Although the term nitrocellulose is used, the product is actually an ester and it will be refered to as cellulose nitrate. The plasticized product will be refered to as cellulose nitrate plastic or celluloid (Yarsley et al., 1964).

The anhydroglucose unit in cellulose has three hydroxyl groups which may be substituted. Commercially produced cellulose nitrate (Figure 9.2) has a nitrogen content of between 10 - 14 % and the degree of substitution is determined by the intended use of the material (Table 9.1). Cellulose nitrate for plastics production is close to the value for a dinitrate with a nitrogen content of 10.7 to 11.1 %. A slightly higher degree of substitution desirable for the production of lacquers to obtain a decrease in water sensitivity. Material for the explosive cordite has a degree of substitution close to the theoretical value for trinitrate (Yarsley et al., 1964).

The substitution of the hydroxyl groups by the nitrate groups reduces the hydrogen bonding which results in compatibility of cellulose nitrate with a large number of plasticizers and the solubility of the material in common solvents. Camphor is the most widely used plasticizer and the structure of camphor is given in Figure 9.3 (Bean, 1972). X-ray diffraction and optical birefringence results (Yarsley et al., 1964) indicate that the camphor and the cellulose nitrate form a fairly stable complex with the camphor bonding to the cellulose nitrate molecule. Camphor and the substituted glucose ring are thought to react in equal molecular proportions to form a complex structure. It is thought that a hydrogen bond is created between the carbonyl group in the camphor molecule and the hydroxyl group which is not nitrated on the glucose molecule. As an excess of cellulose nitrate is used in proportion to the camphor, the mixture probably contains both cellulose nitrate and cellulose nitrate-camphor complex (Yarsley et al., 1964).

Plasticity results from increased movement of the chain. This enables the material to move or be deformed under pressure. The action of the plasticizer can be illustrated as having a solvent effect. The plasticizer is thought to become attached to the polar groups on the cellulose chain. This increases the distance between the cellulose chains which in turn decreases the bonding between them. However, there is still some bonding between adjacent chains which keeps the material from flowing at ordinary temperatures (Yarsley et al., 1964).

Production Method

Preparation of cellulose linters

The source for cellulose which is used for the plastics industry is cotton linters which are obtained as a by-product from the cotton industry. The cotton is passed through a gin which removes the cotton staple fibre from the seeds. Short buff coloured fibres remain attached to the seed hull which are known as linters. They are separated from the hull by a linter machine. There are three grades of linters, first cuts, second cuts and mill runs. The cotton staple fibre and the first cut linters are used in the textile industry and the second cut linters are used to produce chemical cellulose (Yarsley et al., 1964).

The cellulose is prepared for use by a process of mechanical cleaning, digesting, bleaching, washing and drying. The first step of mechanical cleaning takes place in a breaker. The bales of linters ae broken up by bronze spikes attached to rotating cylinders. The linters are then picked up in an air stream which carries them up into an air separator at the top of the building. The air blowing process removes the heavy impurities. The linters are then deposited onto a conveyor where the are treated with a 3% caustic soda solution and introduced into the digester (Yarsley et al., 1964).

The digestion process ensures that seed hull remnents and other non cellulosic impurites are chemically changed to substances which can be eliminated with water. In a typical example, 7,000 lbs of linters are placed in a digester with 10 times the weight of the linters of 3% caustic soda . The alkaline mixture is then boiled under pressure for two to six hours. The steam is introduced below the level of the solution and the the air in the digester is then displaced. The time required is determined by the desired viscosity and the content are thoroughly mixed during the entire process. The contents are released through a valve and taken up through a steam separator. The linters and the alkali solution are then directed into a steel wash tank where the liquid is drained off. The linters are rinsed very thoroughly at this stage to remove the alkali and the degradation products of the impurities. 30,000 gallons of water are used for one ton of linters (Yarsley et al., 1964).

A continuous operation process for digestion and washing has been found to be more efficient in promoting chemical reaction and washing. The continous Dorr-Oliver digester is equipped with a rotary table with a spray jet and removes the alkali and small grit particles more rapidly (Yarsley et al., 1964).

The next step is the bleaching of linters. It is usually done in two or more steps to lessen the possible degradation of the cellulose fibres. The treatment is carried out in wooden tubs with perforated false bottoms. Bleaching agents employed are gaseous chlorine and sodium or calcium hypochlorites with chlorine content ranging from 0.75 to 1.25%. The bleach is most often acidified with sulphuric acid. It is vital that the time, temperature, pH and concentration be strictly monitered throughout the bleaching procedure to ensure that the resultant product has a white colour and is not degraded. Continuous bleaching methods are also being developed to obtain a more uniform product.

After each step of the bleaching procedure, the product is thoroughly rinsed. The purity of the water is important. Impurities such as iron have a pronounced effect on the colour of the product. The product is washed with an oxalic acid solution to lower the iron content after bleaching.

The linters are introduced into a large container where they are blended thoroughly to ensure a chemically and physically uniform product. The linters are then put into a solution of water with a concentration less than 0.5% and the slurry is pumped through a machine where the last of the heavy impurities settle out of the slurry (Yarsley et al., 1964).

The linters are then dried to lower the water content to 50% of the dry weight. The material is drained through rubber covered rolls. The linters are then introduced to a continuous tunnel-drier in which heated air 150 - 160 °F is circulated. When the moisture content falls below 5%, the dried linters are pressed compressed into bales (Yarsley et al., 1964).

Esterification or "nitration" of cellulose

To produce cellulose nitrate, the cellulose must be dried and then reacted with a solution of concentrated sulphuric and nitric acids. The acid is then recovered and the resultant ester is stabilized, bleached, rinsed and then dehydrated by replacing the water with ethyl alcohol (Yarsley et al., 1964).

The moisture content of the linters must be lowered as the water content is often raised to 7 - 8% during transportation and storage. It is critical to remove as much of the excess moisture as possible before treatment. Excess water decreases the acidity of the solution and irregular nitration results. This causes reduced solubility of the product. The heat generated during the dilution of the acid in the fibre structures causes degradation and thus decreased product. The material is dried in the same manner as in the final step of the purification process by passing the material through a tunnel heated by circulating air. The final moisture level should be 0.5 - 1.0 % (Yarsley et al., 1964).

The cellulose can be converted to various derivatives by either homogeneous or heterogeneous techniques. The production of cellulose nitrate is a heterogeneous technique where the fibre structure is retained throughout the process. This differs from the methods used to produce cellulose acetate where the product dissolves into the solution as it is produced, and ethyl cellulose where the fibre structure is destroyed, but the material does not disperse into the medium. Cellulose nitrate may be produced by direct esterification with concentrated nitric acid or with nitric acid vapour under reduced pressure. However, the standard technique is to use concentrated sulphuric acid as a condensing agent in addition to the concentrated nitric acid. A solution consisting of 25% nitric acid, 55% sulphuric acid and 20% water is typical for the production of 11% nitrogen. The composition is very similar to that used by Schonbein (Yarsley et al., 1964).

There have been many improvements in the nitrating procedure. The DuPont process, which was first developed in the USA and is now commonly used, employs a mechanical dipping process. The stainless steel unit is composed of four dipping pots called dippers, a centrifuge and a drowning tank which are positioned vertically with the dipping pots at the top. The actual chemical reaction takes place in the dippers where 30 lbs. of cotton are combined with 1,200 lbs. of the acid mixture at a temperature of 35-40 °C for 30 - 60 minutes. The product is then dropped into the centrifuge and the acid is "spun off" and retained to be reused. The cotton, which still contains a high percentage of acid, is then dropped into a drowning tank where the acid is diluted in a large quantity of water. The resultant slurry is then transferred into large stainless steel vessels where large quantities are collected for further processing (Yarsley et al., 1964).

The next stage is the stabilization of the cellulose nitrate. This is a very important step as the unstabilized material is explosive. Several early disasters led to research, and in 1865 Abel found that the instability was caused by traces of the nitrating acids which were retained in the structure of the material. It was found that the nitration reaction produced sulphuric-nitric mixed esters as a secondary product of the nitration reaction. Sulphuric acid was created as the groups "split off" which instigated autocatalytic decomposition. In 1906, Robertson discovered that boiling the cellulose nitrate in weakly acidic water would almost completely eliminate the acid ester groups. The material is stabilized in the large collection vats. The slurry is washed and the water continously replaced until the acidity of the water is about 0.2%. The solution is then brought to a boil using steam and heated for 5 to 12 hours. If a product with high stability is needed, the process is carried on for a much longer time. The stabilizing process slightly decreases the nitration content and viscosity of the resulting cellulose nitrate (Yarsley et al., 1964).

Bleaching is necessary to produce clear transparent and light coloured plastic. The natural cellulose nitrate plastic has a brownish yellow tinge. The stabilized cellulose nitrate is placed in lined wooden vessels at low temperatures. Gaseous chloride or sodium hypochlorite are the common bleaching agents. The concentration used is about 0.5% available of the weight of the cellulose nitrate and the treatment lasts from 30 to 60 minutes. The product should be treated with sodium sulphite or weak nitric acid to remove residual chlorine from the material. This is important as residual chlorine would cause breakdown of the product. The cellulose nitrate is rinsed until the wash water is neutral and then the product is transfered into a tile-lined draining stall where the water is drained through holes in the floor. As with the preparation of cotton linters for commercial production, it is important that the water is pure. Cellulose nitrate can absorb metallic ions from water with great ease. For example, iron damages both the appearance and the heat stability of the product. Thus, there must be constant quality control of water supply and it must be treated as necessary (Yarsley et al., 1964).

The cellulose nitrate contains a high percentage of water (35 - 40% of the wet weight) after the draining procedure. It is necessary to remove as much of the water content as possible before it can be used to produce cellulose nitrate plastic. It is necessary to replace as much of the water as possible with denatured ethyl alcohol. There are two methods for this process, the first which involves putting the cellulose nitrate into a centrifuge consisting of two concentric baskets. The alcohol is introduced as a spray while it is in motion. The dehydrated product should contain about 30% alcohol and 5% water. In the second method, the cellulose nitrate is pressed into a cylindrical mass in a hydraulic press at a pressure of 2000 - 3000 lb/in^2. The alcohol is added to the system at a pressure of 600 - 800 lb/in^2. The solution is then forced out under full pressure. This method is more efficient, the dehydration is more complete and less alcohol is needed (Yarsley et al., 1964).

The dehydration also has a stabilizing effect as the cellulose nitrate is not entirely insoluble in the alcohol and about 1% of the material is lost in the process. The material which goes into solution has been found to have a lower nitrogen content (Yarsley et al., 1964).

Production of cellulose nitrate plastic and additives

The dehydrated cellulose nitrate is mixed with camphor to create a uniform dispersion or dough. The material is subjected to hydraulic pressure and then the solvent is partially removed by rolling. The bulk is pressed into a block by heat and pressure in a hydraulic press. The block is cut into sheets, the residual solvent is removed by a process called stoving. The sheets are then polished (Yarsley et al., 1964).

The mixing of the cellulose nitrate with the camphor takes place in cast iron, bronze or stainless steel mixers which are boxes with two pairs of blades which "rotate" in opposite directions, and with external heating components. The average composition of the raw material is three parts cellulose nitrate to one part camphor, however, different amounts of camphor are used for special applications. In some cases, plasticizers such as triphenyl phosphate and diethyl or dibutyl phthalate have been used as a partial substitute for camphor. However, camphor is still the most widely used plasticizer for cellulose nitrate. The mixer is steam heated at the beginning of the reaction, but it is usually turned off as the reaction proceeds as heat resulting from the internal friction in the cellulose nitrate keeps the temperature at 104 - 122 °F. The ethyl alcohol in the cellulose nitrate becomes an effective solvent in the presence of camphor. The cellulose nitrate fibres swell and lose their structure as the material gels. Other additives which include colouring agents and occasionally stabilizers are introduced at the beginning of the mixing process. Colouring agents include soluble dyes and pigments which are either added dry or as a paste. For clear transparent plastics, a small amount of soluble dye or very finely dispersed pigment is used to counteract the yellow tinge in natural cellulose nitrate. It is necessary to obtain a uniform dispersion of colourants to prevent "colour spots" in the finished product. Stabilizers are added in small amounts to neutralize acids which may form which gives greater stability. These include urea or a urea derivitive and zinc oxide which is also utilized in opaque pigments. The mixing process takes 1-2 hours until the colouring matter is uniformly dispersed throughout the mixture (Yarsley et al., 1964).

After nitration, the dust and other impurities are eliminated by passing the dough through a calico sieve under hydraulic pressure of 1.5 tons /in^2. The filtered material is then rolled between differentially heated cylinders for 30 - 40 minutes in a two step process to reduce the solvent (ethyl alcohol) concentration in the compound from 28 - 30% to 12 - 15%. During the first part, the movement of the rolls repeatedly exposes fresh surfaces of the material creating a situation where the solvent is evaporated quickly. It is important to not remove too much solvent and the timing is still based on the experience of the operator. The second step is to roll the material on slower, cooled rolls also known as calenders where the plastic is rolled into 1/2 inch thick sheets which are cut to fit the block press.

The Parkes technique called for squeezing the dough between rolls and then eliminating the volatile solvent content. The Hyatt brothers improved on this procedure by first pressing sheets of plastic into a block in a press and then slicing sheets from the mass. This produced a substance with greater toughness than that produced by earlier methods. In modern processes, the sheets are placed on a steel base scored with grooves in which the cellulose nitrate plastic is firmly attached for the subsequent slicing step. The base is placed inside a steel box which is then put in a hydraulic press. The press is heated to 200 °F and put under 350 lb/in^2 pressure. The period of time necessary is dependent on the thickness of the block, the average time required is usually 4 - 5 hours. It is necessary to allow the apparatus to cool thoroughly. If the block is released from the press while still hot, solvent bubbles form in the material and it must be repressed. After the cooled blocks are removed from the box, they are placed in a cool atmosphere for 24 hours to reach a uniform temperature.

The block is fastened to a movable table which is manipulated by a reversible screw. The screw moves the plastic block backwards and forwards under a knife which is programmed to cut certain thicknesses of sheet. An allowance must be made for the final thickness as a certain amount of shrinkage occurs during seasoning. The thickness of sheet can range from 0.005 to 1.0 inch.

There are two methods for seasoning of the cellulose nitrate, one for thin sheets, up to 0.100 in and a modified one for thick sheets. After slicing, the sheets are hung in a heated chamber where the temperature is kept at 122 °F and the air is circulated ultimately into a solvent recovery system. A hard surface layer forms which does not cause a problem with the curing of thin materials. However, the creation of a hard surface layer makes the seasoning of the interior more difficult. The solvent must diffuse through the outer coating which requires a greater length of time. Thick sheets, 0.100 in and greater, are hung in an unheated chambers for three days to allow the bulk of the solvent to diffuse from the material. Then, the sheets are hung in heated rooms as for thin sheets. This prevents the formation of bubbles when the sheets are placed in the heated rooms. There is a certain amount of distortion due to shrinkage as the solvent is removed. The damage is most evident around the edges of thin sheets. The final moisture content is 2% water and some ethyl alcohol which is almost impossible to eliminate because of the strong affinity of the camphor and alcohol and cellulose nitrate.

The final step in the production of sheet cellulose nitrate is polishing. The knife edge used for slicing leaves marks which make transparent cellulose nitrate plastic appear translucent. It must be polished to remove the imperfections on the surface. The seasoned sheets are press polished by heating the sheet between highly polished, nickel plated steel plates in a hydraulic press. The temperature, pressure and time of polishing are carefully controlled so that only the surface material is affected. The plates are quickly chilled to prevent a reduction in thickness of the sheet. Cellulose nitrate sheets with impressed or etched designs can also be produced by using etched or embossed metal plates (Yarsley et al., 1964).

Trade names and applications

The short lived Parkesine Company (1865-1867) produced buckles, clasps, buttons, beads, mirror backs, medallions, book covers, bracelets, handles, shoe-horns and door knobs. In the USA, the Hyatt brothers first manufactured flesh toned dental plates to be used in place of those made of dark hard rubber (1870). In 1872, the new Celluloid Manufacturing Company produced knife handles, harness trimmings and brush backs. In 1878, their production was extended to manufacture jewelry, necklaces, pendants, earrings, watch chains, pins, buttons, charms, bracelets, checkers, dominoes, thimbles, soap dishes and other domestic objects. The Merchant's Manufacturing Company (Newark, New Jersy) had already been set up in 1881 and produced cellulose nitrate under the name Pasbosene. The trademark was changed to Cellonite in 1883 and in 1885, the company was moved and renamed as Arlington Manufacturing Company. The product was then called Pyralin. The Celluloid Manufacturing Company took over the American Zylonite Company in 1890 and with the Arlington Company, were the major producers of cellulose nitate plastic for 25 years. Dupont eventially took over the Arlington Company, but continued to use the trade-mark Pyralin. In 1927, the Celluloid Manufacturing

Company merged with the Celanese Corporation of America (Kaufman, 1963).

More than 1,200 patents had been taken in the USA and Great Britain by 1911 on cellulose nitrate plastic application and production. It is impossible to list them all, but an indication of the scope may be summarized. Natural material were sucessfully substituted by cellulose nitrate. These included grained ivory (1883), horn (1891), tortoise-shell (1875), mother of-pearl (1884), coral, amber, onyx (1895) and marble (1898) (Hillman, 1986).

In addition to the early uses of cellulose nitrate plastic for dentures and "linen" collars and cuffs, other uses included knife handles, printers blocks, and "fancy goods" such as hand mirrors (1890's), dressing cases, trinket boxes, photo frames, dolls, car windsheilds, table tennis balls, lacquers, shoe heels, and corset stays (1881). It was widely used for combs and brush backs which were an important part of the market. Different types of brushes made include hair, nail, shaving, clothes, hat, baby and tooth brushes. Other objects made included piano key linings (1878), ice pitcher linings, playing cards, eye-glass frames, pen holders

(1879), syringes (1880), chocolate and bon-bon boxes (1893), trays and dishes (1895), shoe eyelets (1902), golf balls (1903-1905), and "amber" cigar holders (1904). It was also used to manufacture children's toys including the Kewpie doll, baby rattles, straight razor handles. Artificial leathers utilized for upholstry, bookbindings, raincoats, suitcases, dressing cases, automobile trimming and handbags and waterproof coatings for posters, show bills, and exterior sign s were other applications of celluloid. The first important industrial use was in the new photographic and cinematographic industries. Kodak introduced cellulose nitrate film in 1889 (Kaufman, 1963; Yarsley et al., 1964).

The early trademark Celluloid has come to be used for all cellulose nitrate plastics, but there are many other trade-names which have been used. Certain trademarks were only used for a short time while others were used for many years. The trademarks include Bonesilate, Cellonite, Celluline, Cellulodine, Cellulosine, Coraline, Crolithion, Crytalloid, Fiberloid, Fibrolithoid, Ivaleur, Ivoride, Ivorine, Ivoryide, Lignoid, Lithoxyl, Parkesine, Pasbosene, Pearl-Tone, Pegamoid, Pulveroid, Pyralin, Pyrantin, Pyroxyline, Rubberine, Shell Tone, Shelleur, Viscoloid, Vitroloid, Xylonite, Zylonite and Zyl. Artificial leather was first marketed as Tannette (1890) which was later known as Morrocoline (1892). Later tradenames which date from the turn of the century include Fabrikoid, Keretol, Marokene, Meers, Case and Texaderm (Hillman, 1986).

Cellulose acetate

History

The acetylation of cellulose is a more difficult chemical reaction and the development of cellulose acetate was not as straight forward as that of cellulose nitrate plastic (Kaufman, 1963). Cellulose was first acetylated by Schutzenberger in 1865. He treated cotton with acetic anhydride in a sealed tube and heated it to 130 - 140 °C (Kaufman, 1963; Yarsley et al., 1964). The resulting product was severly degraded and the reaction was difficult to control. Brydson, 1975). Sulphuric acid was first used as a catalyst by Francimont. Cross and Beavan developed the first commercial production method of cellulose acetate in the form of spinnable fibres from regenerated cellulose in 1904. The material was known as viscose rayon (Kaufman, 1963, Hillman, 1986). The initial material was cellulose triacetate which is soluble in chloroform and other toxic solvents. In 1905, Miles found that an acetone soluble product could be produced by the treatment of the triacetate with a weak acid. The hydrolysis created a diacetate. This development helped lead to commercial success. The Dreyfus brothers first achieved success with the production of cellulose acetate used to stiffen fabric aeroplane wings during World War I. After the war, the brothers used surplus stocks to develop a cellulose acetate fibre (Kaufman, 1963). With the introduction of plasticizers in 1927, cellulose acetate could be used for a wider range of applications. It became a non-flammable alternative for cellulose nitrate. It was used more extensively for injection moulding during the subsequent ten years and was the leading material for this purpose until the early years of the 1950s (Kaufman, 1963; Brydson, 1975).

Chemical structure and nomenclature

The structure of cellulose has been discussed above. Like cellulose nitrate, cellulose acetate is an ester where one or more of the available hydroxyl groups on the anhydroglucose molecule is replaced with an acetate group (Figure 9.4). The substitution of the hydroxyl groups with the acetyl groups has a similar effect to the replacement in cellulose nitrate, the hydrogen bonding between the cellulose chains is reduced and the space between the chains is increased by the bulk of the acetate groups. Thus, the polarity of the molecule is reduced. Cellulose acetate may be characterized by the degree of substitution and different degrees are required for different uses. Also, the solubility in various solvents changes according to the degree of substitution (Table 9.2).

Production method

Acetylation of cellulose

There are two types of production techniques, the homogeneous method where the acetylated cellulose is dissolved in a solvent as it is produced and a heterogeneous one where the fibrous structure of the material is kept as it is acetylated. The former method is the most common for the manufacture of cellulose diacetate (Yarsley et al., 1964).

The production method for acetylating cellulose consists of five steps, pretreatment, acetylation, saponification or 'ripening', precipitation and after-treatment. The pretreatment is necessary to "open up" the cellulose structure, otherwise only the hydroxyl groups on the surface will be acetylated. Pretreatment is a mild acetylation where the material is usually treated with glacial acetic acid. This precedure ensures faster and more uniform acetylation. It also helps insure that the cellulose structure does not degrade during acetylation (Yarsley et al., 1964).

The acetylation method usually involves three components, the acetylating agent, a catalyst and a diluent. Acetic anhydride is most commonly used as the acetylating agent, however, acetyl chloride and ketene ($CH_2=C=O$) are also mentioned in the literature. Sulphuric acid, which was first used by Francimont in 1879 is the most commonly used catalyst, although other acids have been reported. The diluent increases the homogeneity of the acetylation reaction, and the most common diluent is glacial acetic acid. It is often combined with methylene chloride (which came into use in the 1940's) which, as the solvent boils, can remove excess heat from the reaction as latent heat of evaporation (Brydson, 1975). The bubbling action also increases the mixing of the reactants (Brydson, 1975; Yarsley et al., 1964). There are an extremely large number of patents for the production of cellulose acetate which incorporate acetic anhydride, acetic acid and a catalyst. They vary in the type and amount of catalyst used and the method and degree of temperature control. The mechanism for the chemical reaction which takes place can be represented in Equation 9.1 where X equals the glucose molecule in cellulose (Brydson, 1975).

$$X\text{-}OH + CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 \longrightarrow X\text{-}O\text{-}CO\text{-}CH_3 + CH_3\text{-}COOH \qquad \text{Equation 9.1}$$

However, the mechanism is not completely understood (Yarsley et al., 1964). It is thought that perhaps the catalyst combines with the cellulose in some way and thus, the reaction is not purely catalytic. It has been suggested that acetyl sulphuric acid ($CH_3\text{-}CO\text{-}O\text{-}SO_3H$) is formed when sulphuric acid is used as the catalyst and that this compound causes the acetylation (Yarsley et al., 1964).

The next step is refered to as saponification, ripening or hydrolysis. The acetylation reaction produces a product with a degree of substitution greater than the diacetate. The ripening stage converts the product to the acetone soluble diacetate. The material is treated with dilute acetic acid or water. The length of treatment and conditions are determined by the desired properties for the cellulose acetate. The reaction is continued until the material displays the desired solubility. The solubility indicates the degree of substitution (Brydson, 1975;

Yarsley et al., 1964). Different degrees of acetylation result in different properties (Table 9.2) (Brydson, 1975)

After saponification, the cellulose acetate must be precipitated from solution. If a low boiling solvent such as methylene chloride is used, it can be removed by evaporation. The usual diluent also contains nonvolatile acetic acid. Water is added to the solution to bring down the cellulose acetate. This must be done carefully to avoid the formation of lumps (Yarsley et al., 1964).

The final step in the acetylation process is the after-treatment which includes washing, stabilizing and drying of the material. The cellulose acetate must be washed to remove free acetic acid and excess mineral acid. Some of the sulphuric acid is incorporated into the cellulose acetate structure as acetosulphate. Thus, stabilization is required. After several washings, the cellulose acetate is boiled with stirring in weak acid (0.02%) sulphuric acid) until the acidity of the water is observed to be constant. Then, the material is washed until no more acid is detected in the water. The resulting powder is then dried at temperatures not exceeding 100 °C until the moisture content is between 2 - 3%. This step was not performed in early manufacturing methods and the sulphur content was found to result in an unstable product. If the cellulose is required for photographic or other purposes for which greater clarity is required, the material undergoes further purification. Otherwise, the material is ready for compounding (Yarsley, et al., 1964).

Compounding of cellulose acetate and additives

The acetylated cellulose is then prepared for commercial use by compounding. The aim of this process is to create a homogeneous mixture of the cellulose acetate, plasticizers, colouring matter and fillers in a form which may be used for production methods such as moulding. The most important additive is the plasticizer which changes the properties of the cellulosic material so that it can be manipulated and the plasticizer has a large effect on the properties of the resulting plastic (Yarsley et al., 1964).

The addition of plasticizers is important because cellulose acetate has a high softening point which is very near its decomposition point and will not flow under heat and pressure.

Thus, unplasticized cellulose acetate cannot be used for extrusion or injection moulding. Although some unplasticized material is produced for specialized applications, most film and all moulding powders are plasticized. The plasticizer has four important effects on the cellulose acetate. It decreases the fusion temperature of the cellulose acetate sufficiently so that the materials can be worked without severe degradation of the cellulose structure. It also increases the ability of the cellulose acetate to flow. The plasticizer adds pliability to films and increases the toughness of finished moulded objects (Yarsley et al., 1964).

There are two types of plasticizer, solvent and non-solvent. The theory of solvent action plasticizer is very similar to that of solution. Cellulose and cellulose ester molecules are composed of glucose rings which are attached by glycosidic bonds which form long chains. Hydrogen bonds formed between the hydroxyl groups cause attraction of the chains to each other. The hydrogen bonding thus reduces the movement of the molecules which prevents flexibility. The solvent type plasticizer is thought to become absorbed to the hydroxyl groups in the cellulose molecule. This would decrease the hydrogen bonding and increase the distance between the chains. A greater mobility between the adjacent molecules would be expected to increase in flexibility and a decrease of the softening point of plasticized cellulose acetate (Yarsley et al., 1964).

Non-solvent plasticizers do not act as solvents, but as extending agents. It is thought that they have a mechanical action instead of a chemical reaction. The distance between the cellulose threads is increased by the bulk of the plasticizer molecule. The bulking process is more effective if the intermolecular attraction between the chains has been reduced by forming hydrogen bonds with the plasticizers. Thus, they are almost always used with solvent action plasticizers (Yarsley et al., 1964).

The properties of cellulose acetate materials are largely affected by the plasticizer. For example, cellulose acetate with 53% acetic acid combined in the structure were observed to have high compatibility with plasticizers which have keto or carboxylic ester groups. The terminal groups should contain three or fewer carbon atoms, the most favourable groups should have two or less. For example, methyl esters such as dimethyl phthalate are highly compatible with cellulose acetate, ethyl esters are slightly less compatible and butyl esters exhibit very poor compatibility. Likewise, acetates demonstrate greater compatibility than propyl esters and proprionates which are in turn more compatible that butyrates. Four types of plasticizer have been defined, linear, planar, pyramidal and complex three dimensional. Pyramidal and complex plasticizers result in a hard, more brittle material than linear and planar compounds. Also, plasticizers which are solid at room temperature give harder and more brittle results than liquid ones (Yarsley et al., 1964).

Yarsley et al. (1964) list the requirements of the ideal plasticizer.

1. It would have a high permanent degree of compatibility with the polymer.
2. It would be substantially non-volatile.
3. It would be resistant to extraction by materials with which the plastic would be likely to come into contact in service.
4. It would be colourless, odourless, tasteless and non-toxic.
5. It would be efficient in preventing brittleness in the plastic at sub-zero temperatures.
6. It would be stable at processing temperatures.
7. It would be stable under the influence of ultraviolet light.
8. It would be cheap and readily available.

It has been difficult to find a compound which would fulfill these requirements and research into the problem is still being pursued. Over several hundred substances have been suggested in the patent literature, but only a small number of plasticizers have been used commercially (Table 9.3)(Yarsley et. al., 1964). One of the major plasticizers in use is dimethyl phthalate. In addition to the very high level of compatibility mentioned before, it is cheap and improves flexibility, toughness and ease of flow. Unfortunately, it is highly volatile which makes the resulting plastic more flammable. Diethyl phthalate is sometimes used as it is less volatile and compatible. It is, however, less effective. Triphenyl phosphate is a crystalline solid which, although it has a lower compatibility with cellulose acetate, is often used with dimethyl phthalate to increase water resistance and give flame retardance. It has been shown to be more permanent than dimethyl phthalate. Triacetin was widely used in the past as it was compatible. However, it lessens the water resistance of the plastic material and is also volatile. It has become necessary to use the cheapest materials to keep cellulose acetate production competitive with that of synthetic polymers. Thus, expensive plasticizers such as ethyl phthalyl ethyl glycollate which are compatible are seldom used (Brydson, 1975).

The structures of three common plasticizers are given in Figure 9.5.

The second important additive is the colouring matter or dye. Untreated cellulose acetate has a yellow tinge that is present even in the highest quality grades. It is necessary to add a small amount of blue dye to produce clear films and sheets. Also, it can be made into a wide variety of colours. Organic dyestuffs are used to produce transparent colours. The choice of colouring agents is difficult, since the material must withstand heat and pressure generated during production and it should not induce degradation of the plastic. The dyestuff should be light-fast and it is important that it not be extracted by compounds which come into contact with the cellulose acetate. Although oil and water soluble dyes are sometimes utilized, the principal dyes used are spirit soluble anthraquinones (Yarsley et al., 1964).

Opaque colours are obtained using pigments and organic lakes. Inorganic pigments are entirely light-fast, but less intense than the organic lakes. More pigment must be used to obtain an equivalent intensity. Opaque shades may also be made from soluble dyestuffs used in conjunction with white pigments. However, in some cases, the use of white pigments reduces the light stability of organic dyes (Yarsley et al., 1964).

Cellulose acetate plastics are usually unfilled, however, powdered mica (in quantities up to 25%) is occasionally utilized. In some cases, carbon black, zinc oxide and wood flour are added as fillers. Mineral fillers increase hardness, the modulus of elasticity and flexural strength of the plastic and water absorption is lessened. Impact strength is lessened and the appearance is affected (Yarsley et al., 1964). Castor oil is sometimes used as a cheap extender (Brydson, 1975).

Ultraviolet light can act as an initiator causing the degradation of the cellulose chains. This causes brittleness of the material and oxygen enhances the reaction. Thus, stabilizers which reverse or retard this reaction must be added to cellulose acetate which is to be used out of doors. Plasticizers which contain aromatic groups such as triphenyl phosphate have a stabilizing effect. The use of compounds such as phenol salicylate (salol), hydroquinone (quinol), monobenzyl ether and other phenolic compounds impart more effective retardation (Yarsley et al., 1964; Brydson, 1975). A very small amount of a weak acid such a tartaric acid is added to clear cellulose acetate before processing to reduce the risk of colour change and this additive is also thought to retard the effect of ultraviolet light. Other stabilizers reported include menthyl phenol, amyl phenols, octyl phenols and other derivitives of phenol (Yarsley et al., 1964).

A lubricant is sometimes added to cellulose acetate to aid in the removal of objects from the mould. It also imparts a surface gloss. It is important to add only a very small amount or it will exude to the surface of the finished article. A plasticizer of low compatibility (dibutyl phthalate for example) is used sometimes as it migrates to the surface to a small extent during moulding. Waxes such as paraffin, spermaceti and carnauba wax are also sometimes utilized as lubricants in quantities of 0.03 - 0.3% (Yarsley et al., 1965).

Trade names and applications

In 1904, spinnable fibres were first produced from regenerated cellulose and marketed as viscose rayon. The Dreyfus brothers developed a manufacturing technique using excess stocks of acetate lacquer from World War One and the acetate fibre was first marketed in England under the trade-name Celanese in 1921. The acetate fibres were first manufactured in the USA in 1924 (Hillman, 1986). After the introduction of plasticizers, cellulose acetate was produced in sheet, rod and tube and some of the common trade-names include Bexoid, Lumarith, Rhodoid, Cellon, Tenite Acetate and Fibestos. It was increasingly used as a cellulose nitrate replacement during the 1930's and 1940's and was widely utilized until the early 1950's. It was used to produced toothbrushes, eye-glass frames, brush backs, tool handles, knobs, dresserware sets, bracelets, game pieces, combs, football helmets, toys, shoe heels, flashlight cases, telephone receivers and steering wheels in motor cars. It was utilized for sunglasses which became fashionable in the late 1930's. Cellulose acetate plastic served as a replacement for parchment lampshades and as 'crystal' buttons and was utilized as packaging for other substances, namely flexible tubes for creams and lotions. The plastic could be made to imitate marble, mother-of-pearl, tortoise-shell and onyx and could be made into any translucent or opaque colour and a fluorescent product could be manufactured (Hillman, 1986).

Casein plastic

History

The development of casein plastic was first sparked by a need for white blackboards in German schools (1897). The concept of producing a casein film on white cardboard which would then be rendered water resistant by chemical treatment was developed by a printer from Hanover named W. Krische. A. Spitteler, a chemist from Bavaria, discovered that casein and formaldehyde form a hard, waterproof material which was resistant to acid. The two collaborated and patents were taken out in 1899 in Germany and 1900 in the USA. The material was first produced in Germany and France under the name Galalith (milkstone). In 1904, the International Galalith Gesellschaft Hoff & Co. was formed and was the only producer of casein plastic until the beginning of World War I. The Spitteler and Krische technique is known as the dry method (Kaufman, 1963).

In the United Kingdom, the technique for the production of casein plastic was patented by a Russian student (V. Schutze) in 1909, a method known as the "wet process". The Syrolit company was founded to produce the material which was called Syrolit. The wet process was not economically viable and the company nearly failed. However, the company was placed under new management and the factory was converted to the dry production method. The new company which was called Erinoid gained stability during World War I (Kaufman, 1963). Casein plastic was not produced in America until 1919 by Christensen. The material was called Aladdinite (Kaufman, 1963).

Chemical structure

Casein is a member of a class of natural products known as proteins which are discussed in Chapter 8. They are similar to polyamides, but their structure is more complex. Polyamides such as Nylon 6,6 or 11 have only one omega amino acid in their structure (Figure 9.6a) whereas proteins are composed of a variety of different alpha amino acids (Figure 9.6b) (Brydson, 1975). The structure of casein has not been fully elucidated, but hydrolysis of the protein has produced over 30 amino acids including glutamic acid, hydroxyglutamic acid, proline, valine, leucine and lysine which make up approximately 60% of the total. Also, arginine seems to play a part in the crosslinking of casein with formaldyhyde. Proteins are highly stereospecific, the amino acids have the L-configuration. The casein molecule is associated with nonprotein material called prosthetic groups and known as a conjugated protein. The casein molecule is associated with phosphoric acid. Calcium is involved in the molecule as well. The presence of inorganic components influences the processing and the use of casein polymers. Casein is present in many animal and vegetable substances, but only cow's skimmed milk is used as a commercial source. There is about 3% casein in milk and it is present as colloidally dispersed micelles with a diameter of approximately 10^{-5} cm (Brydson, 1975).

Production method

Isolation of casein from milk

Although casein can be precipitated from milk using heat, alcohols, acid salts, or the enzyme action of rennet, only precipitation by acid or rennet coagulation methods are used for commercial processes. Casein obtained from acid precipitation is not widely used for plastics production as casein isolated by rennet retains the calcium and phosphates and is more desirable for the manufacture of plastics (Brydson, 1975). In a typical process, the milk is treated as soon as possible after collection. The milk is skimmed to remove the cream. The milk is then placed in vats and steam heated to 100 °F. The rennet is then added and the mixture is agitated. The stirring is controlled to obtain the desired curd size which is the size of peas. After the reaction has finished, the remaining greenish liquid whey is drained and the casein is washed three times with warm water, drained, pressed to remove excess water and dried at temperatures of 110 - 115 °F (Yarsley, 1943). It is thought that the calcium caseinate is changed to the calcium paracaseinate which is insoluble and thus coagulates. It is critical to control the temperature and the entire coagulation process as impurities such as other proteins may be precipitated along with the casein under adverse conditions. These contaminants have a negative effect on the transparency of the plastic product. The size of the curd is important. If the agitation is too slow, the resulting product will be large clots, if the agitation is too fast, the curd will be too fine. In both cases, the precipitate is difficult to wash effectively. In additon to controlling the agitation, inorganic ions are added to improve the quality of the product. Phosphorus ions are introduced to prevent a flaky curd and calcium ions may be required for calcium deficient casein which will not coagulate properly. It is also necessary to dry the finished polymer carefully (Brydson, 1975). The moisture content should be 10 -12%. If the casein is dried at too high a temperature, the product will have too little moisture and would not be usable for plastics production (Yarsley, 1943). If the material is dried too rapidly, an impervious outer layer is formed and the interior of the particles would not be dried. Also, if the drying process is too slow, the product will sour (Brydson, 1975).

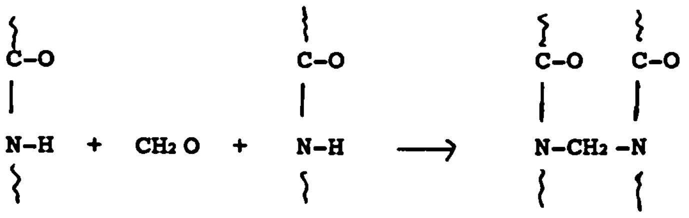
Production of casein plastic and additives

Casein plastic is prepared by mastication of the casein curds under heat and pressure in the presence of moisture. The product is a homogenous plastic mass which can be treated with formaldehyde to create a hard, hornlike material (Yarsley, 1943).

The casein is sieved and then ground in a roller mill. The ground material is then introduced to a purifier where it is sifted and separated from light particles. The final powder should pass through a 40-mesh sieve, but not an 80-mesh sieve. The final cleaning involves the passing the material through a magnetic separator to remove metallic impurities. The ground casein is placed in a dough mixer. In a typical process, 100 kilograms of casein with 10% moisture content are combined with 26 kilograms of distilled water which is introduced as a spray over a period of fifteen minutes. Any dyes or other additives are added at this point. The material is then mixed for one hour. The mixture is then extruded using a horizontal screw extrusion press to produce rods of casein plastic. The material hardens as it is extruded and is cut into the desired lengths and cooled in water. Sheets are produced using two methods. The mixed, coloured casein powder is placed in a mould and pressed or the rods produced by extrusion are cut into uniform lengths and placed in a mould which is heated under high pressure. After the moulds have been filled, the are placed in a multiple hydraulic press and the press is heated to between 180 and 190 °F at a pressure of 600 pounds per square inch (psi) for three minutes. The pressure is increased to two tons psi for three minutes. The moulds are then cooled with cold water while still under pressure for six minutes before the sheets are removed. Initially, the material is soft, but dries and becomes brittle after exposure to the air (Yarsley, 1943).

The next step is to cure the plastic by treating it with formalin which makes the material hard and waterproof. Formalin is a solution of 40% formaldehyde diluted to 5-6%. The concentration used is slightly stronger for thick sheets or rods and weaker for thin sheets. The concentration is important as an excess of formaldehyde will result in a rapid curing of the surface and consequently, insufficient hardening of the center as the formalin cannot permeate the hardened surface. A low concentration lengthens the time needed for hardening (Brydson, 1975). The casein is soaked in the formalin in a cement lined brick tanks and the solution is kept moving by pumps. The amount of time required ranges from two days for very thin sheets of 2 mm in thickness to two months for thich rods of 25 mm in diameter. The reaction between the casein and the formaldehyde is not fully understood and has been described as a condensation reaction (Yarsley, 1943). It is thought that the following three reactions occur (Brydson, 1975).

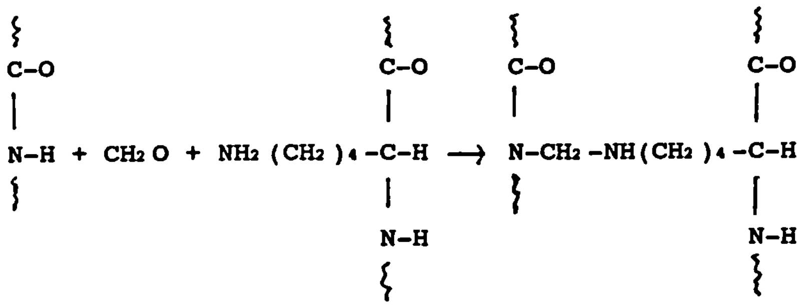
1. There is a crosslinking between the peptide groups.



$$\begin{matrix} \text{C-O} \\ | \\ \text{N-H} \end{matrix} + CH_2O + \begin{matrix} \text{C-O} \\ | \\ \text{N-H} \end{matrix} \longrightarrow \begin{matrix} \text{C-O} & \text{C-O} \\ | & | \\ \text{N-CH}_2 & \text{-N} \end{matrix}$$

(Equation 9.2)

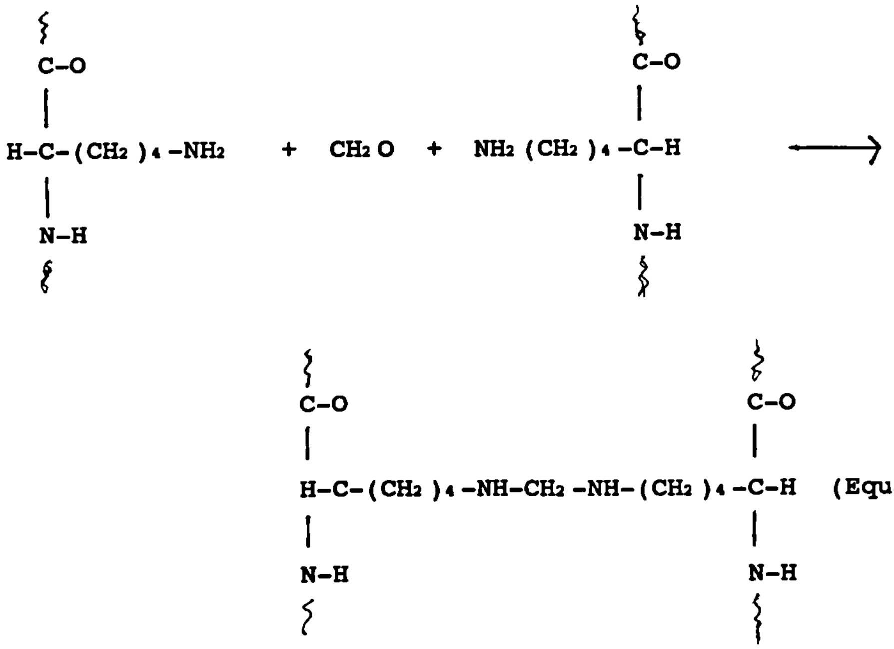
2. There are reactions between the lysine side chains and the peptide groups.



$$\text{N-H} + CH_2O + NH_2(CH_2)_4\text{-C-H} \longrightarrow \text{N-CH}_2\text{-NH}(CH_2)_4\text{-C-H}$$

(Equation 9.3)

3. There are similar reactions between the amino groups on side chains.



$$\text{H-C-}(CH_2)_4\text{-NH}_2 + CH_2O + NH_2(CH_2)_4\text{-C-H} \longrightarrow \text{H-C-}(CH_2)_4\text{-NH-CH}_2\text{-NH-}(CH_2)_4\text{-C-H}$$

(Equation 9.4)

These hypothesized reactions do not explain all of the reactions that occur during formalization. Thus, there are other reactions which are taking place during the process (Brydson, 1975). The formalization can be described as both a physical process of swelling and absorption and as a chemical reaction of consensation in which the hydrogen of the amino group is replaced by a methylene group. They are opposing reactions, the absorption results in swelling and the condensation in shrinkage. Thus, an equilibrium is reached which is determined by the formaldehyde concentration (Yarsley, 1943).

It has been found that the formalization process can be accelerated by adding approximately 1% sodium carboxymethyl cellulose or other water soluble cellulose compounds to the casein mixture. It is thought that a fibrous compound is produced which acts as a wick and provides a network of channels for the formalin to spread more quickly through the structure. The time required is reduced by 25%, but the clarity of the finished material is slightly reduced (Brydson, 1975).

Several alternate methods of hardening have been described by Yarsley (1943). The casein is mixed with 5% water and trithanolamine or a mixture of ethanolamines, or with glyoxal or a homologue. The casein may also be put into alkaline solution with a phenol and an aldehyde in the presence of ammonia. It may also be cured during hot pressing by the addition of methyl ureas and urethanes.

The hardened casein is washed to remove excess water and free formaldehyde and then carefully dried. The drying process must be done slowly to prevent cracking and warping. The product is then polished before manufacture into objects. Only rods and slabs are produced successfully on a large scale. Objects are produced using three techniques; softening the sheet and then shaping, sawing or moulding. It can be turned, drilled, polished, stamped, moulded and engraved like horn and ivory (Yarsley, 1943).

Additives as colouring agents or to add transparency are incorporated during the mixing stage. They include acid dyes, and glycerine (2% of the weight of the casein) has been found to be a successful plasticizer and adds transparency. Tricresyl phosphate and methyl-diphenylamine have also been used as plasticizers (Yarsley, 1943). A later source (Brydson, 1975) lists alkaline water soluble dyes, pigments, and titanium dioxide as a white pigment or a colour base for colouring agents. Clearing agents added to give tansparency include ethyl benzyl aniline, tritolyl phosphate, trixylyl phosphate and chlorinated diphenyls.

Trade names and applications

Casein plastic is rigid and hornlike. It has a pleasant feel and appearance. The material is hygroscopic and can be dyed by acidic or basic alkaline water soluble dyes to obtain a wide range of colours (Brydson, 1975) It is not flammable, harder than cellulose nitrate and easily and economically produced from abundant raw materials. It is also affected by excess humidity Although casein has properties which were more desirable than cellulose nitrate, it never replaced celluloid. it was too brittle to be made into very thin sheets which limited its use for moulding and the sensitivity to water led to cracking and warping in regions of high humidity (Brydson, 1975; Kaufman, 1963). Objects often develop faults due to shrinkage in warm dry atmospheres (Yarsley, 1943). The material could not be used for electrical insulation in outdoor or high tension situations due to its hydroscopic property. Thus it was superceded by synthetic plastics with superior properties as they were developed, but it continued to be widely used for buttons and other decorative objects up until the 1960's.

The trade names Galalith and Erinoid became synonyms for casein in the plastics field (Kaufman, 1963). A related material was manufactured under the trademark Lactoid by the British Xylonite Ltd. (Langton, 1943). In the USA, it first appeared as Aladdinite in 1919. During the 1920's, casein plastics were produced under the tradenames Karolith, Kyloid, Erinoid (Kaufman, 1963) and as India (Langton, 1943). The Button Corporation of America became concerned with the new material and thus assumed control of the Kyloid Company in 1929. The American Plastics Corporation was formed from the combination of the Erinoid Company of America and the Karolith Corporation of America and other firms in 1931 and used the trade-name of Ameroid (Kaufman, 1963). Other trade-marks for casein plastics can be identified by the prefix lac meaning milk (Hillman, 1986).

The climate in the USA limited its use to buttons, buckles and other small objects (Langton, 1943; Kaufman, 1963). It has been used in England to produce buttons, cutlery, combs, spectacle, umbrella handles, fancy goods and electrical units (Yarsley, 1943). In the early years of the twentieth century, it was utilized to produce beads, buckles, poker chips, cigarette holders, boxes and bracelets (Hillman, 1986). It was also used to produce knitting pins, pens and barrels for propelling pencils. A casein fibre was produced in Italy between the two wars which was known as Lanital. Widespread development of synthetic polymers over the past thiry years has sharply decreased the use of casein plastics, but it is still used for buttons, buckles, slides and hair pins. The largest user of casein is the button industry. Casein which has not been treated with formaldehyde is utilized as an adhesive, as a stabilizers for rubber latex and for paper coatings and uses in textile manufacture (Brydson, 1975).

Poly (methyl methacrylate)

History

The history of acrylic polymers began in 1873 when Caspary and Tollens first synthesized methyl, ethyl and allyl acrylate and found that the allyl acrylate polymerized. Methyl acrylate was polymerized by Kahlbaum in 1880, at the same date, it was discovered that methacrylic acid and several of its derivitives polymerize. Otto Rohm researched acrylic polymers and in 1901, published the results of his doctoral dissertation. In 1927, Rohm and his collegue Haas produced poly (methyl acrylate) at their plant in Darmstadt, Germany. It was marketed under the names Acryloid and Plexigum and the gummy material was used for coatings. It was not suitable for producing objects. R. Hill developed poly (methyl methacrylate) (1930) a polymer which had rigid, transparent properties and it was predicted to be of interest to the aircraft industry as glazing material. Early methacrylate esters were produced by dehydration of hydroxyisobutyric esters which were too expensive to be used for commercial processes. A major breakthrough occurred in 1932, when J. W. C. Crawford (ICI) developed a new synthesis of the monomer which utilized acetone, hydrocyanic acid, methanol and sulphuric acid. These materials were inexpensive and easily obtained and this process is still used today worldwide with only minor changes. It was used extensively for aircraft glazing during the Second World War and has found many other uses (Brydson, 1975).

Chemical structure

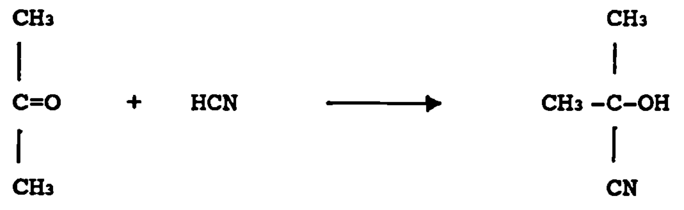
Acrylic polymers are structural derivitives of acrylic acid (Figure 9.7a). Although poly (methyl methacrylate) (Figure 9.7b) is the best known polymer in commercial use, other families of interest include a variety of derivitive polyacrylates (Figure 9.7c) and polymethacrylates (Figure 9.7d). Polyacrylonitrile

(Figure 9.7e) is a widely used polymer for fibre production (Brydson, 1975).

Production method

Synthesis of methyl methacrylate monomer

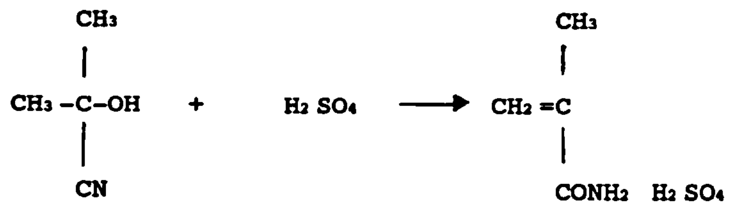
The chemical process which was developed by Crawford is outlined below (Brydson, 1975). The initial step is to add the acetone and the hydrogen cyanide which produces acetone cyanohydrin (Equation 9.5).



$$\overset{CH_3}{\underset{CH_3}{C}}{=}O + HCN \longrightarrow CH_3-\overset{CH_3}{\underset{CN}{C}}-OH$$

(Equation 9.5)

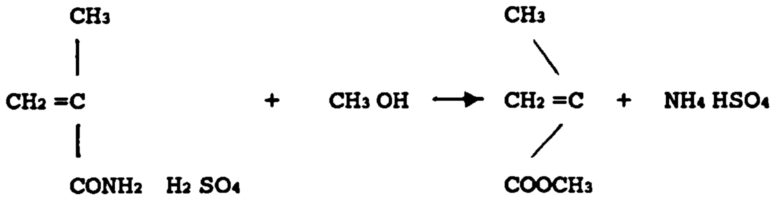
The acetone cyanohydrin is next reacted with 98% sulphuric acid in a cooled hydrolysis container to give methacrylamide sulphate (Equation 9.6).



$$CH_3-\overset{CH_3}{\underset{CN}{C}}-OH + H_2SO_4 \longrightarrow CH_2{=}\overset{CH_3}{\underset{CONH_2\ H_2SO_4}{C}}$$

(Equation 9.6)

The mixture is then reacted with methanol in an esterification vessel without isolation of the sulphate to produce the monomer (Equation 9.7). Inhibitors to prevent polymerization may be added during this step.



$$CH_2{=}C(CH_3)CONH_2\ H_2SO_4 + CH_3OH \longrightarrow CH_2{=}C(CH_3)COOCH_3 + NH_4HSO_4$$

(Equation 9.7)

The esterified material is introduced into a stripping column to remove the residual sulphuric acid, ammonium bisulphate and some of the excess water from the methyl methacrylate, methanol and additional water. The monomer is recovered and purified by additional distillation (Brydson, 1975).

Polymerization

Methyl methacrylate polymerizes easily and the solution should be inhibited to prevent polymerization during storage. An inhibitor such as hydroquinone is added in a concentration of up to 0.10% to the monomer. This is removed before use by distillation under reduced pressure or by treating the monomer with an alkaline solution (Brydson, 1975). For commercial production, a free radical mechanism with peroxides or azo-diisobutyronitrile at temperatures up to 100 °C are used. Methacrylate peroxides are produced in a side reaction if polymerization is carried out in the presence of oxygen. This affects the rate of reaction and the nature of the products. Polymerization should be carried out in a full cell or under an inert gas to exclude oxygen. The rate of conversion accelerates after approximately 20% of the monomer has reacted. This phenomenon is known as the gel effect, the Tromsdorf effect or the autoacceleration effect (Brydson, 1975).

The bulk polymerization method is used on a wide scale to produce sheet polymer and is also used to make a certain amount of rods and tubes. There are several problems in production that must be taken into consideration in order to produce a satisfactory product. It is necessary for commercial success that the product is of even thickness and constant quality and that it contains no impurities or imperfections. Also, excess energy is created during the exothermic reaction and the polymerization rate increases during the course of the reaction. There is also approximately 20% shrinkage of the material after polymerization and the problem of oxygen must be considered (Brydson, 1975).

The first step is to make a 'prepolymer'. This step will decrease the shrinkage in the casting cell and limit the leakage from the cell. After the inhibitor is removed, the monomer is heated for eight minutes at 90 °C in the presence of 0.5% benzoyl peroxide, then returned to room temperature. Additives such as plasticizers, colouring matter and ultraviolet light stabilizers are then added if needed. The product is then filtered and can be stored, if necessary, in a refrigerator. The prepolymer syrup may be considered a solution of the polymer in the monomer. It is thought that the dissolved oxygen in the monomer is reduced by the heating step in the process. This step is difficult to control in large scale commercial situations and must be carefully monitered. Another method is to dissolve some of the polymer in the monomer with some peroxide which will achieve the same results as the preparation of a prepolymer (Brydson, 1975).

Poly (methyl methacrylate) sheet is produced using a casting cell which is made of two sheets of heat resistant polished glass. The glass plates are sealed with a hollow, tube made of rubber or plasticized poly (vinyl alcohol). The syrup is added to the cell making certain that the cell is completely filled. The unit is held together by spring loaded clamps or spring clips. This arrangement allows the glass sheets to come closer together as the material decreases in bulk during polymerization. Thus, the sheet will not have sink marks or voids. The use of rigid glass sheets and even pressure ensures a product of uniform thickness (Brydson, 1975).

The prepared cells are passed through a heating tunnel. The rate of polymerization is slow in the early stages as the temperature is kept at 40 °C. Thus, a rise in temperature due to the exothermic reaction or viscosity-chain termination will have a minor effect on the rate of reaction at this temperature. After 14 hours, most of the monomer has been converted and the cell is exposed to higher temperatures in the heating tunnel. The temperature is raised to approximately 97 °C during a period of one hour and then it is kept at 97 °C for one half an hour. The cell is allowed to cool and then the product is removed from the cell. It is then annealed by heating to 140 °C to decrease internal stress. The sheets are covered with paper attached with gelatine or a pressure sensitive adhesive to protect the surfaces. Large blocks of poly (methyl methacrylate) are difficult to produce because of the excess exothermic energy which builds up during polymerization. In such cases, the process is carried out inside a pressure vessel which elevates the boiling point of the monomer (Brydson, 1975).

Rods of poly (methyl methacrylate) are produced by filling vertical aluminium tubes with the syrup, and then placed in a water bath at 40 °C. As the material at the base of the tube polymerizes, it shrinks and the syrup nearer the top sinks down. The tube is filled from a chamber above. This process allows for shrinkage of the material during polymerization. Tubes are manufactured by placing a given amount of the syrup into a horizontal aluminium tube which is subsequently sealed. the tube is purged with nitrogen, rotated and the apparatus is heated. Polymerization of the material occurs on the wall of the hollow cylinder. The shrinkage problem is not critical and allows the plastic tube to be removed without difficulty (Brydson, 1975).

The average molecular weight of poly (methyl methacrylate) produced by bulk polymerization is too large for the material to have flow properties suitable for applications such injection moulding. The molecular weight can be decreased by mechanical grinding, however, it is not commercially viable the additional cost of mechanical scission increases the price of the already expensive bulk polymerization process. The technique of suspension polymerization was developed to produce material with lower molecular weight. There is no difficulty with excess exothermic energy, thus the process is rapid. The only problems are the control of particle size and agglomeration of the beads. Factors such as the shape and size of the reaction vessel, type and speed of agitation and the suspending agents and protective colloids used control particle size. Talc, magnesium carbonate and aluminium oxide are common suspending agents and poly (vinyl alcohol) and sodium polymethacrylate are frequently utilized protective colloids (Brydson, 1975).

The suspension polymerization process has been described as follows (Brydson, 1975): methylmethacrylate and water in a ratio of one to two are combined with 0.2% benzoyl peroxide as a catalyst and agitated. Eight to 18 grams of Magnesium carbonate in a quantity of eight to 18 grams per litre of reactants is then introduced. A larger quantity is used to produce smaller beads and the use of a smaller amount gives larger particle sizes. The reaction temperature rises from an initial 80 °C to 120 °C due to the excess energy produced in the reaction. Sulphuric acid is added after polymerization is complete (usually after one hour) to eliminate the magnesium carbonate. The beads are then collected, washed thoroughly and dried. The reaction process is sometimes modified by the addition of certain materials. The pH of the reaction may controlled by the addition of a buffer such as sodium hydrogen phosphate. The molecular weight may be modified by chain transfer agents which include lauryl mercaptan or trichloroethylene. Stearic acid and sodium lauryl sulphate may also be added as a lubricant and an emulsifier respectively.

Processing methods for poly (methyl methacrylate) and additives

Acrylic plastics may be processed in the melt phase by injection moulding and extrusion, by mechanical manipulation of sheet, rod and tube, and with monomer-polymer doughs (Brydson, 1975). Production of objects using injection moulding or extrusion is successful as the shrinkage observed after moulding is very low. However, the polymer beads must be stored in dry conditions as the beads absorb water up to 0.3%. The water vapourizes in the heating cylinders creating bubbles and subsequently, a frothy appearance. Also, the equipment used for extrusion or injection moulding must be capable of producing high pressures because the melt viscosity of poly (methyl methacrylate) at the processing temperatures are much higher than those of polystyrene, polyethylene and plasticized poly (vinyl chloride). Also, dependable temperature control throughout the process is vital for consistent quality. Products are frequently made by mechanical manipulation of sheet, rod and tube acrylics using drills, circular saws and bandsaws. It is important not to overheat the plastic. Various forms of cementing have been described as the material cannot be welded together easily. The pieces may be attached by treating the surfaces to be joined with chloroform or by a solution of polymer in a solvent. The use of a monomer-polymer solution has been found to be the most effective technique especially if it is necessary to gap fill. The cement usually contains a photocatalyst which results in polymerization activated by ultraviolet light or a promoter which reacts upon the addition of peroxide to result in rapid polymerization. The manufacture of dentures has been the primary use for monomer and polymer doughs. A plaster of Paris mould is made. The monomer is combined with the polymer powder and an initiator. This results in a dough which is put into the mould. The mould is clamped closed and heated for approximately one half hour and then cooled and opened (Brydson, 1975).

A variety of additives may be incorporated into poly (methyl methacrylate). THe most important are dyes and pigments which must be chosen carefully. They should be stable during processing and use. They should not interfere with polymerization during casting and should exhibit resistance to weathering. Plasticizers are sometimes utilized. Dibutyl phthalate is often used at a composition of approximately 5% It increases the melt properties when used with moulding powders, but impairs the mechanical properties of the object. The inclusion of small amounts of ultraviolet light absorbers such as phenyl salicylate, 2:4-dihydroxy benzophenone, resorcinol monobenzoate, methyl salicylate or stilbene increases the protection against ultraviolet radiation (Brydson, 1975).

Trade names and applications

Poly (methyl methacrylate) in sheet form is marketed under the names Perspex by ICI, Plexiglass by Rohm and Haas, USA and Oroglass by Rohm and Haas, GmbH, Germany. Commercial moulding powders are Diakon by ICI, Acry-ace by Fudow Chemical Co, Japan, Lucite by DuPont, USA and Vedril by Montecatini, Italy (Brydson, 1975).

Figure 9.1 (a) Structure of anhydro-beta-glucose unit (b) structure of cellulose (Yarsley et al., 1964).

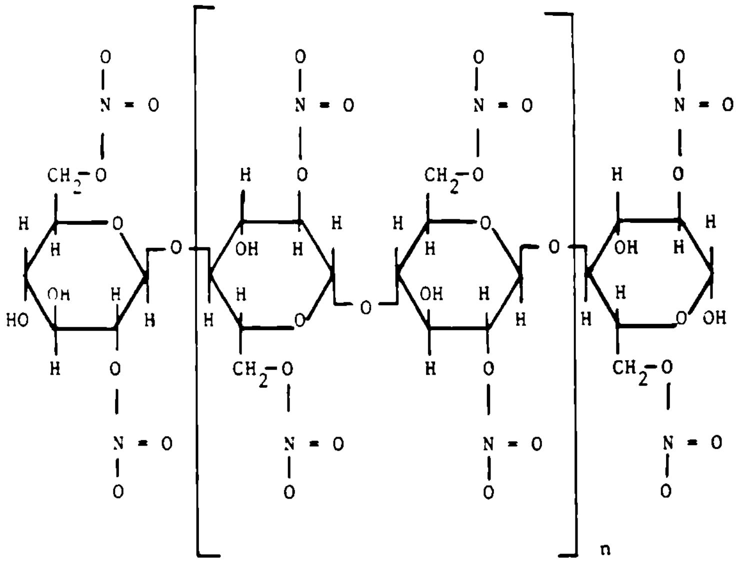


Figure 9.2 Structure of cellulose nitrate.

Figure 9.3 Structure of camphor (Bean, 1973).

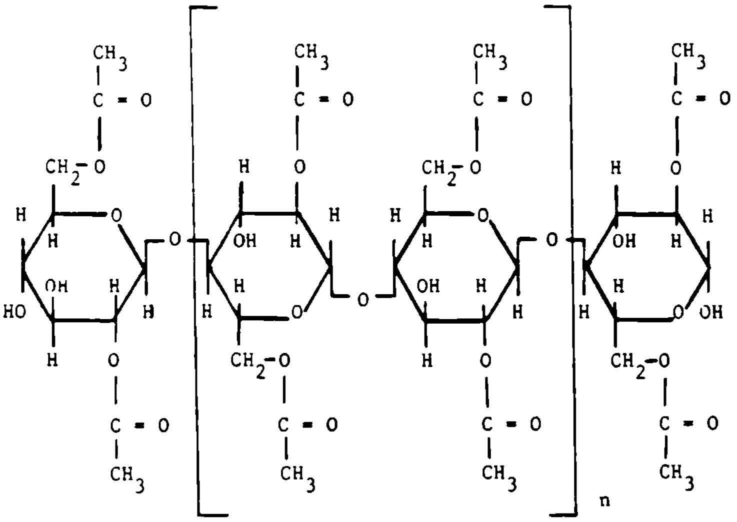


Figure 9.4 Structure of cellulose acetate.

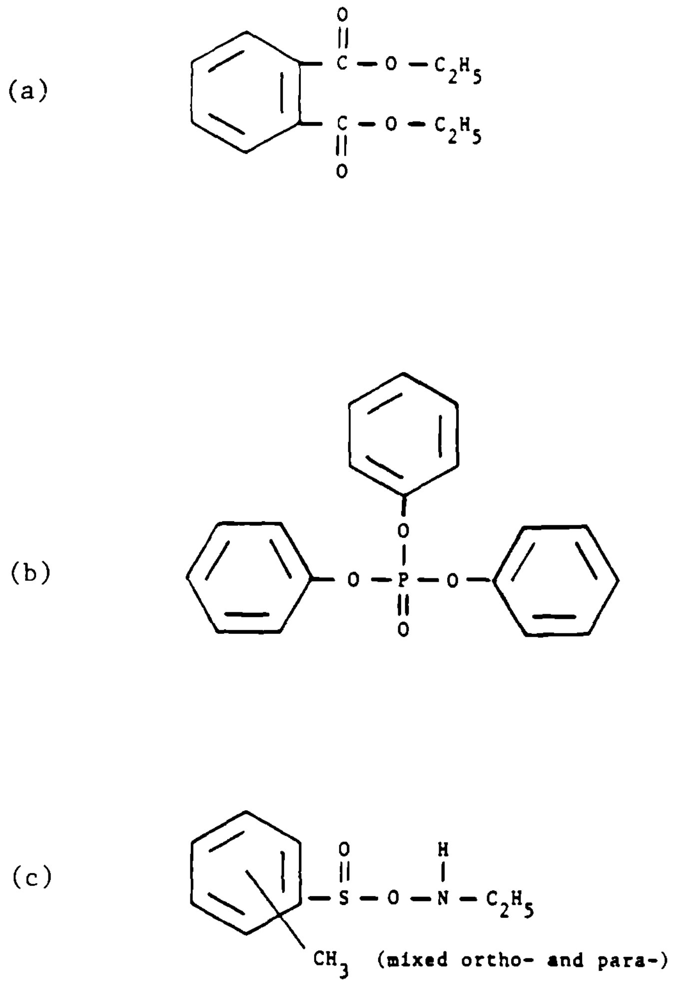


Figure 9.5 Structure of three important plasticizers of cellulose acetate, (a) diethyl phthalate (b) triphenyl phosphate and (c) N-ethyl o,p-toluenesulphonamide.

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Figure 9.6 Structure of (a) omega amino acid and (b) an alpha amino acid (Brydson, 1975).

Figure 9.7 Structure of (a) acrylic acid, (b) poly (methyl methacrylate), (c) polyacrylates, (d) polymethacrylates and (e) polyacrylonitrile (Brydson, 1975).

TABLE 9.1

Degree of nitration and typical usage for cellulose nitrate (Yarsley, et al., 1964)

Degree of nitration	Nitrogen content (%)	Typical usage
Cellulose mononitrate	6.76 (theor.)	Not made commercially
Cellulose dinitrate	11.11 (theor.)	
	10.7 - 11.1	Plastics, lacquers
	11.2 - 12.3	Lacquers
	12.4 - 13.5	Cordite
Cellulose trinitrate	14.14 (theor.)	Not made commercially

TABLE 9.2

Influence of degree of substitution on the properties and uses of cellulose acetate (Brydson, 1975)

Degree of substitution	Acetyl content (% - $COCH_3$	Acetic acid yield (%)	Solubility	Uses
2.2 - 2.3	36.5 - 38.0	52.1 - 54.3	soluble in acetone	injection moulding
2.3 - 2.4	38.0 - 39.5	54.3 - 56.4		film
2.4 - 2.6	39.5 - 41.5	56.4 - 59.3		lacquers
2.8 - 3.0	42.5 - 44.0	60.7 - 62.8	insoluble in acetone, soluble in chloroform	triacetate film and fibre

TABLE 9.3

Plasticizers of cellulose acetate

(Yarsley et al., 1964)

Plasticizer	Molecular Weight	Boiling point (°C)	Maximum Permanent Compatibility (1)
Triethyl acetylcitrate	318	127/0.7 mm	--
Butyl phthalyl butyl glycollate	336	219/5 mm	50
Butyl stearate	340	360	--
Dibutyl phthalate	278	325	30
Dibutyl sebacate	314	345	<10
Diethyl phthalate	222	295	30
Di(2-ethoxyethyl) phthalate	310	345	25
Diethyl sebacate	258	308	10
Dimethyl phthalate	194	285	15
Di(2-methoxyethyl) phthalate	282	209-261/20 mm	25
Dioctyl phthalate	390	229/5 mm	--
Ethyl phthalyl ethyl glycollate	280	190/5 mm	40
Methyl phthalyl ethyl glycollate	266	189/5 mm	40
N-ethyl o- and p-toluene sulphonamides	199	--	35
Triacetin	218	259	12
Tributyl phosphate	266	289	17
Triolyl phosphate	368	295/13 mm	20
Triphenyl phosphate	326	245/11 mm	30
Tripropionin	260	177-182/20 mm	35

1. Expressed as parts of plasticiser per 100 parts of cellulose acetate (56.5% acetic acid).

CHAPTER 10 INTERPRETATION OF REFERENCE PLASTIC SPECTRA

Description of reference materials

The unknown plastic samples were identified by comparison of their spectra with those of reference material, and the absorption frequencies of the major bands with those given in the literature. The standard materials were obtained from chemical companies and in some cases, samples of commercial plastics were also used. Spectra were also obtained from several known plasticizers which were obtained from chemical companies (see appendix). The commercial spectral atlases were used to confirm the validity of the reference spectra (Hummel, 1978; Chicago Society of Coatings Technology, 1980; Hanson, 1987). All of the spectra were collected using diffuse reflectance spectroscopy unless noted otherwise. The band assignments given in this chapter are summarized in Tables 11.4 - 11.9.

A spectrum was obtained of cellulose powder from Whatman. A cellulose nitrate sample of Millipore SC (8 micron) was used as one standard and a sample of fresh scrap cellulose nitrate was obtained from the Wardle-Storey factory in Brantham, Essex. A spectrum of camphor was also obtained of material marketed by P. Boulton, dispensing chemist.

The cellulose acetate systems were identified by comparison with two types of chemical cellulose acetate produced by Aldrich; cellulose triacetate and cellulose acetate, acetyl content 39.8%. An example of commercial sheet triacetate, Bexfilm, was also used. Transmission spectra were also obtained of three known plasticizers of cellulose acetate; o,p-toluenesulphonamide (Ketjenflex, Monsanto), diethyl phthalate (Aldrich) and triphenyl phosphate (Aldrich).

The two spectra used to identify casein plastics were spectra of casein which has not been masticated or formalized. The chemical casein was obtained from BDH and probably precipitated by rennin. The second sample was prepared by R. White of the National Gallery by acid precipitation in the presence of lime.

The identification of poly (methyl methacrylate) plastics was accomplished by comparison of the spectra with a transmission spectrum of poly (methyl methacrylate) obtained from Aldrich and two diffuse reflectance spectra of commercial acrylic plastics, one of Visijar Tuckers Perspex and one of Plexiglass given by the Conservation Analytical Laboratory (Smithsonian Institution, USA).

Interpretation of reference spectra

Cellulose nitrate

The spectrum of cellulose nitrate may be identified by absorption bands arising from the cellulose structure and the nitrate groups. The standard cellulose nitrate spectra (Millipore SC 8 micron; Wardle-Storey) are compared with that of cellulose powder in Figure 10.1. The broad absorption band which is centered at 3460 cm^{-1} which is due to the O-H stretching vibration. The extremely polar nature of the hydroxyl group results in hydrogen bonding with any molecules that are even slightly polar. Thus it is only possible to see the free O-H stretching absorption when examining the material in the vapour phase or in dilute solution in a non-polar solvent. The band observed in most examples is due to the O-H stretches of the hydrogen bonds. In certain rare cases, the free hydroxyl stretching mode can be observed in molecules where there is steric hindrance reduces or stops the hydrogen bonding. In the cellulose nitrate spectra (Figures 10.1b and 10.1c), the frequencies of the hydroxyl absorption (3447 cm^{-1} and 3442 cm^{-1}) are slightly higher than the range given in the literature for polymeric intermolecular bonds (3400 - 3200 cm^{-1})(Bellamy, 1974) and higher than the value observed for cellulose in Figure 10.1a (3358 cm^{-1}) and the range quoted in the literature (3347 cm^{-1} - 3324 cm^{-1})(Marrinan and Mann, 1954). Although it is difficult to make quantitative comparisons due to the effects of sample loading, the intensity of the O-H band relative to the carbon-hydrogen stretching absorptions and the ether linkage absorptions is much greater in the cellulose powder spectrum than in the cellulose nitrate spectra. The loss of intensity is probably caused by the loss of hydrogen bonding between the cellulose chains by the introduction of the nitrate groups and the plasticizer camphor. The increase in frequency may result from the hydrogen bonds which are thought to form between the camphor molecules and the free hydroxyl groups.

The most characteristic features in the spectrum are the absorption bands arising from the stretching of the N-O linkages in the nitrate groups. The literature (Brown, 1955) lists the range of values and the assignments for nitrate esters including cellulose nitrate and the values of the standard spectra are listed with the band assignments in Table 11.4. The first band is very strong and occurs in the region 1653 - 1629 cm^{-1} which results from the asymmetric N-O stretch in the nitrate group. Brown also observed that the value for polynitrates can range to

1667 cm^{-1}. The second band is also very intense and falls within the range 1285 - 1272 cm^{-1} and is assigned to the symmetric stretch of the N-O bond. The third intense band occurs from 872 to 841 cm^{-1} and is due to the N=O bond stretch in the nitrate ester. Brown also states that the range extends to 833 cm^{-1} in polynitrates. There are two bands of medium intensity which occur in the regions of 761 - 745 cm^{-1} and 710 - 689 cm^{-1} and are assigned to an out of plane deformation and a N-O bond bending mode respectively. The spectra of the cellulose nitrate samples have bands which correspond to these regions, but some of the frequencies are beyond the range stated in the literature. The value of the band at 1671 cm^{-1} in the spectrum of the Milipore sample is somewhat beyond the upper range for cellulose nitrate (1667 cm^{-1}) and the absorptions at 1288 cm^{-1} and 1286 cm^{-1} are slightly beyond the limit of 1285 cm^{-1}. However, the spectrum of cellulose nitrate has absorption bands at 846, 751 and 692 cm^{-1} which fall well within the ranges stated by Brown (1955). The deviations in the cellulose nitrate spectrum may be caused by differences in conformation of the samples, the resolution of the instrument and by degradation of the standard cellulose nitrate material.

A strong band occurs at 1748 cm^{-1} (Millipore) and 1732 cm^{-1} (Wardle-Storey) in the reference spectra of cellulose nitrate which has been identified as the carbonyl stretching frequency arising from the camphor. It corresponds to the band at 1735 cm-1 in spectra of cellulose nitrate plastic (Sirkis, 1982). Sirkis noted that the frequency of the carbonyl band of the camphor combined with the cellulose nitrate was slightly lower than the band in the spectrum of free camphor. This was also observed in this study. A diffuse reflectance spectrum of camphor gave a strong, sharp absorption band at 1757 cm^{-1}.

Cellulose acetate

Cellulose acetate plastics have an infrared spectrum which is characterized by absorptions of the hydroxyl groups and ether linkages of the glucose units in the cellulose and the ester linkages between the acetate groups and the cellulose. It is possible to see bands indicative of the plasticizer which do not occur in the unplasticized chemical cellulose acetate.

The three reference spectra include two of chemical cellulose acetate (Figures 10.2a and 10.2b) and one commercial sheet cellulose triacetate plastic (Figure 10.2c) which have certain bands in common which are characteristic of the cellulose acetate structure. The broad absorption band which ranges from 3499 - 3482 cm^{-1} is due to the O-H stretching modes which are similar in nature to the hydroxyl groups in cellulose nitrate plastic. The same behaviour is observed with a slightly higher frequency and much less relative intensity than polymeric intermolecular bonds and in cellulose and the probable causes are also the same. The presence of the acetate groups and the hydrogen bonding of the free hydroxyl group with the plasticizers reduce the hydrogen bonding between the cellulose chains.

There are bands present in all three spectra which are characteristic of C-H stretching modes due to the methyl functionalities in the acetate groups. The stronger absorption falls at 2959 cm^{-1} in all three cases and the less intense band ranges from 2892 - 2893 cm^{-1}. The ranges quoted in the literature for the methyl group are 2962 $\pm$ 10 cm^{-1} (asymmetrical stretch) and 2872 $\pm$ 10 cm^{-1}. The bands at 2959 cm^{-1} fall within the range, but the symmetrical stretch is 10 cm^{-1} beyond the limit of the standard values. This may be caused by the adjacent carbonyl group in the ester linkage, although the literature (Bellamy, 1975) states the presence of a carbonyl group linked to the methyl group does not result in very significant frequency shifts. It is possible that the absorption includes the weak tertiary C-H band which occurs at 2890 cm^{-1} and that it is not possible to resolve the bands. The C-H deformation bands in the reference spectra occur at 1433 - 1434 cm^{-1} and 1373 - 1374 cm^{-1} which falls within the range for the methyl group asymmetrical (1450 ± 20 cm^{-1}) and symmetrical (1380 - 1370 cm^{-1}) C-H deformations (Bellamy, 1975).

The cellulose acetate can also be characterized by the absorptions due to the ester linkage. There is an intense band which results from the C=O stretching mode and one or more bands in the region of 1250 - 1100 cm^{-1} which are caused by the carbon-oxygen single bond stretching absorption. The strong band which occurs in the standard spectra at 1758 - 1764 cm^{-1} is outside the range for most esters (1750 - 1730 cm^{-1}). The standard spectra contain a very intense, split absorption band which is centered at 1245 cm^{-1} which is characteristic for an acetate ester (1250 - 1230 cm^{-1})(Bellamy, 1975). There is a second, less intense band which is also due to the C-O stretch which has been observed to appear in the region 1060 - 1000 cm^{-1} (Bellamy, 1975). This peak would be impossible to see in cellulose acetate, because it falls in the region of the ether linkages in the glucose units. In the cellulose acetate spectra, the ether linkages form a broad band which is centered at 1065 cm^{-1} in the chemical cellulose triacetate spectrum (Figure 10.2b) and at 1087 cm^{-1} in the other two spectra (Figures 10.2a and 10.2c). The frequencies of the ether link in large ring systems is equivalent to values for open chain compounds (1150 - 1060 cm^{-1})(Bellamy, 1975).

There are two sharp bands in the regions 904 - 905 cm^{-1} and 604-605 cm^{-1} which appear in all three spectra. The former is unassigned, but the latter absorption has been described as a skeletal vibration of the acetate group which reported to occur at 605 cm^{-1} (Hummel, 1966) and 612 cm^{-1} (Thompson and Torkington, 1945).

The commercial cellulose acetate sheet contains plasticizers and other possible additives. It would be difficult to identify them from the diffuse reflectance spectrum. However, the absorption bands at 1591, 1490, 1189, 963, 782 and 760 cm^{-1} appear in the spectrum of the commercial cellulose triacetate (Figure 10.2c) which do not occur in the spectra of chemical cellulose acetate which are not plasticized (Figures 10.2a and 10.2b). The bands may be attributed to plasticizers of cellulose acetate (Figure 9.5). There is strong evidence in the spectrum for the presence of an aromatic compound. The aromatic ring is identified by the C-H stretching mode which results in sharp, weak bands near 3070 and 3030 cm^{-1} and four bands in the region 1650 - 1450 cm^{-1} which represent the skeletal ring breathing modes. In the spectrum of the commercial cellulose triacetate, there is a weak band at 3069 cm^{-1} which corresponds to the conjugated C-H stretching mode in an aromatic compound. The band expected at 3030 cm^{-1} is masked in this spectrum by the aliphatic C-H stretching vibrations.

The four bands resulting from skeletal breathing modes are actually two pairs which are degenerate in benzene and thus appear as two bands in the spectrum. When the ring is substituted, the bands split to form four bands. The first band at 1591 cm^{-1} in Figure 10.2c occurs within the range stated in the literature, 1625 - 1575 cm^{-1} and the band at 1490 cm^{-1} is in good agreement for values suggested for monosubstituted aromatics, 1510 - 1480 cm^{-1} (Bellamy, 1975). There are two other bands which are the pairs to the bands near 1600 and 1500 cm^{-1} which may be resent in aromatic compound, one in the region of

1600 - 1560 cm^{-1} and one in the area of 1450 cm^{-1}. The absorption band in the 1600 - 1560 cm^{-1} region is often not present or only appears as a weak shoulder on the band near 1600 cm^{-1} in the spectra of most compounds. The band at 1450 cm^{-1} is often masked by the C-H deformation modes which occur in the same region. In the commercial cellulose triacetate sheet spectrum (Figure 10.2c), there is a shoulder on the band at 1434 cm^{-1} which does not occur in the spectra of chemical cellulose acetate. The absorptions in the region of 1600 and 1500 cm^{-1} coupled with the bands in the area of 3060 - 3030 cm^{-1} are considered good evidence for the presence of an aromatic ring (Bellamy, 1975).

In addition, the presence of an aromatic compound is supported by several bands in the fingerprint region. There is a band of medium intensity which is split at 782 and 760 cm^{-1} which corresponds to the out of plane C-H bending mode for monosubstituted aromatic rings. The band is reported to fall in the 770 - 730 cm^{-1} region and has been observed to be split in the spectra of several compounds. The presence of a monosubstituted aromatic ring is furthur supported by the presence of a sharp band at 692 cm^{-1} in the commercial cellulose triacetate spectrum which falls in the region quoted in the literature (700 - 675 cm^{-1}) and is used to differentiate between monosubstituted and orthosubstituted aromatic systems (Bellamy, 1975). There are absorptions in this region in the chemical cellulose acetates, but they are very weak shoulders near 692 cm^{-1} (Figures 10.2a and 10.2b).

The band at 1189 cm^{-1} in the commercial cellulose triacetate spectrum occurs in the range 1242 - 1100 cm^{-1} which is characteristic of the P-O-C (aromatic) system asymmetric stretch in aromatic phosphates (Thomas and Chittenden, 1964). There is a second band in the region 996 - 905 cm^{-1} which is also due to the P-O-C aromatic system (Thomas and Chittenden, 1964). There is a strong band in the commercial cellulose triacetate spectrum at 963 cm^{-1} which coreesponds to the literature value.

Casein

Proteins, although they are complex structures, can be characterized by bands which correlate to the peptide bond. Other bands are due to the amino acid side chains and in more complex peptides and proteins, it is difficult to elucidate the structure further on the basis of the infrared spectrum. A broad absorption band in the region of 3450 - 3300 cm^{-1} occurs in protein spectra and is assigned to the N-H stretches in the molecule (Bellamy, 1975). It has been suggested that a band near 3300 cm^{-1} is due to the trans- type hydrogen bonding between chains and that a weaker bands near 3200 cm^{-1} is due to intramolecular bonds (Bellamy, 1975). In the reference casein spectrum (Casein I) (Figure 10.3a), there is a broad band centred at 3287 cm^{-1} which may be due to an overlapping of peaks in the region 3450 cm^{-1} - 3200 cm^{-1}. There is a weak band at approximately 3100 cm^{-1} which at one time was thought to be due to the intramolecular hydrogen bonds of the N-H groups, but is now assigned as an overtone of the amide II absorption.

The bands in the 1650 and the 1550 cm^{-1} regions are characteristic of the amide bonds which occur in all proteins and can be useful in differentiating between proteins and other classes of compounds. The band that absorbs in the 1650 cm^{-1} region is due to the C=O in the amide bond and is referred to as the amide I band (Bellamy, 1975). This occurs in the casein I spectrum (Figure 10.3a) at 1661 cm^{-1}. The value for alpha casein given in the literature (D'Esposito and Koenig, 1978) for the amide I band in the solid state is 1656 cm^{-1}. The absorption band in the area of 1550 cm^{-1} is referred to as the amide II band and is thought to be due to a N-H bending mode coupled with a C-N stretching mode. In the casein standard spectrum obtained in this study (Figure 10.3a), this absorption appears at 1546 cm^{-1}. The literature value for this absorption is 1538 cm^{-1} (D'Esposito and Koenig, 1978).

The casein I spectrum contains absorptions at 1450 and 1400 cm^{-1}. The literature lists two bands of medium intensity at 1448 and 1399 cm^{-1} which are assigned to C-H deformations of the methyl and methylene groups and the ionized carboxyl groups (COO-) respectively (D'Esposito and Koenig, 1978).

There is a band that occurs in the 1305 - 1200 cm^{-1} region in the secondary amides which is called the amide III band and is less intense than the amide I and II absorptions. The amide III band is also due to a coupling of the C-N stretching mode and a N-H bending vibration. In the casein I spectrum, there is a band at 1315 cm^{-1} and one at 1241 cm^{-1} which are both relatively weak and one or both may be indicative of a mixed vibration in this region. The literature lists two bands at 1312 and 1242 cm^{-1}

which are assigned to methylene deformations and the amide III absorption respectively (D'Esposito and Koenig, 1978).

The casein I spectrum exhibits bands at 1175, 1106 and 950 cm^{-1} which are difficult to assign but correspond somewhat to the values reported for solid alpha-casein, 1158, 1101 and 980 cm^{-1} (D'Esposito and Koenig, 1978). The rather significant variations in frequency are probably caused by the variations in conformation. There is an ill-defined absorption that is reported to occur in the region of 700 cm^{-1} that is considered characteristic of proteins and secondary amides and has been assigned to an out-of-plane N-H deformation (Bellamy, 1975). In the standard spectrum, there is a very weak peak centred at 703 cm^{-1}. The region between 800 - 400 cm^{-1} in the casein spectrum is a broad, ill-defined band which is caused by the overlapping of many absorptions due to overtones from the amide bonds and the vibrations of the amino acid side chains.

The second casein standard which was prepared by acid precipitation in the presence of lime (White) has a spectrum (Figure 10.3b) which is somewhat different than that of the casein I sample (Figure 10.3a). In the N-H stretching region, the broad band has three distinct peaks at 3495, 3399 and 3246 cm^{-1}. The bands at 3246 and 3399 cm^{-1} are characteristic of bonded N-H structure. The band at the higher frequency of 3495 is credited to free N-H stretches in secondary amides in the trans configuration. The differences between the two spectra in this region may be due to differences in hydrogen bonding and configuration resulting from the alternate method of preparation. The spectrum of casein II does not have the weak band in the region of 3080 cm^{-1} and has relatively weak bands at 2925 and 2854 cm^{-1} which indicate C-H stretches. There are two bands at 2228 and 2117 cm^{-1} which do not appear in the first standard spectrum.

The carboxyl absorption or the amide I band is also slightly different in the casein II spectrum. There is a strong absorption centred at 1621 cm^{-1}, a less intense band at 1684 cm-1 and a very weak band at 1501 cm^{-1} which is almost completely masked. The appearance of two bands in the carbonyl region may be indicative that the protein exists in two conformations, folded and the extended forms. This would affect the bonding. This splits the band and shifts the frequencies. The weak band at 1501 cm^{-1} is probably the amide II band. The band at 1621 cm^{-1}

may also be due to the presence of an ionized carboxyl group which have been observed to absorb in the region of 1600 cm^{-1} (Bellamy, 1975).

The remaining absorption bands are difficult to assign with certainty, but there are some similarities to the casein I spectrum. The absorption at 1431 cm^{-1} is a broad, ill-defined band which may relate to the doublet at 1450 and 1400 cm^{-1} in casein I and correlate to a nitrogen-hydrogen deformation mode. There is a band at 1235 cm^{-1} which has a parallel in the casein I spectrum at 1241 cm^{-1} which may be the result of a coupled N-H bending mode and a carbon-nitrogen stretching vibration. The band that absorbs at 1099 cm^{-1} in casein II may correspond to the band at 1106 cm^{-1} in casein I, however, the casein II absorption is much more intense in relation to the other bands than the band at 1106 cm^{-1}. In the casein II spectrum, there are weak absorptions at 1007, 958, 869 and a very weak band at approximately 700 cm^{-1} which may be due to a number of factors either by the side chains or deformations of the peptide bonds. The band around 700 cm^{-1} is indicative of and out of plane N-H deformation which is characteristic of proteins, but it is extremely weak. Unlike the casein I spectrum, the region between

700 and 400 cm^{-1} is not a broad, ill-defined band. This region has three distinct bands at 667, 592 and 433 cm^{-1}, but it is impossible to assign these bands.

Poly (methyl methacrylate)

Unlike the natural polymers such as proteins, acrylic plastics are composed of uniform monomers and it is possible to interprete the spectra more clearly. The structure of the poly (methyl methacrylate) unit is shown in Figure 9.7. The absorption bands are due to the C-H stretching and deformation vibrations and the stretching modes of the ester linkages.

The transmission spectrum of the secondary standard poly (methyl methacrylate) (Figure 10.4) was compared to the plexiglass (Figure 10.5a) and the perspex (Figure 10.5b) sample spectra and no additional bands appear in the spectra of the commercial materials. In these examples, the additives are not present in sufficient quantities in the diffuse reflectance spectrum. The diffuse reflectance spectrum of the secondary standard poly (methyl methacrylate) was somewhat distorted, most probably due to the fact that the sample was not finely enough ground. The baseline in the transmission spectrum is slanted upwards which is due to the KBr cell whereas the diffuse reflectance spectra slant downwards which may be caused by the influence of the silicon carbide paper. The spectra of the commercial products are very similar to the transmission spectrum. There are differences in relative intensities, the most striking being the increased intensities of the C-H stretching absorptions in the diffuse reflectance spectra. This is caused by the sample overloading effects discussed in Chapter 3. The resolution of the transmission spectrum is slightly better. A doublet is apparent at 1450 and 1436 cm^{-1} which appears as a single band at 1448 cm^{-1} in the perspex spectrum (Figure 10.5b) and at 1450 cm^{-1} in the plexiglass spectrum (Figure 10.5a). A weak band is observed in the transmission spectrum of the secondary standard at 703 cm^{-1} which does not appear in the spectra of the commercial products which may be due to residual solvent used to make the thin film.

The standard spectra have three absorptions in the C-H stretching region. The frequency values range from 2995 - 2997 cm^{-1}, 2951 - 2952 cm^{-1} and 2843 - 2844 cm^{-1}. The values of the latter two bands fall within the ranges for the carbon-hydrogen stretches given in the literature (Bellamy, 1975) for the methyl group (2962 and 2872 + 10 cm^{-1}) and for the methylene groups (2926 and

2853 ± 10 cm^{-1}). However, the bands at 2872 and 2926 cm^{-1} are not evident. The band in the 2995 - 2997 cm^{-1} region is also due to a C-H stretching mode. The values quoted above have been obtained from measurements of unstrained hydrocarbons where the atoms adjacent to the carbon are also carbon atoms. The presence of electronegative atoms attached to the carbon cause a shift in the frequency (Bellamy, 1975). The band in the 2995 - 2997 cm^{-1} region is most probably due to the C-H stretching in the methyl group that is adjacent to the oxygen atom in the ester linkage. McKean et al. (1973) obtained values of 3010 (s) and 2976 cm^{-1} (a) for the methyl group which is adjacent to the single bonded oxygen atom in acetate group where a and s refer to the skeletal plane of the molecule.

The region between 1485 and 1370 cm^{-1} is characteristic of the C-H deformation frequencies. The frequency values for the standard spectra are 1479 - 1484 cm^{-1}, 1448 - 1450 cm^{-1} and 1386 - 1389 cm^{-1}. The transmission spectrum has an extra band at 1436 cm^{-1}. There is a shoulder on the peak in in the region 1386 - 1389 cm^{-1} in all three spectra. The range for the asymmetrical C-H deformation in a methyl group is 1450 + 20 cm^{-1} and the C-H bending resulting from a methylene group is 1465 ± 20 cm^{-1}.

Variations greater than ± 20 cm^{-1} are very unusual except when there is a strongly electronegative atom adjacent to the carbon atom. The range for the symmetrical C-H deformation is 1380 - 1370 cm^{-1} (Bellamy, 1975). Also, it is very difficult to differentiate between the bands in the 1460 cm^{-1} region. The absorption bands in the reference spectra regions 1479 - 1484 and 1448 - 1450 cm^{-1} in the reference spectra fall within the ranges given in the literature. The second band which is found at 1436 cm^{-1} in the transmission spectrum may be indicative of the second type of methyl group in the structure. The frequency values for the symmetrical deformation in the methyl group are higher than those given in the literature, (1380 - 1370 cm^{-1}). This range is fairly consistant for methyl groups which are adjacent to carbon atoms and the frequency can be affected by the presence of electronegative groups in adjacent positions. The band in the region of 1386 - 1389 cm^{-1} with the shoulder may also be indicative of the two types of methyl groups present in the poly (methyl methacrylate) structure.

The poly (methyl methacrylate) can also be distinguished by the presence of absorptions due to the ester linkage. Esters normally have two characteristic bands which are due to the C=O and the C-O bonds in the ester linkage. The frequencies of the carbonyl band in the samples range from 1730 to 1734 cm^{-1} which fit into the range of saturated esters given in the literature (1750 - 1730 cm^{-1}). Esters are characterized by a second band in the region 1200 - 1100 cm^{-1} which is due to the carbon-oxygen single bond stretch. The spectra of the poly (methyl methacrylates) have a common pattern of two bands which are split at 1269 - 1273 cm^{-1} and 1241 - 1243 cm^{-1} and at 1193 - 1194 cm^{-1} and 1150 - 1154 cm^{-1}. The literature indicates that acrylates give two strong bands in the approximate regions of 1310 - 1250 cm^{-1} and 1200 - 1100 cm^{-1} (Colthup, 1950). Although no band assignments are given, the frequency values 1282, 1235, 1170 and 1149 cm^{-1} are given as characteristic for the poly (methyl methacrylate) spectrum (Urbanski et al., 1977).

The standard spectra have a characteristic fingerprint in the region 1065 - 754 cm^{-1} which may be useful in the identification of poly (methyl methacrylate). A band appears as a shoulder on the ester linkage band at 1065 cm^{-1}. In the transmission spectrum of the secondary standard poly(methyl methacrylate), a doublet occurs at 980 and 967 cm^{-1} which appears as a band in the region of 992 - 991 cm^{-1} with a weak shoulder in the diffuse reflectance spectra of the commercial material. A weak band occurs is the area of 913 cm^{-1} in all three spectra. Also, a band falls at 843 cm^{-1} with very weak shoulders around 811 and 827 cm^{-1}. A strong band occurs at 754 cm^{-1} in the diffuse reflectance spectra and at 737 cm^{-1} with a weak shoulder in the transmission spectrum. This band corresponds to the band at 749 cm^{-1} which has been described as characteristic for the poly (methyl methacrylate) spectrum (Urbanski et al., 1977). There is a broad weak band centered at 485 - 482 cm^{-1} in all three. The Visijar Perspex spectrum contains a series of weak bands which are not present in the other spectra from 650 to 485 cm^{-1} which may result from the presence of additives.

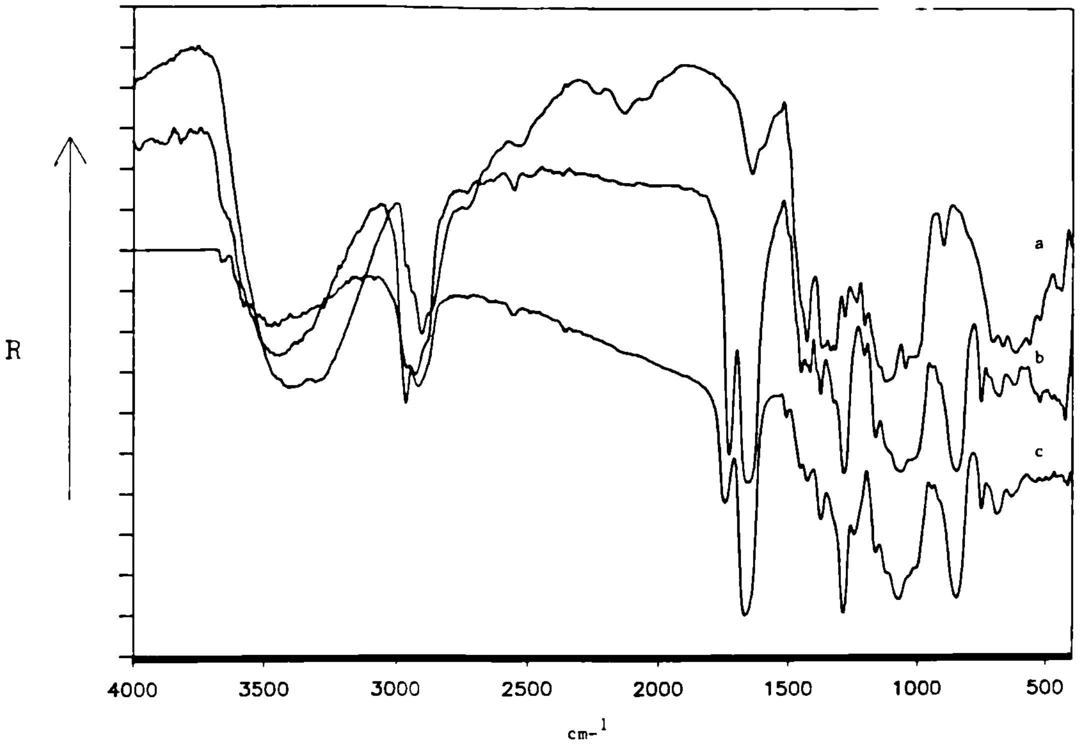

Figure 10.1 Diffuse reflectance FT-IR spectra of (a) cellulose powder, (b) cellulose nitrate plastic (Wardle Storey) and (c) cellulose nitrate plastic (Millipore).

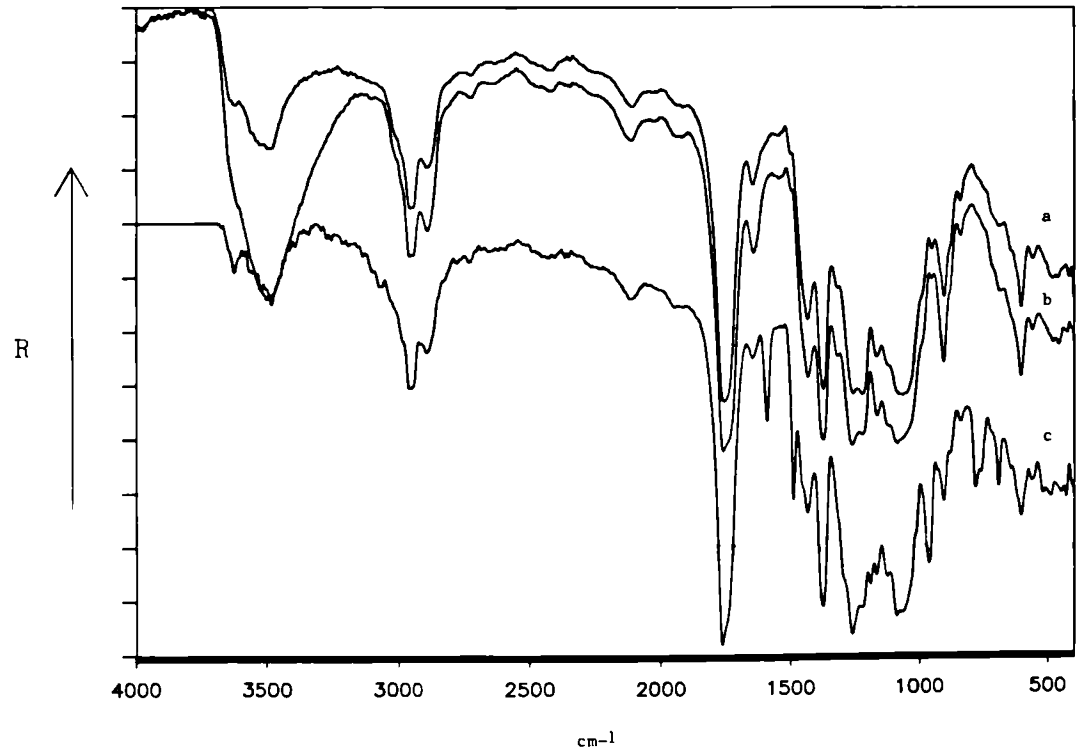

Figure 10.2 Diffuse reflectance FT-IR spectra of (a) chemical cellulose diacetate (acetyl content 39.8%), (b) chemical cellulose triacetate and (c) commercial sheet cellulose triacetate (Bexfilm).

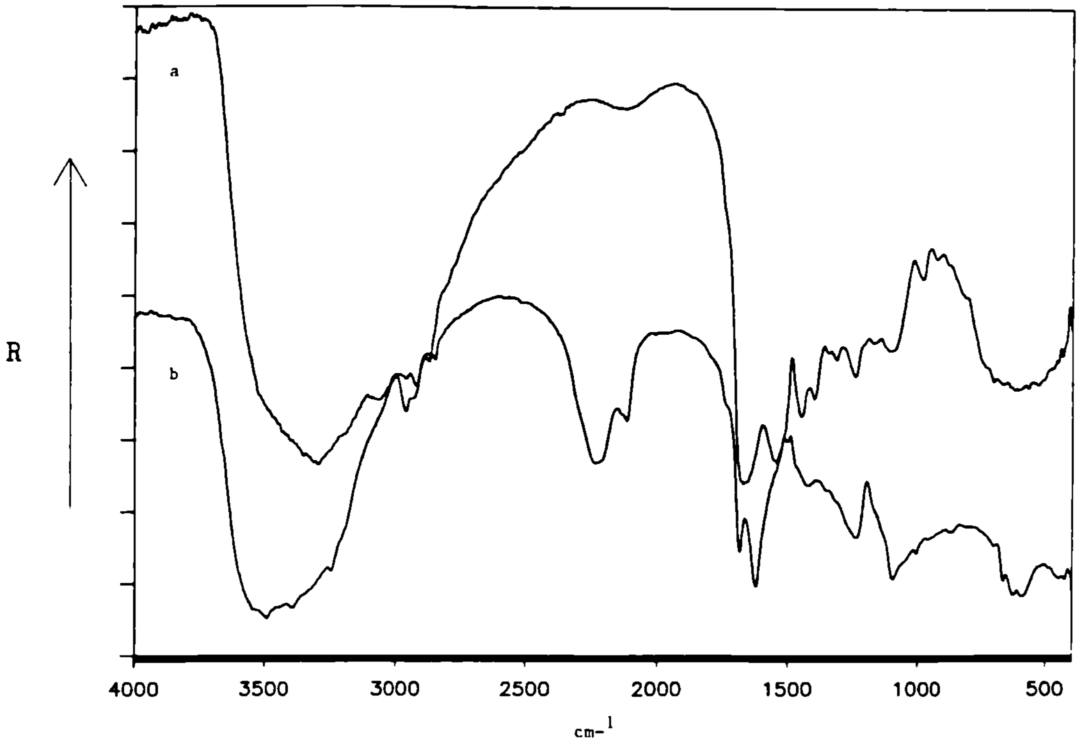

Figure 10.3 Diffuse reflectance FT-IR spectra of (a) commercial casein (BDH) and (b) casein prepared by acid precipitation in the presence of lime.

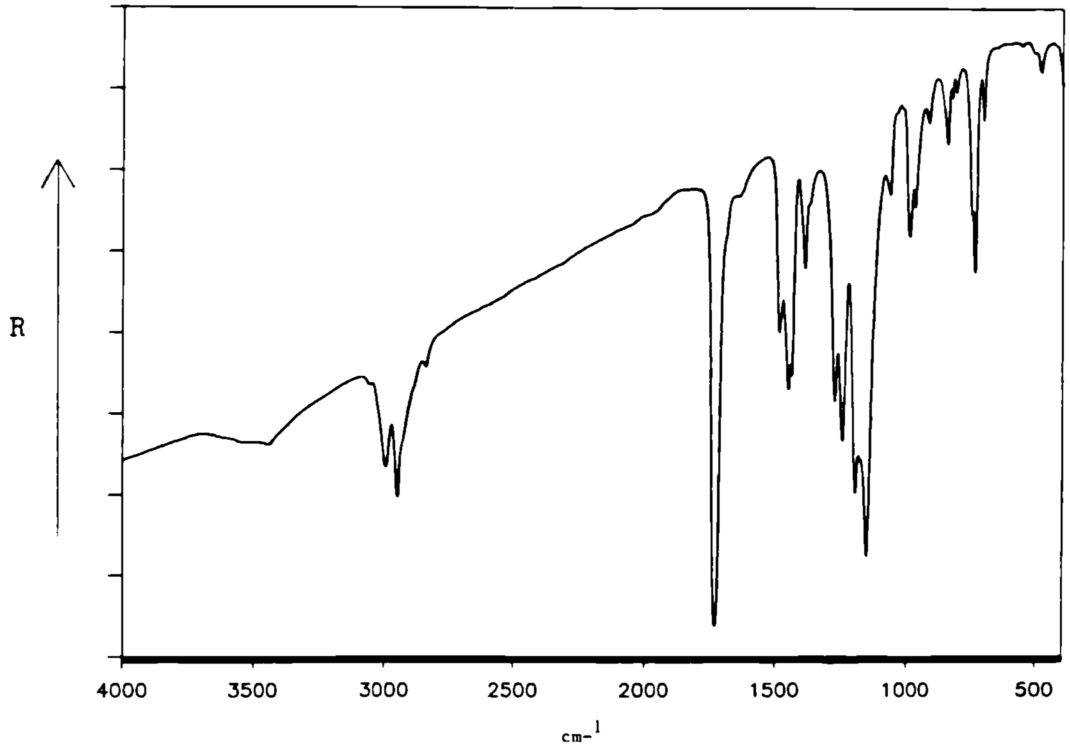

Figure 10.4 Transmission FT-IR spectrum of secondary standard poly(methyl methacrylate).

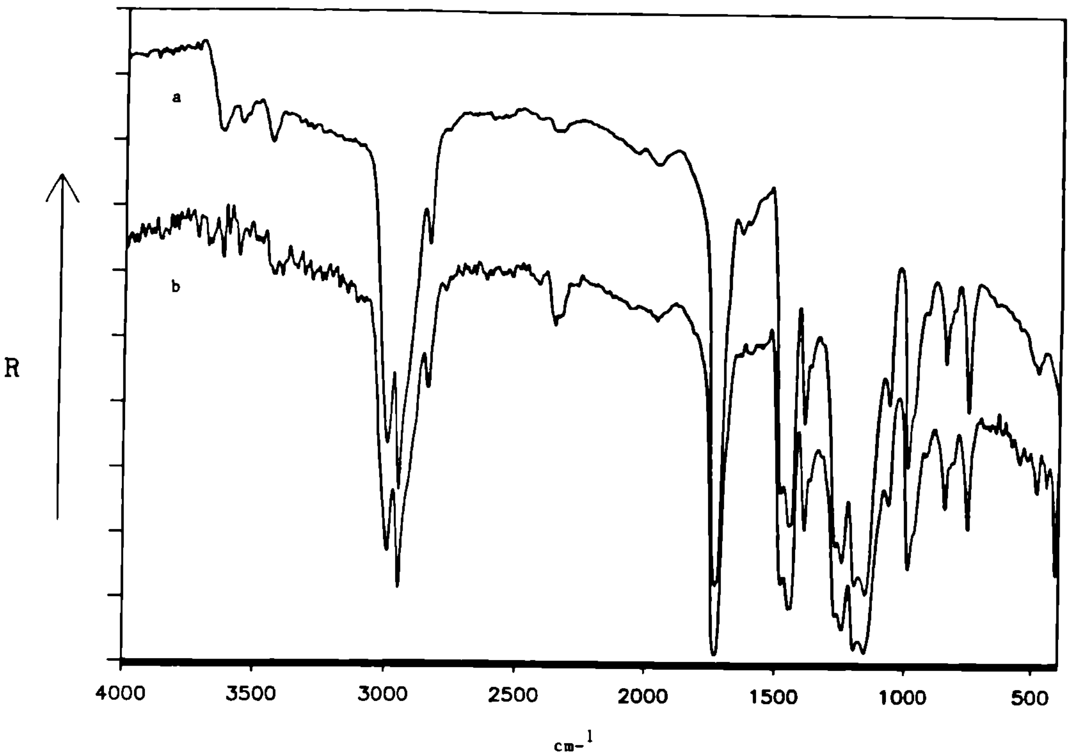

Figure 10.5 Diffuse reflectance FT-IR spectra of (a) commercial sheet "plexiglass" and (b) Visijar Tucker perspex.

CHAPTER 11 IDENTIFICATION OF SCIENCE MUSEUM, VESTRY HOUSE MUSEUM AND TATE GALLERY SAMPLES

Description of samples

Science Museum samples

Six objects from the collection of Parkesine (cellulose nitrate plastic) which were given to the Science Museum by Alexander Parkes in 1934 were sampled using silicon carbide paper. The objects chosen for analysis exhibited no signs of deterioration. There was no exudate visible on the surface and no deformation in shape. The specimens (Science Museum # 1937-30) included a lump of crude Parkesine (#1) (1855-1868). a green marbled door handle (#8) (1855-1868), a billiard ball (#7), and a set of three disks (#3)(1865). The yellow and green disks were stamped with the patent and the green, brown and red marbled one was not.

Vestry House Museum samples

In contrast to the samples taken from the Science Museum, the objects chosen for analysis from the Vestry House Museum were in an advanced state of degradation. Several samples were taken from a hand mirror frame (DB 30.9.65/46) which had broken apart. The plastic was crizzled and cracked and there was a strong odour of camphor given off when the storage box was opened.

Also, the sweat was observed to react with the tissue paper in the box. The mirror frame was composed of an amber coloured plastic on which there was a thin layer of blue and a thicker layer of green plastic on either side. The amber material had discoloured to light yellow. The blue plastic changed to a dark green colour. As the object was severely deteriorated, small samples of each of the three plastics was obtained in addition to the sample removed by silicon carbide paper. An abrasive paper sample was taken from a light green hairbrush (DB 30.9.65/73) which was marked with the Halex trademark and had beads of 'sweat' visible on the surface. A sample of the sweat was collected by rubbing the surface with a cotton swab. A silicon carbide paper sample was taken from the rim of a cylindrical box (DB 30.9.65/97).

Tate Gallery samples

Gabo sculpture samples

Diffuse reflectance spectroscopy was used to identify the polymer system used in a number of sculptures executed in plastic by Naum Gabo located at the Tate Gallery. Several of these sculptures are displaying signs of degradation including distortion and the presence of an exudate or 'sweat' on the surface. The pieces need urgent conservation and the first step was to identify the materials. It was thought that the first piece which was degrading was constructed of cellulose nitrate which is known to be unstable. Initial analysis (Martin, 1987 unpublished results) revealed that the degrading polymer system was in fact cellulose acetate. Thus, the identification of the plastics became an urgent first step (Pullen and Heuman, 1988). A survey of the the sculptures was undertaken using small circles of a finer grade silicon carbide paper to minimize the amount of sample removed. The samples were taken by the conservator by attaching the silicon carbide paper to a wooden dowel and rubbing against the area to be sampled. The sampling marks were visible only under a microscope (Heuman, personal communication). The samples were then taken to the Victoria and Albert Museum to be analysed as soon as possible after sampling. The details of the samples including the works from which they were taken are listed in Table 11.1.

Other Gabo samples

In addition to the pieces of sculpture, several samples plastic from Gabo's workshop were provided for analysis by the Gabo family (Pullen and Heuman, 1988) (Table 11.2). The plastics were subjected to artifical ageing and spectra were obtained of both the unaged and the artificially aged samples. Samples of the exudate or 'sweat' which appeared on the surface of the samples after ageing were also examined. Surface exudate samples from two sculptures were also analysed (Table 11.3). The 'sweat' samples were removed from the surface by using a cotton wool swab and then the swab was rubbed against a potassium bromide cell. The spectrum is obtained by transmission spectroscopy. A sample of adhesive from one of the sculptures was examined using diffuse reflectance spectroscopy. The sample details are presented in Tables 11.2 and 11.3.

Interpretation of sample spectra

Science Museum samples

The six sample spectra from the Parkesine objects all exhibit bands which have been described as characteristic of cellulose nitrate (Figure 11.1), namely in the regions of 1667 - 1693 cm^{-1}, 1272 - 1285 cm^{-1}, 833 - 872 cm^{-1} and 761 - 745 cm-1 which result from vibrations of the nitrate bonds (See Table 11.4). The band which is expected in the region of 710 - 689 cm^{-1} is masked, possibly by overlapping bands in the region, in each of the sample spectra except SM5 (Marbled disk #3) (Figure 11.1b) where a weak band appears at 696 cm^{-1}. There is a weak band at 677 cm^{-1} in SM1 (lump of crude Parkesine)(Figure 11.1a) and in SM4 (green disk #3). However, there are several other indistinct bands in the region which overlap and are difficult to interpret.

In all of the sample spectra, there is a broad band which centred in the range 3441 - 3383 cm^{-1} due to O-H stretches and a broad band in the range 1066 - 1059 which is assigned to the C-O stretch in the ether linkage of the glucose molecules.

The most interesting feature in these spectra is that the band which has been assigned to the C=O stretch due to the camphor molecule is absent in the spectra of sample SM3 (yellow disk #3), SM5 (marbled disk #3) and SM6 (billiard ball). In addition, a band appears at 1541 and 1544 cm^{-1} in the spectra of SM5 and SM6 respectively. In the spectrum of SM4 (green disk #3), the band at 1724 cm^{-1} is very weak in relation to the other bands in the spectrum and there is a weak shoulder in the region of 1550 cm^{-1}. The absence of the absorption credited to the camphor molecule can be explained by the fact that although Alexander Parkes used camphor and other materials as plasticizers, he did not utilize it in large quantities.

Vestry House Museum samples

Four of the five silicon carbide samples from the Vestry House Museum collection were identified as cellulose nitrate. The spectra of the different plastics from deteriorated hand mirrors and the cylindrical box were found to have the bands which are characteristic of the nitrate ester (see Table 11.5) as well as the absorption bands in the O-H stretching region and the C-O ether stretches (Figure 11.2). As in the Science Museum sample spectra, the band in the region 710 - 689 cm^{-1} seems to be masked by multiple overlap in the region 700 - 400 cm^{-1}. In the spectrum of VHN5, the band at 1670 cm^{-1} is slightly beyond the range suggested in the literature, but it is within the range observed experimentally in other samples.

The spectrum of sample VHM3 shows some signs of degradation (Figure 11.2b). The spectrum was identified as cellulose nitrate on the basis of the bands at 1643, 1283, 830 and 752 cm^{-1}. There some differences in band shape between the sample spectrum and those of the cellulose nitrate plastics. The band at 830 cm^{-1} is slightly beyond the range in the literature, but this may be due to degradation. However, the band in the carbonyl region credited to the presence of the camphor molecule is not evident in the spectrum. Also, the band in the C-H stretching region is very weak and a broad ill defined band appears at 2227 cm^{-1}.

The sample taken from the Halex hairbrush (DB 30.9.65/73) was found to be cellulose acetate. The spectrum was identified by the very intense bands at 1758 and 1239 cm^{-1} which are due to the carbonyl stretch and the C-O stretch of the ester linkage (Figure 11.3). The value of the frequency at 1239 cm^{-1} is within the range of acetate esters and both values agree closely with those in the standard spectra of cellulose acetate. The fingerprint bands which occur at 905 and 605 cm^{-1} in the standard cellulose acetate spectra also appear in the spectrum of VHM4. Also, the bands which are observed in the commercial plasticized cellulose acetate sheet can be observed in the Halex spectrum at 1592, 1490, 966, 782, 758 and 692 cm^{-1} which are indicative of an aromatic compound.

The Halex hairbrush was observed to have a surface residue which appeared as a skin. The spectrum of the material seems to indicate an aromatic compound due to the presence of sharp bands at 1604, 1506 and 1456 cm^{-1}.

The identification of the Halex hairbrush illustrates the value of the FT-IR technique. Objects which are stamped with the Halex trademark are considered to be cellulose nitrate, but both cellulose acetate and cellulose nitrate were marketed under the Halex name. As both materials have a tendency to degrade, it is no longer possible to classify all Halex objects as cellulose nitrate without chemical analysis.

Tate Gallery samples

Gabo sculpture samples

The identity of samples taken from the Gabo sculptures are summarized in Table 11.1. There were four polymer systems which were identified in the sculpture, cellulose nitrate, cellulose acetate, casein and poly (methyl methacrylate).

Thirteen samples were identified as cellulose nitrate and are listed in Table 11.1. The spectra were identified by the presence of bands due to the nitrate group bonds and the carbonyl stretch owing to the camphor (Figure 11.4). The range of the frequencies for each characteristic absorption for the samples is listed in Table 11.6.

The sample spectra show some variation in the 630 - 400 cm^{-1} region. This may be due to additives such as pigments and dyes. The spectra of two samples of crizzled cellulose nitrate were not visibly different from the other samples (Figure 11.4b). In sample JH18, the bands in the C-H bending region are very weak. All of the nitrate bands used for identification are not affected. There is a band in the region of 1500 cm^{-1} in the spectra of I-6, I-11, I-13, II-4, II-5, II-13, II-16 and JH17. This may be due to an aromatic additive such as a plasticizer, but there is no other evidence in the spectra.

The samples which were identified as cellulose acetate are listed in Table 11.1. The samples were identified by the presence of bands which have been assigned to features of cellulose acetate structure (Figure 11.5a). The spectra of samples which are visibly degrading are very similar to those of apparently stable plastic (Figure 11.5b). The bands which may be due to aromatic plasticizers are also present. The range of frequency values for the characteristic bands in the sample cellulose acetate spectra are listed in Table 11.7.

The range of the absorption frequencies are slightly greater than the reference spectra, however, they fall within the literature values. Minor variations in composition owing to different manufacturers, age and degradation would affect the infrared spectra slightly, but the frequency values are still valid for identification purposes. The C-H stretching absorptions appear as two bands in the standard spectra. These bands are less resolved in most of the sample spectra where only one band centred from 2920 - 2960 cm^{-1} occurs. Also, there is a band at 839 - 841 cm^{-1} in the reference spectra which appears as a weak band or shoulder in the sample spectra from 828 - 819 cm^{-1}.

The samples which were identified as casein plastic were characterized by comparison to the spectrum of commercial casein (Figure 10.3). Two of the samples taken from the Gabo sculptures were found to be casein and are listed in Table 11.1. The sample spectra (Figure 11.6) have bands which correspond with the standard spectrum in the regions of 3287, 3100, 2962, 1661, 1546, 1450 and 1400 (Table 11.8). Also, there is a band at 1175 cm^{-1} in the standard spectrum of casein which has not been assigned, but which occurs in the sample spectra. There is an absorption at 1106 cm^{-1} in the casein spectrum which may be related to the bands which occur at 1088 and 1084 cm^{-1} in samples I-8 (Figure 11.6a) and II-12 (Figure 11.6b) respectively.

In the standard casein spectrum, there are bands at 1350, 1315 and 1241 cm^{-1}. The latter two were tentatively assigned to a coupled C-N stretching mode and a N-H bending vibration. The bands at 1350 and 1315 cm^{-1} are not present in the sample spectra and a new band occurs in the region 1231 - 1233 cm^{-1}. This effect may be due to several factors. The change in the spectra may be a result of weathering of the polymer structure. It may also be due to changes in the structure caused by the hardening process. It is difficult to say as a sample of fresh casein plastic was not obtained.

In the sample spectra, the amide II band is split with a second band at 1507 and 1511 cm^{-1}. This region is sensitive to changes in conformation and may be due to changes in structure resulting from the hardening process. The region between 800 - 400 cm^{-1} is a broad, ill-defined band with maximum intensity occuring at 826, 656 and 540 cm^{-1}. These are not observed in the standard spectrum and the differences may be due to the hardening process or to additives in the plastic.

The samples which were identified as poly (methyl methacrylate) are listed in Table 11.1. These samples were characterized by comparison of the sample spectra with those of the standard materials (Figure 11.7). The absorptions which have been described as characteristic for poly (methyl methacrylate) are present in the sample spectra except for the band which occurs at 1193 - 1194 cm^{-1} in the standard spectra is not evident in the sample spectra. The sample spectra also have bands in the region 1066 - 1077, 990 - 991 and 753 - 754 cm^{-1} which correspond to those in the reference spectra. The bands which appear near 967 and 913 cm^{-1} in the standards appear as very weak shoulders in some of the sample spectra and the bands at 843, 827 and 811 cm^{-1} do not occur in all of the sample spectra. The frequency values of the Gabo sculpture samples are compared to those of the standards in Table 11.9.

The sample spectra have weak spikey bands from 3900 to 3500 cm^{-1} and a broad band centred in the region 3440 - 3443 cm^{-1}. These bands are most probably due to moisture which is absorbed by the poly (methyl methacrylate) powdered sample from the atmosphere between the time that the sample is collected and the time the spectrum was measured. Poly (methyl methacrylate) beads can absorb 0.3% moisture (Brydson, 1975) and the samples were not kept in a dessicator.

The sample spectra also exhibit very weak bands between 1600 - 1550 cm^{-1}. The bands are characteristic of aromatic compounds and fall in a range where they are not masked by other absorptions. There is a band at 1602 - 1606 cm^{-1} and one in the area 1542 - 1547 cm^{-1} in each example. There is also a band in the region of 1580 cm^{-1}, but it is extremely weak. These absorptions may be skeletal ring breathing modes of the aromatic ring. They would result from the presence of either plasticizers or stabilizers. The plasticizer dibutyl phthalate is an aromatic compound which is sometimes used in poly (methyl methacrylate). The ultraviolet light stabilizers such as phenyl salicylate and 2:4-dihydroxy benzophenone are also aromatic compounds.

The spectrum of sample I-17 has certain anomalies. There are two sharp bands at 3549 and 3408 cm^{-1}, a medium intense band at 1622 cm^{-1} with a shoulder at 1605 and two bands at 672 and 605 cm^{-1} which may result from the presence of additives which cannot be specified.

Gabo experimental plastic samples

Sample G is a transparent grey plastic that resembles the bottom section of the sculpture "Construction in space, Two cones" (T.2143). The material used in the sculpture is reported to be "Rhodoid", a cellulose diacetate, although the sample plastic is of uncertain commercial origin. The grey plastic in the "Two cones" piece is showing signs of degradation. The infrared spectra of samples taken from the surface of the plastic sample G (Figure 11.8a) did show some variations from those of the cellulose acetate standards and those of the sculpture samples identified as cellulose acetate. The strong band in the carbonyl region appears in the range 1724 - 1725 cm^{-1} in the sample spectra which is somewhat lower than in the standard cellulose acetate spectra (1758 - 1764 cm^{-1}). It is also much less intense in relation to the other bands in the spectrum. The strong band in the region of 1240 cm^{-1} in the reference spectra is also much less intense and the frequency has shifted to 1233 - 1235 cm^{-1}. This change indicates that a number of the ester linkages between the acetate groups and the glucose units have been broken. However, several samples were taken at one end after grinding to obtain a fresh surface. The spectra of these samples resemble those of the standard cellulose acetate (Figure 11.8b). The carbonyl band which ranges from 1744 - 1745 cm^{-1} is very intense and the band which falls in the region of 1235 cm^{-1} is also very strong. Thus, the degradation process is not consistent throughout the sample and the degradation seems to be occurring at the surface first.

The grey plastic sample G was subjected to several types of accelerated ageing. Samples were placed in an oven at 50 °C for 30 days under various conditions of relative humidity (RH). Two of the pieces which were aged in 100% RH were examined, one which turned a light brown colour and one which became blue. Both samples had severe lengthwise cracks and sweat was produced on the surface. A third sample was kept at 35% RH but not heated. No significant colour change was noted, but internal cracks occurred. Three spectra were obtained of the low RH material from various locations on the sample and one spectrum was collected of each of the high RH samples (Figure 11.9). The spectra were characterized by a weak band or shoulder in the region of 1723 - 1724 cm^{-1}. The band due to the C-O stretch falls at 1233 - 1234 cm^{-1} and is weak in relation to the other bands in the spectrum (Figure 11.9).

The spectra of the aged samples are very similar to the surface sample spectra of the unaged samples (Figures 11.8 and 11.9). However, the bands in the regions of 1650, 1600 and 1500 cm^{-1} seem to be unaffected by the ageing. A band appears in the region 1315 - 1322 cm^{-1} in the spectra of the surface samples of the unaged and in all of the aged samples. This band is not apparent in the spectra of the fresh surfaces of sample G or in any of the sculpture samples identified as cellulose acetate. The band may reflect the structural changes which result as the cellulose acetate molecule loses acetyl groups. There are some variations in the bands in the region of 800 - 400 cm^{-1} in the aged samples which may be due to weathering.

Sample A is a black plastic and when examined initially, was observed to be cellulose acetate (Table 11.2, sample I-1). However, it was examined a second time and the spectrum was slightly different. The carbonyl band occurred at 1729 cm^{-1} and was less intense in relation to the other bands in the spectrum than the corresponding band in the initial spectrum (Figure 11.10a). After heat ageing at 100% RH and 50 °C there was a dramatic change in the spectrum (Figure 11.10b). The carbonyl band appeared at 1732 cm^{-1} and the relative intensity was sharply decreased. The band at 1652 cm^{-1} is very weak and the bands which occurred at 1236 and 1298 cm^{-1} have disappeared. A new band is present at 1315 cm^{-1} and the broad band in the ether region is replaced by a weak band at 1039 cm^{-1}.

Sample plastic B is a yellowed transparent material which distorted dramatically after heat ageing (Table 11.2). The unaged sample was identified as cellulose acetate (Figure 11.11a). The spectrum of the aged sample shows some variation from those of the unaged plastic (Figure 11.11b). The carbonyl band is shifted from 1758 cm^{-1} in the spectra of the unaged sample to 1732 cm^{-1} in the aged sample spectrum and it is less intense in relation to the other bands in the spectrum. The band at 1246 cm^{-1} in the unaged spectrum is very broad and strong. The corresponding band occurs at 1236 cm^{-1} with a weak shoulder at 1293 cm^{-1} in the aged sample spectrum. The intensity of this band is not greatly affected.

Sample C is a very slightly yellowed, transparent plastic which did not show signs of distortion or signs of sweat on the surface (Table 11.2). It was identified as cellulose acetate and found to be soluble in methylene chloride. Thus, the greater stability is explained as the material is the more stable cellulose triacetate. Sample B was insoluble in both acetone and methylene chloride, but is thought to be the diacetate ester due to its instability. Unfortunately, the spectrum of the unaged sample B is almost identical to that of unaged sample C, thus it does not seem that the degree of substitution can be determined by the diffuse reflectance spectrum.

Sample D is a very yellowed transparent material. The sample did not show signs of degradation. The spectrum indicated that it was cellulose nitrate (Table 11.2).

The red plastic E was identified as casein. The spectrum (Figure 11.12a) exhibits bands at 3313, 3072, 2962, 1671, 1552, 1452 and 1409 cm^{-1} which correspond to the standard casein spectrum (Figure 10.3). Bands are also found at 1510, 1236 and 1176 cm^{-1} which correspond to the spectra of the sculpture samples which were identified as casein plastic. In addition, the bands which are observed at 1350 and 1315 cm^{-1} in the standard casein spectrum and are not apparent in the casein plastic sample spectra are also missing in the sample E spectrum. The region from 800 - 400 cm^{-1} is a broad, ill-defined band, but an absorption occurs at 826 cm^{-1} which corresponds to the bands at 826 and 824 cm^{-1} in the spectra of the samples I-8 and II-12.

After heat ageing at 50 °C and 100% RH for 30 days, sample E was observed to expand and when left to cool returned to almost the same weight as before ageing (Heuman, personal communication). The spectrum of the aged material is somewhat different to that of the unaged sample (Figure 11.12b). Two sharp absorptions occur at 3539 and 3488 cm^{-1} and a broad band is observed at 3311 cm^{-1}. The amide I and amide II bands occur at 1659 and 1549 cm^{-1} but there is no evidence of a band in the 3070 - 3100 cm^{-1} region. There are also bands at 1508, 1452 and 1408 cm^{-1} which occur in the unaged sample. However, there are variations in the region 1230 - 400 cm^{-1}. The band at 1236 cm^{-1} in the unaged sample is shifted to 1225 cm^{-1} after ageing. The band at 1099 cm^{-1} in the unaged sample spectrum does not occur, but two bands appear at 1141 and 1081 cm^{-1} in the aged sample spectrum. The band at 1140 cm^{-1} masks the band which occurs at 1176 cm^{-1} in the unaged sample spectrum. New bands occur at 990, 873, 797 and 665 cm^{-1} in the aged sample spectrum and a broad band which occurs at 559 cm^{-1} in the unaged sample spectrum is split into bands at 577 and 550 cm^{-1} in the spectrum of the aged plastic.

Gabo plastic sample F is a transparent sheet of mustard yellow plastic. The diffuse reflectance FT-IR spectrum of the material is not similar to those of the four polymer systems identified in the the Gabo sculptures and samples. The polymer was tentatively identified by comparison of the spectrum to an infrared atlas of polymers (Hanson, 1987). The sample F spectrum (Figure 11.13) is similar to the spectrum of poly (vinyl chloride) (PVA) in the region 1450 - 400 cm^{-1}, but also has a carbonyl absorption at 1733 cm^{-1} which is not expected in a spectrum of PVA. The spectrum was found to be most similar that of a vinyl chloride/vinyl acetate copolymer which contained 97.5% vinyl chloride. Copolymers of vinyl chloride and vinyl acetate exhibit properties similar to those of PVC, but are more flexible. The copolymer has between 97 and 85% chloride (Sax and Lewis, 1987). The spectral atlas contained spectra of several copolymers with increasing percentages of vinyl acetate (Hanson, 1987). The region 1450 - 400 cm^{-1} is altered by increasing amounts of vinyl acetate. The similarity of the sample F spectrum to that of PVC and the copolymer with a small percentage of vinyl acetate indicates that the material also contains a small amount of vinyl acetate.

The sample F spectrum (Figure 11.13) contains a fairly strong absorption at 1733 cm^{-1} which corresponds to a band in the literature spectrum which occurs near 1735 cm^{-1}. It is slightly more intense in relation to the other bands in the sample F spectrum than the comparable band in the reference spectrum. This variation may be caused by the sample loading on the silicon carbide paper. The literature spectrum was collected by transmission of a cast film. The sample F spectrum contains a strong band at 616 cm^{-1} with a less intense absorption at 700 cm-1. This pattern corresponds to the doublet near 630 and 605 cm^{-1} and the band near 685 cm^{-1} in the atlas spectrum. These bands fall in the C-Cl stretching frequency range for poly (vinyl chloride), 768 - 540 cm^{-1} (Krimm et al., 1963).

The bands at 1433, 1330, 1250, 1103 and 971 cm^{-1} in the spectrum of sample F correspond fairly well with those occurring in the region of 1420, 1325, 1245, 1095 and 955 cm^{-1} in the literature spectrum. The literature spectrum also contains a valley in the region of 1145 cm^{-1} which is absent in the diffuse reflectance spectrum. The diffuse reflectance spectrum has a band at 1197 cm^{-1} which appears as a shoulder near 1195 cm^{-1} in the literature spectrum.

The sample F plastic underwent a dramatic colour change after heating at 50 °C and 100% RH (Table 11.2). The material became an opaque peach colour. The spectrum of the aged material was not dramatically altered from that of the unaged material. The band at 1197 cm^{-1} in the original spectrum appears as a doublet shoulder near 1201 cm^{-1} which is much less intense. The shoulder near 900 cm^{-1} in the original sample F spectrum occurs as a sharp band at 831 cm^{-1} which is similar to the band near 830 cm^{-1} in the literature spectrum. Also, the band at 971 cm^{-1} in the original sample F spectrum occurs at 970 cm^{-1} and is much less intense in the artificially aged spectrum. The sample spectrum of the artificially aged material is slightly more similar to the literature spectrum than that of the unaged material.

The crizzled plastic sample 801 was found to be poly (methyl methacrylate) (Table 11.9). The spectrum of the material (Figure 11.14) is very similar to those of the visibly undegraded sample spectra of poly (methyl methacrylate)(Figure 11.7). There are no new bands which might indicate the creation of degradation products. There is an absence of bands in the region 845 - 810 cm^{-1}. However, there is a fourth C-H stretching band present at 2925 cm^{-1} which is also evident in the sample spectrum of II-7.

Gabo surface exudate samples

The sculptures "Construction in space, Two cones" and "Circular relief" are displaying signs of physical distortion and the presence of a material on the surface. The material was thought to be plasticizer exudate and is described as "sweat". Two samples were collected from "Two cones", one clear substance from the transparent grey plastic and one black substance from the black plastic, by rubbing the surface of the plastic gently with a cotton swab. The swab was then rubbed against a potassium bromide cell and the transmission spectrum of the material was recorded at 2 cm^{-1} resolution and 10 scans. The initial analysis of the "Two cones" samples were performed at the Victoria and Albert Museum (Martin, 1987, unpublished results).

The report on the sweat samples from the "Two cones" sculpture concluded that the spectra of the two samples were similar, but that there were variations in intensity between the two. Several of the absorption bands occurred in different ratios. It was concluded that the samples consisted of two or more substances which have exuded from the polymer system. Also, the sweat mixture may have undergone chemical alteration such as oxidation. It was not possible to make a conclusive identification of the samples, however, there were indications that the mixture may contain a sulphonamide, a phthalate ester or triphenyl phosphate. All three of the materials are documented plasticizers of cellulose acetate and mixtures of phthalates and triphenyl phosphate are often used. It is thought that triphenyl phosphate which is known to sweat out of polymers, is migrating from the polymer system and bringing a certain amount of the other plasticizers to the surface (Martin, 1987, unpublished results).

Four samples of exudate were examined in this study which were obtained using the same sampling technique and examined under the same conditions as the samples from the "Two Cones" sculpture (Table 11.3). The samples JH4 (black) (Figure 11.15a) and JH5 (clear) (Figure 11.15b) were obtained from the artificially aged plastic samples A and G. Sample JH34 was collected from the surface of "Circular Relief" (T.2142) (Figure 11.16a) where it appeared as crystals on the surface. Sample JH40 was a black exudate which appeared on the surface of the "Construction in Space, Two Cones" sculpture which has appeared since the initial analysis (Figure 11.16b). The sample spectra of the artificially induced sweat and the samples from the sculptures were compared to those obtained from the earlier samples. In general, the four sample spectra show similarities to those of the earlier samples and to each other, but there are differences in band intensities. The spectra of samples JH34 and JH5 are not as strong as the other two as less sample was available.

The spectra of the four samples were compared visually with those of triphenyl phosphate (Figure 11.17), diethyl phthalate (Figure 11.18), and Ketjenflex which is N-ethyl o,p-toluenesulfonamide (Figure 11.19). The comparisons must be approached with caution as all three of the types of plasticizer are aromatic compounds and there are certain similarities in all of the spectra which result from aromatic compounds. However, there are some variations in the spectra which can be used to interpret the sample spectra. A table of the absorption frequencies for the four samples are compared to those of the standard materials in Table 11.10.

There is a weak absorption in the region of 3070 cm^{-1} which corresponds to the C-H stretch in an aromatic system. In the spectra of samples JH5 and JH34, the band is very weak. There is a band in the range 1588 - 1590 cm^{-1} and one in the range 1488 - 1489 cm^{-1} which are characteristic of an aromatic system resulting from the skeletal ring breathing modes. In substituted aromatics, these two bands are split to produce four bands. The band in the region of 1600 cm^{-1} is usually strong and the band in the area of 1560 - 1600 cm^{-1} is often weak or non-existent in the infrared spectrum. In the spectrum of triphenyl phosphate and in the four sample spectra, the band near 1580 is strong with the band in the region of 1600 cm^{-1} occurring as a shoulder. In the spectrum of N-ethyl o,p-toluenesulphonamide, there is one sharp band at 1599 cm^{-1}. The diethyl phthalate spectrum has two sharp bands at 1600 and 1580 cm^{-1}. The second set of bands occurs in the range 1510 - 1480 cm^{-1} and at approximately 1455 cm^{-1}. The band in the region of 1455 cm^{-1} is often masked by C-H bending vibrations which occur in the same area. In the spectrum of triphenyl phosphate, the bands occur at 1484 cm^{-1} and 1455 cm^{-1}. The sulphonamide spectrum has a single sharp band at 1495 cm^{-1} and the diethyl phthalate has a multiplet of bands at 1488, 1476, 1466 and 1448 cm^{-1}. In the spectra of sample JH5 and JH34, there is a strong absorption at 1489 and 1488 cm^{-1} with a weak band in the region of 1450 cm^{-1}. In the sample JH4 and JH40 spectra, there are two bands at 1489 and 1450 cm^{-1} and 1489 and 1457 cm^{-1} respectively.

Aromatic compounds exhibit a series of low intensity absorptions in the region 1225 - 950 cm^{-1}. Bands in the regions of 1175 - 1125 cm^{-1}, 1110 - 1070 cm^{-1} and 1070 - 1000 cm^{-1} are characteristic of C-H in-plane deformations in mono-substituted aromatic compounds. Ortho and para-substituted compounds exhibit weak bands in the region 1225 - 1175 cm^{-1}, 1125 - 1090 cm^{-1} and 1070 - 1000 cm^{-1} (two bands). In addition, ortho-substituted compounds also absorb in the region 1000 - 960 cm^{-1}. This region is less useful for identification as the bands are weak. They are used to confirm evidence from other regions in the spectrum (Bellamy, 1975). In the spectrum of triphenyl phosphate, bands occur at 1176, 1162, 1153, 1071, 1030, 1023 and 1009 cm^{-1}. Diethyl phthalate, which is an ortho-substituted compound, has absorptions at 1174, 1124, 1097, 1074, 1041 and 1018 cm^{-1}. The spectrum of Ketjenflex, which is a mixture of ortho and para-substituted compounds contains bands at 1162, 1120, 1095, 1067, 1037 and 1019 cm^{-1}. In the sample spectra of JH4 and JH40, there are bands at 1162 - 1163 cm^{-1}, 1123 - 1124 cm^{-1}, 1072 - 1073 cm^{-1}, 1041, 1026 and 1011 cm^{-1}. Some but not all of these bands are also apparent in the weaker spectra of JH5 and JH34.

The region 1000 - 650 cm^{-1} is characteristic for aromatic compounds and strong bands appear which result from C-H out-of-plane deformations. The occurrence of these bands is due to the position of the substituents and is characteristic of the substitution pattern of the ring (Bellamy, 1975). Mono-substituted aromatic materials absorb very strongly in the region 770 - 730 cm^{-1} with an additional strong band in the region 710 - 690 cm^{-1}. Ortho-substituted compounds also absorb in the region 770 - 735 cm^{-1}, however, the compound does not absorb in the region 710 - 690 cm^{-1} which makes this band diagnostic for mono-substituted compounds. Para-substituted aromatics are characterized by a strong band in the region 860 - 800 cm^{-1}. The spectrum of mono-substituted triphenyl phosphate contains a strong doublet at 770 and 752 cm^{-1} and a strong band at 691 cm^{-1}. The diethyl phthalate spectrum has strong absorptions at 745, 706, and 651 cm^{-1}. The spectrum of the sulphonamide, which is a mixture of ortho and para compounds, exhibits strong bands at 815 and 664 cm^{-1} with a band of medium intensity at 707 cm^{-1}. The sample spectra exhibit an intense doublet in the region of 770 cm^{-1} and another band at 689 - 690 cm^{-1} and are most similar to that of triphenyl phosphate. However, smaller amounts of ortho-substituted compounds may be present as one of the two bands in the region 770 cm^{-1} may be due to both ortho and mono substitution. There is no evidence of para substitution which may indicate that if it is present, it is only in very small quantities.

The three types of plasticizer have unique functional groups which can be used to differentiate between them in the infrared spectrum. Triphenyl phosphate can be characterized by the phosphorus linkages. The P=O vibration is recorded in the literature as absorbing in the region 1300 - 1250 cm^{-1} (Bellamy, 1975). The band occurs at 1295 cm^{-1} in the triphenyl phosphate spectrum. However, there is a very strong band in this region in the diethyl phthalate spectrum, so it is not useful for isolating triphenyl phosphate. The P-O-C (aromatic) stretching vibration results in two absorptions in the regions 1242 - 1110 cm^{-1} and 996 - 905 cm^{-1} (Thomas and Chittenden, 1964). There is a band in the region of 1185 cm^{-1} in the spectrum of Ketjenflex, but there are no possible interferences from diethyl phthalate. The second band, however, is very diagnostic. It is a strong and often complex band. In the spectrum of triphenyl phthalate, a strong multiplet occurs in this region with a maximum intensity at 953

cm^{-1}. There are no strong bands in this region in the spectrum of the sulphonamide mixture or the diethyl phthalate. The sample spectra have bands at 1187 - 1188 cm^{-1} and 954 - 964 cm^{-1}. In the sample spectra JH5, JH34 and JH40, the band occurs from 954 - 964 cm^{-1} and is the strongest absorption in relation to the other bands in the spectrum. In the spectrum of JH4, the band occurs at 961 cm^{-1} and is less intense than the bands at 1728 and 1288 cm^{-1}. The band in the area of 1187 - 1188 cm^{-1} may be due to a combination of the P-O-C (aromatic) vibration and the absorption in the sulphonamide mixture.

Diethyl phthalate is an ester which is distinguished by the presence of two strong absorptions resulting from the ester linkage. The ester linkage in phthalate esters are characterized by absorptions in the regions 1730 - 1717 cm^{-1} (C=O stretch in aryl esters), 1310 - 1250 cm^{-1} and 1150 - 1100 cm^{-1} (C-O stretching vibration) (Bellamy, 1975). In the diethyl phthalate spectrum, there are strong absorptions at 1728, 1284 and 1124 cm^{-1}. The band in the region 1310 - 1250 cm^{-1} is subject to confusion due to the P=O absorption in phosphates, although in the phthalate spectrum, it is very broad. The band in the region of 1150 - 1100 cm^{-1} is not diagnostic as there is a strong multiplet in the area of 1200 - 1140 cm^{-1} which might mask the absorption in a mixture. The carbonyl absorption is useful, however. In the spectrum of triphenyl phosphate, there are very weak absorptions at 1952, 1881, 1800 and 1739 cm^{-1} which are aromatic overtone and combination bands. In the Ketjenflex spectrum, these bands occur at 1920, 1808, 1765, 1726, 1709 and 1687 cm^{-1} and are also very weak. Thus, the presence of a strong absorption in the region of 1726 - 1728 cm^{-1} is indicative of a phthalate.

It is slightly harder to characterize the sulphonamide when in combination with other aromatic compounds. There are strong bands at 1325 cm^{-1} (with shoulders at 1306 and 1290 cm^{-1}) and 1161 cm^{-1} in the standard spectrum of Ketjenflex which may be used. The bands correspond to the characteristic regions for sulphonamides which exhibit strong bands, one in the region 1180 - 1160 cm^{-1} and one in the region 1360 - 1330 cm^{-1}. The bands are assigned to S=O stretches in the sulphone group ($-SO_2-$) (Bellamy, 1975). The band at 1162 cm^{-1} is not as diagnostic as it may be confused with the C-H in-plane deformations of the aromatic ring in all the compounds. The band in the region of 1325 cm^{-1} is possibly more diagnostic as there are no strong bands in the corresponding region of the other plasticizer spectra. A weak band occurs at 1350 cm^{-1} in the spectrum of JH5, but no absorption is evident in the spectrum of JH35. In the spectrum of sample JH4, there are bands at 1339 and 1369 cm^{-1} which are medium in intensity and a band occurs at 1369 cm^{-1} in the spectrum of sample JH40.

The exudate sample spectra give indications of an aromatic material and although it is not possible to match the spectra with that of a pure compound, it is possible to determine the identity of the mixture by characteristic bands of each material. The identification of triphenyl phosphate as one of the possible components is supported by the literature as it has been reported to exude from cellulose acetate. It is also reported to be used in conjunction with phthalate plasticizers, so the identification of a phthalate plasticizer as one of the components is also supported. It is also possible that the phthalate is being carried out with the triphenyl phosphate. The physical appearance of sample JH34 as crystals on the surface indicated that the material was triphenyl phosphate which is a solid at room temperature. However, the presence of weak bands in the aliphatic C-H stretching region in addition to the strong band at

1726 cm^{-1} indicate that a second compound must be present which is probably a phthalate ester. The presence of the sulphonamide is more difficult to confirm. It is very compatible with cellulose acetate, so it is not expected to exude in great quantities. It is difficult to say whether or not the sweat samples actually contain a sulphonamide from the spectra obtained in this study.

Gabo sculpture adhesive sample

A sample of adhesive was removed from the sculpture "Construction in space, Two cones" and analysed by diffuse reflectance spectroscopy (Table 11.3). The sample was held with forceps and lightly rubbed against the silicon carbide paper. The sample spectrum was found to resemble those of the poly (methyl methacrylate) standards and a diffuse reflectance spectrum of an acrylic resin adhesive (HMG) which is made of Paraloid B-72 acrylic resin. The sharp bands in the C-O region which are evident in the poly (methyl methacrylate) standard spectra are not as distinct in the sample spectra where two bands appear 1235 and 1173 cm^{-1}. The same effect is evident in the spectrum of the acrylic adhesive where absorptions occur at 1237 and 1169 cm^{-1}. The sample spectrum is very similar to that of the acrylic resin adhesive with only minor variations and they are compared in Figure 11.20. There is a band at 1475 cm^{-1} in the Paraloid B-72 spectrum which appears as a shoulder on the band at 1450 cm^{-1} in the sample spectrum. A weak band occurs near 1525 cm^{-1} in the Paraloid B-72 spectrum which is very indistinct in the sample spectrum. The band which appears at 837 cm^{-1} as a shoulder on the band at 863 cm^{-1} in the acrylic resin spectrum occurs at 828 cm^{-1} in the sample spectrum and a new, weak band occurs at 691 cm^{-1} in the sample spectrum. There are slight variations in the region 600 - 400 cm^{-1} between the spectra, however, the agreement between the strong bands in the spectra is strong evidence for the identity of the unknown adhesive to be an acrylic resin.

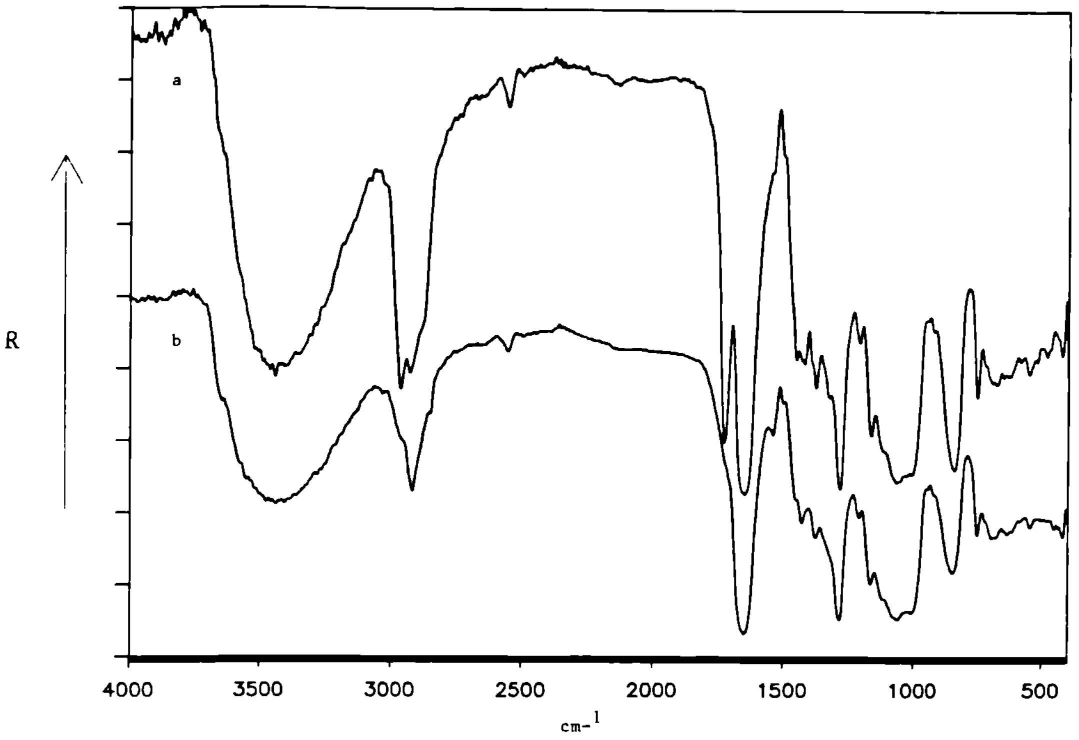

Figure 11.1 Diffuse reflectance FT-IR spectra of (a) lump of crude Parkesine (SM1) and(b) Parkesine marble coloured disk (SM5).

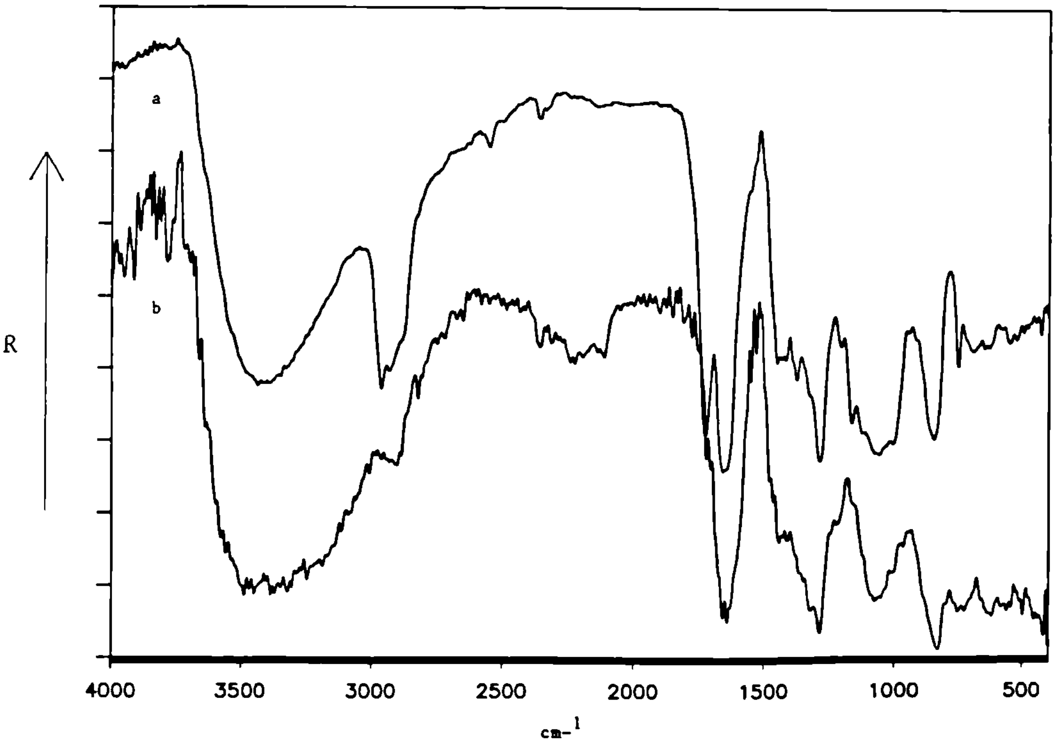

Figure 11.2 Diffuse reflectance spectra of samples from a degraded hand mirror from Vestry House Museum(a) yellow section (vhm1) and (b) dark green section (vhm3).

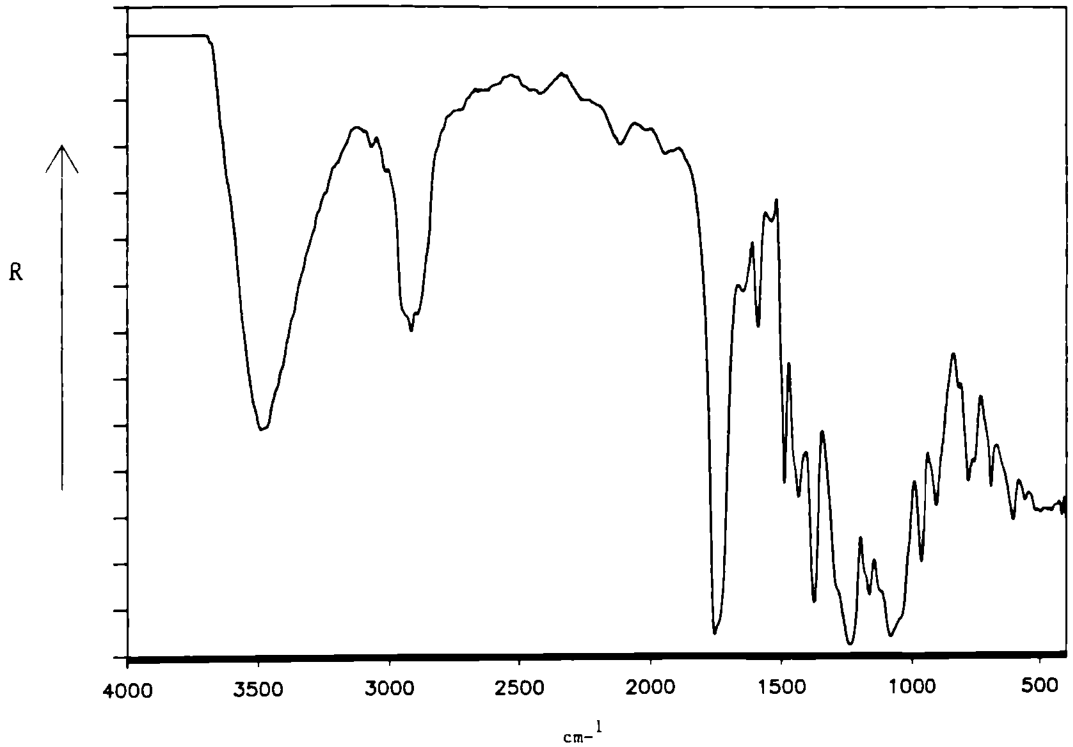

Figure 11.3 Diffuse reflectance FT-IR spectrum of a "Halex" hairbrush (vhm4) from Vestry House Museum.

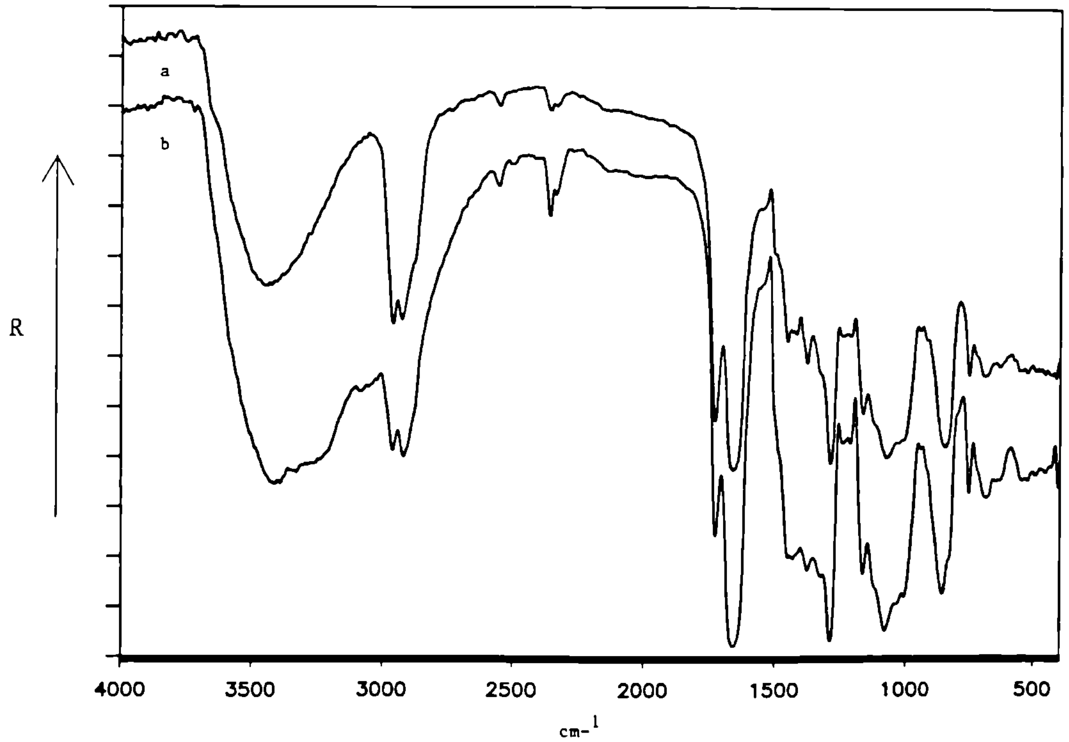

Figure 11.4 Diffuse reflectance FT-IR spectra of two Gabo samples identified as cellulose nitrate plastic. (a) Material in good condition from Model for 'Monument for an Airport' (T.2168) and (b) Crizzled plastic from Model for 'Double relief in a niche' (T.2170).

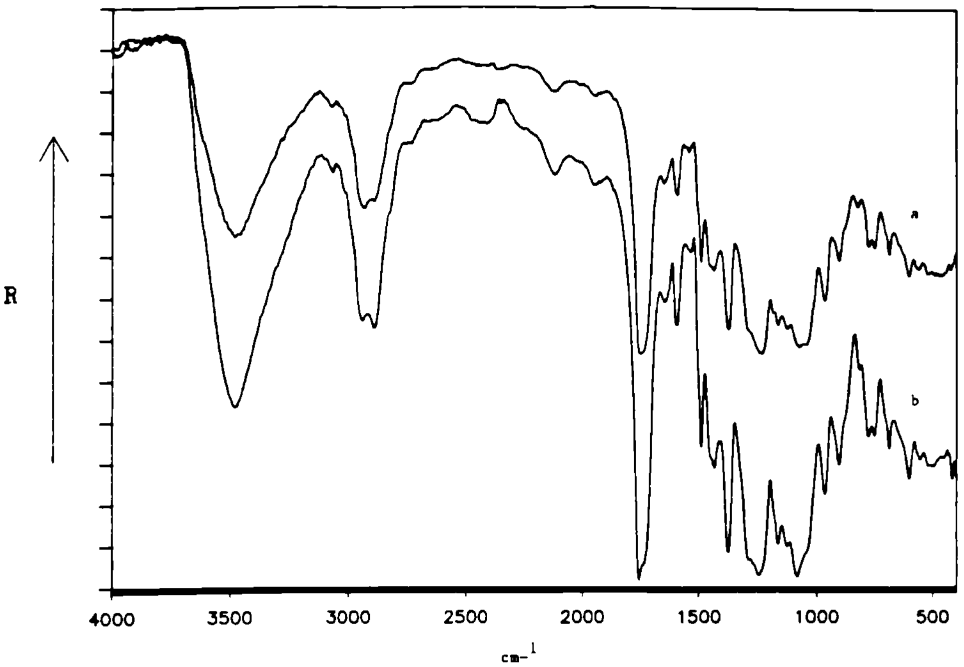

Figure 11.5 Diffuse reflectance FT-IR spectra of samples from Gabo sculptures which were identified as cellulose acetate plastic, (a) material in good condition from 'Torsion' (T.2146) and (b) Material observed to "sweat" from 'Construction in space, Two cones' (T.2143).

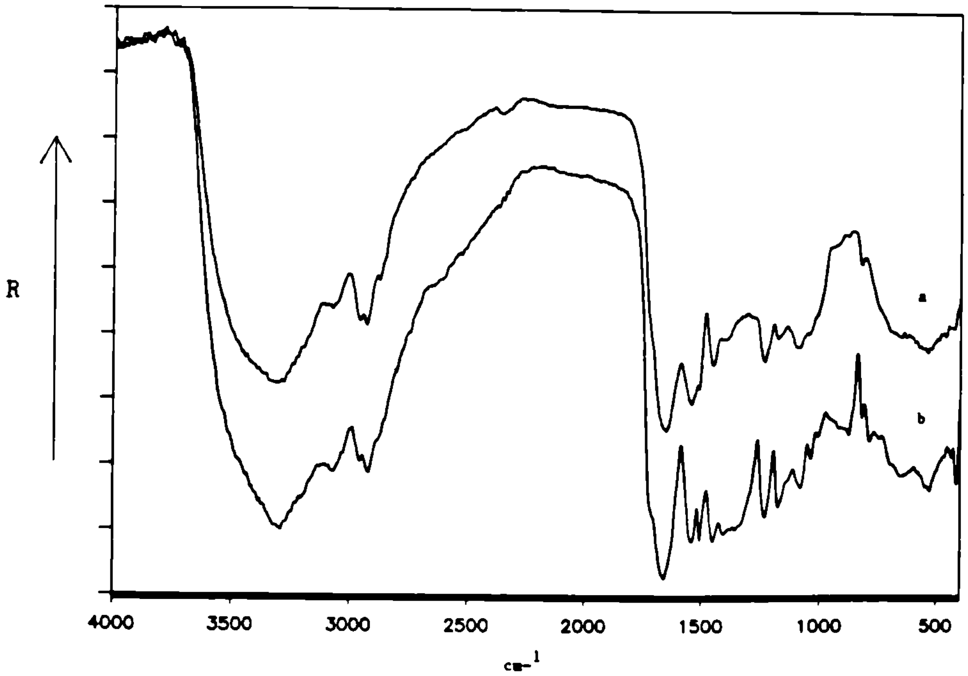

Figure 11.6 Diffuse reflectance FT-IR spectra of samples from Gabo sculptures identified as casein plastic, (a) material from Model for 'Construction in space, Two cones' (T.2169) and (b) sample from Model for 'Double relief in a niche' (T.2170).

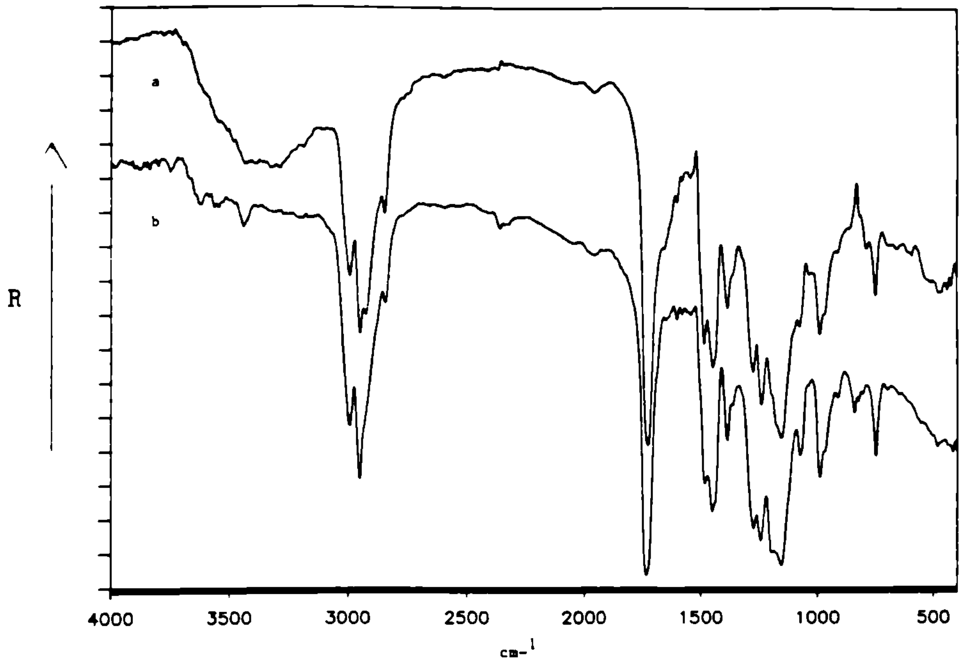

Figure 11.7 Diffuse reflectance FT-IR spectra of samples from Gabo sculptures identified as poly(methyl methacrylate), (a) material from First model for 'Monument to the unknown political prisoner' (T.2186) and (b) sample from Model for 'Monument to the unknown political prisoner' (T.2187).

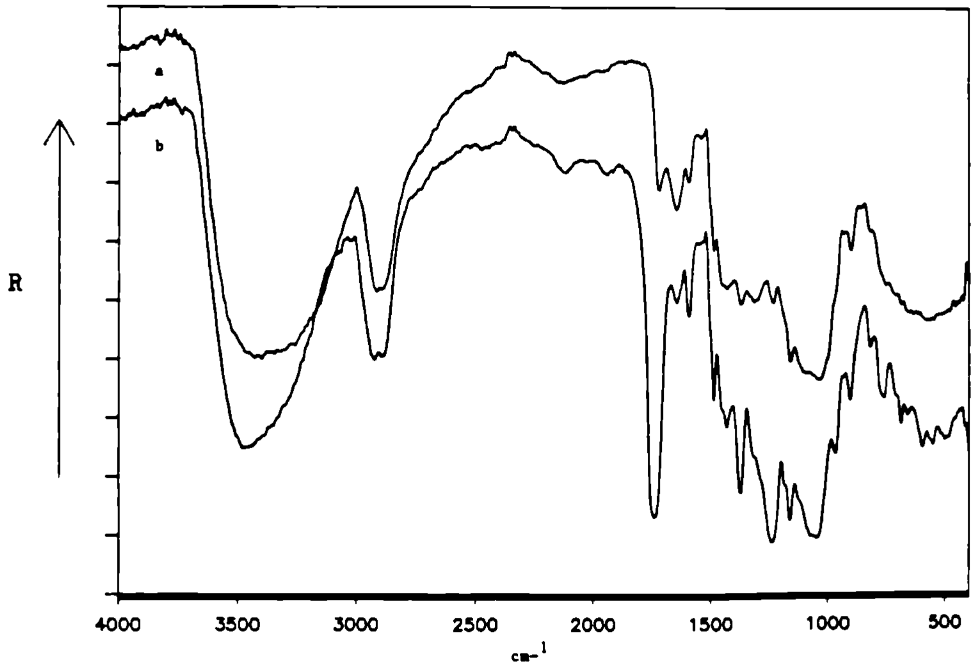

Figure 11.8 Diffuse reflectance FT-IR spectra of Gabo sample plastic G (transparent grey) identified as cellulose acetate, (a) sample taken from original surface and (b) sample obtained after grinding to obtain a fresh surface.

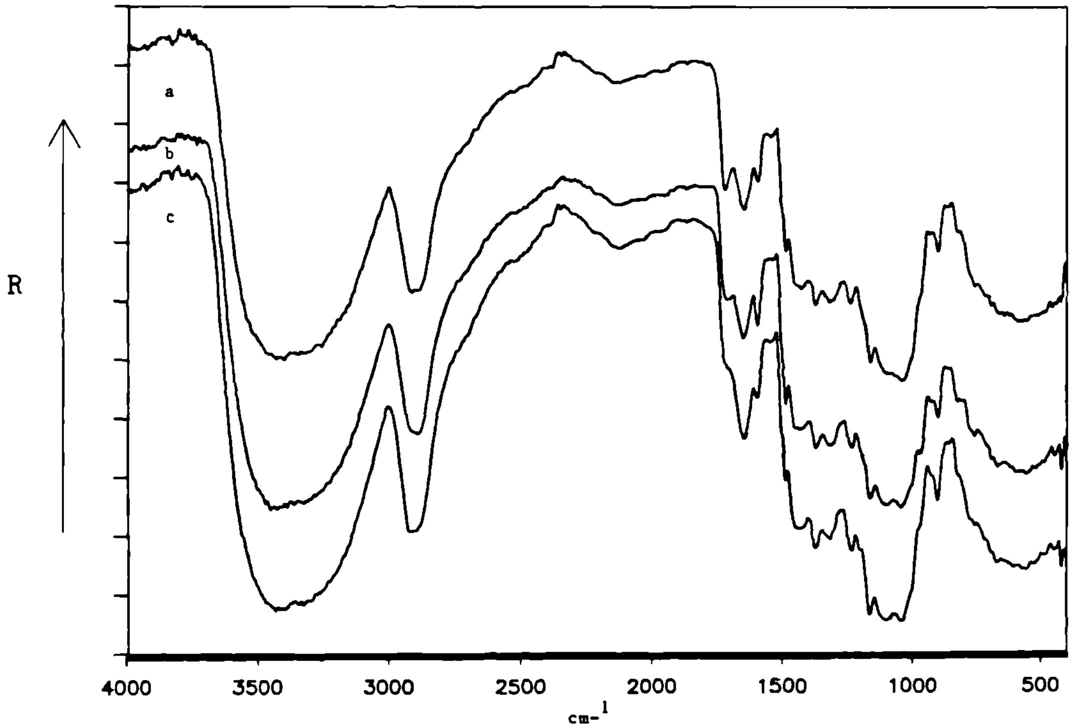

Figure 11.9 Diffuse reflectance FT-IR spectra of artificially aged samples of Gabo sample plastic G, (a) sample aged at 35% RH, (b) sample aged at 100% RH and 50 °C and (c) sample aged at 100% RH and 50 °C which turned blue.

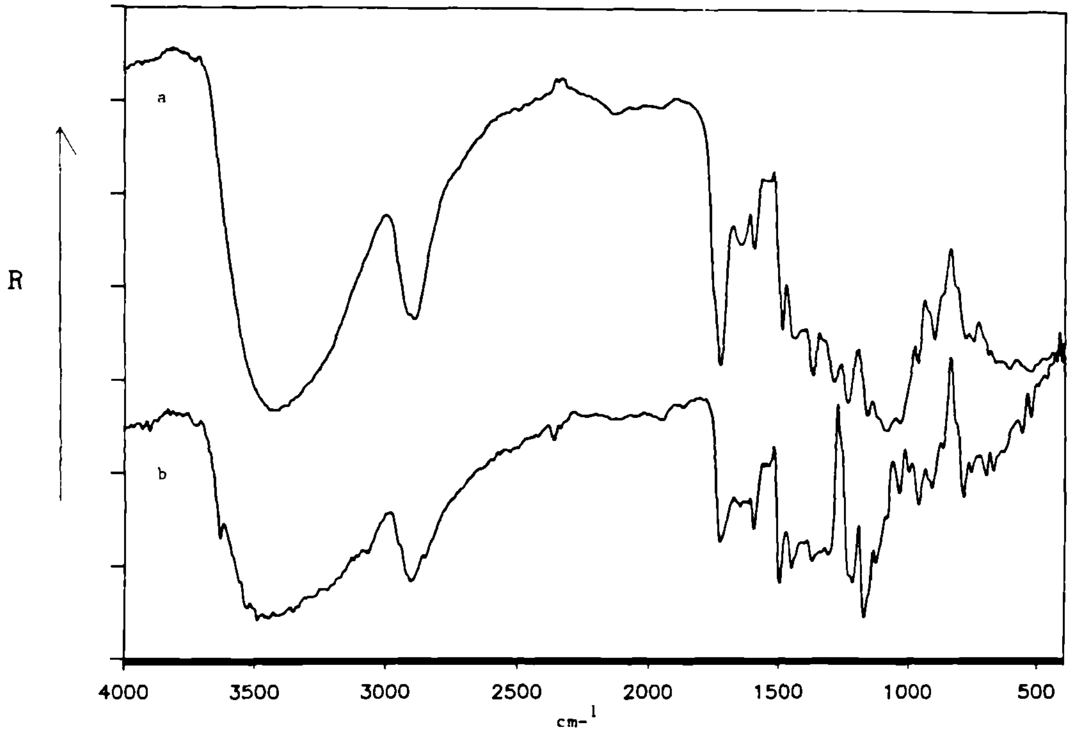

Figure 11.10 Diffuse reflectance FT-IR spectra of Gabo sample plastic A (black) identified as cellulose acetate (a) before artificial ageing and (b) after ageing at 100% RH and 50 °C.

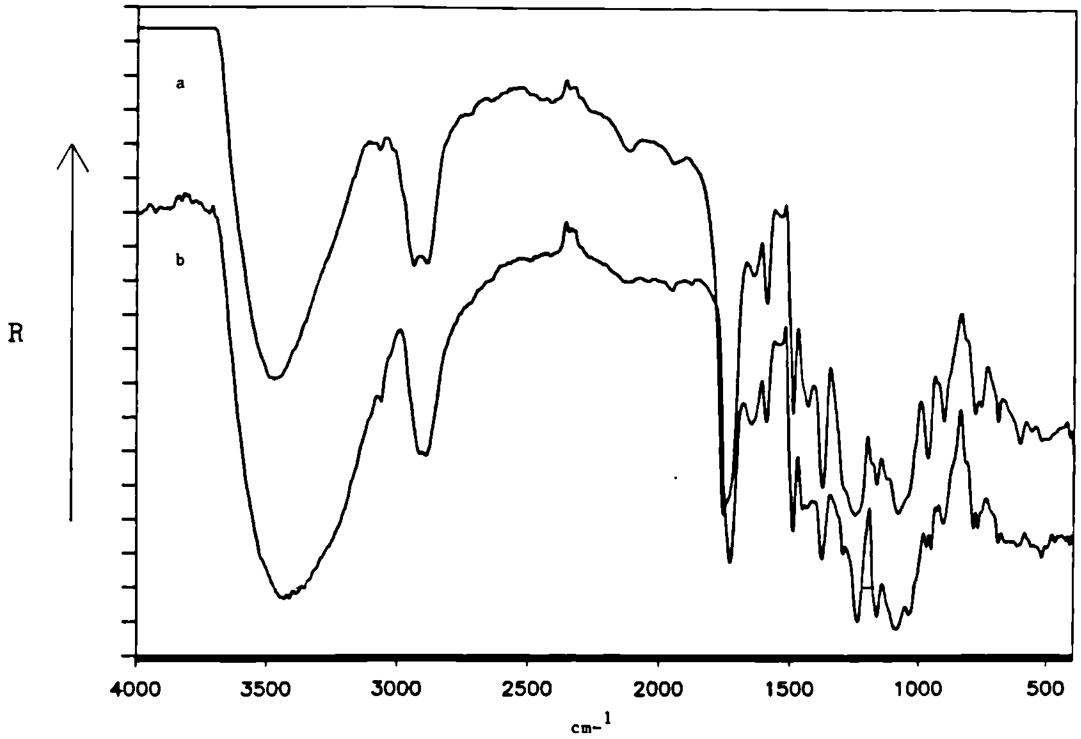

Figure 11.11 Diffuse reflectance FT-IR spectra of Gabo sample plastic B (clear) idnetified as cellulose acetate (a) before artificial ageing and (b) after ageing at 100% RH and 50 °C.

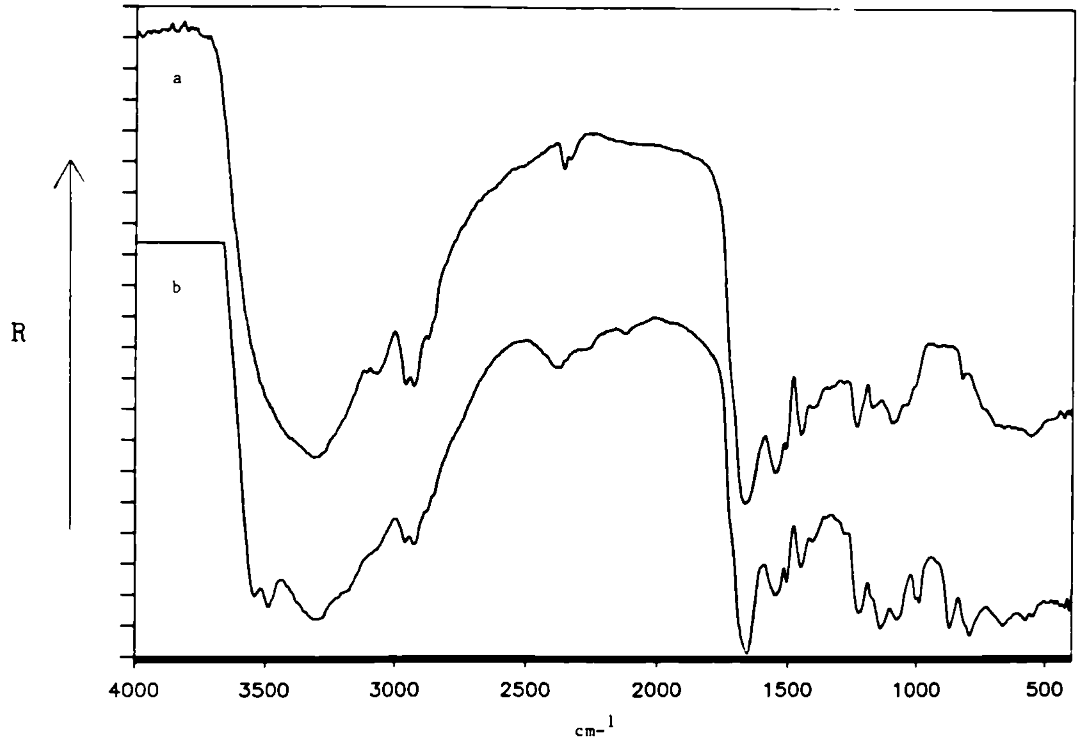

Figure 11.12 Diffuse reflectance FT-IR spectra of Gabo sample plastic E (red) identified as casein (a) before artifical ageing and (b) after ageing at 100% RH and 50 °C.

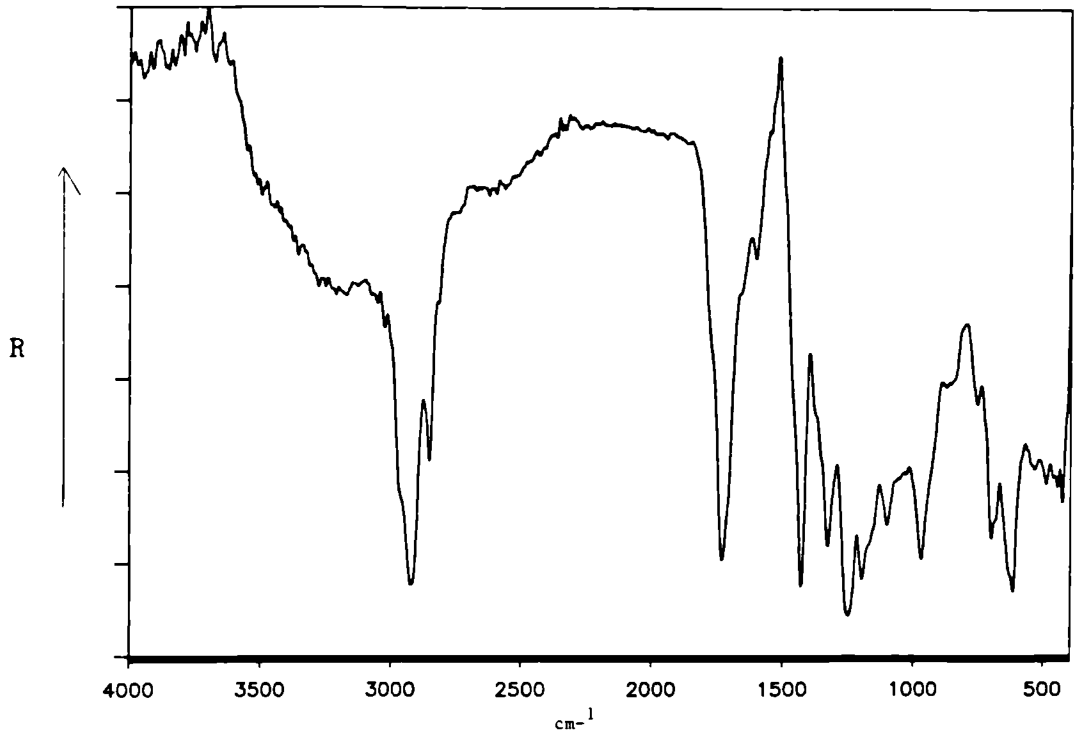

Figure 11.13 Diffuse reflectance FT-IR spectrum of Gabo sample plastic F (transparent yellow).

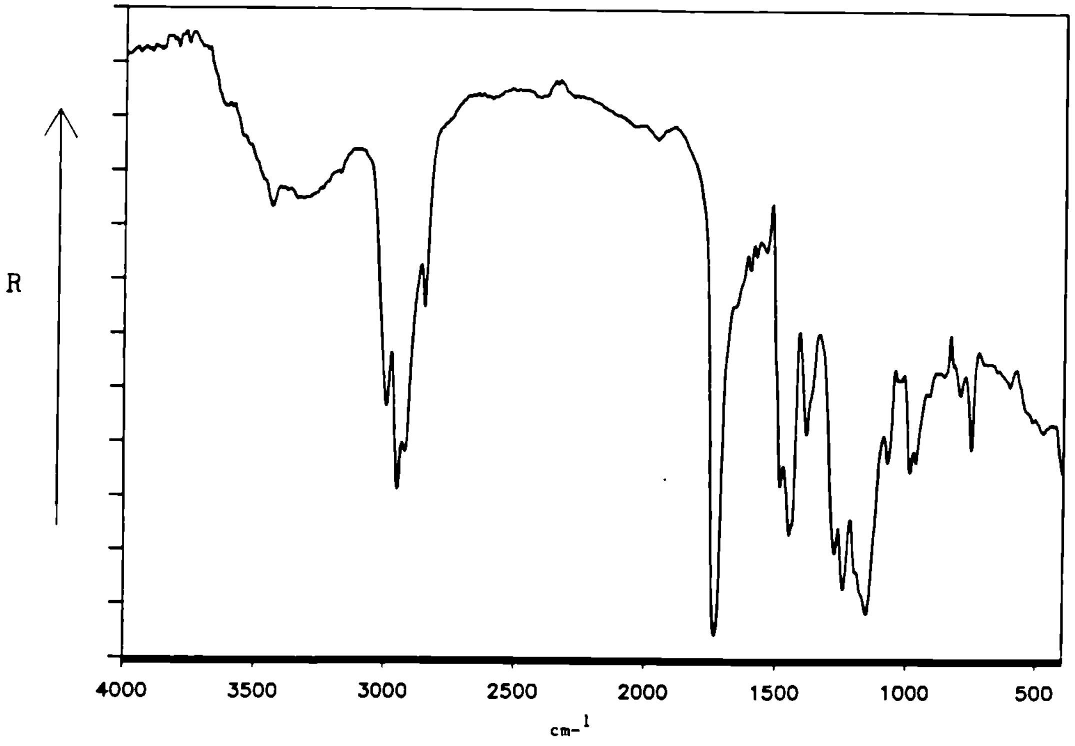

Figure 11.14 Diffuse reflectance FT-IR spectrum of Gabo archive sample 801 identified as poly (methyl methacrylate).

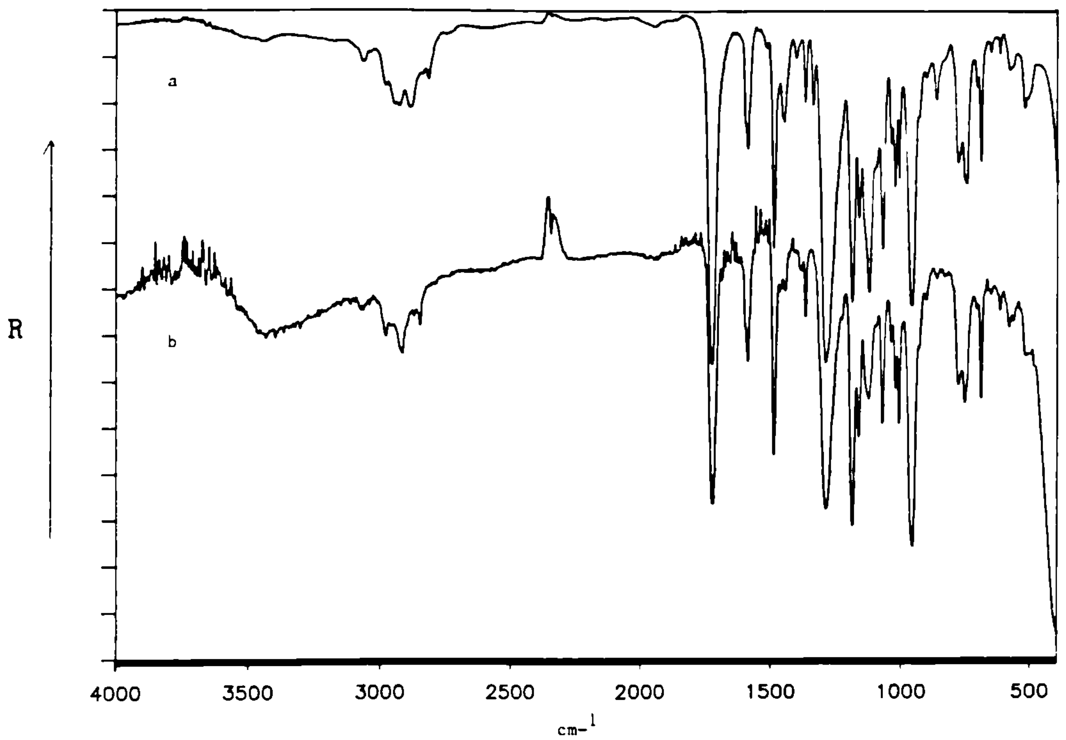

Figure 11.15 Transmission FT-IR spectra of surface exudate produced after artificial ageing of (a) Gabo plastic sample A and (b) Gabo plastic sample G.

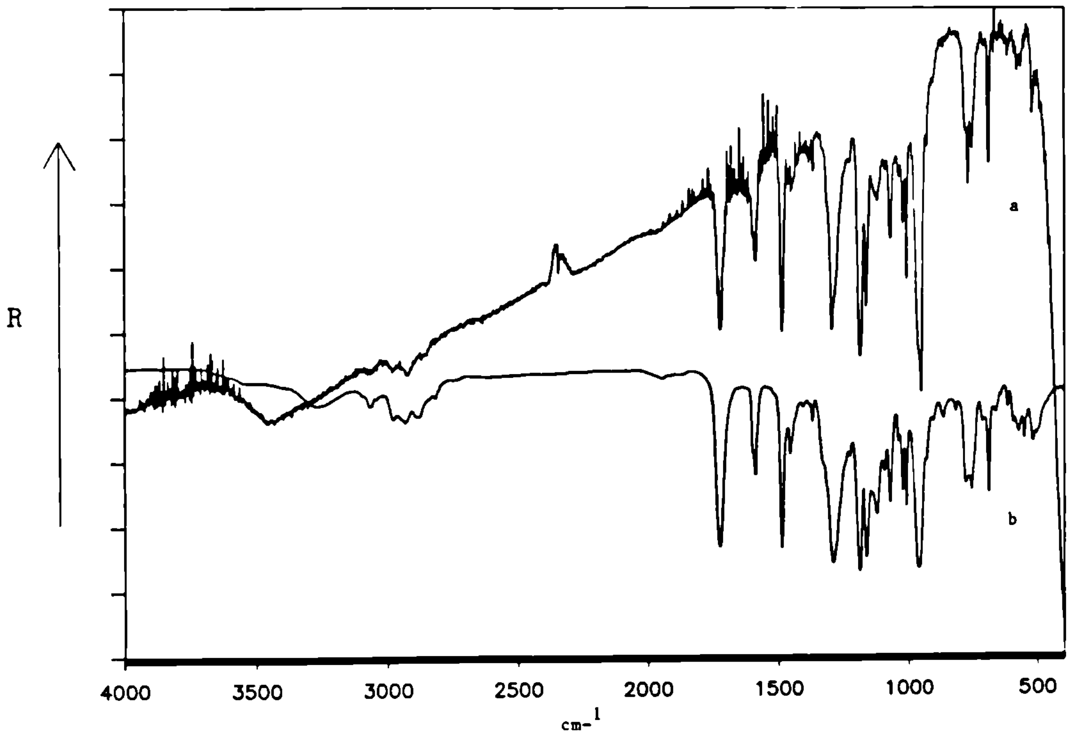

Figure 11.16 Transmission FT-IR spectra of surface exudate observed on the surface of (a) 'Circular relief' (T.2142) as crystals and (b) 'Construction in space, Two cones' (T.2143).

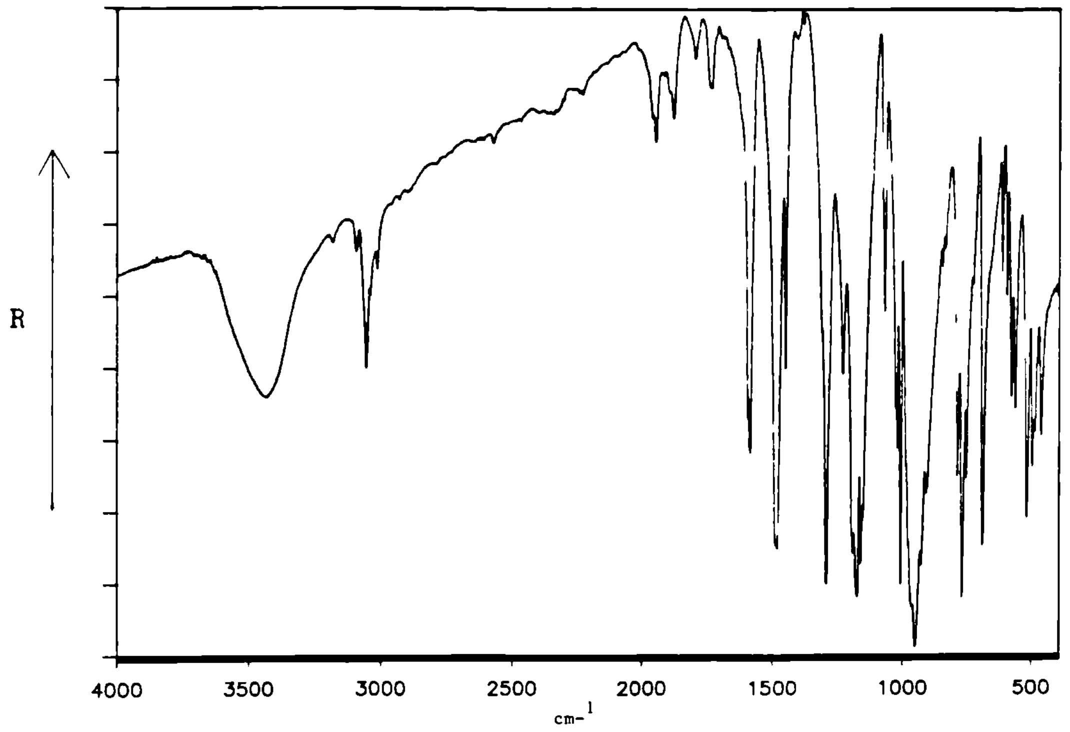

Figure 11.17 Transmission FT-IR spectrum of triphenyl phosphate.

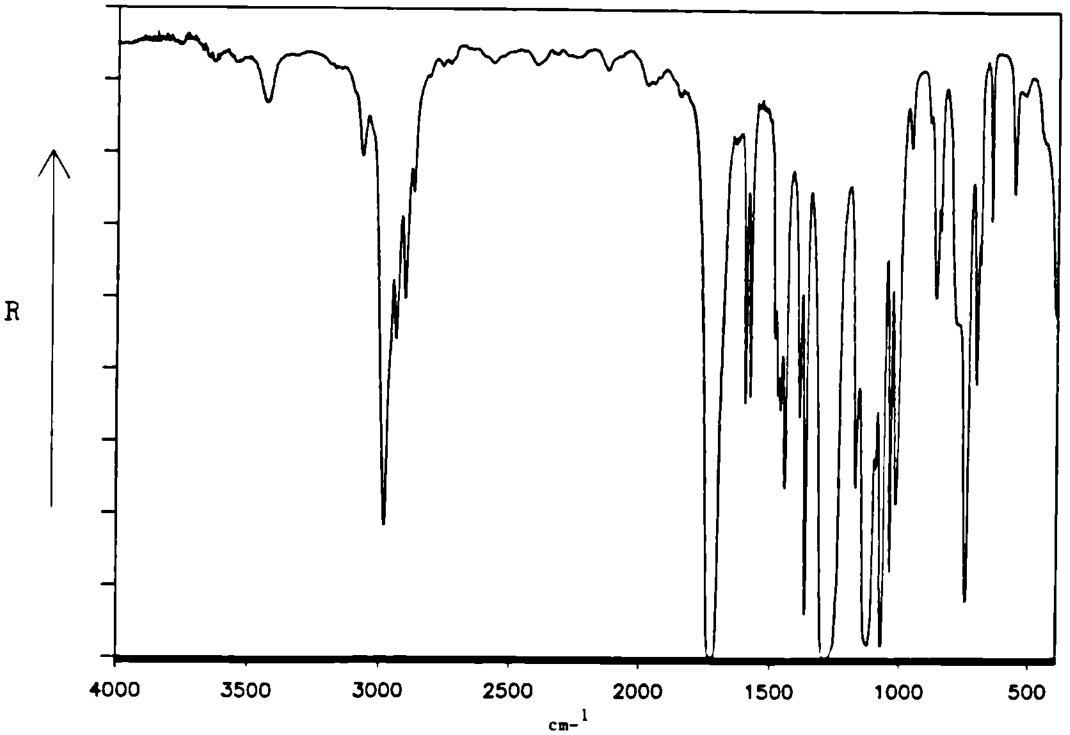

Figure 11.18 Transmission FT-IR spectrum of diethyl phthalate.

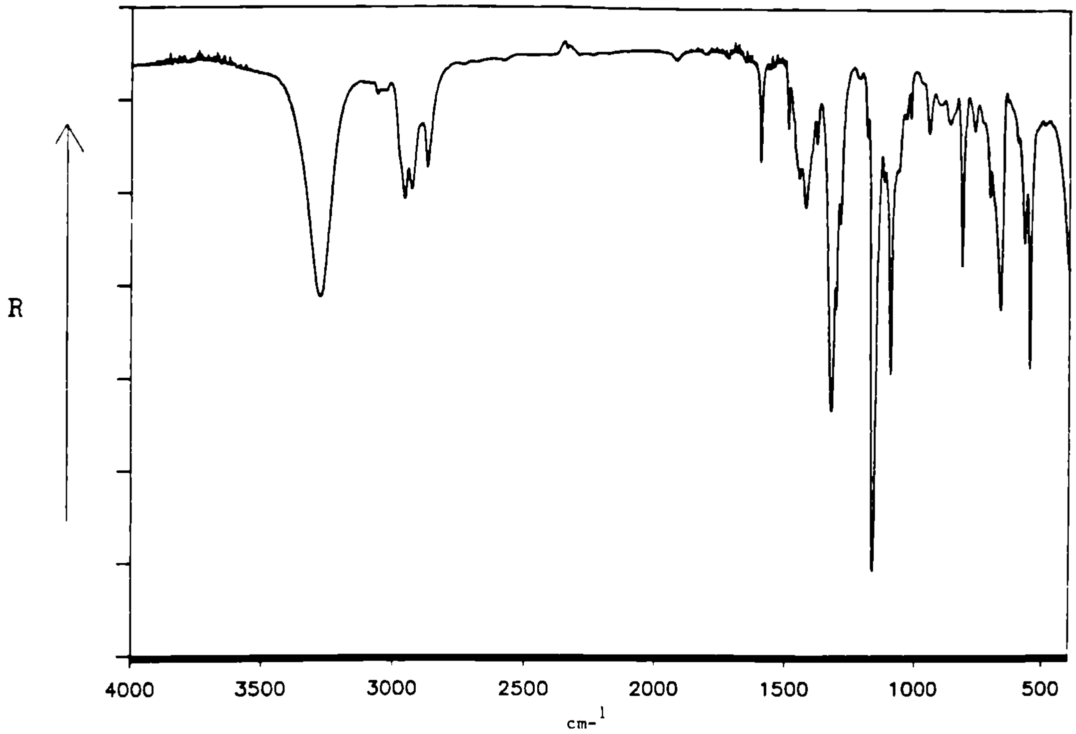

Figure 11.19 Transmission FT-IR spectrum of Ketjenflex 8 (N-ethyl o,p-toluenesulphonamide).

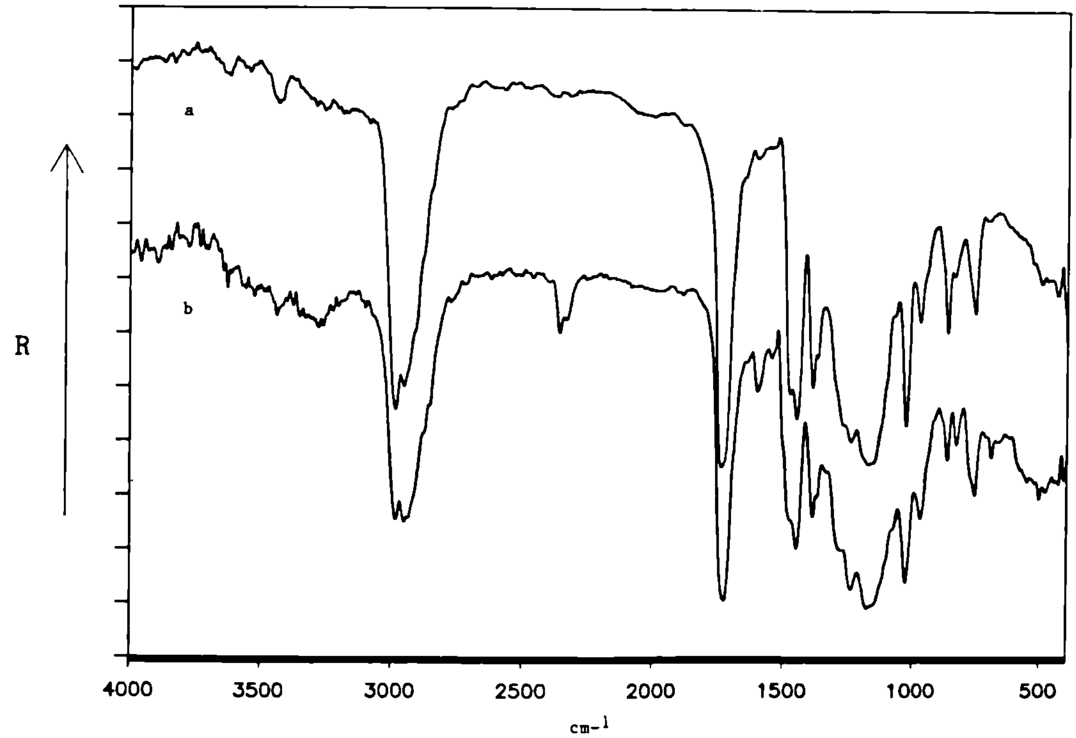

Figure 11.20 Diffuse reflectance spectra of (a) HMG Paraloid B-72 acrylic adhesive and (b) adhesive sample (JH3) from 'Construction in space, Two cones' (T.2143).

TABLE 11.1

Description and identification of Gabo sculpture samples

Sample number	Museum number	Title	Date	Location of sample	Colour	Condition	Identification
I-3	T.2168	Model for 'Monument for an airport'	c.1932	black parallelogram	black	OK	cellulose nitrate
I-4	T.2178	Model for 'Construction on a line'	c.1937	clear plastic in front	clear, yellowed	distorted with bubbles	cellulose acetate
I-5	T.2178	Model for 'Construction on a line'	c.1937	thin clear back sheet	clear	distorted	cellulose acetate
I-6	T.2178	Model for 'Construction on a line'	c.1937	black strip	black	slightly distorted	cellulose nitrate
I-7	T.2169	Model for 'Construction in space, Two cones'	c.1927	bottom layer of base section	black	OK	cellulose nitrate
I-8	T.2169	Model for 'Construction in space, Two cones'	c.1927	triangular section inside cones	red	OK	casein
I-9	T.2169	Model for 'Construction in space, Two cones'	c.1927	grey upper layer of base section	trans grey	OK	cellulose acetate
I-10	T.2145	Construction in a niche	c.1930	large curved backdrop section	trans orange	OK	poly(methyl methacrylate)
I-11	T.2167	Model for 'Column'	c.1920-21	long black strip	black	OK	cellulose nitrate
I-12	T.2179	Model for 'Construction in space' crystal	c.1937	thick base section	clear, yellowed	slight distortion	cellulose acetate
I-13	T.2170	Model for 'Double relief in a niche'	c.1929-30	strip at bottom of rectangular section	black	OK	cellulose nitrate
I-14	T.2142	Circular relief	c.1925	black strip	black	slight distortion crystals of sweat	cellulose acetate
I-15	T.2146	Torsion	c.1929-37	black top	black	OK	cellulose acetate
I-16	T.2146	Torsion	c.1929-37	upper arm	clear	OK	poly(methyl methacrylate)
I-17	T.2187	Model for 'Monument to the unknown political prisoner'	c.1952	black wedge	black	OK	poly(methyl methacrylate)
I-18	T.190	Spiral theme	c.1941	thick side section	clear, slightly yellowed	OK	cellulose acetate
I-19	T.2187	Model for 'Monument to unknown prisoner'	c.1952	center section, scratched	clear	OK	poly(methyl methacrylate)
I-20	T.190	Spiral theme	c.1941	thin side section, not bloomed	clear	OK	cellulose acetate
II-1	T.2206	Model for 'Construction in space, arch'	c.1937	transparent side	clear, yellowed	collapsed	cellulose acetate
II-3	T.2177	Model for 'Construction through a plane'	c.1935-37	outer surround	clear	slight distortion	cellulose acetate
II-4	T.2177	Model for 'Construction through a plane'	c.1935-37	triangle in front	clear, slightly yellowed	distorted	cellulose nitrate
II-5	T.2177	Model for 'Construction through a plane'	c.1935-37	star in center	black	OK	cellulose nitrate
II-6	T.2181	Model for 'Spiral theme'	c.1941	top section	clear	OK	cellulose acetate

TABLE 11.1 contd.

Description and identification of Gabo sculpture samples

Sample number	Museum number	Title	Date	Location of sample	Colour	Condition	Identification
II-7	T.2187	Model for 'Monument to the unknown political prisoner'	c.1952	N/A	clear	OK	poly(methyl methacrylate)
II-8	T.2145	Construction in a niche	c.1930	orange shape	orange	OK	poly(methyl methacrylate)
II-9	T.2145	Construction in a niche	c.1930	curved shape at top	clear, slightly yellowed	OK	cellulose acetate
II-10	T.2145	Construction in a niche	c.1930	wedge shape in rear	frosted	OK	poly(methyl methacrylate)
II-11	T.2145	Construction in a niche	c.1930	curved spiral section at bottom	clear, slightly yellowed	OK	cellulose nitrate
II-12	T.2170	Model for 'Double relief in a niche'	c.1929-30	rectangle base	orange	OK	casein
II-13	T.2170	Model for 'Double relief in a niche'	c.1929-30	plastic beneath cone	clear, yellowed	OK	cellulose nitrate
II-14	T.2144	Red cavern	c.1926	black strip	black	OK	cellulose nitrate
II-15	T.2144	Red cavern	c.1926	triangle shape	frosted	OK	cellulose nitrate
II-16	T.2144	Red cavern	c.1926	long, thin rectangle at front	white	OK	cellulose nitrate
II-17	T.2142	Circular relief	c.1925	top section	white	OK	poly(methyl methacrylate)
II-18	T.2142	Circular relief	c.1925	large circular panel	black	slight distortion where laminated	cellulose acetate
JH13	T.2143	Construction in space 'Two cones'	c. 1968	base section	trans grey	distorted, sweat	cellulose acetate
JH15	T.2143	Construction in space 'Two cones'	c. 1968	base section	black	distorted, sweat	cellulose acetate
JH17	T.2168	Model for 'Monument for an airport'	c. 1932	vertical plane, yellow piece	yellow	crizzled	cellulose nitrate
JH18	T.2170	Model for 'Double relief in a niche'	c.1929-30	adhered on base	orange	crizzled	cellulose nitrate
JH26	T.2142	Circular relief	c.1925	top section	clear	OK	poly(methyl methacrylate)
JH29	T.4146	stage set 'La Chatte' (Pevsner)	c.1925-26	model in back	clear, slightly yellowed	OK	cellulose acetate
JH30	T.4146	state set 'La Chatte'	c.1925-26	back piece	black	OK	see text
JH32	T.4146	state set 'La Chatte'	c.1925-26	diamond riveted in #B	clear, yellowed	OK	cellulose nitrate
JH38	T.2188	Model for 'Construction outside Bijenkorf building, Rotterdam	c. 1955	greenish clear base	clear	OK	cellulose acetate
JH39	T.2186	First model for 'Monument to the unknown political prisoner	c. 1952	clear section at bottom edge	clear	OK, acrylic appearance	cellulose acetate

TABLE 11.2

Description and identification of Gabo plastic samples

Sample	Sample number	Treatment	Colour	Condition	Identification	Comments
A	I-1	none	black	OK	cellulose acetate	
	JH21	none	black	OK	cellulose acetate	**some loss of C=O band**
	JH22	heat + 100% RH	black	sweat + distortion		**spectrum much altered see text**
B	II-2	none	yellowed	OK	cellulose acetate	
	JH19	none	yellowed	OK	cellulose acetate	
	JH20	heat + 100% RH	yellowed	sweat + distortion		**spectrum altered - some loss of C=O and C-O bands**
C	JH33	none	very slightly yellowed	OK	cellulose acetate	
	JH36	heat + 100% RH	no change	OK	cellulose acetate	
D	JH16	none	yellowed transparent	OK	cellulose nitrate	
E	I-1	none	red	OK	casein	
	JH31	heat + 100% RH	red	expanded see text	casein	**some alteration in spectrum see text**
F	JH8	none	mustard yellow transparent	OK	poly(vinyl chloride)/ poly(vinyl acetate) copolymer	
	JH37	heat + 100% RH	opaque peach	OK	poly(vinyl chloride)/ poly(vinyl acetate) copolymer	**slight alteration in spectrum**

TABLE 11.2 contd.

Description and identification of Gabo plastic samples

Sample	Sample number	Treatment	Colour	Condition	Identification	Comments
G	JH2	none	transparent grey	OK	cellulose acetate	loss of C=O and C-O bands
		none-ground end			cellulose acetate	loss of C=O and C-O bands
		none-smooth side surface			cellulose acetate	loss of C=O and C-O bands
		none-rough side surface			cellulose acetate	loss of C=O and C-O bands
		none-ground end			cellulose acetate	
		none-further grinding			cellulose acetate	
	JH10	35% RH	transparent grey	internal cracks	cellulose acetate	loss of C=O and C-O bands
					cellulose acetate	loss of C=O and C-O bands
					cellulose acetate	loss of C=O and C-O bands
	JH11	heat + 100% RH	transparent light brown	sweat + lengthwise cracks	cellulose acetate	loss of C=O and C-O bands
	JH12	heat + 100% RH	transparent blue	sweat + lengthwise cracks	cellulose acetate	loss of C=O and C-O bands
801	II-1A	none	transparent	crizzled	poly (methyl methacrylate)	

TABLE 11.3

Description and identification of Gabo adhesive and surface exudate samples

Sample number	Museum number	Title/Sample	Date	Sample	Sampling technique	Sample location	Colour	Identification
JH3	T.2143	Construction in space 'Two cones'	c. 1968	adhesive	sample removed, rubbed onto silicon carbide paper	between laminated layers in base	clear	acrylic adhesive
JH4		Gabo plastic sample A artificially aged - see text	N/A	sweat	removed with swab, rubbed onto KBr plate	surface	black	plasticizers see text
JH5		Gabo plastic sample B artificially aged - see text	N/A	sweat	removed with swab, rubbed onto KBr plate	surface	clear	plasticizers see text
JH34	T.2142	Circular relief	c. 1925	sweat	removed with swab, rubbed onto KBr plate	black circular section see text	crystals	plasticizers see text
JH40	T.2143	Construction in space 'Two cones'	c. 1968	sweat	removed with swab, rubbed onto KBr plate	base	black	plasticizers see text

TABLE 11.4

Frequency values and band assignments for cellulose nitrate and Parkesine samples

Millipore	Wardle-Storey	Parkes SM1	SM2	SM3	SM4	SM5	SM6	Intensity	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1				cm-1	
3447	3442	3441	3406	3400	3397	3438	3383	m,b	O-H stretch hydrogen bonded	O-H group	3400 - 3200(vs) polymeric intermolecular	1
2961	2965							m	C-H stretch	methyl group	2962 ± 10(s)	1
2917	2928	2929	2921	2918	2933	2919	2920	m	C-H stretch	methylene group	2926 ± 10(s)	1
1748	1732	1731	1728		1724			s	C=O stretch	carbonyl group	1735(s,sp)	2
1671	1663	1651	1652	1651	1652	1652	1651	s	N-O asym. stretch	nitrate group	1667 - 1629(vs)	3
1511						1541	1544	w	unassigned			
1455	1452							m	C-H asym. deformation	methyl group	1450 ± 20(m)	1
									C-H deformation	methylene group	1465 ± 20(m)	1
1429	1418	1419	1431		1428	1429	1400	m	unassigned			
1374	1376	1375			1375	1375		m	C-H sym. deformation	methylene group	1380 - 1370(s)	1
1288	1286	1280	1281	1282	1281	1282	1283	s	N-O sym. stretch	nitrate group	1285 - 1272(vs)	3
1246								m	unassigned			
	1205	1206				1207		m	unassigned			
1162	1163	1162			1163	1163		s	C-O stretch	ether linkage	1150 - 1060(vs)	1
1073	1066	1066	1062	1062	1059	1061	1064	s,b	C-O stretch	ether linkage	1150 - 1060(vs)	1
945	near 945							w	unassigned			
846	846	840	841	843	846	847	846	s	N=O stretch	nitrate group	872 - 833(s)	3
751	752	752	750	753	752	752	749	m	out-of-plane deformation	nitrate group	761 - 745(m)	3
692	683	677			677	696		m	N-O deformation	nitrate group	710 - 689(m)	3

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.5

Frequency values and band assignments for cellulose nitrate and Vestry House Museum samples

Millipore	Wardle-Storey	Vestry House Museum Samples				Intensity	Vibration	Functional group	Frequency range given in literature	Ref.
		VHM1	VHM2	VHM3	VHM5					
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1				cm-1	
3447	3442	3437	3386	3488	3445	m,b	O-H stretch hydrogen bonded	O-H group	3400 - 3200(vs) polymeric intermolecular	1
2961	2965	2964	2963			m	C-H stretch	methyl group	2962 ± 10(s)	1
2917	2928	2934			2928	m	C-H stretch	methylene group	2926 ± 10(s)	1
1748	1732	1739	1728		1728	s	C=O stretch	carbonyl group	1735(s,sp)	2
1671	1663	1661	1643	1643	1670	s	N-O asym. stretch	nitrate group	1667 - 1629(vs)	3
1511						w	unassigned			
1455	1452	1451	1451			m	C-H asym. deformation	methyl group	1450 ± 20(m)	1
							C-H deformation	methylene group	1465 ± 20(m)	1
1429	1418				1420	m	unassigned			
1374	1376	1375	1368		1378	m	C-H sym. deformation	methylene group	1380 - 1370(s)	1
1288	1286	1285	1283	1283	1282	s	N-O sym. stretch	nitrate group	1285 - 1272(vs)	3
1246						m	unassigned			
	1205	1204	1204			m	unassigned			
1162	1163	1162	1161		1162	s	C-O stretch	ether linkage	1150 - 1060(vs)	1
1073	1066	1058	1061	1075	1053	s,b	C-O stretch	ether linkage	1150 - 1060(vs)	1
945	near 945					w	unassigned			
846	846	847	840	830	845	s	N=O stretch	nitrate group	872 - 833(s)	3
751	752	752	753	752	752	m	out-of-plane deformation	nitrate group	761 - 745(m)	3
692	683	694			674	m	N-O deformation	nitrate group	710 - 689(m)	3

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.6

Frequency values and band assignments for cellulose nitrate standards and Gabo sculpture samples

Millipore cm-1	Wardle-Storey cm-1	Gabo samples cm-1	Intensity	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
3447	3442	3494 - 3411	m,b	O-H stretch hydrogen bonded	O-H group	3400 - 3200(vs) polymeric intermolecular	1
2961	2965	2964 - 2962	m	C-H stretch	methyl group	2962 ± 10(s)	1
2917	2928	2929 - 2915	m	C-H stretch	methylene group	2926 ± 10(s)	1
1748	1732	1732 - 1728	s	C=O stretch	carbonyl group	1735(s,sp)	2
1671	1663	1678 - 1662	s	N-O asym. stretch	nitrate group	1667 - 1629(vs)	3
1511		1504 - 1488	w	unassigned			
1455	1452	1454 - 1451	m	C-H asym. deformation	methyl group	1450 ± 20(m)	1
				C-H deformation	methylene group	1465 ± 20(m)	1
1429	1418	*1419 - 1416	m	unassigned			
1374	1376	1378 - 1375	m	C-H sym. deformation	methylene group	1380 - 1370(s)	1
1288	1286	1297 - 1287	s	N-O sym. stretch	nitrate group	1285 - 1272(vs)	3
1246		*1240 - 1230	m	unassigned			
	1205	*1213 - 1208	m	unassigned			
1162	1163	1166 - 1162	s	C-O stretch	ether linkage	1150 - 1060(vs)	1
1073	1066	1095 - 1073	s,b	C-O stretch	ether linkage	1150 - 1060(vs)	1
945	near 945	* 945	w	unassigned			
846	846	870 - 846	s	N=O stretch	nitrate group	872 - 833(s)	3
751	752	755 - 752	m	out-of-plane deformation	nitrate group	761 - 745(m)	3
692	683	699 - 685	m	N-O deformation	nitrate group	710 - 689(m)	3

* Absorption is weak or does not appear in some spectra

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.7

Frequency values and band assignments for cellulose acetate standards and Gabo samples identified as cellulose acetate

cellulose acetate			Gabo samples	Intensity	Vibration	Functional group	Frequency range given in literature	Ref.
VA13	VA14	Bexfilm						
cm-1	cm-1	cm-1	cm-1				cm-1	
3499	3494	3482	3493 - 3464	m,b	O-H stretch	O-H group hydrogen bonded	3400 - 3200 (b)	1
		3069	3073 - 3068	w	C-H stretch	aromatic ring	near 3070 (w)	1
2959	2959	2959	2960 - 2891	m	C-H stretch	methyl group	2962 ± 10 (s)	1
2892	2893	2893		m	C-H stretch	methine group	2890 ± 10 (w)	1
1762	1758	1764	1760 - 1736	s	C=O stretch	ester	1750 - 1730 (s)	1
1644	1647	1648	1651 - 1646	m	unassigned			
		1591	1600 - 1592	m	skeletal ring stretch	aromatic ring	1625 - 1575(va)	1
1547	nr 1547	nr 1535	* 1551 - 1536	vw	unassigned			
		1490	1492 - 1490	m	skeletal ring stretch	aromatic ring	1525 - 1475(va)	1
1433	1434	1434	1436 - 1433	m	C-H asym. deformation	methyl group	1450 ± 20 (m)	1
1374	1373	1374	1375 - 1373	s	C-H sym. deformation	methyl group	1380 - 1370 (s)	1
1262	1258	1260	1246 - 1232	s	C-O stretch	acetate ester	1250 - 1230 (s)	1
1221	1222				unassigned			
		1189		s	P-O-C (aromatic)	triphenyl phosphate	1242 - 1110 (s)	2
1164	1166	1166	1164 - 1162	s	C-O stretch	ether linkage	1150 - 1060 (vs)	1
1087	1065	1087	1085 - 1040	s,b	C-O stretch	ether linkage	1150 - 1060 (vs)	1

TABLE 11.7 contd.

Frequency values and band assignments for cellulose acetate standards and Gabo samples identified as cellulose acetate

cellulose acetate			Gabo samples	Inten-sity	Vibration	Functional group	Frequency range given in literature	Ref.
VA13	VA14	Bexfilm						
cm-1	cm-1	cm-1	cm-1				cm-1	
954(vw)	954(vw)	963	975 - 965	s	P-O-C (aromatic)	triphenyl phosphate	996 - 905 (s)	2
905	904	904	907 - 904	m	unassigned		near 901 (m)	3
840	841	839	* 828 - 819	m	unassigned		near 837 (vw)	3
		782	785 - 761	m	C-H out-of-plane deformation	aromatic ring	810 - 750 (vs) meta-substitution	1
		760		m			770 - 735 (vs) ortho-substitution	1
							770 - 730 (vs) mono-substitution	1
nr 692(vw)	692 (vw)	692	692 - 691	m	C-H out-of-plane deformation	aromatic ring	710 - 690 (s) mono-substitution	1
605	604	604	607 - 603	m	bending vibration	acetate group	605 (m)	3
					skeletal vibration	acetate group	612 (s)	4

* Absorption is absent in some sample spectra.

1. Bellamy, 1975
2. Thomas and Chittenden, 1964
3. Hummel, 1966
4. Thompson and Torkington, 1945

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 11.8

Frequency values and band assignments for casein and Gabo samples identified as casein

Casein I	Gabo samples				Vibration	Functional group	Frequency range given in literature	Ref.
RW1	I-8	II-12	I-1	JH31				
cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
				3539(sp)	unassigned			
				3488(sp)	unassigned			
3287(s,b)	3313(s,b)	3291(s,b)	3313(s,b)	3311(s,b)	N-H stretch hydrogen bonded	peptide bond	3320 - 3270(m) (trans-)	1
3100(sh)	3076(sh)	3068(sh)	3072(sh)		amide II overtone	peptide bond	3100 - 3070(w) (cis- and trans-)	1
2962(m)	2959(m)	2959(m)	2962(m)	2962(m)	C-H stretch	methyl group	2962 ± 10(s)	1
	2932(m)	2923(m)	2931(m)	2927(m)	C-H stretch	methylene group	2926 ± 10(s)	1
2876(m)					C-H stretch	methyl group	2872 ± 10(s)	1
2120(w)				2129(w)	unassigned			
1661(s)	1652(s)	1661(s)	1671(s)	1659(s)	amide I C=O stretch	peptide bond	1680 - 1630(s)	1
					amide I	peptide bond	1656(vs)	2
1546(s)	1544(s)	1544(s)	1552(s)	1549(s)	amide II - coupled N-H deformation and C-N stretch	peptide bond	1570 - 1515(s) (solid)	1
					amide II	peptide bond	1538(s)	2
	1511(s)	1507(s)	1510(s)	1508(s)	unassigned			
1450(m)	1453(s)	1452(s)	1452(s)	1452(s)	C-H deformation	methyl and methylene groups	1448(m)	2
1400(m)	near 1400(m)	1408(s,b)	1409(s,b)	1408(m)	C-O resonance bond	carboxylic acid ionized	1399(m)	2
1350(m)					unassigned			
1315(m)					C-H deformation	methylene groups	1312(w)	2

TABLE 11.8 contd.

Frequency values and band assignments for casein and Gabo samples identified as casein

Casein I	Gabo samples				Vibration	Functional group	Frequency range given in literature	Ref.
RW1	I-8	II-12	I-1	JH31				
cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
1241(m)	1233(s)	1231(s)	1236(s)	1225(s)	amide III - coupled N-H deformation and C-N stretch	peptide bond	1305 - 1200(m)	1
					amide III	peptide bond	1242(m)	2
1175(m)	1177(m)	1176(s)	1176(m)	1141(s)	unassigned		1158(w)	2
1106(m)	1088(m)	1084(m)	1099(s)	1081(s)	N-H deformation	peptide bond	1101(m)	2
	near 1050(m)	1040(m)			unassigned			
950(w)		1009(m)		990(s)	unassigned		980(m)	2
900(w)		880(m)		873(s)	unassigned			
	826(w)	824(w)	826(m)		unassigned			
		793(m)		797(s)	unassigned	broad area of absorption - see text		
703(b)					unassigned			
626(b)	656(b)	650(b)		665(s)	unassigned			
569(b)	540(b)	532(b)	559(b)	577(s)	unassigned			

1. Bellamy, 1955

2. D'Esposito and Koenig, 1978

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.9

Frequency values and band assignments for poly (methyl methacrylate) standards and Gabo samples identified as poly (methyl methacrylate)

Aldrich trans cm-1	Plexiglass DR cm-1	Perspex DR cm-1	Gabo samples cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
2995	2997	2995	2998 - 2995	C-H stretch	methyl group	3010; 2976	2
2951	2952	2952	2953 - 2951	C-H stretch	methyl group	2962 ± 10 (s)	3
2843	2844	2844	2852 - 2844	C-H stretch	methylene group	2853 ± 10 (s)	3
1730	1734	1734	1739 - 1729	C=O stretch	ester	1750 - 1730 (s)	3
	1641	1601		unassigned			
1484	1480	1479	1489 - 1485	C-H deformation	methylene group	1465 ± 20 (m)	3
1450	1450	1448	1453 - 1451	C-H asym. deformation	methyl group	1450 ± 20 (m)	3
1436	nr 1430(sh)	nr 1430(sh)		C-H asym. deformation	methyl group	1450 + 20 (m)	3
1386	1389	1389	1389 - 1388	C-H sym. deformation	methyl group	1380 - 1370 (s)	3
1273	1269	1270	1276 - 1271	C-O stretch	ester	1310 - 1250 (s)	4
				unassigned		1282	5
1242	1243	1241	1243 - 1239	C-O stretch	ester	1310 - 1250 (s)	4
				unassigned		1235	5
1193	1193	1194	**1196 - 1195	C-O stretch	ester	1200 - 1100 (s)	4
				unassigned		1170	5
1150	1152	1154	1161 - 1153	C-O stretch	ester	1200 - 1100 (s)	4
				unassigned		1149	5
1065	1065	1065	1077 - 1066 (1)	unassigned			
990	991	992	991 - 990	unassigned			
967	nr 960(sh)	nr 960(sh)	* 968	unassigned			
913	nr 910(sh)	nr 910(sh)	* 915 - 911	unassigned			
843	843	843	* 844 - 843	unassigned			

TABLE 11.9 contd.

Frequency values and band assignments for poly (methyl methacrylate) standards and Gabo samples identified as poly (methyl methacrylate)

Aldrich trans cm-1	Plexiglass DR cm-1	Perspex DR cm-1	Gabo samples cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
827	nr 825(sh)	nr 825(sh)	* 828 - 827	unassigned			
811	nr 810(sh)	nr 810(sh)	* 810	unassigned			
			* 795 - 793	unassigned			
737	754	754	754 - 753	unassigned		749	5
703				unassigned			

* Absorption is weak or does not appear in some spectra ** Absorption only appears in sample spectra I-19 and II-10.

1. Band appears at 1035 cm-1 in spectrum of sample II-8
2. McKean et al., 1973
3. Bellamy, 1975
4. Colthup, 1950
5. Urbanski et al., 1977

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 11.10

Frequency values and band assignments for plasticizer standards and unknown 'sweat' samples

JH4 cm-1	JH5 cm-1	JH34 cm-1	JH40 cm-1	Triphenyl phosphate cm-1	Sulphonamide* cm-1	Diethyl phthalate cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
					3281(s)			unassigned	
				3097(w)			C-H stretch	aromatic carbon	3070 and 3030(w)
3070(w)	near 3070(w)	near 3070(w)	3070(w)	3059(m)	3064(w)	3072(w)	C-H stretch	aromatic carbon	3070 and 3030(w)
				3019(w)			C-H stretch	aromatic carbon	3070 and 3030(w)
			2980(w)		2960(m)	2983(s)	C-H stretch	methyl group	2962 ± 10(s)
2931(m)	2918(m)	near 2900(w)	2936(w)		2934(m)	2939(m)	C-H stretch	methylene group	2926 ± 10(s)
						2906(m)	C-H stretch	methine group	2890 ± 10(w)
2891(m)			2882(w)		2874(m)	2874(m)	C-H stretch	methyl group	2872 ± 10(s)
2821(w)			2821(w)				unassigned		
				1739(w)			unassigned		
1728(s)	1726(s)	1726(s)	1727(s)			1728(s,b)	C=O stretch	ester, aryl	1730 - 1717(s)
			1597(sh)	1598(s)	1599(m)	1600(s)	skeletal ring stretch	aromatic ring	1625 - 1575(va)
1590(m)	1590(m)	1588(m)	1589(m)	1588(s)		1580(s)	skeletal ring stretch	aromatic ring	1600 - 1560(w unless conjugated)
1489(s)	1489(s)	1488(s)	1489(s)	1484(s)	1495(w)	1488(m)	skeletal ring stretch	aromatic ring	1525 - 1475(va)
						1476(s)	C-H asym. deformation	methyl group	1450 ± 20(m)
1450(m)			1457(m)	1455(m)	1453(m)	1466(s)			
					1426(m)	1448(s)	C-H deformation	methylene group	1465 ± 20(m)
							skeletal ring stretch	aromatic ring	near 1450((m)
1405(w)			1405(w)				unassigned		
				1384(w)	1383(m)	1391(s)	unassigned		
1369(m)			1369(w)			1369(s)	C-H sym. deformation	methyl group	1380 - 1370(s)

TABLE 11.10 contd.

Frequency values and band assignments for plasticizer standards and unknown 'sweat' samples

JH4 cm-1	JH5 cm-1	JH34 cm-1	JH40 cm-1	Triphenyl phosphate cm-1	Sulphonamide* cm-1	Diethyl phthalate cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
1339(m)					1325(s)		S=O stretch	sulphonamide	1358 - 1336(s)
					1306(sh)		unassigned		
					1290(sh)		unassigned		
1289(s)	1287(s)	1294(s)	1289(s)	1295(s)		1284(s,b)	P=O stretch	phosphate	1300 - 1250(s)
							C-O stretch	phthalate ester	1310 - 1250(s)
			1227(m)	1233(m)			unassigned		
1188(s)	1188(s)	1187(s)	1188(s)	1194(s)	1185(w)		P-O-C (ar)/ P-O stretch	phosphate aromatic	1242 - 1110(s) (2)
				1176(s)		1174(s)	C-H in-plane deformation	aromatic ring	1225 - 950(w)
1163(s)	near 1160(s)	1163(s)	1162(s)	1162(s)	1161(s)		S=O stretch	sulphonamide	1169 - 1152(s)
				1153(s)			unassigned		
1123(s)	1124(s)	near 1125(m)	1124(s)		1120(m)	1124(s)	C-O stretch	phthalate ester	1150 - 1100(s)
			1094(m)		1094(s)	1097(s)	C-H in-plane deformation	aromatic ring	1225 - 950(w)
1073(s)	1073(s)	near 1080(m)	1072(s)	1071(m)	1067(w)	1074(s)			
1041(m)	near 1040(m)	near 1040(w)	1041(m)	1030(s)	1037(w)	1041(s)			
1026(m)	near 1025(m)	near 1025(m)	1026(s)	1023(s)	1019(w)	1018(s)			
1011(m)	1011(s)	1010(s)	1011(s)	1009(s)					
				981(s)			P-O-C (ar)	phosphate aromatic	996 - 905(s) (2) often complex
961(s)	959(s)	954(s)	964(s)	953(vs)	948(w)	963(w)			
				931(s)					
			906(w)	913(s)		893(w)			
866(m)			866(w)		864(w)	864(m)	unassigned		
				846(w)		847(m)	unassigned		
				835(w)			unassigned		

TABLE 11.10 contd.

Frequency values and band assignments for plasticizer standards and unknown 'sweat' samples

JH4 cm-1	JH5 cm-1	JH34 cm-1	JH40 cm-1	Triphenyl phosphate cm-1	Sulphon-amide* cm-1	Diethyl phthalate cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
			817(w)		815(s)		unassigned		
				787(s)			unassigned		
779(m)	770(m)	770(m)	778(s)	770(s)	767(w)		C-H out-of-plane	aromatic ring	770 - 730(vs)
747(m)	753(s)	near 750(m)	755(s)	752(s)			deformation		mono-substitution
						745(s)	C-H out-of-plane	aromatic ring	770 - 735(vs)
							deformation		ortho-substitution
706(w)			714(w)		707(m)	706(s)	C-H out-of-plane	aromatic ring	710 - 690(s)
690(m)	689(s)	690(m)	689(s)	691(s)		692(sh)	deformation		mono-substitution
652(w)			663(w)		664(s)	651(m)	unassigned		
618(w)			617(w)	616(w)			unassigned		
			595(w)	596(w)			unassigned		
579(m)			573(m)	579(s)	572(s)		unassigned		
			551(m)	564(s)	551(s)	563(m)	unassigned		
520(sh)			519(m)	519(s)			unassigned		

* N-ethyl o,p-toluenesulphonamide (Monsanto)

1. Bellamy, 1975

2. Thomas and Chittenden, 1964

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

CHAPTER 12 POLYMER DEGRADATION MECHANISMS

Introduction

A detailed study of the degradation of polymers was not undertaken in this research. However, most samples which are examined in the conservation context will have undergone some degradation and a brief discussion of degradation mechanisms is appropriate.

Degradation is defined as a change of properties or loss of characteristics which generate the specific requirements necessary for the product to fulfil its desired function (Crighton, 1988). The most important characteristic is mechanical performance. In the polymer industry, it is necessary to produce materials with mechanical properties which are specific to its intended use. The mechanical properties are dependent on the polymer type, length of polymer chain and the structural arrangements of the molecules such as areas of crystallinity, cross links between chain and preferred orientation of the chains affect the properties (Crighton, 1988). A variation in molecular size, namely chain length, has the greatest effect on properties and these changes in turn affect the chain interactions and areas of ordered structure.

Variations in appearance resulting from creation or loss of a chromophore can be undesirable and are considered to be degradation (Crighton, 1988). This is especially true in works of art and objects in museum collections.

Some of the properties which are affected by chain length include strength, toughness, elasticity, abrasion resistance, processability and clarity (in films). Breakage of bonds in the polymer backbone causes changes in mechanical properties. There are two types of reactions, a step reaction and a chain reaction. The step reaction involves breakage of bonds in random locations in the chain to produce large fragments. This results in a rapid alteration of the properties which are dependent on chain length as only a few reactions are needed to reduce the chain length by 50%. In the chain degradation mechanism, the terminal backbone linkage is repeatedly broken producing the monomer. It has been described as an unzipping depolymerization. This is a slower degradation process as 50% of the reactions must occur before the chain length is reduced by half. The crosslinks between polymer chains affect the mechanical properties and are also affected by the step degradation process. Crosslinks give strength and elastic recovery and prevent excessive movement of the chains. There is a favoured concentration of crosslinks for desired properties and an excess causes greater stiffness and brittleness. Thus, the rapid reduction of chain length by random scission will result in a higher percentage of crosslinks for each molecule (Crighton, 1988).

Sources of energy for bond scission

Chemical bond scission requires a discrete amount of energy. In certain molecules there are imperfections in the chain structure which often provide weak bonds which are more susceptible to breakage. Thus, the energy required is reduced. The sources of energy are mechanical, thermal or electromagnetic radiation. The energy from the ultraviolet region (<320 nm) causes much damage and is a major source of degradation energy. Chemical reactions also cause degradation by weakening links in the back bone or by direct reaction with the bond. Examples of chemical reaction include hydrolysis which occurs in the presence of water and oxidation which requires oxygen or ozone (Crighton, 1988).

Hydrolysis is the reverse of the reaction used to produce polymers by the condensation process. Water is often a byproduct of condensation polymerization and polymers such as polyesters and polyamides which are produced by condensation are particularly subject to hydrolysis by scission of the ester or amide backbone linkages. The rate of degradation is controlled by the severity of the environmental conditions, the chemical structure of the monomer units and the ease of access of the linkages to the reactive agents (Crighton, 1988).

Thermal or heat energy is a second source of energy which can break chemical bonds. Weak bonds due to structural irregularities and "activated" bonds in the polymer backbone are susceptible to thermal degradation. In addition-type polymers, thermal degradation produces one polymer chain with a free radical end which is very reactive. In polymers which are produced by a free radical initiated chain reaction, the presence of a free radical end can cause a depolymerization or unzipping reaction. The chain length of the polymer gradually reduces and monomers are liberated. Poly (methyl methacrylate) is particularly susceptible to thermal degradation, the polymers is entirely reduced to monomer units where poly (ethylene) is only degraded by 3%. Other degradation reactions can be caused by thermal energy. For example, poly (vinyl chloride) loses hydrochloric acid. After a large amount of the acid is lost, the remaining polymer absorbs energy from the visible region of the electromagnetic spectrum and the residual polymer darkens and turns black (Crighton, 1988).

The presence of oxygen increases the rate of thermal degradation. The oxygen reacts chemically at the reactive sites in the polymer chain causing backbone scission. Areas of unsaturation in the polymer chain are susceptible to oxidation. Peroxides are easily attacked at the O-O bond and a very reactive free radical is formed. This type of reaction is accelerated by heat, light or metal ions. The free radicals which are produced then react with other polymer chains causing further degradation. The rate of degradation is related to both the chemical structure of the polymer system and the physical changes which result from the degradation. Thus, there is no antioxidant which will be efficient for all polymers. In vulcanized rubber, the crosslinks are sensitive to heat and oxygen. The properties of rubber are severely affected by the number of crosslinks and too few or too many result in a degraded product. Ozone which is present in the atmosphere in small quantities and other materials such as oxidizing acids (H_2SO_4) can have the same effect (Crighton, 1988).

When a molecule is exposed electromagnetic radiation, the molecule absorbs some of the energy and becomes 'excited'. The energy in the region 290 - 400 nm is the most critical as many of the bond energies fall within this region. If the radiation is equal to the bond energies of 'weak' chemical bonds due to structural irregularities, the bond may break. Also, free radical species are often produced by this reaction which cause further chain scission. The free radicals are referred to as photo-initiators. Additives in the polymer matrix such as dyes, pigments, delustrants and other additives. can also act as sensitizers when they absorb light energy and transfer it to the polymer by molecular collisions. Impurities which include residues of catalysts used in the polymerization, trace metals absorbed during productions or processing and atmospheric pollutants have a similar sensitizing effect (Crighton, 1988).

If the impurity in the polymer structure when activated by the light energy removes a hydrogen atom from the polymer creating a radical which then in turn may remove a hydrogen atom from another chain. It can also react with oxygen in the air or form a crosslink with another polymer radical (Crighton, 1988).

Photo-oxidation is a chain reaction which creates further light absorbing molecules which cause degradation. Thus, the presence of only a few radicals can result in a significant variation in the mechanical properties of the polymer (Crighton, 1988).

The oxidation reaction also forms carbonyl groups which are potentially very reactive and after a quantity is formed, they absorb a large amount of active incident light. This energy absorption causes bond scission or it may activate another oxygen molecule which causes further oxidation (Crighton, 1988).

When polymers are subjected to tensile stress, the polymer chains which are in an amorphous arrangement are extended which causes strain in localized lengths. These bonds are more reactive and susceptible to attack. It is possible to observe localized differences in degradation rates in strained fibres and fabrics (Crighton, 1988).

Plasticizers modify mechanical properties of polymers such as stiffness and hardness (Chapter 9). They are only active in the amorphous areas within the polymer. With mobile chains, some of the plasticizer is lost by diffusion over time which will change the properties. Fillers such as carbon black, which are added to reinforce polymer systems, result in increased stiffness, strength, toughness and abrasion resistance. This occurs due to forces between the additive molecules and those of the polymer Loss of filler additives will also alter the properties. Liquids which come into contact with polymers cause them to swell and extract additives (Crighton, 1988).

Polymers of natural origin, such as cellulose or protein derivatives, are also susceptible to bacterial and insect attack in a warm and moist environment. Polymers may be treated by an insecticide or a bacteriocide and should be stored in a dry cool air environment to retard degradation (Crighton, 1988).

Degradation of plastics

Cellulose nitrate

Cellulose nitrate is affected by both thermal and photochemical decomposition. In thermal degradation, it is thought that the primary reaction is the breaking of the N-O bond of the nitrate ester (Sirkis, 1982).

$\mathrm{R{-}O{-}NO_2} \longrightarrow \mathrm{R{-}O^{\bullet}} + \mathrm{NO_2}\uparrow$ (Equation 12.1)

However, the secondary reactions are not fully understood. One possible situation is that the free radicals may form an aldehyde and an alcohol (Equation 12.2).

$\mathrm{R{-}O^{\bullet}} + \mathrm{R{-}O^{\bullet}} \longrightarrow \mathrm{ROH} + \mathrm{RCHO}$ (Equation 12.2)

The free radical may attack the remaining nitrate to form an aldehyde and $\mathrm{NO_2}$ gas.

$\mathrm{R{-}CH_2{-}O^{\bullet}} + \mathrm{R{-}CH_2{-}O{-}NO_2} \longrightarrow \mathrm{R{-}CH_2{-}OH} + \mathrm{R{-}\overset{\bullet}{C}H{-}O{-}NO_2}$ (Equation 12.3)

$\mathrm{R{-}\overset{\bullet}{C}H{-}O{-}NO_2} \longrightarrow \mathrm{R{-}CHO} + \mathrm{NO_2}\uparrow$ (Equation 12.4)

where $\mathrm{R{-}\overset{\bullet}{C}H{-}O{-}NO_2}$ is a radical nitrate (Sirkis, 1982).

The reactions are strongly exothermic at room temperature and are autocatalyzed by unstable sulphate esters which are formed as a byproduct of the nitration, residual acids remaining from the nitration, and free radicals. The presence of moisture further accelerates the degradation as moisture swiftly converts the $\mathrm{NO_2}$ to nitric acid which causes additional denitration and hydrolysis of the cellulose chain. It is thought that the glucose ring is destroyed as well (Ott, 1943). The number of terminal aldehydes which are possible reducing agents is increased each time the cellulose chain is shortened.

Ultraviolet radiation is thought to cause dramatic colour changes to cellulose nitrate by the production of nitrogen dioxides. Photochemical degradation also causes scission of the backbone bonds which results in a loss in viscosity and embrittlement. All of the wavelengths in the ultraviolet result in denitration. Shorter wavelengths, however, cause changes in viscosity and the most rapid change is seen with light of 253.6 nm. The presence of oxygen with light causes photo-oxidation and fluctuating environmental conditions increase the rate of degradation. The exact reactions of photodegradation are not fully elucidated. They are thought to be a series of peroxide and free radical reactions (Sirkis, 1982).

The cellulose chain is sensitized by metal ions, anthraquinone dyes, azo dyes, reactive and dispersive dyes which make the material more sensitive to ultraviolet radiation. The mechanism for the sensitization can be represented either by Equation 12.5

$$\text{DYE} + \text{O}_2 \xrightarrow{\text{light}} \text{O}_2^* + \text{DYE}^* \qquad \text{(Equation 12.5)}$$

or by Equations 12.6 and 12.7

$$\text{DYE} \xrightarrow{\text{light}} \text{DYE}^* \qquad \text{(Equation 12.6)}$$

$$\text{DYE}^* + \text{Cell-H} \longrightarrow \text{Cell}^* + \text{DYE-H} \xrightarrow{\text{O}_2} \text{Cell}^*\text{-O}_2 \qquad \text{(Equation 12.7)}$$

The metal ions are incorporated into the cellulose as trace metals and catalyst residues from the production method and these "foreign atoms" are found in most polymers after production (Crighton, 1988).

It is interesting to note that as the most complete experiments on cellulose nitrate degradation have been performed with pure uncombined cellulose nitrate, the effect of camphor is not known. It has been assumed that camphor could be involved in a number of possible reactions. The role of camphor in cellulose nitrate degradation should be studied to obtain a better understanding of cellulose nitrate deterioration (Sirkis, 1982).

The progress of cellulose nitrate film degradation has been studied and the stages are documented. The stages of object deterioration are more complex because of compositional differences such as the presence of fillers, dyes, and stabilizers and the shape of the object. Also, the production method and what the object was utilized for will have an effect on the degradation and will differ from object to object. The first sign of deterioration may be observed in the packing materials. Paper, which is mainly composed of cellulose, is sensitive to gaseous NO_2 and the hygroscopic nature of the paper provides a matrix for the manufacture of nitric acid from the NO2 given off by the objects (Weseloh, 1981). The paper darkens and/or becomes brittle. Acid-free tissue paper can almost completely disintegrate after contact of less than 48 hours with actively deteriorating cellulose nitrate. Other observable deterioration in objects include increased brittleness, cracking, discolouration, especially yellowing, a greasy feel on the surface, droplets of sticky moisture appearing on the surface and a strong odour. More severe degradation includes excessive warping and cracking and a characteristic crizzling pattern. The object may after a time completely fall apart (Sirkis, 1982).

The conventional dispersive infrared analysis of cellulose nitrate in the Sirkis study did not show any marked changes between the spectra of visibly stable and degraded material. No new bands were formed and there was no evidence of major destruction of the glucose rings or of the ether linkages between them. Nor was there any evidence of aldehyde formation. Another study using FT-IR to analyse artificially aged fresh cellulose nitrate films concluded that there were no differences apparent in the spectra of six modern cellulose nitrates after heat or light ageing. However, there was some visible yellowing of the samples (Green and Bradley, 1988). In the same study, severely deteriorated cellulose nitrate Somali beads were examined. The degradation was not uniform and there were three deterioration 'zones' which were straw coloured, dark yellow and brown which were analysed separately by FT-IR. The spectrum of the brown material did show evidence of degradation. The bands which are due to the nitrate bonds were much less intense in relation to other bands in the spectrum than in the straw coloured material or the other cellulose nitrate sample spectra. The ratio of the carbonyl peak height to that of the nitrate band in the region of 1660 cm^{-1} is higher in the spectrum of the brown sample than in that of the straw coloured sample. The authors concluded that the age of the sample does not seem to be related to the degree of deterioration and that the non-uniformity of the deterioration seems to be due to the bulk of the sample (Green and Bradley, 1988).

The results of the studies by Sirkis (1982) and Green and Bradley (1988) are similar to those observed in this research. No strong evidence of degradation can be seen in the spectra. The Tate samples JH17 and JH18 are described as crizzled, but there are no major variations between the spectra of the samples and those of the visibly undegraded cellulose nitrate and the cellulose nitrate standards. The Gabo sample D was very yellowed, but no change was observed in the spectrum (see Chapter 11).

Cellulose acetate

Cellulose acetate is generally considered to be more stable than cellulose nitrate and shortly after it was invented, it was widely used as a replacement for cellulose nitrate. Since the early 1950's, cellulose triacetate has completely replaced cellulose nitrate as an archival material for cinema and photographic film. It is one of the few polymer systems which meets specifications for use as a photographic film support as it is considered to have archival permanence (physical and chemical stability over long periods of time when stored under a controlled environment). Images from older cellulose nitrate films have been transferred to cellulose acetate film. However, it is now evident that cellulose acetate is also subject to degradation. The decomposition is characterized by the release of acetic acid when the film container is opened and by the appearance of liquid/crystalline plasticizer deposits on the surface of the film. The phenomenon has become known as the "vinegar syndrome" in the film industry (Allen et al., nd).

The degradation mechanism of cellulose acetate is described as a deacetylation reaction in which acid is produced, which in turn causes chain scission. As the acetate groups are lost, and subsequently, the degree of substitution is lowered, the rate of reaction increases. Thus, an autocatalytic effect similar to that in cellulose nitrate degradation seems to be occurring. The reaction is thought to be acid catalyzed as the maximum rate of hydrolysis occurs at a pH of 4 and the degradation increases with increasing moisture concentration and temperature (Edge et al., 1988).

Work is being carried out on degradation of photographic film (Allen, et al., 1988; Edge, et al., 1988). Samples of naturally aged and artifically aged films were analysed. The study found that the rate of degradation was higher in the presence of 1M acetic acid than in 100% RH and that the slowest rate was observed in dry conditions. It was also found that the rate of degradation increases with increasing temperature and that the atmosphere is more critical than the temperature in degradation. The presence of acetic acid accelerates or perhaps catalyzes the hydrolytic degradation of the films. The effect of film storage materials were also examined and the enclosure of reels in metal storage cans was found to accelerate the degradation. Analysis of cross sections revealed that degradation was more extensive near to the spool and at the outer edges of the reel where the film would come into contact with the metal. The degradation of polymeric materials is known to be catalyzed by transition metals such as iron and decomposition was observed to be delayed by the use of inert glass containers. The emulsion layer was observed to inhibit deterioration of the base polymer to a certain extent, probably due to its acting as an acid neutralizer.

Plasticizers are used in cinematographic film to make the base more flexible. Triphenyl phosphate is usually used at a concentration of 20% of the weight of the acetate base. Diffusion or migration of the plasticizer was found to be associated with hydrolysis and deacetylation of the film and was observed to be dominant in the regions of the film reel which show higher moisture regain after dessication. White crystalline deposits, which were identified as triphenyl phosphate, were found on films which have characteristics of lowered acetyl content (i.e. high degree of insoluble polymer, high moisture regain and low pH) (Edge et al., 1988).

The results of the study support the mechanism of acid catalyzed hydrolytic deacetylation and degradation of the polymer structure and the subsequent loss of plasticizer. Moisture absorption was found to be the most important controlling factor in the decomposition process. Also, the build up of acetic acid in the film containers is thought to promote the degradation.

The stability of cellulose acetate is related to its structure. Different degrees of substitution result in differences in physical and chemical properties. Solubility can be used to distinguish between undegraded cellulose triacetate and diacetate. Cellulose triacetate with a substitution factor of 2.7 is soluble in methylene chloride/methanol and insoluble in ketonic solvents where the diacetate with a substitution factor of 2.3 is soluble in ketonic solvents such as acetone and not soluble in the methylene chloride/methanol solution (Edge et al., 1988). The absorption of moisture by cellulose acetate is attributed to hydrogen bonding between water molecules and available hydroxyl groups of the glucose units. The greater the degree of substitution, the lower the uptake of moisture (Edge et al., 1988). The chemical stability of cellulose diacetate was found to be lower than that of cellulose triacetate. Analysis of cellulose diacetate and cellulose triacetate dispersed in buffer solutions of pH rangeing from 2 - 10 at 30 °C indicated that the overall rate of hydrolysis was faster for the diacetate than that of the triacetate. This is an important consideration as the degradation mechanism in cellulose acetate is thought to be a hydrolysis reaction.

The initial methods used in the studies (Allen et al., 1988; Edge et al., 1988) were infrared and Fourier transform infrared spectroscopy. The spectroscopic methods were not successful owing to the thickness of the photographic film and its insolubility in the later stages of degradation (Allen et al., 1988). It was decided that cast thin films from a solvent would not be used as it would not be indicative of the real situation and because of the solubility problems of the heavily degraded film stock. Also, thin films that were made were poor in quality and there was a loss in clarity (Allen et al., 1988). The infrared results did not give detailed data on the changes in structure due to degradation. No obvious chemical or functional group variation was noted in the spectra. Only small decreases in acetate content and "variable" qualitative change in the hydroxyl region were seen. Thus, indirect measurement of deacetylation was made by monitoring changes in physical properties. This included changes in moisture regain, solubility, and pH (formation of free acetic acid) and the molecular weight was measured by dilute solution viscometry which gave an indication of chain scission.

The degradation of cellulose acetate used in Gabo's sculpture "Construction in Space, Two Cones" has been recorded. The sculpture was made in 1968 as a replica of a piece originally constructed in 1937 (material unidentified) which had fallen apart. The replica was produced from a variety of cellulose acetate sheets of different thicknesses and colours which are joined together with a solvent based adhesive. The deterioration of the replica has been described (Pullen and Heuman, 1988) as follows:

1. Distortion and warping without damage to adhered joints (1982).
2. Acetic acid odour (first detected in 1982).
3. The appearance of small beads of an oily substance on the laminate base (2/87).
4. Minor crack appeared on base (5/87).
5. Severe cracking and delamination on base, pH 3.5 (6/87).
6. Advanced deterioration and internal cracking (12/87).

The changes which are due to oxidation and hydrolysis are thought to have been occurring over a long period of time even when the sculpture appeared stable. The deterioration seems to be related to the induction phenomenon which has been observed in studies of organic polymer degradation (Pullen and Heuman, 1988). During the induction period, apparent stability suddenly ceases and rapid deterioration is observed. In the "Two Cones" piece, the warping and cracking of the base has completely changed it from its original form and it was necessary to make detailed photographic documentation. Little research has been done on the effect of light on cellulose acetate. It is thought that ultraviolet and possibly visible radiation can supply the activation energy for degradation reactions of oxidation and chain scission. As stabilizers are lost or altered over time, the polymer system is more vulnerable to photolytic degradation (Pullen and Heuman, 1988).

There are several factors which might have affected the stability of the "Two Cones" sculpture. The composition of the material is important. As mentioned earlier, the triacetate form is more stable, but the use of triacetate has in the past been limited to the production of photographic film and fibres. The sheet acetate used in the sculptures is thought to be the diacetate which is inherently less stable. Stability varies from batch to batch and may be masked by the addition of stabilizers (Pullen and Heuman, 1988).

Additives such as fillers, pigments, anti-oxidants and ultraviolet light absorbers are added to cellulose acetate to change properties and extend the lifespan of the product. Additives influence polymer stability, but are gradually lost over time by evaporation, volatilization on heating, or leaching out by water or other solvents. This results in brittleness, shrinkage, warping and lower resistance to moisture penetration (Pullen and Heuman, 1988). A lower resistance to moisture will lead to hydrolysis of the polymer material.

A third element affecting stability is the environmental history of the object. The "Two Cones" piece was exposed to a wide range of unrecorded conditions (temperature, relative humidity and light levels) before coming to the gallery and was subjected to some variations afterwards. The original "Two Cones" was kept in an air-tight case for many years and when the case was removed, a strong odour was noted and cracks developed on parts of the piece. On the following day, the base and the thick centre section were shattered. The Tate replica had also been kept stored under an acrylic cover and acetic acid was detected as having built up. Attempts were made to ventilate the piece, but the degradation continued. The cover was removed, but rapid deterioration has followed (Pullen and Heuman, 1988).

It is interesting to note that although the replica was made 40 years after the original, the initial degradation appeared in the same area. The first signs of break-down occurred on the laminated structure of the base. The sculpture base was constructed with a 4 mm thick transparent sheet "sandwiched" between two opaque black layers adhered with a solvent based acrylic adhesive system. It is thought that internal stresses are created by shrinkage as the solvent evaporates from the laminated joint and are relieved by cracking. The stresses remain locked into the polymer and make the system more susceptible to degradation (Pullen and Heuman, 1988).

In the artificial weathering tests, beads of exudate were only visible on the surface of samples kept at 100% RH at 50°C and 19°C. At 50 °C, sweat appeared after 5 days followed by severe cracking and yellowing. At 19 °C, plasticizer appeared after 16 days and slight cracking occurred without colour change. However, although 0% RH has been recommended for photographic film, the 4 mm thick samples which were exposed to 35% RH exhibited severe cracking. Gradual reconditioning of samples from 50 to 40 °C over 72 hours has resulted in saml1 cracks extending inwards from the cut edges. The effect of cyclic variations of humidity have not yet been investigated (Pullen and Heuman, 1988).

As with the cellulose nitrate samples, no strong evidence of the cellulose acetate degradation can be seen in the diffuse reflectance spectrum of the samples taken from "Construction in space, Two cones", JH13 (transparent grey) and JH15 (black). In the Gabo plastic sample G (see chapter 11), there is strong evidence for the hydrolysis of the acetate ester bond on the surface of the unaged sample and the aged sample. The degradation did not seem to be uniform throughout the sample. The question remains as to why the sample spectra from the actively degrading sculpture did not show evidence of degradation. As mentioned before, only a few random breaks in the backbone polymer chain drastically reduces the molecular weight and adversely affects the physical properties of the plastic. The plastics used in the sculpture have been subjected to stresses that the samples have not, and a change in the physical properties may be more evident in the material subjected to stress. The number of broken ester linkages needed to catalyze or accelerate the degradation are probably just a few of the total within the molecule and the loss of the ester linkages would not be seen in the spectrum until after the degradation has proceeded to a large degree.

Casein

The casein samples from the Gabo pieces seem to be in good condition (Pullen and Heuman, 1988) and casein is considered to be fairly stable. Casein is hygroscopic and tends to warp and shrink in warm, dry conditions (Langton, 1943; Yarsley, 1943). Thus, extreme environmental conditions are harmful, but ambient conditions seem to be satisfactory for the plastic. As no acids are involved in the production method for obtaining casein by the rennin method or by the hardening process, there does not seem to be an inherent risk of autocatalyzed degradation. The chemical reactions involved in compounding the plastic and hardening with formaldehyde seem to affect the conformation of the protein and cause crosslinking between elements along the chain. They do not seem to derivatize the protein as in the modification of cellulose. Additives such as dyes or pigments may affect long term stability which has not become evident as yet.

The Gabo sample plastic E which was identified as casein returned to almost the same size after expansion during ageing in high humidity. The material seems to recover from the ageing process. This situation is not realistic for objects as stresses in construction would cause cracks and warping. There are also differences in the diffuse reflectance spectra measured before and after the artificial ageing. Namely, the sharp bands which appear in the region of 3600 cm^{-1} in the aged sample spectra which indicate that water molecules have been incorporated into the structure. The spectrum of the aged plastic does not show any evidence of significant amino acid production which would indicate hydrolysis of the protein chain.

Poly (methyl methacrylate)

Poly (methyl methacrylate) is considered to be extremely stable. The longterm stability may be due to the fact that the structure is less susceptible to autocatalyzed degradation. Acid is used in the production of the monomer, but care is taken in its removal. Also, potential acid forming functional groups in the structure seem to be more stable. However, surface crazing has been observed on several of the Gabo sculptures and the archive piece which have been identified as poly (methyl methacrylate) (Pullen and Heuman, 1988). Several organic materials such as aliphatic alcohols (but not solvents) cause crazing and cracking in poly (methyl methacrylate)(Brydson, 1975; ICI 1987). The crazing in the Gabo pieces is thought to be due to treatment with propan-2-ol. Isopropyl alcohol was "commonly used" to clean Gabo's work (Pullen and Heuman, 1988).

CHAPTER 13 SURVEY OF OBJECTS FROM THE PLASTICS HISTORICAL SOCIETY

Introduction

A series of plastic objects from the collection of the Plastics Historical Society was surveyed using silicon carbide paper and diffuse reflectance spectroscopy. The objects which were selected for analysis were stamped or marked with a patent or trademark which enabled identification of the material and an approximate date. In some cases, the objects were identified on the basis of examination by plastic experts (Plastics Historical Society, Publishers of "Plastiquarian - Journal of the Plastics Historical Society). The collection was to form a reference library for the identification of a wide range of early plastics. The types of plastic identified may be separated into three major groups, natural plastics, semi-synthetic plastics and synthetic plastics.

Natural plastics

Proteins

This group includes protein containing materials such as horn and tortoiseshell which were discussed in chapter 8. Three objects identified as horn by Colin Williamson (Plastics Historical Society were sampled. They included a black stamp seal in the shape of a bust of John Wesley (PHS25) which was marked 'John Wesley Centenary, 1839', a black broach in the shape of a wreath (PHS26) which was marked 'reg. 18/5/1880' and a bow shaped broach (PHS27) with mother-of-pearl inlay which was stamped 'reg. 13/10/1880'. A spectrum of tortoiseshell was obtained from a hairbrush made from Hawksbill turtle (PHS55). The results are summarized in chapter 8.

Other natural products which have been used as moulding materials include gutta percha, rubber and shellac. The composition of these materials have been discussed in earlier chapters. Another protein, albumen, was also utilized. These materials are discussed in the following section.

Gutta percha

Three objects of gutta percha of early date were sampled in addition to one example of modern gutta percha. The first example was an inkwell (PHS1) marked 'Gutta Percha Co. Patent' (c. 1860's), the second was a medallion (PHS2) marked 'Gutta Percha Company London' (c. 1860's), and the third was a photo frame (PHS3) impressed with 'Hancock's Patent West Ham, Essex' (c. 1850). The modern sample was a Silvertown Dental Impression

Sheet (1987)(PHS4). The three older samples were resinous and crystalline. Two samples were removed from the inkwell, one from the rough surface on the base and the second one from the rim around the inkwell where the black lacquer had broken away. A sample was taken from the medallion and the frame in a location where the brown coating had worn away to prevent the possibility of contamination from the lacquer and to minimize the damage to the object.

The spectra of the three older objects were observed to be very similar to each other and very different from that of the modern sample. The first three sample spectra are marked by several strong, broad bands in the regions 3452 - 3384 cm^{-1}, 2971 - 2970 cm^{-1}, 2942 - 2932 cm^{-1}, 1714 - 1712 cm^{-1}, 1453 - 1452 cm^{-1}, 1380 - 1379 cm^{-1} and a broad, indistinct absorption with maximum intensities in the regions of 1172 - 1170 cm^{-1} and 1097 - 1051 cm^{-1} (Figure 13.1a). A weak absorption is evident in the area 1320 - 1319 cm^{-1} and near 803 - 801 cm^{-1}. The region from 800 to 400 cm^{-1} in the spectra is a broad area of absorbance with several weak bands. The band in the carbonyl region (1714 - 1712 cm^{-1}) has a distinct shape. The band has a slight shoulder in the region of 1770 cm^{-1} and a stronger shoulder in the region near 1660 cm^{-1}.

The spectrum of the modern material is similar to those of the other gutta percha samples in the region 4000 - 1800 cm^{-1}. However, the carbonyl region of the modern material contains a series of bands which are less intense in relation to the remaining bands in the spectrum and exhibit frequencies of 1711, 1663, 1625 and 1600 cm^{-1}. This is in sharp contrast to the corresponding region in the older samples. In the modern sample spectrum, there are bands at 1449 and 1381 cm^{-1} and a broad area of absorption with maximum absorptions at 1207, 1105 and 1032 cm^{-1}. The region from 950 to 400 cm^{-1} is marked by a series of distinct, sharp bands at 878, 798, 752, 671, 603, 539 and 472 cm^{-1}. This area differs greatly from that observed in the spectra of the older gutta percha samples.

Crude gutta percha contains a portion of resinous material in addition to the rubber hydrocarbon. The spectrum of crude gutta percha has been published along with the spectra of the resinous extract and that of the residual elastomer (Saunders and Smith, 1949). The spectrum of the unextracted gutta percha has a complex area of absorption in the carbonyl region. Two bands of medium intensity are located near 1739 and 1709 cm^{-1} with weaker bands in the regions of 1667 and 1639 cm^{-1}. With the exception of the band near 1667 cm^{-1}, the bands are not evident in the spectrum of the purified rubber hydrocarbon. The spectrum of the resinous material exhibits a strong band near 1709 cm^{-1} with a shoulder in the region of 1739 cm^{-1} and a weak band in the area of 1639 cm^{-1}. This pattern is similar to that observed in the carbonyl region in the spectra of the old gutta percha obtained in this study.

The spectra of the gutta percha objects contain bands which are characteristic of both the hydrocarbon elastomer and the resinous portion. The tentative band assignments are listed in Table 13.1.

The differences between the spectra of the older materials and the modern sample may be due to contamination of the sample by the presence of a resinous lacquer. However, this is unlikely as great care was taken to obtain samples from areas where the lacquer had worn away. Also, to confirm this, the sample of the photo frame (PHS3) (<0.5 mg) was taken from the back of the frame (PHS3) in a place where the brown coating material had worn away.

This sample was yellow, brittle and resinous and was crushed onto the silicon carbide paper to ensure that no lacquer was removed with the sample. The spectrum of this material was very similar to those obtained of the other objects. The differences in the spectra may also reflect changes which occur over time or during moulding. It is more likely that the objects made in earler times were produced from unextracted gutta percha. Thus, a resinous component would be present in the material. This would explain the presence of the strong carbonyl absorption and other bands which may be attributed to resins (carboxylic acids) in the diffuse reflectance spectra of the older objects examined in this study. Also, gutta percha exists in one of two possible crystalline orientations (alpha or beta) at room temperature (Saunders and Smith, 1949). The crystalline nature of gutta percha would explain the crystalline appearance of the material which is so different to that of the modern material. This difference in the spectra supports the opinion of plastics authorites that the material used in the past differs from that which may be obtained today.

Rubber

Vulcanized rubber

Two examples of rubber were examined, a piece of Spencer Moulton rubber hose (c. 1936) (PHS18) and a section of a Michelin tyre (PHS19). The rubber hose was exhibiting signs of degradation on the interior. The external surface of of the hose was black, but the interior was a grey colour and a strong odour was noticed. The tyre section was in good condition.

Two spectra were obtained of the rubber hose, one sample was taken from the interior and one from the exterior. The rubber materials examined in this study did not powder well. The diffuse reflectance spectra of the tyre and hose obtained in this study do not resemble those of natural rubber and vulcanized rubber which have been published (Linnig and Stewart, 1958). The variations in shape between the spectra are most probably due to differences in sample preparation. The silicon carbide paper did not produce a suitable sample to obtain a good quality spectrum. An early report of the silicon carbide method recommended moistening the silicon carbide paper with dichloroethane before obtaining the sample. This was not done in this study due to the possible detrimental effects of the solvent to the objects.

The spectrum of the exterior of the hose is similar to that of the Michelin tyre. The spectrum of the hose exterior has bands at 3375, 2926, 1662, 1429, 1138, 757, 672 and 606 cm^{-1} which correspond to those at 3385, 2922, 1660, 1411 (very broad), 1141, 757, 670 and 602 cm^{-1} in that of the tyre. However, the intensities are not consistent. The spectrum of the exterior of the hose has a band with maximum intensity at 1048 cm^{-1} which is in contrast to the spectrum of the tyre which contains two distinct bands at 1099 and 1022 cm^{-1}. Also, the spectrum of the hose contains a sharp, weak absorption at 1377 cm^{-1}. In the tyre spectrum, a sharp, weak band appears at 1322 cm^{-1} and a weak band occurs at 820 cm^{-1}.

The spectrum of the interior of the hose is similar to that of the gutta percha with bands at 3387, 2934, 1712, 1450, 1378 and 1085 cm^{-1}. The carbonyl band has a sharp absorption at 1712 cm^{-1} with a very pronounced shoulder in the region of 1650 cm^{-1}. The band with maximum intensity at 1085 cm^{-1} is very broad.

The frequency values for the vulcanized rubber obtained in this study are listed in Table 13.2 where they are compared to those given in the literature for vulcanized rubber (Linnig and

Stewart, 1958) and given tentative band assignments. The bands which are evident near 1661, 1639, 1631 and 1600 cm^{-1} in the literature spectrum (Linnig and Stewart, 1958) are due to the presence of double bonds and suggest that a large number of double bonds exist after vulcanization. The band near 1661 cm^{-1} in the literature is evident in both the spectrum of natural rubber and the vulcanized rubber and these absorptions are evident in the diffuse reflectance spectra in this study near 1661 cm^{-1} (hose exterior) and at 1660 cm^{-1} (tyre). The band at 1600 cm^{-1} appears in the spectra of vulcanized rubber and is characteristic of conjugated double bonds.

Also, the band located at 837 cm^{-1} in unvulcanized rubber (Linnig and Stewart, 1958) decreases in intensity in the spectra of vulcanized rubber. A band appears near 962 cm^{-1} in the spectra of vulcanized rubber. The bands are assigned to the C-H deformations of hydrogens attached to double bonded carbons in the trans- configuration. The band at 962 cm^{-1} is due to the double bonds which were shifted in the vulcanization process and the band near 837 cm^{-1} results from the original double bonds (Linnig and Stewart, 1958). These bands are not evident in the spectra obtained in this study. A weak band is evident near 820

cm^{-1} in the tyre spectrum and a medium band is seen at 808 cm^{-1} in the spectrum of the hose exterior.

The literature also lists weak bands at 699 and 676 cm^{-1} for rubber containing more than 12% sulphur and a single band at 690 cm^{-1} for rubber containing between 2 and 12% sulphur which were assigned to the hydrogens on the carbon double bonds in the cis-configuration (Linnig and Stewart, 1958). These bands are evident in the hose exterior spectrum at 672 cm^{-1} and in the tyre spectrum at 694 and 670 cm^{-1}.

In addition to these bands, a band is evident in the vulcanized rubber spectrum in the literature near 1111 cm^{-1} which is not present in that of the natural rubber. This band has not been assigned and may be related to the strong band at 1099 cm^{-1} in the tyre spectrum and 1138 cm^{-1} in the hose exterior spectrum. Also, the literature spectrum contains a band near 1307 cm^{-1} and the spectrum of the tyre contains a band at 1322 cm^{-1} which may be assigned to the C-H in-plane deformation of the carbon double bond which falls in the region of 1310 - 1295 cm^{-1}.

The difference in the spectra of the interior and the exterior of the hose may represent the changes in structure which occur when rubber undergoes ageing. The similarity of the interior spectrum to that of gutta percha is interesting and may be due to the loss of sulphur linkages in the vulcanized structure.

Vulcanite

The addition of large amounts of sulphur to natural rubber results in a very hard material known as ebonite, vulcanite or hard rubber. The ratio of rubber to sulphur in these materials is approximately 68 to 32. The material contains a large amount of cross linkage and the empirical formula indicates that one double bond is converted for every sulphur atom present (Brydson, 1975). Three objects of vulcanite were examined and one object which was thought to be a rubber mixture. A Vesta box (PHS14) with the image of Queen Victoria (1897), a Jubilee medal (PHS15) for Queen Victoria (1887) and a cigarette holder (PHS17) made by Dunhill (c. 1920's) which were identified as vulcanite (Williamson, personal communication) were sampled. Also, a medal copy (PHS16) which was stamped 'Facsimilie of Wm. Warne & Co. Prize Medal 1862, Manufactured from their patent Mineralite London and Tottenham'. The material was thought to be rubber plus some sort of additive.

The spectra of the vulcanite specimens obtained in this study resemble the published spectrum of vulcanized rubber (Linnig and Stewart, 1958) more closely than the spectra of vulcanized rubber obtained in this study. This is in fact due to the hardness of vulcanite which led to more satisfactory samples for diffuse reflectance. The frequency values observed for the vulcanite objects are listed with the vulcanized rubber and the literature values in Table 13.2 Tentative band assignments are also given. The spectra of the four objects have fairly simple spectra which exhibit five absorptions which may be considered characteristic (Figure 13.1b). The regions include 2929 - 2927 cm^{-1}, 1453 - 1451 cm^{-1}, 1379 - 1376 cm^{-1}, 1151 - 1129 cm^{-1} and 1040 - 1032 cm-1. The absorptions in the regions 1453 - 1451 cm^{-1} and 1379 - 1376 cm^{-1} are strong and sharp. The absorptions in the regions 1157 - 1129 cm^{-1} and 1040 - 1032 cm^{-1} are very broad. There are variations between the spectra in other regions.

In the spectra of PHS14 and PHS17, the C-H stretching absorptions are very strong and much more intense in relation to the rounded absorption in the hydroxyl region. In the spectra of the samples PHS15 and PHS16, the C-H stretching vibrations are less intense in relation to the hydroxyl absorption. Also, the bands in the region of 1453 - 1451 cm^{-1} and 1379 - 1376 cm^{-1} are more intense than the broad absorption in the regions 1151 - 1129 cm^{-1} and 1040 - 1032 cm^{-1} in the spectra of PHS14 and PHS17. The broad bands are more intense than the bands at 1453 - 1451 cm^{-1} and 1379 - 1376 cm^{-1} in the spectra of samples PHS15 and PHS16. There is a great deal of variation in the carbonyl region in the spectra. The spectrum of PHS17 has very weak bands at 1710, 1652 and 1603 cm^{-1}, the spectrum of PHS16 has two absorptions of medium intensity at 1711 and 1623 cm^{-1}, the spectrum of PHS15 contains a broad band with maximum absorptions at 1709 and 1662 cm^{-1} and the spectrum of PHS14 has a sharp band of medium intensity at 1743 cm^{-1} and a weak band at 1652 cm^{-1}.

The region between 950 and 400 cm^{-1} is fairly weak and there are some variations in the spectra. An exception is the spectrum of the medal copy (PHS16) which contains fairly strong absorptions at 672, 600 and 467 cm^{-1}. The C-S absorptions occur as weak bands in the approximate region 700 - 600 cm^{-1} and S-S linkages are marked by very weak absorptions in the area 500 - 400 cm^{-1} (Bellamy, 1975). The spectra of PHS14 and PHS15 contain weak bands at 598 and 610 cm^{-1} respectively and the spectrum of PHS16 contains two bands at 672 and 600 cm^{-1} which may be due to the

C-S linkage. The spectra of PHS14, PHS16 and PHS17 contain weak bands at 471, 467 and 466 cm^{-1} respectively which may result from disulphide linkages. These bands are normally very weak and not considered to be diagnostic (Bellamy, 1975), however, the vulcanite structure contains a high number of sulphur linkages and it would be reasonable to assume that the weak bands may be due to these bonds.

The variation in the vulcanite spectra are probably due to the presence of colourants. It is interesting to note that the spectra of the two black objects, the Vesta box and the cigarette holder, are very similar with the exception of the band at 1743 cm^{-1} in the spectrum of the vesta box (PHS14) which is apparent as only a weak band at 1710 cm^{-1} in the spectrum of the cigarette holder. This similarity is encouraging from the stand point of identification of objects of unknown constitution. The date of the objects differs by about 20 years, however, the spectra are very similar which suggests similar composition. The spectra of PHS14 and PHS17 exhibit bands at 954 and 955 cm^{-1}, 848 and 822 cm^{-1}, 739 and 740 cm^{-1} and 1312 and 1313 cm^{-1} respectively. The spectrum of the medal copy (PHS16), which was composed of a material refered to as mineralite, displays similarities to that of vulcanite.

Shellac

Several objects which were known or thought to be made from mineral filled shellac were examined. The objects included a union case (PHS9) marked 'S. Peck'. The frame section of the case contained a paper which listed the following information: 'S. Peck's Patent Oct 3d, 1854, Halverson's Patent, Feb 7th, 1855 assigned to S. Peck, S. Peck's Patent, Feb 5th, 1856'. Union cases were used to display ambrotypes and daguerreotypes and the patent disclosed that the objects were moulded from shellac mixed with wood flour (catalogue). The second object was a black hand mirror (PHS8) with an ornate flower pattern on the back which was identified as a filled shellac (Williamson, personal communication). The third object was a black knot brooch (PHS22) which was marked 'Mantons Ware Patent'. This material was described in the patent as a mineral filled shellac (Williamson, personal communication).

In addition to the objects described, three other objects were found to be shellac materials as the spectra obtained display bands which correspond to those obtained of the three objects previously described. These include a photograph frame (PHS6) stamped 'Smith's American Patent Composite', a belt buckle (PHS20) identified as D&C Patent and a brooch (PHS21) stamped with 'D&C Patent'.

The absorption frequencies and the band assignments of these samples are compared to those of shellac in Table 13.3. The spectra of the objects include a broad, strong band with maximum intensity in the range 3409 - 3353 cm^{-1}, strong bands in the region 2931 - 2922 cm^{-1} and 2858 - 2855 cm^{-1}, a strong band in the region 1726 - 1713 cm^{-1}, a weaker absorption in the region 1658 - 1640 cm^{-1} (a band occurs at 1605 cm^{-1} is observed in the spectrum of PHS20) and weak bands in the regions 1465 - 1461 cm^{-1} and 1379 - 1375 cm^{-1}. In the spectrum of PHS21, the band occurs at 1429 cm^{-1} with a shoulder in the higher frequency region and the band at 1379 - 1375 cm^{-1} is not apparent in the spectrum of PHS22. The regions observed in these pieces correspond to those observed in the spectra of the shellac standards (chapter 7); 3421 - 3326 cm^{-1}, 2933 - 2923 cm^{-1}, 2858 - 2854 cm^{-1}, 1717- 1713 cm^{-1}, 1641 - 1638 cm^{-1}, 1469 - 1464 cm^{-1} and 1377 - 1375 cm^{-1}.

The presence of mineral fillers would be expected to affect the spectrum and this is seen in the variation in the spectra in the region 1250 - 400 cm^{-1}. The spectra of the reference shellacs exhibit a series of broad absorptions with maximum intensity at 1253 - 1235 cm^{-1}, 1170 - 1162 cm^{-1} and 1048 - 1030 cm^{-1}. However, there is considerable variation in this region between the various object spectra. A weak band is evident at 723, 723 and 725 cm^{-1} in the spectra of PHS9, PHS6 and PHS20 respectively which correspond to a weak band apparent in the range 725 - 723 cm^{-1} in the reference shellac spectra.

The spectrum of the Manton's Ware sample (PHS22) is marked by bands at 2515, 1796, 878 and 753 cm^{-1} which are indicative of calcium carbonate (Miller and Wilkins, 1952). The broad band which is expected near 1430 cm^{-1} in the spectrum of calcium carbonate (Miller and Wilkins, 1952) is apparent in the broad, intense band with maximum intensity at 1465 cm^{-1} which may be due to overlap of several absorptions due to different vibrations.

Bois durci (Albumen and wood flour)

An early moulding material was produced from the combination of albumen from egg whites or dried blood with wood flour. The material was placed in steel moulds and transformed by high heat and pressure. The precess was developed by C. Lepage who established English and French patents in 1855. The material was refered to as Bois Durci and was used to manufacture commemorative plaques of famous personalities and royal personages in addition to items such as combs, jewelry, knife handles, pipes and frames. It is thought that the material was no longer produced by 1887 (Williamson, 1988).

A circular, dark brown plaque which depicts the head of Leopold (PHS13) and was thought to be Bois Durci was examined (c. 1860's). The resulting spectrum bears certain variations from that obtained of dry egg white which is probably the result of interference from the fillers. The Bois Durci spectrum is marked by a strong, broad band with maximum intensity in the region 3410 - 3304 cm^{-1} and a band of medium intensity at 2921 cm^{-1}. This region is similar to that of the dried albumen spectrum where a strong band is apparent with maximum intensity at 3276 cm^{-1} and a less intense absorption is present at 2942 cm^{-1}. However, the weak band at 3071 cm^{-1} in the albumen spectrum is not evident in that of the Bois Durci. The amide I absorption in the Bois Durci spectrum is very wide and the amide II band expected near 1550

cm^{-1} is not evident. The shape of the amide I region is very different to that observed in the albumen spectrum. The Bois Durci spectrum contains a sharp band at 1511 cm^{-1} and a wide band with maximum intensities at 1463 cm^{-1} and near 1430 cm^{-1}. The albumen spectrum has one broad absorption centered at 1449 cm^{-1}. The major difference between the spectra is in that of the Bois Durci, a very intense, broad area of absorption is evident in the region 1300 - 1000 cm^{-1} with bands at 1235, 1115 and 1061 (very strong) cm^{-1}. The corresponding region in the albumen spectrum contains two broad, weak regions of absorption with maximum absorptions at 1309 and 1049 cm^{-1}. The region from 800 - 400 cm^{-1} is a broad envelope of absorption in both spectra which is typical for proteins.

A second object , a black lacquered knot brooch (PHS23) which had the pin broken off, was examined. The small sample was removed from where the fastener broke off to avoid contamination from the lacquer. The spectrum of the material shows some similarities to that of the albumen although it does not closely resemble that of the Bois Durci plaque. The spectrum was thought to be of a protein material due to the strong, broad band in the region 3450 - 3298 cm^{-1}, a band of medium intensity at 2929 cm^{-1}, and bands at 1661 (amide I), 1549 (amide II) and 1431 cm^{-1} which are found in the spectra of proteins (chapter 8). The band assignments are summarized in Table 13.4.

Semi-synthetic plastics

Cellulose nitrate

Parkesine

Three objects which were identified as Parkesine were sampled: a black knife handle with a blade which was stamped 'Patent Parkesine Handle (PHS28), a mottled green and yellow knife handle with no blade (PHS29) and a white billiard ball (PHS30). The objects date from the 1860's. The objects were in good condition, only the green handle being slightly distorted.

All three pieces gave spectra which contained the characteristic nitrate absorptions near 1651, 1282, 846 and 752 cm^{-1} (Brown, 1955). The band which is expected in the region 710 - 690 cm^{-1}, however, seems to be masked by overlapping bands in the region. The spectra contain broad bands in the range 3450 - 3394 cm^{-1} and 1076 - 1031 cm^{-1} which are due to the hydrogen bonded hydroxyl groups and the C-O ether linkages respectively in the cellulose molecule. The spectra are similar to those obtained from the

Parkesine objects from the Science Museum (Chapter 11). It is also interesting to note that the intense band in the carbonyl region which is characteristic of the camphor molecule is not apparent in these spectra (Chapter 10). In the spectrum of the black knife handle, a relatively weak band occurs at 1727 cm^{-1} and only a very slight shoulder occurs in the region of 1725 cm^{-1} in the other spectra. The frequency values and band assignments are listed in Table 13.5.

Xylonite

Four examples which were identified as Xylonite were examined: a white cuff (PHS31) which was stamped with the elephant and tortoise Xylonite trademark (c. 1890's), a red photo developing tray (PHS32) which was marked 'Xylonite trademark' (c. 1900's) and a blue powder box (PHS34) stamped 'Xylonite trademark' (c. 1930's). The fourth object was a 'tortoise-shell' tray which was exhibiting signs of degradation, namely the appearance of plasticizer 'sweat' on the surface. Also, two of the four knob 'feet' had come loose. The tray had been treated with soya bean oil in an effort to arrest the degradation (Williamson, personal communication). The material beneath the knob feet was discoloured and cracked. The other three objects were in good condition.

A small sample was removed from the degraded material beneath the knob feet with a scalpel to avoid contamination from the vegetable oil. A spectrum was measured of the degraded material and two samples were taken of the surface with silicon carbide paper, one of the very top surface and one of the surface obtained by stronger rubbing. The spectra of the degraded material and the very top surace show some evidence of denitration. The bands located near 1660, 1290 and 850 cm^{-1} are less intense in relation to the broad band in the region of 1065 cm^{-1}. This is in contrast to the intensities observed in the spectra of cellulose nitrate objects which do not show visible evidence of degradation. The degradation does not prevent the identification of the material as cellulose nitrate as the characteristic nitrate bands are still evident. The vegetable oil did not cause visible distortion of the spectrum.

The spectrum of the deeper surface contained strong nitrate bands. This spectrum and those obtained of the other Xylonite objects display the characteristic nitrate absorptions which are discussed in chapters 10 and 11. Also, the spectra of the Xylonite samples contain a strong absorption in the region of 1730 cm^{-1} which is characteristic of camphor (Table 13.5).

Cellulose acetate

A transparent orange phonograph record (PHS47) was sampled. It was marked 'Filmophone Flexible Record Ltd. British Made Cat. No. 236 (F13 U7H I)'. The spectrum, which was identified as cellulose acetate, is characterized by bands at 3491, 2943, 1746, 1647, 1432, 1373, 1230, 1162, 1051, 905 and 603 cm^{-1} which are indicative of the cellulose acetate structure (chapter 10). Bands are also evident at 1592, 1488, 970, 780 and 691 cm^{-1} which are characteristic of aromatic structures and indicate the presence of aromatic plasticizers (Table 13.6).

Casein

Three objects were examined which were tentatively identified as casein (Williamson, personal communication). These included a green nail brush with a roughened, worn surface (PHS35), a flat circular hat adornment which depicts a woman's head (PHS36) and a mottled brown, blue and white pen which had a silver end pieces with an image of George V and Queen Mary (PHS37). The side was stamped 'Jubilee Souvenir 1910-1935'.

The spectra of the three materials exhibit the bands which are characteristic of proteins and which have been discussed in chapter 8. The values for these samples are summarized in Table 13.7. The spectra include a broad band in the range of 3320 - 3293 cm^{-1} and a weak shoulder in the region of 3070 cm^{-1}. The spectra also contain the characteristic bands at 1662 - 1661 cm^{-1} (amide I), 1551 - 1550 cm^{-1} (amide II) and 1449 - 1447 cm^{-1}. The region between 1300 and 400 cm^{-1} varies greatly between samples, however. The spectrum of the nail brush is marked by a broad, fairly flat band between 1235 - 1000 cm^{-1} which is probably the result of several overlapping bands. There is also a broad area of absorption in the region 800 - 400 cm^{-1}. The spectrum of the hat adornment is characterized by a broad absorption centered at 1123 cm^{-1} flanked by minor absorptions at 1234 and 999 cm^{-1}. The spectrum also contains a broad band of absorption from 800 to 400 cm^{-1} with maximum intensity near 600 cm^{-1}. The spectrum of the pen is marked by a very strong, broad absorption centred at 1101 cm^{-1}. The spectrum contains several bands of medium intensity in the area 900 - 400 cm^{-1} at 917, 799, 782, 696, 515, 468 and 414 cm^{-1} which is in contrast to the region in the other spectra. The analysis of these objects indicates that the materials are indeed protein, but there is a great deal of variation between various objects which is most likely due to the presence of additives such as colourants.

Synthetic plastics

Phenol formaldehyde

Phenol formaldehyde was the first synthetic plastic. The process was developed by Leo Baekeland. The patent for this material was taken out in 1899. It was already known that phenols and aldehydes form a resin-like material. In Baekeland's patent, the material which has come to be known as Bakelite is produced by a reaction of phenol and formaldehyde under high heat and pressure. The process also includes the addition of fillers, namely wood flour. The major difficulty with the material was that is was a dark colour which limited the colours to dark brown or black. A later development in the procedure involved heating the liquid resin in lead moulds at lower temperatures for a longer period of time. This material was not coloured and could be dyed to create both transparent and opaque colours (Kaufman, 1963). These materials are known as cast phenolics (Williamson, personal communication).

Two objects of Bakelite were examined. The first was a small, brown bowl (PHS45) which is marked with the Bakelite logo and marked 'Bakelite Limited reg'd trademark' (c. 1940's) and the second object was a black desk tidy (PHS46) made in the shape of the Bakelite logo. It was produced to commemorate the coronation of George VI and Queen Elizabeth (1937). It is marked with the Bakelite logo and trademark. A third example of phenol formaldehyde, a black aerial link (PHS44) which was produced by Mouldensite, was also sampled.

Several cast phenolic objects were also examined. These include a orange-red coloured napkin ring (PHS41), a Carvercraft ash tray marked with a mallet and chisel trademark (PHS42), a handle which was originally a pale amber colour which had turned black (c. 1925)(PHS43) and a bright orange sample plaque made by Dekorit and marked 'Dekorit L222' (PHS48)(c. 1987).

The spectra which were obtained are very similar for the dark phenol formaldehydes and the cast phenolics (Figure 13.2). This is not surprising as the chemical structure of the materials is similar. The structure consists of phenol groups linked by methylene groups (Candlin, 1988). The frequency values and band assignments are listed in Table 13.8.

A broad band is evident in the spectra which is centered in the region 3400 - 3305 cm^{-1} which has been assigned to the intermolecular hydrogen bonded O-H groups. The value given in the literature for solid polymeric phenol is 3225 cm^{-1} (Evans, 1960).

The spectra exhibit strong bands in the regions 1609 - 1597 cm-1, 1510 - 1508 cm^{-1} and 1483 - 1477 cm^{-1} with a less intense band or shoulder in the region 1652 - 1644 cm^{-1}. In the spectra of samples PHS43, PHS44, PHS45 (Figure 13.2b) and PHS46, there is a strong band in the region 1510 - 1508 cm^{-1}. In the spectra of the remaining samples (PHS41, PHS42 and PHS48(Figure 13.2a)), however, only a weak shoulder is apparent. In the spectra of samples PHS44 and PHS45, there is no strong band evident in the region 1483 - 1477 cm^{-1} (see table 13.8). These bands are indicative of the skeletal ring stretching modes of the aromatic ring (chapters 10 & 11) (Bellamy, 1975). The frequency values recorded for solid phenol are 1605, 1598, 1501 and 1473 cm^{-1} (Evans, 1960).

In the sample spectra, strong, fairly broad bands are observed in the regions 1369 - 1334 cm^{-1} and 1234 - 1217 cm^{-1}. The first absorption corresponds to a band reported to occur at 1370 cm^{-1} in the spectrum of solid phenol which has been assigned as a ring stretching mode coupled with an O-H deformation (Evans, 1960). The second absorption, which has a weak shoulder in the approximate region of 1250 cm^{-1}, may be related to the bands which have been reported to occur in solid phenols at 1252 and 1230 cm^{-1}. The bands have been assigned to the C-O stretch and to the in-plane O-H deformation coupled with ring stretch in polymeric phenols respectively (Evans, 1960).

A broad area of absorption is observed in the region 1200 - 1000 cm^{-1} with maximum absorptions in the regions 1154 - 1152 cm^{-1}, 1102 - 1097 cm^{-1} and 1065 - 1043 cm^{-1}. The band near 1102 - 1097 cm^{-1} is not, however, evident in all of the spectra and the intensities vary somewhat. The bands are due to the C-H in-plane deformations of the aromatic ring (Bellamy, 1975) and correspond approximately to the frequency values reported for solid phenol, 1169, 1152, 1072 and 1024 cm^{-1} (Evans, 1960).

The spectra are also marked by a band in the region of 897 - 883 cm^{-1}, a band at 826 - 822 cm^{-1} (variable intensity) and a band of medium intensity in the region 763 - 757 cm^{-1}. The bands in this region are due to C-H out-of-plane deformations of the aromatic ring and are indicative of the substitution pattern on the ring (Bellamy, 1975). In a highly cross-linked polymer, the rings would be highly substituted and the pattern would not be consistent. This would explain the variation in the intensities of the bands in this region. The region would also be affected by the presence of fillers and the spectra of the cast phenolics might also by affected by the colouring matter. The values reported for solid phenol, 888, 828 and 754 cm^{-1} (Evans, 1960), are fairly close to those observed for the phenolic plastics in this study.

Amino plastics

The condensation reaction between urea and formaldehyde was first discovered in 1884. The first commercially successful plastic (1928) was prepared from a mixture of urea and thiourea in equal parts, formaldehyde and wood flour or cellulose pulp. This material was dried and ground to form a moulding powder. The product was called Beetle and later Beatl. In 1931 - 1930, a technique was developed for the production of a urea formaldehyde plastic in which an accelerator was added to decrease the time needed for moulding. Plastics produced by the reaction of melamine with formaldehyde were established around 1935 (Kaufman, 1963).

Two objects of thiourea/urea formaldehyde were sampled. A yellow and green cup (PHS38) marked 'Beatl ML137 made in England' (1926 - 1935) and a green, blue and yellow marbled beaker (PHS39) stamped on the base with 'Bandalasta Ware Reg'd trademark Made in England' and the Bandalasta trademark (1928). The spectra of the urea formaldehyde plastics were obtained from a white sample plaque (PHS49) marked 'BIP x8132' (c. 1987) and a cream coloured shaving cream box (PHS50) stamped 'Wardonia Patent Nos 296,597, 376644 Reg'd trademark Made in England' (c. 1950's). A sample was also taken from a yellow saucer (PHS40) composed of melamine formaldehyde which was marked on the base 'Melaware'.

Thiourea/urea, urea and melamine formaldehyde plastics may be differentiated by their spectra (Urbanski et al., 1977) and the diffuse reflectance spectra obtained of these samples are observed to be characteristic for each type of plastic. The spectra of thiourea/urea formaldehyde (Figure 13.3a) and urea formaldehyde (Figure 13.3b) are fairly similar to each other and exhibit features also found in the spectra of proteins (chapter 8). The spectra of the urea formaldehyde plastics are marked by strong absorptions near 1650 and 1550 cm^{-1} which correspond to the amide I and amide II bands and a broad band near 3335 cm^{-1} which is indicative of N-H stretching vibrations. These absorptions are consistent with the structure of the urea molecule and agree well with values quoted in the literature for urea resins, 1639, 1563 and 3333 cm^{-1} (Urbanski et al., 1977).

The spectra of the urea plastics obtained in this study also contain absorptions near 2922 cm^{-1} (PHS50) and 1479 cm^{-1} which indicate methylene linkages in the polymer structure. They also show a broad absorption in the region of 1048 - 1040 cm^{-1} which corresponds to ether linkages and there is some evidence for methyl end groups due to the bands near 2961 cm^{-1} (PHS49) (Bellamy, 1975) and 1380 cm^{-1}. These bands correspond with the values given in the literature for condensation polymerization of urea and formaldehyde carried out in butanol, 1087 and 1383 cm^{-1} (Urbanski et al., 1977).

The thiourea/urea formaldehyde spectra exhibit absorptions due to both the urea and thiourea structures. The literature states that thiourea resin spectra contain two bands near 1538 and 1333 cm^{-1} and that the amide I band is not present. The band at 1538 cm^{-1} is assigned to a C=S vibration and the second band is also tentatively related to the C=S functional group (Urbanski et al., 1977). In the spectra of the thiourea/urea formaldehyde resins, the amide II absorption masks the absorption near 1538 cm^{-1} in part but the band near 1333 cm^{-1} is not blocked and is thus a characteristic feature for amino resins containing thoiurea (Urbanski et al., 1977). The spectra of the thiourea/urea formaldehyde plastics in this study contain absorptions at 1341 cm^{-1}. The bands at 1541 and 1548 cm^{-1} in these spectra are probably due to both the amide II and C=S vibrations. This may explain why these bands are more intense in relation to the other bands in the spectra, than the amide II absorption in the urea formaldehyde spectra. The band assignments are summarized in Table 13.9.

Melamine formaldehyde has a somewhat different spectrum (Figure 13.3c) which is due to the melamine structure. The region 1667 - 1250 cm^{-1} is characteristic for melamine formaldehyde spectra where a series of strong absorptions occur. A particularly characteristic band is observed near 1563 cm^{-1} in the literature. These bands are assigned to the triazine ring and to methylene and ether linking groups in the structure (Urbanski et al., 1977). A band which is observed near 813 cm^{-1} is also credited to the triazine ring. The ether group is also observed due to a weak band near 1064 cm^{-1} (Urbanski et al., 1977).

The melamine formaldehyde spectrum obtained in this thesis is marked by strong bands at 1586, 1501 and 1478 cm^{-1} which overlap to a great extent, in addition to an equally intense band apparent at 1356 cm^{-1}. The spectrum of the melamine formaldehyde has a strong, sharp band at 815 cm^{-1} and a strong broad band at 1048 cm^{-1}. The frequency values are listed in Table 13.9.

All five spectra are marked by a broad envelope of absorption with no strong bands in the region 800 - 400 cm^{-1}. This feature is also observed in the protein spectra obtained in this study. The complex structures of the polymers would result in many overlapping bands.

Figure 13.1 Diffuse reflectance FT-IR spectra of samples from (a) a gutta percha inkwell (PHS1) and (b) a vulcanite Vesta box (PHS14) from the Plastics Historical Society collection.

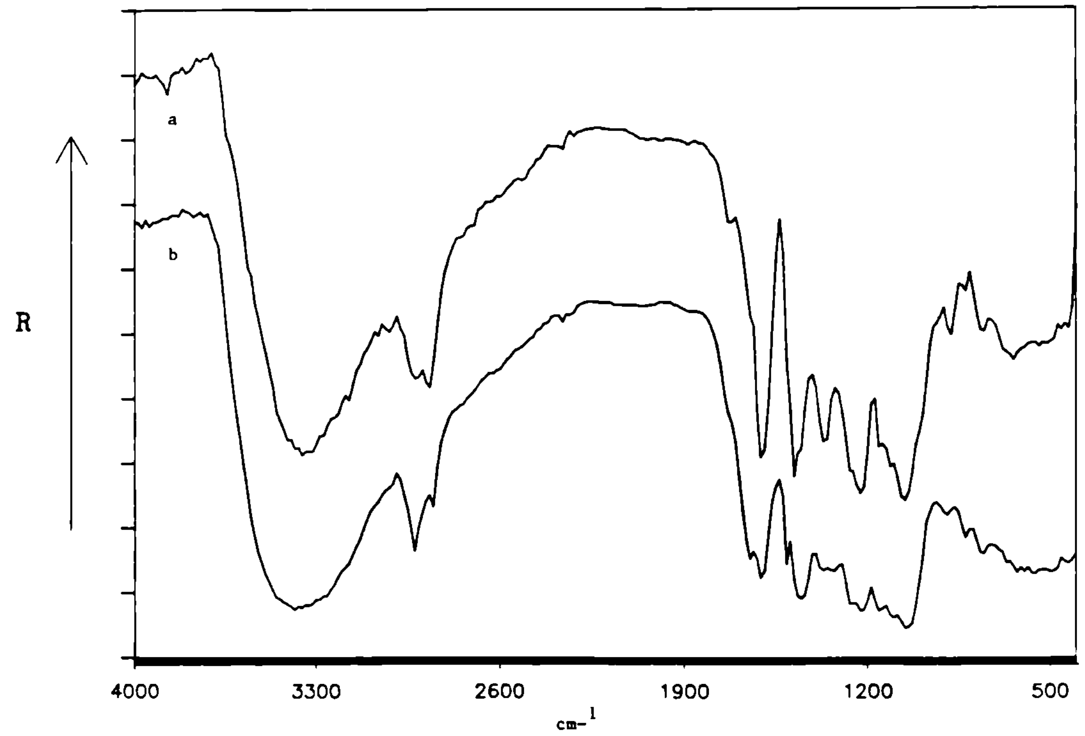

Figure 13.2 Diffuse reflectance FT-IR spectra of samples from (a) a 'Dekorit' cast phenolic sample plaque (PHS48) and (b) a Bakelite bowl (PHS45) from the Plastics Historical Society collection.

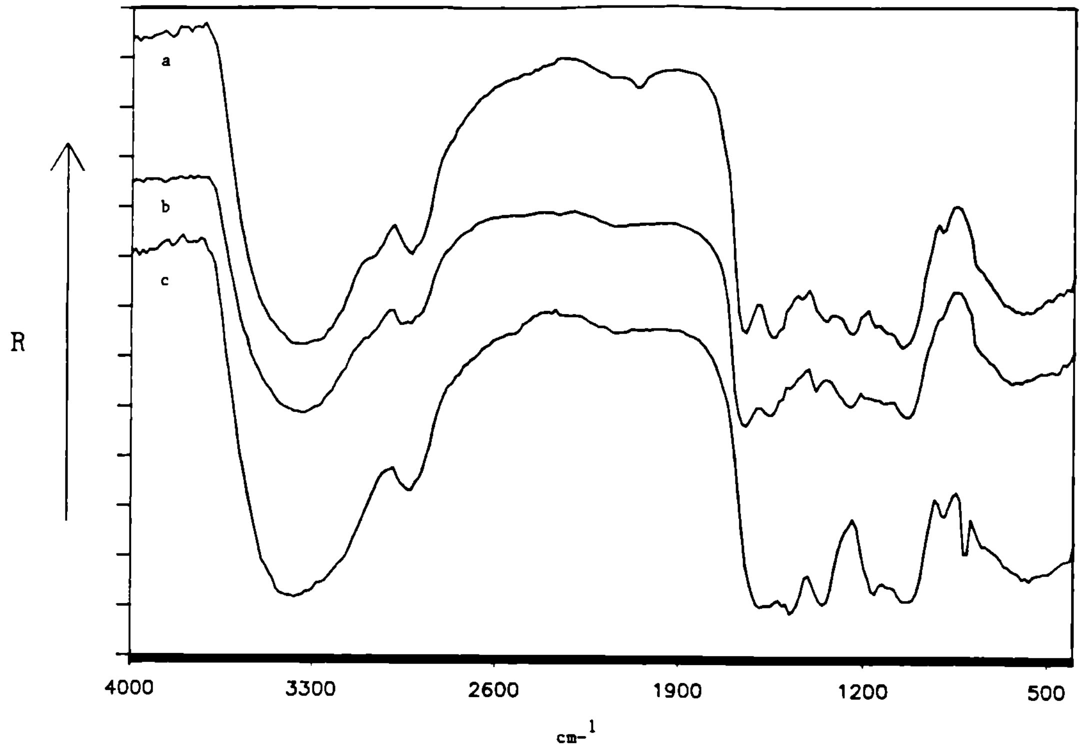

Figure 13.3 Diffuse reflectance FT-IR spectra of samples from (a) a thiourea/urea formaldehyde 'Beatl' cup (PHS38), (b) a urea formaldehyde BIP sample plaque (PHS49) and (c) a melamine formaldehyde 'Melaware' saucer (PHS40) from the Plastics Historical Society collection.

TABLE 13.1

Frequency values and band assignments for Plastics Historical Society gutta percha samples

PHS1 cm-1	PHS1 cm-1	PHS2 cm-1	PHS3 cm-1	PHS4 cm-1	Crude gutta percha (1) cm-1		Vibration	Functional group	Frequency range given in literature (3) cm-1
3421	3415	3421	3431	3414	3448(w,b)		O-H stretch hydrogen bonded	carboxylic acid water	3000 - 2500(b)
3387	3385	3387	3384	3390			O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)
near 2970(sh)	2971(s)	near 2970(sh)	2970(s)	near 2970(sh)			C-H stretch	methyl group	2962 ± 10(s)
2932(s)	2941(s)	2937(s)	2942(s)	2926(s)	2941(s)		C-H stretch	methylene group	2926 ± 10(s)
				2857(s)			C-H stretch	methylene group	2853 ± 10(s)
********** (weak shoulder near 2700) *********					2740(sh)		O-H stretch hydrogen bonded	carboxylic acid	near 2650(w)
************ (shoulder near 1770) ************					1739(sh)	R	C=O stretch	ester	1750 - 1730(s)
1712(s)	1714(s)	1714(s)	1714(s)	1711(m)	1709(s)	R	C=O stretch	carboxylic acid	1725 - 1700(s)
************ (shoulder near 1660) ************				1663(m)	1667(m)	E	C=C stretch	C=C bond non-conjugated	1680 - 1620(va)
				1625(m)	1639(w)	R	unassigned		
				1600(m)			C=C stretch	C=C bond, C-O or C=C conjugated	near 1600(va)
1452(s)	1453(s)	1452(s)	1452(s)	1449(s)	1449(s)		C-H asym. deform.	methyl group	1450 ± 20(m)
							C-H deformation	methylene group	1465 ± 20(m)
1380(s)	1380(s)	1379(s)	1380(s)	1381(s)	1379(s)		C-H sym. deform.	methyl group	1380 - 1370(s)
near 1320(sh)	1320(w)	near 1320(w)	1319(w)		1325(m)	E	C-H in-plane deformation	C=C bond	1310 - 1295(s-w)
					1242(s)	R	C-O stretch/ O-H deformation	carboxylic acid	1320 - 1211(s)
				1207(s)	1205(s)	E	unassigned		
near 1170(sh)	1172(s,b)	near 1170(b)	1170(s,b)		1163(s)	R	C-O stretch	ester	1300 - 1000(s)
					1143(s)	E	unassigned		
				1105(s)			unassigned		

TABLE 13.1 contd.

Frequency values and band assignments for Plastics Historical Society gutta percha samples

PHS1 cm-1	PHS1 cm-1	PHS2 cm-1	PHS3 cm-1	PHS4 cm-1	Crude gutta percha (1) cm-1		Vibration	Functional group	Frequency range given in literature (3) cm-1
1083(s,b)	1051(s,b)	1064(s,b)	1097(s,b)		1093(s)	E	unassigned		
				1032(s)	1047(s)	E	unassigned		
					1026(s)	R	C-O stretch	ester	1300 - 1000(s)
					990(m)	E	C-H out-of-plane deformation	C=C bond (trans-)	970 - 960(s)
					971(sh)				
					922(w)	R	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)
			881(w)	878(m)	885(m)	E	C-H out-of-plane deformation	C=C bond	1000 - 800(s)
					862(m)	E			
					848(m)	E			
803(w)	803(w)	near 800(w)	801(w)	798(m)	803(m)	E			
			752(w)	752(m)	766(w)	R	unassigned		
					741(w)	E	unassigned		
660(w)	659(w)			671(m)	(2)		C-H out-of-plane deformation	C=C bond (cis-)	near 690
607(w)	579(w)		601(w)	603(m)	(2)		unassigned		
	561(w)						unassigned		
	516(w)	544(w)	517(w)	539(m)	(2)		unassigned		
				472(s)	(2)		unassigned		

1. The wavelength values were estimated to the nearest + 0.05 microns from an enlarged copy of the spectrum from Saunders and Smith, 1949. The wavenumber conversions were taken from the table in Hummel, 1966.
   Bands which are marked R are apparent in the spectrum of the resinous extract only.
   Bands which are marked E are apparent in the spectrum of the elastomer extract only. See text
2. Spectrometer range ends at 700 cm-1.
3. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.2

Frequency values and band assignments for vulcanized rubber and vulcanite Plastics Historical Society samples.

Vulcanized rubber			Vulcanite					Vibration	Functional group	Frequency range given in literature	Ref.
PHS18 int.	PHS18 ext.	PHS19	PHS14	PHS15	PHS16	PHS17	vulcanized rubber (1)				
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
					3483(sp)			unassigned			
					3411(sp)			unassigned			
3412(s,b)	3375(s,b)	3404(s,b)	3304(m,b)	3387(s,b)	3304(m,b)	3304(m,b)	3279(w)	O-H stretch	water		
								O-H stretch hydrogen bonded	carboxylic acid (resin fraction)	3000 - 2500(b)	2
2963(s)	near 2960(s)	2961(m)						C-H stretch	methyl group	2962 ± 10(s)	2
2934(s)	2926(s)	2922(m)	2928(s)	2927(s)	2927(s)	2929(s)	* 2941(s)	C-H stretch	methylene group	2926 ± 10(s)	2
	near 2850(sh)	2853(m)	2856(s)	near 2859(sh)	near 2850(sh)	2858(s)		C-H stretch	methylene group	2853 ± 10(s)	2
							* 2740(w)	O-H stretch hydrogen bonded	carboxylic acid (resin fraction)	near 2650(w)	2
							2041(w)	unassigned			
			1743(s)				1739(w)	C=O stretch	carbonyls in hydrocarbon chain,		1
1712(s)				1709(s)	1711(s)	1710(m)	1709(w)	C=O stretch	oxidation products or resinous fraction. additives to plastic		
1650(sh)	1662(s,b)	1660(s,b)	1652(m)	1662(s)	1623(m)	1652(m)	1661(m)	C=C stretch	C=C bond	1680 - 1620(va)	2
							1639(m)	C=C stretch	C=C bond	1680 - 1620(va)	2
							1631(m)	C=C stretch	C=C bond	1680 - 1620(va)	2
			1505(w)			1603(m)	1600(m)	C=C stretch	C=C bond conjugated	near 1600(va)	1,2
							1538(w)	unassigned			
1450(s)			1453(s)	1452(s)	1451(s)	1452(s)	* 1449(s)	C-H deformation	methylene group	1465 ± 20(m)	2
	1429(s)	1411(s,b)						C-H asym. deform.	methyl group	1450 ± 20(m)	2
1378(s)	1377(s)		1376(s)	1379(s)	1378(s)	1376(s)	* 1379(s)	C-H sym. deform.	methyl group	1380 - 1370(s)	2

TABLE 13.2 contd.

Frequency values and band assignments for vulcanized rubber and vulcanite Plastics Historical Society samples.

Vulcanized rubber			Vulcanite					Vibration	Functional group	Frequency range given in literature	Ref.
PHS18 int. cm-1	PHS18 ext. cm-1	PHS19 cm-1	PHS14 cm-1	PHS15 cm-1	PHS16 cm-1	PHS17 cm-1	vulcanized rubber (1) cm-1			cm-1	
		1322(m)	1312(m)			1313(m)	* 1307(m)	C-H in-plane deformation	C=C bond	1310 - 1295(s-w)	2
							* 1227(m)	unassigned			
						1194(s)		unassigned			
	1138(s,b)	1141(s)	1151(s,b)	1129(s,b)	1147(s,b)	1139(s)	* 1136(sh)	unassigned			
							* 1111(m)	unassigned	not present in natural rubber spectrum		1
1085(s,b)		1099(s)					* 1087(m)	unassigned			
	1048(s)	1022(s)	1034(s)	1040(s)	1039(s)	1032(s)	* 1036(m)	unassigned			
							* 1020(sh)	unassigned			
			954(m)			955(w)	962(s)	C-H out-of-plane deformation	C=C bond (trans-)		1
								C-H out-of-plane deformation		970 - 960(s)	2
							* 889(m)	unassigned			
	808(m)	820(w)	848(m)		872(m)	822(w)	837(s)	C-H out-of-plane deformation	C=C bond (trans-)		1
									C=C bond (trans-)	1000 - 800(s)	2
	757(w)	757(m)	739(m)			740(w)	* 761(m)	unassigned			
							* 741(m)	unassigned			
		694(m)				701(w)	699(w)	C-H out-of-plane deformation	C=C bond (cis-)		1**
								C-H out-of-plane deformation	C=C bond (cis-)	near 690	2
	672(w)	670(m)			672(s)		676(w)	C-H out-of-plane deformation	C=C bond (cis-)		1**

TABLE 13.2 contd.

Frequency values and band assignments for vulcanized rubber and vulcanite Plastics Historical Society samples.

Vulcanized rubber			Vulcanite					Vibration	Functional group	Frequency range given in literature	Ref.
PHS18 int.	PHS18 ext.	PHS19	PHS14	PHS15	PHS16	PHS17	Vulcanized rubber (1)				
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
617(m)	606(m)	602(m)	598(w)	610(m)	600(s)		588(w)	unassigned			
							571(w)	unassigned			
493(w)				512(w)			505(w)	unassigned			
467(w)	467(m)	452(m)	471(w)		467(m)	466(w)	472(w)	S-S linkages			1
							441(w)	S-S linkages			1
							410(w)	S-S linkages			1

1. Linnig and Stewart, 1958. Wavenumber conversions were made using the table in Hummel, 1966.
2. Bellamy, 1975
* Absorption values were estimated from enlarged copy of spectrum in Linnig and Stewart, 1958.
** Reference also suggests bands may be due to C-S linkages or non-characteristic skeletal vibrations.
KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.3

Frequency values and band assignments for shellac and mineral filled shellac objects from Plastics Historical Society

Shellac samples cm-1	PHS8 cm-1	PHS9 cm-1	PHS6 cm-1	PHS20 cm-1	PHS21 cm-1	PHS22 cm-1	Vibration	Functional group	Frequency range in literature (1) cm-1	Ref.
3421 - 3326(b)	3388(m,b)	3390(s,b)	3387(s,b)	3353(m,b)	3353(s,b)	3405(m,b)	O-H stretch hydrogen bonded	carboxylic acid	3000 - 2500(b)	1
							O-H stretch	alcohol	3400 - 3200(vs,b) polymeric inter-molecular bonds	1
2933 - 2923(s)	2924(s)	2922(s)	2931(s)	2930(s)	2925(s)	2928(s)	C-H stretch	methylene group	2926 ± 10(s)	1
2858 - 2854(s)	2855(s)	2857(s)	2855(s)	2858(s)	2856(s)	2856(s)	C-H stretch	methylene group	2853 ± 10(s)	1
						2515(w)	calcium carbonate		2530(vw)	2
						1796(w)	calcium carbonate		1785(vw)	2
1717 - 1713(s)	1724(s)	1726(s)	1714(s)	1713(s)	1726(s)	1717(s)	C=O stretch	ester, aryl	1730 - 1717(s)	1
							C=O stretch	carboxylic acid aryl	1700 - 1680(s)	1
							C=O stretch	aldehyde, aryl	1715 - 1695	1
* 1641 - 1638(m)	1642(w)	1642(m)	1640(w)	1605(m)	1658(m)	1640(m)	unassigned			
1469 - 1464(m)	1465(w)	1464(w)	1465(m)	1461(m)	nr 1450(sh)	1465(s,b)	C-H asym. deformation	methyl group	1450 ± 20(m)	1
							C-H deformation	methylene group	1465 ± 20(m)	1
					1429(m)		calcium carbonate		1430(vs,b)	
* 1418 - 1414(w)			nr 1420(sh)	nr 1420(sh)			C-H in-plane deformation	aldehyde	near 1400(w)	1
1377 - 1375(m)	1379(w)	1375(w)	1378(m)	1375(m)	1375(m)		C-H sym. deformation	methylene group	1380 - 1370(s)	1
					1319(w)		unassigned			
1253 - 1235(s)	nr 1230(sh)	1237(s)	1236(s)			1253(s)	C-O stretch/O-H deformation	alcohol primary or secondary	1350 - 1260(s)	1
							C-O stretch/O-H deformation	carboxylic acid	1320 - 1211(s)	1
1170 - 1147(s)	1197(m)	nr 1160(sh)	1166(s)	1166(s)	1163(s)	1149(s)	C-O stretch	ester	1300 - 1000(s)	1

TABLE 13.3 contd.

Frequency values and band assignments for shellac and mineral filled shellac objects from Plastics Historical Society

Shellac samples	PHS8	PHS9	PHS6	PHS20	PHS21	PHS22	Vibration	Functional group	Frequency range in literature (1)	Ref.
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
* 1114(vw)		nr 1120(sh)	1115(w)	nr 1115(s)	1112(s)	1111(s)	C-O stretch/O-H deformation	alcohol, secondary	near 1100(s)	1
1048 - 1030(s)	1085(s)	1048(s)	1041(s)	1059(s)	1058(s)	1037(s)	C-O stretch/O-H deformation	alcohol, primary	near 1050(s)	1
948 - 945(m)	970(vs)		947(w)		nr 950(w sh)	921(s)	O-H out-of-plane deformation	carboxylic acid	950 - 900(va)	1
	882(w)					878(s)	calcium carbonate		877(s)	2
**799 - 772(w)		803(m)	781(w)			791(w)	C-H out-of-plane deformation	aldehyde	975 - 780(m)	1
* 725 - 723(m)		723(m)	723(m)	725(w)		753(w)	chain rocking vibration	long chain hydrocarbons with four or more methylene units	750 - 720(m)	1
						714(m)	calcium carbonate		715(w)	2
**664 - 639(w)	617(s)	662(m)	660(w)	607(w)	613(w)		unassigned			
**565 - 513(w)	572(s)	536(m)	518(w)	564(w)	521(w)	543(s)	unassigned			

* Absorption is weak or occurs as a shoulder in some sample spectra.

** Absorption is not present is some sample spectra.

1. Bellamy, 1975
2. Miller and Wilkins, 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 13.4

Frequency values and band assignments for Bois Durci and albumen Plastics Historical Society samples

Albumen GS1 cm-1	PHS13 cm-1	PHS23 cm-1	Vibration	Functional group	Frequency range given in literature (1) cm-1
3276(m,b)	3410(s,b) 3304(s,b)	3450(s,b) 3298(s,b)	N-H stretch hydrogen bonded	peptide bond	3320 - 3270(m) trans-
3071(m)			amide II overtone	peptide bond	3100 - 3070(w) cis- and trans-
2942(m)	2921(m)	2929(m)	C-H stretch	methylene group	2926 ± 10(s)
nr 2050(w)	2139(w)	2151(w)	unassigned		
1648(s)	1661(m,b)	1661(s)	amide I C=O	peptide bond	1680 - 1630(s)
1554(s)		1549(m)	amide II - coupled N-H deformation and C-N stretch	peptide bond	1570 - 1515(s)
	1511(m)	1502(w)	unassigned		
1449(m,b)	1463(m,b)	1431(m,b)	C-H deformation	methylene group	1465 ± 20(m)
	nr 1430(m,b)		C-H asym. deformation	methyl group	1450 ± 20(m)
	1372(m)	1345(m)	C-H sym. deformation	methyl group	1380 - 1370(s)
1309(m,b)	nr 1310(m)		unassigned		
	1235(s)		amide III - coupled N-H deformation and C-N stretch	peptide bond	1305 - 1200(m)
	nr 1160(s)	1164(s,b)	unassigned	possible interference from mineral fillers	
	1115(s)		unassigned		
1049(m,b)	1061(vs)	1060(s)	unassigned		
		926(m)	unassigned		
	899(w)		unassigned		
		848(s)	unassigned		
**** (see text) ****		804(s)	unassigned		
		716(s)	unassigned		

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder;
b = broad; va = variable; sp = sharp; nr = near

TABLE 13.5

Frequency values and band assignments for Plastics Historical Society Parkesine and Xylonite samples

Milli-pore	Wardle-Storey	PHS28	PHS29	PHS30	PHS31	PHS32	PHS33	PHS34	Inten-sity	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1				cm-1	
3447	3442	3450(m,b)	3448(m,b)	3394(m,b)	3453(m,b)	3441(m,b)	3406(m,b)	3448(m,b)	m,b	O-H stretch hydrogen bonded	O-H group	3400 - 3200(vs) polymeric intermolecular	1
2961	2965					2965(m)	2964(m)	2965(m)	m	C-H stretch	methyl group	2962 ± 10(s)	1
2917	2928	2927(m)	2924(m)	2922(m)	2929(m)	2928(m)	2925(m)	2930(m)	m	C-H stretch	methylene group	2926 ± 10(s)	1
1748	1732	1727(m)			1729(m)	1731(s)	1730(m)	1732(s)	s	C=O stretch	carbonyl group	1735(s,sp)	2
1671	1663	1651(s)	1651(s)	1651(s)	1662(s)	1662(s)	1662(s)	1671(s)	s	N-O asym. stretch	nitrate group	1667 - 1629(vs)	3
1511									w	unassigned			
1455	1452	1452(m)			1453(m)	1452(m)		1452(m)	m	C-H asym. deformation	methyl group	1450 ± 20(m)	1
										C-H deformation	methylene group	1465 ± 20(m)	1
1429	1418		1426(m)	1428(m)	1430(m)	1419(m)	1430(m)	1418(m)	m	unassigned			
1374	1376	1378(m)	1377(m)	1377(m)	1376(m)	1376(m)	1376(m)	1376(m)	m	C-H sym. deformation	methylene group	1380 - 1370(s)	1
1288	1286	1280(s)	1282(s)	1282(s)	1284(s)	1286(s)	1288(s)	1290(s)	s	N-O sym. stretch	nitrate group	1285 - 1272(vs)	3
1246									m	unassigned			
	1205					1206(m)	1207(m)	1205(m)	m	unassigned			
1162	1163	1162(m)	1163(m)	near 1160(w)	1163(s)	1163(s)	1162(s)	1163(s)	s	C-O stretch	ether linkage	1150 - 1060(vs)	1
1073	1066	1031(s,b)	1061(s,b)	1076(s,b)	1061(s,b)	1065(s,b)	1061(s,b)	1066(s,b)	s,b	C-O stretch	ether linkage	1150 - 1060(vs)	1
945	near 945							946(w)	w	unassigned			
846	846	842(m)	846(s)	847(s)	840(s)	841(s)	848(s)	850(s)	s	N=O stretch	nitrate group	872 - 833(s)	3
751	752	750(m)	752(m)	752(m)	752(s)	752(m)	752(m)	752(m)	m	out-of-plane deformation	nitrate group	761 - 745(m)	3
692	683		676(m)		695(s)	694(m)	695(m)	695(m)	m	N-O deformation	nitrate group	710 - 689(m)	3

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.6

Frequency values and band assignments for cellulose acetate standards and Plastics Historical Society sample

cellulose acetate VA13	 VA14	 Bexfilm	Intensity	PHS47	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1		cm-1			cm-1	
3499	3494	3482	m,b	3491(m,b)	O-H stretch	O-H group hydrogen bonded	3400 - 3200 (b)	1
		3069	w		C-H stretch	aromatic ring	near 3070 (w)	1
2959	2959	2959	m	2943(m)	C-H stretch	methyl group	2962 ± 10 (s)	1
2892	2893	2893	m	near 2890(m)	C-H stretch	methine group	2890 ± 10 (w)	1
1762	1758	1764	s	1746(s)	C=O stretch	ester	1750 - 1730 (s)	1
1644	1647	1648	m	1647(m)	unassigned			
		1591	m	1592(m)	skeletal ring stretch	aromatic ring	1625 - 1575(va)	1
1547	nr 1547	nr 1535	vw		unassigned			
		1490	m	1488(m)	skeletal ring stretch	aromatic ring	1525 - 1475(va)	1
1433	1434	1434	m	1432(m)	C-H asym. deformation	methyl group	1450 ± 20 (m)	1
1374	1373	1374	s	1373(s)	C-H sym. deformation	methyl group	1380 - 1370 (s)	1
1262	1258	1260	s	1230(s)	C-O stretch	acetate ester	1250 - 1230 (s)	1
1221	1222				unassigned			
		1189	s	near 1190(w)	P-O-C (aromatic)	triphenyl phosphate	1242 - 1110 (s)	2
1164	1166	1166	s	1162(s)	C-O stretch	ether linkage	1150 - 1060 (vs)	1
1087	1065	1087	s,b	1051(s,b)	C-O stretch	ether linkage	1150 - 1060 (vs)	1

TABLE 13.6 contd.

Frequency values and band assignments for cellulose acetate standards and Plastics Historical Society sample

cellulose acetate			Inten-	PHS47	Vibration	Functional group	Frequency range given	Ref.
VA13	VA14	Bexfilm	sity				in literature	
cm-1	cm-1	cm-1		cm-1			cm-1	
954(vw)	954(vw)	963	s	970(s)	P-O-C (aromatic)	triphenyl phosphate	996 - 905 (s)	2
905	904	904	m	905(m)	unassigned		near 901 (m)	3
840	841	839	m	834(m)	unassigned		near 837 (vw)	3
		782 760	m m	780(m)	C-H out-of-plane deformation	aromatic ring	810 - 750 (vs) meta-substitution	1
					C-H out-of-plane deformation	aromatic ring	770 - 735 (vs) ortho-substitution	1
					C-H out-of-plane deformation	aromatic ring	770 - 730 (vs) mono-substitution	1
nr 692(vw)	692 (vw)	692	m	691(m)	C-H out-of-plane deformation	aromatic ring	710 - 690 (s) mono-substitution	1
605	604	604	m	603(m)	bending vibration	acetate group	605 (m)	3
					skeletal vibration	acetate group	612 (s)	4

1. Bellamy, 1975
2. Thomas and Chittenden, 1964
3. Hummel, 1966
4. Thompson and Torkington, 1945

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 13.7

Frequency values and band assignments for Plastics Historical Society samples identified as casein

Casein I RW1	PHS35	PHS36	PHS37	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1			cm-1	
3287(s,b)	3320(s,b)	3305(s,b)	3293(s,b)	N-H stretch hydrogen bonded	peptide bond	3320 - 3270(m) (trans-)	1
3100(sh)	near 3070(sh)	near 3070(sh)	near 3070(sh)	amide II overtone	peptide bond	3100 - 3070(w) (cis- and trans-)	1
2962(m)		2963(m)		C-H stretch	methyl group	2962 ± 10(s)	1
	2929(m)	2934(m)	2920(s)	C-H stretch	methylene group	2926 ± 10(s)	1
2876(m)		2877(sh)	2852(s)	C-H stretch	methyl group	2872 ± 10(s)	1
2120(w)	near 2100(w)	2130(w)	1879(w)	unassigned			
1661(s)	1661(s)	1662(s)	1661(s)	amide I C=O stretch	peptide bond	1680 - 1630(s)	1
				amide I	peptide bond	1656(vs)	2
1546(s)	1550(s)	1551(s)	1550(s)	amide II - coupled N-H deformation and C-N stretch	peptide bond	1570 - 1515(s) (solid)	1
				amide II	peptide bond	1538(s)	2
1450(m)	1448(m)	1447(m)	1449(s)	C-H deformation	methyl and methylene groups	1448(m)	2
1400(m)				C-O resonance bond	carboxylic acid ionized	1399(m)	2
1350(m)				unassigned			
1315(m)		1320(m)		C-H deformation	methylene groups	1312(w)	2
1241(m)	1235(m,vb)	1234(m)		amide III - coupled N-H deformation and C-N stretch	peptide bond	1305 - 1200(m)	1
				amide III	peptide bond	1242(m)	2

TABLE 13.7 contd.

Frequency values and band assignments for Plastics Historical Society samples identified as casein

Casein I RW1	PHS35	PHS36	PHS37	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1			cm-1	
1175(m)				unassigned		1158(w)	2
1106(m)			1101(vs,b)	N-H deformation	peptide bond	1101(m)	2
950(w)				unassigned		980(m)	2
900(w)			917(m)	unassigned			
			799(s)	unassigned	broad area of absorption - see text		
			782(s)	unassigned			
703(b)			696(s)	unassigned			
626(b)				unassigned			
569(b)			515(s)	unassigned			
			468(s)	unassigned			

1. Bellamy, 1955
2. D'Esposito and Koenig, 1978

KEY: v = very; s = strong; m = medium; w =weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.8

Frequency values and band assignments for phenolic plastic samples from Plastics Historical Society

PHS45	PHS46	PHS41	PHS42	PHS43	PHS44	PHS48	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1	cm-1	cm-1	cm-1			cm-1	
3353(s)	3335(b)	3305(b)	3344(b)	3400(b)	3351(b)	3334(s)	O-H stretch	phenol polymeric	3225	1
	3013(w)			3017(m)			C-H stretch	aromatic ring	3019	1
2921(m)	2922(m)	2923(m)	near 2920(m)	2915(m)	2925(m)	near 2920(m)	C-H stretch	methylene group	2926 ± 10(s)	2
2853(m)	near 2860(sh)	near 2860(sh)	2876(m)	2843(w)		2869(m)	C-H stretch	methylene group	2853 ± 10(s)	2
1646(m)	near 1650(sh)	1651(m)	1652(m)	near 1650(sh)	1644(w)	near 1640(w)	unassigned			
1604(s)	1606(s)	1609(s)	1608(s)	1598(s)	1597(s)	1600(s)	skeletal ring stretch	aromatic ring	1605	1
1509(s)	1508(s)	near 1500(sh)	near 1500(sh)	1510(s)	1510(s)	near 1500(sh)	skeletal ring stretch	aromatic ring	1501	1
	1477(s)	1483(s)	1483(s)	1477(s)		1483(s)	skeletal ring stretch	aromatic ring	1473	1
1450(s)	near 1450(sh)	near 1450(sh)	near 1450(sh)	1442(s)	1457(s)	near 1450(sh)	C-H deformation	methylene group	1465 ± 20(m)	2
1334(b)	1338(b)	1359(s)	1362(s)	1337(s)	1369(b)	1363(s)	coupled ring stretch and O-H deformation	phenol	1370	1
near 1250(sh)	near 1250(sh)	near 1250(sh)	near 1250(sh)	near 1250(sh)	near 1250(sh)	near 1250(sh)	C-O stretch	phenol	1252	1
1220(s)	1217(s)	1234(s)	1232(s)	1225(s)	1228(s)	1223(s)	coupled O-H deform. and ring stretch	phenol polymeric	1230	1
1154(s)	1153(s)	1153(s)	1152(s)		1154(s)	1153(s)	C-H in-plane deformation	aromatic ring	1152	1
near 1100(s)	1099(s)	near 1100(sh)		1102(s)	1097(s)		C-H in-plane deformation	aromatic ring	1072	1
1051(s)	1054(s)	1064(s)	1060(s)	1043(w)	1048(s)	1065(s)	C-H in-plane deformation	aromatic ring	1024	1
				1000(w)			unassigned			

TABLE 13.8 contd.

Frequency values and band assignments for phenolic plastic samples from Plastics Historical Society

PHS45 cm-1	PHS46 cm-1	PHS41 cm-1	PHS42 cm-1	PHS43 cm-1	PHS44 cm-1	PHS48 cm-1	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
895(w)	near 900(w)	885(m)	885(m)	887(w)	897(w)	883(m)	C-H out-of-plane deformation	aromatic ring	888	1
822(m)	823(m)	826(m)	826(m)	823(s)	822(m)	825(m)	C-H out-of-plane deformation	aromatic ring	828	1
757(m)	758(m)	763(m)	757(m)	758(s)	759(m)	759(m)	C-H out-of-plane deformation	aromatic ring	754	1

1. Evans, 1960
2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.9

Frequency values and band assignments for amino plastic samples from Plastics Historical Society

PHS38 T/UF cm-1	PHS39 T/UF cm-1	PHS49 UF cm-1	PHS50 UF cm-1	PHS40 MF cm-1	Vibration	Functional group/ compound	Frequency value given in literature cm-1	Ref.
3334(s,b)	3335(s,b)	3337(s,b)	3335(s,b)	3369(s,b)	N-H stretch	urea, thiourea melamine	3333(b)	1
		2961(m)			C-H stretch	methyl group	2962 ± 10(s)	2
2922(m)	2923(m)		2922(m)	2925(m)	C-H stretch	methylene group	2926 ± 10(s)	2
2061(w,b)	2059(w,b)		2151(w,b)		unassigned			
1650(s)	1647(s)	1650(s)	1644(s)		amide I C=O stretch	urea	1639(s)	1
				1586(s)	triazine ring	melamine	* 1667 - 1250(s)	1
1541(s)	1548(s)	1550(s)	1553(s)		amide II C-N stretch	urea	1563(s)	1
					C=S vibration	thiourea	1538(s)	1
				1501(s)	triazine ring	melamine	* 1667 - 1250(s)	1
				1478(s)	triazine ring	melamine	* 1667 - 1250(s)	1
1434(w)	1433(w)	1479(m)	nr 1479(m)		C-H deformation	methylene group	1443	1
		1381(m)	1380(m)		C-H deformation	methyl group	1383	1
				1356(s)	triazine ring	melamine	* 1667 - 1250(s)	1
1341(m)	1341(m)				C=S vibration	thiourea	1333	1
1238(s)	1237(s)	1251(s)	1244(s)		unassigned			
	1159(m)			1161(s)	unassigned			
1056(s)	1059(s)	1048(b)	1040(b)	1048(s,b)	C-O stretch	ether linkage	nr 1087(s)	1
					C-O stretch	ether linkage melamine	1064(vw)	1
901(m)	900(m)	nr 900(sh)	nr 900(sh)	899(m)	unassigned			
				815(s)	triazine ring	melamine	813(s)	1
		nr 800(sh)	nr 800(sh)		unassigned			

T/Uf = thiourea/urea formaldehyde UR = urea formaldehyde MF = melamine formaldehyde

* A series of strong bands occur in region 1667 - 1250 cm-1

1. Urbanski et al., 1977; Wavelengths were converted using table from Hummel, 1966 2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

CHAPTER 14 IDENTIFICATION OF OLD CONSERVATION MATERIALS FOUND ON OBJECTS

Introduction

In addition to being able to identify the synthetic materials used to construct objects (discussed in the previous chapter), it is also important to be able to identify the synthetic materials that have been used in conservation treatments. Modern materials have been used extensively in conservation almost from the time that they became available (Horie, 1987). Unfortunately, it has only recently become standard procedure to keep detailed treatment records. Several materials were encountered during the course of this research project which were identified as synthetic substances and the results of the infrared spectroscopy of these samples will be summarized below.

Nimrud ivories

Some Nimrud ivory writing boards were examined as part of an undergraduate dissertation (Norman, 1988). Several types of materials applied during previous conservation, including consolidants, adhesives and gap filling materials were present on the objects. No records had been kept of the treatments carried out during the period 1958 - 62 and the person who performed much of the early conservation treatment is no longer alive. Ivory has a tendency to laminate. Some of the treatment materials had yellowed and were pulling away from the surface and causing damage by bringing some of the ivory with it. FT-IR was utilized in an attempt to identify the materials which were used.

It was thought that the residues might be poly (vinyl acetate) (PVAC) as it was known to have been used as a consolidant when the objects were excavated (Norman, 1988). The use of PVAC homopolymers in conservation was first published in 1932 and the material was widely used by the mid 1950's (Horie, 1987). PVAC has been observed to be stable to light aging. It oxidizes to a certain extent in air, but has not been observed to severely crosslink or otherwise degrade. It has been reported that PVAC can be dissolved after 30 to 40 years. PVAC is also made as a dispersion and dispersions of vinyl copolmers have been used in conservation. However, they have been found to be less stable and more susceptible to yellowing due to the emulsifiers used which are somewhat unstable. Early emulsions used in conservation were plasticized and the plasticizers are thought to be lost after several decades. Also, PVAC dispersions have been observed to degrade and produce acetic acid (Horie, 1987).

A summary of the field conservation of the Nimrud ivories is given as an appendix in the publication on Nimrud (Mallowan, 1966). After uncovering and preliminary cleaning, the objects were coated with PVAC in acetone. When the solvent had evaporated, the piece was lifted and the other side was consolidated. The post excavation treatment of the ivories incorporated further cleaning and consolidation. Also, the pieces were reinforced and the lost portions were filled if necessary (Wales, 1966). It has been recorded that PVAC was used to consolidate the fragile ivories which were excavated at Fort Shalmaneser during the final seasons (cir. 1958 - 1962). The ivories had to be consolidated in the field as the original condition was described as having the consistency of processed cheese (Reade, 1982).

A further material which could have been used on the ivories was cellulose nitrate. Cellulose nitrate in solution can be used as an adhesive. A solution of celluloid dissolved in a 50/50 solution of acetone and amyl acetate was first recommended in 1926 for use as an adhesive and consolidant. However, cellulose nitrate has long been recognized as an unstable material and its use in other fields such as the film industry has been superceded by more stable materials. As early as 1867, it was discovered that cellulose nitrate became acidic in the presence of strong light. The degradation products included nitric, formic and oxalic acids, cyanogen and glucose. Cellulose nitrate is sensitive to acid and alkaline hydrolysis which produces a reduction of chain length and denitration. This may be catalyzed by residual acid impurities retained from the nitration process. Also, the loss of volatile stabilizers and plasticizers produce a brittle film with impaired mechanical properties. Thus, in addition to a loss of adhesion qualities with time, acidic degradation products are formed which are harmful to the objects. However, cellulose nitrate is still widely used in conservation (Koob, 1982).

The composition of a typical cellulose nitrate adhesive includes 100 parts by weight cellulose nitrate (11.4% nitrogen content), 40 parts camphor, 75 parts acetone, 300 parts ethyl alcohol and 165 parts amyl acetate (Skeist, 1977). Different solvents are utilized by manufacturers to achieve various working properties. The solvents make up the largest portion of the composition by weight. Camphor is not used by every company as a plasticizer (Koob, 1982)

There are two methods which can be used to identify cellulose nitrate. The first technique is a spot test utilizing acidic diphenylamine which turns a very intense blue colour in the presence of cellulose nitrate (Koob, 1982; Haslem et al., 1972; Braun, 1982). The second method is infrared spectroscopy. Cellulose nitrate has a distinctive spectrum which has been discussed in detail in chapter 10.

Fourteen samples were removed from the ivories by the conservator for analysis. The sample details are listed in table 14.1. The samples were prepared for analysis by the standard procedure of rubbing them gently onto a piece of silicon carbide abrasive paper and measuring the spectrum directly from the paper. In many cases, the samples were thin films, but they were too thick to obtain a satisfactory transmission spectra when mounted in a microaperture holder. It was difficult to generate a powder by rubbing the film on to the abrasive paper. The samples were held with fine forceps and very gently rubbed against the silicon carbide paper. The hard waxlike materials were simply crushed onto the paper with the back of a microspatula and the excess was shaken off and retained.

The results of the infrared analysis are summarized in Table 14.1. Six of the samples were identified conclusively as cellulose nitrate. In all of these spectra, the bands characteristic of the nitrate group (Chapter 10) appear, except for the absorption in the region 689 - 710 cm^{-1} (Table 14.2). It is thought that the band in that region is masked by the overlapping of several bands. The spectra were also compared to a diffuse reflectance spectrum of a fresh cellulose nitrate adhesive (HMG) (Figure 14.1). In sample CWN1 (Figure 14.2b), the bands at 1673 and 1296 cm^{-1} fall slightly above the regions suggested in the literature for cellulose nitrate, but the second absorption occurs at 1298 cm^{-1} in the HMG spectrum. The frequencies of the absorption bands are affected by the immediate environment of the of the functional group it represents. The value may be shifted by the crosslinking and denitration which occur on ageing or by plasticizers and additives present. Two types of cellulose nitrate adhesive seem to have been used, as spectra of samples CWN5 (Figure 14.2a) and CWN12 have a strong band at 1737 and 1735 cm^{-1} respectively which is characteristic of the plasticizer camphor (Sirkis, 1982). In the other four spectra, only a very weak shoulder appears at 1720 - 25 cm^{-1} which may be due the presence of other additives (Figure 14.2b).

Two of the sample spectra, CWN6 (Figure 14.3b) and CWN11, have very similar spectra which are somewhat difficult to interpret. There are bands at 1647 - 1651 cm^{-1} and 1282 - 1284 cm^{-1} which are less intense in relation to the other bands in the spectrum which may indicate a heavily denitrated cellulose nitrate. However, there are indications of a second material with very weak bands in the regions of 2516, 1797 and 875 cm^{-1}. These bands are characteristic of calcium carbonate (Miller and Wilkins, 1952).

The spectra of CWN9 and CWN 14 are extremely difficult to interpret. There is an absence of sharp or intense bands. There is a broad band centered at 3374 cm^{-1}, an indistinct band at 2924 cm^{-1} and a broad band at 1646 cm^{-1} which correlate with those in the spectrum of cellulose powder. There is also a doublet at 988 and 921 cm^{-1} which may be due to the ether linkages in the cellulose. There is no evidence of bands at 1280 and 840 cm^{-1}, so it is difficult to say that it is severely degraded cellulose nitrate. None of the sample spectra resembled that of ivory.

Only one sample, CWN13, was identified as poly (vinyl acetate) which has been recorded as being used. It was identified by comparison with a diffuse reflectance sectrum of chemical poly (vinyl acetate) (Aldrich secondary standard) and to a spectrum of PVAC adhesive (UHU, Beecham). The spectrum of CWN13 (Figure 14.4b) has absorptions at 1435, 1375, 1265, 1227, 1125, 1026, 948, 631 and 606 cm^{-1} which correspond very closely to absorptions in the spectrum of the secondary standard poly (vinyl acetate) (Figure 14.4a). The spectra are compared in Figure 14.4. The sample spectrum has a strong band which is most intense at 1739 cm^{-1}; however,the corresponding absorption in the standard spectrum is a broad band with the maximum intensity occurring at 1752 cm^{-1}. The frequency values are compared in Table 14.3.

Sample CWN3 was described as a wax fill and identified as beeswax. The sample spectrum is discussed in the chapter on wax. However, there are several bands at 2522, 1788, 874 and 857 cm^{-1} and are due to some sort of impurity or additive. A spectrum of beeswax taken from a comb of *Apis dorsata* was subtracted from the sample spectrum by the computer and the difference spectrum was obtained. It was found to have the bands at 2522, 1788, 874, 857

cm^{-1} and a very strong band at 1539 cm^{-1}. The beeswax sample CWN3 contains other components which may include calcium carbonate, which is characterized by bands which occur at 2530, 1785, 1430, 877 and 715 cm^{-1} (Miller and Wilkins, 1952).

Two samples which were described as a hard waxlike substance (CWN7) and a possibly original grey wax (CWN10) were found to have similar, distinctive spectra. The spectrum is characterized by four sharp bands which fall in the regions 2515 - 2516 cm^{-1} (doublet), 1797, 875 - 877 and 715 - 716 cm^{-1}. These bands fall into the regions given above for calcium carbonate. Initially, the identification of this spectrum was difficult. The confusion is due to the the effect of specular reflectance which causes the bands near 2530 and 1785 cm^{-1} to be disproportionately intense. There is no strong evidence for the presence of cellulose nitrate in these spectra. However, the description of the materials as a hard wax-like substance (CWN7) and possibly original wax indicate that the consistancy of the material was somewhat different to that of the adhesive and consolidants. In an early textbook on conservation (Plenderleith, 1956), a recipe is given for a mixture of cellulose nitrate in a solution of amyl acetate and acetone (50/50) and fine white sand. This mixture was described as having the "consistancy of soft putty" and was recommended as a anhydrous cement which would not shrink. The dry material had the colour of light sandstone and was recommended for stone. However, it might have been used for these materials as it would have been desirable to have a gap filling material which would not shrink. Presumably calcium carbonate was used in place of sand as a filler.

It is not surprising that many of the samples were identified or thought to be cellulose nitrate because it has been a popular conservation material and was available from the date of excavation of the ivories. Although the Nimrud ivories were not specifically mentioned, commercial cellulose nitrate adhesives such as Durofix and HMG were "safely recommended" as an adhesive for ivories in a textbook on conservation (Plenderleith and Werner, 1971). It is interesting to note that samples which were described both as yellowed and as white were identified as cellulose nitrate. Also, there seem to be two types of cellulose nitrate used, one with camphor as a plasticizer and one with very little or none. There may also be samples of denitrated cellulose nitrate. It is important to be able to detect whether cellulose nitrate has been used on objects such as the ivories so that it can be removed. It has been noted in the literature that the acidity of the cellulose nitrate may be harmful to sensitive materials such as ivory (Koob, 1982).

The weak bands which have been assigned to the presence of calcium carbonate in several of the spectra may indicate that a mineral filler was prepared with cellulose nitrate. It is also possible that the traces of calcium carbonate result from the traces of soil which were found to adhere in some cases to the ivory and consolidant (Norman, 1988).

The presence of PVAC and beeswax on the object are also not surprising as both materials have been widely used in conservation for many years. There is no evidence of degradation in the CWN13 spectrum and it has been reported that poly (vinyl acetate) can be dissolved after 30 - 40 years (Horie, 1987).

Stone consolidation material from marble frieze

A sample of gap filling material was taken from a marble frieze located at the British Museum. The material was thought perhaps to be a resin of some sort. The restoration was thought to have been carried out in the nineteenth century. The diffuse reflectance spectrum of the material is characterized by bands at

2516, 1797, 1442 (very strong), 877 and 714 cm^{-1} which are characteristic of calcium carbonate. The spectrum also contains a shoulder which commences near 3400 cm^{-1} and runs into the band at 2934 cm^{-1}. Also, a strong band is observed at 1696 cm^{-1}. These bands are indicative of an organic acid which suggests that the material contains a resin of some sort. It may be that an material similar to the later putty material described by Plenderleith (1956) was prepared with a resin and a filler containing calcium carbonate.

Materials from glass painting sample

A sample was analyzed which had been separated from the inorganic pigments from a painting on glass. The material was thought to be an organic binder. A diffuse reflectance spectrum was measured and it was found to correspond very closely to that of cellulose nitrate adhesive. This was somewhat surprising as it was not obvious from a visual inspection that the painting had been treated. It is not known if cellulose nitrate was used as the medium. The material was also examined with the infrared microscope to see if traces of the painting media were evident in the cellulose nitrate. The sample examined appeared to be homogeneous and was found to be cellulose nitrate.

Coating from glass lithograph fragment

A sample (York3) was analyzed from a fragment of glass which was thought to be a lithograph which was attached to the glass with turpentine and then covered with a white material which was thought to be paint (Skeldergate, York, 1983.25 context 2005, small finds number 96). The glass fragments were found in a fill from the cellar of a building erected between 1718 and 1786. There are a wide range of dates given to the material in the fill, however, the picture represents a building which was not built until around 1833. It is thought that the fill material was deposited in the 1880's. The material was excavated in 1983 and the surface was consolidated with a PVAC emulsion. The material is almost certainly Vinamul (poly (vinyl acetate) dispersion) (Little, 1988, personal communication).

A fragment was sent for identification and a small sample was removed for analysis. Diffuse reflectance spectroscopy was not successful as the material did not powder well. A sliver of the thin film was transfered to a copper TEM grid and examined with FT-IR microscopy without any mounting medium which might have obscured the spectrum. The sample was transparent in some areas and appeared to be folded over in others forming grey areas.

There were also several yellowed areas which were thought to be residual adhesive, perhaps resin. Spectra were recorded of the very transparent section and one of the yellowed sections. A second set of two samples of the white material thought to be paint was also examined. The paint samples appeared as an opaque grey colour under the microscope.

The first sample was the clear, transparent section and the resulting spectrum (Figure 14.5) was identified as PVAC by comparison with reference spectra. The unknown sample spectrum contains absorptions due to the C=O and the C-O stretching vibrations of the acetate ester functional group which are assigned in Table 14.3. The spectrum was found to correspond closely to a published spectrum of poly (vinyl acetate) (Hummel, 1978). The sample spectrum was also observed to correspond to spectra of secondary standard poly (vinyl acetate) and of a PVAC adhesive (UHU, Beecham) which were collected using diffuse reflectance FT-IR spectroscopy. Minor variations in band intensity were observed between the published transmission spectrum and the diffuse reflectance. This effect is discussed in Chapter 2. The frequencies values of the diffuse reflectance spectra are fairly close to those of the transmittance spectrum in the literature. The frequency values of the unknown are compared with the standards in Table 14.3. The weaker bands at 1697 and 1433 cm^{-1} in the unknown spectrum (Figure 14.5) are greater in relative intensity in the diffuse reflectance spectra of the secondary standard poly (vinyl acetate) (see Figure 14.4a). The band which occurs as a doublet near 1270 and 1224 cm^{-1} in the diffuse reflectance spectra appears as a single band at 1238 cm^{-1} in the unknown spectrum and as a single band near 1245 cm^{-1} in the spectrum from the literature. The most serious variation between the spectrum of the unknown and the reference spectra is the shape of the band with maximum intensity at 1024 cm^{-1}. The band at 1127 and 1123 cm^{-1} in the spectra of the chemical standard PVAC and the PVAC adhesive respectively are not apparent in the sample spectrum where a weak shoulder occurs at 1115 cm^{-1}. The presence of a broad band centered at 3458 cm^{-1} which is indicative of hydroxyl groups suggested that the material might contain poly (vinyl alcohol) (PVAL). This absorption is not present in the PVAC reference spectra. PVAL is produced from PVAC and often actually contains some acetate groups in the structure (Horie, 1987). The diffuse reflectance FT-IR spectra obtained of two types of Gelvatol (poly (vinyl alcohol)) exhibited evidence of acetate content. It is more likely that the PVAC dispersion has undergone a degree of deacetylation through time resulting in the presence of some hydroxyl groups in the structure, or that the band may be due to residual water in the structure.

The second sample of the yellowed area was thicker and the resulting spectrum is less clear. The bands in the region 3454 - 2860 cm^{-1} are more intense in relation to the other bands in the spectrum than in that of the clear sample. The band which occurs at 1738 cm^{-1} is much wider in the thicker sample spectrum and the weak shoulder at 1697 cm^{-1} is stronger and occurs at 1659 cm^{-1}. Also, the band at 1433 cm^{-1} is stronger and the region between 1248 - 1024 cm^{-1} is indistinct with no major bands. Several new, weak bands appear in the region between 2400 - 2000 cm^{-1}. However, the differences are probably due to the distortions caused by the thickness of the sample and not by the presence of additional materials. Unfortunately, the data processing capabilities of the microscope do not allow spectral subtraction which would remove the bands due to PVAC and so possibly reveal the presence of other materials.

The spectra of the paint material are very similar. Most of the bands present are due to the PVAC. However, two very broad, strong bands occur with maximum intensities at 3393 and 1074 cm^{-1}. The shape and the location of these very broad bands suggest that an inorganic compound is present. The only statement which can be made is that it is not calcium carbonate which is marked by a very strong, broad band near 1430 cm^{-1} with lesser bands near 877, 1785 and 2530 cm^{-1} (very weak). The broad band in the paint sample spectra is indicative of inorganic constituents.

Paraffin wax

Another type of synthetic treatment which has been discussed earlier is that of paraffin or hydrocarbon wax. It has been widely used in conservation since the end of the last century (Horie, 1987) and, as it is produced from petroleum distillation, has only been available since the nineteenth century (Mills, 1972). It has also been recommended for lifting fragile objects in an early text on archaeological excavation techniques (Droop, 1915). The wax is merely heated and then the hot wax is deposited over the object. Paraffin oil or wax was recommended in an early textbook on conservation (Plenderleith, 1956) as a treatment for corroded steel, coating for leather, and as a moisture barrier in the treatment of stone. Also, a recipe is given for a paraffin wax/polyethylene wax paste which is recommended as a polish for, among other things, paintings (Plenderleith, 1956). The use of paraffin wax has largely been discontinued. Thus, when identified on an art or archaeological object, it must be assumed to be the result of treatment and not original unless the object is of very recent date. Examples of the use of thiis material have been encountered in this study on the bronze figure from the Fitzwilliam Museum and the two mummy masks from the Boston Museum of Fine Arts (Chapter 4).

Material from Mask of Thay

A very good example of the desirability of identifying old treatments may be seen with an object from the Fitzwilliam Museum, the Mask of Thay (E.198.1903). The object, a Middle Kingdom mummy mask, was excavated from the Tomb of Beni Hasan and acquired by the museum in 1903 as a gift of the excavation committee. It is thought that all subsequent treatment was performed at the museum and no documentation of any sort was kept. The piece was again conserved in 1987 in preparation for an exhibition. The mask was composed of three layers, a plaster layer which was thought to have been treated with shellac, linen which was coated with some sort of resin and the top layer which was plaster which had been painted. The bottom layer was cracked in some places, but was fairly intact. The top layer of plaster was made up of about forty fragments which were reassembled presumably at the museum. Several samples were removed from the mask to attempt to identify some of the early materials which had been utilized during conservation.

A sample of material which was thought to be modern was removed from the repair above the left eye (FW16). The diffuse reflectance spectrum of this material was found to resemble that of cellulose nitrate adhesive. It is interesting to note that the material does not show any evidence of degradation in the spectrum. All of the characteristic bands of the nitrate group are strong (Table 14.2) and a band which is indicative of camphor is present at 1714 cm^{-1}. A second sample (FW17) which was removed from the lower right cheek gave a very complex diffuse reflectance spectrum which was difficult to interpret. The sample was then examined by FT-IR microscopy. The sample was a dirty white colour with a few specks of a yellow-red material which may be shellac. The spectrum of the grey material (Figure

14.6) was observed to correspond closely with that of the PVAC from the painted glass (York3) and the PVAC standards (Table 14.3). The spectrum of the yellow area was much less clear. The spectrum was very difficult to interpret which indicates that a mixture is present.

In situ analysis of coatings on metal objects

It was hoped that the FT-IR microscope could be used to examine coatings and residues on metal objects in the reflectance mode. Such an examination procedure could be carried out completely non-destructively. Earlier attempts to analyze black, presumably organic, deposits on highly burnished Cypriot ceramic ware were unsuccessful as an insufficient amount of energy was reflected back to the detector to record a signal. Two metal objects were also examined. The first object was a Saxon brooch (Institute of Archaeology laboratory number 5528) which had several organic inlays. It was thought that the object had been coated with a synthetic varnish. The metal surface was sufficiently reflective to record a signal and a spectrum was recorded against a background spectrum of an aluminum mirror. However, the resulting spectrum was very difficult to interpret. A series of sharp bands were observed above the baseline. These might arise from the metal of the brooch itself. The spectrum is not thought to be in any way related to that of a synthetic organic material. An attempt was made to examine one of the resinous inlays in the brooch but the inlay area was not sufficiently reflective to record a signal. The second piece which was examined was a bronze pin (Institute of Archaeology laboratory number 2743) which was known to have been coated with Incralac, an acrylic resin commonly used to coat bronze objects. The surface did not, however, reflect sufficient energy to record a spectrum.

It is thought that in the first case, a larger number of scans would improve the measurement from highly reflective surfaces. However, the problem of insufficiently reflective surfaces has yet to be overcome with the FT-IR microscope used in this research.

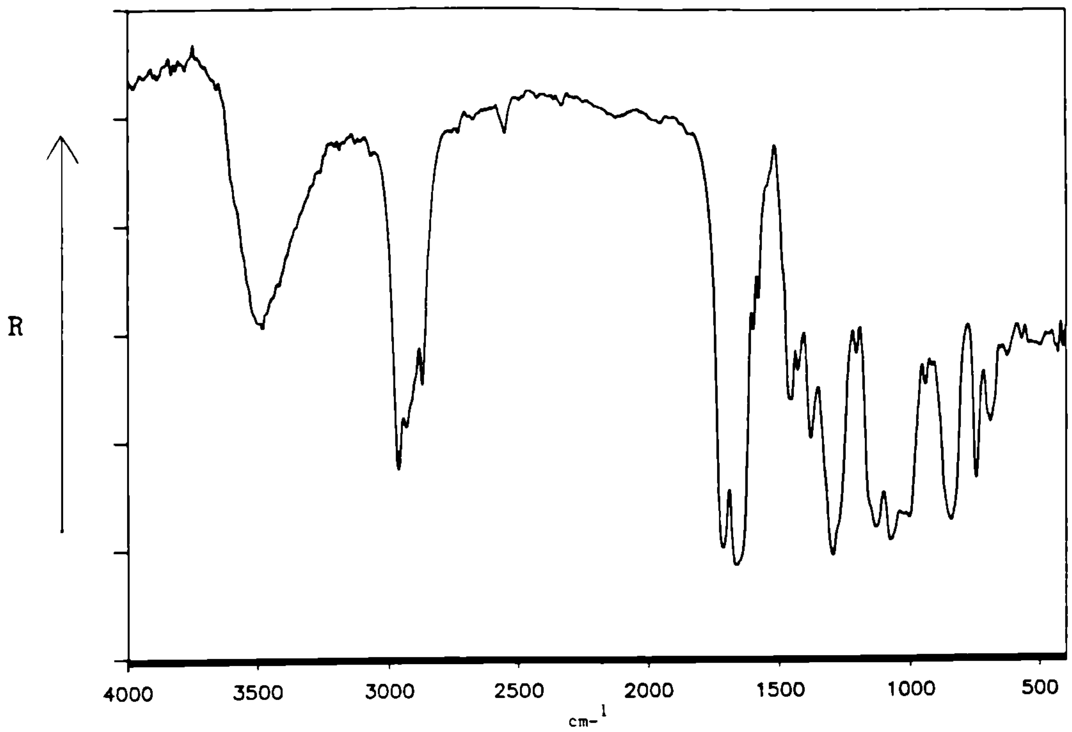

Figure 14.1 Diffuse reflectance FT-IR spectrum of HMG cellulose nitrate adhesive.

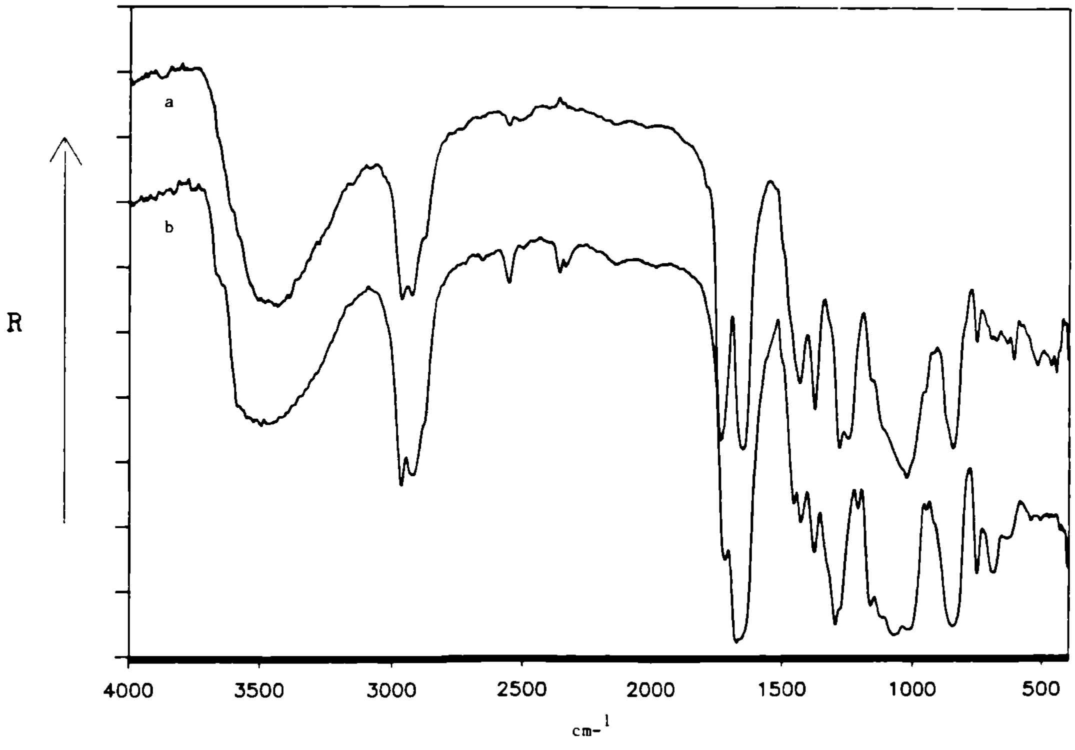

Figure 14.2 Diffuse reflectance FT-IR spectra of consolidant/adhesive samples from Nimrud ivories identified as cellulose nitrate, (a) CWN5 and (b) CWN1.

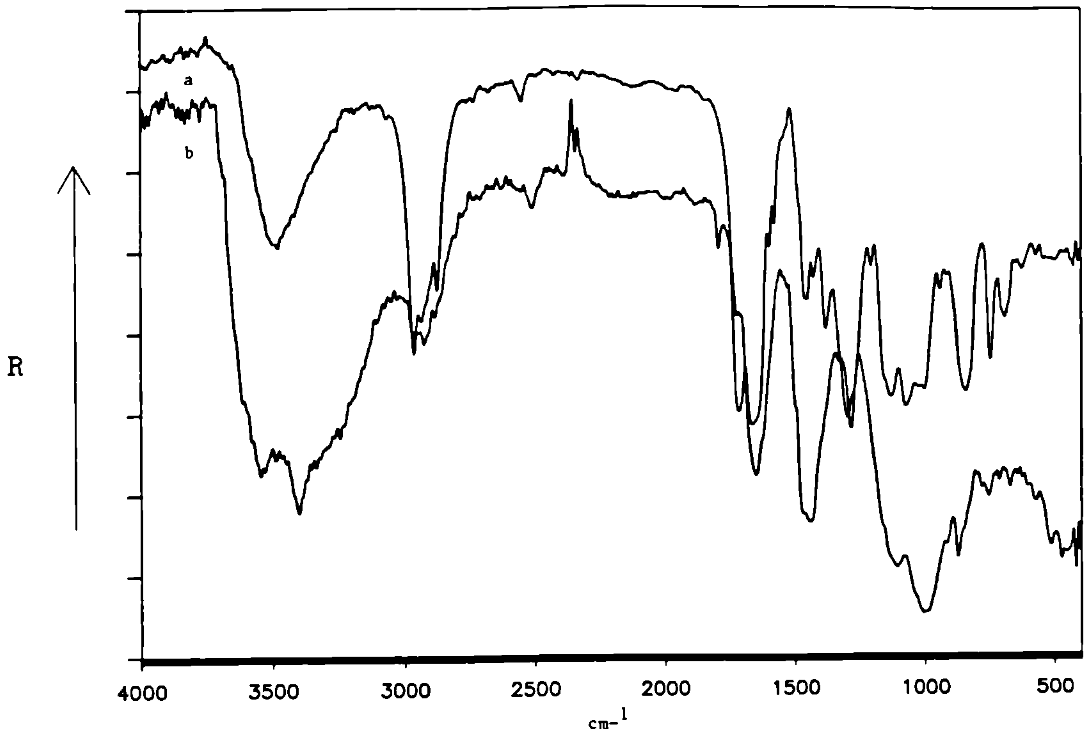

Figure 14.3 Diffuse reflectance FT-IR spectra of (a) HMG cellulose nitrate adhesive and (b) consolidant film from Nimrud ivories identified as degraded cellulose nitrate (CWN6).

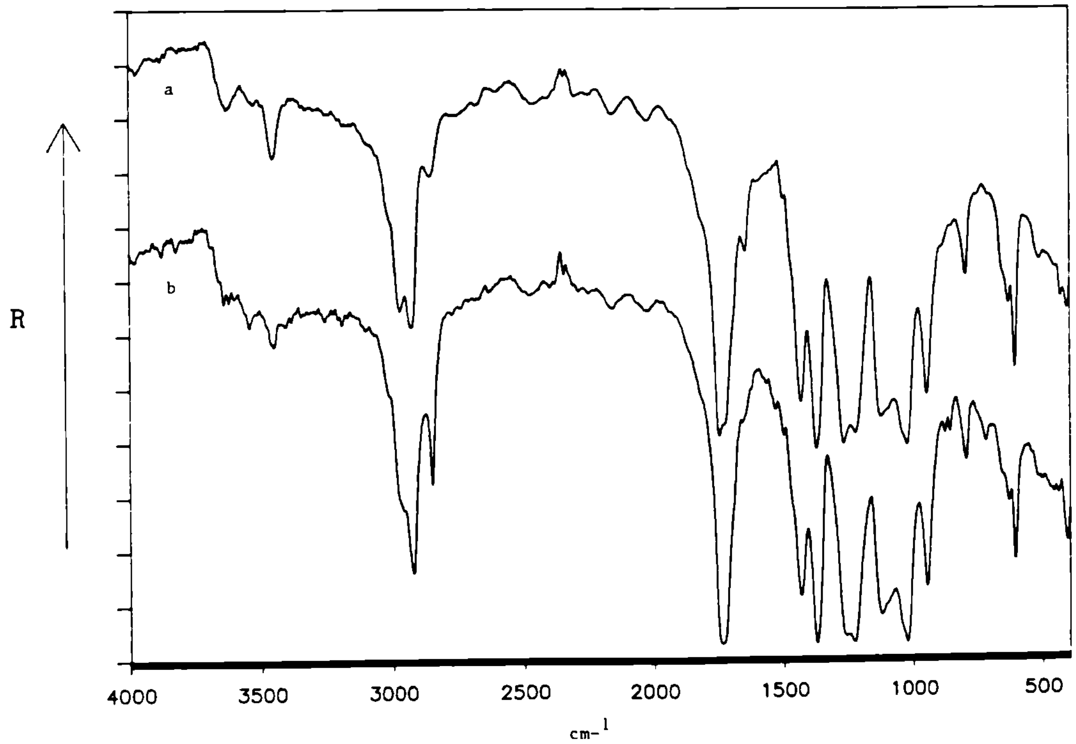

Figure 14.4 Diffuse reflectance FT-IR spectra of (a) secondary standard poly (vinyl acetate)(Aldrich) and (b) adhesive/consolidant from Nimrud ivories identified as poly (vinyl acetate)(CWN13).

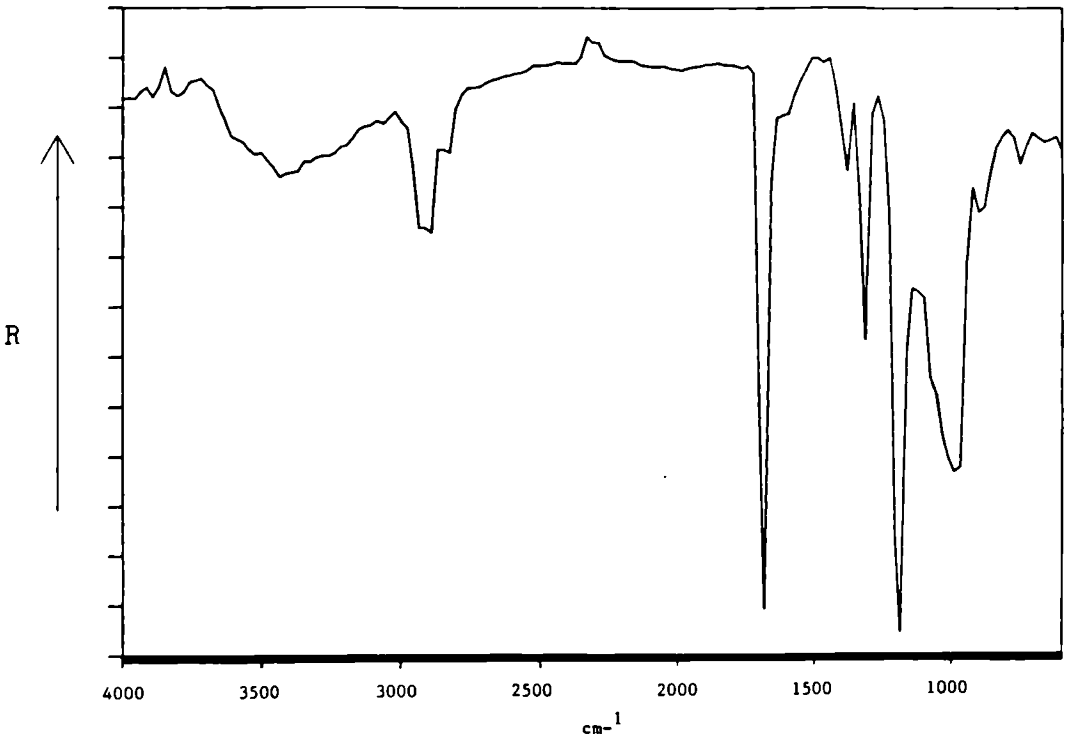

Figure 14.5 Transmission FT-IR spectrum of coating from glass lithograph (York3) obtained using Bruker FT-IR microscope. The material was identified as poly (vinyl acetate).

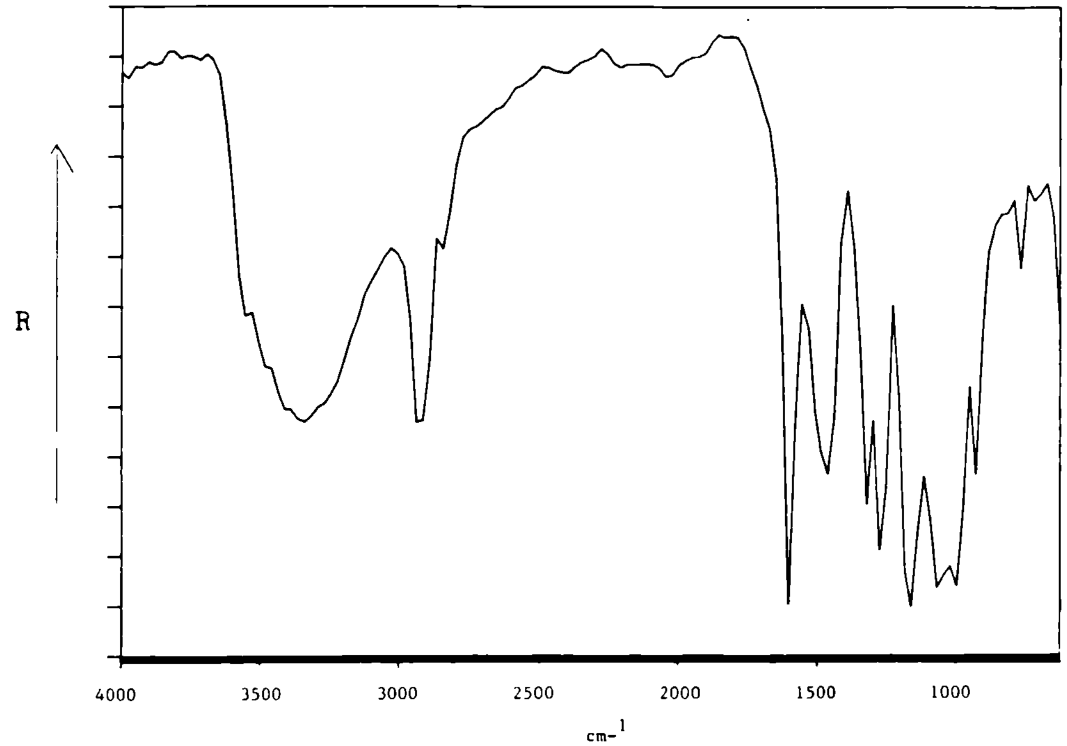

Figure 14.6 Transmission FT-IR spectrum of old restoration material from the lower reight cheek of the Mask of Thay (FW17) obtained using Bruker FT-IR microscope. The sample was identified as poly (vinyl acetate).

TABLE 14.1

Description and identification of Nimrud ivory samples

Sample number	Sample description	Object number (1)	Identification	Spectrum number
CWN1	consolidant/adhesive		cellulose nitrate	gsva0356
CWN2	yellowed, hard adhesive		cellulose nitrate	gsva0357
CWN3	waxfill from surface of burnt fragment w/ corner		beeswax + calcium carbonate	gsva0358
CWN4	consolidant layer from wax surface of burnt fragment		cellulose nitrate	gsva0553
CWN5	adhesive		cellulose nitrate	gsva0360
CWN6	white consolidant film		degraded cellulose nitrate	gsva0554
CWN7	hard waxlike substance from long point hinge fragment		calcium carbonate	gsva0362
CWN8	adhesive from burnt fragment		cellulose nitrate	gsva0548
CWN9	possible original wax from grey uneven surface of writing board	ND 3572	possible degraded cellulose nitrate	gsva0564
CWN10	possible original wax from writing board	ND 3572	calcium carbonate	gsva0522
CWN11	consolidant layer from writing board	ND 3572	degraded cellulose nitrate	gsva0551
CWN12	white consolidant film from writing board	ND 3572	cellulose nitrate	gsva0552
CWN13	adhesive/consolidant from reverse of writing board	ND 3572	poly (vinyl acetate)	gsva0552
CWN14	Hard waxlike material		possible degraded cellulose nitrate	gsva0526

1. If available

TABLE 14.2

Frequency values and band assignments for synthetic samples identified as cellulose nitrate

Millipore	Wardle-Storey	HMG adhesive	Nimrud ivory samples	Mask of Thay	Intensity	Vibration	Functional group	Frequency range given in literature	Ref.
cm-1	cm-1	cm-1	cm-1	cm-1				cm-1	
3447	3442	3482	3496 - 3404	3480	m,b	O-H stretch hydrogen bonded	O-H group	3400 - 3200(vs) polymeric intermolecular	1
2961	2965	2964	* 2966 - 2962	2963	m	C-H stretch	methyl group	2962 ± 10(s)	1
2917	2928	2936	2928 - 2921	2935	m	C-H stretch	methylene group	2926 ± 10(s)	1
1748	1732	1719	**1737 - 1735	1714	s	C=O stretch	carbonyl group	1735(s,sp)	2
1671	1663	1664	1673 - 1651	1673	s	N-O asym. stretch	nitrate group	1667 - 1629(vs)	3
1511					w	unassigned			
1455	1452	1461	* 1464 - 1455	1468	m	C-H asym. deformation	methyl group	1450 ± 20(m)	1
						C-H deformation	methylene group	1465 ± 20(m)	1
1429	1418	1431	1433 - 1429		m	unassigned			
1374	1376	1384	1376 - 1375	1379	m	C-H sym. deformation	methylene group	1380 - 1370(s)	1
1288	1286	1298	1296 - 1278	1292	s	N-O sym. stretch	nitrate group	1285 - 1272(vs)	3
1246			* 1247 - 1243		m	unassigned			
	1205	1208	* 1209 - 1208		m	unassigned			
1162	1163	1134	* 1163 - 1161	1143	s	C-O stretch	ether linkage	1150 - 1060(vs)	1
1073	1066	1079	1073 - 1022	1058	s,b	C-O stretch	ether linkage	1150 - 1060(vs)	1
945	near 945	944	* 946	near 945(sh)	w	unassigned			
846	846	845	846 - 838	842	s	N=O stretch	nitrate group	872 - 833(s)	3
751	752	749	753 - 750	751	m	out-of-plane deformation	nitrate group	761 - 745(m)	3
692	683	694	694 - 670	693	m	N-O deformation	nitrate group	710 - 689(m)	3

* Absorption is weak or does not appear in some spectra

** Strong band occurs in samples CWN5 and CWN12, a weak shoulder occurs near 1719 cm-1 in other sample spectra.

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 14.3

Frequency values and band assignments for samples identified as poly (vinyl acetate)

PVAC standard cm-1	PVAC adhesive cm-1	PVAC (1) cm-1	CWN13 diffuse reflect. cm-1	York3 micro-scope cm-1	FW17 micro-scope cm-1	Inten-sity	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
3457	3451	3470	3452	3458	3358	w	O-H stretch hydrogen bonded	alcohol water	3400 - 3200 (b) polymeric	3
2975	2973	2985	near 2960(sh)	2961	2963	m	C-H stretch	methyl group	2962 ± 10 (s)	3
2929	2927	2930	2922	2930	2935	m	C-H stretch	methylene group	2926 ± 10 (s)	3
2861	near 2860(sh)	near 2860(sh)	2851	2860	2860	w	C-H stretch	methyl group	2872 ± 10 (s)	3
							C-H stretch	methylene group	2853 ± 10 (s)	3
1752	1730	1745	1739	1738	1749(b)	s	C=O stretch	ester	1750 - 1730 (s)	3
					1738(b)	s	C=O stretch	ester	1750 - 1730 (s)	3
1651	1656	near 1650	near 1650	1697(vw)		sh	unassigned			
					1582	s	unassigned			
1436	1435	1435	1435	1433	1433	s	C-H asym. deformation	methyl group	1450 ± 20 (m)	3
1375	1374	1375	1375	1373	1373	s	C-H sym. deformation	methyl group	1380 - 1370 (s)	3
1270	near 1270(sh)		near 1250(sh)		1250(b)	s	C-O stretch	acetate ester	1250 - 1230 (s)	3
1224	1225	1245(b)	1227	1238	1238(b)	s	C-O stretch	acetate ester	1245(s)	
				1171		w	unassigned			
1127	1123	1130	1125	1115(w)	1124	s	unassigned			
1028	1025	1025	1026	1025	1024	s	C-O stretch	acetate ester	1060 - 1000 (m)	3

TABLE 14.3 contd.

Frequency values and band assignments for samples identified as poly (vinyl acetate)

PVAC standard cm-1	PVAC adhesive cm-1	PVAC (1) cm-1	CWN13 diffuse reflect. cm-1	York3 micro- scope cm-1	FW17 micro- scope cm-1	Inten- sity	Vibration	Functional group	Frequency range given in literature cm-1	Ref.
948	948	950	948	947	947	s	unassigned			
798	797	795	797	795	795	m	unassigned			
632	632	630	631	(2)	(2)	m	bending vibration	acetate group	630	4
							skeletal deformation	acetate group	640(s)	5
607	607	605	606	(2)	(2)	s	bending vibration	acetate group	605	4
							skeletal deformation	acetate group	612(s)	5

1. Values were estimated to nearest 5 cm-1 from transmission spectrum in Hummel, 1978.
2. Microscope range ends at 650 cm-1
3. Bellamy, 1975
4. Hummel, 1966
5. Thompson and Torkington, 1945

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

CHAPTER 15 CONCLUSIONS

For natural products, diffuse reflectance infrared spectroscopy was useful in identifying the type of material but rarely allowed a more specific identification. Waxes can be identified with a high degree of certainty and in several examples, waxes were identified as components of a mixture. Shellac and amber have distinct infrared spectra. Proteins and gums may be identified as a class of materials. Some samples of fats and resins were identified as being such, but no very specific identification could be made as to type of resin or fat. Bituminous materials were very difficult to identify because of their compositional complexity. These results support the conclusions of earlier workers (Chapter 1).

Many of the samples examined in this study which were not identified were characterized by several broad, overlapping bands. These broad features may be due to several factors. They may be indicative of severe degradation of the sample or of the presence of inorganic materials. Both of these factors are common in archaeological samples. As was mentioned in Chapter 3, the infrared analysis of complex substances is difficult due to overlapping bands and polymerization reactions that take place over time decrease the detail which may be observed in infrared spectra (Mills and White, 1987). More sensitive separation techniques such as GC-MS are required for more specific characterization of natural products. FT-IR can, however, be recommended as a preliminary screening technique as very little sample is required and the procedure is rapid.

In the case of semi-synthetic and synthetic materials, the technique was far more successful for the identification of these materials. All but one of the unknown plastic samples provided by the Museums was identified with certainty. The need for this type of analysis for both the identification of previous conservation treatments and the characterization of materials in twentieth century objects is vital. The identity of modern synthetics should be determined before any type of treatment is carried out and it is very difficult or impossible to identifiy the materials with certainty by visual or microscopic examination. The importance of this technique in the future of conservation cannot be underestimated.

The FT - IR microscopy did not produce the kind of results that were expected from reports in the literature. A major problem was sample preparation. It is very important to have a sufficiently transparent sample and many of the samples analysed in this thesis were not sufficiently transparent to produce acceptable spectra. Also there is the problem of finding a suitable sample support. The TEM grids used in this study were adequate for some samples, but were difficult to work with in the laboratory conditions available to the author. There is a wide area for future research using other types of FT-IR microscopes.

Other areas for future work in the application of FT-IR within conservation include gathering reference spectra of collection of early plastic materials and of early conservation treatments. Another important consideration is the use instruments which utilize J-CAMP-DX programming language (McDonald and Wilks, 1988). This language permits the interlaboratory exchange of spectra irrespective of the brand of spectrometer used. Readily exchangable data is an important consideration in the field of conservation research as there are few research laboratories in the field.

The results of this thesis indicate that FT-IR is a valid technique for the identification of modern organic materials of interest in conservation and has use in the characterization of natural product encountered in archaeological and art contexts. FT-IR is recommended for conservation research since, after the initial expenditure, it is cheap in terms of analyst time and running costs. Also, the speed and portabilty of the silicon carbide technique make the analysis of samples from other museums easily possible.

REFERENCE COLLECTION

Sample Number RW1
Sample Name Common Name Softwood tar
Chemical Name Genus and Species: Pix liquida BP
Source Raymond White
Museum Laboratory National Gallery Trafalgar Square London
WC2N 5DN Telephone 01-839-3321 x 233
Provenance N A
Number: N A
Spectra: GSIA0010
GSIA 031
GSIA0069
GSIA 54
GSIA0155
GSVA0015
GSVA 097
GSVA0288
GSVA0387
Library Number: DR0015 GSVA0015)
DR0142 GSVA0097)
DR0207 (GSVA0387

Sample Number RW2
Sample Name Common Name Bitumen
Chemical Name Genus and Species N A
Source Raymond White
Museum Laboratory: National Gallery Trafalgar Square, London
WC N 5DN Telephone 01-839-3321 x 233
Provenance: Middle East
Number N A
Spectra: GSIA0001
GSIA0026
GSIA0032
GSIA0070
GSVA0016
GSVA0098

Library Number: DR0016 GSVA0016)
DR0143 (GSVA0098)

Sample Number RW3
Sample Name Common Name Asphaltite
Chemical Name Genus and Species N A
Source Raymond White
Museum Laboratory National Gallery, Trafalgar Square London
WC2N 5DN Telephone 01-8 9-3321 x 233
Provenance Middle East
Number N A
Spectra: GSIA0002
GSIA0027
GSIA0029
GSIA0030
GSIA0071
GSVA 017
GSVA0101
Library Number DR0017 (GSVA0017)
DR0144 (GSVA0101)

Sample Number: RW4
Sample Name Common Name: Pine rosin tar
Chemical Name Genus and Species: N/A
Source: Raymond White
Museum, Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N A
Spectra: GSIA0011
GSIA0033
GSIA0072
GSIA0156
GSIA0157
GSVA0018
GSVA0102
GSVA0289
GSVA0388
Library Number: DR0018 (GSVA0018)
DR0145 (GSVA0102)
DR0208 (GSVA0388)

Sample Number: RW5
Sample Name Common Name Asphaltum
Chemical Name Genus and Species: N/A
Source: Raymond White
Museum Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0003
GSIA0028
GSIA0034
GSIA0073
GSVA0019
GSVA0103
Library Number: DR0019 (GSVA0019)
DR0146 (GSVA0103)

Sample Number: RW6
Sample Name Common Name: Coal tar (aged film spread '78)
Chemical Name Genus and Species: N A
Source Raymond White
Museum Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number. N/A
Spectra: GSIA0012
GSIA0035
GSIA0074
GSIA0098
GSVA0020
GSVA0104
Library Number: DR0020 (GSVA0020)
DR0147 (GSVA0104)

Sample Number: RW7
Sample Name/Common Name: Coarse birch bark bistre
(Hardwood pitch)
Chemical Name Genus and Species: from Betula species
Source: Raymond White
Museum Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N A
Spectra: GSIA0013
GSIA0036
GSIA0075
GSIA0099
GSVA0021
GSVA0105
Library Number: DR0021 (GSVA0021)
DR0148 (GSVA0105)

Sample Number: RW8
Sample Name Common Name: Egyptian mummy
Chemical Name Genus and Species: N/A
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN Telephone. 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0004
GSIA0037
GSIA0076
GSVA0022
GSVA0106
Library Number: DR0022 (GSVA0022)
DR0149 (GSVA0106)

Sample Number: RW9
Sample Name Common Name: Softwood pitch (aged 11 years)
Chemical Name/Genus and Species: Pix liquida BP
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0151
GSIA0152
GSVA0228

Library Number: DR0198 (GSVA0228)

Sample Number: RW10
Sample Name Common Name: Casein
Chemical Name Genus and Species: Casein
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: BDH
Number: N/A
Spectra: GSIA0297
GSVA0322
Library Number: DR0191 (GSVA0322)
P00035 (GSVA0322)

Sample Number: RW11
Name Common Name: Casein (precipitated with acid)
Chemical Name Genus and Species: Casein
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number. N/A
Spectra: GSIA
GSVA0323
Library Number: DR0199 (GSVA0323)
P00045 (GSVA0323)

Sample Number: RW12
Sample Name Common Name: Abietic acid
Chemical Name/Genus and Species: 1,2,3,4,4a,4b,5,6 10,10a-Decahydro-1,4a-dimethyl-7-(1-methylethyl)-1-phenanthrene-carboxylic acid
($C_{20}H_{30}O_2$)
Source: Raymond White
Museum Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233
Provenance: N A
Number N/A
Spectra: GSIA0299
GSVA0324
Library Number: DR0200 (GSVA0324)

Sample Number: RW13
Sample Name/Common Name. Umbelliferone
Chemical Name/Genus and Species: 7-Hydroxy-2H-1-benzopyran-2-one
($C_9H_6O_3$)
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: Sigma U 7626
Number: N/A
Spectra: GSVA0336
Library Number: DR0192

Sample Number: RW14
Sample Name Common Name: Hexatriacontane
Chemical Name Genus and Species: Hexatriacontane ($CH_3(CH_2)_{34}CH_3$)
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: Fluka AG Bucks SG
Number: N/A
Spectra: GSVA0337
Library Number: DR0193

Sample Number: RW15
Sample Name/Common Name: Beechwood bistre (hardwood pitch)
Chemical Name Genus and Species: from *Fagus grandifolia* Ehrh.
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance:
Number: N/A
Spectra: GSVA0515
GSVA0516
Library Number:

Sample Number: MW1
Sample Name/Common Name: Gum myrrh
Chemical Name/Genus and Species: from Commiphora ssp.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC1
Spectra: GSIA0014
GSIA0038
GSIA0077
GSVA0023
GSVA0107
Library Number: DR0023 (GSVA0023)
DR0150 (GSVA0107)

Sample Number: MW2
Sample Name Common Name Frankincense (olibanum)
Chemical Name/Genus and Species. from *Boswellia* species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC2
Spectra: GSIA0015
GSIA0039
GSIA0078
GSVA0024
GSVA0108
Library Number: DR0024 (GSVA0024)
DR0151 (GSVA0108)

Sample Number: MW3
Sample Name/Common Name: Gum olibanum
Chemical Name/Genus and Species: from *Boswellia* species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC3
Spectra: GSIA0016
GSIA0040
GSIA0079
GSVA0025
GSVA0109
Library Number: DR0025 (GSVA0025)
DR0152 (GSVA0109)

Sample Number: MW4
Sample Name/Common Name: Gum karaya
Chemical Name/Genus and Species: from Sterculia urens
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC4
Spectra: GSIA0005
GSIA0041
GSIA0080
GSVA0026
GSVA0110
Library Number: DR0026 (GSVA0026)
DR0153 (GSVA0110)

Sample Number: MW5
Sample Name/Common Name: Gum dammar
Chemical Name/Genus and Species: N/A
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC5
Spectra: GSIA0017
GSIA0042
GSIA0081
GSVA0027
GSVA0111
Library Number: DR0027 (GSVA0027)
DR0154 (GSVA0111)

Sample Number: MW6
Sample Name/Common Name: Locust bean gum
Chemical Name/Genus and Species: from *Ceratonia siliqua* L.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC6
Spectra: GSIA0018
GSIA0043
GSIA0082
GSVA0028
GSVA0112
Library Number: DR0028 (GSVA0028)
DR0155 (GSVA0112)

Sample Number: MW7
Sample Name/Common Name: Gum tragacanth
Chemical Name Genus and Species: from *Astragalus* species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC7
Spectra: GSIA0019
GSIA0044
GSIA0083
GSVA0029
GSVA0113
Library Number: DR0029 (GSVA0029)
DR0156 (GSVA0113)

Sample Number: MW8
Sample Name/Common Name: Gum arabic
Chemical Name/Genus and Species: from *Acacia* species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: RC8
Spectra: GSIA0006
GSIA0045
GSIA0084
GSVA0030
GSVA0114
Library Number: DR0030 (GSVA0030)
DR0157 (GSVA0114)

Sample Number: MW9
Sample Name/Common Name: Gum myrrh
Chemical Name/Genus and Species: from *Commiphoria* species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: W62
Spectra: GSIA0020
GSIA0046
GSIA0085
GSVA0008
GSVA0031
GSVA0120
Library Number: DR0031 (GSVA0031)
DR0158 (GSVA0120)

Sample Number: MW10
Sample Name/Common Name: Gum benzoin sumatra
Chemical Name/Genus and Species: from *Styrax benzoin*
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: W63
Spectra: GSIA0007
GSIA0047
GSIA0053
GSIA0086
GSVA0032
GSVA0121
Library Number: DR0032 (GSVA0032)
DR0159 (GSVA0121)

Sample Number: MW11
Sample Name Common Name: Gum tolu balsam
Chemical Name Genus and Species: from *Myroxylon balsamum* (L.) Harms.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: W64
Spectra: GSIA0021
GSIA0048
GSIA0052
GSIA0087
GSVA0033
GSVA0122
GSVA0174
GSVA0291
Library Number: DR0033 (GSVA0033)
DR0160 (GSVA0122)
DR0180 (GSVA0291)
DR0196 (GSVA0174)

Sample Number: MW12
Sample Name/Common Name: Gum labdanum
Chemical Name/Genus and Species: from *Cistus ladaniferus* L.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: W65
Spectra: GSIA0008
GSIA0009
GSIA0050
GSIA0051
GSIA0088
GSVA0034
GSVA0123
GSVA0175
GSVA0290
GSVA0389
GSVA0390
Library Number: DR0034 (GSVA0034)
DR0161 (GSVA0123)
DR0179 (GSVA0290)
DR0197 (GSVA0175)
DR0209 (GSVA0390)

Sample Number: NJS1
Sample Name Common Name: Natural stick lac
Chemical Name/Genus and Species: from *Laccifer lacca* Kerr.
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSIA0022
GSIA0054
GSIA0089
GSVA0002
GSVA0014
GSVA0124
GSVA0217
Library Number: DR0002 (GSVA0217)
DR0162 (GSVA0124)

Sample Number: NJS2
Sample Name/Common Name: Shellac
Chemical Name/Genus and Species: from *Laccifer lacca* Kerr.
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSIA0023
GSIA0055
GSIA0090
GSVA0001
GSVA0013
GSVA0125
GSVA0216
Library Number: DR0001 (GSVA0216)
DR0163 (GSVA0125)

Sample Number: NJS10
Sample Name/Common Name: Jet
Chemical Name/Genus and Species: N/A
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Whitby beach
Number: N/A
Spectra: GSVA0230
Library number: DR0194

Sample Number: NJS20
Sample Name/Common Name: Hematite
Chemical Name/Genus and Species: Iron oxide (Fe_2O_3)
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0335
Library number: DR0195

Sample Number: NJS24
Sample Name/Common Name: Ivory
Chemical Name/Genus and Species: N/A
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0519
Library number: DR0227

Sample Number: NJS25
Sample Name/Common Name: Asphalt
Chemical Name/Genus and Species: N/A
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dead Sea, Khurbet Qumran, Jordan
Number: N/A
Spectra: GSVA0607
GSVA0608
Library number: DR0234 (GSVA0607)
DR0235 (GSVA0608)

Sample Number: VA1
Sample Name/Common Name: Carnauba wax (fatty grey)
Chemical Name/Genus and Species: from *Copernicia cerifera*
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: John Myland, 18 Norwood High Street, London, SE29 9NW
Number: N/A
Spectra: GSIA0061
GSIA0092
GSVA0035
GSVA0036
GSVA0127
Library Number: DR0035 (GSVA0035)
DR0036 (GSVA0036)
DR0165 (GSVA0127)

Sample Number: VA2
Sample Name/Common Name: Paraffin wax
Chemical Name Genus and Species: Hydrocarbon wax
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: John Myland, 18 Norwood High Street, London, SE29 9NW
Number: N/A
Spectra: GSIA0062
GSIA0093
GSVA0037
GSVA0128
Library Number: DR0037 (GSVA0037)
DR0166 (GSVA0128)

Sample Number: VA3
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: N/A
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: John Myland, 18 Norwood High Street, London, SE29 9NW
Number: N/A
Spectra: GSIA0060
GSIA0094
GSVA0038
GSVA0129
Library Number: DR0038 (GSVA0038)
DR0167 (GSVA0129)

Sample Number: VA4
Sample Name/Common Name: White shellac
Chemical Name/Genus and Species: from *Laccifer lacca* Kerr
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0063
GSVA0039
GSVA0223
Library Number: DR0039 (GSVA0039)
DR0176 (GSVA0223)

Sample Number: VA5
Sample Name/Common Name: Sandarac
Chemical Name/Genus and Species: from *Tetraclinis articulata*
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0064
GSVA0040
Library number: DR0040 (GSVA0040)

Sample Number: VA6
Sample Name/Common Name: Mastic
Chemical Name/Genus and Species: from *Pistacia lentiscus*
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0065
GSVA0041
Library number: DR0041 (GSVA0041)

Sample Number: VA7
Sample Name/Common Name: English mandrek

Chemical Name Genus and Species. N/A
Source J Kitchin
Museum Laboratory· Conservation Department. Victoria and Albert Museum. Cromwell Road. London SW7
Provenance· N/A
Number: N/A
Spectra: GSIA0066
GSIA0068
GSVA0042
Library number: DR0042 (GSVA0042)

Sample Number: VA8
Sample Name Common Name· Kaolin
Chemical Name/Genus and Species: N/A
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0067
GSVA0043
Library number: DR0043 (GSVA0043)

Sample Number: VA9
Sample Name/Common Name: Microcrystalline wax
Chemical Name/Genus and Species: Hydrocarbon wax
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSVA0100
GSVA0229
Library Number: DR0177 (GSVA0100)
DR0178 (GSVA0229)

Sample Number: VA10
Sample Name Common Name: Rabbit skin glue
Chemical Name/Genus and Species: N/A
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum. Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSVA0194
Library Number: DR0133

Sample Number: VA11
Sample Name Common Name· Animal glue
Chemical Name Genus and Species: N/A
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra· GSVA0195
Library Number: DR0134

Sample Number: VA12
Sample Name/Common Name: Hide glue
Chemical Name/Genus and Species: N/A
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSVA0196
Library Number: DR0135

Sample Number: VA13
Sample Name/Common Name: Cellulose acetate acetyl content 39.8%
Chemical Name/Genus and Species: Cellulose diacetate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich
Number: N/A
Spectra: GSVA0350
Library number: P00037

Sample Number: VA14
Sample Name/Common Name: Cellulose acetate
Chemical Name/Genus and Species: Cellulose triacetate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich
Number: N/A
Spectra: GSVA0351
Library number: P00038

Sample Number: VA15
Sample Name/Common Name: Poly (vinyl acetate) PVAC
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich secondary standard
Number: N/A
Spectra: GSVA0352
Library number: P00039

Sample Number: VA16
Sample Name Common Name: Poly (vinyl chloride) PVC
Chemical Name/Genus and Species: Poly (vinyl chloride)
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich secondary standard
Number: N/A
Spectra: GSVA0353
pvc4
Library Number: P00040 (GSVA0353)
P00041 (pvc4)

Sample Number: VA17
Sample Name/Common Name: Cellulose acetate butyrate
Chemical Name/Genus and Species: Cellulose acetate butyrate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich
Number: N/A
Spectra: GSVA0386
Library Number: P00043

Sample Number: VA18
Sample Name/Common Name: Oleic acid
Chemical Name/Genus and Species: 9-Octadecenoic acid
$(COOH(CH_2)_7CH=CH(CH_2)_7CH_3)$
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: BDH Chemicals Ltd., Poole, England
technical grade
Number: N/A
Spectra: GSVA0471
Library number: DR0228

Sample Number: VA19
Sample Name/Common Name: Myristic acid
Chemical Name/Genus and Species: Tetradecanoic acid
$(COOH(CH_2)_{12}CH_3)$
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: BDH Chemicals Ltd., Poole, England
biochemical grade, specially pure
Number: N/A
Spectra: GSVA0472
Library number: DR0229

Sample Number: VA20
Sample Name/Common Name: Palmitic acid
Chemical Name/Genus and Species: Hexadecanoic acid
$(COOH(CH_2)_{14}CH_3)$
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: BDH Chemicals Ltd., Poole, England
general purpose reagent (GPR)
Number: N/A
Spectra: GSVA0473
Library number: DR0230

Sample Number: VA21
Sample Name/Common Name: Stearic acid
Chemical Name/Genus and Species: Octadecanoic acid
$(COOH(CH_2)_{16}CH_3)$
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: BDH Chemicals Ltd., Poole, England
general purpose reagent (GPR)
Number: N/A
Spectra: GSVA0474
Library number: DR0231

Sample Number: VA22
Sample Name/Common Name: Poly (methyl methacrylate)
Chemical Name/Genus and Species: Poly (methyl methacrylate)
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich secondary standard
Number: N/A
Spectra: pmethmel
GSVA0530
Library Number: P00008 (pmethmel)

Sample Number: VA23
Sample Name/Common Name: Polycarbonate resin
Chemical Name/Genus and Species: Polycarbonate resin
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich secondary standard
Number: N/A
Spectra: carbonate
Library Number: P00032

Sample Number: VA24
Sample Name Common Name: Cellulose nitrate
Chemical Name Genus and Species: Cellulose nitrate
Source. G Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Millipore SC 8 micron
Number: N/A
Spectra: cno3
Library number: DR0008
P00027

Sample Number: VA25
Sample Name Common Name: Cellulose nitrate plastic
Chemical Name Genus and Species: Cellulose nitrate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Wardle-Storey Factory, Brantham, Essex
Number: N/A
Spectra: GSVA0555
Library number: P00049

Sample Number: VA26
Sample Name Common Name: Camphor
Chemical Name/Genus and Species: from *Cinnamomum camphorae* Nees $(C_{10}H_{16}O)$
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: P. Bolton, Dispensing Chemist
Number: N/A
Spectra: camphor2
GSVA0531
Library number: P00031 (camphor2)

Sample Number: VA27
Sample Name Common Name: Bexfilm T cellulose acetate sheet
Chemical Name/Genus and Species: Cellulose triacetate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Bexford plc
Number: N/A
Spectra: Bexfilm
Library number: DR0175
P00029

Sample Number VA28
Sample Name Common Name Triphenyl phosphate
Chemical Name Genus and Species: Triphenyl phosphate
Source G Martin
Museum Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich 99+%
Number: N/A
Spectra: Tripphos
Library number: N/A

Sample Number: VA29
Sample Name/Common Name: Diethyl phthalate
Chemical Name/Genus and Species: Diethyl phthalate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Aldrich 99%
Number: N/A
Spectra: Diethylp
Library Number: N/A

Sample Number: VA30
Sample Name/Common Name: Santicizer 8 (Ketjenflex8)
Chemical Name/Genus and Species: N-ethyl o,p-toluenesulfonamide mixture
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Monsanto
Number: N/A
Spectra: Ketjen8
Library Number: P00028

Sample Number: VA31
Sample Name/Common Name: Perspex (Plexiglass)
Chemical Name/Genus and Species: Poly (methyl methacrylate)
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert Museum, Cromwell Road, London SW7
Provenance: Visijar Tuckers Perspex VE
Number: N/A
Spectra: Perspex
Library Number: P00030

Sample Number: VA32
Sample Name Common Name: Plexiglass (Perspex)
Chemical Name/Genus and Species: Poly (methyl methacrylate)
Source: Furniture conservation
Museum/Laboratory: Smithsonian Institution, Conservation Analytical Laboratory, Washington D.C.
Provenance: unknown commercial
Number: N/A
Spectra: plex320
Library Number: P00034

Sample Number: LA1
Sample Name/Common Name: Amber
Chemical Name Genus and Species: Succinite (Baltic amber)
Source: Leena Airola
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square London, WC1E 0PY, 01-387-7050
Provenance: possibly from Russia
Number: 34
Spectra: GSIA0056
GSIA0095
GSVA0007
GSVA0011
GSVA0131
GSVA0219
Library Number: DR0004 (GSVA0219)
DR0169 (GSVA0131)

Sample Number: LA2
Sample Name Common Name: Amber
Chemical Name Genus and Species: Succinite (Baltic amber)
Source: Leena Airola
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square London, WC1E 0PY, 01-387-7050
Provenance: possibly from Russia
Number: 35
Spectra: GSIA0057
GSIA0096
GSVA0004
GSVA0132
GSVA0220
Library Number: DR0005 (GSVA0220)
DR0170 (GSVA0132)

Sample Number: LA3
Sample Name/Common Name: Amber
Chemical Name/Genus and Species: Succinite (Baltic amber)
Source: Leena Airola
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square London, WC1E 0PY, 01-387-7050
Provenance: Denmark
Number: 36
Spectra: GSIA0058
GSIA0059
GSIA0097
GSVA0005
GSVA0006
GSVA0130
GSVA0221
GSVA0222
Library Number: DR0006 (GSVA0221)
DR0007 (GSVA0222)
DR0168 (GSVA0130)

Sample Number: Kew1
Sample Name/Common Name: Kauri resin (white, rerasped)
Chemical Name/Genus and Species: from *Agathis australis*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New Zealand (T. Hedley Barry)
Number: 36.1932
Spectra: GSIA0103
GSIA0104
GSVA0044
GSVA0045
GSVA0213
Library Number: DR0044 (GSVA0044)
DR0045 (GSVA0045)

Sample Number: Kew2
Sample Name/Common Name: East Indian copal (medium-hard grade)
Chemical Name/Genus and Species: from *Agathis dammara*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Dutch East Indies (T. Hedley Barry)
Number: 36.1932
Spectra: GSIA0105
GSIA0106
GSVA0046
GSVA0047
GSVA0214
Library number: DR0046 (GSVA0046)
DR0047 (GSVA0047)

Sample Number: Kew3
Sample Name Common Name: Resin
Chemical Name/Genus and Species: from *Agathis dammara*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Singapore (India Museum)
Number: N/A
Spectra: GSIA0107
GSIA0108
GSVA0048
GSVA0049
GSVA0215
Library number: DR0048 (GSVA0048)
DR0049 (GSVA0049)

Sample Number   Kew4
Sample Name Common Name   Resin
Chemical Name Genus and Species: from Araucaria columnaris
Source   Rupert Hastings
Museum Laboratory: Museum of Economic Botany, Kew
Provenance   New Caledonia (J. McGillivray)
Number. N A
Spectra: GSIA0109
GSIA0110
GSVA0050
GSVA0051
GSVA0239
GSVA0240
Library number: DR0050 (GSVA0050)
DR0051 (GSVA0051)

Sample Number: Kew5
Sample Name Common Name: Resin
Chemical Name Genus and Species: from Abies spectabilis
Source   Rupert Hastings
Museum Laboratory: Museum of Economic Botany, Kew
Provenance: Simla, India (Indian Office, India Museum)
Number: 18.1898
Spectra: GSIA0111
GSIA0112
GSVA0052
GSVA0053
GSVA0054
Library number: DR0052 (GSVA0052)
DR0053 (GSVA0053)
DR0054 (GSVA0054)

Sample Number: Kew6
Sample Name Common Name. Resin
Chemical Name Genus and Species: from Cedrus brevifolia
Source: Rupert Hastings
Museum Laboratory: Museum of Economic Botany, Kew
Provenance: Cyprus (Forest Exhibition, Edinburgh)
Number: 167.1884
Spectra: GSIA0113
GSIA0114
GSVA0055
GSVA0056
Library Number: DR0055
DR0056

Sample Number   Kew7
Sample Name Common Name   Burgandy pitch as sold in market)
Chemical Name Genus and Species   from Picea abies
Source: Rupert Hastings
Museum Laboratory   Museum of Economic Botany, Kew
Provenance   Geneva (Dr. Hanbury, 1874)
Number: N/A
Spectra: GSIA0115
GSIA0116
GSVA0057
GSVA0058
GSVA0059
Library Number: DR0057 (GSVA0057)
DR0058 (GSVA0058)
DR0059 (GSVA0059)

Sample Number: Kew8
Sample Name Common Name: Resin
Chemical Name Genus and Species: from Picea glauca
Source: Rupert Hastings
Museum Laboratory: Museum of Economic Botany, Kew
Provenance: Carlton, Saskatchewan, Canada
Number: N/A
Spectra: GSIA0117
GSIA0118
GSVA0065
GSVA0066
Library Number: DR0062 (GSVA0065)
DR0063 (GSVA0066)

Sample Number: Kew9
Sample Name/Common Name: Htin Yoo resin (used for soldering)
Chemical Name/Genus and Species: from Pinus kesiya
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: India (Indian Forestry Department)
Number: N/A
Spectra: GSIA0119
GSIA0120
GSVA0067
GSVA0068
Library Number: DR0064 (GSVA0067)
DR0065 (GSVA0068)

Sample Number: Kew10
Sample Name/Common Name: Resin
Chemical Name Genus and Species: from Pinus massoniana
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Ningpo, China (W. M. Cooper)
Number: 149.1884
Spectra: GSIA0121
GSIA0123
GSVA0069
GSVA0070
Library number: DR0066 (GSVA0069)
DR0067 (GSVA0070)

Sample Number: Kew11
Sample Name Common Name: Resin
Chemical Name Genus and Species: from Pinus merkusii
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Sumatra   (T. Hedley Barry)
Number: 23.1938
Spectra: GSIA0124
GSIA0125
GSVA0071
GSVA0072
Library number: DR0068 (GSVA0071)
DR0069 (GSVA0072)

Sample Number: Kew12
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Pinus roxburghii
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: India
Number: N/A
Spectra: GSIA0126
GSIA0127
GSVA0073
GSVA0074
Library number: DR0070 (GSVA0073)
DR0071 (GSVA0074)

Sample Number: Kew13
Sample Name/Common Name: Common yellow resin
Chemical Name Genus and Species: from Pinus sylvestris
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: North Europe
Number: N/A
Spectra: GSIA0129
GSIA0130
GSVA0060
GSVA0061
Library number: DR0060 (GSVA0060)
DR0061 (GSVA0061)

Sample Number: Kew14
Sample Name Common Name: Resin
Chemical Name/Genus and Species: from Callitris endlicheri
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New South Wales, Australia (F. M. Bail)
Number: 73.1891
Spectra: GSIA0131
GSIA0132
GSVA0075
GSVA0076
Library Number: DR0072 (GSVA0075)
DR0073 (GSVA0076)

Sample Number: Kew15
Sample Name/Common Name: White pine resin
Chemical Name Genus and Species: from Callitris verrucosa
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New South Wales, Australia
Number: N/A
Spectra: GSIA0133
GSIA0134
GSVA0077
GSVA0078
Library Number: DR0074 (GSVA0077)
DR0075 (GSVA0078)

Sample Number: Kew16
Sample Name/Common Name: Gunisht resin
Chemical Name/Genus and Species: from Juniperus phoenicea
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Morocco
Number: N/A
Spectra: GSIA0135
GSVA0079
GSVA0080
Library Number: DR0076 (GSVA0079)
DR0077 (GSVA0080)

Sample Number: Kew17
Sample Name/Common Name: Gum sandarach
Chemical Name/Genus and Species: from Tetraclinis articulata
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Bombay, India
Number: N/A
Spectra: GSIA0136
GSIA0137
GSVA0081
GSVA0082
Library Number: DR0078 (GSVA0081)
DR0079 (GSVA0082)

Sample Number: Kew18
Sample Name/Common Name: East Africa gum copal
Chemical Name/Genus and Species: from Hymenaea verrucosa
(Trachylobium verrucosa)
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A
Number: 66.1924
Spectra: GSIA0138
GSIA0139
GSVA0083
GSVA0084
Library number: DR0080 (GSVA0083)
DR0081 (GSVA0084)

Sample Number Kew19
Sample Name Common Name Resin
Chemical Name Genus and Species. from *Hymenaea courbaril*
Source. Rupert Hastings
Museum Laboratory: Museum of Economic Botany, Kew
Provenance: Bahea, Brazil (Coll. T.S.)
Number N/A
Spectra: GSIA0140
GSIA0141
GSVA0085
GSVA0086
Library number: DR0082 (GSVA0085)
DR0083 (GSVA0086)

Sample Number: Kew20
Sample Name/Common Name: Chio mastic
Chemical Name Genus and Species: from *Pistacia lentiscus*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Turkey
Number:
Spectra: GSIA0142
GSIA0143
GSVA0088
GSVA0089
Library number: DR0084 (GSVA0088)
DR0085 (GSVA0089)

Sample Number: Kew21
Sample Name/Common Name: Mastic
Chemical Name/Genus and Species: from *Pistacia lentiacus*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A
Number: N/A
Spectra: GSIA0145
GSIA0146
GSVA0090
GSVA0091
Library number: DR0086 (GSVA0090)
DR0087 (GSVA0091)

Sample Number: Kew22
Sample Name/Common Name: Chian turpentine
Chemical Name/Genus and Species: from *Pistacia terebinthus*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A
Number: 7.1927 (Burroughs and Wellcome)
Spectra: GSIA0147
GSIA0148
GSVA0092
GSVA0093
Library Number: DR0088 (GSVA0092)
DR0089 (GSVA0093)

Sample Number: Kew23
Sample Name Common Name: Larch manna
Chemical Name Genus and Species: from *Larix decidua* Miller
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Canton Valais, Switzerland (Prof. A. Henry)
Number: 51.1924
Spectra: GSIA0178
Library Number: DR0171

Sample Number: Kew24
Sample Name/Common Name: Swiss turpentine
Chemical Name/Genus and Species: from *Picea abies*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Messrs Menier and Co.
Number: N/A
Spectra: GSVA0292
GSVA0391
Library Number: DR0181 (GSVA0292)
DR0210 (GSVA0391)

Sample Number: Kew25
Sample Name/Common Name: American turpentine
Chemical Name/Genus and Species: from *Pinus palustris*
(*Pinus australis*)
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A (D. Hanbury)
Number: N/A
Spectra: GSVA0293
GSVA0392
Library Number: DR0182 (GSVA0293)
DR0211 (GSVA0392)

Sample Number: Kew26
Sample Name/Common Name: Carnauba wax (yellow)
Chemical Name/Genus and Species: from *Copernicia cerifera*
(*Copernicia prunifera*)
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Brazil (Prices patent candle Co.)
Number: 23.1853
Spectra: GSVA0197
Library number: DR0172

Sample Number: Kew27
Sample Name/Common Name: Candelilla wax
Chemical Name/Genus and Species: from *Euphorbia cerifera*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Coahula, Mexico
Number: 24.1935
Spectra: GSVA0198
Library number: DR0173

Sample Number: Kew28
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from *Cedrus libani* (var. *brevifo*
same as Kew6
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Cyprus (Museum Pharm. Soc. of Great Britain)
Number: 167.1884
Spectra: GSVA0475
GSVA0476
Library number: DR0232 (GSVA0475)
DR0233 (GSVA0476)

Sample Number: NHM1
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Longmynd beds, Houghmond Hill, Shrewsbury, Shropshire
Number: 1911,298 (Bought of H. F. H. Butler, 1911)
Spectra: GSIA0182
GSVA0135
Library number: DR0090 (GSVA0135)

Sample Number: NHM2
Sample Name/Common Name: Asphalt
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Eastwell, Croftymine, Camborne, Cornwall
Number: 14433
Spectra: GSIA0183
GSVA0136
Library Number: DR0091 (GSVA0136)

Sample Number: NHM3
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: floating on the Dead Sea, Palestine (Dr. J W. Evans
1928)
Number: 1928,245
Spectra: GSIA0184
GSVA0137
Library Number: DR0092 (GSVA0137)

Sample Number: NHM4
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: bitumen mines between Hasheya and Jezzen, Syria
(H. Davidson)
Number: 26775
Spectra: GSIA0185
GSVA0224
Library Number: DR0093 (GSVA0224)

Sample Number: NHM5
Sample Name/Common Name: Mineral pitch
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: south beach of Mustique Island, (Grendine), West Indie
Number: 80896
Spectra: GSIA0186
GSVA0225
Library Number: DR0094 (GSVA0225)

Sample Number: NHM6
Sample Name/Common Name: Asphalt or bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: France
Number: 39698
Spectra: GSIA0187
GSVA0140
Library number: DR0095 (GSVA0140)

Sample Number: NHM7
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Derbyshire (Alan-Gregg collection)
Number: AG5
Spectra: GSIA0188
GSVA0141
Library number: DR0096 (GSVA0141)

Sample Number: NHM8
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: found as coating on quartz from chocdolomite, Strencno
(18.8°E, 49.3°N), Zilna, Slovakia (V. Rosicky, 1939)
Number: 1939,92
Spectra: GSIA0189
GSVA0142
Library number: DR0097 (GSVA0142)

Sample Number: NHM9
Sample Name Common Name: Asphaltum
Chemical Name Genus and Species: N/A
Source. Department of Mineralogy
Museum/Laboratory British Museum Natural History, London, SW7
Provenance: Trinidad, West Indies (F. C. Garrett, 1904)
Number: 87147
Spectra: GSIA0190
GSVA0143
Library number: DR0098 (GSVA0143)

Sample Number: NHM10
Sample Name Common Name: Bitumen
Chemical Name Genus and Species: N/A
Source. Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: in anhydrite rock, Billingham, Co. Durham (Directors of ICI, Ltd., 1943)
Number: 1943.9
Spectra: GSIA0191
GSVA0144
Library Number: DR0099 (GSVA0144)

Sample Number: NHM11
Sample Name Common Name: Bitumen
Chemical Name Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Mt. Sorrell, Leicestershire
Number: 48372
Spectra: GSIA0192
GSVA0145
Library Number: DR0100 (GSVA0145)

Sample Number: NHM12
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from comb of Apis dorsata
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Goalparah, Bengal
Number: N/A
Spectra: GSVA0311
Library Number: DR0185

Sample Number: NHM13
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from comb of Apis floralis
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: N/A
Number: N/A
Spectra: GSVA0312
Library Number: DR0186

Sample Number NHM15
Sample Name Common Name Resin
Chemical Name Genus and Species from tree which hosted Trigona loeviceps
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Singapore (Smith, 1857)
Number: N/A
Spectra: GSVA0314
Library number: DR0187

Sample Number: NHM16
Sample Name/Common Name: Beeswax
Chemical Name Genus and Species from Apis dorsata
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: India
Number: N/A
Spectra: GSVA0315
Library number: DR0187

Sample Number: NHM17
Sample Name/Common Name: Beeswax
Chemical Name Genus and Species: from Trigona species
Source: Department of Entomology, Hymenoptera collection
Museum Laboratory: British Museum Natural History, London, SW7
Provenance: India and Burmah (East Indian Museum)
Number: N/A
Spectra: GSVA0316
Library number: DR0188

Sample Number: NHM18
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from queen cells of Apis mellif
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Southall (Abbott Brothers, 1902)
Number: N/A
Spectra: GSVA0317
Library number: DR0189

Sample Number: NHM19
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from comb of Apis mellifera
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Dorset, ·77
Number: N/A
Spectra: GSVA0318
Library Number: DR0190

Sample Number: IA1
Sample Name/Common Name: Wood tar pitch
Chemical Name/Genus and Species: Pix liquida BP
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSIA0193
GSVA0146
Library Number: DR0101 (GSVA0146)

Sample Number: IA2
Sample Name/Common Name: Wood or Stockholm tar
Chemical Name/Genus and Species: Pix liquida BP
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0177
GSVA0294
GSVA0393
Library Number: DR0174 (GSVA0177)
DR0183 (GSVA0294)
DR0212 (GSVA0393)

Sample Number: IA3
Sample Name Common Name: Dopplerite
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Garry castle, Althone, County Westmeath
Number: N/A
Spectra: GSVA0147
Library Number: DR0102

Sample Number: IA4
Sample Name/Common Name: Dopplerite
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Mount shannon, Limerick
Number: N/A
Spectra: GSVA0148
Library number: DR0103

Sample Number: IA5
Sample Name/Common Name: Glance pitch
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dead Sea
Number: N/A
Spectra: GSIA0196
GSVA0149
Library number: DR0104 (GSVA0149)

Sample Number: IA6
Sample Name/Common Name: Gilsonite
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Utah, USA
Number: N/A
Spectra: GSIA0197
GSVA0150
Library number: DR0105 (GSVA0150)

Sample Number: IA7
Sample Name/Common Name: Asphalt (refined)
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Trinidad Lake
Number: N/A
Spectra: GSIA0198
GSVA0151
Library number: DR0106 (GSVA0151)

Sample Number: IA8
Sample Name/Common Name: Rock asphalt
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Syria
Number: N/A
Spectra: GSIA0199
GSVA0152
Library Number: DR0107 (GSVA0152)

Sample Number: IA10
Sample Name Common Name Glycerol
Chemical Name Genus and Species. 1,2 3-Propanetriol

Source: Department of Conservation
Museum/Laboratory Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY. 01-387-7050
Provenance: BDH General Purpose Reagent GPR)
Number: N/A
Spectra: GSVA0379
Library number: DR0201

Sample Number: IA11
Sample Name Common Name Ketone Resin N
Chemical Name Genus and Species Probably cyclohexanone polymer
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0380
Library number: DR0202

Sample Number: IA12
Sample Name/Common Name: Paraloid B-48N
Chemical Name/Genus and Species: Uncertain methyl methacrylate copolymer
Source: Department of Conservation
Museum Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Rohm & Haas (UK) Ltd.
Number: N/A
Spectra: GSVA0381
Library number: DR0203

Sample Number: IA13
Sample Name/Common Name: Poly (vinyl acetate) PVAC
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N A
Spectra: GSVA0382
Library Number: DR0204

Sample Number: IA14
Sample Name Common Name: Dammar resin
Chemical Name Genus and Species: N/A
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Hopkins and Williams Laboratory
Number: N/A
Spectra: GSVA0383
Library Number: DR0205

Sample Number IA15
Sample Name Common Name Soluble nylon
Chemical Name Genus and Species N-methoxymethyl nylon
Source: Department of Conservation
Museum Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Calaton
Number. N/A
Spectra: GSVA0563
GSVA0581
GSVA0583
GSVA0585
GSVA0598
GSVA0600
GSVA0602
Library Number: N/A

Sample Number: IA16
Sample Name/Common Name: Urea
Chemical Name/Genus and Species: Carbamide (H_2NCONH_2)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Urea SLR Fisons Laboratory Reagent
Number: N/A
Spectra: GSVA0385
Library Number: DR0206
P00042

Sample Number: IA17
Sample Name/Common Name: HMG adhesive
Chemical Name/Genus and Species: Cellulose nitrate
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: H. Marcel Guest Ltd. (HMG)
Number: N/A
Spectra: GSVA0540
GSVA0586
GSVA0587
GSVA0596

Library number: P00046 (GSVA0540)

Sample Number: IA18
Sample Name/Common Name: Paraloid B-72 adhesive
Chemical Name/Genus and Species: Methyl acrylate/ethyl methacrylate copolymer
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: H. Marcel Guest Ltd. (HMG)
Number: N/A
Spectra: GSVA0541
GSVA0595
Library number: P00047 (GSVA0541)

Sample Number: IA19
Sample Name Common Name: UHU adhesive
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Beecham UHU
Number: N/A
Spectra: GSVA0542
GSVA0597
Library number: P00048 (GSVA0542)

Sample Number: IA20
Sample Name/Common Name: Gelvatol 40:20
Chemical Name/Genus and Species: Poly (vinyl alcohol)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0622
Library number: N/A

Sample Number: IA21
Sample Name/Common Name: Gelvatol 20:90
Chemical Name/Genus and Species: Poly (vinyl alcohol)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0623
Library Number: N/A

Sample Number: BM1
Sample Name/Common Name: Shellac flakes
Chemical Name/Genus and Species: from Laccifer lacca Kerr.
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0158
Library Number: DR0108

Sample Number: BM2
Sample Name Common Name: Bleached shellac (insoluble in alcohol)
Chemical Name Genus and Species. from Laccifer lacca Kerr.
Source: S. Bradley
Museum/Laboratory British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0159
Library Number: DR0109

Sample Number: BM3
Sample Name/Common Name: Gum arabic
Chemical Name/Genus and Species: from Acacia species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0160
Library Number: DR0110

Sample Number: BM4
Sample Name/Common Name: Gum sandarac
Chemical Name/Genus and Species: from Tetraclinis articulata
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0161
Library number: DR0111

Sample Number: BM5
Sample Name/Common Name: Gum ammoniacum
Chemical Name/Genus and Species: from Dorema ammoniacum
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0162
Library number: DR0112

Sample Number: BM6
Sample Name/Common Name: Gum acacia
Chemical Name/Genus and Species: from Acacia species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0163
Library number: DR0113

Sample Number: BM7
Sample Name Common Name: Copaiba balsam
Chemical Name/Genus and Species: from Copaifera species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0164
Library number: DR0114

Sample Number: BM8
Sample Name Common Name Ketone resin
Chemical Name Genus and Species Probably cyclohexanone polymer
Source: S Bradley
Museum Laboratory: British Museum Research Laboratory, London, WC1
Provenance: BASF replacement for A W 2, similar to M.S.2
Number: N/A
Spectra: GSVA0165
Library Number: DR0115

Sample Number: BM9
Sample Name Common Name: Spermaceti wax (cetaceum)
Chemical Name Genus and Species: from *Physeter macrocephalus* L.
Source: S Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: Trinity College, Dublin
Number: N/A
Spectra: GSVA0166
Library Number: DR0116

Sample Number: BM10
Sample Name/Common Name: Gum copal
Chemical Name Genus and Species: possibly from *Daniella similis*
Source: S. Bradley
Museum Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0167
Library Number: DR0117

Sample Number: BM11
Sample Name Common Name: Guaiacum resin
Chemical name Genus and Species: from *Guaiacum sanctum*
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0168
Library Number: DR0118

Sample Number: BM12
Sample Name/Common Name: Gum benzoin
Chemical Name Genus and Species: from *Styrax benzoin*
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0169
Library number: DR0119

Sample Number BM13
Sample Name Common Name Gum dammar
Chemical Name Genus and Species. N A
Source: S. Bradley
Museum Laboratory: British Museum Research Laboratory, London, WC
Provenance: N/A
Number: N/A
Spectra: GSVA0170
Library number: DR0120

Sample Number: BM14
Sample Name Common Name: Canada balsam
Chemical Name Genus and Species: from *Abies balsamea*
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0171
Library number: DR0121

Sample Number: BM15
Sample Name/Common Name: Button shellac
Chemical Name/Genus and Species. from *Laccifer lacca* Kerr
Source: S Bradley
Museum Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0172
Library number: DR0122

Sample Number: BM16
Sample Name/Common Name: Colophony (Rosin)
Chemical Name/Genus and Species: probably from *Pinus* species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0179
Library Number: DR0123

Sample Number: BM17
Sample Name/Common Name: Asphalt
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0180
Library Number: DR0124

Sample Number: BM18
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0181
Library Number: DR0125

Sample Number: BM19
Sample Name/Common Name: Stockholm tar
Chemical Name/Genus and Species: *Pix liquida* BP
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0182
Library Number: DR0126

Sample Number: BM20
Sample Name/Common Name: Paraffin wax
Chemical Name Genus and Species: Hydrocarbon wax
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0183
Library number: DR0127

Sample Number: BM21
Sample Name/Common Name: Badische A wax
Chemical Name/Genus and Species: Hydrocarbon wax
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0184
Library number: DR0128

Sample Number: BM22
Sample Name/Common Name: Carnauba wax (yellow)
Chemical Name/Genus and Species: from *Copernicia cerifera*
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: BDH
Number: N/A
Spectra: GSVA0185
Library number: DR0129

Sample Number: BM23
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC
Provenance: N/A
Number: N/A
Spectra: GSVA0186
Library number: DR0130

Sample Number: BM24
Sample Name/Common Name: PVAC vinylite
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC
Provenance: AYAF
Number: N/A
Spectra: GSVA0187
Library Number: DR0131

Sample Number: BM25
Sample Name/Common Name: Beeswax (yellow foreign)
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: BDH
Number: N/A
Spectra: GSVA0188
Library Number: DR0132

Sample Number: BM26
Sample Name/Common Name: Hard wax mixture 1 part dammar resin,
1 part grey carnauba wax, 1 part paraffi
and 3 parts beeswax
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: National Museum of Copenhagen
Number: N/A
Spectra: GSVA0226
Library Number: DR214

Sample Number: BM27
Sample Name/Common Name: Venice turpentine
Chemical Name/Genus and Species: from *Larix decidua* Miller
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0227
GSVA0394
Library Number: DR0184 (GSVA0295)
DR0213 (GSVA0394)

Sample Number GS1
ample Name/Common Name: Egg white (3 hours UV exposure)
Chemical Name/Genus and Species: Albumen
ource: G Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
pectra: GSVA0199
Library number: DR0136

Sample Number: GS2
Sample Name/Common Name: Egg yolk (3 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0200
Library number: DR0137

Sample Number: GS3
Sample Name/Common Name: Egg yolk and white (3 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0201
Library number: DR0138

Sample Number: GS4
Sample Name/Common Name: Egg white (3 hours UV exposure)
Chemical Name/Genus and Species: Albumen
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0202
Library number: DR0139

Sample Number: GS5
Sample Name/Common Name: Egg yolk (12 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0203
Library Number: DR0140

Sample Number: GS6
Sample Name/Common Name: Egg yolk and white (12 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0204
Library Number: DR0141

Sample Number: GS7
Sample Name/Common Name: Cellulose powder
Chemical Name/Genus and Species: Cellulose
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Whatmen standard grade, W & R Balston Ltd.
Number: N/A
Spectra: GSVA0334
Library Number: DR0010
P00044

Sample Number: GS8
Sample Name/Common Name: Lamb suet
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0434
Library Number: DR0217

Sample Number: GS9
Sample Name/Common Name: Olive oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Sainsbury's brand
Number: N/A
Spectra: GSVA0465
Library number: DR0218

Sample Number: GS10
Sample Name/Common Name: Safflower oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dove brand pure safflower oil
Number: N/A
Spectra: GSVA0466
Library number: DR0219

Sample Number: GS11
Sample Name/Common Name: Grapeseed oil
Chemical Name Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dufrais Pure Grapeseed Oil
Number: N/A
Spectra: GSVA0467
Library number: DR0220

Sample Number: GS12
Sample Name/Common Name: Walnut oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Planoix brand
Number: N/A
Spectra: GSVA0468
Library number: DR0221

Sample Number: GS13
Sample Name/Common Name: Hazelnut oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: 'La fleur de Noisetier' brand
Number: N/A
Spectra: GSVA0469
Library Number: DR0222

Sample Number: GS14
Sample Name/Common Name: Olive oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0470
Library Number: DR0223

Sample Number: GS15
Sample Name/Common Name: Shale
Chemical Name/Genus and Species: N/A
Source: D Moffat
Museum/Laboratory: Institute of Archaeology, 31-34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: possibly Kimmeridege
Number: N/A
Spectra: GSVA0512
GSVA0546
Library Number: DR0224 (GSVA0512)

Sample Number: GS16
Sample Name/Common Name: Jet
Chemical Name/Genus and Species: N/A
Source: John Laveson Gower
Museum/Laboratory: The Square, Winscombe, Avon, BS25 1DA
Provenance: Whitby Museum
Number: N/A
Spectra: GSVA0517
Library Number: DR0225

Sample Number: GS17
Sample Name/Common Name: Shale
Chemical Name/Genus and Species: N/A
Source: Dennis Sloper
Museum/Laboratory: Ringwood, Hampshire
Provenance: Kimmeridge
Number: N/A
Spectra: GSVA0518
GSVA0547
Library number: DR0226 (GSVA0518)

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