THE DEGRADATION AND STABILISATION OF CELLULOSE TRIACETATE CINEMATOGRAPH FILM

by

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DEDICATION

To my family with love.

CHOICES

Up front
or last row
Out there
or hidden
Speaking up for
Speaking out against
or shutting up
into safety
Be heard, visible,
criticized, attacked
Be quiet, unnoticed
left alone, peaceful

To learn, to understand
To educate, to change
To mumble in corners,
grumble with friends,
protect myself from
learning,
protect others from
changing.

DECLARATION

The following is a record of research carried out in the Chemistry Research Laboratories of the Faculty of Science and Engineering at Manchester Polytechnic. It has not been previously submitted in candidacy for a higher degree of the Council or any University. The work described is wholly that of the author except where indicated otherwise.

Michele Edge

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ABSTRACT

Cellulose triacetate support cinematograph films exhibit degradation when stored under archival (dark storage) conditions. Degradation is manifested by the evolution of acetic acid and white crystalline surface deposits with accompanying image erosion. The purpose of this study has been to identify and prevent any degradation mechanisms which may operate in such circumstances. With respect to this under both natural (archival) and accelerated ageing conditions it has been shown that there is a direct correlation between moisture regain, acidity and decrease in viscosity of the support material. Two degradation processes have been identified utilising these techniques along with FTIR and FTNMR. The first is an acid catalyzed hydrolytic de-acetylation of ester functionality and the second is an acid catalyzed oxidative scission of the cellulose backbone. With respect to both mechanistic routes, the emulsion layer, which is acutely sensitive to surrounding moisture from the atmosphere, serves as a source of protoic catalyst (H_3O^+). Here redistribution of moisture in the emulsion occurs to adjacent cellulose triacetate support. As a consequence a moisture gradient exists throughout the length and width of wound cinematograph film. Degradation apparently grows into the reel from the outer circumference and sprocket areas. The presence of hydroperoxides, which have been identified within the film materials, supports the existence of an oxidative degradation pathway. It has also been shown that iron is absorbed, from metal storage cans, into the support via facile uptake as the material becomes progressively more hygroscopic. Subsequently, iron then acts as a powerful catalyst in accelerating the degradation, probably by catalyzing the decomposition of active peroxides. This is confirmed by doping films with iron. The emulsion layer also serves to impart some stability to the support material by scavenging any acid degradation products and in so doing its gelatin constituent undergoing hydrolysis. It also likely serves as a diffusion barrier to oxygen attack. The support plasticiser, triphenyl phosphate, also enhances film stability. Other than improving resistance to moisture uptake it possibly complexes with any metal ions taking part in the degradation and behaves to some extent as an antioxidant. As the cellulose triacetate support degrades the plasticiser is rendered incompatible with it and is pushed to the surface where it crystallises out as a white deposit. The stabilisation of cellulose triacetate support cinematograph film has also been examined using a number of potential stabiliser systems. These include acid scavengers, primary hindered phenolic antioxidants, secondary hindered piperidine stabilisers, metal dialkyldithiocarbamates, metal deactivators, secondary thioesters and phosphites. Stabilisation efficiency was assessed by measuring percentage retention in viscosity of the polymer support. None of the stabiliser systems was found to be effective when used alone, indicating that more than one type of mechanism is operative in degradation. Effective stabilisation is achieved through a synergistic tris system of stabilisers namely, Tinuvin 770, Irganox MD1024 and Sodium Phenyl Phosphinate. This combination has the ability to scavenge acetic acid and free radicals, and deactivate any peroxides and transition metal ions.

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INTRODUCTION

When we consider that imaging systems house a vast proportion of information the significance of preservation becomes apparent. At present audio-visual archives have adopted cinematograph film as the medium by which we can retain and transmit a visual record of data and events. Newer media, such as magnetic tape and optical disc, are not as yet considered archival due to unproven longevity and the rate of obsolescence of play-back equipment.

Unfortunately, typical signs of deterioration of cinematograph films have been manifested almost universally in archives over the past two decades. Currently, there is no practicable way of halting, much less reversing, the course of self-destruction. Some of the film can be preserved by copying but this process is slow, costly and results in loss of image resolution. Other than solving an immediate problem, copying onto the same material, which obviously has insufficient longevity, seems to be defeating the object of the exercise. However, at present an alternative material which meets all the requirements of an archival medium is not available; and many historians would argue that the original material has innate value anyhow.

An additional problem presents itself in the huge quantities of films housed in archives. It has been optimistically estimated that it would take an archive holding around two million reels of film in the region of two hundred years (working 24 hours a day!) to copy this quantity. It follows that even if a more stable material were available some method of prioritisation of copying would be necessary to prevent loss of more deteriorated stocks.

The aim of the present project is thus to identify those mechanisms operating under archival conditions which lead to film decomposition, and to utilise this knowledge to design appropriate methods of testing the stability of filmstocks and of stabilisation.
With regard to this the thesis is divided into three sections. The first presents an overview of the literature pertaining to those processes which lead to degradation of the materials composing cinematograph films. It also identifies the critical degradation steps of cellulose acetate films, concentrating on suitable methods of assessing and accelerating the degradation process. The second concentrates on design of suitable methods for predicting the longevity of such filmstocks; and the final section on increasing the effective lifetime of these materials i.e. stabilisation.

Chapter 1

1. THE COMPOSITION OF CINEMATOGRAPH FILM

Photographic emulsions consist of dispersions of light-sensitive materials in a colloidal medium, usually gelatin. They are extremely fragile in nature and require support. Historically this support was supplied by coating the emulsion onto glass plate or paper. However, with the development of the cinematograph in the late 1800s came the need for a flexible film base. Typically, cinematograph film is composed as illustrated in Figure 1.1.

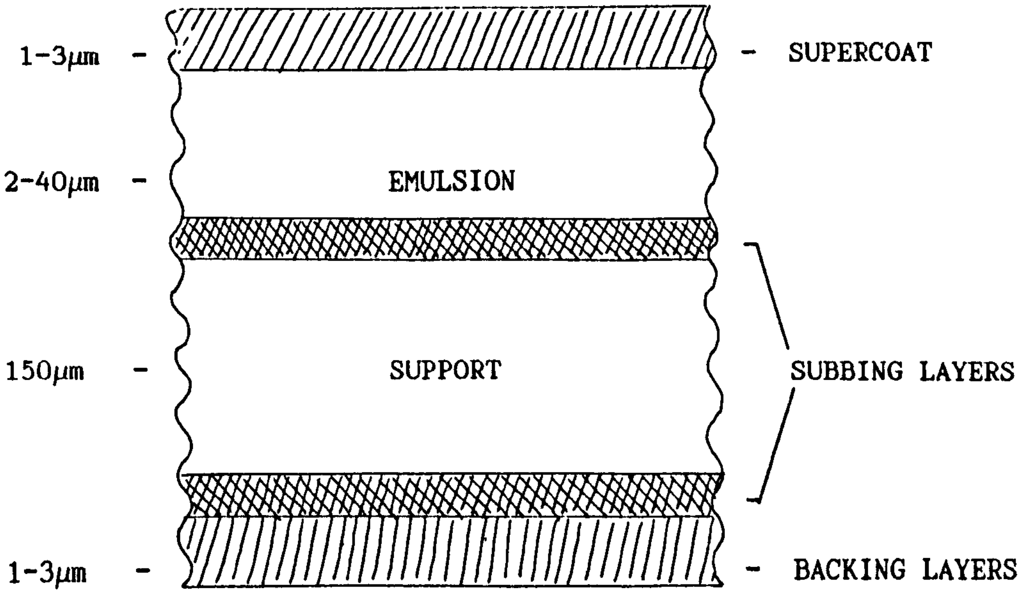


Figure 1.1

Schematic Representation of a Cross-Section Taken Through a Typical Cinematograph Film.

1.1 Cinematograph Film Support 1889-1990

The first recorded use of flexible film base as support for photographic emulsions was by Fortier and David in 1881, utilising cellulose nitrate. However, it was in 1889 that the first successful cellulose nitrate base coating was formulated. This was subsequently adopted by George Eastman who offered the standard format which remains to date for cinematograph film. Unfortunately, even in the early stages of its introduction reservations as to the stability of this material were expressed [1.1] and it was evident that a replacement material was necessary. With the production in 1903 of the so called 'diacetate' an alternative was available. Eastman Kodak Co. cast photographic film base from cellulose acetate as early as 1908. However, introduction though now commercially feasible was tentative due to inferior physical properties of nitrate film [1.2]. This resulted in the introduction of mixed esters of cellulose; cellulose acetate propionate and cellulose acetate butyrate; which gradually replaced cellulose diacetate from around 1940. Still more desirable properties were available in the form of the so-called 'high-acetyl' or 'triacetate' formulations. This film base offered the advantages of reduced fire hazard, reduced static build up and less residual solvent retention after manufacture. However, dichloromethane is about the only practicable coating solvent for high acetyl content cellulose acetate; and this solvent was not available in commercial quantities until after World War II. This difficulty retarded the use of cellulose triacetate film base for a number of years. As soon as it was possible Eastman rapidly introduced the new 'safety' base. This occurred principally between the years 1948 and 1951 when the manufacture of cellulose nitrate by Eastman Kodak Co. was completely discontinued [1.3].

1.2.1 Manufacture of Film Base

All cellulose-ester base photographic film is manufactured by the solvent casting technique. The polymer, manufactured as in chapter 3,is dissolved in suitable solvents to form a 'dope'. Plasticisers are added to the dope solution which is concentrated and very viscous, having the consistency of honey.The first production methods involved coating the dope onto glass top tables. The solvent was then allowed to evaporate and the resulting film support stripped from the tables [1.4]. In later years continuous coating was developed (see Figure 1.2).

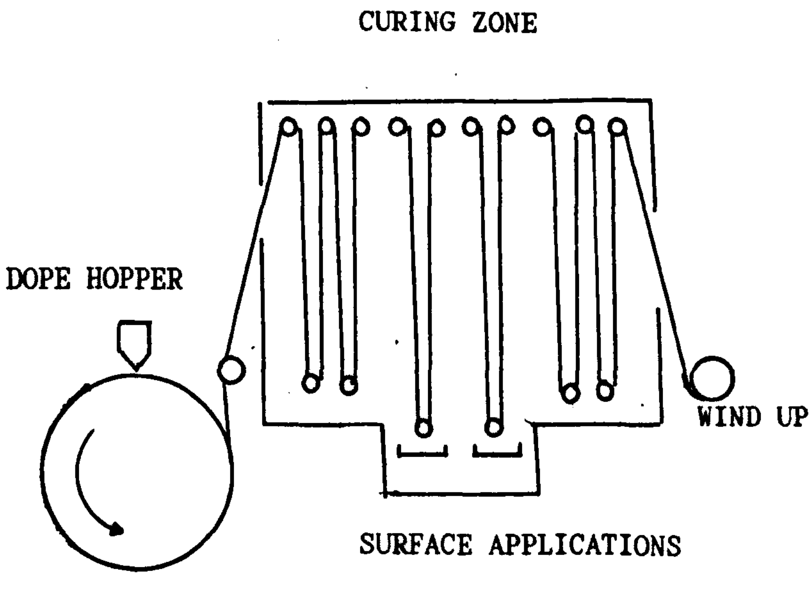


Figure 1.2

Schematic Diagram of a Machine for Solvent Casting of Film Base

Here the dope solution is cast by spreading a uniform layer on a large, heated, chromium-faced drum which slowly rotates. The solvent is then allowed to evaporate, as previously. Alternatively, the base is allowed to 'coagulate'. This is done by use of a good solvent/poor solvent mixture, i.e. use of a dope in which the polymer is barely soluble, and the film is then chilled and the good solvent evaporated. The base is thus firm enough to be stripped off in a continuous sheet before the drum has made a complete revolution. The base is then passed through a series of heated chambers to remove the remaining solvent. This is known as 'curing'. In this operation the tension of the sheet is carefully controlled because stretching the base tends to orient the cellulose-ester molecules in the direction of the stretch, which will affect the mechanical and dimensional properties of the film [1.5, 1.6].

1.2.2 Plasticisers used in the Manufacture of Film Base

Plasticisers are added to the dope to render the resulting film base resistant to moisture uptake. They are incorporated at a proportion of up to 20% w/w of the film base. For cellulose acetate, a triphenyl phosphate/phthalate ester composition is used. This combination is used to prevent the former crystallising out and the latter imparting a greasy character to the film surface [1.7].

1.2.3. Surface Coatings Applied to the Film Base

There are at least four different types of surface coating applied to the base prior to the final coating of the emulsion layer [1.8].

(a) *The Subbing Layer*

Since gelatin emulsions do not directly adhere to the base a subcoating or adhesive layer is necessary to prevent frilling of the emulsion layer when wet or cracking when dry. The formulations of these subbing layers vary widely, but usually consist of water, gelatin and a polymer similar in composition to the base material, e.g. cellulose nitrate or extensively hydrolysed cellulose triacetate. These are usually dissolved in an organic water-miscible solvent such as ethanol or acetone, to effect some etching of the base.

(b) *Anti-Curl Layers*

It is usual to sub both sides of the base, as this helps counteract the uneven shrinkage which otherwise occurs when the coated emulsion dries, which causes the dried film to curl up towards the emulsion. This effect is due to the fact that gelatin, its major constituent, swells at a different rate to the base (see chapter 5).

(c) *Anti-Halation Layers*

Pigments such as 'rem jet' or dyes such as tartrazines are added to backing layers (which are removed during photographic processing) to prevent light scattering within the film. For some materials (usually negatives) a neutral density, grey dye is incorporated into the film base and this is retained after processing.

(d) *Anti-Static Layers*

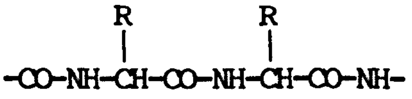
These may be either conducting layers or layers containing matt particles which prevent close surface-to-surface contact and the resulting static generation upon separation. A comprehensive review of antistatic agents for photographic materials is provided by Glafkides [1.9].

1.3 Emulsion Composition

According to given standards [1.10],"A photographic emulsion consists of dispersions of light-sensitive materials, in a colloidal medium, usually gelatin, coated as a thin layer on film base."

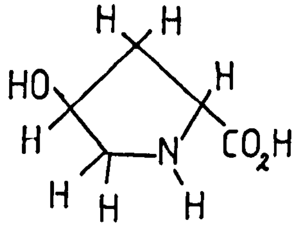
1.3.1 Photographic Gelatins

Photographic gelatins are obtained from two sources; bones or hide and skin. The major constituent of these two sources is collagen - gelatin being obtained by a controlled partial hydrolysis and is thus a heterogeneous mixture of polypeptides. The structure may be represented simply as:



$$\text{-CO-NH-}\overset{\overset{\displaystyle R}{|}}{\text{C}}\text{H-CO-NH-}\overset{\overset{\displaystyle R}{|}}{\text{C}}\text{H-CO-NH-}$$

i.e. a series of amino acids combined by peptide linkages. At least nineteen different amino acids have been isolated from collagen [1.11], the most characteristic of which is hydroxyproline:



1.3.2 Properties of Gelatin

To date gelatin remains the only acceptable colloidal medium for preparation of photographic images. Other than its part in the growth and distribution of silver halide crystals, gelatin also plays an interactive role in photolysis and subsequent image formation. However, of the most desirable features of this colloid the most important are its reversible gelling properties and ability to undergo controlled swelling in aqueous solutions to allow penetration of image processing agents [1.12].

1.3.3 Other Emulsion Constituents Pertaining to Gelatin

Bactericides

Gelatin is particularly susceptible to microbial attack: it provides an ideal medium to sustain bacterial growth. Thus, even if the film is to be kept only a short time, it is necessary to add a bactericide to the emulsion layer. These are usually phenols or its derivatives, such as p-chloro-m-cresol; incorporated at 0.1 to 5% of the weight of the gelatin dependent on their activity [1.13].

Plasticisers

When gelatin is dry it is extremely brittle. It is important to retain flexibility of cinematograph emulsions under low humidity conditions. This is usually achieved by the addition of a humectant. Many compounds have been referred to in the patent literature but they are generally derivatives of ethylene glycol [1.14].

Emulsion Hardeners

A gelatin emulsion in its original state would, since it is 'soft', be susceptible to mechanical abrasion and the action of dust. In addition excessive swelling of the emulsion would occur during photographic development, causing reticulation when the layer was subsequently re-dried. Emulsion hardeners are therefore added prior to coating. These are essentially cross-linking agents, which interact with the carbonyl and amino groups between different collagen chains. Both organic and inorganic cross-linking agents are used; incorporated at 0.5-2% of the gelatin weight. To increase rate of cross-linking accelerators are also often added. These are phenols or phenolic aldehydes incorporated at 0.1-1.0g per 100g gelatin.

Wetting Agents

When an emulsion is coated, a wetting agent is required to reduce surface tension of the liquid emulsion in order that a uniform coating thickness be attained. Many surfactants have been utilised for this purpose, both anionic (e.g. lauryl sulphate), cationic (hexadecyltrimethylammonium bromide) and non-ionic (saponin). These are added as an aqueous solution at 20mg-1g per 100g gelatin.

Anti-Foaming Agents

These agents are incorporated to counteract the tendency of emulsions to froth; a problem enhanced by the addition of wetting agents. Anti-Foaming agents are aliphatic alcohols of intermediate chain length e.g amyl and nonyl; although glyceryl monolaurate which is also effective is often used.

1.3.4 Light-Sensitive Materials

All modern photographic materials utilise silver halides as light sensitive addenda. Silver halide grain size is correlated to emulsion speed and contrast. For fine grain panchromatic and fine grain negative films, typically those used for cinematograph films, emulsion grain sizes are 0.7 and 2μm respectively.

1.3.5 Other Emulsion Constituents Pertaining to Silver Halide Crystals

Chemical and Spectral Sensitizers

For most photographic applications it is necessary to enhance the sensitivity of silver-halide crystals to light. Chemical sensitizers (e.g. sodium thiosulphate, potassium aurothiocyanate) cause emulsion grains to make more efficient use of the light they absorb. Spectral sensitizers (typically cyanine dyes) enable grains to use light in a region of the spectrum in which they would not normally absorb. Sensitizers are added at 0.02-0.2g per g mole of silver.

Stabilizers and Anti-Foggants

Stabilizers confer sensitometric stability upon coated emulsions with subsequent storage. Organic and metal compounds are used, they includes tetrazaindenes and cadmium or mercury salts respectively.

Antifoggants are commonly benztriazole and 5-nitrobenziminzole.

These are incorporated at 1-10mg/mole silver.

1.3.6 Emulsion Preparation and Coating

The processes involved in the preparation of a photographic emulsion are summarized by the flow chart in Figure 1.3 [1.15].

The coating of the emulsion to base (to which has been applied sub-adhesive layers) is then as follows:-

The emulsion held accurately at the proper temperature in a liquid state, is coated onto the film base and is passed directly into a chilling chamber, where gelatin is solidified as quickly as possible at 10°C or below. From the chilling chamber, the emulsion coated film goes into a drying alley where it hangs in loops from rods. Temperature, humidity, air purity and time of drying are all carefully controlled. The tendency of modern photographic emulsions to utilize less gelatin results in greater susceptibility to physical abrasion. To avoid this a thin protective layer is coated onto the film, which is usually a thin gelatin layer consisting of <10% of the gelatin composing the emulsion. More recently other reagents have been used e.g. polyvinyl alcohol, polyamide mixtures, polyvinyl pyrrolidine and acrylic copolymers.

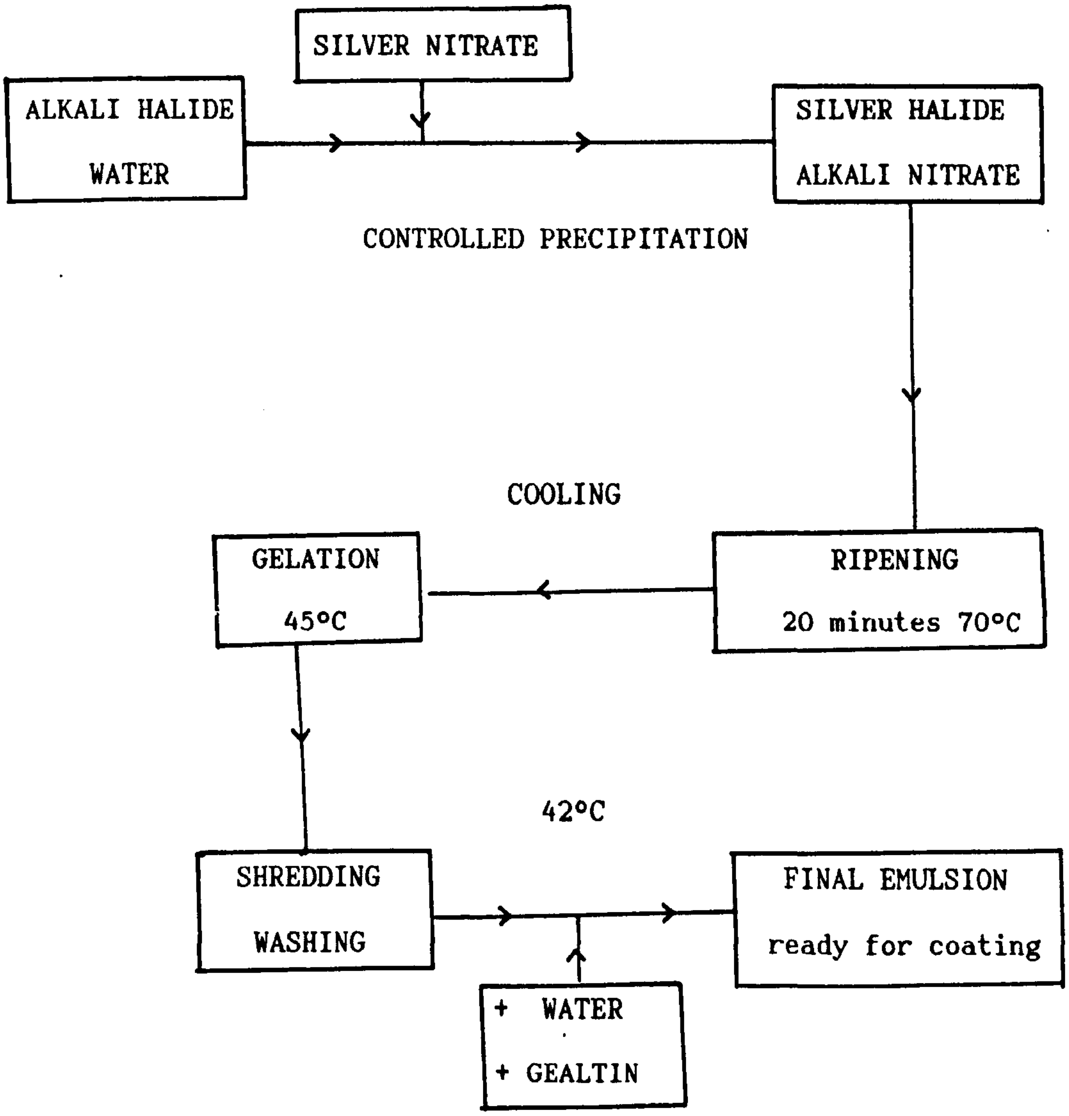
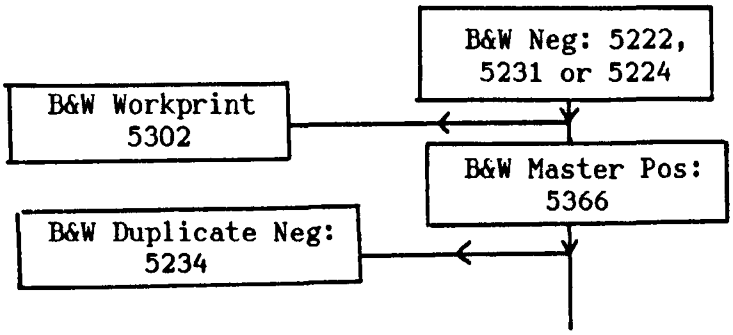


Figure 1.3

Schematic of the Processes Involved in Emulsion Preparation

1.3.7 Emulsion Types used for Archival Cinematograph Film



The flow chart above is an exemplification of Eastman Kodak emulsion types for archival (Black and White) cinematograph films. These include:-

Negative Master/Original ('camera film') : Types 5231/5222/5224

Here all three types are general purpose panchromatic films, with speed being the major difference among them, in the order
5224 > 5222 > 5231 [1.16].

Master Positives and Duplicate Negatives : Types 5234/5302/5366

Type 5234, has a high resolving power and is used to make duplicate negatives from master positives. Type 5302, is a low-speed, blue-sensitive print film with high resolving power and used for general release printing. Type 5366 is a low speed, blue-sensitive duplicating film with high resolving power.

1.4 Photographic Processing

Photographic processing of black-and-white negatives and positives may be summarized as follows [1.17]:-

Development

Here exposed silver halide grains are converted to image metallic silver. Developer solutions are characterized by their high alkalinity (pH ≥ 10).The following developer composition is typical for cinematograph film.

KODAK DEVELOPER D-76

Water	750.0 cm^3
(N,N-dimethyl)-p-aminophenol	2.0 g
Sodium sulphite	100.0 g
p-hydroxyphenol	5.0 g
Borax	2.0 g
Water, to make to	1000.0 cm^3

Stopping Development

It is necessary to arrest the action of the developer. Here an acid stop bath (typically acetic acid) is used to neutralize the high alkalinity of the developer.

Fixation

This is the removal of unexposed silver halide grains. The insoluble silver halides are converted to water soluble salts, which can be washed out of the emulsion. This is achieved by use of 'hypo' (sodium thiosulphate).

Washing and Drying

The film is washed to remove last traces of fixer, or sometimes placed in a 'hypo' eliminator solution. Modern eliminators are dilute solutions of oxidizing agents e.g sodium hypochlorite, potassium perborate, hydrogen peroxide.

Drying, in an environment of warm circulating air, removes any surface moisture from processing.

1.5 Treatments to Processed Film

Any cinematograph film which has undergone projection will have received lubrication; this is usually a mixture of silicone and 1,1,1-trichloroethane, or paraffin wax in 1,1,1-trichloroethane.

1.6 Implications from Structural Composition with respect to Stability

The complexity of the photographic matrix and the wide variety of processes to which it is subjected is such that any 'impurities' instigating film instability may be present in the film already i.e prior to storage. Despite the complexity of cinematograph film it is essentially a combination of two polymers, the cellulose-ester support and gelatin: It is these components which will dictate image longevity. However, as will be discussed in the following chapters many of the reagents added in trace quantities will significantly influence the stability of the surrounding polymer matrix.

Chapter 2

2. POLYMER DEGRADATION

Degradation of a polymer structure is manifested by property changes resulting from both physical and chemical modifications.
The type and degree of such modifications are a reflection of factors inherent to the polymeric material and of external environmental factors.

Intrinsic Factors

These include:-
the structure of the polymer; e.g. presence of functional groups within the main chain or as pendant groups;
the physical form of the polymer; e.e bulk, thin film, powder;
presence of incorporated additives; e.g. plasticisers, colourants, anti-static agents.

Extrinsic Factors

These include:-
high temperatures; oxygen; sunlight; high relative humidities; polluted atmospheres,

2.1 General Mechanisms of Degradation[2.1]

2.1.1 Initiation

There is much debate as to the initiation steps in polymer degradation. The presence of impurities is thought to significantly influence initiation. Here impurities may be weak links in the polymer chain, metallic impurities or impurity functional groups (carbonyl and carboxylic acid groups). The latter two are particularly significant features of autoxidation of polymers.

2.1.2 Depropagation

This is essentially a reversal of the polymerisation process. Transfer of an atom or functional group to the active chain-end results in splitting off a single monomer unit or by direct loss from a free-radical chain end.

2.1.3 Random Chain-Scission

Random chain scission is the most common route to polymer degradation. This arises as a consequence of the statistical equivalence of bond dissociation energies within a polymer network.
Hydrolytic, high-temperature thermal and radiolytic reactions are typical examples of processes which characterise random chain scission.

2.1.4 Degradation without Chain-Scission

Degradation without chain scission is typified by reactions which occur in the side groups on a polymer chain. On the whole such reactions are analogous to those which occur in low molecular weight compounds and differ only as a consequence of the macromolecular nature of the material. That is accessibility etc. Small proportions of modified pendant groups do not therefore result in significant deterioration of the physical properties of the polymer.

2.2 Thermal Degradation

Thermal degradation processes occur during the manufacture, processing and practical use of polymers. Degradation is accentuated by high temperatures; under ambient conditions such processes are slow and largely dependent on the chemical nature of the polymer repeat unit and the presence of "impurity centres".

Unfortunately, it is not possible to determine thermal stability of polymers simply utilising experimentally determined bond energies of small molecule model compounds. This essentially neglects the long-chain character of a polymer, which renders possible reactions along chains and between adjacent chains. In addition it neglects the effects due to the presence of low concentrations of structural irregularities which often determine initiation of degradation. Any extrapolations on this basis, especially kinetic ones are therefore invalid. Furthermore, thermal reactions are markedly influenced by environment. Degradation is for example usually more complex in air than nitrogen due to additional oxidation reactions. Other features such as a static or dynamic surrounding atmosphere also play a major role. Often any primary degradation products if not quickly removed from the microenvironment of the polymer will induce secondary reactions.

However, the general mechanism of thermal degradation is believed to occur as follows [2.2];-

Random Initiation : $M_n \longrightarrow M_j + M_{n-j}$
Terminal Initiation : $M_n \longrightarrow M_{n-1} + M$
Depropagation : $M_i \longrightarrow M_{i-1} + M$
Transfer : $M_i + M_n \longrightarrow M_i + M_n$
Scission : $M_n \longrightarrow M_j + M_{n-j}$
Termination : $M_i + M_j \longrightarrow M_i + M_j$ or M_{i+j}

Initiation may occur either at polymer chain-ends or randomly anywhere along the polymer backbone. One of two processes may then take place. Depropagation, which involves loss of a single monomer unit or alternatively radical transfer may occur to another polymer chain. Another possibility is that random chain scission may occur anywhere along the polymer backbone.[2.3]

2.3 Autoxidation

Autoxidation takes place when organic polymers interact with molecular oxygen. The mechanism of autoxidation was first characterized by Bolland and Gee [2.4]. The pathway of autoxidation is believed to occur as follows;-

INITIATION	$RH \longrightarrow R\cdot$
PROPAGATION	$R\cdot + O_2 \longrightarrow ROO\cdot$
	$ROO\cdot + RH \longrightarrow ROOH + R\cdot$
CHAIN BRANCHING	$ROOH \longrightarrow RO\cdot + \cdot OH$
	$2ROOH \longrightarrow RO\cdot + ROO\cdot + H_2O$
TERMINATION	$2ROO\cdot \longrightarrow \text{inactive products} + O_2$
	$R\cdot + ROO\cdot \longrightarrow ROOR$
	$2R\cdot \longrightarrow R\text{-}R$

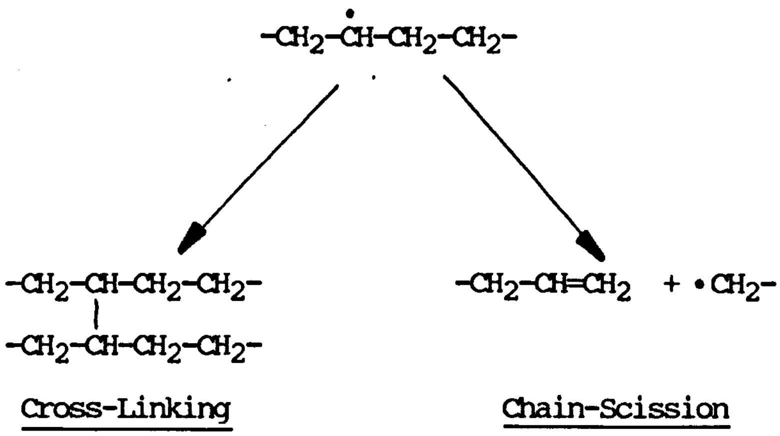
Mechanisms of initiation are not yet fully understood. It is believed the oxidation initiating polymer radical (R•) is formed by heat, light, mechanical stress or by reactions with radicals originating from foreign sources. Initial generation of a free-radical then leads to the formation of alkyl and alkylperoxy radicals (R• & ROO•) The chain-branching reactions have high activation energies and are thus negligible at ambient temperatures.

The formation of hydroperoxides becomes significant in the presence of metal ions [2.5]. Metal ions, usually transition metal ions, of the same parent metal whose oxidation states differ by a factor of one, are active catalysts for the decomposition of hydroperoxides. This has the effect of producing radicals able to trigger further breakdown. i.e.;-

$$\begin{array}{ll} \mathrm{ROOH + M^{+}} & \mathrm{RO\cdot + M^{2+} + {}^{-}OH} \\ \mathrm{ROOH + M^{2+}} & \mathrm{ROO\cdot + M^{+} + H^{+}} \\ \hline \mathrm{2ROOH} & \mathrm{ROO\cdot + RO\cdot + H_2O} \\ \hline \end{array}$$

The effect of autoxidation is either cross-linking or chain-scission.

e.g.



Chapter 3

3. MANUFACTURE AND PROPERTIES OF CELLULOSE-ESTERS

All stages in the production, processing and subsequent storage of cellulose-esters will influence their longevity. No examination of stability is therefore complete without a consideration of each of these steps. Manufacture will determine the initial stability of the material but subsequent to this the properties of a given cellulose-ester, both chemical and physical, will play a significant role. The properties of cellulose-esters vary with the type of substituent, degree of susbstitution (D.S.) and degree of polymerisation (D.P.). Furthermore, the properties of plastics films and coatings will also be influenced by any incorporated additives e.g. plasticiser and residual coating solvents.

3.1 MANUFACTURE

3.1.1 Chronology

The first organic ester of cellulose was cellulose acetate as prepared by Schutzenberger in 1865, by heating cotton and acetic anhydride to 180°C in a sealed tube until the cotton dissolved [3.1].
In 1879 Franchimont acetylated cotton at lower temperatures with the aid of a sulphuric acid catalyst [3.2]. Later investigations by Cross and Bevan [3.3] and Miles [3.4] though still using comparatively high temperatures utilised much milder conditions than those of earlier studies. Following this lower temperature esterifications were

introduced, such as those described by Dreyfus [3.5]. Most current day commercial processes utilise temperatures not exceeding 50-60°C. Subsequent processes describe the use of catalysts other than sulphuric acid, for example zinc chloride by Ost [3.6], but none of these met with the advantages offered by sulphuric acid.
However, the most notable development was that by Miles in 1903 [3.7] when he described the preparation of a partially hydrolysed cellulose acetate, which was easily distinguished from the fully acetylated product by its solubility in common inexpensive solvents. This naturally led almost immediately to commercial applications.
Around 1950 Eastman Kodak Co. adopted cellulose triacetate as cinematograph film substrate to circumvent the undesirable characteristics experienced in the use of cellulose nitrate [3.8]. Cellulose acetate is is now used in a variety of areas, principally as a filter in cigarettes, as film and sheet and in the protective coatings field. Solution grades of cellulose acetate occupy a small sector of more specialised markets such as membranes for reversal osmosis applications (e.g. artificial kidneys), desalination of water and purification of industrial waste [3.9].
As a result of its varied applications, the process used for the production of cellulose acetate is very dependent on the type of downstream requirement [3.10]. Thus, the process chosen for a particular application will vary with respect to starting materials, extent of esterification and after treatment of the product; though the basics of manufacture will be that as described below.

3.1.2 Manufacture

The commercial manufacture of cellulose acetate involves the following operations (as summarised by the flow chart in Figure 3.1) [3.11];-

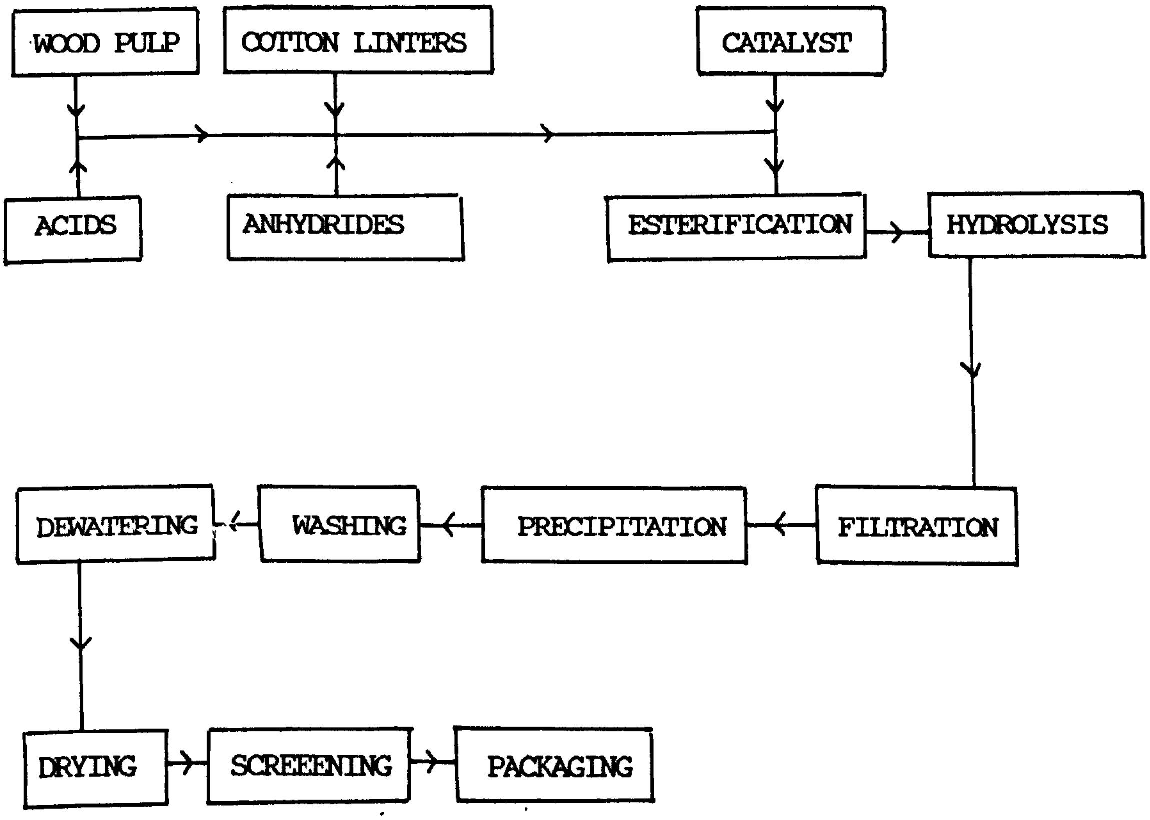


Figure 3.1

Manufacturing Steps in the Production of Cellulose-Esters

i) Pre-Treatment of Cellulose

Prior to esterification cellulose is activated in order to increase reactivity. Here the cellulose is "soaked" in water and allowed to swell so separating the normally closely packed fibres. Once activation is complete, the water is flushed out and replaced by acetic acid. The purpose of this is to improve the accessibility of the hydroxyl groups to the acid anhydrides used in the esterification process.

ii) The Acetylation Stage

In the course of the production of cellulose acetate, esterification is performed by mixing cellulose with acetic acid (glacial), acetic anhydride and the appropriate catalyst, usually sulphuric acid. The course of the reaction is permitted to continue until the three hydroxyl groups on each anhydroglucose unit have been replaced by the acetyl group.

It has been found that the fully acetylated product, the triester, is of limited value in the production of plastics and coatings; some free hydroxyl groups are necessary along the polymer chain to effect solubility, flexibility etc.. Unfortunately, esterification to a predetermined degree, less than the triester, is not possible directly if a uniform soluble product is required. Therefore the triester is initially produced and subsequently hydrolysed to the desired hydroxyl level.

ii) Precipitation

Precipitation of the filtered water-acid solution of the hydrolysed cellulose-ester is accomplished by controlled addition of demineralized water. Additional water is added as precipitation proceeds to prevent acid build up to the point of redissolving the product. Normally, the cellulose-ester is precipitated as fibrous flake, hammer milled to the desired particle size and washed neutral with demineralized water. Water is removed from the product by a two-step operation. The first step centrifugation lowers the water content of the cellulose by about 65% by weight whereupon the product is transferred to vacuum dryers for continued drying to a moisture level not exceeding 3%. Upon complete drying the free-flowing powder is passed through screens to remove over-sized particles that are retained for reprocessing.

3.1.3 Composition

The composition of typical commercial grades of cellulose acetate are represented in Table 3.1 [3.12].

Table 3.1

The Composition of Typical Commercial Grades of Cellulose Acetate

ACETIC ACID YIELD %	ACETYL CONTENT %	DEGREE OF SUBSTITUTION OF ACETATE GROUPS	AVERAGE DEGREE OF POLYMERISATION
52-54	37.3-38.7	2.2-2.3	200-250
54-56	38.7-40.1	2.3-2.4	250-300
56-58	40.1-41.6	2.4-2.6	-
61-62.5	43.7-44.8	2.9-3.0	-

As stated previously fully acetylated cellulose or a formula containing 44.8% acetyl groups per molecule is not utilised commercially since its properties are undesirable. Originally the acetates manufactured were 40% acetylated, i.e. diacetate. More recently produced acetates typically referred to as "triacetate" or "high-acetyl" cellulose acetate are 42% acetylated. Such materials have superior properties and are less susceptible to physical deformation on handling.

The structure typical for cellulose acetates, as deduced by infra-red and nmr analysis [3.13,3.14] is represented here in Figure 3.2 by that of "high-acetyl" cellulose acetate.

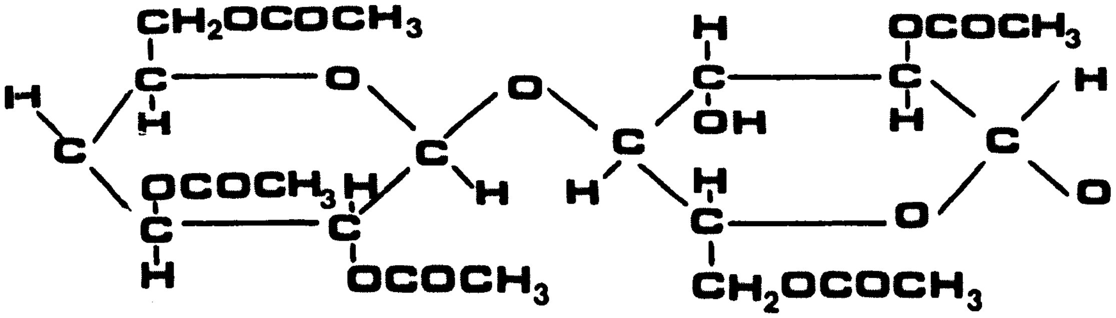


Figure 3.2

Structural Representation of Cellulose 'Triacetate'

However, strictly speaking incomplete esterification and hydrolysis of cellulose 'triacetate' can give rise to eight regioisomers (as depicted in Figure 3.3) providing the opportunity for a variety of degradation reactions.

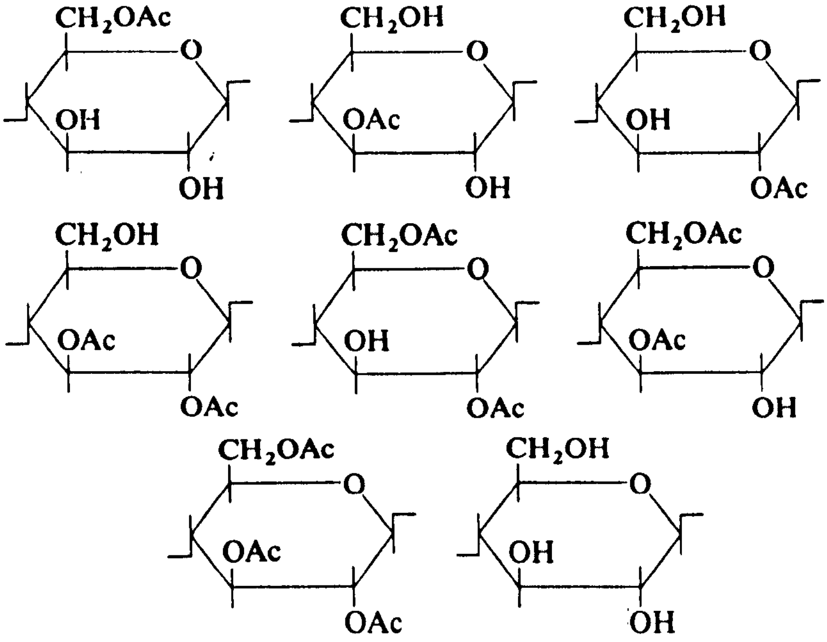


Figure 3.3

Possible Regioisomers of Cellulose Triacetate

3.2 PHYSICAL PROPERTIES

A number of physical properties of cellulose acetate are shown in Table 3.2[3.15].

Table 3.2

Typical Properties of Commercial Cellulose Acetate

PROPERTY	
Specific Gravity (g/cm^3)	1.22 - 1.34
Refractive Index	1.46 - 1.50
Tensile Strength (MN/m^2)	3.5 - 11
Flow Temperature (°C)	115 - 165
Water Absorption (%)	1.7 - 6.5
Tg (°C)	100 - 130

The properties which follow are described in detail since they have particular relevance to the physical and chemical stability of a given cellulose acetate.

3.2.1 Crystallinity

Although the crystal structure of a cellulose derivative is frequently associated with a definite chemical composition such as cellulose triacetate, the actual crystal structure may remain constant over a wide range of chemical composition; e.g. the crystalline structure of secondary cellulose acetate (D.S.=2.5) is identical to that found in crystalline cellulose triacetate.

It is to be noted also that;

- the surface of the cellulose fibres will have reacted more than the interior;
- the low-order non-crystalline regions will be substituted to a greater extent than crystalline regions;
- even though the substituents may react randomly along the molecule, the D.S. of an individual anhydroglucose unit may vary randomly from zero to three.

Variations in crystallinity will also be induced by heat, solvents and plasticisers in addition to the afore mentioned variations in chemical composition [3.16]. X-ray studies on cellulose triacetate has showed that good solvents give films with higher crystallinity than poor solvents [3.17]. Many of the compatible plasticisers used in cellulose-esters cause permanent disordering by association of the plasticiser with specific groups of the polymer and subsequent weakening of interchain forces. In these cases the plasticiser is not concentrated in amorphous regions, but gradually disorders the whole structure [3.18].

3.2.2 Moisture Sorption

One of the most important properties of cellulose-esters is their susceptibility to the sorption of moisture and consequent dimensional change when exposed to atmospheres of different relative humidities. In plasticised compositions this property is determined by the combined effects of the cellulose-ester and plasticiser [3.19].

Since sorption of moisture in cellulose derivatives is generally considered to be attributable to hydrogen bonding of the water molecules to the available hydroxyl groups of the substrate, the moisture regain of a cellulose-ester in given conditions will be dependent on the nature of the substituted group, the degree of substitution and the extent of crystallisation (in a triester) [3.20].

As illustrated below, it can be seen that the higher the degree of substitution of a cellulose acetate the more resistant it is to the uptake of moisture [3.21].

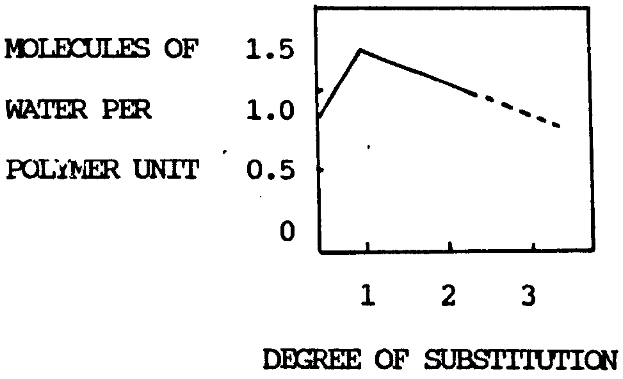


Figure 3.4

Moisture Regain of Cellulose Acetates of Varying Degree of Substitution

A variety of other factors influence such relationships, Sheppard and Newsome [3.22] found that the relationship between degree of substitution and moisture regain is dependent upon the method of preparation of the ester. Moisture regain of cellulose esters is also contingent upon relative humidity; increasing with lowered D.S. [3.23, 3.24].

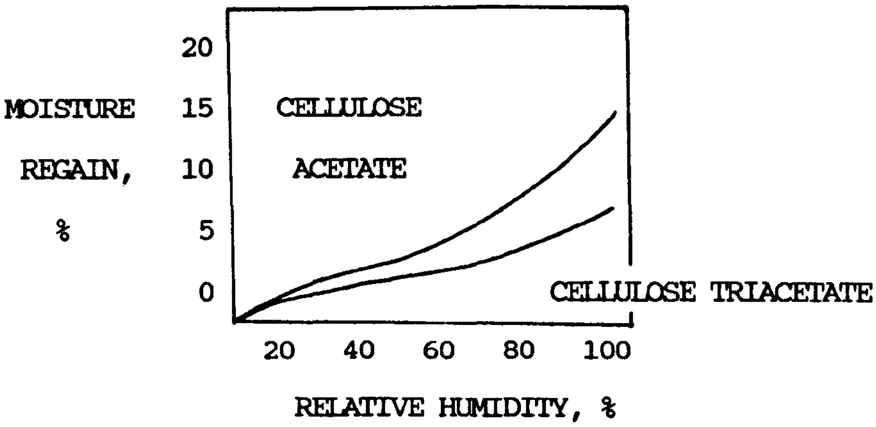


Figure 3.2

Absorption of Water by Cellulose Acetate and Cellulose Triacetate with Varying Relative Humidity

3.2.3 Solubility

Polymer dissolution occurs in two stages;-

Firstly, solvent is slowly absorbed into the polymer to produce a swollen gel. Then the gel gradually disintegrates into a true solution. If the polymer is cross-linked by primary valence bonds, or strong hydrogen bonds or is highly crystalline only swelling may take place.

For a given cellulose derivative solubility changes drastically with degree of substitution [3.25]. As the degree of substitution is varied an interesting phenomenon is observed. In all cases the widest range of solubility is found somewhere between no substitution and complete substitution. Coupled with this is the expected trend of solubility with substitution, derivatives of low D.S. being predominantly soluble in water or solvents of high hydroxyl content, and completely substituted derivatives being soluble in non-hydroxylic solvents.

Solvents for cellulose acetates of varying D.S. [3.26] are listed below;-

Table 3.3

Solvents for Cellulose Acetates of Varying D.S.

D.S. Cellulose Acetate	Solvents	Non-Solvents
0.6 - 0.8	water;	
1.3 - 1.7	2-methoxyethanol	acetone water
2.0 - 2.3	acetone	CH_2Cl_2/CH_3OH
2.3 - 3.0	CH_2Cl_2/CH_3OH ethyl acetate glacial acetic acid aniline	hydrocarbons aliphatic ethers weak mineral acids acetone

Other factors such as degree of polymerisation, concentration and temperature also effect solubility [3.27].
It has also been observed that solubility varies somewhat with the method of manufacture [3.28].

3.2.4 Mechanical and Dimensional Properties

The mechanical and dimensional proerties of cellulose-ester fibres, films and bulk plastics are largely influenced by the afore-mentioned moisture and crystallinity characteristics, although other factors such as temperature do play a part.
Dimensional change in cellulose-esters is in the main caused by loss or gain of moisture. Dimensional stability in cellulose acetates is markedly influenced by varying relative humidity. This is seen to be a reflection of their hygroscopicity. Mechanical properties are also influenced by relative humidity resulting in consequent change in tensile strength, elongation and brittleness [3.29].

Chapter 4

4. Mechanisms by which Cellulose Acetate Degrades

While an enormous volume of work pertaining to the effects of temperature, relative humidity and oxygen on cellulose-esters can be found in the literature investigations have invariably led to the accumulation of a sizeable quantity of empirical information concerning changes in physical properties and considerable speculation regarding underlying mechanistic rationale.

4.1 Primary Decomposition Pathways

(a) Hydrolytic Degradation

Studies on the hydrolytic decomposition of cellulose acetate are numerous. Hiller [4.1] has shown that the reaction follows kinetics as for the random degradation of polymers. He also found the rate of reaction to be temperature dependent, increasing with increasing temperature and to be greatly influenced by the presence of strong acids.

Continuing studies by the same author, indicate the degradation reaction to have a larger activation energy than the deacetylation reaction, implying the degradative reaction is to be more temperature dependent than the de-esterification. Furthermore, for the uncatalysed reaction, the activation energy for deacetylation of primary hydroxyls is much less than that for secondary hydroxyls.

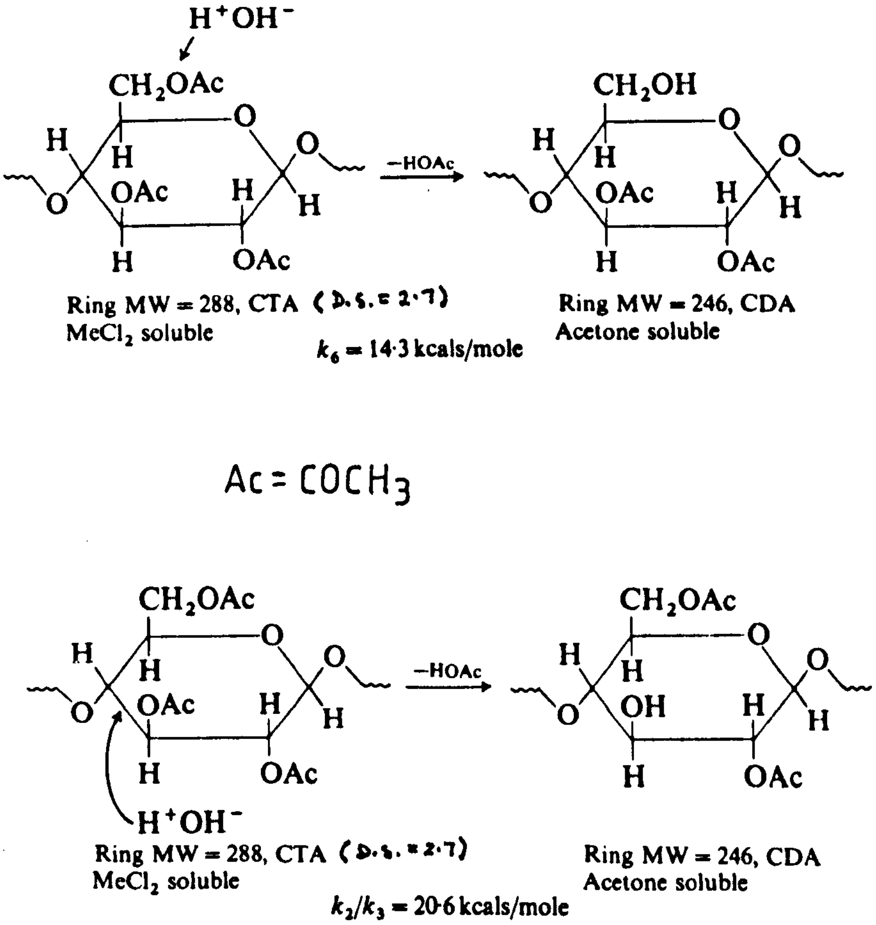


Figure 4.1

Schematic of Hydrolytic Degradation Pathway in Cellulose Acetates

In the presence of a strong acid however, for example sulphuric acid, the activation energy for hydrolysis of secondary hydroxyls is markedly decreased and the reaction is apparently faster than that for primary hydroxyls. According to Lenz [4.2] C_2 or C_3 acetyl groups are likely to undergo hydrolysis prior to cleavage of 1,4-glycosidic linkages which have a higher activation energy (see secondary decomposition pathways).

Later studies by Richau, Schwarz and Kudela [4.3] have shown rate of hydrolysis of cellulose acetate to be minimal at a pH value between 4 and 5. These results have been confirmed by Vos, Floyd and Riley [4.4]. Other studies on cellulose di- and tri-acetate, dispersed in buffer solutions in the pH range 2-10 at 30 C, have shown the overall rate of hydrolysis of cellulose diacetate to be more rapid than that for cellulose triacetate and that for both acetate types the hydrolysis rate has a maximum and minimum at pH=10 and pH=4 respectively [4.5] (see Figure 4.2).

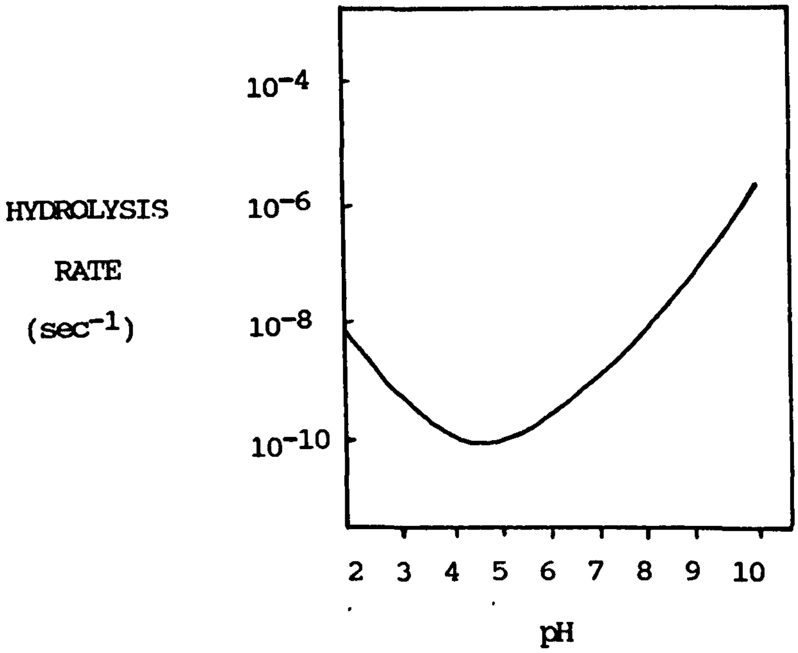


Figure 4.2

Influence of pH on Hydrolysis Rate of Cellulose Acetate

More recent work on cellulose acetate by Cantillo et al. [4.6,4.7] indicates that the rate of hydrolysis increases with increasing moisture concentration and temperature, and that hydrolysis is zero order with respect to acetyl content [4.6]. In contrast to deacetylation they have shown that depolymerisation by hydrolysis is independent of moisture concentration, but proceeds by first order kinetics of removal of acetate groups [4.7].

However, such studies have generally been performed under homogeneous conditions, i.e. are essentially solution reactions. Little attention has been directed towards heterogeneous hydrolysis of cellulose-esters. Here accessibility of degrading agencies to linkages susceptible to hydrolysis may play a significant part in the overall deterioration process. Studies on the heterogeneous hydrolytic degradation of cellulose acetate have shown significant deacetylation to be accompanied by negligible depolymerisation [4.8].

(b) Thermal/Oxidative Degradation

The oxidative chemistry of cellulose-esters has centred mainly on oxidation of cellulose-esters with a wide variety of reagents under both acidic and basic conditions. Specific studies employing unmodified cellulose-esters degraded thermally in oxygen or air are very few in number.

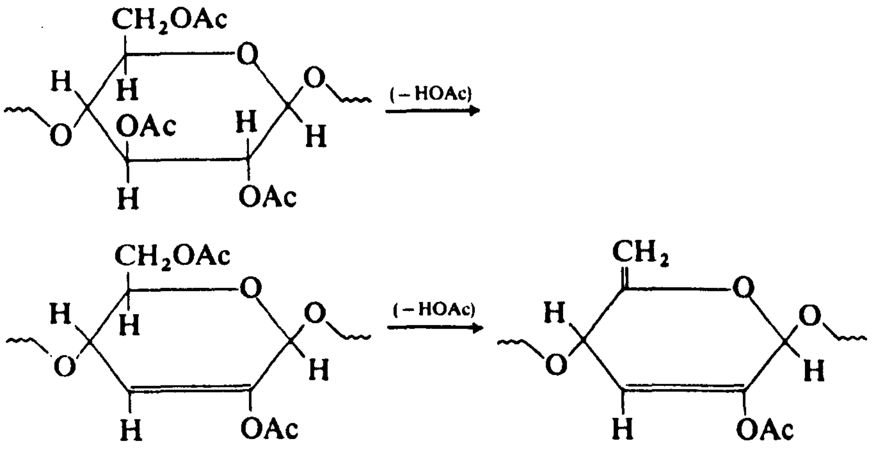
The heat stability of cellulose acetate has been shown to be a function of its ease of oxidation. Evans and Mcburney [4.9] report that during oxidation volatile products were formed, an orange-yellow colour developed, and viscosity decreased. They have also shown that small quantities of sulphuric acid catalyze autoxidation.

Other workers have treated powdered cellulose acetate with moist oxygen containing a small percentage of ozone. This induced oxidative degradation which occurred gradually initially and finally resulted in an abrupt drop in specific viscosity and formation of peroxide, carbonyl and carboxyl groups. On subsequent storage they found that the peroxide groups decomposed in proportion to the duration of 'ozonization'.

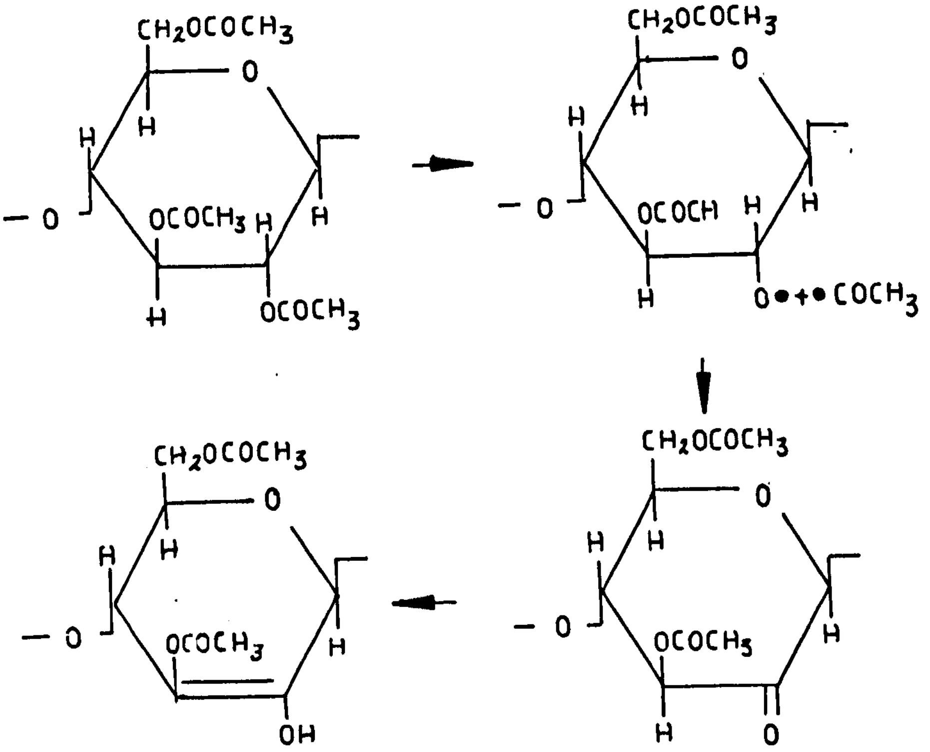
Other studies have concentrated on the effects of impurity groups such as carboxylic acid groups on the thermal degradation of cellulose acetate. They conclude that such groups decrease the induction time prior to onset of oxidative breakdown.

In all cellulose-esters degradation has been found to proceed more rapidly in the presence of oxygen than nitrogen. Mechanisms of oxidation are on the whole rather obscure. Studies have established that the reaction is of the autocatalytic free-radical type; they show an induction period followed by a linear zero order reaction, which is characteristic of such a process [4.10].

Work by Scotney [4.11] suggests that thermal decomposition of cellulose triacetate in vacuo, air or an inert atmosphere begins with random deacetylation of the polymer chain. i.e.

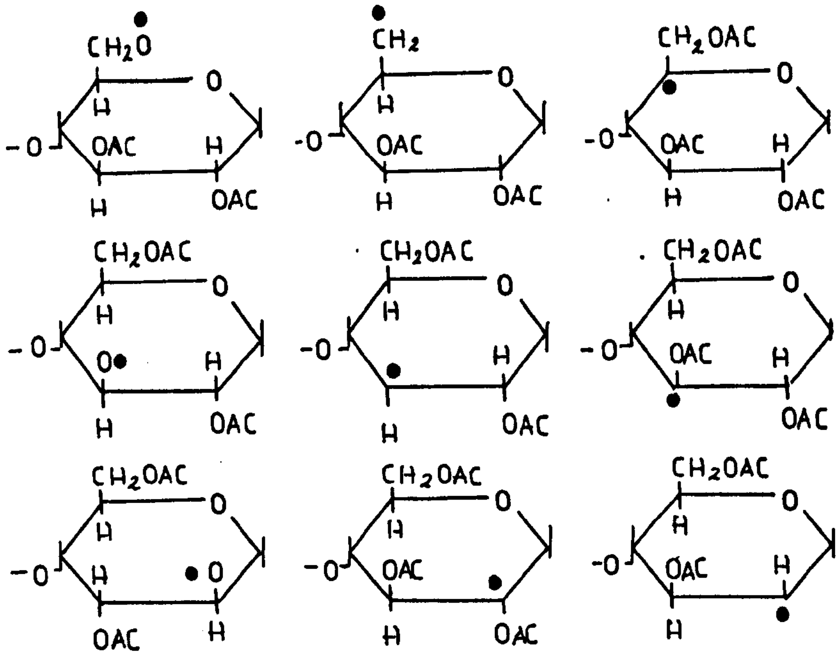


This may be a simple process of elimination of acetic acid as suggested above or may be the result of a more complex radical decomposition as follows;-



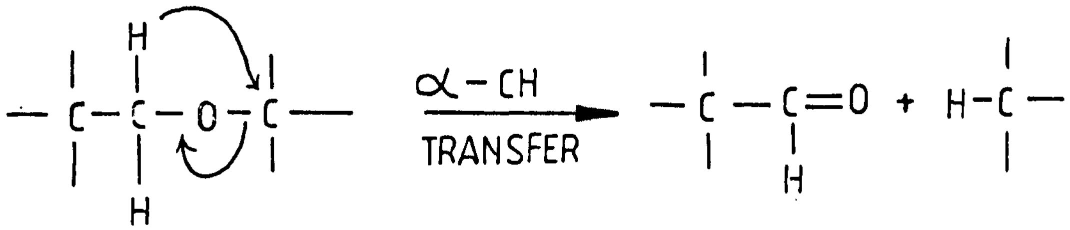
Here deacetylation may result in either carbonyl formation or unsaturation, though this is purely speculative since there is insufficient evidence to support it. Disregarding this, if the process is indeed a radical reaction as the kinetics of degradation imply, radicals could be formed at any of the following positions in the polymer structure, leading to a whole range of possible degradation products. Here any radicals formed could participate in both bond scission or cross-linking reactions.

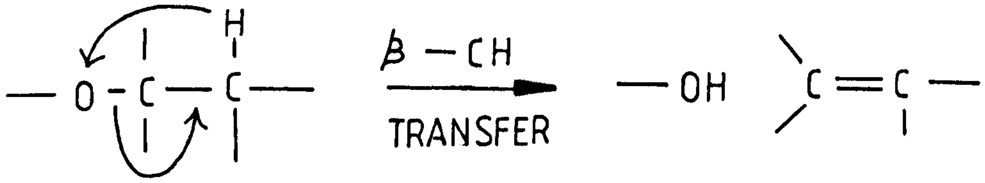
$AC = COCH_3$



Repeating this process for each of the eight possible regioisomers formed in the production of cellulose triacetate (see chapter 3) - the possible combinations of radical reactions increases markedly.

Alternatively, any primary thermal degradation processes operating in polyethers, such as cellulose triacetate, may give similar degradation products but by a process of α-CH or ß-CH transfer reactions.





However, contrary to findings by Scotney, work by Zitomer suggests primary decomposition products are environment dependent [4.12] Products of thermal breakdown of both cellulose triacetate and cellulose diacetate were compared in air and helium by thermogravimetry/mass spectrometry and are illustrated in Table 4.1.

Table 4.1

Thermal Degradation Products of

Cellulose Triacetate (CTA) and Cellulose Diacetate (CDA)

Compound	Atmosphere	Volatile (wt%)					First Evolved
		CO	CO_2	H_2O	CH_3CHO	CH_3COOH	Product
CTA	Air	1.2	34.8	5.9	0.3	56.4	CO_2
CDA	Air	4.4	48.9	5.5	0.3	38.9	CO_2
CTA	He	3.2	24.2	4.5	0.5	64.3	CH_3COOH
CDA	He	1.4	19.8	7.2	0.6	66.3	CH_3COOH

The results bring to light several interesting features regarding the thermal decomposition of cellulose triacetate and diacetate. Firstly, they suggest that oxygen is not involved in deacetylation reactions since more acetic acid is evolved in Helium than air. Secondly, they suggest that in the presence of oxygen a different degradation mechanism dominates. This is reflected by the fact that the first evolved decomposition product in air is carbon dioxide but in an inert atmosphere it is acetic acid.

Other studies, labelling acetate groups during oxidative degradation of cellulose acetate have shown that volatile products arising from the degradation though principally acetic acid, also include methanal, formic acid, carbon dioxide and carbon monoxide. It is interesting to note that only acetic acid retains the label. Where the pyran ring has been labelled chain degradation is shown to take place through the rupture of the C_1-C_2 bond [4.13] Furthermore, it has been shown that of the identified volatile decomposition products,volatiles other than carbon monoxide decrease with oxidation. The evolution of this specie appears to be autocatalytic. Again few studies are in evidence which concern heterogeneous thermo-oxidative decomposition of cellulose acetates.

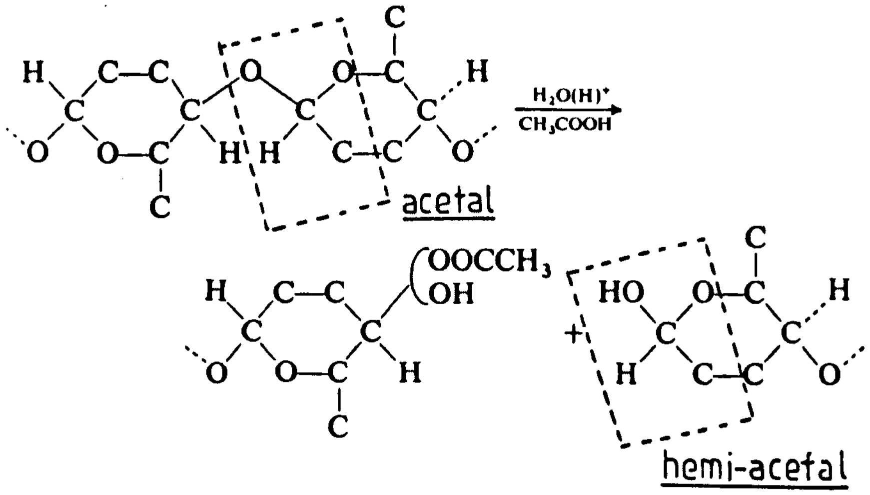
4.2 Secondary Decomposition Pathways

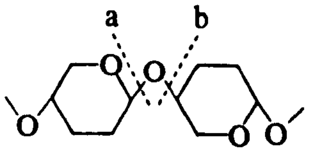
In secondary degradation the initial decomposition products accumulate and may themselves react with the polymer to instigate further degradation processes.

Where acid groups are formed as a result of hydrolysis, there is evidence that these moieties then catalyze further reaction conferring autocatalytic properties on the overall process [4.13] Here moisture trapped within the polymer network from processing may play a significant role.

Properties peculiar to cellulose-esters such as increased hygroscopic nature with decreasing degree of substitution of ester groups may be seen to exacerbate the overall situation.

Depending upon primary decomposition pathways chain degradation may occur in a number of ways. In the main further degradation reactions are attributed to acid cleavage of the 1,4-glycosidic linkage; although this will be accompanied by further de-esterification reactions. 1,4-glycosidic bond scission may occur by both hydrolysis or acetolysis as depicted below;-

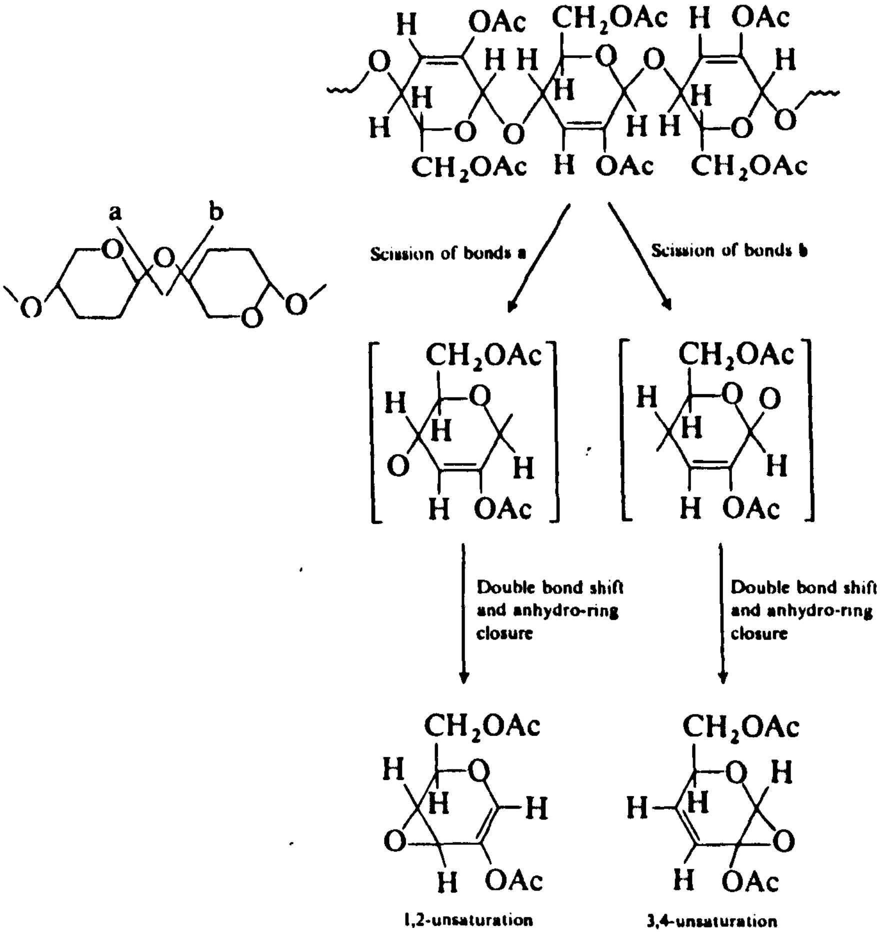




$k_{\text{chain-scission}}$ = 29·6 kcals/mole
(1,4-glycosidic link)

This would give rise to the formation of reducing and non-reducing end-groups. As illustrated the activation energy for this process is higher than that for deacetylation and is therefore less likely to be a primary hydrolytic process.

If chain scission takes place at sites in the polymer network where deacetylation has already occurred the scission process may result in degradation products of the following kind;-



Again it should be emphasized that the nature of such mechanisms and the extent to which they participate under particular degradation condition have by no means been satisfactorily resolved.

4.3 Influence of Additives

Since cellulose-esters are invariably used in combination with plasticisers. The work of Decroes and Tambyln [4.14] shows that the inherent oxidative sensitivity of cellulose-esters is magnified by the plasticiser system with which they are formulated. Here plasticisers which contain methylene or methylidene groups were found to be particularly susceptible to attack themselves by oxygen: e.g. plasticisers such as diethyl phthalate and dibutyl phthalate are unstable to oxidative attack c.f. dimethyl phthalate and triphenyl phosphate which appear relatively inert (see Table 4.2).

Table 4.2

The Effect of Oxygen on Phthalate-Ester and Aryl Phosphate Plasticisers

Plasticiser	Apparent Oxygen Absorbed, ml	Acid Produced, meq.	Peroxide Produced, meq.
Dimethyl Phthalate	0	0	0
Diethyl Phthalate	26	2.0	1.3
Dibutyl Phthalate	52	2.3	0.5
Triphenyl Phosphate	0	0	0

4.4 Manufacturing Impurities and Initiation of Degradation

Since the raw starting material for esterification is cellulose, a natural polymer, it must be accepted that there will be impurities present within the structure which may sensitize degradation.

Other than this the manufacturing process itself may be responsible for the introduction of impurities into the final cellulose triacetate.

A large amount of data pertaining to the effects of residual manufacturing chemicals is evident in the literature [4.15]. Here the effect of the catalyst is seen to be particularly significant.

The majority of esterifications use a strong acid catalyst. Where this is sulphuric acid, along with the substitution of hydroxyl groups by the required ester a certain proportion will react to give the hydrogen sulphate ester, cellulose-OSO_2OH (and to some extent the dicellulose sulphate, cellulose-OSO_2O-cellulose). Alkyl hydrogensulphates are hygroscopic and therefore enhance the possibility of hydrolytic decomposition. While modern manufacturing techniques minimize this reaction, it cannot be totally excluded (see chapter 12).

The stability of the resultant triacetate will also be influenced by particular choice of acetylation method. Brems [4.15] highlights the advantages of the fibrous 'inhomogeneous' acetylation process over any 'homogeneous' method. In the latter 'solution' process, cellulose fibres are dissolved in the reaction medium during esterification - reaction is stopped by addition of water which not only reduces acid concentration but causes a certain amount of hydrolysis to occur. In the former case cellulose acetate is prevented from passing into solution by the addition of a non-solvent and a fibrous acetylation results. Here washing is with the non-solvent and any competing hydrolytic reaction are thus suppressed.

4.4 Influence of Downstream Application

Exposure of a cellulose-ester to a given environment will be determined by its particular end use. Taking the example of cinematograph film, all the materials which constitute this matrix will determine its overall stability: Not only will the cellulose-ester itself influence stability of other constituents, but they in turn may influence cellulose-ester stability. i.e. The degradations of the total combination of constituents and their surrounding environment are unlikely to be mutually exclusive.

It is therefore important that the material under investigation is considered as a whole and not merely with respect to is constituent parts.

Chapter 5

5. PROPERTIES OF CELLULOSE-ESTER BASE CINEMATOGRAPH FILM

The properties of cellulose-ester base motion picture film are a reflection of both the proerties of the base and emulsion layer.

5.1 Moisture Properties

The behaviour of photographic film under the influence of varying relative humidity as a consequence of varying water uptake may be considered to be the major determining factor with regard to many other physical properties.

At low moisture levels photographic film can show brittleness, static and dimensional changes; while at high moisture levels problems arise due to stickiness, ferrotyping or high friction.

Figure 5.1 illustrates the moisture sorption of uncoated cellulose triacetate base [5.1].

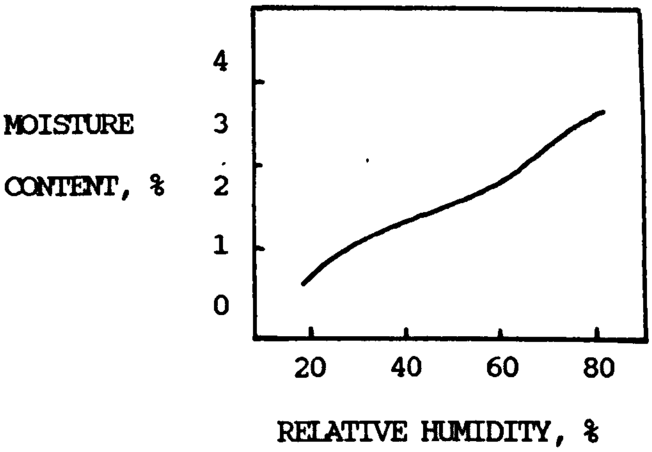


Figure 5.1

Variation of Moisture Content of CTA Base Cinematograph Film with RH.

Figure 5.2 shows the moisture absorption of both gelatin and a photographic emulsion. It can firstly be seen that the ratio of gelatin to silver halide will influence moisture absorption: a photographic emulsion absorbs less moisture than gelatin. Secondly, the weight percentage moisture in the gelatin layer is more than ten times greater than that of the cellulose-ester base [5.2].

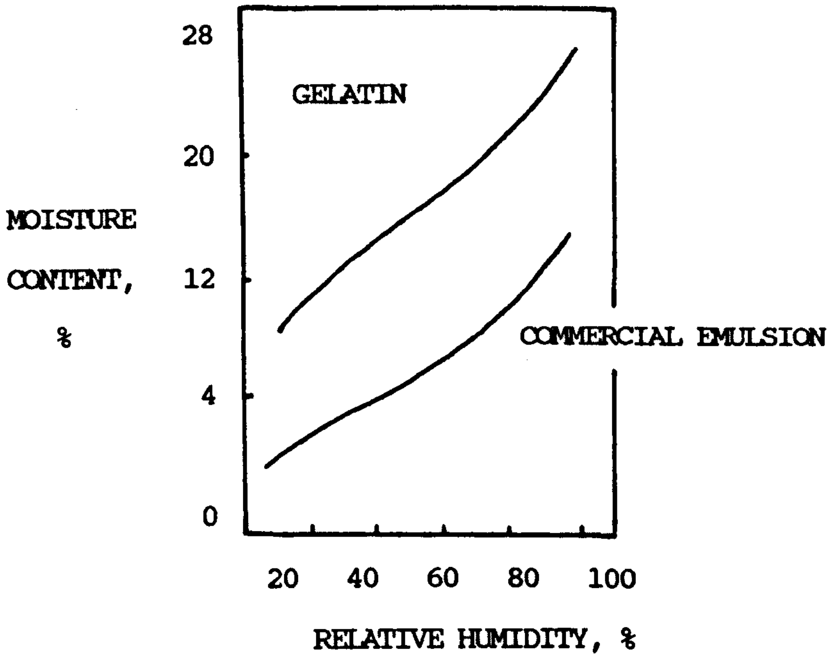


Figure 5.2

The Moisture Content of a Photographic Emulsion Layer

It follows therefore that the final moisture content of the film will be dependent upon both the moisture uptake and relative thickness of the individual components.

The influence of parameters such as relative humidity and temperature are illustrated in Figure 5.3 [5.3]. It can be seen that moisture content has a strong dependence upon relative humidity but is relatively independent of temperature.

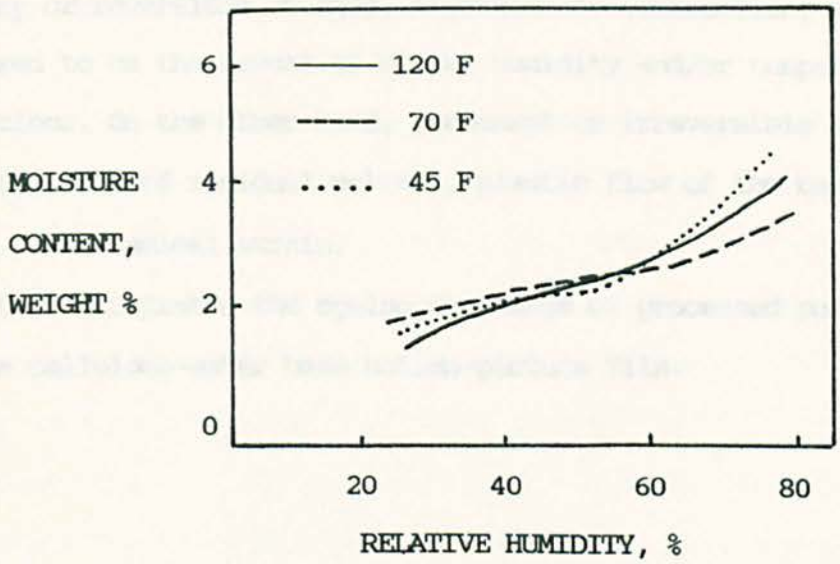


Figure 5.3

Effect of Temperature and Relative Humidity on the Moisture Content of Cellulose Triacetate Cinematograph Support

5.2 Dimensional Properties

The retention of exact dimensions in motion-picture film is important with respect to projection, printing and copying. Any deviation from the given standards may mean that the film is no longer projectable and cannot therefore be copied or viewed. Standards have thus been adopted to ensure that such requirements are stringently met [5.4].

Unfortunately, unavoidable dimensional changes in film do occur. Calhoun, in an excellent review of "the physical properties and dimensional behaviour of motion-picture film" has classified these changes as temporary or permanent [5.5].

Temporary or reversible changes, expansion or contraction, are considered to be the result of either humidity and/or temperature fluctuations. On the other hand, permanent or irreversible shrinkage is due to the loss of residual solvent, plastic flow of the base or the release of mechanical strain.

Figure 5.4 illustrates the ageing shrinkage of processed positive and negative cellulose-ester base motion-picture film.

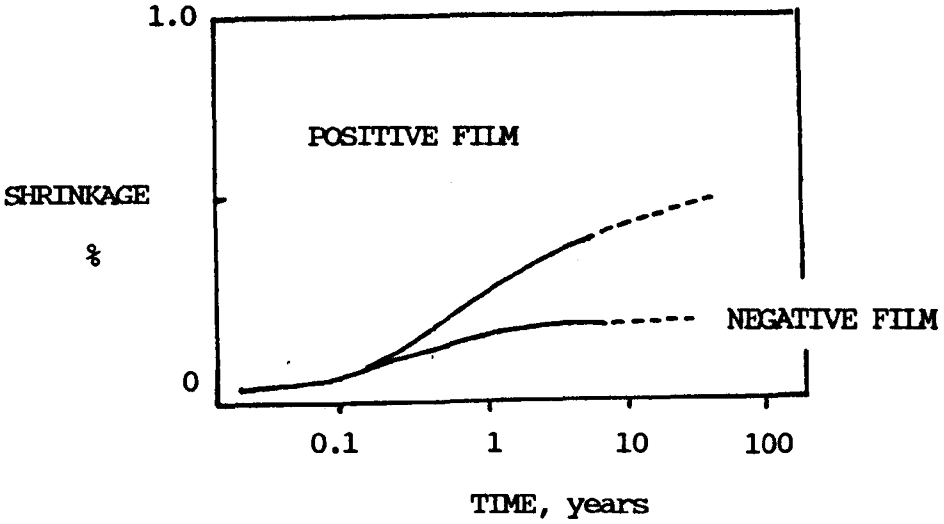


Figure 5.4

Ageing Shrinkage of Processed Cellulose-Triacetate Base Cinematograph Film

Thus, dimensional stability is an all inclusive term, with size changes being complex and occurring for a number of reasons.

5.3 Mechanical Properties

Cinematograph film during the course of its life is exposed to considerable mechanical stress, strain and abrahsion (particularly in the case of release positives which are subjected to repeated projections). The importance of mechanical properties such as tensile strength, elongation, fold endurance, tear resistance and brittleness are thus implied [5.6]. As is the case with dimensional characteristics both temperature and relative humidity play a role. The strength properties of photographic film are best evaluated by the standard tensile stress-strain curve [5.7]. Such properties are determined by the characteristics of the base rather than the emulsion. On the other hand brittleness is determined by the influence of the emulsion layer. Above 30% RH film is not normall brittle, but below 20% RH brittleness increases rapidly. This is because the gelatin of the emulsion becomes brittle due to moisture loss; any sudden cracks which develop in the emulsion will tend to propagate throughout the base. Perforated film is more subject to emulsion cracking than non-perforated film.

Chapter 6

6. THE DEGRADATION OF CELLULOSE-ACETATE BASE CINEMATOGRAPH FILM

6.1 Requirements for Archival Cinematograph Films

According to present standards only Black-and-White cinematograph film is considered to be archival (i.e. to have long-term, dark-keeping stability) [6.1]. Furthermore, this applies only to cellulose-acetate base film. Standards have also been established for the correct storage of these materials and suggest storage at < 21°C and within a relative humidity range of 15-50 % [6.2].

6.2 Observed Degradation Characteristics of Cellulose-Acetate Base Cinematograph Film

Under the correct conditions of storage it was generally considered cellulose acetate base motion-picture film would remain stable almost indefinitely. Unfortunately, as is the case with other polymeric materials, cellulose-esters decompose. Patterns of decomposition were first observed by archivists in the early 1970s.

The degradation of cellulose acetate cinematograph film is characterized firstly by evolution of acetic acid; this occurs prior to any observable changes in image quality. A progressive deterioration then follows which is manifested by the following features;-

As loss of acetic acid becomes more apparent the film material distorts, with frilling around the sprocket regions;
In latter stages of degradation, the deposition of liquid/crystalline materials on the film surface are apparent;
In some films yellowing and embrittlement of the cellulose acetate support occurs but in many cinematograph films the cellulose acetate support does not embrittle but becomes flaccid, with a corresponding decrease in mechanical properties, such as tensile strength;
Eventually fading and erosion of the silver image results.
Figures 6.1 and 6.2 depict new and degraded cellulose acetate support cinematograph films.

In humid climate archives growth of microbes on the emulsion surface has also been observed; leading to loss of the image carrier: though this is essentially a separate problem to that of the "vinegar syndrome".
Because the major cause for concern, as regards cellulose-acetate base materials, is the decomposition which occurs as a result of base degradation, such modes of degradation will only be considered briefly here.

Figure 6.1
New Cellulose Triacetate Support Cinematograph Film

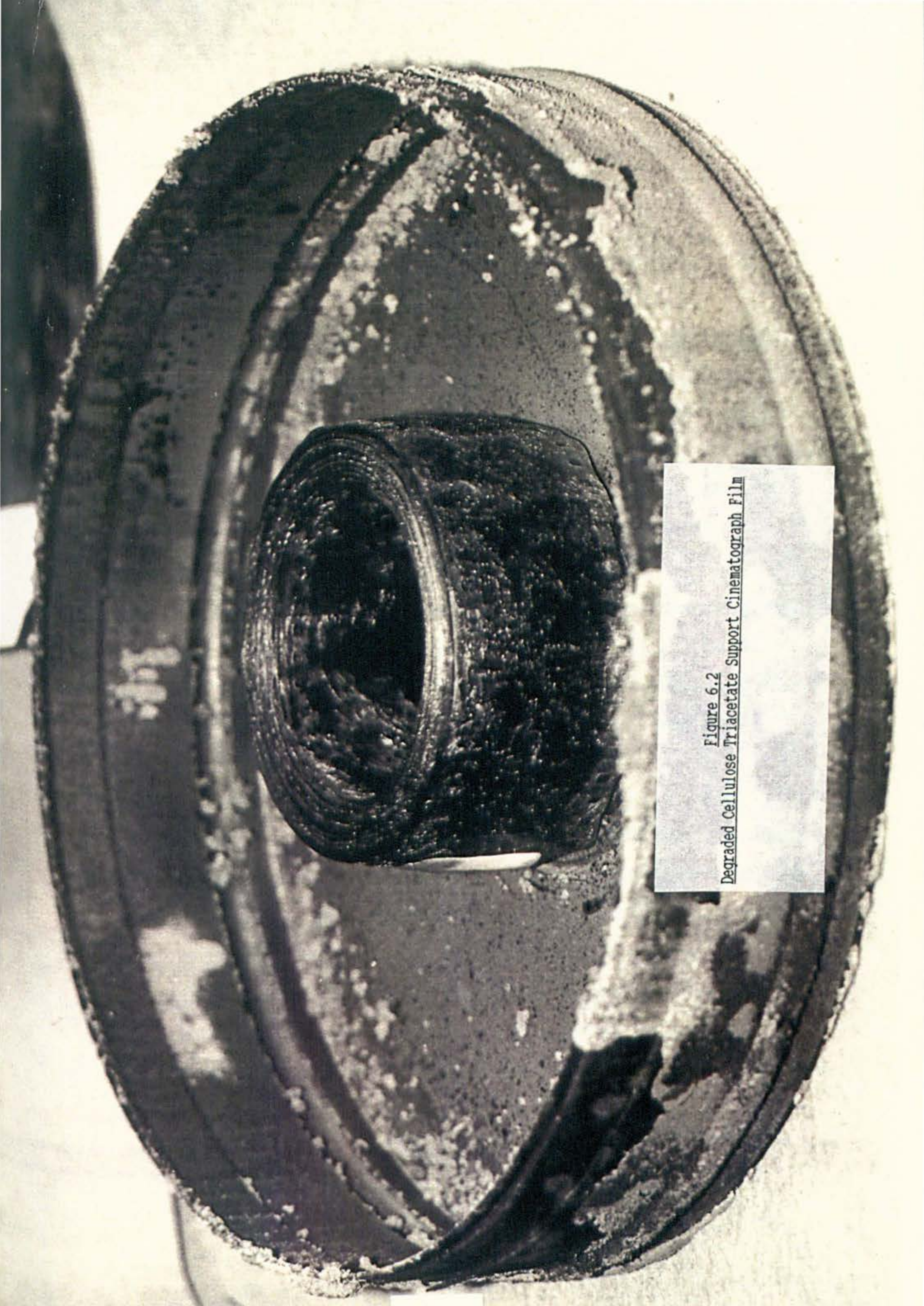


Figure 6.2

Degraded Cellulose Triacetate Support Cinematograph Film

6.3 Stability Characteristics of Emulsion Layer

6.3.1 The Silver Image

Studies on the ageing of emulsion coatings have shown that significant changes in image quality occur on storage [6.3]. Photographic characteristics change as a result of agents contained within the original coating, or agents from the atmosphere, film base or packaging materials.

Effect of Relative Humidity

Although fluctuations in relative humidity do not, on the whole, have a detrimental effect on silver image stability, very high relative humidities may cause recrystallization of the silver filaments. This influences both the covering power and tone of the silver [6.4].

Effect of Oxygen

The major route for the deterioration of the silver image is oxidative. In photographic emulsions silver is present in a finely divided form and thus has a high surface-to-volume ratio; hence, susceptibility to attack by oxygen. Obviously, relative quantitative changes will differ with different materials. In the case of oxidation, grain size along with type and degree of sensitization has a marked influence [6.5]. As a result of oxidation, metallic silver is converted to silver ion (e.g. AgS, AgO).

Many microfilms undergo a spontaneous image degradation upon normal storage [6.6]. Here an interesting phenomenon occurs, which has occasionally been observed in cinematograph emulsions. During ageing many microfilms develop red or yellow spots, 10-150μm in diameter. Such 'microspots' are termed Liesegang rings. Oxidation at a given point of susceptibility causes metallic silver to be converted to silver ions, which then migrate uniformly in all directions from this point. The silver ions are then reduced back to silver which precipitates in a colloidal state; which is thus coloured when viewed by transmitted light and silver or mirror-like by reflected light. Such effects have been considered to be attributable to attack by hydrogen peroxide formed as a result of photographic fixers. Studies by Brown and Jacobson [6.7] on the archival permanence of silver image holograms indicates that while minimal residual thiosulphate retention accelerates image oxidation, higher levels appear to have a stabilising effect. Such observations are attributed to the formation of stable silver tetrathionate complexes.

Sulphides in film enclosure materials and atmospheric pollutants have also been suggested as causal factors in silver image deterioration. However, a more thorough elucidation of detailed mechanisms of silver image degradation are necessary to determine the exact causes of fading.

6.3.2 Gelatin

The properties of gelatin as discussed in chapter 1, will play a large part in determining its subsequent stability.

Hydrolytic Degradation of Gelatin[6.8]

The principle mode of decomposition of gelatin is by hydrolysis to its component amino acids. This may be brought about by chemical or biological means. Chromatographic analysis of gelatin in emulsions which exibit stickiness with evolution of acetic acid indicate the presence of amino acids. Other than this, gelatin is extremely sensitive to microbial attack, namely by bacteria, funghi and mildews. Fortunately, sensitivity to silver inhibits growth of bacteria and funghi in conditions other than that of high temperature and relative humidity. Mildews however, have been found to tolerate even extremes of temperature, RH and high silver content

Oxidative Degradation of Gelatin[6.9]

Oxidative breakdown of gelatin is largely a reflection of the presence of oxidizable microcomponents. For example, carbohydrates are present in gelatin in amounts up to 0.5% (hexoses, pentoses). The majority is found in collagen - (glucose, galactose) and is linked to hydroxylysine by glyciside bonding. Smaller amounts originate from nucleic acids and from mocopolysaccharides, impurities which occur in gelatin. Oxidation of the carbohydrate component can lead to the production of aldehydes and carboxylic acids. The latter may act as impurity centres for further breakdown.

6.4 The Subbing Layer

The influence of adhesive layers, which link the cellulose-ester support and emulsion, have recently been the subject of much debate. As stated in chapter one, these layers are initially hydrophobic where they contact the base and become progressively hydrophilic where they contact the emulsion. The layers are composed of gelatin and either cellulose diacetate or cellulose nitrate in varying ratios. It seems likely therefore that stability will be largely dependent upon the stability of the cellulose-ester constituting them..

Pollakowski [6.10] recently proposed a mechanism of degradation based on the principle that small quantities of cellulose nitrate which are present in some subbing layers trigger the hydrolysis of safety base films. Brems [6.11] also quotes studies undertaken comparing non-cellulose nitrate and cellulose-nitrate subbed films. After accelerated ageing at

67°C and 50% RH free acidity was measured for each film type. Although for the fourteen days of testing acidity remained within the recommended tolerances, it was shown that free acidity increased more in the film base containing nitrate substratum than in the one without. However, this evidence is by no means conclusive since in a survey of 44 film samples exhibiting vinegar syndrome, by the same author, only 25 contained cellulose nitrate and 19 did not. Further work is thus necessary to uphold the original hypothesis purported by Pollakowski.

6.5 Cellulose-Acetate Base Cinematograph Degradation

Due to the more recent discovery of this problem little work has been undertaken on degradation of cellulose acetate as a constituent of photographic film materials. The majority of studies which have been carried out concentrate on the permanent changes in physical properties which result on deterioration of these film materials. Theoretical studies discussing the degradation are rare.

A significant but somewhat dated investigation in this respect was undertaken by Kozlov [6.12]. Kozlov considers depolymerization to be a major factor in the ageing of cellulose-ester films. He also described studies showing the interrelation between plasticizers, composition and proportion of solvent mixtures, and conditions of manufacture on cellulose acetate stability.

Since the first observable evidence of degradation is the evolution of acetic acid another interesting area of investigation is the examination of volatiles arising from film breakdown. Olsen, Bruryes and Sabetta [6.13] have studied the gases produced during the decomposition of cellulose acetate photographic films. They observed that two major gases were evolved, namely acetic acid and carbon monoxide. In this respect degradation is apparently emanating from film base, since an analogous pathway occurs in cellulose acetate material alone (see chapter four).

A number of comparative studies, examining the relative stabilities of cellulose acetate and polyester as support materials, have been undertaken by Adelstein and Mccrea [6.14]. Here the tensile and viscometric properties of both materials were taken as indicators of degradation. The results show two significant features with respect to cellulose acetate. Firstly that there is a significant decrease during ageing in the intrinsic viscosity and tensile strength of film support. Secondly, attempts to predict archival lifetimes of film materials are conflicting. Arrhenius extrapolations of accelerated ageing data to ambient conditions based on time taken to a given property loss vary in their lifetime estimation for the same material. The literature also suggests that triacetate film base, if not contaminated by other products, and if kept under the correct storage conditions, should last at least a hundred years: An obvious discrepancy with respect to recent practical experience in the archival world.

Horvath [6.15] in a survey of acetate negatives, has considered the effect of enclosure materials. For the cross-section of films he examined, he claims that highly acidic envelopes seem to accelerate the degradation process. Many degraded negatives showing separation of the base and emulsion along the seam of such envelopes. Negatives also stored in glassines often show signs of deterioration before similar unsleeved negatives or those in paper sleeves. From this it is implied that the physical microenvironment of the film may influence rate of degradation.

Horvath also observed that "pockets" of degradation occur, where materials already exhibiting degradation seemingly infest other surrounding materials; which he terms a "bad apple" phenomenon. Another important point illuminated from this report pertains to manufacture. Prior to 1940 all cinematograph support stock was manufactured by a batch process; replicate composition of such product groups is therefore unlikely. Horvath's survey graphing percentage degraded filmstock versus year of manufacture shows definite peaks relating to specific years of production for a given film manufacturer. Unfortunately this data is only complete to the year 1950; it would be interesting to see if similar trends exist for continuously processed materials.

Much more investigation is necessary if we are to elucidate the factors which contribute to instability in cinematograph materials. Studies which link together the effects of environment with initial and subsequent degradation pathways are vague and incomplete. Furthermore, the majority of works do not relate to practical archival storage conditions and their validity in any real sense is therefore questionable.

AIM

It should by now be apparent that the complex interplay between innate structural features of a cinematograph film and external environmental variables result in many possible degradative routes. Since no film will ever be exposed to only one degrading agency and even the most easily identified factors are often acting in combination attack often occurs in a complex and little understood manner. Possible and highly probable synergism and antagonism between competing degrading agencies further adds to the difficulty of understanding the effects of a given environment on a film.

Little information is as yet available regarding cinematograph film stability. If we are to establish the limits of stability of this material we require the following objectives to be achieved:

To identify the nature of degrading agencies present within a particular film environment;
To understand the nature of the physical and chemical effects that these agencies have on film component structures;
To understand and quantify the interactions following combined agency attack.

The chapters which follow therefore concern the experimental undertakings in this present project relating to the establishment of an underlying mechanistic rationale for the degradation process.

Chapter 7

7. EXPERIMENTAL

Initial attempts to follow mechanistic pathways leading to film decomposition were fraught with problems associated with assessment of such a complex matrix. Difficulties were experienced in separating film support from subbing layers and emulsion, to carry out testing; without either extracting degradation impurities or accelerating any artificial ageing effects to which the film was subjected. The methodologies which follow are those which best minimized any errors which resulted as a consequence of such factors.

7.1 Materials

The cinematograph films used in all studies were 35mm, processed, commercial fine grain recording materials coated onto cellulose triacetate support. In all studies negative materials were emulsion type 5224 and positive materials were emulsion type 5336.

All films contained phosphate and phthalate ester plasticisers along with a small percentage of residual coating solvent, and were supplied by the National Film Archive, U.K..

Cellulose Triacetate flake, to produce solvent cast films, was supplied by Courtaulds Acetate, U.K..

All solvents were analar grade supplied by Fisons, U.K..

Triphenyl phosphate, and metal oxides were supplied by Aldrich.

Film containers were supplied by the National Film Archive.

7.2 Ageing

The inter-relationship between naturally and artificially-aged films is necessary not only for a reliable assessment of film condition but for a realistic interpretation of the mechanistic processes involved. Thus, at all points in the study results were compared for naturally-aged films and for those films which had been subjected to accelerated ageing.

7.2.1 Natural Ageing

Film samples in a variety of conditions were analyzed, which had been taken randomly from the National Film Archive storage vaults.

7.2.2 Accelerated Ageing

Film Strips

Film samples were cut into strips, ten frames in length, and suspended in glass containers which simulated the following environments:

0%	relative humidity	(using anhydrous calcium chloride);
100%	relative humidity	(using distilled water);
	Acid conditions	(using molar acetic acid).

The glass containers were then placed in constant temperature ovens at 50, 70 and 90°C.

Films were analyzed by moisture regain, pH, viscometry and % insoluble polymer.

Film Reels : Cross-Sectional Analysis

Four naturally-aged film reels were chosen for analysis. These comprised relatively new film, one which exhibited acetic acid odour but no visible signs of degradation, and a film which was visibly degraded). Films were sampled across the reel radius from the core outwards at distances of approximately 0.1, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 5.5 and 5.9 mm.

Further studies were carried out on artificially-aged film material at 90°C in 100% RH, for films 60mm in diameter . All films were wound under the same tension.

Both naturally and artificially-aged samples were analyzed by moisture regain.

7.3 Viscometry

Dilute solution viscometry provides a rapid, reproduicible means of determining bond-scission, and hence lowering of molecular weight in a polymer.

For a dilute solution;-

$$N_{sp} = \frac{t - t_o}{t_o}$$

where N_{sp} = specific or relative viscosity

t_o = flow time (in seconds) of pure solvent

t = flow time (in seconds) of the cellulose-ester solution.

The viscosity number (V.N.) is obtained using the relationship;-

$$V.N. = \frac{N_{sp}}{c}$$

where c = concentration of polymer in g/cm^3

The percentage viscosity retention is then simply the viscosity number of the polymer prior to degradation related to the sample viscosity number at time t of degradation.

$$\text{i.e. \% viscosity retention} = \frac{V.N._o - V.N._t}{V.N._o} \times 100$$

where,

$V.N._o$ = viscosity number prior to degradation of the sample, and

$V.N._t$ = viscosity number at time t of the degradation.

In the present study, the emulsion layer was first removed by dipping the film in dilute sodium hypochlorite solution. The plasticiser was removed by soxhlet extraction with methanol for 12 hours. Samples were then dissolved in dichloromethane : methanol mixture (9:1 v/v) at 0.5% w/v. Solutions were filtered through glass wool to remove insoluble subbing layers and a flow time obtained using an Ubbelhode viscometer. at 25°c ± 0.2.

7.4 Determination of Free and Combined Acetic Acid

Since the first observable evidence of film degradation is apparently the evolution of acetic acid it was felt that one route to extricating degradative information was to test quantitatively for volatile acid decomposition products within the film. Information relating to the degree of acetic acid which is present as combined acetyl groups or combined acetic acid is important in assessing whether lowering of degree of substitution is occurring on degradation.

7.4.1 Free Acid

Any acid formed during the degradation was determined potentiometrically. Film samples (1g) were soaked in distilled water (100cm^3) for 3 hours. Results were cross-checked by titrating film samples (1g) to a phenolphthalein end point with 0.1M sodium hydroxide in a medium of 1:1 v/v ethanol:acetone.

7.4.2 Combined Acid

All techniques concerned with measuring combined acetic acid directly are difficult since the integrity of the polymer material as a whole suffers.

Apparent Acetyl

Esters are commonly determined by saponification with a measured quantity of standard base. The excess base is then titrated with standard acid.

Esters vary widely in their reactivity towards saponification; some require several hours of heating with a base and some react rapidly enough to permit direct titration. In the case of cellulose-esters, typically, the ester is refluxed with standard 0.5M base for 1-2hours. After cooling the base is titrated with standard acid.
However, difficulty arises as a consequence of the pH sensitivity of cellulose-triacetate. Both acetate groups and ß-anhydroglucose linkages are stable to hydrolysis only with in the pH confines of 4 and 5. This places restrictions on any reagents used for such determinations.
It is as a consequence of this that extensive variability of results is found upon saponification. Because of this saponification as a method for determining combined acid content was disregarded. It is however, interesting to note that samples exhibited a yellowing when refluxed in 0.5M NaOH reagent which increased in intensity the more degraded the sample. This is highly likely to be the result of carbonyl groups within the polymer forming an aldol condensation type product.

Combined acetic acid determination was therefore tried according to other methods.

Selective Ammonolysis

This was undertaken according to a method described by Mansson [7.1]. Here acyl groups were split by ammonolysis with pyrrolidine, and the 1-acetylpyrrolydine formed vacuum distilled off and determined quantitatively by g.l.c. (Shimadzu miniature coupled to a microprocessor printer of the same make). This method was used not only because of the reactivity of the pyrrolidine in removing the ester but primarily because it causes negligible degradation of the cellulose backbone.

UV Absorption

Cellulose triacetate exhibits a characteristic $n \text{ —— } \pi^*$ transition in the region 200-230nm. Any decrease in this absorption band will correspond to loss of acetate functionality. In the present study change in absorbance of the ester band in cellulose triacetate was monitored at 222nm, using a Perkin-Elmer Lambda-7 absorption spectrometer.

Because of the tedious nature of methodology pertaining to selective ammonolysis and the lack of specificity of uv absorption in the region corresponding to acetate absorption supporting data on acetyl content has also obtained indirectly.

7.5 Moisture Regain

Since cellulose acetates become progressively more hygroscopic with lowering of degree of substitution, determination of moisture regain may be utilised as an indirect method of loss of ester groups.

Film samples (1g) were dried for 2 hours at 100-105°C cooled and then reweighed. The moisture content was then reported as percentage by weight of the original polymer. The results were cross-checked using the Karl-Fischer titration method.

7.6 Insoluble Polymer

Again this is an indirect measure of the lowering of degree of substitution of the polymer. This utilises the specificity of a cellulose acetate of given degree of substitution for solubility in a particular solvent. As the degree of acetylation of the polymer decreases it will become insoluble in any organic liquid originally used as a solvent.

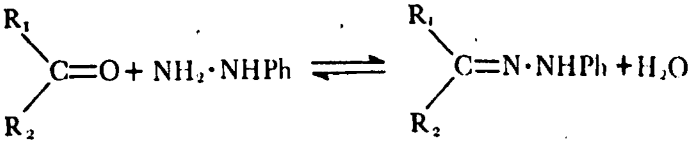
Samples of the film (1g) were subjected to continuous extraction by a dichloromethane/methanol mixture (90:10 v/v) in a soxhlet apparatus for 6 hours. Samples were then dried for 2 hours at 80°C and reweighed. Insoluble polymer was reported as a percentage by weight of the original material.

7.7 Functional Group Analysis

The following functional groups may be introduced into cellulose-esters upon degradation;- aldehyde groups, potential aldehyde groups (hemiacetals), ketone, carboxyl and hydroxy groups. As yet no satisfactory method exists for the determination of such groups, although certain methods give reliable results for particular types of material. All claims to have measured either aldehyde or total carbonyl contents of cellulosic materials should therefore be examined critically.

7.7.1 Determination of Carbonyl Groups

Most of the methods for determining carbonyl groups in cellulose-esters employ well known addition or condensation reactions.
e.g phenyl hydrazine.



These reactions are all reversible and the extent of addition or condensation at equilibrium is dependent upon pH; so also is the rate of attainment of equilibrium. Phenyl hydrazine itself has not proved a very satisfactory although several authors have proposed more promising methods [7.2].

The most widely used reagent for determining carbonyl groups in degraded cellulosics is hydroxylamine. The usual procedure is to treat the material with a solution of hydroxylamine hydrochloride under such conditions that the final pH is between 3.5 and 5.0.

A number of naturally-aged films samples were tested for carbonyl content after removal of any support additives.

7.8 Determination of Hydroperoxides

Iodometry is one of the most widely used methods for the estimation of hydroperoxide concentrations. In this method iodide is oxidised quantitatively to iodine by the hydroperoxide in an acid medium.

$$ROOH + 2I^- + H^+ \longrightarrow ROH + H_2O + I_2$$

This method involves experimental conditions which are highly influential on the reproducibility of results and many modifications have been published.

In the present study iodine is determined spectrophotometrically and not by titration. The medium of reaction,propan-2-ol, containing glacial acetic acid and sodium iodide is used as the source of iodine, instead of potassium iodide because of its higher solubility, which helps keep the equilibrium;-

$$I_2 + I^- \rightleftharpoons I_3^-$$

far to the right, thus preventing the loss of liberated iodine due to boiling; as the tri-iodide ion is non-volatile. Further the tri-iodide ion will not add to unsaturated systems so errors due to unsaturation are eliminated.

The use of propan-2-ol as solvent decreases the likelihood of atmospheric oxidation of the iodide and the absence of water in the system avoids low results due to retardation of the iodine-hydroperoxide reaction.

Initial experimental analysis involved duplicate samples of polymer (1g) cut into small pieces and transferred to a medium containing sodium iodide (0.5g), propan-2-ol : glacial acetic acid (9.5:0.5 v/v). This highly acid environment also acts to eliminate discrepancies due to the presence of acetic acid as a degradation product of cellulose triacetate breakdown. The mixture was refluxed for 30 minutes. Following rapid cooling, the iodine generated as tri-iodide was measured spectrophotometrically at 420nm in 1cm cells. The corresponding hydroperoxide concentration was read off a calibration curve set up using cumene hydroperoxide as a standard. Unfortunately, initial studies indicated not only very low peroxide values but highly conflicting results. This was probably due to reaction of iodine with some of the degradation products in the cellulose triacetate other than peroxide. The method was thus modified to eliminate any heating, to establish whether or not this was a contributor to non-reproducibility. The samples were thus prepared as previously but left to stand at room temperature in the dark for 1 hour.

7.9 Plasticizer Analysis

Cellulose triacetate films 150μm thick (comparable to that of cinematograph film base) were cast from a 10% w/w solution of triacetate flake in 90:10 v/v dichloromethane:methanol. Films were cast 20% (by weight of the polymer) triphenyl phosphate plastisizer. A number of solvent cast and 35mm cinematograph films were then artificially-aged at 50,70 and 90°C at both 100% RH and in molar acetic acid environments.

Samples of cast film and cinematograph film (after removal of emulsion layer) were soxhlet extracted with methanol for 12 hours; followed by drying at 80°C. Plasticizer content was then reported as % weight loss, after first correcting for moisture content and acetic acid loss.

Samples aged at 90°C and 100% RH were also analyzed by viscometry and for moisture regain.

Naturally-aged and artificially-aged (90°C, 100% RH) films were also analyzed by the above method for plasticizer content throughout their cross-section.

Samples of crystalline deposits taken from naturally-aged cinematograph film surfaces, which were suspected to be plasticizer, were examined by infra-red analysis. Samples of the same films with crystalline deposits scraped away were then subjected to soxhlet extraction in methanol for several hours to remove any plasticizer material. All infra-red spectra were obtained using a Nicolet SX Fourier-transform infra-red spectrometer.

7.10 Metal Ion Analysis

Since the presence of metal ions, particularly iron from processing and storage cans, may possibly catalyze decomposition of peroxides which could be present in cinematograph films; naturally-aged film samples were analyzed for the presence of iron. This was achieved by application of atomic absorption spectroscopy. Samples were subjected firstly to acid digestion. Duplicate determinations were made and the iron content reported as micrograms per gram of film.

Small reels of film were also prepared with and without emulsion layer. The reels were then placed in contact with film cans and artificially-aged in desiccators at 90°C and 100% RH. The films were analysed by viscometry and for moisture regain.

In addition, various metal oxides, namely iron, silver and chromium were added to a cellulose triacetate dope at concentration levels of 0 (control), 5, 10, 20, 50, 100 and 200 ppm. The resulting films (approximately 150μm thickness) were cast from this dope and artificially-aged at 90°C and 100% RH. The films were analyzed by viscometry and for moisture regain.

7.11 Infra-Red Analysis

Studies on the infra-red spectra of celullose triacetate [7.3] have assigned specific vibrations in the molecule to the following frequencies:

The valence vibration of CH_2 groups located at C_6 are found in the region 3000cm^{-1}; while the symmetric valence vibrations of the methyl group are localized at 2875-80cm^{-1}. The absorption band at 1720-50cm^{-1} results from the valence vibrations of C=O bonds. The 1300-1500cm^{-1} domain (primarily 1370 and 1430cm^{-1}) is assigned to the antisymmetric and symmetric deformations of methyl groups. The domain of 1000-1300cm^{-1} (primarily wide bands at 1220-40 and 1040-60cm^{-1}) is assigned to acetate groups.
The region 800-950cm^{-1} is ascribed to C-0 bond vibrations: At 950cm^{-1} C-O-C and C-C-O groups localised at C_5 and C_6; and at 840cm^{-1} C-O of the acetate at C_2 and C_3. At 400-700cm^{-1} is found the vibrations of acetate groups and anhydroglucose segments, containing O_1, O_4 and O_6. The region 840cm^{-1} is also thought to be particularly useful in evaluating the effects of heat and plasticizers.

In this study, initial infra-red analysis proved to be quite difficult due to the thickness of the cellulose triacetate base (approx. 150μm) and the fragility of more degraded samples. Recasting the base as a thin film proved ineffective due to the insolubility of samples at later stages of deterioration.

Furthermore, as a consequence of this, any information regarding the condition of surface layers in contact with the emulsion and subbing layers was lost. Removal of small sections of the film, as layer was attempted by microtoming. However, microtoming a highly glossed surface, such as that of photographic film base, results in very small sample sizes which require the use of a microscope attachment to a Fourier-Transform Infra-Red (FTIR) spectrometer. Fortunately, this then allowed analysis of progressive layers.

Both naturally and artificially-aged (90°C, 100% RH) films were investigated according to the above method. In addition samples were also taken from a naturally-aged cellulose-acetate sculpture, provided by the Tate Gallery, London U.K..

7.12 Nuclear Magnetic Resonance (NMR) Analysis

Both naturally and artificially-aged (90°C, 100% RH) films have been analyzed by FTnmr spectroscopy. This was performed by dissolving samples in trifluoroacetic acid. A 270 MHz Jeol GSX FTnmrinstrument was used to produce all spectra.

Solution studies were undertaken because in the solid state chain motions of polymers are relatively slow and as a consequence resonances tend to be broad owing to the local dipolar field at each observed nucleus. This 'dipolar broadening' tends to abolish all structural information. in solution chain motion is fast and this effect is negligible, i.e. averaged to zero, and detailed structural information results.

7.13 Open and Enclosed Environments

Since film materials are stored in containers (i.e. within a fixed volume of non-circulating air), an intercomparison between this condition and a more open environment (i.e. large volume of freely-circulating air) has been undertaken. Artifically-aged film samples were analyzed by moisture regain, viscometry and for the presence of peroxides.

7.14 Role Played by Containers

Because film reels are stored in containers any interaction which may occur between the two may play a role in stability. A number of film reels have therefore been aged in contact with tin-plated iron and aluminium coated iron cans, plastic (HDPE) and glass containers. This has been performed at 50 and 100% RH and at a series of elevated temperatures to permit an Arrhenius extrapolation to room temperature conditions (see sections 9.4 and 10.1).

Chapter 8

8. RESULTS AND DISCUSSION

8.1 Influence of Temperature and Relative Humidity

8.1.1 Analytical Data for Naturally-Aged Cellulose Triacetate Films

The first study concentrated on the properties of cinematograph films which had been stored over a period of time in archival conditions; but which had unknown pre-history prior to archival storage. The results in Table 8.1 compare the full set of analysis data on films of this type.

Table 8.1

Analytical Data for Naturally-Aged Cellulose Triacetate Films of Unknown Pre-History Prior to Archival Storage

Sample	Appearance	pH	Viscosity number	% Insoluble polymer	% Moisture regain	|Fe| (μg/g)
1. ۱۹۸۶	good	4.2	120.6	7.6	1.20	<1
2. ؟	good	4.9	121.0	9.4	2.40	5.3
3. ؟	good	4.5	104.8	10.7	2.68	7.8
4. ؟	acetic acid odour	5.9	—*	68.1	8.92	12.2
5. ۱۹۶۵	plasticiser deposit on film surface	5.8	—*	73.5	11.95	16.8
6. ۱۹۴۰	image loss	3.2	—*	75.1	26.09	31.2

* Samples were insoluble in the solvent used for viscometric determinations.

The dates of films 1 & 2 are unknown. Comparing films of known age it is seen that those made in the year 1950 (i.e around the inception of the use of cellulose triacetate as a base material) have acquired a far higher moisture content than the later films manufactured in the 1980s. Degree of insolubility of the polymer also relates to this data. Both undated films show a similar relationship. Extent of degradation is also consistent with lower pH (i.e. higher acidity), except for the two 1950 films. A possible explanation for this anomaly may be that acidity may have been neutralised as a result of some treatment process. Certainly this is not an unusual procedure in archives to facilitate copying. Viscosity measurements further corroborate previous data; viscosity number decreasing with films in poorer condition (as typified by decline in image quality). Viscosity values on films 4,5 and 6 were not possible due to their insolubility in the solvent system used for the determinations.

Since samples in Table 1 have unknown pre-history it is not possible to make definite conclusions as to any age related changes which may be taking place under a given set of conditions over an extended ageing period. Therefore, to investigate effects of film chronology a cross section of films were taken spanning a period of two decades from 1968-1985. The results of analysis of these films are given in Table 8.2.

Table 8.2

Analytical Data for Naturally-Aged Cellulose-Triacetate Films Stored Under Archival Conditions (25°C and 15-40% RH)

Sample Number and Type	Year of Manufacture	Viscosity Number	% Moisture Regain	pH	% Insoluble Polymer
7. (Positive)	1968	111.9	2.61	3.8	12.2
8. (Positive)	1975	114.8	2.30	3.8	11.3
9. (Positive)	1977	113.0	1.69	3.9	10.7
10. (Positive)	1981	122.1	1.44	4.1	10.1
11. (Positive)	1985	127.2	1.24	4.7	7.7

The results in Table 8.2 do indicate age related changes. The film sample dated 1985 through to the film sample dated 1968 show progressive lowering of pH and viscosity number, with increase in percentage moisture regain and percentage insoluble polymer.

Both sets of tabulated data signpost a hydrolytic degradation process to be occurring. Parameters such as moisture regain, pH and percentage insoluble polymer may all be considered to be relevant to polymer de-acetylation supporting this. On the other hand, viscometric data may be considered to be an indicator of both de-acetylation and chain-scission.

8.1.2 Analytical Data for Artificially-Aged Cellulose Triacetate Films

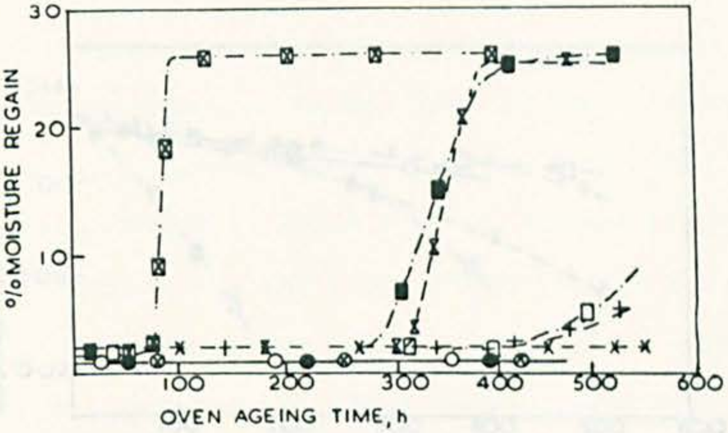
Those parameters which may be considered to be relevant to polymer de-acetylation are depicted in Figures 8.1-8.4 and compare changes at 50, 70 and 90°C in three different atmospheres; namely, dry, 100% RH and molar acetic acid. In all cases, it is seen that rates of degradation follow the order molar acetic acid > 100% RH > dry conditions. The degree of degradation also increased, as might be expected with increasing temperature, the effect being particularly marked at the highest temperature.

Figure 8.1 depicts percentage moisture regain as a function of oven-ageing time. It is interesting to note that under dry conditions temperature has no effect over the time period studied; while at 70 and 90°C in molar acetic acid the rate of regain of moisture is autocatalytic.

The results on polymer insolubility are compared in Figure 8.2 and are consistent with those in Figure 8.1. The material becomes progressively insoluble particularly in the presence of acetic acid.

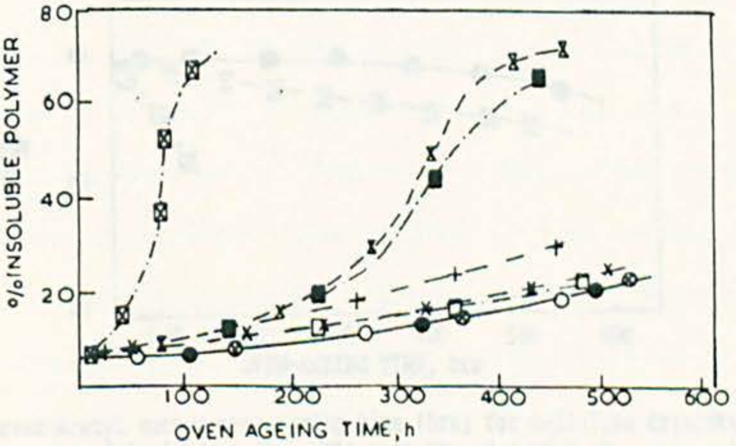
The results in Figure 8.3 compare changes in absorbance at 222nm with oven-ageing time. Again it is seen that in a dry atmosphere the effect of temperature is not discernible but under moist and acid conditions degradation is pronounced at the higher temperature. The most significant feature of this direct measure of deacetylation is that lowering cf acetate content is slight; only 0.1 absorbance unit even under the most severe degradation conditions (90°C; 100%RH).

Figure 8.1



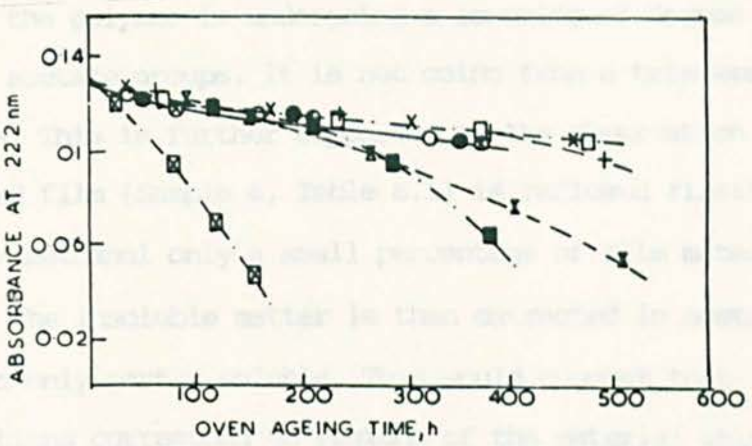
Percentage moisture regain versus oven ageing time (h) for cellulose triacetate photographic film in (——) dry, (– – – –) 100% RH and (–·–·–) 1M acetic acid conditions at 50 (○, ×, □), 70 (⊗, +, ■) and 90°C (●, ⧖, ⊠).

Figure 8.2



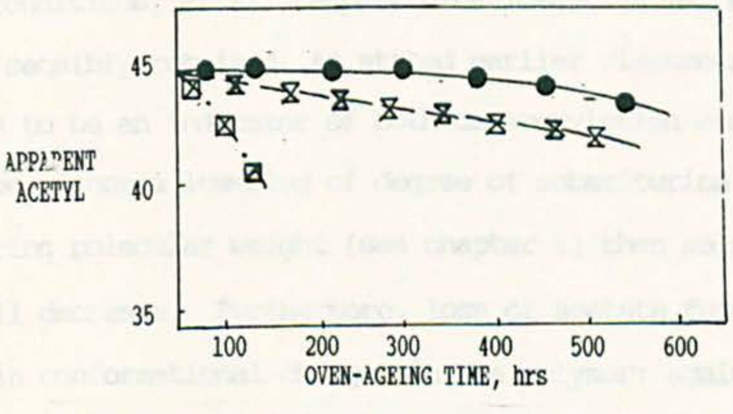
Percentage insoluble polymer versus oven ageing time (h) for cellulose triacetate photographic film in (——) dry, (– – – –) 100% RH and (–·–·–) 1M acetic acid conditions at 50 (○, ×, □), 70 (⊗, +, ■) and 90°C (●, ⧖, ⊠).

Figure 8.3



Absorbance at 222 nm versus oven ageing time (h) for cellulose triacetate photographic film in (——) dry, (- - - -) 100% RH and (-·-·-) 1M acetic acid conditions at 50 (○, ×, □), 70 (⊗, +, ■) and 90°C (●, ⧗, ⊠).

Figure 8.4

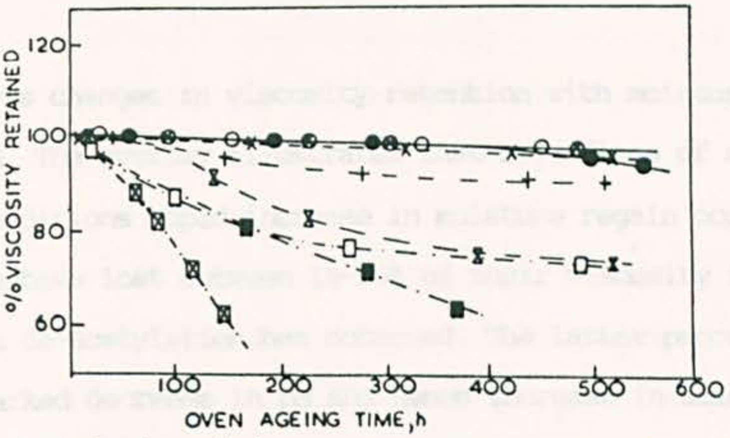


Apparent acetyl versus oven-ageing time (hrs) for cellulose triacetate photographic film in (●) dry; (⧗) 100% RH and (-⊠-) 1M acetic acid conditions at 90°C.

Figure 8.4 gives changes in apparent acetyl content under dry, 100% RH and molar acetic acid conditions. The data support that in Figure 8.3, i.e. the acetyl content of the cellulose triacetate support material is undergoing only a minimal decrease, even when exposed to relatively severe degradation conditions. Typically, the acetyl content of cellulose triacetate is 44.8 and that of cellulose diacetate is 34.9 [8.1]. Although the polymer is undergoing a lowering of degree of substitution of acetate groups, it is not going from a triacetate to a 'true' diacetate. This is further supported by the observation that if severely degraded film (Sample 6, Table 8.1) is refluxed firstly in dichloromethane/ methanol only a small percentage of film material is solubilised. If the insoluble matter is then extracted in acetone this material is also only partly soluble. This would suggest that successive fractions correspond to regions of the material which are tri- and di- substituted.

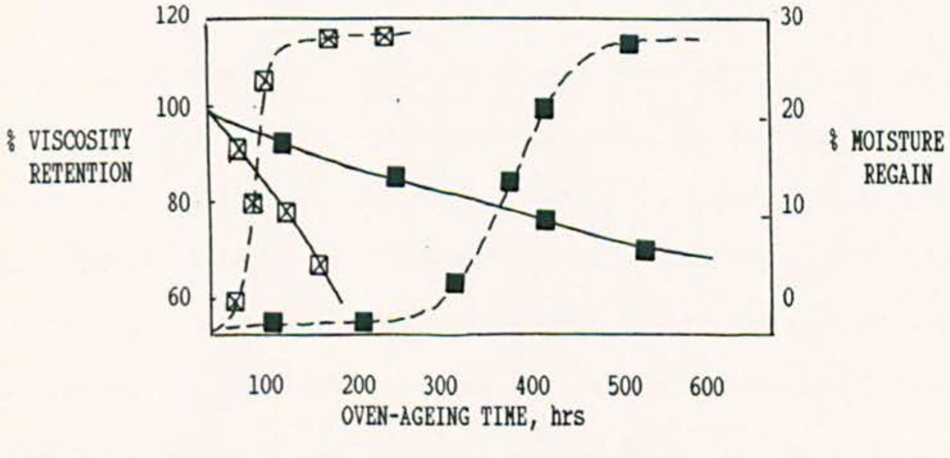
Viscometric data is presented in Figure 8.5. In molar acetic acid conditions film rapidly loses around 20% viscosity at 90°C. Compared to this in dry conditions, at all temperatures investigated, support viscosity is sensibly retained. As stated earlier viscometric data may be considered to be an indicator of both de-acetylation and chain-scission. Since a lowering of degree of substitution results in a lowering of ring molecular weight (see chapter 4) then solution viscosity will decrease. Furthermore, loss of acetate functionality will result in conformational changes in the polymer; again this will result in a decrease in solution viscosity. Thus, it is not possible by viscometric means to to make the distinction between changes which may

Figure 8.5



Percentage viscosity retained versus oven ageing time (h) for cellulose triacetate photographic film in (———) dry, (- - - -) 100% RH and (-·-·-) 1M acetic acid conditions at 50 (○, ×, □), 70 (⊗, +, ■) and 90°C (●, ⧖, ⊠).

Figure 8.6



Percentage viscosity retention (—) and percentage moisture regain (--) versus oven-ageing time (hrs) for cellulose triacetate photographic film at 90°C under ■ : 100% RH and ⊠ : 1M acetic acid conditions.

occur due to lowering of molecular weight via chain-scission and those which may occur due to de-acetylation. The problem is further complicated by the fact that as samples degrade they become progressively more insoluble in the solvent system used for viscometric determinations.

Figure 8.6 compares changes in viscosity retention with moisture regain in the same graph. The overlay illustrates that regardless of severity of degradation conditions rapid increase in moisture regain occurs only after the samples have lost between 15-20% of their viscosity i.e. after significant de-acetylation has occurred. The latter process is indicated by a marked decrease in pH and hence increase in acidity of the materials.

8.2 Cross-Sectional Analysis

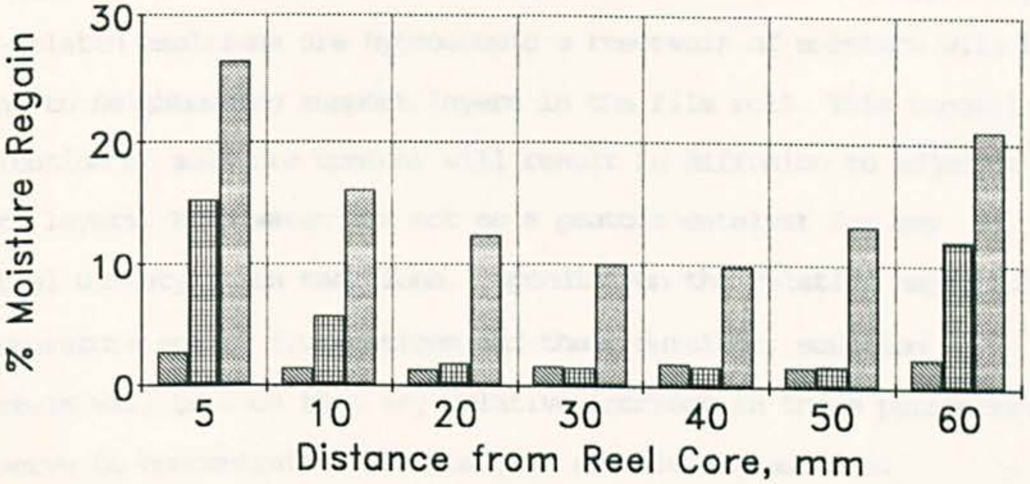
All the results in section 8.1 were obtained using samples which were strips of film taken from the same recently manufactured and processed reel. Archives, on the other hand, store film as 1000′ strips wound tightly into reels. Here the film is essentially a sandwich of emulsion and support layers. The next stage of the study was thus to emulate film breakdown when stored as reels.

The bar chart in Figure 8.7 depicts results for analysis of moisture regain across the radius of the film reel. Moisture regain is higher at the reel core and outer circumference of the film; the effect becoming more marked with more severely degraded films.

A similar pattern is evident from accelerated ageing data presented again for moisture regain in Figure 8.8. Here outer parts of the reel exhibit a more rapid onset of increase in moisture regain compared to other sections of the reel.

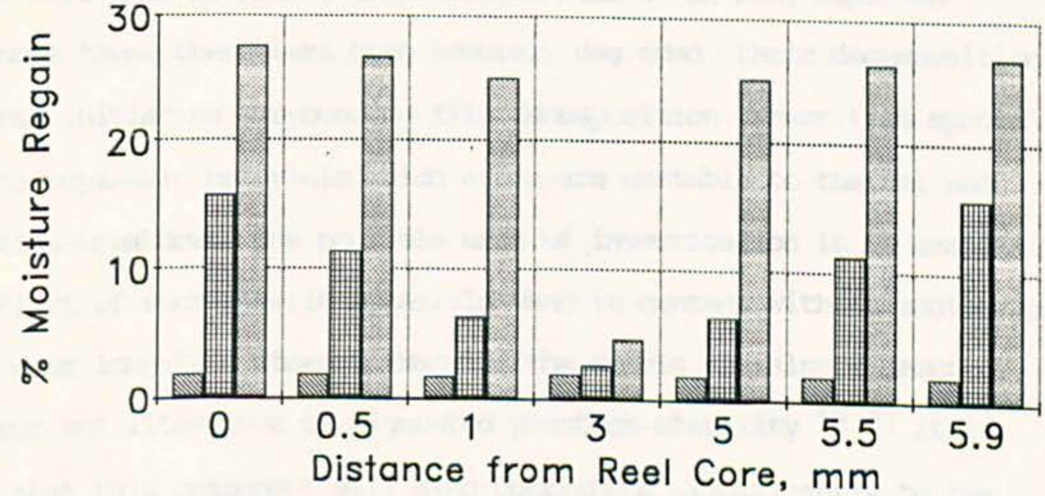
In the case of outer sections of the reel, this part of the reel is one which is in close contact with immediate surroundings. Diffusion of moisture and oxygen will occur much more readily to areas in contact with the enveloping atmosphere. Correspondingly, ready loss of acetic acid to the environment will occur operating in favour of further acid release; consequently, shifting any de-esterification reaction in the direction of degradation. Inner sections of the reel will be protected to a degree by their surrounding counterparts. Thus, a moisture

Figure 8.7



Percentage moisture regain versus sample distance from reel spool (core) for naturally-aged 35mm cellulose triacetate films which are ▨ :relatively new; ▦ :exhibiting acetic acid odour and ▩ :degraded.

Figure 8.8



Percentage moisture regain versus sample distance from reel spool (core) for artificially-aged 35mm cellulose triacetate films which have been aged for ▨ : 50; ▦ : 200 and ▩ :400 hours at 90°C and 100% RH.

gradient is established in both the length and width directions of wound 'roll'cinematograph film. The moisture content of the film will tend towards redistribution until an equlibrium is attained. Typically, since gelatin emulsions are hygroscopic a reservoir of moisture will be present to neighbouring support layers in the film roll. This unequal distribution of moisture content will result in diffusion to adjacent support layers. Here water can act as a protoic catalyst for any potential deacetylation reactions. Depending on the relative magnitude of temperature and RH fluctuations and their duration, sorption hysteresis will be such that any relative increase in these parameters will serve to concentrate such catalysts and aid degradation.
The final result being that film reels exhibit more degradation at their exposed surfaces and that this decomposition gradually 'grows' into inner sections of the reel.

The higher moisture regain with sections of film close to the reel core may be associated with the presence of the plastic spool. Earlier spools were made of phenol-formaldehyde resins; in many reported instances these themselves have severely degraded, their decomposition products initiating surrounding film decomposition. Newer film spools are thermoplastic materials which again are unstable to thermal and oxidative breakdown. One possible area of investigation is to examine the effect of such plastic materials when in contact with cinematograph films over long-term storage. Many of the spools are also pigmented; from current literature on pigmented plastics stability [8.2] it is known that this component will also contribute significantly to the stability of the polymeric matrix within which it is contained.

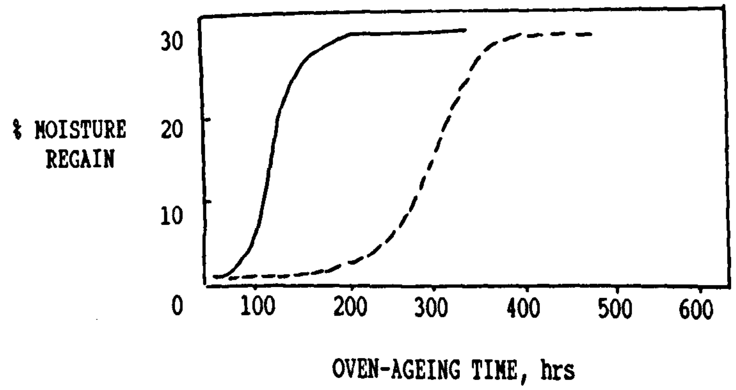
8.3 Influence of Emulsion Layer on Support Stability

Since film material is a composite of both emulsion and support layers possible interaction between the two cannot be disregarded. Several features were examined in this respect.

Films were aged firstly with and without emulsion layers to assess the effect of this component. Results are depicted in Figure 8.9 and 8.10 for moisture regain and viscosity retention versus oven-ageing time respectively.
Secondly, a comparison between negative and positive 35mm cinematograph materials was undertaken. Full analysis data is represented in Table 8.3 for films aged at 90°C and 100% RH.

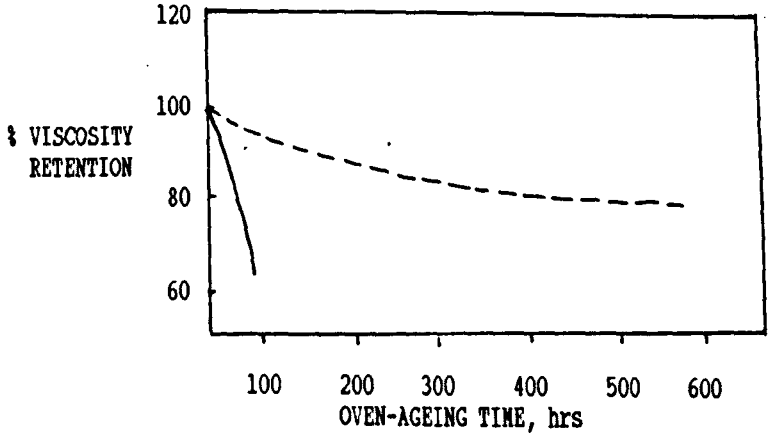
Apart from their obvious image characteristics negative and positive film materials differ in the thickness of the emulsion layer; in the order negative > positive. As Table 8.3 depicts, this has an influence on the degradation rate of the material. Over a period of 400 hours, the viscosity decrease is more marked for positive than negative film; this difference is consistent with a higher increase in moisture regain and in insoluble polymer material for the former. Deacetylation as measured by decrease in uv absorption at 222nm is also greater for the positive film, but the pH decreases at the same rate.
In addition Figures 8.9 and 8.10 show that for both physical parameters assessed, the presence of an emulsion layer serves to retard onset of degradation.

Figure 8.9



Percentage moisture regain versus oven-ageing time (hrs) for cellulose triacetate base cinematograph film in contact with metal can --: with and —: without an emulsion layer at 90°C and 100% RH.

Figure 8.10



Percentage viscosity retention versus oven-ageing time (hrs) for cellulose triacetate base cinematograph film in contact with metal can --: with and —: without an emulsion layer at 90°C and 100% RH.

Table 8.3

Degradation Effects on Negative and Positive 35mm Cellulose Triacetate Films Oven-Aged at 90°C and 100% RH

	Negative Film				Positive Film			
	Oven Ageing Time, hr							
	0	100	200	400	0	100	200	400
Viscosity Retained (%)	100	100	98	88	100	97	92	82
Moisture Regain (%)	2.9	2.9	2.9	17.0	1.2	1.3	1.4	25.0
Insoluble Polymer (%)	4.0	6.0	12.0	56.0	4.0	8.0	14.0	64.0
Absorbance at 222 nm	0.13	0.13	0.13	0.10	0.13	0.13	0.12	0.09
pH	4.62	3.75	3.55	3.48	4.62	3.75	3.55	3.48

This 'protective' effect of the emulsion layer may be associated with a number of inherent features. The layer as a whole may be operating as an effective diffusion barrier, both to components entering the film support and to loss of support additives, such as plasticiser (see section 8.4). The major constituent of the emulsion layer, gelatin, may also be operating (due to the amphoteric nature of its constituent amino acids) as an acid scavenger. It follows that the thicker this emulsion layer the more effective an acid 'mop' it will be; as reflected by the differences in stability between negative and positive materials. The tendency to thinner emulsion coatings in modern cinematograph materials can be seen therefore as a negative aspect of film stability.

8.4 Influence of Plasticisers

A significant feature of the degradation of cellulose triacetate support film, is the presence of white crystalline deposits on the surface (Figure 8.11). Analysis, by infra-red, showed this to be triphenyl phosphate, i.e. a component of base plasticiser (Figure 8.12). Quantities of plasticiser were also extracted from the film base after removal of any surface deposits (Figure 8.13). In both cases there was no evidence for the hydrolysis of this component.

Furthermore, all other infra red spectra (see section 8.8) which analyse base after plasticiser extraction, show no evidence of P-OH formation in the non-extractable, bound plasticiser; and hence no plasticiser hydrolysis. It is inferred that any surface plasticiser deposits result from migration of this component as it becomes increasingly incompatible with the degraded polymer. In the light of this information studies were undertaken to examine the conditions leading to plasticiser loss. The results in Table 8.4 summarize the effects of plasticiser on the moisture regain and viscosity retention of cellulose triacetate film during oven ageing at 90°C and 100% RH.

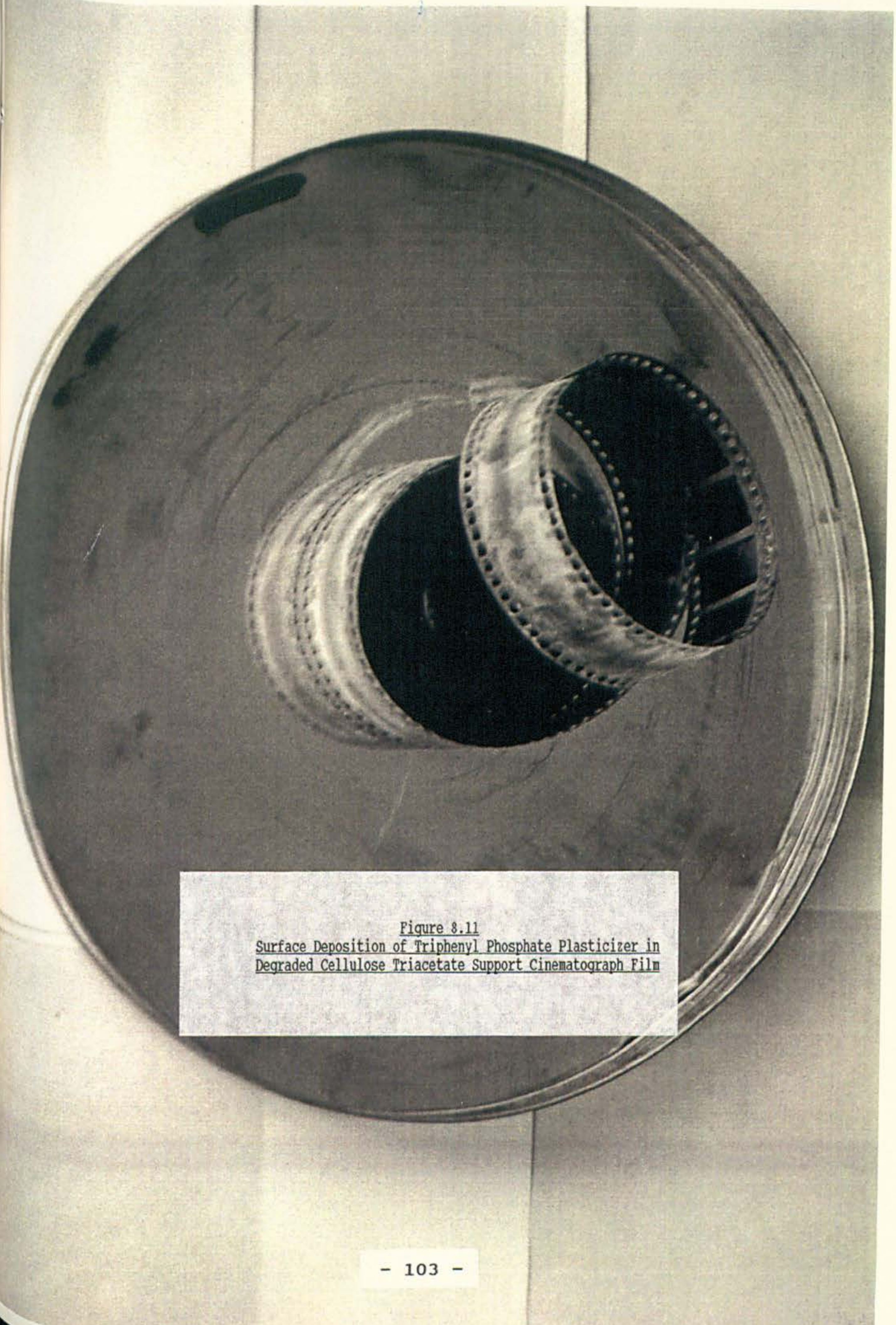
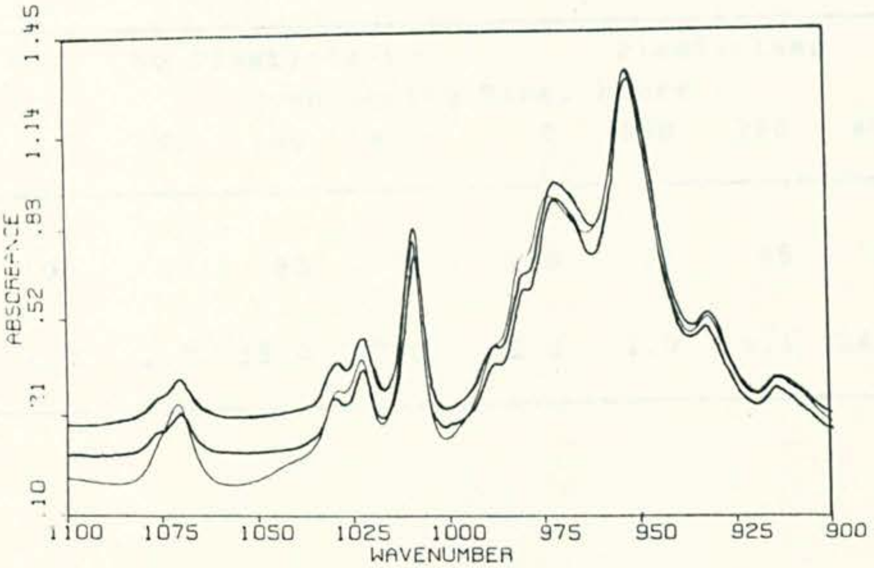


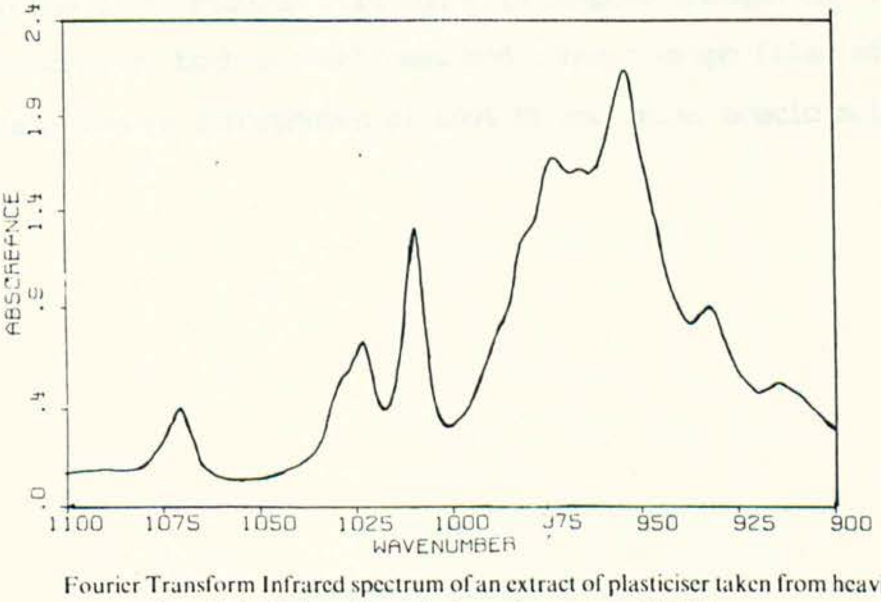
Figure 8.11
Surface Deposition of Triphenyl Phosphate Plasticizer in Degraded Cellulose Triacetate Support Cinematograph Film

Figure 8.12



Fourier Transform Infrared spectra of the white crystalline deposits taken from the surface of heavily degraded, naturally aged cellulose triacetate base cinematographic film.

Figure 8.13



Fourier Transform Infrared spectrum of an extract of plasticiser taken from heavily degraded cellulose triacetate base cinematographic film.

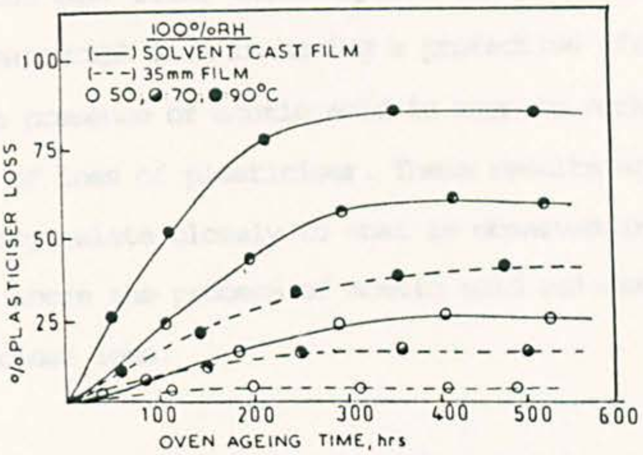
Table 8.4

Degradation Effects on Unplasticised and Plasticised Cellulose Triacetate Cinematograph Films at 90°C and 100% RH

	No Plasticiser				Plasticiser			
	Oven Ageing Time, hours							
	0	100	200	400	0	100	200	400
Viscosity Retained (%)	100	85	80	75	100	91	85	80
Moisture Regain (%)	1.3	2.0	15.0	27.0	1.3	2.0	5.1	26.5

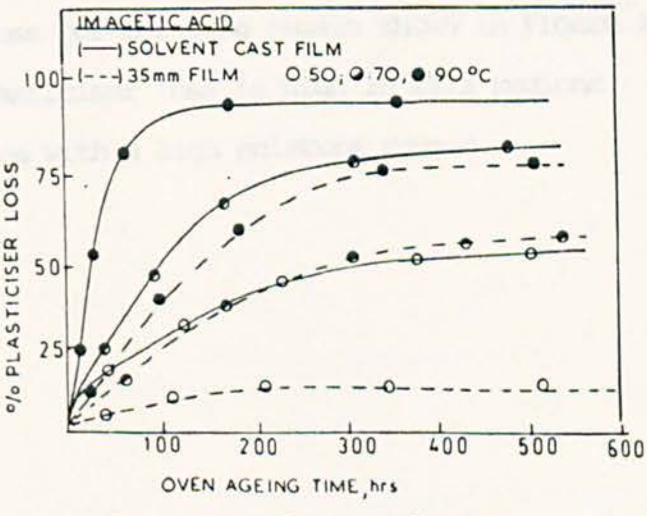
It is seen that moisture regain is markedly inhibited by the plasticiser and this is consistent with a better retention of viscosity. The plasticiser is therefore imparting some degree of protection to the film. Figures 8.14 and 8.15 compare changes in plasticiser content of both solvent cast and cinematograph films at various temperatures in atmospheres of 100% RH and molar acetic acid respectively.

Figure 8.14



Percentage plasticizer loss versus oven ageing time in hours for (_______) solvent cast and (------) 35 mm cellulose triacetate films at ○: 50; ○: 70 and ●: 90°C in 100% RH.

Figure 8.15

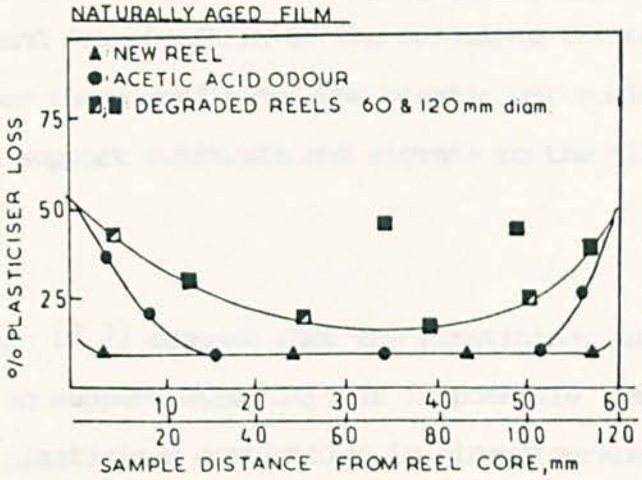


Percentage plasticizer loss versus oven ageing time in hours for (_______) solvent cast and (------) 35 mm cellulose triacetate film at ○: 50; ○: 70 and ●: 90°C in 1 molar acetic acid.

As might be expected rate of loss of plasticiser follows the order 90 > 70 > 50°C in both atmospheres. More significantly, the rate is greater in the case of solvent cast film, which implies that the emulsion layer in the case of cinematograph film is having a protective effect on the polymer support. The presence of acetic acid is seen to markedly accelerate the rate of loss of plasticiser. These results are interesting since they relate closely to what is observed in practical archival situations where the process of acetic acid release is a precursor to plasticiser loss.

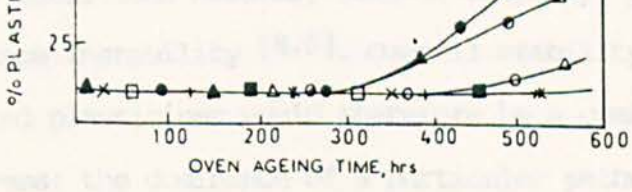
Figure 8.16 compares the loss of plasticiser in naturally-aged film reels. The results are consistent with the effects of cross-sectional analysis discussed previously. In this case plasticiser loss is greatest at the spool core and outer layer of the film. These results are in agreement with those for the same film samples shown in Figure 8.7. Figure 8.17 compares the effect of plasticiser loss from film samples taken from different regions of the film reel. The results are in agreement with those for moisture regain shown in Figure 8.7; and clearly show that plasticiser loss is high in film regions corresponding to those with a high moisture regain.

Figure 8.16



Percentage plasticizer loss versus sample distance from reel spool (core) for 35 mm cellulose triacetate films which are ▲: relatively new; ●: giving acetic acid odour and □; ■ degraded 60 and 120 mm in diameter respectively.

Figure 8.17



Percentage plasticizer loss versus oven ageing time in hours for film samples taken at ●: 0.1; ○: 0.5; ○: 1.0; □: 1.5; X: 2.0; *: 3.0; +: 4.0; ■: 4.5; △: 5.0; △: 5.5 and ▲: 5.9 mm from the reel spool (core) at 90°C in 100% RH.

On the whole, plasticiser loss appears to be dominant in regions of the film reel which are in contact with the environment. In these regions it would appear that diffusion/migration of plasticiser is associated more with hydrolysis and deacetylation of the cellulose triacetate support material. Under these conditions the plasticiser would be incompatible with the support substrate and migrate to the film surface and crystallize out.

However, Studies by Ram [8.3] suggest that the plasticiser has a destabilising effect on support stability. It is possible that as the more volatile of the plasticiser combination in cinematograph film is lost (i.e phthalate ester; see section two) film is rendered less stable to degradation. If this were the case 'pockets' would be created rendering the film more susceptible to moisture and oxygen diffusion and attack. During the course of degradation as triphenyl phosphate is lost this process would be enhanced. However, the triphenyl phosphate component of the plasticiser combination when present may act as an agent to complex any metal ions participating in the degradation. Indeed this has been observed with phosphate/phosphite systems in other polymers [8.4]. This latter process would serve to retard any oxidative degradation pathways which may occur in the presence of metal ions. In the absence of any metal ions however, loss of triphenyl phosphate would be seen to enhance instability [8.5]. Overall stability with respect to incorporated plasticiser would therefore be a combination of such competitive process; the dominance of a particular pathway being dependent upon external environmental parameters.

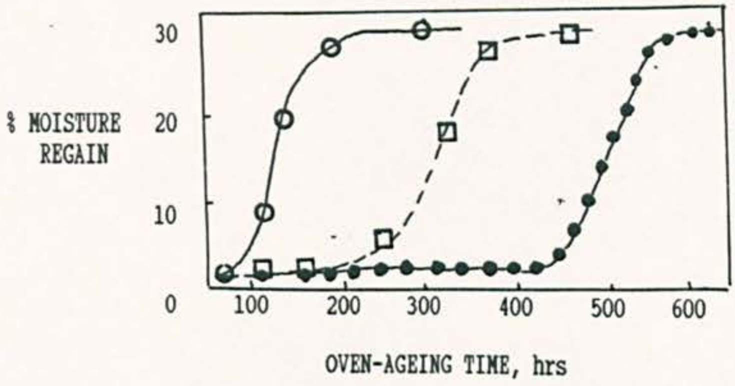
8.5 Influence of Metal Ions

The data in Table 8.1, for naturally-aged film samples, indicate that as both viscosity retention decreases and moisture regain increases, the iron content of film samples increases. From these results it is difficult to determine if iron is a contributor to degradation pathways in cellulose triacetate, or whether it is merely a feature of facile uptake as the film material becomes progressively more hygroscopic. However, subsequent results from artificially aged film samples suggest this is not the case. Figures 8.18 and 8.19 show that for film aged in contact with metal containers, the degradation rate as measured by both moisture regain and viscosity retention is markedly increased in comparison to film aged in contact with glass containers. Furthermore, it can be seen that the presence of an emulsion layer acts to retard decomposition.

Figures 8.20 and 8.21 illustrate photographically films aged with and without an emulsion layer in contact with glass and metal containers respectively at 90°C and 100% RH for the same time period. The results are self-evident.

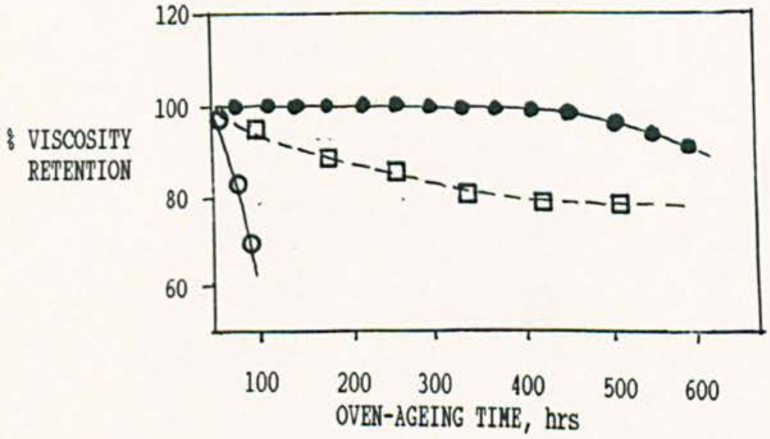
To consolidate these findings, studies on the incorporation of iron into solvent cast films at concentration levels of 5, 10, 20, 50, 100 and 200ppm were undertaken. Results, as presented in Figures 8.22 and 8.23, affirm the implication that iron is a significant contributor to the degradation.

Figure 8.18



Percentage moisture regain versus oven-ageing time (hrs) for cellulose triacetate base cinematograph film in contact with metal can -□-: with and -⊖-: without an emulsion layer and in contact with glass container -●-: with emulsion layer at 90°C and 100% RH.

Figure 8.19

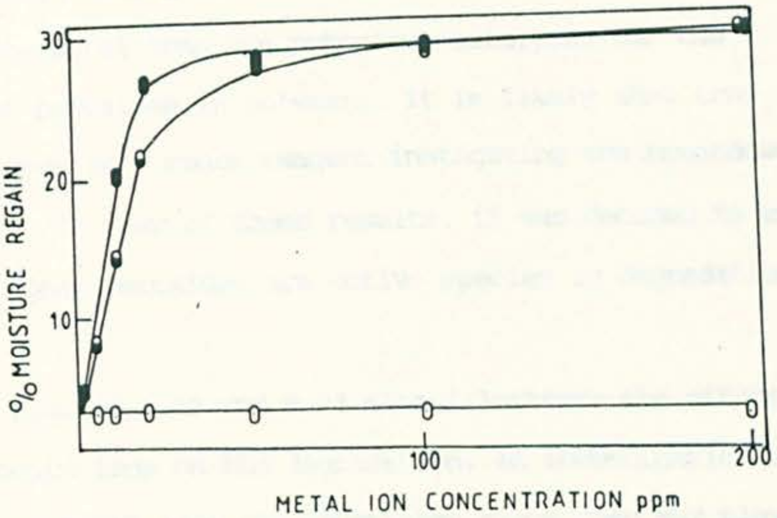


Percentage viscosity retention versus oven-ageing time (hrs) for cellulose triacetate base cinematograph film in contact with metal can -□-: with and -⊖-: without an emulsion layer and in contact with glass container -●-: with emulsion layer at 90°C and 100% RH.

Figure 8.20
Cellulose Triacetate Support Cinematograph Film
Oven-Aged for 50 hours at 90°C and 100% RH
in Contact with Glass Container and Metal Can.

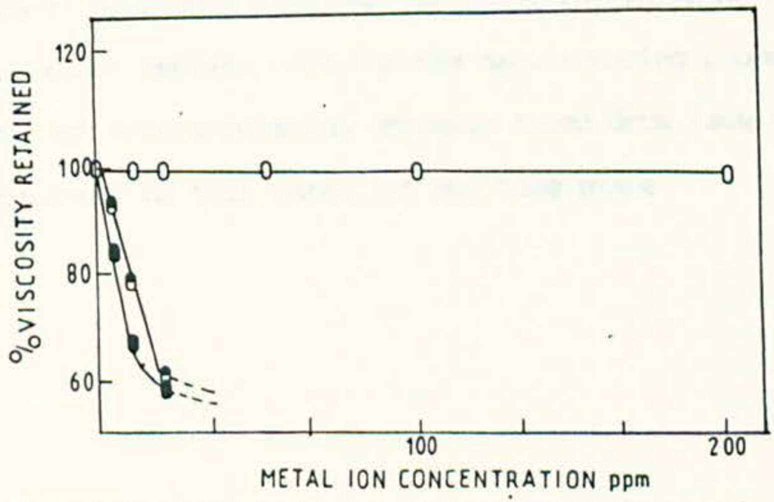
Figure 8.20
Cellulose Triacetate Support Cinematograph Film
Oven-Aged for 50 hours at 90°C and 100% RH
in Contact with Glass Container and Metal Can
with Emulsion Layer Removed.

Figure 8.22



Percentage moisture regain versus metal ion concentration (ppm) for solvent cast cellulose triacetate films (150 μm); ●, iron; ◒, chromium; ○, silver.

Figure 8.23



Percentage viscosity retention versus metal ion concentration (ppm) for solvent cast cellulose triacetate films (150 μm); ●, iron; ◒, chromium; ○, silver.

Up to concentrations of 10-20ppm iron, a marked increase is seen in moisture regain (Figure 8.22) with a corresponding rapid decrease in viscosity retention (Figure 8.23). At higher concentrations there is little further change. It is evident that only trace quantities are necessary to bring about an accelerated breakdown of the cellulose triacetate. Since metal ions are notorious catalysts for the decomposition of peroxides in polymers, it is likely that iron is acting in this case as a redox reagent instigating the breakdown of active peroxides. In view of these results, it was decided to examine the implication that peroxides are active species in degradation (see section 8.8).

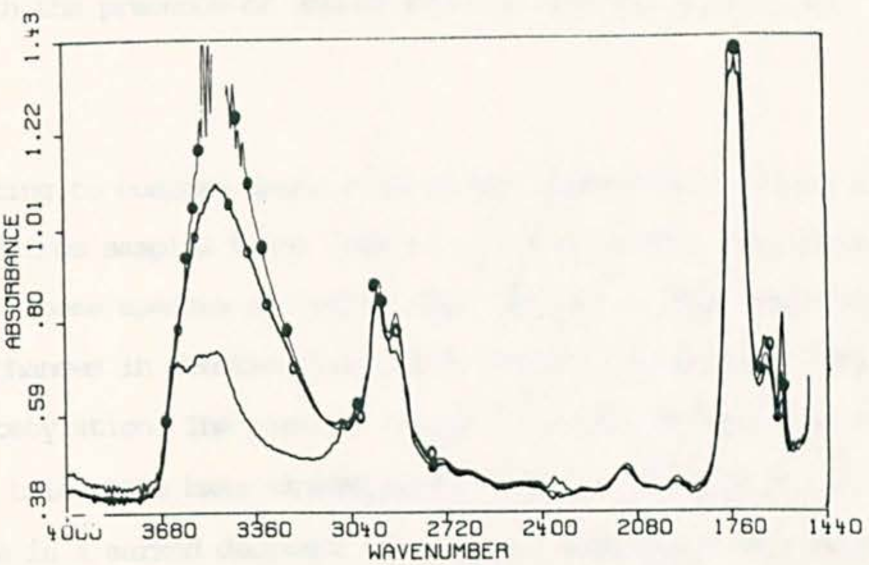
The results in Figures 8.22 and 8.23 also illustrate the effect of silver and chromium ions on the degradation. An investigation of these latter transition metal ions was undertaken since they may play a significant role in film stability; silver obviously is a major constituent of the emulsion layer and chromium may be picked up during the manufacturing process. Silver itself apparently has a negligible effect on film stability, but chromium on the other hand has a detrimental effect comparable with that of iron. The influnce of chromium has important implications for the manufacturing process since film support is cast onto a rotating chromium faced drum (see section 1.2.1) where 'pick-up' of this metal ion may take place.

8.6 Infra-Red and NMR Analysis

Figures 8.24-8.26 illustrate FTIR spectra of both naturally and artificially aged (90°C at 100% RH) samples of cellulose triacetate cinematograph film base in the regions 4000-1440cm^{-1} (Figure 8.24) and 1200cm^{-1}-800cm^{-1} (Figures 8.25 and 8.26).

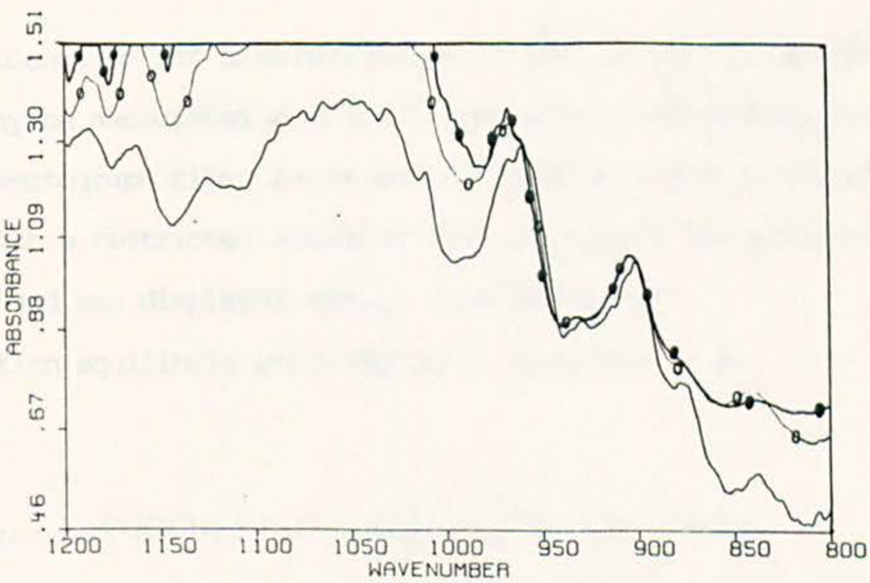
Figure 8.24 illustrates the infra-red spectra of samples of cellulose triacetate base film in the region 4000-1440 cm^{-1} for control and naturally aged materials showing strong signs of acetic acid release. There are noticeable changes in the hydroxyl region at 3360 cm^{-1}, especially for the film surface which lies in contact with the emulsion layer. This is evidently due to the uptake of moisture, which would be expected to be higher in concentration on the emulsion side of the film. In addition to this there are changes in the alkyl stretching region (2800-3000 cm^{-1}) and also in the carbonyl region (1760 cm^{-1}). The most significant feature of the spectra are the relatively small changes which occur in both the latter regions. Any changes which have occurred are likely to be due to deacetylation and the relatively small differences signify relatively little change in this respect. However, infra-red analysis is relatively insensitive and any small changes in acetate content which occur may be masked by the greater absorption of those remaining in place. It should be noted however that the more sensitive technique of uv absorption spectrophotometry also indicated minimal changes in acetate content of the materials. Figure 8.25 shows spectra for the same sample in the region 1200-800cm^{-1}. No significant changes are apparent.

Figure 8.24



Fourier Transform Infrared spectra of cellulose triacetate base cinematographic films in the region 4000–1440 cm^{-1}. ———, Control before ageing and naturally aged film; ●, emulsion side of base; ○, non-emulsion side of base.

Figure 8.25

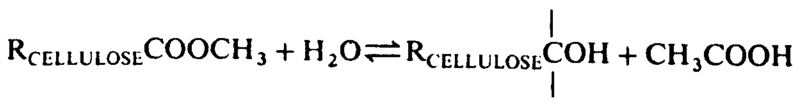


Fourier Transform Infrared spectra of cellulose triacetate base cinematographic films in the region 1200–800 cm^{-1}. ———, Control before ageing and naturally aged film; ●, emulsion side of base; ○, non-emulsion side of base.

However, Figure 8.26 for artificially aged film samples does exhibit changes in the region 1000cm^{-1}. Such changes are likely to be associated with the presence of unsaturation within the structure.

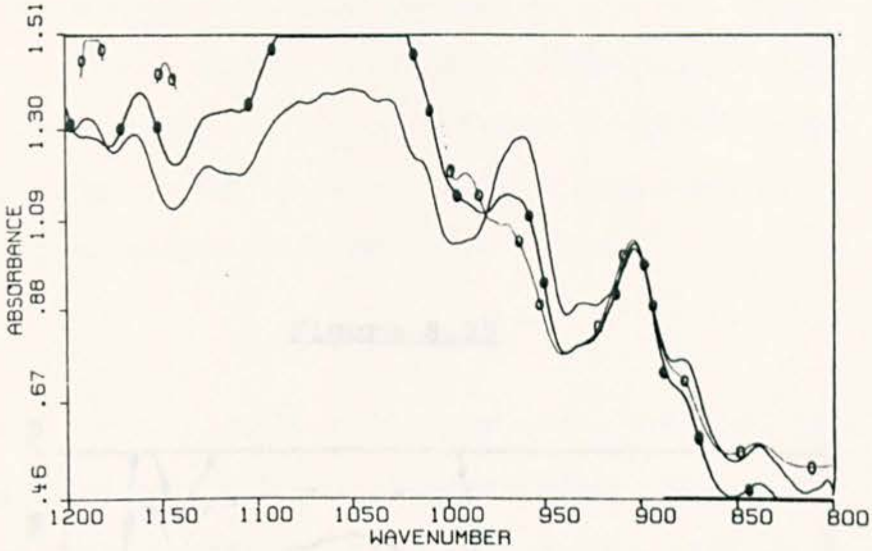
It is interesting to compare these results for cinematograph films with those obtained from samples taken from a cellulose acetate sculpture (Figure 8.27). These spectra are quite informative, in that they show quite marked changes in functionality. The changes are characteristic of marked deacetylation. The peak at 3360cm^{-1} is much broader than that for cellulose triacetate base cinematograph film in Figure 8.24. In addition there is a marked decrease in carbonyl absorption at 1760cm^{-1} along with corresponding changes in alkyl stretching region. Figure 8.28 shows no changes in the region 1000cm^{-1} which would be indicative of unsaturation.

A possible explanation for this difference in the quantity of acetate groups lost may be associated with the volume of air surrounding the material. Cinematograph films are stored in containers i.e. a closed environment with a restricted volume of free air-space. The sculpture on the other hand was displayed openly. Considering any de-esterification equilibria which may be in operation; i.e.



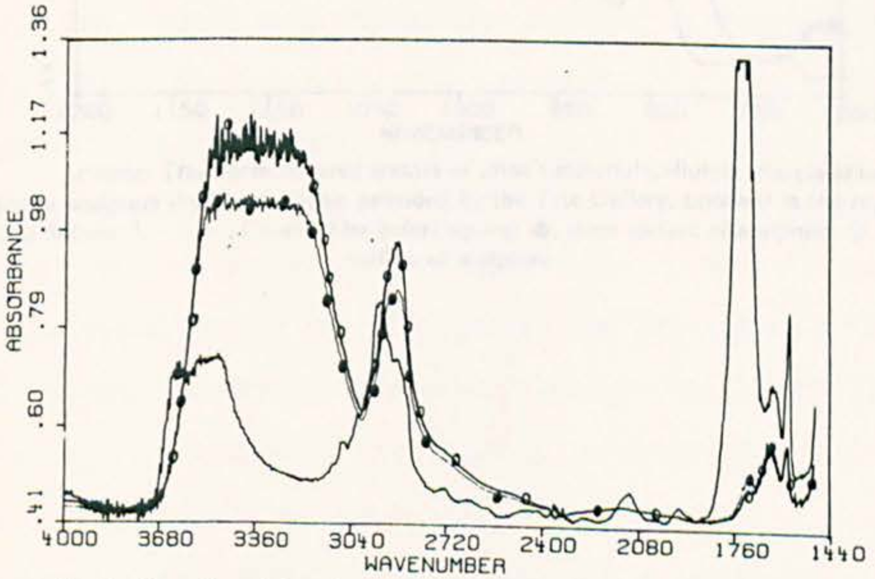
$$R_{CELLULOSE}COOCH_3 + H_2O \rightleftharpoons R_{CELLULOSE}\overset{|}{\underset{|}{C}}OH + CH_3COOH$$

Figure 8.26



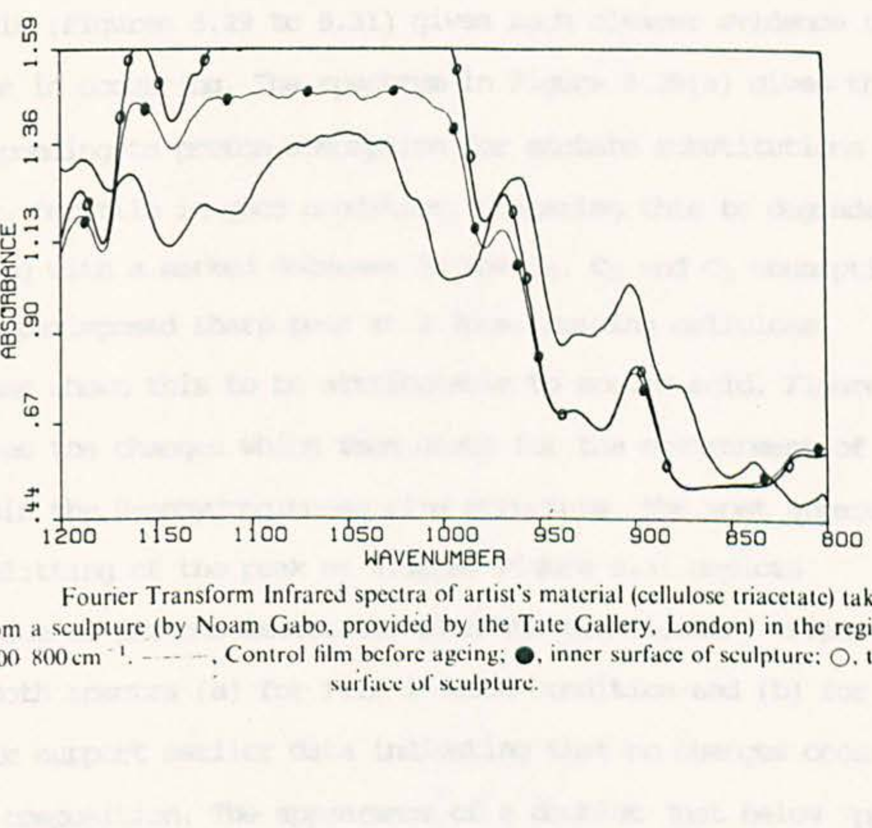
Fourier Transform Infrared spectra of cellulose triacetate base cinematographic films in the region 1200–800 cm^{-1}. ———, Control before ageing and artificially aged film; ●, emulsion side of base; ○, non-emulsion side of base at 90°C and 100% RH.

Figure 8.27



Fourier Transform Infrared spectra of artist's material (cellulose triacetate) taken from a sculpture (by Noam Gabo, provided by the Tate Gallery, London) in the region 4000–1440 cm^{-1}. ———, Control film before ageing; ●, inner surface of sculpture; ○, top surface of sculpture.

Figure 8.28

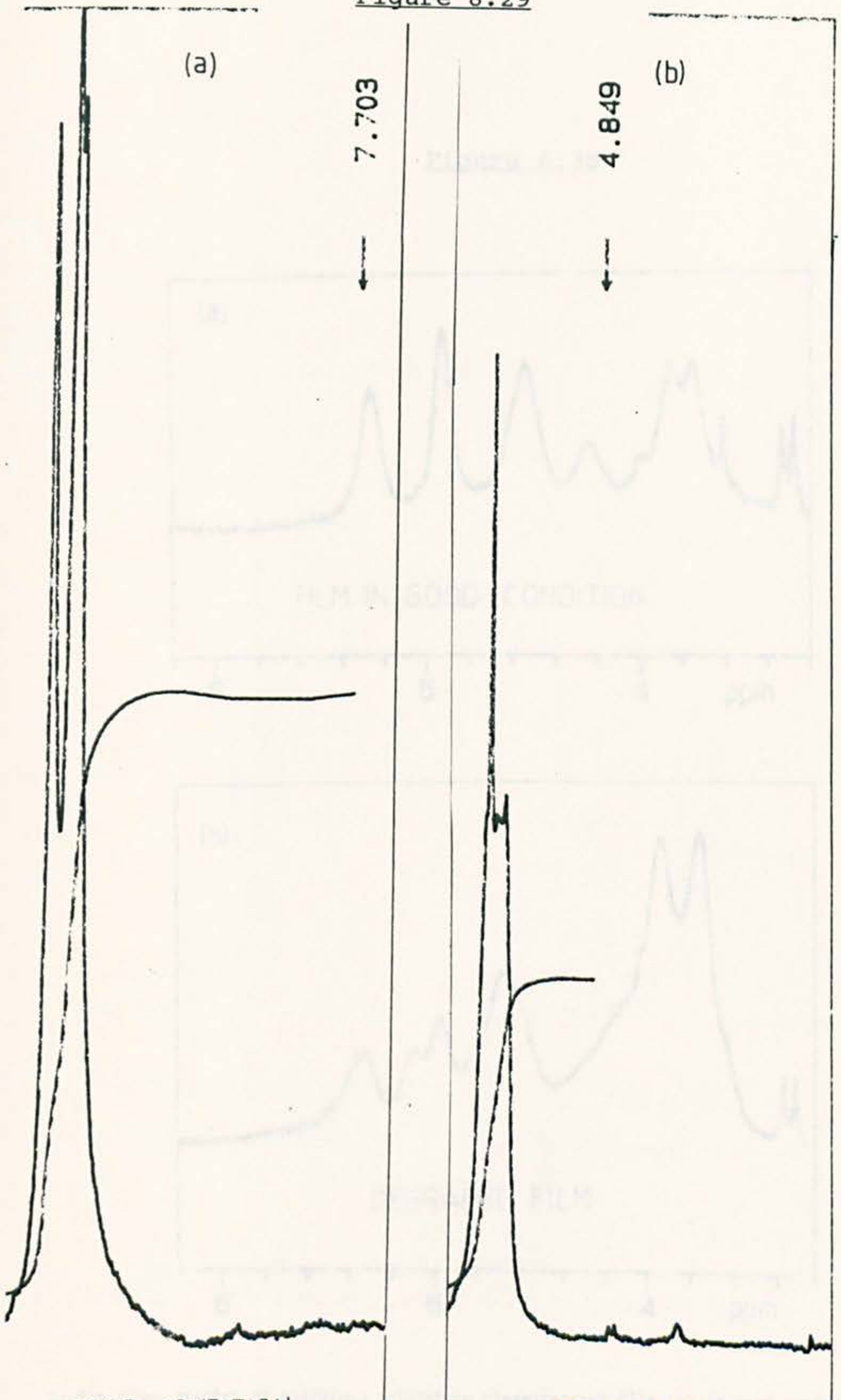


Fourier Transform Infrared spectra of artist's material (cellulose triacetate) taken from a sculpture (by Noam Gabo, provided by the Tate Gallery, London) in the region 1200–800 cm^{-1}. ------, Control film before ageing; ●, inner surface of sculpture; ○, top surface of sculpture.

the release and consequent build up of acetic acid within the closed environment of the cinematograph film will slow the rate of de-esterification; whereas continued release of acid to a large volume of circulating air will operate in favour of further loss. It is felt that this intercomparison was not too unreasonable since both the sculpture and cinematograph films are stored as bulk polymer; the cinematograph film being wound tightly into a reel.

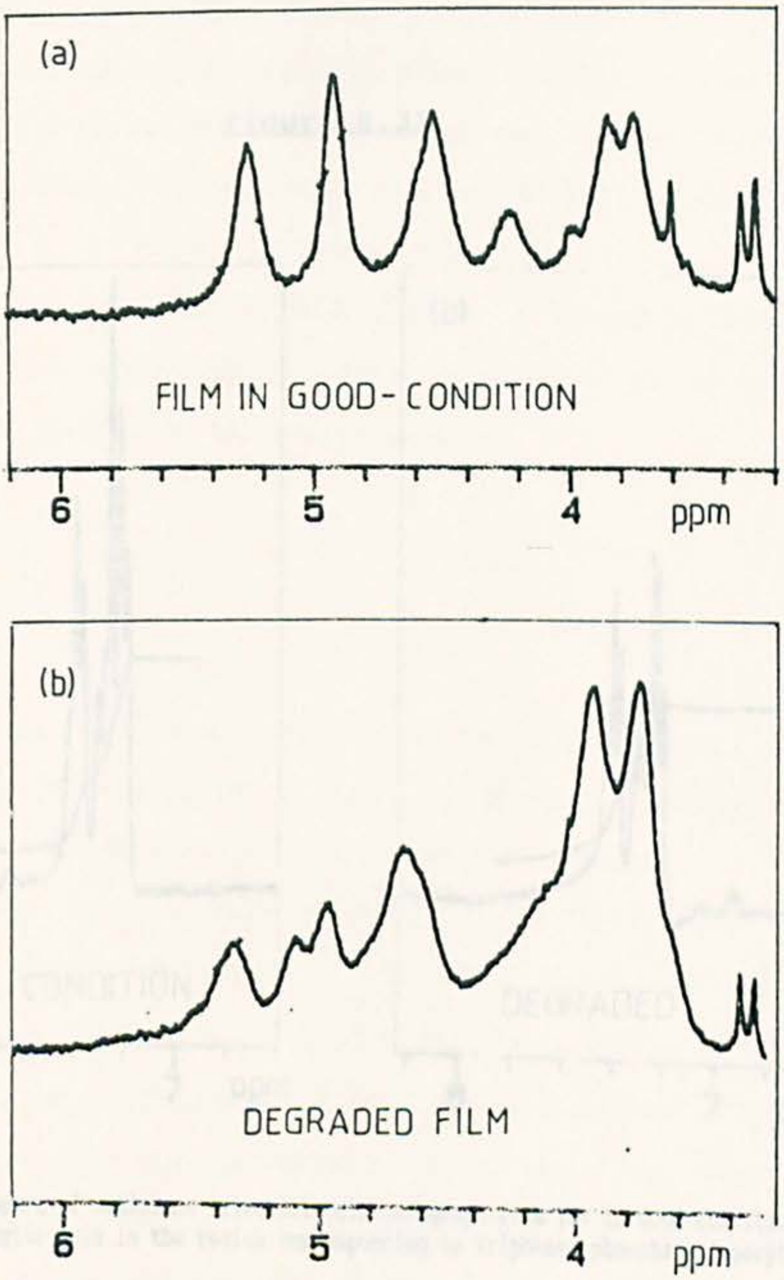
FTnmr analysis (Figures 8.29 to 8.31) gives much clearer evidence that deacetylation is occurring. The spectrum in Figure 8.29(a) gives the peaks corresponding to proton absorption for acetate substitutions at C_6, C_2 and C_3 for film in good condition. Comparing this to degraded material along with a marked decrease in the C_6, C_2 and C_3 absorptions there is a superimposed sharp peak at 2.2ppm. Spiking cellulose triacetate has shown this to be attributable to acetic acid. Figure 8.30 indicates the changes which thus ensue for the environment of protons within the ß-anhydroglucose ring structure, the most apparent being the splitting of the peak at 4.9ppm. Figure 8.31 depicts absorptions due to protons associated with the plasticiser, triphenyl phosphate. Both spectra (a) for film in good condition and (b) for degraded film support earlier data indicating that no changes occur in plasticiser composition. The appearance of a doublet just below 7ppm is indicative of the development of unsaturation. Although this was not detected by infra-red analysis for naturally-aged material as it was here. This supports the indication of development of unsaturation as shown for artificially aged material.

Figure 8.29



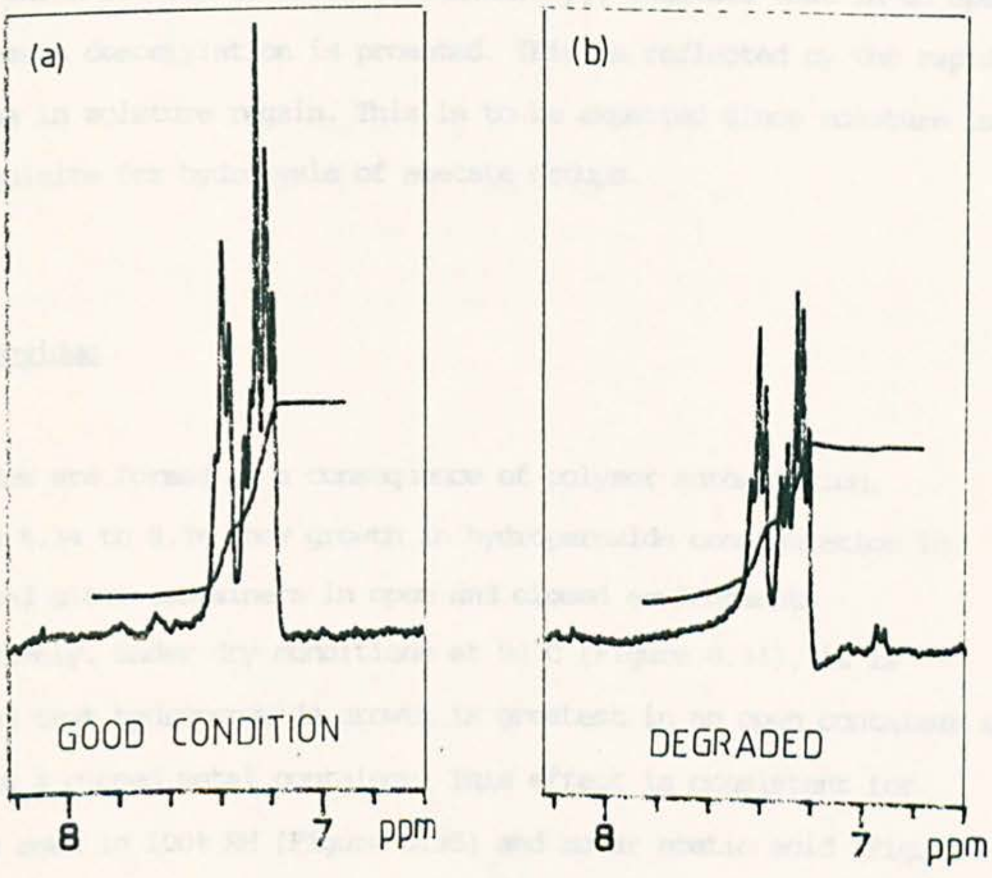
Proton FTnmr spectra of cellulose triacetate cinematograph film (a) in good condition and (b) releasing acetic acid in the region corresponding to acetate absorption.

Figure 8.30



Proton FTnmr spectra of cellulose triacetate cinematograph film (a) in good condition and (b) releasing acetic acid in the region corresponding ß-anhydroglucose ring structure.

Figure 8.31



Proton FTnmr spectra of cellulose triacetate cinematograph film (a) in good condition and (b) releasing acetic acid in the region corresponding to triphenyl phosphate absorption.

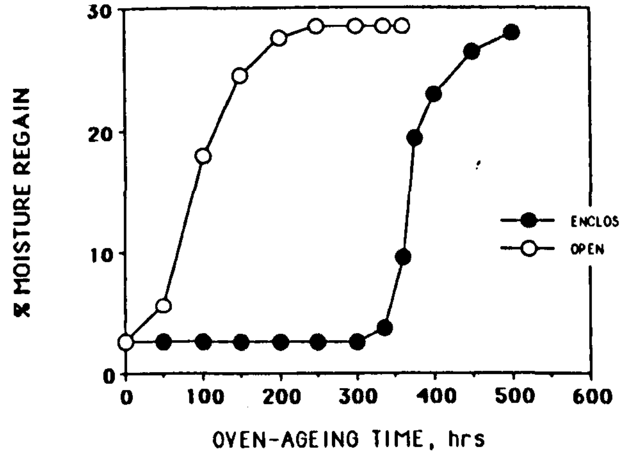
8.7 Open and Enclosed Environments

Additional analytical data on film conditioned in open and enclosed environments, supports earlier infra-red studies. Figure 8.32 graphs viscosity retention against oven-ageing time: It indicates that deacetylation and chain-scission are promoted when film is kept within an enclosed environment. In contrast a plot of moisture regain (Figure 8.33) (which relates to ester functionality), suggests that in an open environment deacetylation is promoted. This is reflected by the rapid increase in moisture regain. This is to be expected since moisture is a pre-requisite for hydrolysis of acetate groups.

8.8 Peroxides

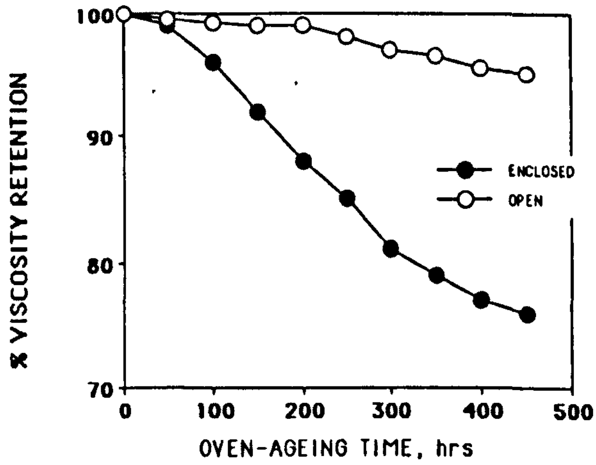
Peroxides are formed as a consequence of polymer autoxidation. Figures 8.34 to 8.36 show growth in hydroperoxide concentration in metal and glass containers in open and closed environments respectively. Under dry conditions at 90°C (Figure 8.34), it is observed that hydroperoxide growth is greatest in an open container and least in a closed metal container. This effect is consistent for samples aged in 100% RH (Figure 8.35) and molar acetic acid (Figure 8.36) conditions, but is more pronounced. In all cases the suppressed rate of hydroperoxide growth in an enclosed environment is evidently due to the rapid initial consumption of oxygen. In comparison oxygen equilibration would be maintained in an open environment. In the metal container reduced hydroperoxide growth may be taken to be associated

Figure 8.32



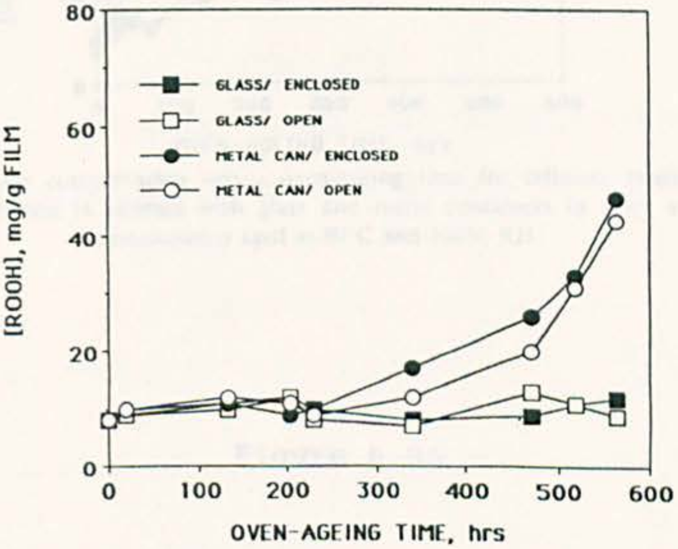
Percentage moisture regain versus oven-ageing time (h) for cellulose triacetate base cinematograph film in open and closed environments, oven-aged at 90°C and 100% RH.

Figure 8.33



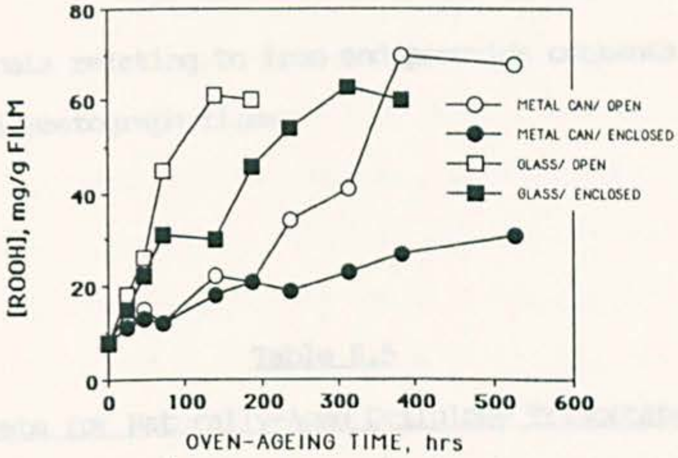
Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film in open and closed environments, oven-aged at 90°C and 100% RH.

Figure 8.34



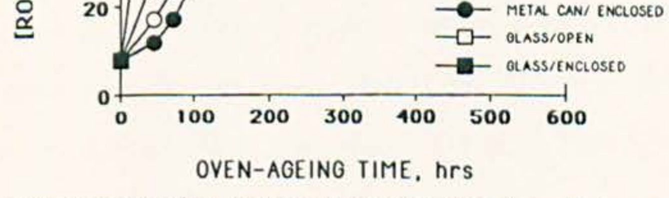
Peroxide concentration versus oven-ageing time for cellulose triacetate base cinematograph film in contact with glass and metal containers in open and closed environments aged at 90°C in dry conditions.

Figure 8.35



Peroxide concentration versus oven-ageing time for cellulose triacetate base cinematograph film in contact with glass and metal containers in open and closed environments aged at 90°C and 100% RH.

Figure 8.36



Peroxide concentration versus oven-ageing time for cellulose triacetate base cinematograph film in contact with glass and metal containers in open and closed environments aged at 90°C in a 1M acetic acid environment.

with an accelerated decomposition of this group induced by the catalytic activity of iron. This supports previous data on the influence of metal ions and further infers that peroxides are key initiators in the mechanism of main chain degradation.

Table 8.5 gives data relating to iron and peroxide contents for naturally-aged cinematograph films.

Table 8.5

Analytical Data for Naturally-Aged Cellulose Triacetate Support Cinematograph Films of Unknown Pre History Prior to Archival Storage

Sample	Appearance	[Fe] (μg/g)	[ROOH] (mg/g)
1	good	<1	<5
2	good	5.3	7
3	good	7.8	23
4	acetic acid odour	12.2	17
5	plasticiser deposit on film surface	16.8	<5
6	image loss	31.2	<5

The results in Table 8.5 are interesting compared to the results obtained by artifical ageing methods discussed previously. Firstly, they indicate that naturally-aged materials contain much lower levels of peroxides than do artificially-aged materials. All the ageing studies in this project have been performed at temperatures well below the Tg (glass transition temperature) of the polymer to minimize any effects which may come into play as a result of conformational changes and a more 'open' polymer network. However, at the higher temperatures oxidation will logically be more rapid and ease of oxygen diffusion will be enhanced by ready loss of any residual coating solvents or plasticiser. Peroxides are seen to build up in the polymer but are presumably quickly decomposed by the presence of iron which is apparently taken up by the polymer as it becomes progressively more degraded (see Table 8.1). Peroxide levels are lower in more severely degraded filmstocks, since an autocatalytic process is evidently occurring and by this stage most will have been converted. However, it should be stated that the data presented here requires corroboration from Electron Spin Resonance (ESR) studies which would confirm the presence of any free radicals resulting from peroxide decomposition.

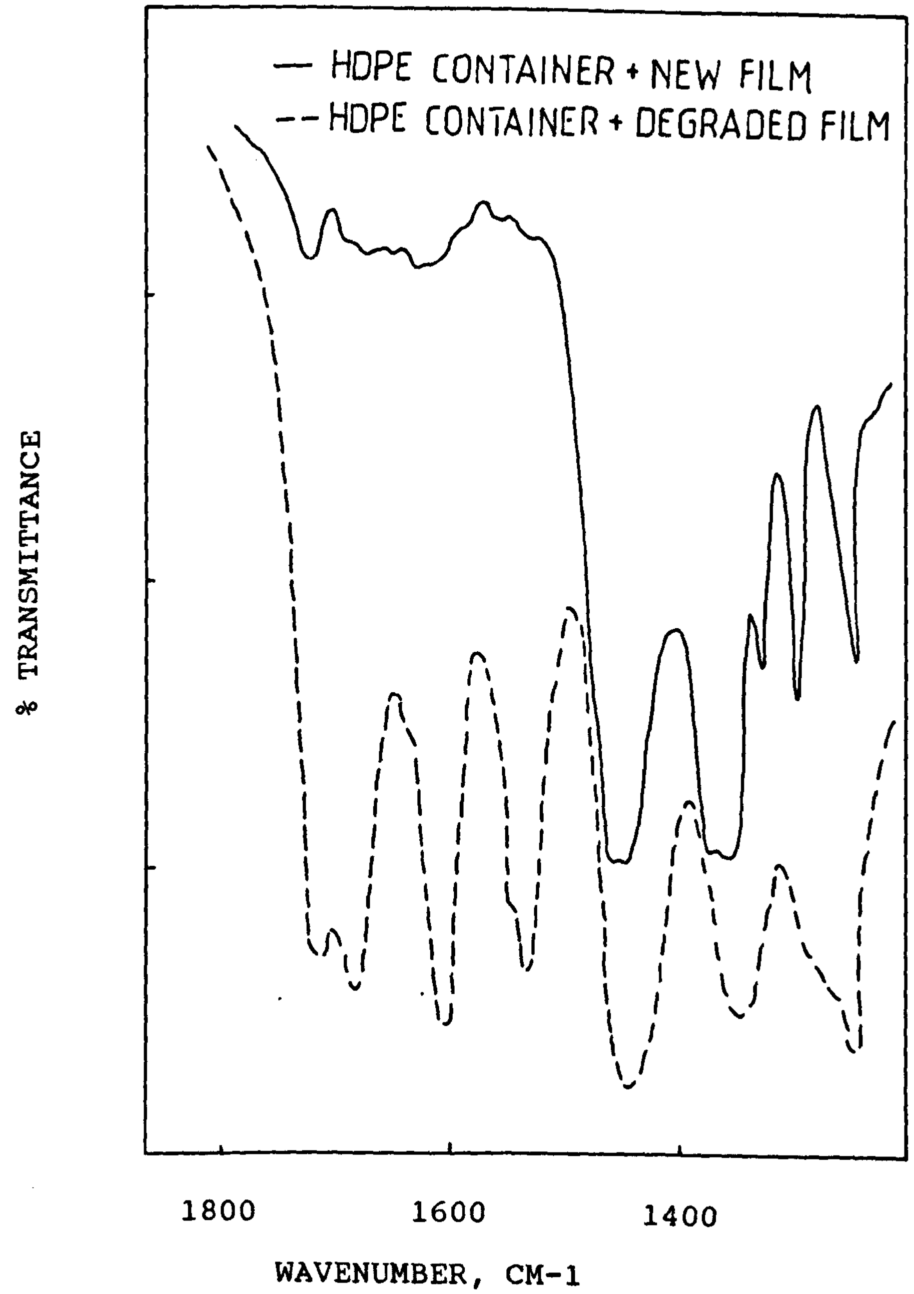
Carbonyl determinations were also attempted to complement the peroxide analysis. As stated in section 7.7.1 hydroxylamine was the reagent used to determine carbonyl content. Unfortunately the results were both difficult to reproduce and didn't seem to show any obvious relationship to other data. This may be due to a number of factors: the instability of hydroxylamine in solution; complexation with metal ions or reaction with any peroxy radicals.

8.9 Influence of Containers

It has already been stated that the metal container within which film reels are enclosed during storage will have a significant effect on the degradation characteristics. This is an important aspect of stability since the majority of cinematograph films are stored in tin-plated iron containers. However, a variety of other containers are also used. These include aluminium coated cans and a range of pigmented plastic containers. Film reels were thus aged in contact with tin-plated, aluminium coated, plastic and glass containers to effect a comparison. Results are illustrated in Figures 11.1 and 11.2 (section two) but the results essentially indicate the order of stability to be glass > plastic > aluminium-coated > tin-plated containers. In the case of the two metal cans it was observed that formation of acetic acid had served to erode the coating, thus exposing iron.

Plastic cans will themselves have their own degradation characteristics, which may influence or be influenced by the decomposition of the film materials they contain. The infra-red spectra in Figure 8.37 correspond to changes in the structural characteristics, on natural ageing, of a high density polyethylene (HDPE) container in contact with cellulose acetate support cinematograph film. In one of the spectra it can be seen that the surface of one can has heavily oxidised reflected by the growth in carbonyl absorption at 1700cm^{-1}.

Figure 8.37



Infra-red spectra of samples taken from the surface of HDPE containers in contact with — new and ---degraded cellulose triacetate cinematograph film reels respectively.

This particular can contained cellulose triacetate support cinematograph film which had degraded and was losing acetic acid. It is difficult to tell at this late stage whether or not the film is having a detrimental effect on its container or the container has initiated film breakdown. It should however be borne in mind that in the oxidative breakdown of the HDPE container the formation of carbonyl and carboxylic groups may act to sensitize film breakdown. Furthermore, studies have also shown that when two different plastics are in contact over long periods of time some inter-migration of additives occurs. Unfortunately, additives which are beneficial to one polymer may be detrimental to another i.e. most additive packages are specific to the polymer they were designed for.

Part two

Chapter 9

9. STABILITY TESTING

9.1 Introduction

The enormity of material to be transferred in copying programmes necessitates a method for prioritisation, with film materials of poorer condition being given precedence. In order to achieve this and so prevent loss of valuable material, archivists require an accurate, standardised scheme of surveillance, i.e. a predictive stability test. Ideally some method of temporary stabilisation would also be of benefit to extend available copying time (this is discussed in section three). Such objectives require an in-depth understanding of the mechanisms leading to the deterioration of filmstocks. To make accurate lifetime predictions regarding cinematograph film stability, or at least establish the limits of its stability, requires the generation of accelerated ageing tests, which alongside of real-life exposure tests, enable realistic lifetime predictions to be made.

Currently, effective lifetime prediction is in its infancy as a science. It is obvious that the small physico-chemical changes which occur during the early stages of ageing i.e during the induction period prior to the onset of degradation will be of prime importance with respect to subsequent stability. Any predictive stability test must monitor this induction stage effectively.

9.2 Requirements of Stability Testing

The quantity of material housed in archives dictates that any test must be simple and quick to perform;

To conserve valuable film it is essential that any method used must be applicable to small quantities which do not impair the usefulness of the film, or preferably be non-destructive;

Sampling error should be minimised so as to give highly reproduicible results; and sensitivity maximised to enable the small changes in the induction period to be measured quantitatively.

9.3 Current Stability Testing

At present there is no stability test available to archives for cellulose acetate filmstocks. Safety film is merely inspected at its location site for presence or absence of acetic acid odour.

9.4 Predictive Stability Testing:

9.4.1 The Arrhenius Approach

Application of the Arrhenius expression is common to follow polymer degradation reactions.

From classical kinetics, the rate of a first order reaction is;-

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

where k = the rate constant;
a = the initial concentration of the reactant;
x = the decrease of the reactant after time, t.

Using the Arrhenius approach this expression may be modified to express the above as a function of temperature. i.e.;-

$$\frac{d\ln k}{dt} = \frac{E}{RT^2}$$

where E = the activation energy;
R = the gas constant;
T = the absolute temperature.

Rate constants can thus be obtained at two or preferably more temperatures and a graph plotted of lnk versus 1/T. The straight line obtained indicative of a first order equation and this can then be extrapolated to the desired temperature.

Here versions adapted from classical kinetics allow extrapolation of high temperature ageing data to ambient conditions. However, care must be taken when interpreting data obtained from such relationships since errors may arise as a consequence of the following;-

Experimental error (testing technique);

Incubation conditions;

Number of data points;

Data processing (use of logarithmic scale for dependent variable).

9.4.2 Statistical Analysis

An alternative method of predicting film longevity would be to compile data of incidences of degradation in an analagous manner to the Horvath survey (see section 6.5). A large population of films could be sampled and incidences of degradation within a given sample be recorded. A statistical analysis could be performed to predict the number of films likely to be degraded in the total population. If the stock dates of films sampled were known and the general enviromental conditions under which they were kept (temperature, relative humidity) then the overall picture obtained would at least give an indication of the limits of stability of film materials which are stored in current archival conditions.

9.5 Film Characterization Approach

9.5.1 Microwave Technique

Since the moisture content of a given film material will be a feature of both the relative humidity of its surrounds and its condition, such parameters will (as previously mentioned) reflect upon stability.

A variety of techniques are currently available for determining moisture content in polymers [9.1]. These include oven-drying, Karl-Fischer and infra-red methods. While these techniques are undoubtedly useful in determining moisture they lack the sensitivity which is desirable to enable the induction period prior to degradation to be followed closely. One technique which has perhaps been neglected until recently in this respect is microwave spectroscopy; but this does afford excellent sensitivity. Microwave spectroscopy measures those changes which arise as a consequence of the rotation of a three dimensional body. A molecule possessing a permanent dipole moment appears to be a fluctuating dipole when it rotates and the observer is in the plane of rotation. The observer sees no fluctuating dipole if the molecule carries no permanent dipole. Therefore, only molecules with permanent electric dipole moments can absorb or emit radiation by making a transition between different states of rotation [9.2]. Water which is an asymmetric top molecule can thus absorb energy in the microwave region of the electromagnetic spectrum.

9.5.2 Thermal Analysis

Here the temperature dependence of some physical (or mechanical) property of the polymer is correlated to structure.

Differential scanning calorimetry is widely applicable since most physical processes involve either a change in heat content or heat capacity sufficiently large as to be detected; if carried out at a reasonably high rate. Thermal analysis can give information regarding rates of physical ageing, glass transition temperatures, crystallinity, thermal and oxidative decomposition kinetics and the effect of additive and processing conditions on polymer stability. Studies by Jain et al. [9.3] have examined the thermal decomposition of cellulose acetate by differential scanning calorimetry (DSC) and thermogravimetry (TG) from ambient temperatures to 450°C. They conclude that degradation occurs in three stages. The first stage is due to deacetylation, the second due to oxidative degradation and the third due to ring decomposition. Endotherms below 100°C were attributed to evaporation of moisture.

9.5.3 Colorimetric Analysis

Here chemical degradation products are detected by a reagent which develops colour or undergoes a colour change. This type of testing is analogous to that already undertaken by many archives for nitrate film materials; where rate of evolution of nitrogen oxides is measured as a function of their ability to decolourize paper impregnated with alizarin red. In the case of cellulose triacetate materials any colorimetric test should be aimed at measuring rate of acetic acid loss.

Chapter 10

10. EXPERIMENTAL

10.1 Arrhenius Testing

In the studies undertaken here, 'a' is taken as the initial physical property of the film e.g. viscosity retention, and 'a-x' as the property remaining after a given time, t.
Film reels were artificially aged in contact with glass, high density polyethylene, aluminium and tin-plated iron containers at a series of elevated temperatures (70, 80, 90, 100 and 110°C) in both 50 and 100% relative humidity conditions. Films were also aged at 100% RH with and without plasticiser and the emulsin layer. Samples were removed from the middle of the film reel for analysis. Time taken for a 10% loss in viscosity was then determined, since this was considered a particularly reliable indicator of film condition.

10.2 Statistical Analysis

Statistical methodology, sampling and analysis is described in the results and discussion in section 11.2 for convenience of data intercomparison.

10.3 Microwave Measurements

The Marconi 6500 automatic amplitude analyser was used for all determinations of moisture in this study. This instrument generates microwave frequencies, which pass through a connecting device e.g. a

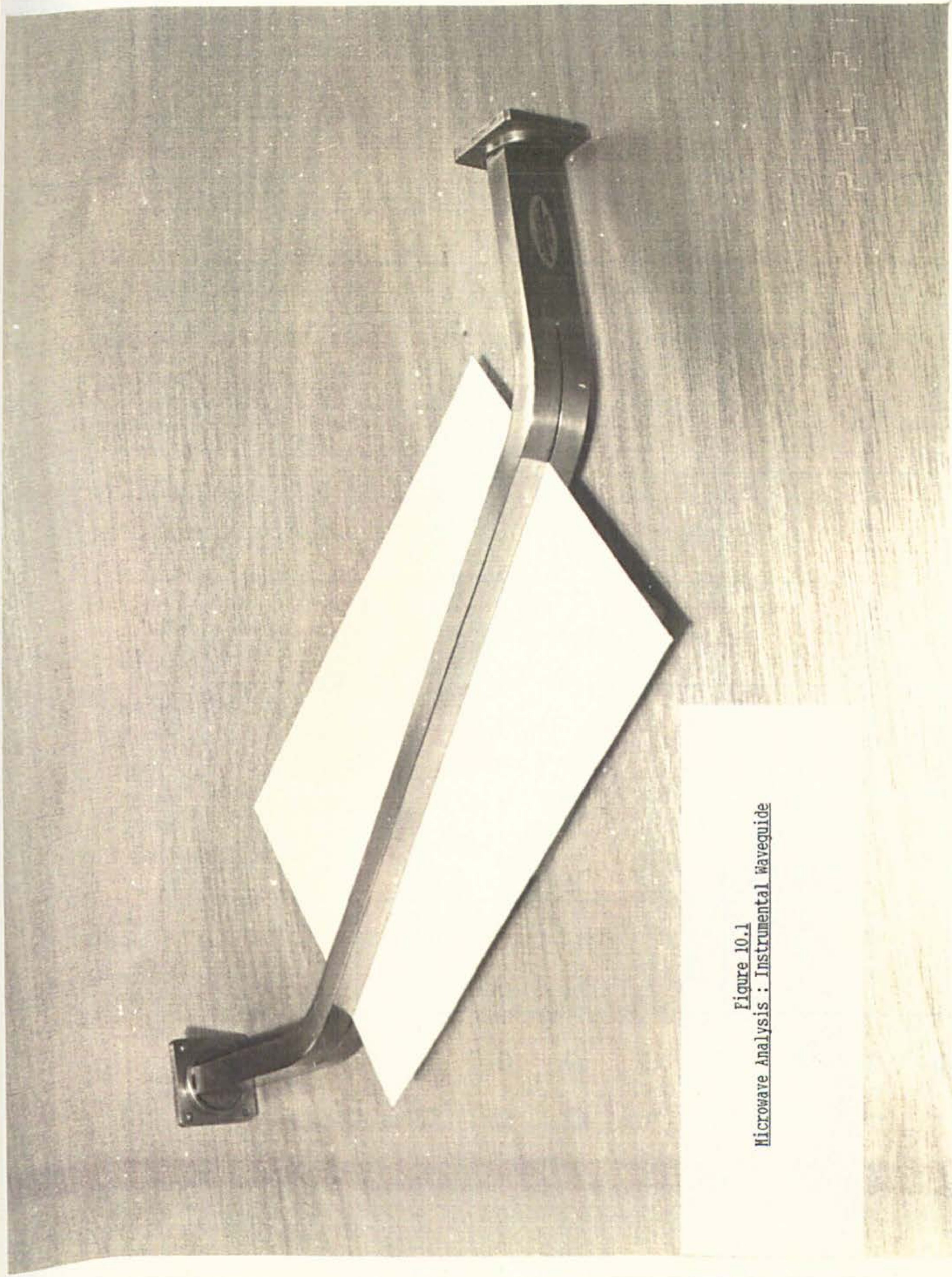


Figure 10.1

Microwave Analysis : Instrumental Waveguide

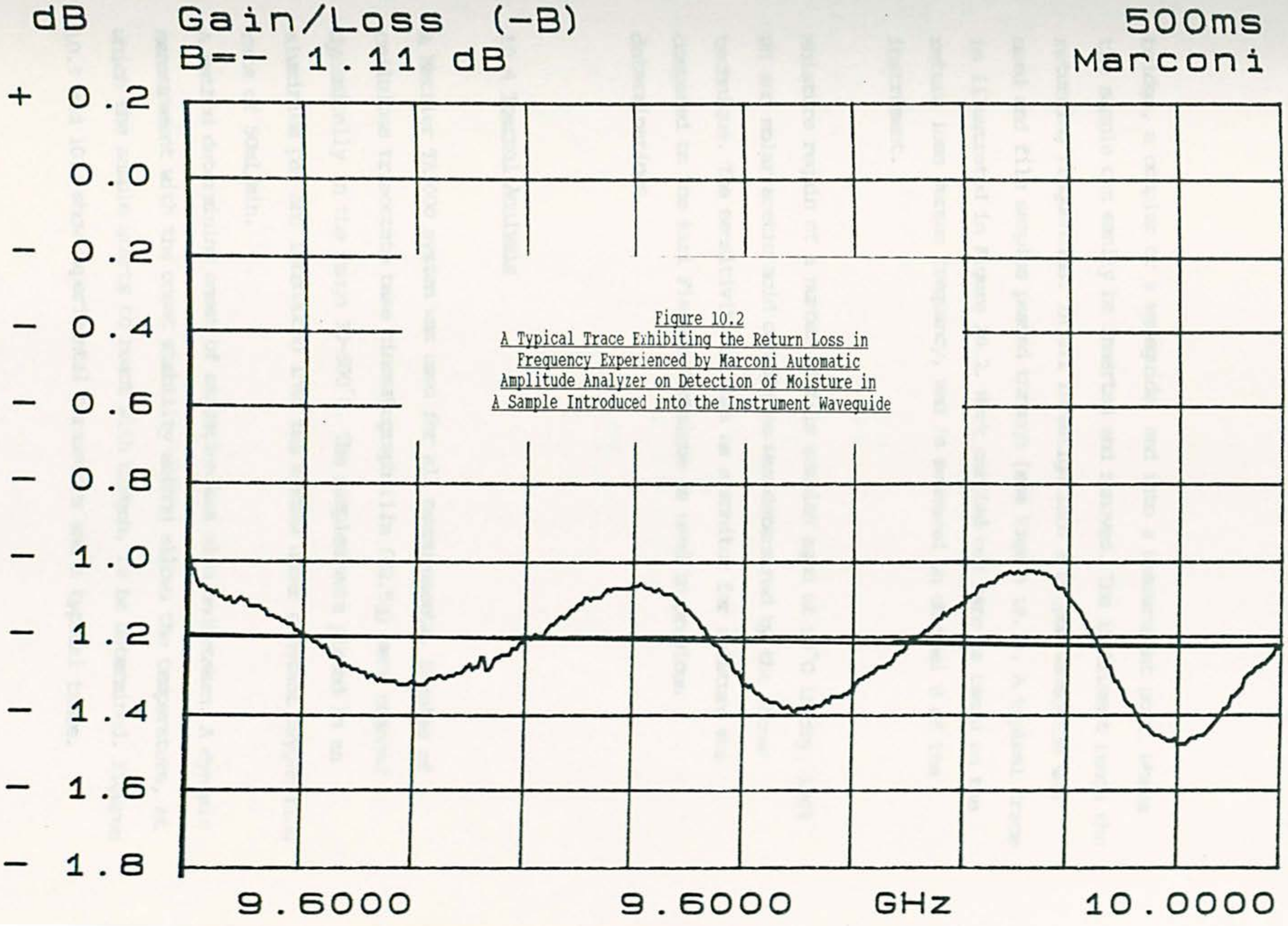


Figure 10.2
A Typical Trace Exhibiting the Return Loss in Frequency Experienced by Marconi Automatic Amplitude Analyzer on Detection of Moisture in A Sample Introduced into the Instrument Waveguide

bridge, a coupler or a waveguide, and into a measurement port, where the sample can easily be inserted and removed. The instrument reads the returning frequencies. In all investigations a copper waveguide was used and film samples passed through (see Figure 10.1). A typical trace is illustrated in Figure 10.2. Work carried out here is based on the return loss versus frequency, and is measured on channel B of the instrument.

Moisture regain of a number of film samples aged at 90°C in dry, 100% RH and molar acetic acid conditions was determined by the above technique. The sensitivity of this as a monitor for moisture was compared tc the Karl Fischer Technique as used in previous determinations.

10.4 Thermal Analysis

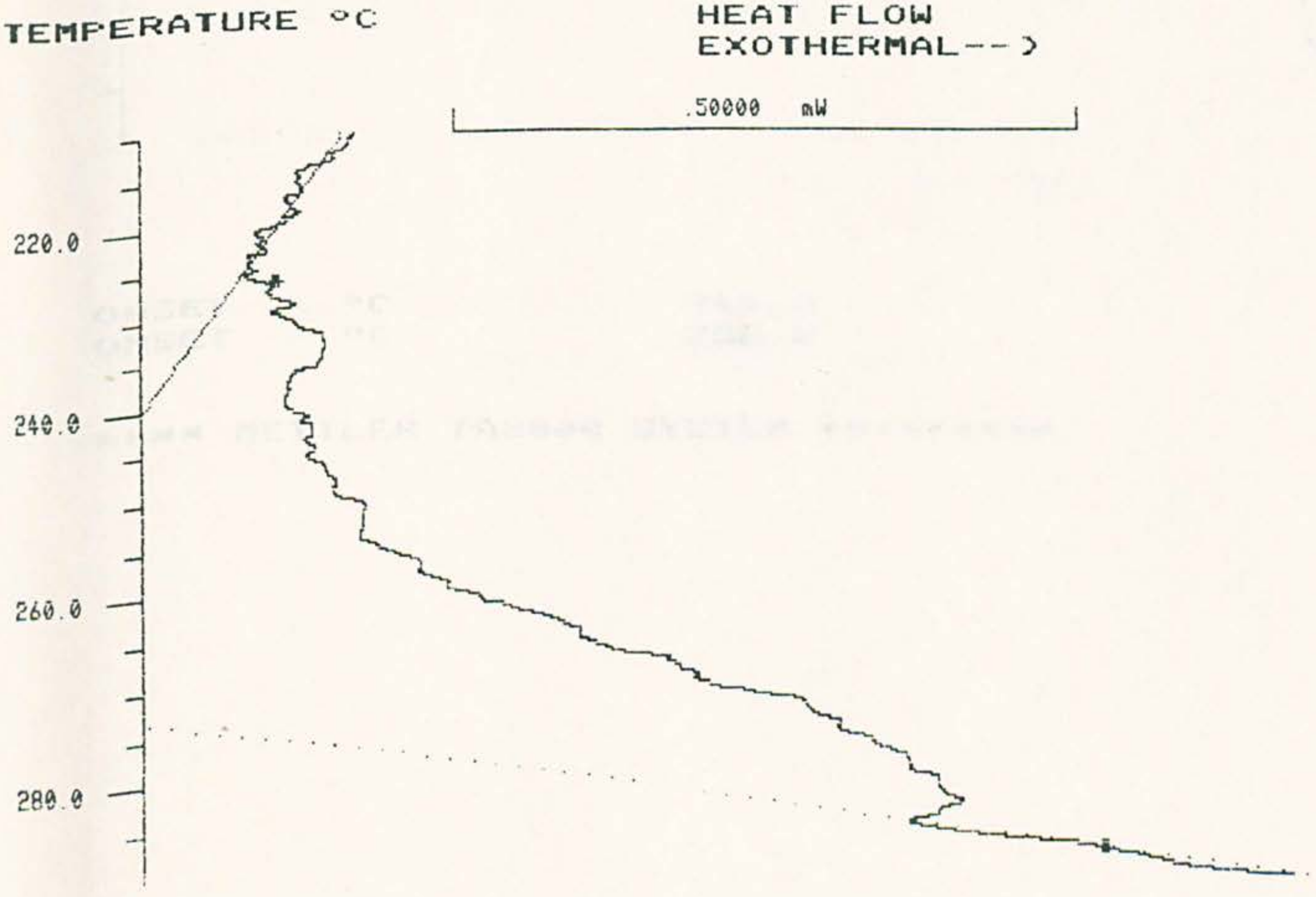
A Mettler TA3000 system was used for all measurements. Samples of cellulose triacetate base cinematograph film (@2.5g) were scanned dynamically in the range 30-500°C. The samples were placed in an aluminium pan and introduced into the system under constant oxygen flow rate of 50ml/min.

A method determining onset of oxidation was also undertaken. A dynamic measurement with the onset stability method allows the temperature, at which the sample starts to react with oxygen, to be determined. Figures 10.3 and 10.4 show experimental parameters and a typical trace.

ONSET

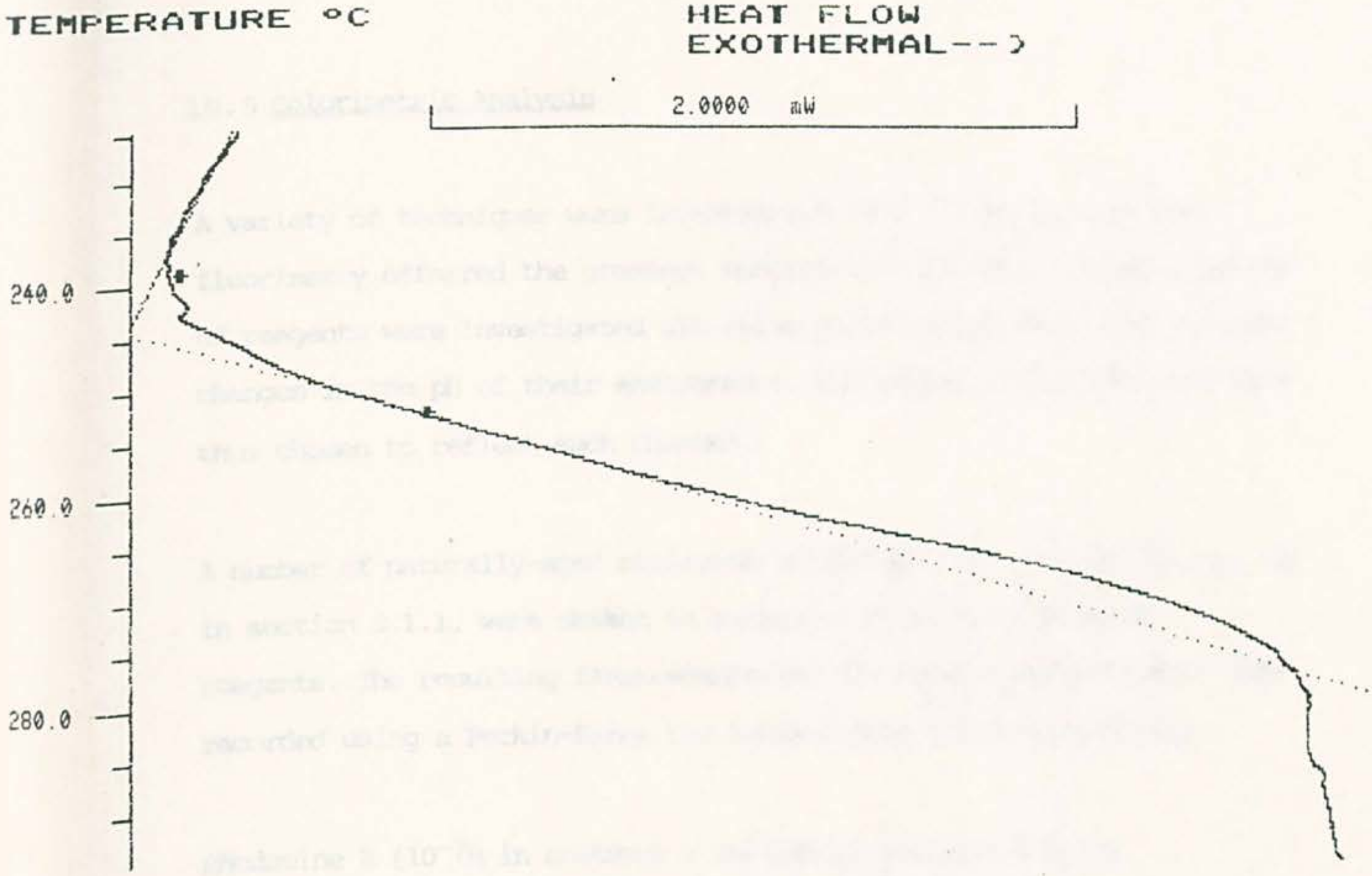
1-OCT-89 2:48

ONSET		
DYN/ISO	1/2	1
START		210
END		290
THRESHOLD	mW	1
BASELINE TYPE		1
PLOT	CM	10
PLOT MODE		101



ONSET	°C	270.3
ONSET	°C	287.0

******** METTLER TA3000 SYSTEM *********



ONSET °C 244.0
ONSET °C 252.2

******** METTLER TA3000 SYSTEM *********

10.5 Colorimetric Analysis

A variety of techniques were investigated, but it was decided that fluorimetry offerred the greatest sensitivity. In this respect a number of reagents were investigated all being particularly sensitive to small changes in the pH of their environment. Fluoresein and Rhodamine B were thus chosen to reflect such changes.

A number of naturally-aged cellulose triacetate film samples (0.1g), as in section 8.1.1, were shaken in solutions of both fluorescent reagents. The resulting fluorescence for all sample solution were then recorded using a Perkin-Elmer LS5 Luminescence spectrophotometer.

Rhodamine B (10^{-7}M in acetone)	: Excitation Maximum = 544nm Emission Maximum = 578nm
Fluorescein (0.01g in 500cm^3 x 4 dilution in 80:20 v/v acetone:water)	: Excitiation Maximum = 496nm : Emission Maximum = 545nm

Chapter 11

11. RESULTS AND DISCUSSION

11.1 Archival Predictions

Figures 11.1 to 11.4 depict the time taken in years for a 10% loss in viscosity of cellulose triacetate films at a series of oven-ageing temperatures. The plots are then extrapolated to give a prediction of actual film life when stored under ambient temperature conditions.

Figures 11.1 and 11.2 examine the effects on film life of ageing film reels when in contact with glass, polyethylene, aluminium and tin-plated iron containers at 50 and 100% relative humidity respectively.
Linear plots for degradation were obtained and the degradation rate increases, as expected, with increasing temperature. These results show two interesting features with regard to the degradation rate of film reels. The first and most significant result is that the film stability increases in the order tin < aluminium < polyethylene << glass.
The second feature is that the degradation rate is greater at 100% RH than at 50% RH and effectively illustrates the hydrolytic effect of moisture in the degradation mechanism. From the results in Figure 11.1, the archival lives are found to be 110, 60, 50 and 35 years for glass, polyethylene, aluminium and tin-plated iron respectively. The least squares method was used in each case to obtain the best fit for the points and all graphs were originally plotted by micro-computer. The most important aspect of the data is that the life of 35 years found

Figure 11.1

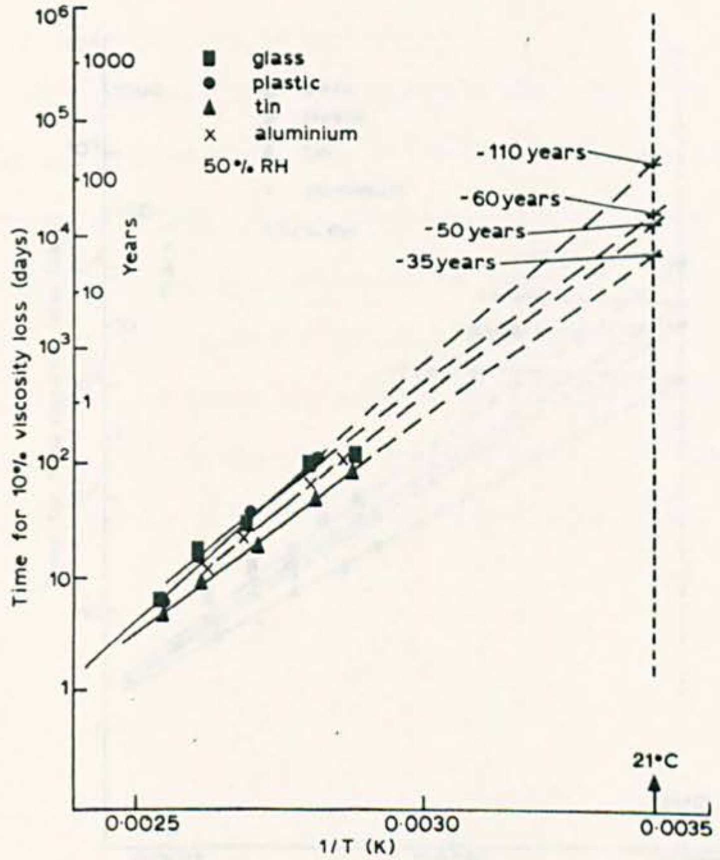


Fig. 1. Time for a 10% loss in viscosity of the cellulose triacetate film (days and years) versus the reciprocal temperature of degradation (K) in ■, glass; ●, polyethylene; ▲, tin-plated iron; ×, aluminium containers at 50% RH.

Figure 11.2

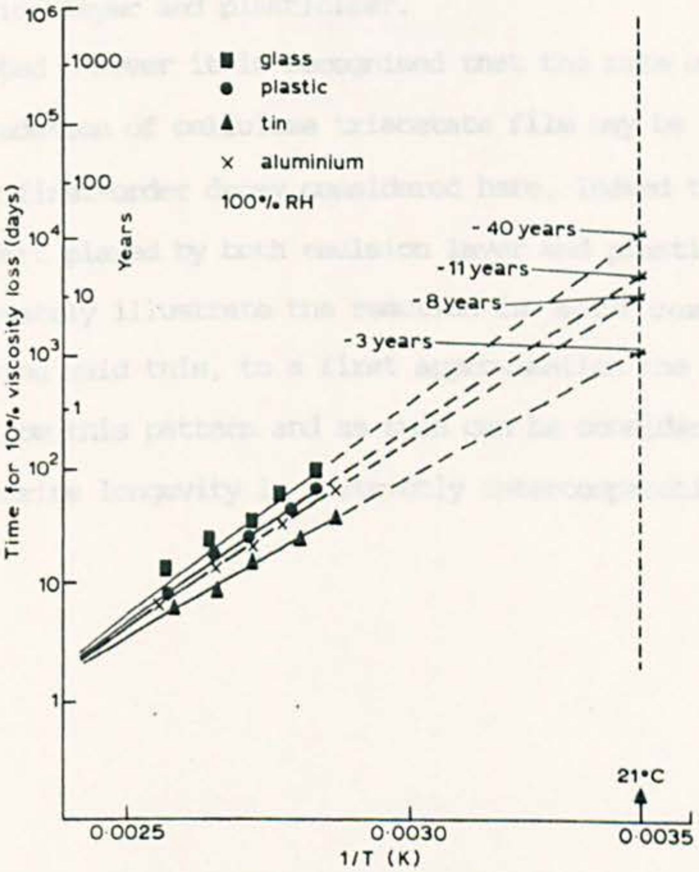


Fig. 2. Time for a 10% loss in viscosity of the cellulose triacetate film (days and years) versus the reciprocal temperature of degradation (K) in ■, glass; ●, polyethylene; ▲, tin-plated iron; ×, aluminium containers at 100% RH.

for the film reel aged in the tin-plated iron container corresponds closely to that found for actual archival storage conditions. This further supports earlier inferences that iron acts as a catalyst for the degradation mechanism in archival situations.

The results in Figures 11.3 and 11.4 show the effects of the emulsion layer and plasticiser on the rate of degradation of the film. In both cases it is seen that each imparts some degree of stability to the cellulose triacetate film base. Again this supports earlier data on the effects of emulsion layer and plasticiser.

It should be stated however it is recognised that the rate controlling step in the degradation of cellulose triacetate film may be more complex than the first-order decay considered here. Indeed the evidence confirming the part played by both emulsion layer and plasticiser composition adequately illustrate the reaction *is* more complex than first-order. Having said this, to a first approximation the kinetics do 'apparently' follow this pattern and as such can be considered to sufficiently describe longevity in a strictly intercomparative sense.

Figure 11.3

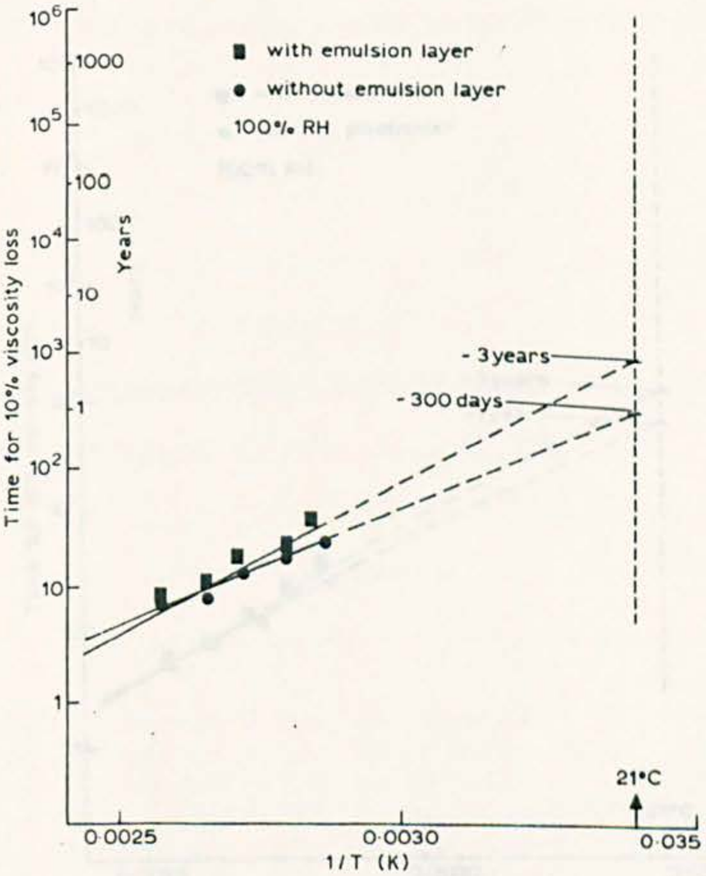


Fig. 3. Time for a 10% loss in viscosity of the cellulose triacetate film (days and years) versus the reciprocal temperature of degradation (K) in a tin-plated iron can at 100% RH ■, with and ●, without the emulsion layer.

Figure 11.4

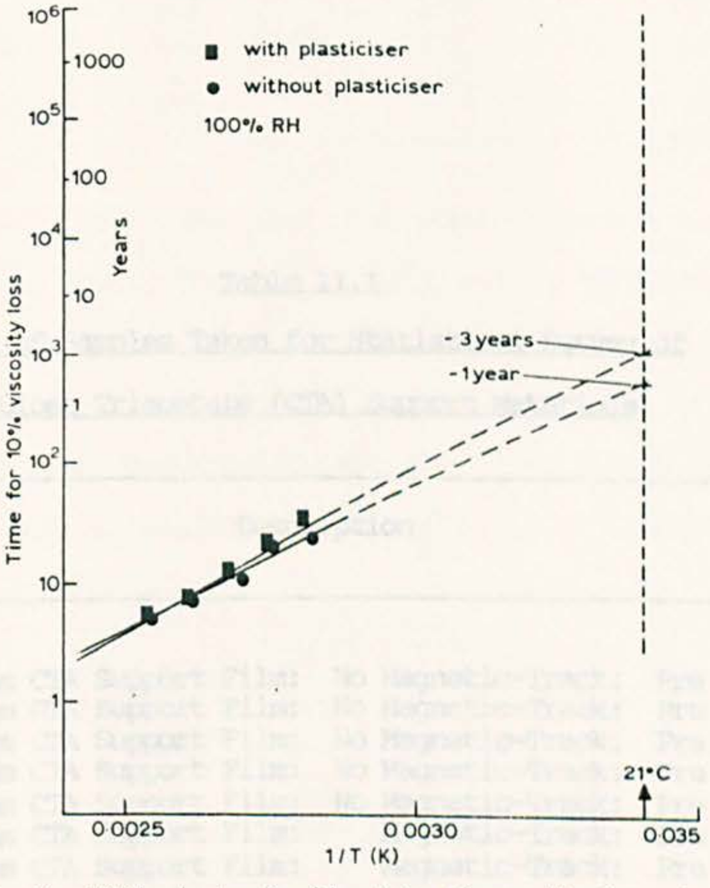


Fig. 4 Time for a 10% loss in viscosity of the cellulose triacetate film (days and years) versus the reciprocal temperature of degradation (K) in a tin-plated iron can at 100% RH ■, with and ●, without the plasticiser.

11.2 Statistical Survey of Cellulose Triacetate Support Materials held in a Temperate Climate Archive and Exhibiting Acetic Acid Loss

To corroborate earlier studies a survey of materials housed in a typical temperate climate archive was undertaken. A total population of 58,490 Cellulose Triacetate Support Materials was investigated. This was split into 7 groups for sampling covering a typical range of coatings (e.g gelatin emulsion, magnetic track) held on a Cellulose Triacetate Support. Data categorizing each group is presented in Table 11.1

Table 11.1

Listing of Samples Taken for Statistical Survey of Cellulose Triacetate (CTA) Support Materials

Code	Description
Group 1	35mm CTA Support Film: No Magnetic-Track: Pre 1982
Group 2	35mm CTA Support Film: No Magnetic-Track: Pre 1982
Group 3	16mm CTA Support Film: No Magnetic-Track: Pre 1982
Group 4	16mm CTA Support Film: No Magnetic-Track: Pre 1955
Group 5	35mm CTA Support Film: No Magnetic-Track: Pre 1954
Group 6	35mm CTA Support Film: Magnetic-Track: Pre 1982
Group 7	16mm CTA Support Film: Magnetic-Track: Pre 1982

Table 11.2

Sampling Data and Incidences of Acetic Acid Loss in the Cellulose Triacetate Support Materials Examined

Description	Population Sizes	Sample Sizes	Incidences
Group 1	53,300	292	0
Group 2	23	22	0
Group 3	2,850	156	2
Group 4	14	14	0
Group 5	29	29	0
Group 6	1,443	170	55
Group 7	831	242	35
Totals	58,490	925	92

Statistical analysis infers that the true number defective, i.e. within the total population examined, to within 95% and 99% confidence intervals is that given in Table 11.3.

Table 11.3

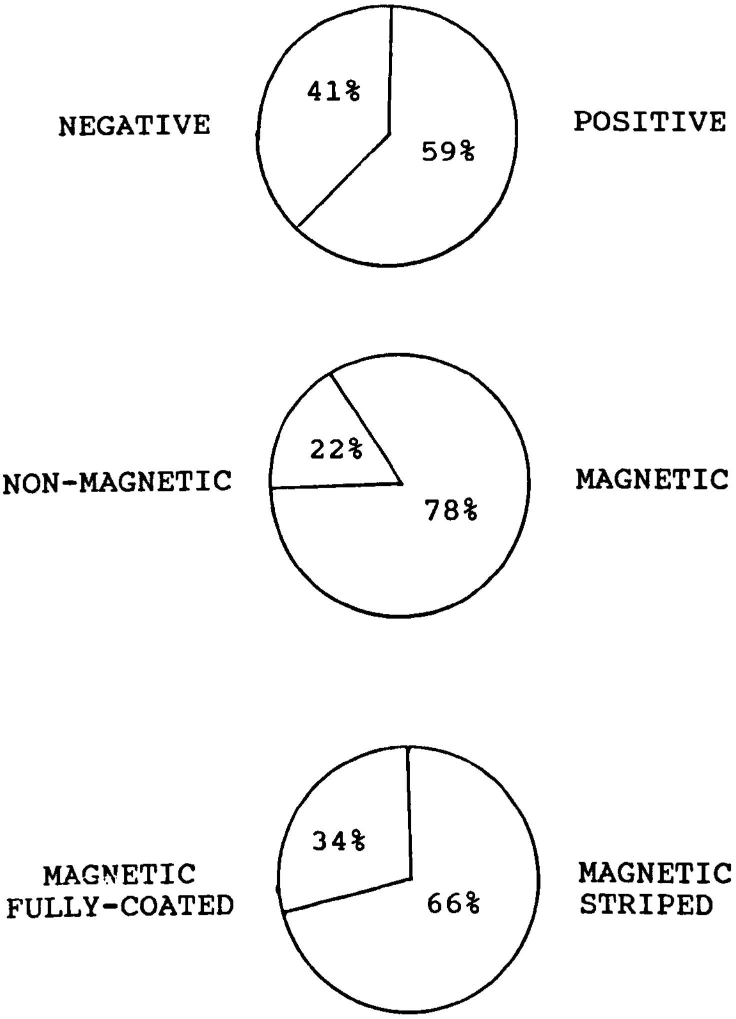
Statistically Predicted Incidences of Degradation for Total Population of Cellulose Triacetate Support Materials Examined

	# Incidences	
Confidence Limit:	95%	99%
Group 1	< 533	< 800
Group 2	0	0
Group 3	< 74	< 90
Group 4	0	0
Group 5	0	0
Group 6	375-563	346-592
Group 7	91-150	83-158
Maximum	1,320	1,640

Groups 1 to 5 are optical track materials (silver/gelatin emulsion only) and of this cross-section it can be concluded that only 0.4% of this sample (i.e. 2 out of 513 reels) exhibit degradation.
The results also clearly indicate that the majority of decomposing reels are associated with magnetic sound tracks (Groups 6 and 7). It was therefore decided to test all materials on Cellulose Triacetate support which were known to contain a magnetic sound track. In addition to this an intercomparison of negative and positive optical track materials exhibiting degradation was undertaken. Collating the previous data with this yielded the results which are illustrated in Figure 11.5.

The results of the statistical survey are interesting since they support earlier chemical test data for naturally and artifically aged films related in chapter 8 and the Arrhenius predictions in the present chapter. The implication from chemical test data that there is a difference in stability between negative and positive (negative > positive) filmstocks is upheld with 59% of degraded films being positive materials compared to 41% negative materials.
The evidence that metal ions particularly iron decrease the expected lifetime of cellulose triacetate support films is confirmed by the analagous situation whereby 78% of degraded materials are in contact with a magnetic track (iron oxide) compared to only 22% non-magnetic materials.
Arrhenius predictions at 50% RH suggest that film materials kept in contact with tin-plated iron cans has a lifetime of around 35 years (95% confidence limits). The majority of materials sampled had stock

Figure 11.5



Pie charts representing relative percentages of specific types of cellulose triacetate film materials taken from a random cross-section of archive materials exhibiting acetic acid odour.

dates between 1958 and 1964. Degradation should thus be apparent around 1993-1999 ± 5 years. The fact that only a small percentage of optical material has degraded seems to support this. On the other hand, a more significant quantity of magnetic track materials exhibit deterioration. Here iron oxide is closely in contact with the support material and any metal-ion catalysed degradation will be promoted. Furthermore, the binder for magnetic particles is often cellulose nitrate, which again is particularly susceptible to iron-catalysed decomposition. The degradation products of the cellulose nitrate may in turn instigate breakdown of the triacetate.

This survey been limited by constraints on time and human resources and as such can only provide preliminary insight into the current situation. A more exhaustive study should consider a much larger population for accuracy and should also intercompare incidences of "vinegar syndrome" in tropical and dry climate archives for a more complete picture of the problem.

11.3 Thermal Analysis

Tables 11.4 and 11.5 give TG and DSC data for the same naturally-aged film samples which were analysed in 8.1.1.

Table 11.4

% Mass Loss at Peak Temperatures in TG Thermograms for Naturally-Aged Cellulose-Triacetate Support Cinematograph Films

	Sample Appearance	Peak Temperatures (°C)	Mass Loss %
1.	good	85, 275, 555	6.3, 70.1, 21.5 (residue = 2.3)
2.	good	85, 274, 553	6.5, 70.0, 20.1 (residue = 2.5)
3.	good	84, 270, 549	6.9, 71.2, 21.0 (residue = 1.9)
4.	acetic acid odour	84, 270, 547	8.0, 73.5, 23.0 (residue = 0.6)
5.	plasticiser deposit on surface	85, 271, 547	10.3, 74.1, 25.0 (residue = 1.9)
6.	image loss	85, 273, 551	9.0, 73.9, 26.7 (residue = 1.9)

Table 11.5

Onset of Oxidation Peak Temperatures in the DSC Thermograms for Naturally-Aged Cellulose-Triacetate Support Cinematograph Films

	Sample Appearance	Onset Temperature (°C)	H J/G
1.	good	292.8	2612.0
2.	good	290.9	1064.3
3.	good	287.9	768.4
4.	acetic acid odour	262.9	221.5
5.	plasticiser deposit on surface	256.8	256.8
6.	image loss	243.9	141.6
7.	'triacetate' support	280.0	1987.0

The first point to note, with respect to all samples, is that thermal analysis data is for the cinematograph film complete with emulsion and not merely for the cellulose triacetate alone. The resulting thermograms (as exemplified by Figures 10.3 and 10.4) were as a consequence more complex and difficult to interpret initially. Fortunately, a closer examination reveals that the major peaks as found by Jain et al. for cellulose triacetate flake are preserved.

With respect to thermogravimetry, the first information of interest arises as a consequence of moisture loss 45-150°C; this is quite significant due to the presence of the emulsion layer. The value also increases as the film tends towards acetic acid loss, as one might expect from previous studies. In the second stage of decomposition 150-430°C, essentially that due to deacetylation, relative mass loss is seen initially to increase significantly and then decrease slightly; i.e. deacetylaticn 'levels off'. In the third stage 430-870°C, for films 1-6 which are apparently progressively more degraded, there is a steady increase in the mass loss corresponding to volatile decomposition products resulting from oxidative breakdown.

The data obtained from DSC supports that of TG. As samples become progressively more deteriorated onset of oxidation occurs at lower temperatures. The enthalpy change associated with onset of oxidation is endothermic and large initially, but subsequently undergoes a corresponding decrease. That is the film matrix is becoming increasingly unstable. Onset temperatures occurred in the range 300-240°C, the region which according to Jain et al. signifies deacetylation. Comparing these results to those from thermogravimetry it is obvious that as cinematograph film loses acetate groups this favours further loss.

Another point to observe is that in the presence of an emulsion layer, which has not been affected by the presence of acetic acid,onset of oxidation is at a much higher temperature than that of cellulose triacetate alone. This again affirms the stabilising influence of the emulsion layer. It is also interesting to note that in the original dynamic scans, all the endotherms obtained were broad, indicating a slow change in enthalpy.

11.4 Colorimetric Analysis

Fluorescence values for naturally-aged films in both fluorescein and Rhodamine B reagents are depicted in Table 11.6.

Table 11.6

Fluorescence Values for Solutions of Fluorescein and Rhodamine B contacted with Naturally-Aged Cellulose-Triacetate Support Cinematograph Films

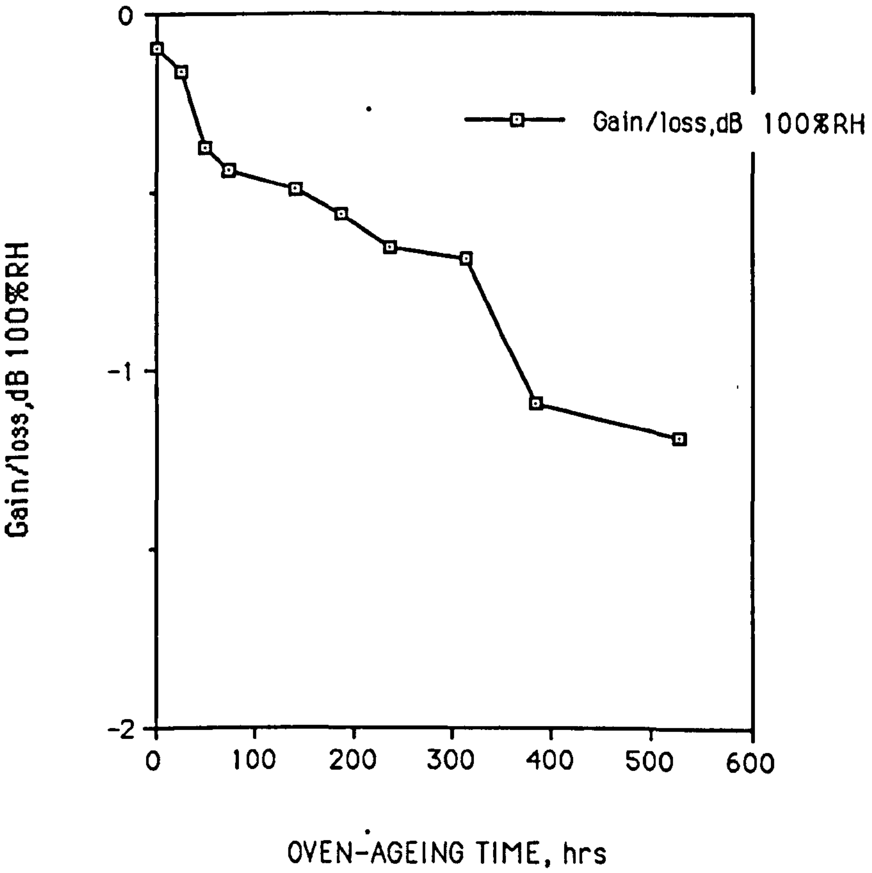
Sample Appearance	Fluorescence	
	Fluorescein	Rhodamine B
1. good	99	78
2. good	99	79
3. good	90	67
4. acetic acid odour	62	26
5. plasticiser deposit on surface	50	113
6. image loss	34	125
7. control	100	100

Both of the tests have the advantage in that they are simple and rapid. The potential sensitivity of Fluorescein as a test reagent is reflected by the progressive decrease in fluorescence with film condition. The observed trends for Rhodamine B on the other hand are more complex; with both an enhancement and quenching of fluorescence being seen. Unfortunately, when the tests were repeated, although trends in Fluorescence quenching were retained relative values were not reproducible. As such this does not represent a satisfactory test for acetate film. However, a colorimetric test as a means of assessing film stability should not be entirely abandoned, it may be that more accurate and reproducible results are obtained if the reagent is impregnated in a test paper and rate of evolution of acetic acid is measured in a similar manner to current tests on nitrate filmstocks. This would certainly circumvent discrepancies due to more than one specie reacting with the reagent in question.

11.5 Microwave Analysis

Figure 11.6 shows changes in return frequency with oven-ageing time for cinematograph film aged at 100% RH. Comparing this to Figure 8.1 (which shows moisture regain as determined by more conventional methods) it can be seen that in the former case changes which occur in the induction period prior to onset of degradation are much more apparent. Microwave aanalysis thus provides a particularly sensitive means of measuring the moisture regain of cinematograph films.

Figure 11.6



Moisture Regain as a Function of Return Loss in Frequency versus Oven-Ageing Time, hrs for Cellulose Triacetate Base Cinematograph Film Aged at 90°C and 100% RH.

11.6 Intercomparison and Assessment of Techniques

Arrhenius testing albeit the only real tool which we have to date to make longevity predictions, has proven time and again to be largely ineffective, unless used in a strictly comparative sense. Since the unpredictability of long-term practical situations means a continuing reassessment of stability, Arrhenius or other stability testing should be an ongoing procedure. It is difficult to make definite lifetime projections if external factors are indefinite. Extensive testing in an acceptable time span is a necessity. In this respect Arrhenius testing is inappropriate. Arrhenius testing may be useful to assess the limits of stability of a given material but it is impractical for repetitive testing. This is discussed further in the overview and conclusion.

Apart from its value in the latter respect, the advantages offered by the microwave technique are its sensitivity and its non-destructive nature. Unfortunately, in the case of photographic film materials different emulsions contain different silver:gelatin ratios and thus absorb different amounts of water. Moisture determinations by this method would thus have to be correlated to measurements on silver image density. To standardize this technique would thus require an exhaustive survey of commercial materials to provide a baseline against which to compare measurements. However, since background moisture content is automatically subtracted from any measurements this technique could be used to monitor changes in moisture content of a given film during the course of a day, week or year at no detriment to the film material. This would not require the extensive background study previously described and would provide the archivist with extremely valuable information relating directly to his particular film collection.

Colorimetric tests while providing another measure of film condition are particularly sensitive to the presence of interferences. It is also extremely difficult, considering the complex matrix of cinematograph films, to elucidate exactly what colorimetric reagents are reacting with. In view of such unknown variables testing by these methods should be regarded with caution.

It is therefore considered that by far the best assessment of film condition, from the methods considered here, is thermal analysis. The major advantages of TG and DSC are that they provide information regarding *all* stages in the degradation reaction: moisture content, deacetylation, oxidation and change in order of the system. The drawbacks of these techniques are that they are however time consuming and destructive; although in this latter respect only small samples of film are necessary. If this were to be used as a means of random analysis, rather than for testing every single film reel, the large amount of information obtained for a single test should offset test time. Furthermore, other than sample gathering it is relatively labour free. However, if a non-destructive, labour-free test proves to be the only realistic answer to the analysis of vast quantites of film materials an alternative method may be required. Since acetic acid is the first observable evidence of degradation future studies could concentrate on designing a suitable probe to measure acetic acid levels in the film can e.g. by means of a gas sensing electrode.

Part three

Chapter 12

12. STABILISATION

The compounds which are used to retard or arrest breakdown of polymers are referred to as "stabilisers" or "antioxidants". To stabilise an individual polymer requires a recognition of those factors which under the prevailing conditions affect its stability. Appropriate procedures or the incorporation of additives is then necessary to circumvent this.

12.1 Stabiliser Classification and Mechanistic Action

Scott [12.1] has classified antioxidants into two types, viz; kinetic chain-breaking (radical scavengers) and initiation preventative (hydroperoxide decomposers). Figure 12.1 is a diagrammatic representation of the points at which antioxidants can prevent or retard polymer degradation mechanisms.

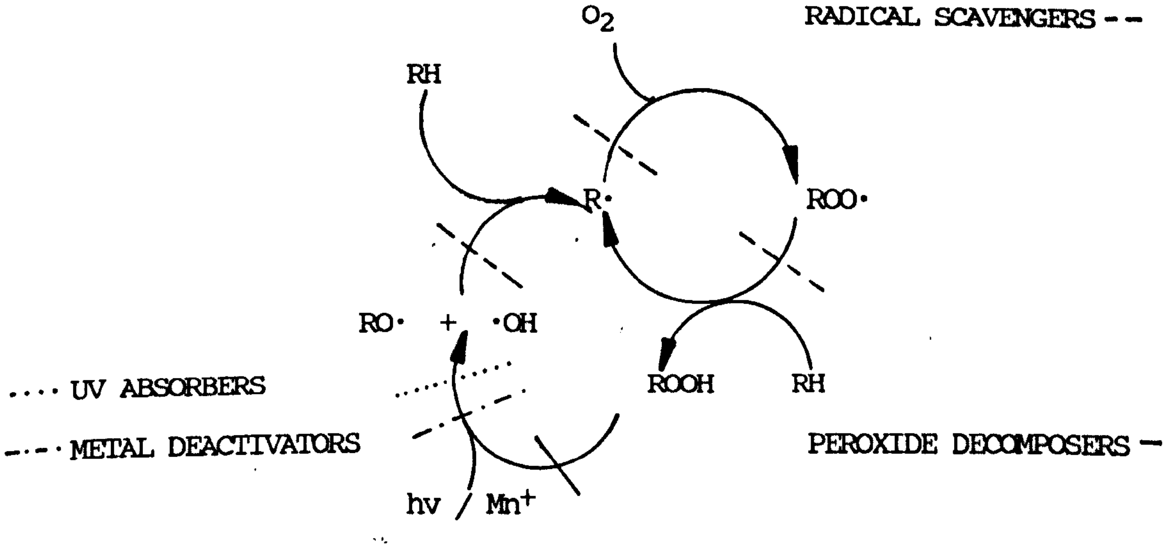


Figure 12.1 : Mechanisms of Stabiliser Action

12.1.2 Radical Scavengers (Primary Antioxidants)

The most effective systems used for this purpose are hindered phenols and alkylarylamines. They operate basically as free-radical terminators. Essentially radicals generated in polymer degradation reactions are "transferred" to the antioxidant whose structure is such that radical stability is enhanced and hence the rate of chain transfer reactions are reduced. Thus, efficient antioxidant behaviour is dependent upon both the structure of the antioxidant and the stability of the radical intermediate. From this it follows that the stability of the transformation products of the latter will also be of importance.

Hindered Phenols

Hindered phenols terminate autoxidation in polymers by trapping both oxygen centred (alkoxy, $RO\cdot$ and alkylperoxy, $RO\cdot_2$) and alkyl ($R\cdot$) radicals; thus limiting the rate of propagation of degradation reactions. As already stated, the performance of a given phenolic antioxidant will be influenced not only by its innate structural composition but also by the nature of its transformation products (Figure 12.2). The complexity of such reactions results in the possibility that the oxidation products of phenols may be either degradation sensitisers or improve stabilisation efficiency. In Figure 12.2 whilst the bis-phenol product may be a more efficient antioxidant, the stillbene quinone may act as a sensitiser.

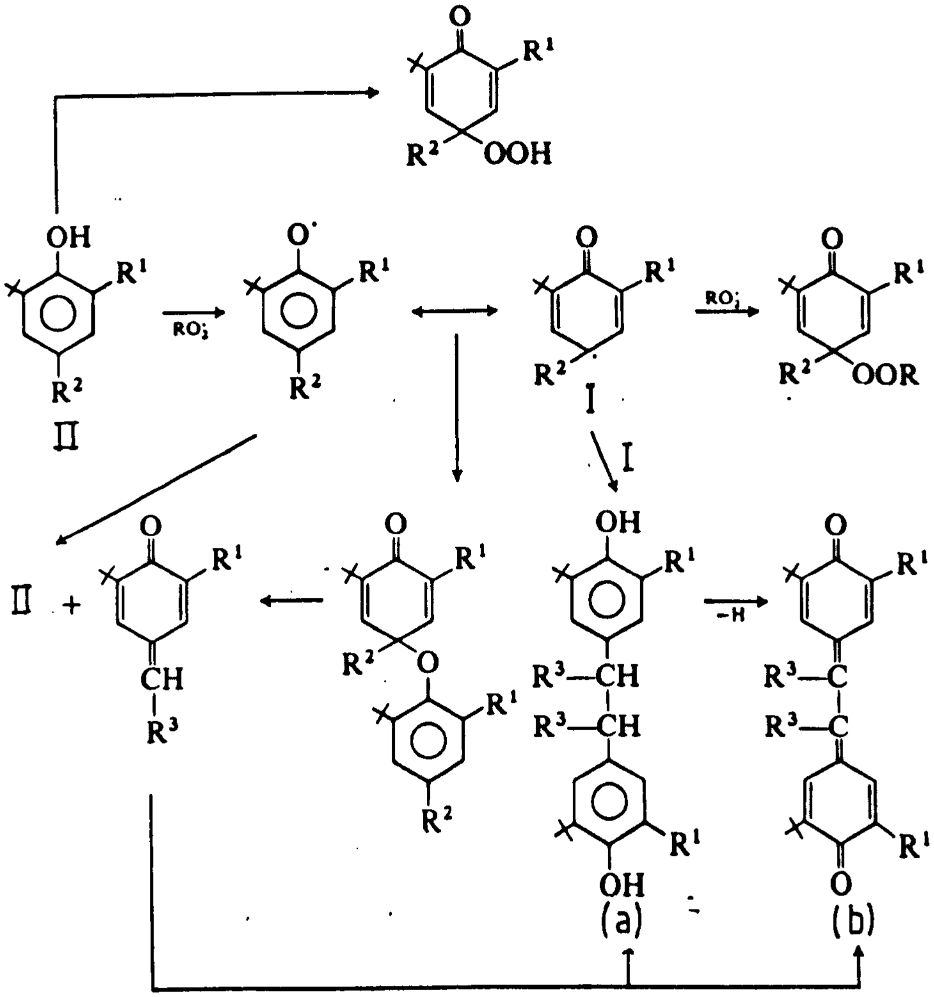


Figure 12.2
Oxidative Transformations of Phenolic Antioxidants

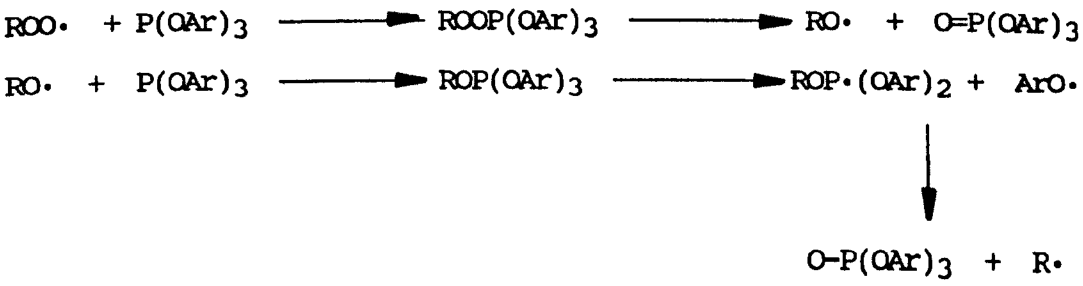
12.1.3 Hydroperoxide Decomposers (Secondary Antioxidants)

Phosphorous Esters

Here stabilising action may be explained by an ability to decompose peroxide in a non-radical manner. Here the phosphorous ester essentially stoichiometrically reduces hydroperoxides to alcohols:

$$P(OR)_3 \ + \ R'OOH \longrightarrow O{=}P(OR)_3 \ + \ R'OH$$

Aryl phosphites may also operate to some extent as chain-breaking antioxidants:



$$\begin{aligned}
&ROO\cdot \ + P(OAr)_3 \longrightarrow ROOP(OAr)_3 \longrightarrow RO\cdot \ + \ O{=}P(OAr)_3 \\
&RO\cdot \ + \ P(OAr)_3 \longrightarrow ROP(OAr)_3 \longrightarrow ROP\cdot(OAr)_2 + \ ArO\cdot \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O{-}P(OAr)_3 \ + \ R\cdot
\end{aligned}$$

However, phosphorous ester antioxidants are limited in their application by poor hydrolytic stability [12.2]. Despite evidence to support this it cannot be excluded that the hydrolysis products are not necessarily detrimental but themselves inhibit the oxidative process, i.e. internal synergism results:

$$(RO)_3P + H_2O \longrightarrow (RO)_2P(H){=}O + ROH$$
$$ROH + R'OO\cdot \longrightarrow R'OOH + RO\cdot$$
$$RO\cdot + O{=}P(OR)_2 \longrightarrow (RO)_2P\cdot{=}O + ROH$$
$$(RO)_2P\cdot{=}O + RO\cdot \longrightarrow (RO)_2P(OR){=}O$$

Sulphur Compounds

Sulphur compounds destroy hydroperoxides by a catalytic mechanism.

i.e. $R{-}S{-}S{-}R + R'OOR \longrightarrow R{-}S{-}O{-}S{-}R \longrightarrow SO_2$

The disulphide is converted to a thiosulphinate and then sulphur dioxide which is itself a good peroxide decomposer.

Typical sulphur containing antioxidants are the thioesters, dilaurylthiodipropionate (DLTDP) and distearylthiodipropionate (DSTDP).

Use of sulphur compounds is limited by the insolubility of some of this group in organic media, and corrosive tendencies. A number also give acidic species on oxidation with hydroperoxides and therefore act as reservoirs for peroxidolytic species.

Aromatic Amines

These compounds operate as chain-breaking donors and acceptors as indicated by Figure 12.3. The alkylarylamine donates a hydrogen atom to a peroxyl radical giving an alkylarylamine radical. The latter will then react with peroxyl radicals, the product of which is unstable and will decompose to give nitroxyl radicals. These nitroxyl radicals will then act as chain-breaking acceptors for macroalkyl radicals to give a substituted hydroxylamine. This is itself in turn unstable and will react with peroxy radicals and so repeat the whole cycle.

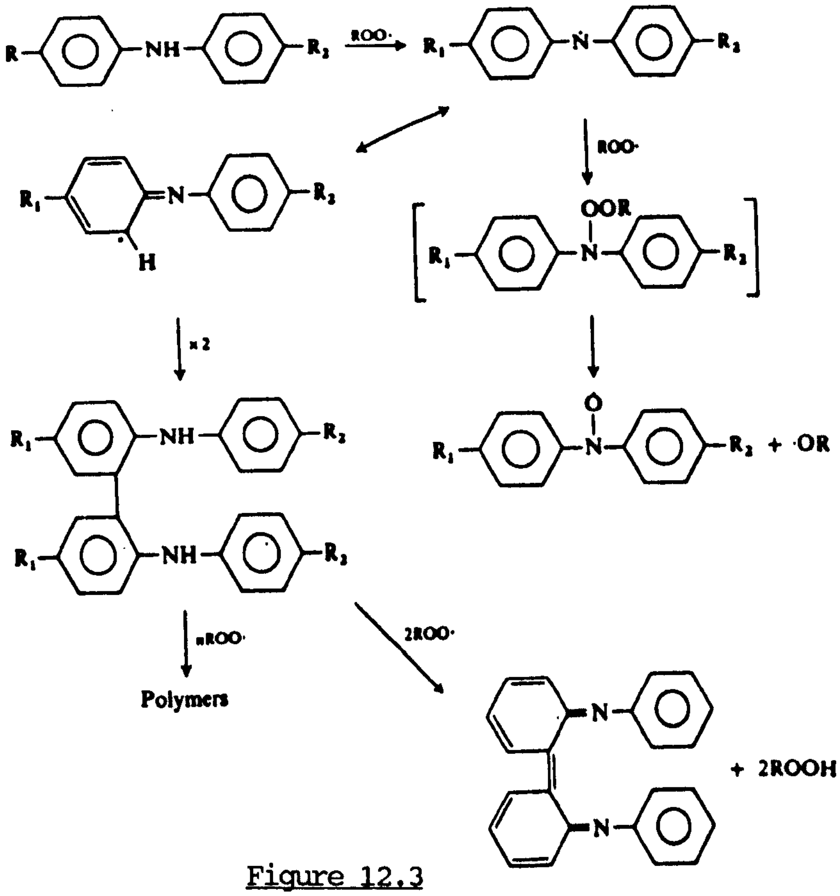


Figure 12.3

Oxidative Transformations of Alkylarylamines

12.1.4 Metal Deactivators

Metallic compounds may act either as accelerators or retarders for the degradation of polymers. The role of the metal ion is complex and is influenced by a variety of factors.

Other than their photosensitizing action metallic compounds may operate in the following ways;-

(i) Catalytic Decomposition of Hydroperoxides

Here the metal ion acts in its capacity as a redox reagent decomposing hydroperoxides to give alkoxy and alkyl peroxy species thus promoting free-radical reactions.

i.e $\quad ROOH + M^{n+} \longrightarrow RO\cdot + M^{(n+1)+} + OH^-$

$ROOH + M^{(n+1)+} \longrightarrow ROO\cdot + M^{n+} + H^+$

i.e. $\quad 2ROOH \longrightarrow RO\cdot + ROO\cdot + H_2O$

(ii) *Direct Reaction with the Substrate*

$$RH + MX_2 \longrightarrow R\cdot + MX + HX$$

$$RH + MX \longrightarrow R\cdot + M + HX$$

(iii) *Activation of Oxygen*

Interaction with oxygen may lead to a charge-transfer complex or active oxygen.

$$Mn^{+} + O_2 \rightleftharpoons Mn^{+}\ldots\ldots O_2$$

$$Mn^{+}\ldots\ldots O_2 + RH \longrightarrow Mn^{+} + R\cdot + \cdot OOH$$

Effective inhibition of metal-catalysed degradation is brought about by complexation. Alternatively an effective hydroperoxide decomposer will also serve as a metal deactivator. However, the effect of a metal complex is rarely as simple as this. Often the ligand itself has a superimposed antioxidant function. Although many compounds have been proposed as metal deactivators [12.3] only hydrazones [12.4] (Figure 12.4, I), bishydrazones [12.5] (Figure 12.4, II) of aliphatic and aromatic aldehydes, bis-acylated hydrazine derivatives [12.6] (Figure 12.4, III) and molecular combinations of sterically hindered phenols and metal complexing groups [12.7]

(Figure 12.4, IV) are used in practice.

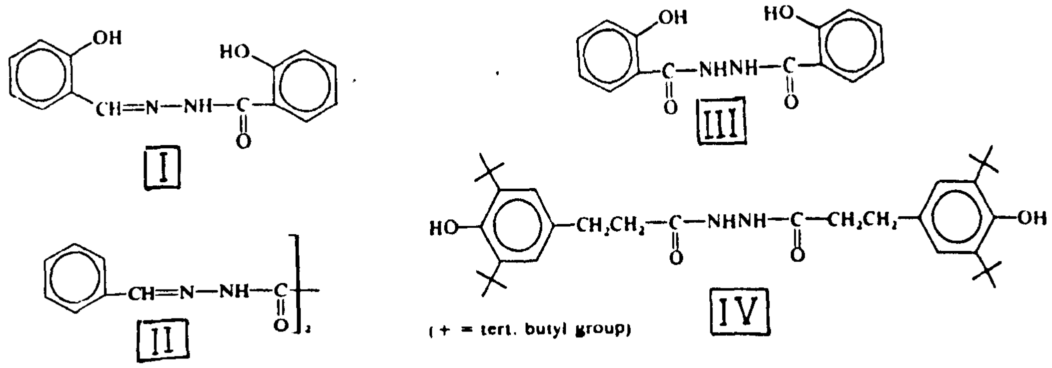


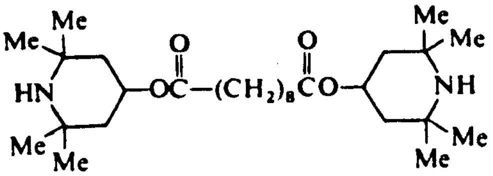
Figure 12.4

Commercial Metal Deactivators

12.2 Light-Stablisers

Although compounds which absorb/screen light are not relevant to the studies considered here, since archival cinematograph film materials are stored in the dark, hindered amine light stabilisers (HALS) are important. With respect to the latter, it is the transformation products of HALS, particularly the hindered piperidines, which offer stabilising action.

Considering Tinuvin 770, an important commercial example,



This is transformed by both thermal- and photo-oxidation processes to the corresponding nitroxyl radical. In common with other nitroxyl radicals, these are effective chain-breaking anti-oxidants.

12.3 Acid Scavengers

Acid scavengers are essentially acid "mops" neutralising any free acid. Commonly used acid scavengers are based on metal soaps, which are frequently used in synergistic combinations [12.8].

12.4 Co-Operative Interaction of Stabiliser Combinations

Where combinations of antioxidants produce an overall antioxidant effect which is greater than the sum of the individual effects synergism is observed. Antioxidants working by possible different and complimentary mechanisms co-operate by mutual conservation.

12.4.1 Phenolic Antioxidants and Peroxide Decomposers

Heterosynergism results from the combination of phenolic antioxidants and peroxide decomposers. This may be explained (see Figure 12.5) by a concentrated scavenging of alkylperoxy radicals and a non-radical decomposition of hydroperoxides.

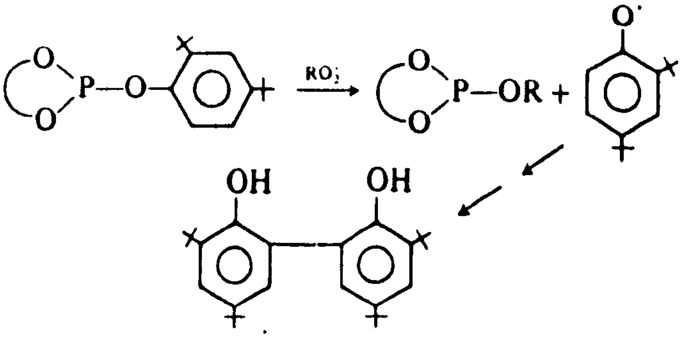


Figure 12.5

Interaction between Hindered Phenolic Antioxidants and Phosphite Peroxide Decomposers

12.4.2 Phenolic Antioxidants and Hindered Amines

Homosynergism occurs between phenolic antioxidants and HALS with respect to both photo and thermal stabilisation. An understanding of the respective transformation products is necessary to explain mechanisms operating and is indicated in Figure 12.6. Synergism is thought to result from possible interactions between phenol/nitroxide and phenoxyl/hydroxylamine leading to cyclical regeneration of the hindered amine via an o-alkylhydoxylamine [12.9].

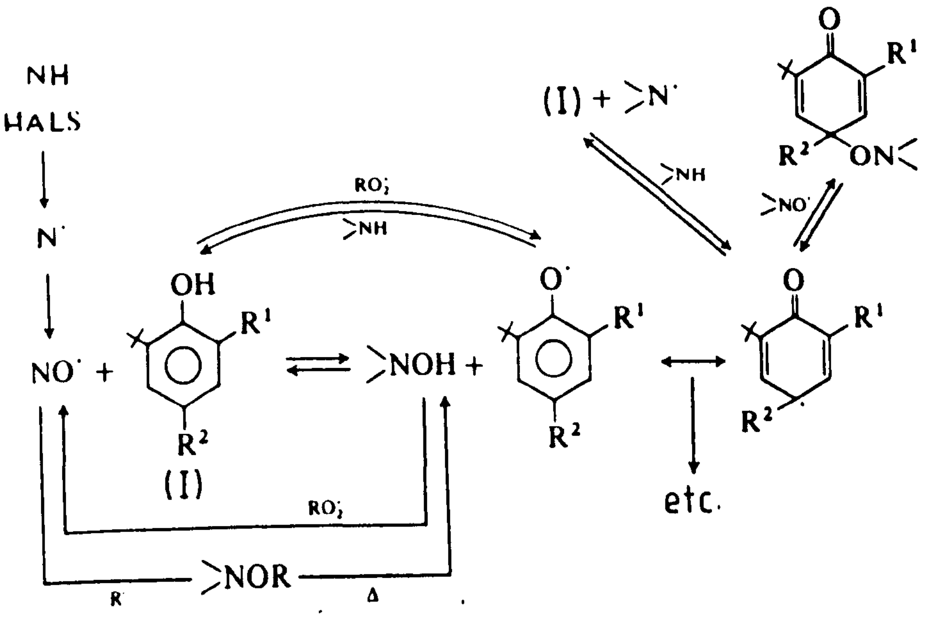


Figure 12.6

Possible Interactions between Hindered Amine and Phenolic Antioxidants

12.4.3 Hindered Amines and Peroxide Decomposers

Although when used alone the efficiency of hydroperoxide decomposers is usually such that sulphur compounds > phosphorous esters, when used in combination with hindered amines the former proves antagonistic whereas the latter is rather synergistic.

12.5 Physical Loss of Stabilisers from Polymers

Extensive investigations [12.10-12.13] have shown that the main factors which determine the effectiveness of stabilisers in a polymer matrix are:-

- the intrinsic stabiliser behaviour which is determined primarily by the chemical structure of the stabiliser; and
- the permanence of the stabiliser in the polymer.

The effectiveness of a particular stabiliser is largely dependent on its concentration in the polymer, which in a polymer matrix decreases during long term use [12.14]. Concentration changes in polymers may arise as a result of two processes :

- chemical reactions of the stabilisers, and
- physical loss from the polymer.

Since chemical loss is essentially via the operation of the stabiliser, and has already been discussed, we are concerned here only with the physical loss. Obviously retention of the stabiliser within the polymer matrix is a pre-requisite for effective chemical operation. Any processes which contribute to a reduction in stabiliser content must be accounted for when choosing a particular stabiliser system. The physical loss of stabilisers may be seen as a function of the following:

Compatibility

It may be generally stated that the more similar is the character of the components in a system the better is the compatibility.

Volatility

Volatility due to thermal motion of molecules on the surface of a sample, is another cause of physical loss of stabilisers in polymers. During heating of a pure stabiliser, vapour pressure arises over the surface by evaporation of a certain amount of stabiliser. Because of high diffusion coefficients in the gaseous phase, the equilibrium in the surface layer is disturbed and this results in further evaporation of the sample. A disturbance of the thermodynamic equilibrium may also be induced by temperature or fluid flow over a sample. Assuming a uniform distribution of the stabiliser in the bulk polymer, the evaporation from the surface layer, results in the formation of a concentration gradient which is the driving force for diffusion to take place.

Extractability

Extraction of stabiliser components from a polymer system results from contact of the polymer with organic solvents or other extraction media. As a consequence extraction reduces the content of the stabiliser, especially in the surface layers, which are usually those most sensitive to degradation during ageing.

When a polymer system is in contact with solvents, we cannot only consider a one-sided process involving a concentration decrease of the stabiliser in the polymer. The reverse process, diffusion of solvent molecules into the polymer must also occur, characterized by a high solvent concentration gradient at the interface. Since solvent molecules are usually smaller than stabiliser molecules, the diffusion rate of the solvent must be greater than that of the stabiliser. The presence of the solvent in the polymer has a plasticising effect which improves the flexibility of the molecules and contributes to the increase in diffusion rate of stabilisers to the surface of polymers thus leading to higher extractability.

Diffusion

As implied, the diffusion of a stabiliser doesn't produce any stabiliser loss itself, but it does play a significant role in the evaporation and leaching process. In general, rate of diffusion will depend on the degree of packing of polymer chains and hence polymer density. It will also depend on segmental chain mobility and thus the cohesive energy of the polymer [12.15]. Diffusion in polymers also decreases with an increase in content of polar and methyl groups [12.16].

Another important factor which affects diffusion is the presence of cross-links in the polymer. Studies have confirmed that on the whole crystalline regions in polymers are impenetrable to organic molecules, it is implicit within this statement that the thermal history of a given polymer will determine crystallinity and hence diffusion characteristics [12.17]. Associated with this is that chain branching also lowers diffusion.

The diffusing agent itself will also influence rate of penetration into or out of the polymer network. Molecular weight and steric factors will be an important factor here. Essentially the higher the molecular weight and the more bulky the diffusing agent the more free space required for diffusion.

12.6 A Review of Cellulose Triacetate Stabilisation

Little work has been undertaken in this area of cellulose-ester chemistry, principally because the mechanism of degradation is so poorly understood. Attempts to stabilise cellulose triacetate to date can be divided into two categories; those methods which are concerned with the neutralisation or removal of residual manufacturing chemicals and those which incorporate antioxidants into the polymer.

12.6.1 Removal of Residual Manufacturing Reagents

Staud [12.18] has summarised the major factors affecting stability arising from the manufacturing process as;-
the presence of free acetic acid,
the presence of bound and residual free sulphuric acid, and
excessive degradation of the cellulose during acetylation and hydrolysis.
In modern day processing, where sulphuric acid is utilised as a catalyst, most of the bound and free sulphate is removed after esterification, on addition of aqueous acetic acid during the hydrolysis stage (although it is not practicable to remove the last traces). The literature pertaining to this aspect of stabilisation is extensive. It ranges from the addition of simple compounds, such as alkali metal salts, to more dubious methods, such as boiling in water or use of superheated steam [12.19].

12.6.2 Addition of Stabilisers

A number of compounds have been proposed and evaluated as stabilisers for cellulose acetate. The majority of these are concerned with the inhibition of uv degradation. A number of phenolic type antioxidants have however been suggested to minimise the oxidative degradation and discoloration of cellulose acetate [12.20-12.23]. Acid scavengers, namely epoxy resins and magnesium acetate, have also been proposed [12.24]. One particularly interesting, and reasonably effective, combination of stabilisers is represented by potassium citrate with a phenol and magnesium stearate [12.25]. This has the potential to operate as a stabiliser to oxidative and hydrolytic breakdown of cellulose acetate. A variety of other similar systems have also been patented.

However, investigations of such stabiliser systems have as yet not been the subject of a systematic investigation. Furthermore, many of the systems investigated are outdated with regard to current technology and inappropriate for the application with which this project is concerned; many for instance lack the physical aspects required by cinematograph film base. The purpose of this investigation is to apply current knowledge of commercially available stabilisers and to extrapolate this, using the knowledge of the degradation pathways elucidated previously, to cinematograph film.

Chapter 13

13. EXPERIMENTAL

13.1 Materials

The films used were all 35mm, processed, commercial fine grain recording materials; coated onto cellulose triacetate support (containing phosphate and phthalate ester plasticisers, along with a small percentage of residual coating solvent) and supplied by the National Film Archive, U.K..

The commercial names of the stabilisers tested, along with their chemical formulae and suppliers are listed in Table 13.1 [13.1].

Table 13.1

Commercial Names, Chemical Formulae and Suppliers of Anti-Degradants utilised in the Stabilisation of 35mm Cellulose Triacetate Base Cinematograph Film

Commercial name	*Chemical formula*	*Supplier*
Irganox 1010	Pentaerythrityl tetrabis(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Ciba-Geigy Corp. UK Ltd.
Ethanox 330	1,3,5-Tris(3′,5′-di-tert-butyl-4′-hydroxybenzyl) 2,4,6-trimethylbenzene	Ethyl Corp. USA
Cyanox 1790	1,3,5-Tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate	American Cyanamid Co. USA
Goodrite 3114	1,3,5-Tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate	B.F. Goodrich Co. USA
Tinuvin 770	Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Ciba–Geigy Corp.
Irgafos 168	Tris(2,4-di-tertbutylphenyl) phosphate	Ciba–Geigy Corp.
DLTDP	Dilauryl-tin-dithiocarbamate	American Cyanamid Co.
Naugard XL1	2,2-oxamido-bis-(ethyl-3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Uniroyal Chemical Co. USA
Irganox MD1024	*N,N′*-Bis(beta-3,5-di-tert-butyl-4-hydroxyphenyl-propiono) hydrazide	Ciba–Geigy Corp.
—	Nickel & Zinc di-iso-nonyl-dithiocarbamates	Robinson's Ltd. UK
Lankromark LZ440	—	Harcros Lankro Ltd. UK
Lankromark LC68	—	
Lankroflex ED6	—	
—	Sodium phenyl phosphinate	ICI Wilton UK

13.2 Stabiliser Incorporation

Film samples were immersed in a bath containing a solution of stabiliser components in a 50:50 propan-2-ol:water mixture for a period of 2 hours to allow diffusion of the stabilisers into the swollen film material. The stabiliser bath also contained plasticiser to prevent loss of this component from the film to the bath. "Stabilised" film samples were then wound into reels.

N.B. With this solvent/non-solvent ratio some film distortion was apparent due to the different rates of swelling and subsequent drying of the gelatin emulsion layers and cellulose-triacetate base composing the film material. However, this was not considered to be of prime concern here, the main objective being incorporation of an optimum concentration of stabiliser compounds, in order to assess their effectiveness.

13.3 Ageing

Film reels with incorporated stabilisers were aged in contact with metal cans at a constant temperature of 90°C and a constant relative humidity of 100%. Samples were periodically removed, from the outer circumference of the film reel, and tested for retention of viscosity and moisture regain (same methodology as in chapter 7, section one).

13.4 Arrhenius Predictions

In order to extrapolate the high temperature ageing results to normal archival conditions the data were treated by a modified Arrhenius approach (see section two). Film samples which were treated with the tris stabiliser combination: Tinuvin 770 / Irganox MD1024 / Sodium Phenyl Phosphinate were oven-aged at temperatures of 70, 80, 90 and 100°C at 50%RH and the time taken for a 10% decrease in viscosity retention noted. Unstabilised samples of the same film type were also aged under the same conditions.

13.5 Optimising Tris-Stabiliser Incorporation

With respect to tris-stabiliser incorporation some difficulty was experienced in solubilising Irganox MD1024. Saturated solutions of Irganox MD1024 were thus left to stand, with agitation, for 24 hours. The solutions were then filtered and absorption spectra recorded in the range 400-200nm, using a Perkin-Elmer Lambda-7 uv/visible spectrophotometer.

Irganox MD1024 absorbs at 310-250nm dependent on the solvent system used.

Chapter 14

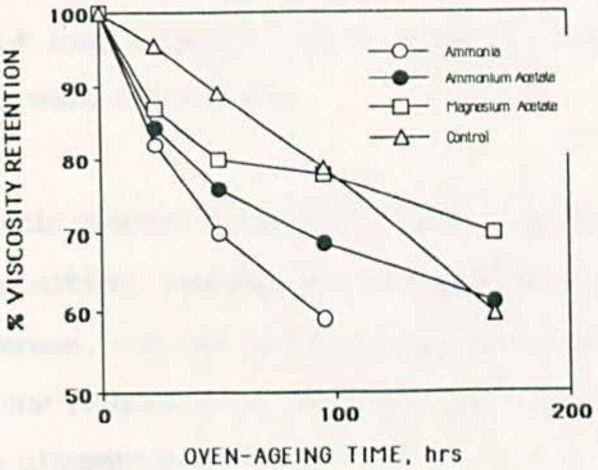
14. RESULTS AND DISCUSSION

14.1 Stabiliser Performance

The first study was to determine the influence of simple stabiliser systems capable of deactivating the species which were earlier deduced to significantly influence stability.

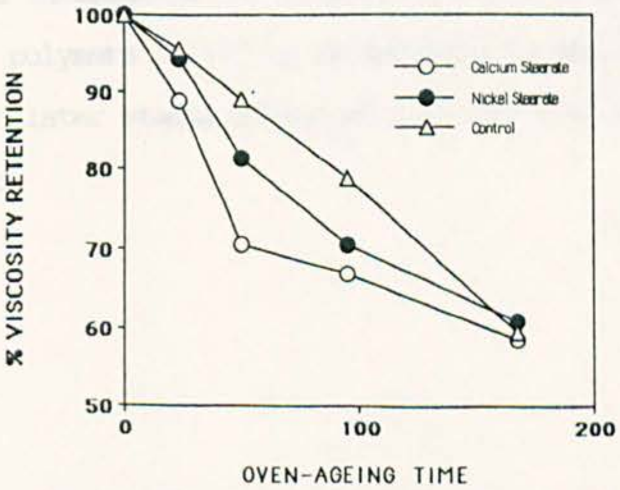
Bearing in mind, the sensitivity of cellulose triacetate cinematograph film to changes in pH and that the presence of acetic acid will be a major factor in influencing this parameter the primary step in improving stability would logically be to control pH. Figure 14.1 shows preliminary attempts to achieve this; on the one hand the use of an ammonia wash; and on the other the use of buffers such as ammonium and magnesium acetates. Retention of the viscometric properties of the base material is taken here as being indicative of degradation. The inability in all three cases to stabilise the material; and in the case of ammonia to significantly promote onset of degradation implies two things. Firstly, that it is not enough to merely neutralise any acid impurity by use of a system which is significantly basic since it will act itself as an instigator of hydrolysis. Secondly, buffering the system is not a sufficient measure against decomposition.

Figure 14.1



Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film washed with ammonia and containing ammonium and magnesium acetate buffers (0·5% w/w) aged at 90°C and 100% RH.

Figure 14.2



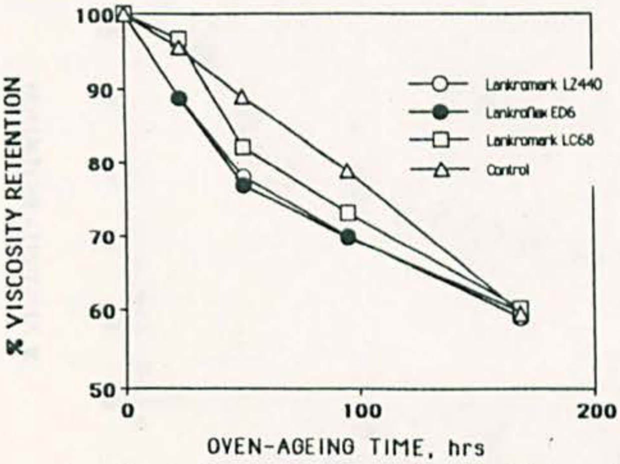
Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing calcium and nickel stearates (0·5% w/w) aged at 90°C and 100% RH.

This observation is supported by the data in Figures 14.2 and 14.3 which examine the effects of weak acid scavengers, calcium and nickel stearates, and typical PVC stabilsers. Although these compounds operate in a similar manner to magnesium acetate they have the added advantage in that they are more compatible with the cellulose triacetate polymer due to the presence of long aliphatic chains. However, again all are not only inactive but weak sensitisers.

From earlier mechanistic studies hydroperoxides are implied as being key species in decomposition. However, peroxide decomposers of established effectiveness, such as metal di-isononyl-dithiocarbamates (Figure 14.4) and DLTDP (Figure 14.5) show poor performance in cellulose triacetate cinematograph film.

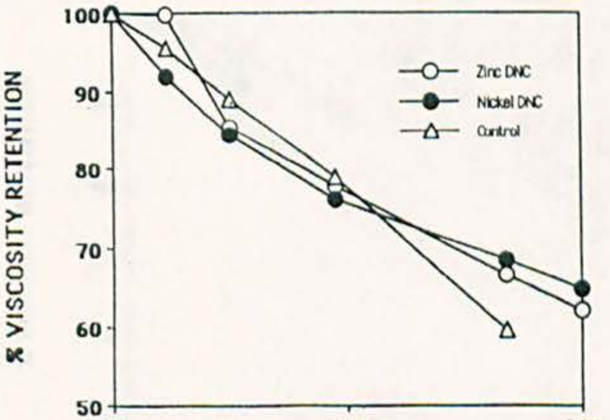
If any peroxide induced decompositions were occurring the presence of metal ions would noticeably influence this parameter. It would be considered therefore that metal deactivators such as Naugard XL1 and Irganox MD1024 would significantly deccelerate decomposition. Although these compounds are instrumental in inhibiting metal catalysed breakdown in other polymers [14.1] in cellulose triacetate they are significant only at later stages of ageing and their effect is not particularly marked.

Figure 14.3



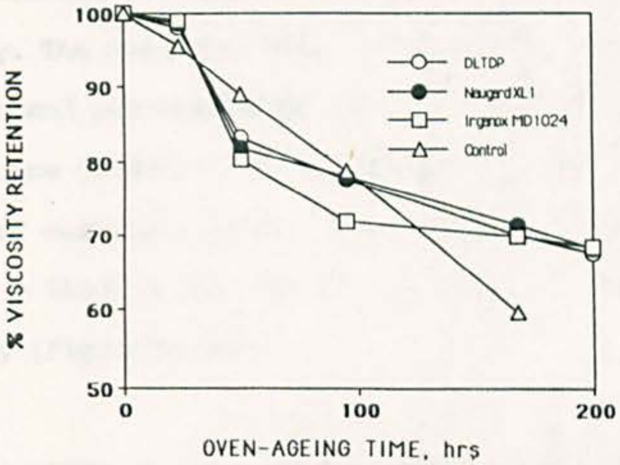
Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing the PVC stabilisers Lankromark LZ440, Lankroflex ED6 and Lankromark LC68 (0·5% w/w) aged at 90°C and 100% RH.

Figure 14.4



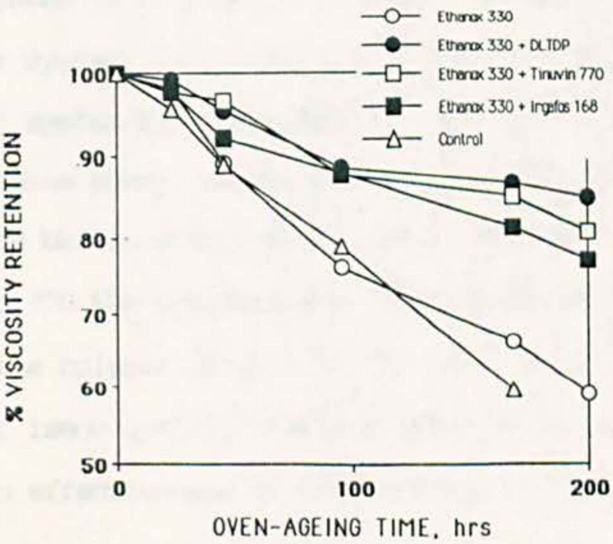
Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing zinc and nickel di-isononyl-dithiocarbamates (0·5% w/w) aged at 90°C and 100% RH.

Figure 14.5



Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing the metal deactivators DLTDP, Naugard XL1 and Irganox MD1024 (0·5% w/w) aged at 90°C and 100% RH.

Figure 14.6

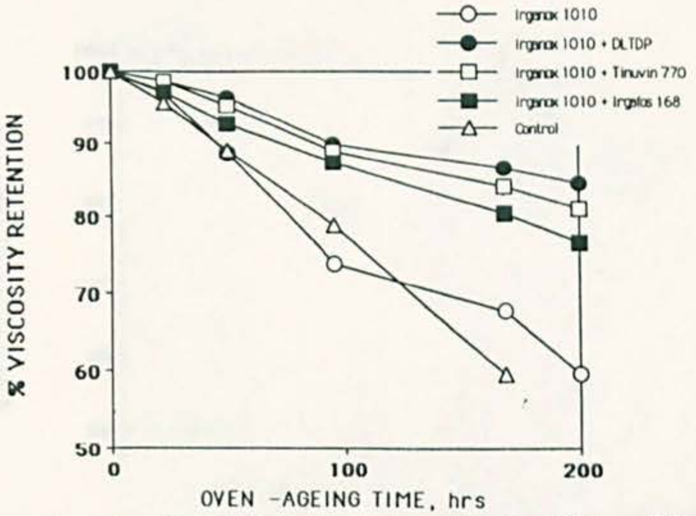


Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing Ethanox 330, alone (0·5% w/w) and in combination with DLTDP, Tinuvin 770 and Irgafos 168 (0·5% w/w) aged at 90°C and 100% RH.

Bis-stabiliser systems were then considered. Combinations of peroxide decomposers and hindered piperidines with the antioxidants Ethanox 330 (Figure 14.6), Irganox 1010 (Figure 14.7) and Cyanox 1790 (Figure 14.8) were evaluated. The results show three interesting features. The first is that a primary phenolic antioxidant itself has little or no effect on polymer stability. The second is that combinations of primary phenolic antioxidant and peroxide decomposers (DLTDP & Irgafos 168) or the hindered piperidine (Tinuvin 770) are strongly synergistic. Thirdly, the order of stability in all three areas is of the order Irgafos 168 > DLTDP > Tinuvin 770. Tinuvin 770 used alone has no effect on polymer stability (Figure 14.9).

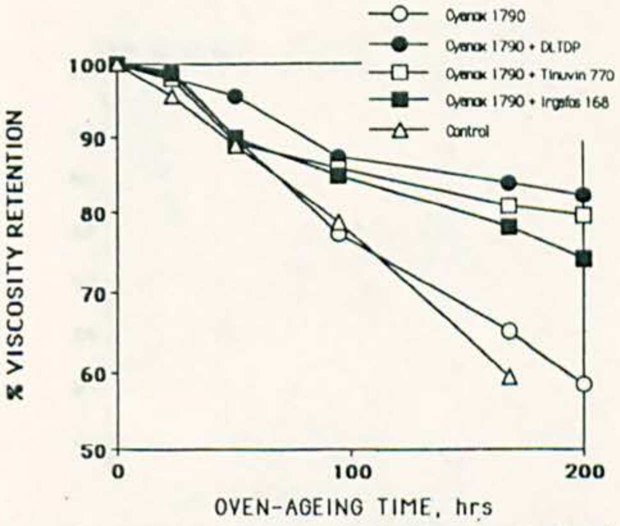
The two metal deactivators (Irganox MD1024 & Naugard XL1) when used in combination with Tinuvin 770 increase the induction period prior to loss of viscosity retention. It should be noted however, that the metal deactivators studied here, as well as complexing metal ions are also phenolic antioxidants, and are therefore capable of scavenging free-radicals. The system could therefore be regarded as a tris rather than a bis-stabiliser system. This examination was then extended to the use of a "quaternary" system by incorporating a water-soluble peroxide decomposer namely, sodium phenyl phosphinate. Alone this component exhibits no protection but in combination with Irganox MD1024 or Naugard XL1 & Tinuvin 770 the system almost completely retains the molecular weight of the polymer (Figure 14.10) over the time period studied. The superior image quality observed after 50 hours of oven-ageing makes the effectiveness of this combination self-evident (Figure 14.11).

Figure 14.7



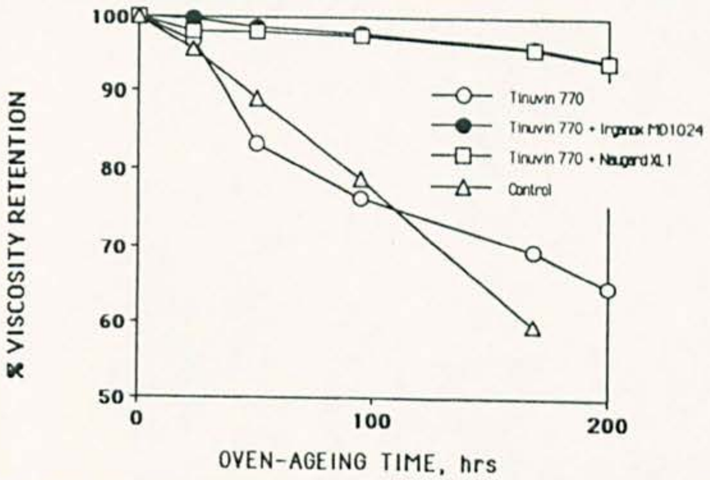
Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing Irganox 1010, alone (0·5% w/w) and in combination with DLTDP, Tinuvin 770 and Irgafos 168 (0·5% w/w) aged at 90°C and 100% RH.

Figure 14.8



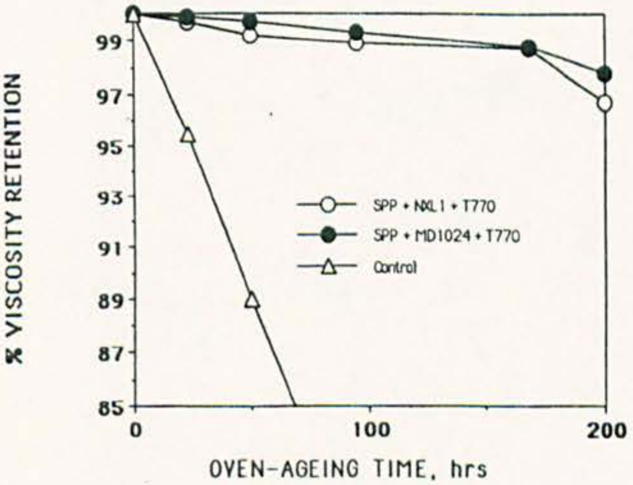
Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing Cyanox 1790, alone (0·5% w/w) and in combination with DLTDP, Tinuvin 770 and Irgafos 168 (0·5% w/w) aged at 90°C and 100% RH.

Figure 14.9



Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing Tinuvin 770, alone (0·5% w/w) and in combination with Irganox MD1024 and Naugard XL1 (0·25% w/w) aged at 90°C and 100% RH.

Figure 14.10



Percentage viscosity retention versus oven-ageing time (h) for cellulose triacetate base cinematograph film containing tris combinations of stabilisers.

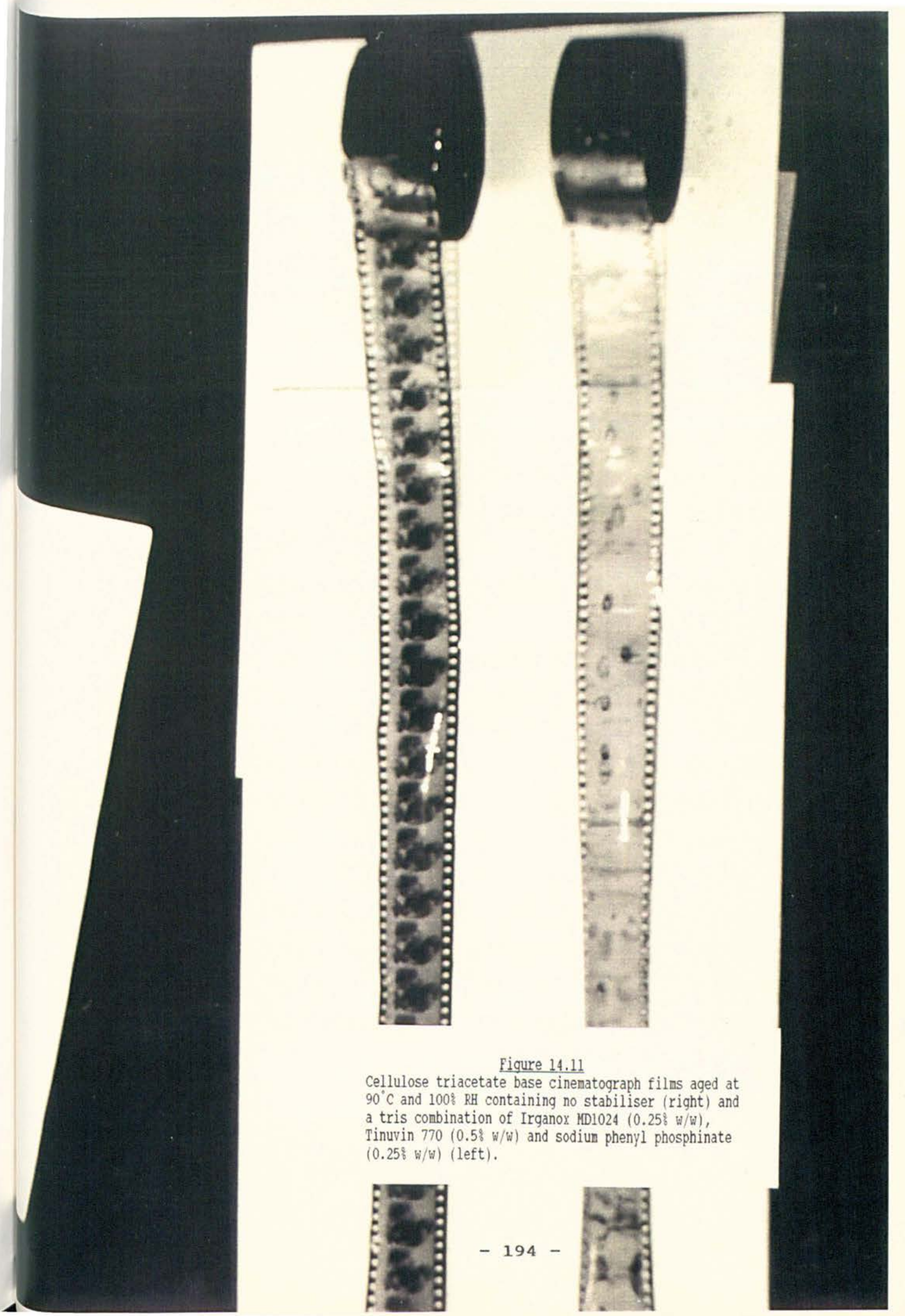
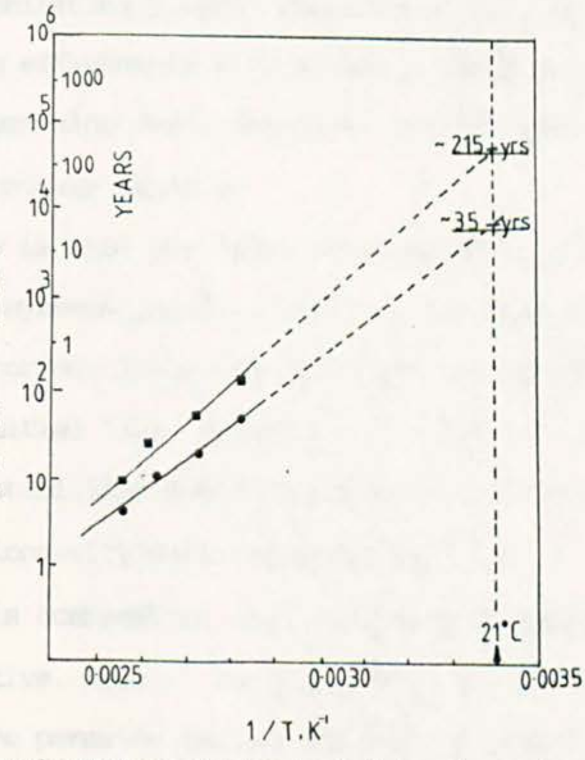


Figure 14.11
Cellulose triacetate base cinematograph films aged at 90°C and 100% RH containing no stabiliser (right) and a tris combination of Irganox MD1024 (0.25% w/w), Tinuvin 770 (0.5% w/w) and sodium phenyl phosphinate (0.25% w/w) (left).

14.2 Prediction of Archival Life for Films Containing the Tris-Stabiliser System

Figure 14.12 illustrates the predicted lifetime of stabilised (Tinuvin 770, Irganox MD1024, Sodium Phenyl Phosphinate) and non-stabilised film materials; based on the time taken for a 10% loss in viscosity of the cellulose triacetate support. For stabilised material a six-fold increase in longevity from around 35 years (for unstabilised material) to 215 years is indicated.

Figure 14.12



Time taken for 10% loss in the viscosity of cellulose triacetate base cinematograph film (years) versus the reciprocal temperature of degradation (K) for films aged in contact with metal cans at 50% RH containing no stabiliser (●) and a tris stabiliser (■) combination of Irganox MD1024, Tinuvin 770 and sodium phenyl phosphinate.

14.3 Mechanistic Implications derived from Stabiliser Performance

The results obtained in this stabilisation study are interesting compared with those for other polymers, since it shows that the use of a single stabiliser system is largely ineffective. This would suggest that although all three species discussed previously are implicated in the degradation mechanism they are not necessarily interconnected and may operate independently. This is confirmed by the observation that stabilisation is effective only with bis, or even more so with tris, stabiliser systems capable of deactivating two or all of the reactive degradants.

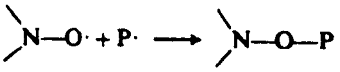
It may be therefore, that the primary phenolic antioxidants are ineffective in inhibiting polymer degradation because they are either unable to compete efficiently with alkoxy or hydroxy radicals (generated from peroxide decomposition); or that this mechanistic route is not the sole primary reaction.

Of course, it may be that the degradation pathway, for some of the single component systems investigated, has not been followed for a sufficient time period; since many peroxide decomposers such as Nickel DNC exhibit an initial 'lag' period [14.2]. Even so, in view of observations of stabiliser combinations it is unlikely that significant prolongation of longevity would necessarily follow.

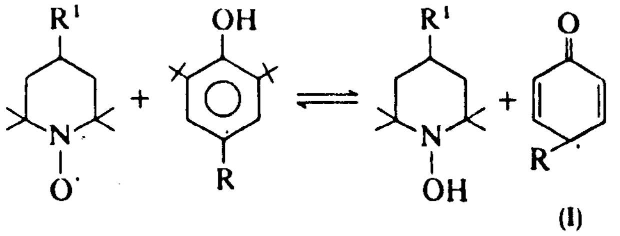
In support of this combination with secondary antioxidants proves reasonably effective. Here it is likely that secondary antioxidants are decomposing active peroxide and protecting the simple alkyl radical terminating operation of the phenolic antioxidant.

The synergism imparted by the hindered piperidine, Tinuvin 770, is interesting since this molecule can operate in three ways. The first is to decompose hydroperoxides to give stable nitroxyl radicals and thus protect primary and secondary antioxidants. i.e.

The second is the ability of the nitroxyl radicals to scavenge macro-alkyl radicals as follows:-



The third is to scavenge the active acid produced by de-esterification. The synergism between the hindered piperidine, Tinuvin 770, and the phenolic antioxidants is described in Figure 12.6.
An important part of this scheme is the interaction of the nitroxyl radical of the hindered amine with the phenolic antioxidant according to:



(I)

However, in the case of cellulose triacetate stabilisation the radical (I), is more probably generated by reaction of the hindered phenol with

$RO_2\cdot$; since the former will be dependent on the local concentration of nitroxyl [14.3]. The presence of hydroperoxides would force both these reactions to the right anyhow and this would be accentuated in the presence of metal ions. The use of a secondary antioxidant (sodium phenyl phosphinate) would therefore serve to destroy the hydroperoxides and maintain equilibrium. The metal deactivator would enhance the overall synergism by complexing out any metal ions. Since this also has a superimposed antioxidant function the overall scheme would be further reinforced. The whole system would be further preserved by the very efficient scavenging ability of >NOH [14.4] regenerating the nitroxyl. Naturally, this is by no means the only mechanism of operation and a more in depth study would be necessary to confirm such proposals. More recent physico-chemical studies, for example, suggest the possibility of oxidation of phenol by hindered nitroxide in a very slow equilibrium reaction. Due to intermolecular donor-acceptor interactions, both reactants form a paramagnetic σ-complex - the strength of the latter dependent on the specific structure of both reactants [14.5].

14.4 Stabiliser Compatibility and Introduction

It should be noted, that some problems were experienced on the introduction of some stabiliser systems. Adequate migration of stabilisers into the film base is dependent upon the extent of solubility of the stabiliser in question in the solvent system used. Irganox MD1024 for example exhibited several difficulties in this respect. Figure 14.13, illustrates improved solubility of this component in an alternative solvent system, demonstrating that such difficulties can be overcome.

Having said this it will require much more work to fully optimise stabiliser introduction while minimising film distortion, but this is essentially a technological aspect of the problem.

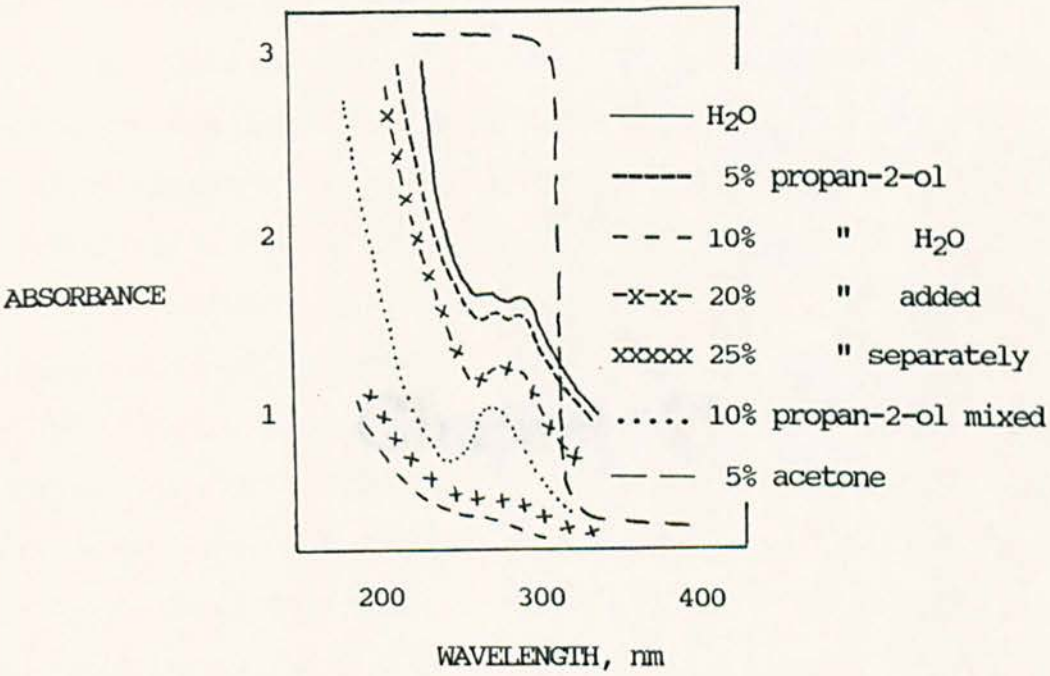


Figure 14.13

The Solubility of Irganox MD1024 in a Range of Solvents

Chapter 15

15. OVERVIEW AND CONCLUSIONS

Good correlation between natural and accelerated ageing tests has been achieved. Results from chemical and physical testing along with statistical surveys on archival materials reflect well implications from artificial-ageing studies.

The dominant feature in the stability of cellulose triacetate support cinematograph film is the emulsion layer. The majority of polymer systems are relatively hydrophobic but in the case of cinematograph film the emulsion layer is in close contact with the cellulose triacetate support and provides a reservoir of moisture necessary for any hydrolytic reactions. The acute sensitivity of the emulsion to fluctuations in temperature and relative humidity will determine the moisture content of the material and hence the potential for hydrolysis. On the other hand the emulsion serves to neutralize any resulting acid degradation products. The complex interplay between the two processes will be important in determining the final lifetime of any film. Moisture uptake will to some extent be inhibited by the presence of the triphenyl phosphate plasticiser. However, as the film material degrades plasticiser becomes progressively incompatible with the support and migrates to the surface where it crystallizes out as a white deposit which obscures the image. In this process areas would be left within the polymer network which would be susceptible to moisture and oxygen attack thus enhancing the potential for any degradation processes which may be taking place.

The container within which the film reel is housed plays both an active and passive role in stability. In the former case, the presence of acetic acid serves to erode any coating in metal cans exposing the underlying iron which apparently accelerates any degradation reactions. High levels of iron have been found within degraded filmstocks. That this is not merely a facile process of 'uptake' as the polymer becomes progressively more hygroscopic has been shown by doping cellulose triacetate with metal oxides. The part played by metal ions in catalysing degradation is apparently associated with the presence of peroxides formed within the polymer. This in turn suggests that some kind of free-radical autocatalytic mechanism is operating. Both free-radical and hydrolytic processes may result in formation of acetic acid which will serve to emphasize any de-esterification reactions occurring by either acid-catalysed hydrolysis or acetolysis.

In the latter case, the passive role played by the can is one of containment. Free-circulation of air surrounding the film reel is inhibited. This has the effect of concentrating any initial degradation products in the immediate vicinity of the film material. This in turn enhances the possibility of primary degradation products instigating secondary degradation reactions. Conversely, ineffective removal of acetic acid also apparently suppresses any significant acetate loss. This build up of acetic acid also has other consequences. At ambient temperatures there will be competition between chain-scission and cross-linking. The latter process is usually dominant at low oxygen concentrations. In the case of many naturally-aged cinematograph films some cross-linking has occurred in addition to chain-degradation. It is likely that oxygen will be initially consumed to produce peroxides but will gradually be displaced by any acetic acid formed. Thus both chain degradation and cross-linking are likely to occur in naturally-aged materials. This would also account for the relatively low levels of peroxides found in naturally-aged materials compared to artificially-aged films. Obviously relative consumption rates of acetic acid and oxygen by the film material when housed in a film can will be important in determining subsequent degradation mechanisms, and any future studies should attempt to elucidate this.

Predicting the longevity of films or at least establishing the limits of their stability is of prime concern. This requires an understanding of the kinetics of degradation. Correlating the findings here to studies performed by other workers provides a more coherent picture of degradation. It has been shown that de-acetylation proceeds by kinetics which are first order with respect to moisture i.e. rate of de-esterification approximately doubles as moisture concentration doubles, but is independent of concentration of acetate groups. Although this information is the result of solution studies it also apparently applies to cinematograph film support; de-acetylation rate increasing with increasing relative humidity. In contrast to homogeneous solution studies the limiting factor of accessibility becomes apparent in the heterogeneous polymer: This factor should be taken into account in any kinetic investigations. This is reflected in cinematograph film reels as the moisture gradient described previously. Furthermore, the initial de-acetylation reaction is largely a feature of surrounding relative humidity and temperature of a cinematograph film. Since these parameters will be fluctuating during film lifetime and kinetics become even more complex. A similar argument applies to any secondary reactions which occur. Here solution studies have shown chain degradation to be independent of moisture concentration but to be first order with respect to acetic acid. Again no account of accessibility or competing reactions is taken. Use of an Arrhenius relationship without taking such factors into consideration i.e. attempting to apply kinetic relationships which have arisen from the study of small molecules, is inappropriate. Hence the wide divergence in results by different workers. Even if these criteria can be satisfied there remains the possibility of misleading results if the same degradation product can be formed by more than one mechanism. Since acetic acid, the major degradation product, can arise by a number of possible mechanistic routes, accurate lifetime predictions are difficult to achieve. Use of the simple Arrhenius relationship provides information in an intercomparative sense i.e to indicate whether one material is more stable than another, but the accuracy of absolute lifetime predictions by this method is questionable. It has been stated previously that a close correlation between artificial and natural ageing studies must be achieved for any accelerated ageing interpretations to be realistic. In this respect the value of both chemical test and statistical data arising from films housed in archives and exhibiting degradation cannot be over emphasized. Although the statistical survey undertaken in the present study was not exhaustive (merely intercomparing incidences of degradation for different types of material e.g. magnetic and non-magnetic track materials, or negative and positive films) it has correlated well with what would be predicted by relating chemical test data obtained from both naturally and artificially-aged films. However, it seems that by far the most appropriate approach to discern film lifetime is to monitor the induction period prior to degradation. Here correlation of how concentration of acetic acid (the degradation product which participates in the rate determining step in breakdown) relates to image quality should establish a concentration limit beyond which film condition is no longer acceptable and should be stabilised or copied.

Stabilisation studies support inferences from mechanistic investigations that a combination of processes lead to degradation. Stabilisation is achieved by a combination of Irganox MD1024, Tinuvin 770 and Sodium Phenyl Phosphinate. The overall picture which emerges has interesting implications within the field of stabilisation because despite dual functionality of individual stabilisers (e.g.Irganox MD1024 acts as a phenolic antioxidant and metal deactivator; Tinuvin 770 as an acid or free-radical scavenger) they are relatively ineffective except when used in combination. That these stabilisers are relatively ineffective when used alone suggests that several mechanisms are operating and that some synergistic interaction is occurring. It would be interesting to follow up the initial studies to determine the extent to which Tinuvin 770 is acting in its capacity as a base to neutralise any acid degradation products and the extent to which it is participating in blocking any free-radical reactions. Tinuvin 770 may as is suggested by recent studies also play a part in complexing with any metal ions [15.1]. Since stabilisation studies also imply the metal deactivator is playing a dominant role an investigation of relative concentration efficiency of each component in the tris-system would be informative. It is necessary also to determine whether the tris-system is penetrating the cellulose triacetate support or merely the emulsion

or both - it may be that effective lifetime is extended as a result of improved emulsion stability rather than support stability.
The role played by the plasticiser is significant. Although original reasoning behind its addition was to resist moisture uptake by the base material results suggest it also has a superimposed antioxidant function and as such may complement the functioning of the stabiliser system. Subsequent to completion of this project ongoing studies using FTnmr have shown that where the plasticiser is a phthalate ester this serves as a stabiliser. Results indicate that any acetate released substitutes itself on the phthalate ring and is so prevented from reacting further with either moisture or the polymer.

A more in depth mechanistic study is now required to identify the extent to which hydrolysis, acetolysis and free-radical reactions are separate or whether (and how) they influence each other and exactly how the stabilisers are operating. Here any free-radical reactions of both polymers and stabilisers could be followed by ESR spectroscopy. Relative stabiliser concentrations may be followed by uv spectroscopy (for phenolic antioxidants) and HPLC (for hindered amines and phosphates/phosphinates). In addition, ESCA could provide a valuable tool in determining any processes which may be taking place at the surfaces where an interface occurs. In particular the role played by the subbing layer, which has not been considered here, could be elucidated by this technique. A more in depth understanding of the mechanistic aspects of any degradation processes will be important in refining the stability tests and stabiliser systems which have been described in this study.

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