

Charles Selwitz

Cellulose Nitrate in Conservation

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nitrate

THE GETTY
CONSERVATION
INSTITUTE

$C_6H_7O_2(ONO_2)_3$

Cellulose Nitrate in Conservation

Charles Selwitz

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in Conservation**

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Dr. Charles Selwitz received his Ph.D. in organic chemistry at the University of Cincinnati in 1953. After graduation he was with the Gulf Research and Development Company in Marmarville, Pennsylvania until 1982 where he was Director of Synthetic Chemistry. During that period he published 121 papers and patents, mostly in the fields of acetylene chemistry, oil field chemicals, high performance polymers, and hydrocarbon oxidation. He is now an independent consultant, but works primarily for the Getty Conservation Institute on problems of stone consolidation.

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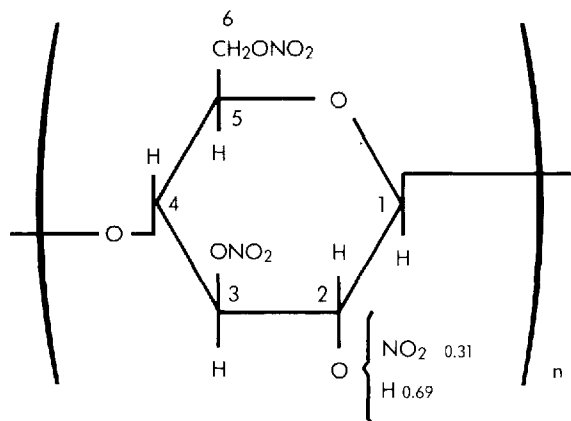
Contents

Chapter 1	The Use of Cellulose Nitrate in Art Conservation	1
Chapter 2	The Structural Chemistry of Commercial Cellulose Nitrate	9
Chapter 3	Causes of Instability	15
	Hydrolytic Decomposition via Acid Catalyzed Ester Cleavage	15
	Thermal Decomposition.....	17
	Decomposition by Ultraviolet Radiation	22
	Mechanisms of Primary Decomposition	25
	Secondary Modes of Decomposition	25
Chapter 4	Cellulose Nitrate Stability at Ambient Conditions	33
	Structural Factors for a More Stable Cellulose Nitrate	34
	Avoidance of Acid Catalyzed Ester Cleavage.....	36
	Thermal Cleavage.....	38
	Ultraviolet Degradation	38
Chapter 5	The Use of Cellulose Nitrate as an Adhesive for Ceramics	41
Chapter 6	The Use of Cellulose Nitrate as a Metals Coating	49
	Introduction	49
	Compositions.....	50
	Special Properties.....	52
	Stability.....	55
Appendix	Proprietary Material Cited in the Text	57
	References	59
	Index	67

The Use of Cellulose Nitrate in Art Conservation

Cellulose nitrate is the polynitrate ester of the natural polysaccharide, cellulose, and for a polymer averaging 2.3 nitrate groups per glucose unit has the structure shown in Figure 1. The molecular weight for most commercial products ranges between 20,000 and 250,000. This semisynthetic polymer was first produced more than 150 years ago and is the most important and only commercially available inorganic ester of cellulose. Due to its unique physical properties and low cost it has been an important factor in many advances in the industrial arts and sciences over the years. Cellulose nitrate was initially used in the manufacture of military explosives where it came to be known as "gun cotton," the first major development in explosives since the introduction of black powder. When it was discovered that cellulose nitrate could be stabilized with camphor (in the ratio of 4:1), the resultant product, celluloid, inaugurated the advent of engineering plastics.

Figure 1.
Cellulose nitrate structure
for polymer with a 2.31 degree
of substitution.



In the years following World War I, cellulose nitrate lacquers and coatings were developed. While these have since been superseded by better materials, the largest industrial use today of cellulose nitrate (now also referred to as nitrocellulose) continues to be in its capacity as a lacquer, although substantial quantities are still used in explosives and propellants, printing inks, and plastics. Currently, the total commercial production of cellulose nitrate in the United States approaches 100 million pounds a year.

Criteria for polymeric material to be used in conservation and particularly in coatings have been developed by Feller (1976:137). Considerations of solubility, stability, and hardness consign cellulose nitrate to his low molecular weight group of polymers (i.e., damar, mastic, polyketones, etc.), materials that are readily soluble in many solvents to give solutions with good working properties. These solutions form hard, often brittle films, and since they possess high refractive indices, a penetrating lay down and other related properties, they provide coatings with good optical qualities.

In terms of stability, however, cellulose nitrate is a very suspect material. It does not have the resistance to degradation possessed by most other polymers used in conservation. Only when stability is defined as "the maintenance of solubility and reversibility" can cellulose nitrate, which degrades, but generally does not crosslink, be said to have stability.

A consideration of the molecular structure elucidates why the polymer is relatively unstable. These same factors lead, however, to properties that make its use attractive to many conservators. These beneficial properties are to a large extent products of the extraordinarily high nonionic polarity of the molecule, a polarity that is provided by the extensive network of nitrate ester groups and hydroxyl groups. This combination forms a multiplicity of strong but reversible coordinate bonds with oxygen-bearing substrates, both organic and inorganic. The high polarity of the polymer limits its use to high dielectric constant solvents—esters and ketones—and excludes the use of aromatic and aliphatic hydrocarbons.

Adhesive-grade cellulose nitrate, comparable in degree of substitution to the structure of Figure 1, provides a much more viscous, thixotropic solution than a polymer of similar molecular weight that is completely nitrated and thus has no hydroxyl groups. This uncommon combination of intra- and intermolecular coordinate bonding enables these relatively low molecular weight polymers to have unique tackiness, thinness, and solvent release properties sought after in many conservation applications. Consequently, cellulose nitrate has found broad usage in art conservation. In her article, "New Methods for the Consolidation of Fragile Objects," Rosenquist gives further theoretical insight into the relationship between polymer structure and adhesive properties.

Existing literature amply describes how the polymer has been successfully employed as an adhesive for stone and ceramic ware, as a consolidant, and as a coating for fine metal objects. The same literature also points out the less desirable aspects of using cellulose nitrate in conservation. Meryl Johnson (1976:66-75) provides an excellent review of cellulose nitrate as a conservation hazard. Johnson discusses the history of the growth of this polymer in commercial applications and points out a generally concurrent growth of its use in art. He also points to a critical need to determine the long-term reversibility of cellulose

nitrate, the chances of preserving and safely storing objects made of it, and the necessity of continuing to use it as a conservation material.

Mibach, writing in *Conservation and Archaeology and the Applied Arts* (1975:58), describes the suitability of cellulose nitrate for ceramic restoration in terms of having the correct levels of plasticization and viscosity required for good workability, physical and chemical stability, rapid drying, and reversibility. Several brands and suppliers of cellulose nitrate are named in the appendix; HMG is recommended with the comment "experience has shown this brand to be useful, durable and lastingly reversible." Dowman (1970:71) recommends cellulose nitrate as one of only a few adhesives that have been found satisfactory for joining pottery and other porous objects found in excavations. She, too, prefers HMG brand, although a formulation for preparing the adhesive from celluloid is described that can be used when HMG is not available. Furthermore, directions are given for balancing the use of acetone and amyl acetate solvents to control solvent loss and viscosity and for the addition of plasticizer to prevent film cracking.

Plenderleith and Werner's *The Conservation of Antiquities and Works of Art* (1971:338), considered to be among the most reliable handbooks available on conservation, recommends cellulose nitrate under the tradename Durofix for repairing broken pottery, earthenware, and tile. They favor the use of poly(vinyl acetate) or poly(methyl methacrylate) as consolidants when fragile pottery fragments need to be strengthened. A 1979 UNESCO publication claims that cellulose nitrate is probably the most convenient adhesive for mending archaeological pottery and recommends Balsa or HMG brands. The article cautions that certain commercial brands are deficient in plasticizer and offers a method for the preparation of a glue by following the procedure essentially provided by Dowman.

Cellulose nitrate has also been used as an adhesive for glass, although it can be expected to be much less successful in this application than for pottery. Glass, which does not have the porosity of ceramics and has different adhesive requirements, will also transmit light to the polymer, and light transmission has long been known to provide an additional mechanism of decomposition. Furthermore, discoloration, which can occur through trace contamination and without significant loss of bond strength, is much more apparent within a glass structure. Koob (1986:7-14) shows that Acryloid B-72 is a stronger adhesive than poly(vinyl acetate) or cellulose nitrate (Duco cement) for non-porous ceramics such as porcelain or glass slides.

Despite its drawbacks, the use of cellulose nitrate as a glass adhesive has drawn favorable comment from a number of conservators. Davison (1984:191-4) reviews adhesives and consolidants used on glass antiquities. She comments on Koob's work and notes that it draws attention to the long-term instability of cellulose nitrate, but feels cellulose nitrate still

remains a most useful adhesive in the absence of anything more suitable. Davison (1978:3-8) particularly favors cellulose nitrate for joining glass surfaces that are delicate or uneven because she has found it to be very fast setting. This is surprising in view of Koob's finding that glass slides glued at butt ends with Duco cement showed absolutely no adhesion, even after 72 hours.

Plenderleith and Werner underscore the difficulty of repairing broken glass objects and recommend a cellulose nitrate formulation such as Durofix or HMG as probably the most useful adhesive for this general purpose. The previously mentioned UNESCO publication also recommends the polymer for glass and porcelain. Davison cites a number of other papers on the use of cellulose nitrate for repairing glass (Davison 1984; Jackson 1983:10-1 to 10-7).

Cellulose nitrate has been used to repair crazed enamel. Enamel is basically a glass colored by the addition of metal oxides and fused onto a metal base. It is a composition that often exists under high strain without apparent cause and can become loose from the base and even fracture. Both Plenderleith and Werner (1971:71) and Mills (1964:39) recommend repair by freely covering the object with a cellulose nitrate lacquer, then carefully removing the excess with an acetone swab. Plenderleith also recommends the polymer for the repair of ivory, a purpose where ease of application, good adhesive properties, and reversibility are important considerations. The ivory comb of St. Cuthbert, which had split into many fragments, was readily restored using Durofix, and the repair is expected to be permanent under museum conditions.

The volume of cellulose nitrate sold commercially as a lacquer and or coating is much larger than that sold as an adhesive. It has been proposed and tried in art conservation for most situations where coatings are required, but in recent years, its most popular application has been as a protective lacquer for silver objects. Commercial silver lacquers such as Frigilene are thin, low-viscosity cellulose nitrate solutions that also contain stabilizers and plasticizers in a suitable blend of solvents. Both Mills and Plenderleith and Werner recommend Frigilene for covering silver and discuss the cleaning and degreasing of the object that must be carried out prior to its use. Plenderleith also comments on the use of a cellulose-nitrate-based coating, Ercolene, to protect both bronze and iron. This polymer gets high marks for its transparency. Moncrieff (1966:6-7) compares cellulose nitrate, a silicone, and Inctalac (an acrylic polymer containing benzotriazole) for coating silver and prefers the latter for protection against tarnish, resistance to abrasion, and ease of application. Most of the references noted above provide only a brief mention of the use of cellulose nitrate as a metals coating. More recent research and examination in depth of this application by Don Heller (1983:57-64) of the Winterthur Museum and others will be discussed in a later section on coatings.

Cellulose nitrate has been recommended for a variety of uses in archaeology. One of these is the "Lackfilm" method for collecting mirror-image replications of paleontologically and archaeologically important surfaces (Voight and Gittens 1977:449-57). The method involves initially spraying an acetone-diluted cellulose nitrate lacquer onto a previously prepared surface. This first application is then set afire to burn off the acetone and stabilize the impregnation. Subsequently, two or three applications of more viscous solutions are made and the solvent is allowed to evaporate. Finally, a gauze backing is applied and, after another 30 minutes of drying, the film is stripped from the surface and rolled on a core for transport.

It is interesting to note that, when flame is applied to the cellulose nitrate coating, the unevaporated acetone burns and the polymer does not. There is a feeling among conservators who are apprehensive about the use of cellulose nitrate that after some aging the material is liable to burst into flame spontaneously. The Lackfilm experience suggests this is not likely. In addition, the peeling film procedure has been advocated for removing stains from marble, and Plenderleith and Werner (1971:317) provide several lacquer formulations for doing this. They also mention the use of cellulose nitrate to repair marble, unbaked clay, and cuneiform tablets.

In addition to Meryl Johnson, many other conservators, particularly those with a more scientific background, do not favor the use of cellulose nitrate in conservation. Van Zelst states,

The adhesives which have been used historically to mend broken ceramics include stick shellac, a paste of white lead (lead hydroxy carbonate) in oil, and cellulose nitrate. None of those is used anymore because of the undesirable properties of these adhesives, notably their discoloration upon aging and the large changes in solubility characteristics for some of them (1984:437).

In an article on the "Instability of Cellulose Nitrate Adhesives," Koob concludes,

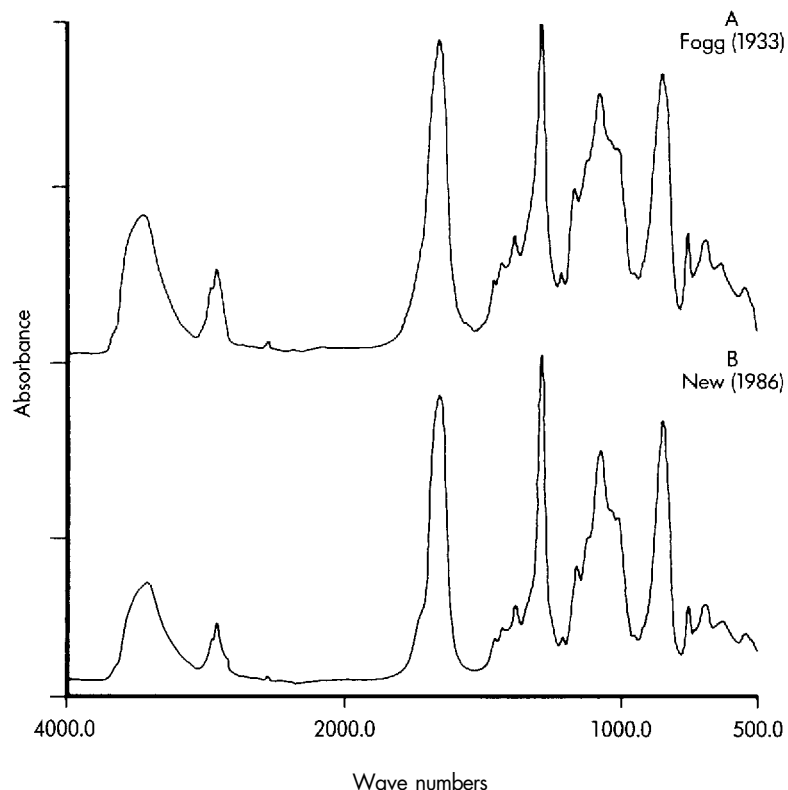
Research shows that cellulose nitrate cannot be depended on as a stable compound, even with the addition of stabilizers. Commercially available adhesives based on cellulose nitrate are no exceptions. It is only a matter of time before the deleterious combination of acid impurities remaining from manufacture, the eventual loss of volatile plasticizers and the external environment accelerate the degradation of an already unstable compound. . . . Further research into adhesives for conservation is necessary, but with all due respect to the usefulness that cellulose nitrate has shown, it is no longer the best choice of available adhesives (1982:31-34).

The Canadian Conservation Institute (CCI) has put cellulose nitrate on its list of materials that should not be used for conservation applications under any conditions.

Nevertheless, cellulose nitrate is still being used as an adhesive for ceramics and as a coating for metal objects by many conservators. Considerable effort has been expended in attempting to establish documented examples of failure in situations where this material was used as an adhesive. Koob cites cases where Samerthrace glass has not held up. In compiling this report, other specific examples of failure with ceramics were not available although the conservators contacted had experience going back 30 years.

However, for the present report, two different types of cellulose nitrate products were obtained with authentication that all samples were at least 50 years old. One type was obtained from the Gettens and Stout collection of naturally aged films of the Center for Conservation and Technical Studies of the Harvard University Art Museum. A 1 millimeter cellulose nitrate film was cast on glass by Rutherford Gettens in 1933. The samples in this collection were stored in the dark under ambient conditions. After 54 years, the coating was hard and clear. It possessed the structural integrity of fresh material and showed no apparent yellowing as a very thin film. The original container of lacquer was not available. The infrared spectrum of this sample is shown in Figure 2a and can be compared with the spectrum of a fresh sample of cellulose nitrate that contains 2.3 nitrate groups per cycloanhydroglucose ring (Fig. 2b). The spectra are very similar. There does not appear to be any plasticizer in this material.

Figure 2.
Comparison of new cellulose nitrate and aged Fogg samples



The other type of cellulose nitrate that was obtained was plastic sheeting used as coverings for Walt Disney cartoon cells. These were 50 to 60 years old. Production dates imprinted on the sheets made it possible to determine age with confidence. These materials had been in diffuse light at room temperature over their lifetime. All were flexible, clear, odorless, of good strength, and were discolored, at most, to a very pale yellow tint in some sections. More detailed chemical analyses of both pale yellow and relatively clear sections of these sheets have been made. A discussion of those findings is presented in later sections dealing with the chemistry and mechanism of instability.

It is clear that there is disagreement, if not outright controversy, on the suitability of cellulose nitrate for many conservation applications. It is readily demonstrated that the polymer is unstable if heated moderately or given limited exposure to ultraviolet radiation. Koob clearly shows this in the studies described in his article. He points out, moreover, that there is an inherent instability that leads to degradation even without these factors. Unfortunately, no one has yet measured exactly how much degradation occurs in the protected confinement of an adhesive interlayer, particularly under ambient conditions. It has not at all been demonstrated, for instance, that the integrity of a vase reconstructed with cellulose nitrate will not hold up for the 100 years that Feller (1976) sets as a criterion for Class A polymer stability. What if the durability is not quite that long? Is the durability nonetheless long enough to warrant using cellulose nitrate as a favored adhesive because of its other desired properties?

This report will attempt to isolate and separately examine each of the factors known to lead to cellulose nitrate decomposition, and then relate their contribution to the instability of the polymer when it is used as a bonding agent for ceramics and as a lacquer for metal objects. These factors include deterioration caused by heat, radiation, or acid impurities, or through the loss of plasticizer. There is, moreover, decomposition caused autocatalytically by the initial breakdown products. In particular, we will examine new information on chemical changes under ambient conditions that has been developed recently through advances in analytical procedures such as chemiluminescence, X-ray scanning spectroscopy (ESCA), and more sophisticated viscometry. This new information will be added to the large body of data, collected over the past 150 years, on the instability of cellulose nitrate under more severe conditions. Based upon a consideration of this comprehensive technical data and the unique requirements of art conservation, we hope to develop more soundly based conclusions concerning the suitability of commercial cellulose nitrate for conservation.

The Structural Chemistry of Commercial Cellulose Nitrate

Any cellulose nitrate can be defined with statements on its molecular weight distribution and on the number and positioning of nitrate groups on the anhydroglucose rings. The chain length, expressed as the number of anhydroglucose units in the polymer, is referred to as the degree of polymerization or D.P. This value can be obtained by viscosity measurements. For example, the D.P. of a cellulose nitrate with 12% nitrogen is 170 times the viscosity, in acetone, divided by the concentration, in grams per deciliter, at infinite dilution. Most commercial cellulose nitrates near 12% nitrogen have intrinsic viscosities of 0.4 to above 5.0. This corresponds to a D.P. range of 70-850, or an average molecular weight range of 20,000-250,000 (Spurlin et al. 1955).

The average number of nitrate groups per ring is known as the degree of substitution or D.S. The same information is given by the nitrogen content of the polymer. For a fully esterified molecule, the D.S. is 3.0, and the nitrogen content is 14.1%. When the D.S. is 2.0, the nitrogen content is 11.1%. Most commercial cellulose nitrates range between 10.7% and 12.2% nitrogen. Polymers with higher nitrogen concentrations are used in explosives. D.S. tells nothing about the distribution of nitrate esters. For a typical product of nitration taken to a D.S. of 2.3 (N = 12.2%), the polymer would contain 50% trinitrated rings, 34% dinitrated rings, 16% mononitrated rings, and essentially no rings without nitrate esters. These two properties, D.S. and D.P., are in general use industrially for the characterization of batches of cellulose nitrate. Hercules Incorporated is the only commercial manufacturer of the polymer in the United States. It supplies the material in various grades that depend on the extent of nitration: SS with 11.0% N, AS with 11.5% N, and RS with 12.0% N. The properties of the RS grade of Hercules are shown in Figure 3 (Hercules Powder Company 1965). The specifications sheet indicates that the effect of sunlight in causing discoloration and embrittlement is moderate and aging is slight. In the past, both Monsanto and DuPont also manufactured cellulose nitrate. Hercules additionally operates a plant to make explosives-grade cellulose nitrate for the U.S. Army at its Radford Arsenal. There are a number of foreign manufacturers and at least one of them, Societe Nationale des Poudres et Explosifs (SNPE) of France, markets in the United States through a distributor, the Polychrome Chemicals Corporation of Bloomfield, New Jersey.

Figure 3.
Properties of Cellulose Nitrate

General Properties	
odor	none
taste	none
color of film	water-white
clarity of film	excellent
specific gravity of cast film	1.58-1.65
refractive index, principal	1.51
light transmission, lower limit of substantially complete, Å	3,130
moisture absorption at 21°C in 24 hr, 80% rh, %	1.0
water-vapor permeability at 21°C, g/cm ² /cm/hr X 10 ⁻⁶	2.8
sunlight, effect on discoloration	moderate
effect on embrittlement	moderate
aging, effect of	slight
Electrical Properties	
dielectric constant at 25-30°C	
60 cycles	7-7.5
1,000 cycles	7
1,000,000 cycles	6
power factor at 25-30°C, %	
60 cycles	3-5
1,000 cycles	3-6
electric charge on rubbing with silk	negative
Mechanical Properties	
tensile strength at 23°C, 50% rh, lb/in. ²	9,000-16,000
elongation at 23°C, and 50% rh, %	13-14
flexibility of 3-4-mil film, MIT double folds under 200-g tension	30-500
hardness, Sward, % of glass	90
softening-point range (Parr), °C	155-220
Solubility and Compatibility Characteristics	
solvents, principal types	esters, ketones, ether-alcohol mixtures
resins, examples of compatible types	almost all
plasticizers, examples of compatible types	almost all, including many vegetable oils
waxes and tars, examples of compatible types	none
compatible cellulose derivatives	ethylcellulose, cellulose acetate, ethylhydroxy- ethylcellulose
Resistance to Various Substances	
water, cold	excellent
water, hot	excellent
acids, weak	fair
acids, strong	poor
alkalies, weak	poor
alkalies, strong	poor
alcohols	partly soluble
ketones	soluble
esters	soluble
hydrocarbons, aromatic	good
hydrocarbons, aliphatic	excellent
oils, mineral	excellent
oils, animal	good
oils, vegetable	fair to good
* Unplasticized RS* Nitrocellulose (Hercules Powder Co.).	

Polychrome does not make finished products. Bulk polymer is put into solution and sold to others for conversion to printing inks, furniture coatings, and other products. Guardsman Chemical Company, for example, has been a major converter of SNPE polymer into wood finishes. Similarly Hercules sells only uncompounded, unplasticized polymer. Thus, cellulose nitrate manufactured by Hercules and by basic producers outside of the United States may pass through many hands before it is formulated and packaged in small quantities for art conservation.

Cellulose nitrate is manufactured by a continuous, automatic nitrating procedure that employs a mixed acid of nitric acid, sulfuric acid, and water. The procedures and problems attendant to this process have been extensively reviewed in the literature. The process goes through stages of nitration, purification, digestion, and dehydration. In the purification process, the product and quench water are passed into large stainless steel vats. The quench water is removed and the product is washed with fresh water. Then follows a series of boiling and washing treatments in purified water of controlled pH to further decompose and remove unstable products.

A very clear description of types and grades, properties, modifiers, and testing procedures is given in trade literature available from Hercules. The company monitors its commercial cellulose nitrate through a series of tests that include water content, acidity, ash, color, heat stability, nitrogen content, polymer assay, volatile content, and viscosity measured by the four-ball method. Descriptions of these tests in the form of a laboratory report are available upon request. It is pointed out that cellulose nitrate is a highly effective absorbent for iron and that small amounts of iron have pronounced effects on the color of the polymer and its solutions. A yellowing of lacquer purchased and kept in metal cans is more likely to be the result of iron contamination than polymer decomposition. Conservators should transfer these products to glass containers and then store them in the dark to prevent color formation.

Recent advances in instrumental analysis have made it possible to describe how reaction proceeds as nitric acid interacts with cellulose. Initial work by Wu (1980:74) provides assignments in the C-13 magnetic resonance analysis for 6-mononitrated, 2,6-dinitrated, 3,6-dinitrated, and trisubstituted rings based on the anomeric, i.e., C-1, carbon. Further refinements by Clark and coworkers provides additional assignments to these ring structures based on peaks derived from C-2, C-3, and C-4 (Clark 1981:1112-7; Clark et al. 1982:217-46). This has confirmed the conclusions made by Wu and has sharpened the precision of the analysis. Thus, by simple procedures, product can be isolated during the nitration and analyzed for the distribution of different ring types.

It has been found that the primary hydroxyl group, on C-6, esterifies much more readily than the secondary hydroxyls, and the initial product appears to be essentially only 6-

mononitrate. Higher degrees of esterification then proceed at the secondary hydroxyl groups with the 2-hydroxyl group reacting about twice as fast as the 3-hydroxyl group. Esterification is an equilibrium reaction and when highly nitrated cellulose is placed in concentrated nitric acid with low concentrations of water, some limited hydrolysis occurs. The degree of hydrolysis is dependent on a number of factors including the amount of water present. Clark uses C-13 resonance to study the distribution of substituents as the nitrate group is removed by hydrolytic cleavage. In one experiment, cellulose was first nitrated to a D.S. of 2.83 by using 64% nitric acid, 26% phosphoric acid, and 10% P_2O_3 . The product contained 83% trisubstituted ring, 11% 2,6-disubstituted, and 6% 3,6-disubstituted rings. When this product was put into 95% nitric acid and 5% water for two hours, 9% of the trisubstituted material was converted to disubstituted rings. There was no formation of rings with a D.S. of less than 2. This indicates that under these conditions trinitrated rings were giving up nitrate groups and dinitrated rings were not. The product distribution obtained using 82% nitric acid was 40% tri-, 23% 2,6-di-, 12%-3,6-di- and 25% 6-monosubstituted product and it contained no unsubstituted rings.

In particular, Clark's studies show that there was a difference in the distribution of substitution patterns at the same D.S. when the product was obtained from cellulose by nitration or produced from a more highly nitrated polymer by hydrolysis. Nitration tended to give a broader distribution that favored trisubstituted rings, but still yielded quantities of rings with little or no substitution, while denitration led to a buildup of intermediate degrees of nitration rather than conversion to mono- and unsubstituted rings. These findings argue against a reaction model where the partial equilibrium values at a given carbon atom are independent of the substitution at other carbon atoms of the ring. Hydrolysis of ester groups on trinitrated rings proceeds more readily than would be predicted from partial equilibrium values. Dinitrated rings in turn cleave more readily than mononitrated rings. In the next section, a variety of mechanisms leading to the breakdown of cellulose nitrate will be considered. It is important at this point to stress that trinitrated rings are less stable than dinitrated units and more readily yield decomposition products by the ester cleavage reaction. In addition, Clark's work also provides evidence that esterification and deesterification rates at given carbon atoms are influenced by substitution patterns on adjacent rings as well as the distribution of nitrate groups on the same ring. He has also found that the distribution along the polymer chain of the four types, i.e., tri-, 2,6-, 3,6- and 6-substituted rings, is not random.

In addition to a better understanding of the molecular structure, recent work has provided insight into changes in the bulk, topographical nature of the cellulosic polymer as hydroxyl groups are progressively esterified. Cellulose chains exist as helices that are lined up in a parallel manner. As nitration and

conversion proceed, there is a change in the dimensions of the unit cell in the spiral angle and in the nature of the coil. X-ray diffraction patterns from highly oriented fibers of cellulose nitrate with a D.S. of 3 have shown that the crystalline molecule exists in a right-handed helix with five anhydroglucose rings in each of two turns. Typically this material has a spiral angle of 144° and an axial advancement of 0.519 millimeters. The parallelism of the macro chains is generally maintained but may diminish, reorient, or otherwise change with increased processing, particularly where partial solution or swelling occurs. The nature and degree of parallelism plays a major role in the birefringence properties of cellulose nitrate and Clark describes how this can lead to a range of birefringence values. These values depend on the degree of substitution that affects the macro-molecular chain arrangement. With a degree of substitution of less than 2.2, cellulose nitrate, like cellulose, has positive birefringence. At higher values, with sufficient variation from the molecular ordering of cellulose, birefringence becomes negative. The phenomenon can be used analytically (Kohlbeck and Bolleter 1976:153). It is possible to estimate the D.S. from birefringence measurements, which may be much handier to do than Kjeldahl nitrogen analyses.

The variation in birefringence with the extent of substitution can also be used to shed light on subtle structural considerations. The stable 6-nitrate group projects outward from the helix and can do so in three possible conformations. Lewis (1982:710) describes how calculations based on birefringence have shown that the confirmation in which the 6-nitrate group positioned towards the ring oxygen can be ruled out.

Causes of Instability

Most of the literature on cellulose nitrate instability describes three primary modes of decomposition: hydrolytic, thermal, and photochemical. These modes are examined in this paper with concern for rates and mechanisms most likely to prevail under ambient conditions. Recent research can be interpreted to show that these three modes can be redefined into more fundamental mechanisms for primary decomposition, a finding that may provide additional insight into the properties of the polymer as well as the optimum conditions for its use. Primary decomposition processes slowly lead to breakdown products. If these are not swept away they can lead, catalytically, to a faster and more extensive degradation than that caused by the primary processes that engender them. Conclusions on the chemistry of decomposition caused by these breakdown products, i.e., secondary processes, are integrated with our analyses of the primary modes in the next section—a discussion on the overall stability of cellulose nitrate at ambient conditions.

Hydrolytic Decomposition via Acid Catalyzed Ester Cleavage

The earliest manufacturing processes of cellulose nitrate in the 19th century were concerned almost totally with the production of explosives. After a number of disastrous detonations took place, the search for their causes revealed in 1865 that the retention of small amounts of sulfuric acid from the nitrating mixture was responsible for the instability (Worden 1921:1604 et seq.), and, further, that this instability was roughly proportional to the amount of sulfuric acid left in the polymer (Wiggam 1931:536). It was also recognized that sulfate esters of partially nitrated cellulose were also formed (Hake 1909:457). In no case did the nitration of cellulose with mixed acid ever proceed to a completely nitrated product, i.e., to a D.S. of 3.0 and nitrogen content of 14.1%. The best that could be achieved was a product with 13.8% nitrogen in which only 29 out of 30 hydroxyl groups bore nitrate functionality because the 30th was converted to a sulfate ester. In cases where exhaustive nitration was done without using sulfuric acid, e.g., with nitrogen oxides (Bouchonnet et al. 1938:308) or with nitric acid and phosphorus pentoxide (Lenz et al. 1931:4) or acetic anhydride, a completely nitrated product

with 14.1% nitrogen was obtained. These products were invariably of better stability than high nitrate product made with mixed acid (Barsha 1954:724-30).

While considerations of this type and other studies suggested that most of the sulfate content was in the ester form, at least one report suggested that high (13-14%) nitrogen cellulose nitrate contained only free sulfuric acid while lower nitrogen content polymer (10-12% N) had primarily esterified sulfate. These conclusions followed from work in which the polymer was dissolved in acetone, precipitated in water, and the water and precipitate analyzed for sulfate (Miles 1955:130). The bulk of the evidence strongly indicates, however, that when sulfate is present in cellulose nitrate, it is in the ester form. It occurs primarily as the hydrogen sulfate ester, cellulose-OSO₂-OH, but also to some extent as the dicellulose sulfate, cellulose-OSO₂O-cellulose. Elimination of these esters is important (Barsha 1954:738). Sulfuric acid is hygroscopic, alkyl hydrogen sulfates are hygroscopic, and cellulose nitrate bearing a sulfate hydrogen group is almost certainly hygroscopic. This combination provides all the components needed for hydrolytic decomposition to free nitric acid, i.e., the nitrate ester, water, and a strong acid catalyst.

A great deal of technology in this field is concerned with removing the sulfur content. Water washing can remove most of the free acid, but beating and pulping were found as early as 1865 to be critical in breaking down micellar and larger structures and providing the needed contact for efficient extraction (Abel 1865). A recent U.S. patent (Baumann, Blais and Spiess 1983) describes the use of ultrasonics for this same purpose. However, simple water washing at ambient temperatures, even with perfect dispersion, is not sufficient for removing acid tied onto the molecule as a sulfate ester. Extractions of crude cellulose nitrate product have been done using aqueous alkali or by ammonium hydroxide solutions to provide neutrality as soon as possible. These procedures, however, are not favored (Barsha 1954:739). The foundation for an important part of the stabilization process now used industrially was made with the discovery that most of the unstable sulfate esters are more readily decomposed in boiling water when it contains a small amount of the mixed acid than by treating it with a boiling aqueous alkaline solution. Still higher temperatures provided faster and even more effective results (Robertson 1906:624).

Improvement in the stability of cellulose nitrate has also been effected by extraction with alcohols under various conditions (Scharf 1942; Small 1920). The material so removed by extraction may be reactive, highly degraded cellulose nitrate, as well as sulfate bodies. Muraour (1932:1089), working with commercial cellulose nitrates, claims to be able to stabilize certain samples with boiling alcohol, which is so effective in removing impurities that the product is stable in the presence of water at 15-20°C over a 20- to 30-year period. More recent Polish studies,

which quote Muraour's work, claim that the best procedure is to heat cellulose nitrate in boiling water containing 1% NaOCl and 0.1% sodium acetate for two hours, and follow this with several water washings and a final washing with ethanol at room temperature (Urbanski and Kukulka 1983:98-101).

In the next section, this report will discuss several more practical procedures that have been used to take cellulose nitrate to an acid-free product so that contamination by sulfuric acid or its esters is no longer a cause of decomposition. Following this will be a consideration of the ramifications of these procedures in terms of today's commercially available material.

Thermal Decomposition

High Temperature

Basic factors that can affect the ultimate stability, and thus the usefulness, of cellulose nitrate in conservation are the nature and rate of inherent, uncatalyzed, thermal breakdown. This would be the instability that remains when all catalyzed and correctable causes of decomposition have been eliminated. Thus it should be possible by extensive washing, extraction, and neutralization of cellulose nitrate to arrive at a product that is free of acid and stable.

However, the German chemist Will, in some elegant work done at the turn of the century, shows that there is an uncatalyzed, thermal decomposition that can be studied and measured at temperatures as modest as 135°C (Miles 1955:253). Will evaluates a variety of methods for the stabilization of cellulose nitrate made by the commercial mixed acid method (Fig. 4). For each method, as the stabilization treatment proceeded, samples were taken periodically and the rate of decomposition of each sample was determined at 135°C. This was done by converting all nitrogenous gases in a carbon dioxide offstream to nitrogen, measuring the nitrogen volumetrically and then obtaining the slope of the formation of nitrogen with time. In each case, the slope was found to reach a minimum value, indicating that as much of the catalyzing, acidic impurity as possible had

Figure 4.
Procedures for stabilization by
removal of acids

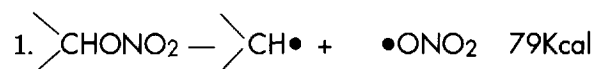
Method	Time for reaching minimum rate of decomposition Hours	Minimum rate of decomposition* mg N ₂ /hour
1. Boil in water	70	208
2. Heat in water at 144°C	4	220
3. Extraction with alcohol	–	212
4. Heat in alcohol	2	220
5. Boil in water for 70 hours alcohol extraction	2	216

* Nitrogen oxides all converted to N₂ and measured volumetrically.

been removed; in each case this limiting slope had the same value. The conclusion one has to draw from this data is that the same acid-free product is produced by each method and that this material undergoes a measurable and reproducible thermal decomposition at 135°C.

All organic substances must ultimately give way to a relatively rapid thermal decomposition as the temperature is increased. For the most stable compounds this will occur at temperatures above 300°C. For cellulose nitrate, because of weak nitrogen oxygen bonds, this occurs measurably at 135°C or even lower. One of the major early breakdown products, formed even under these mild conditions, is the very reactive oxidizing agent NO₂. Will found little formation of formaldehyde at 135°C, but Rideal and Robertson did find this product in decompositions at higher temperatures, i.e., close to 200°C (Miles 1955:253)

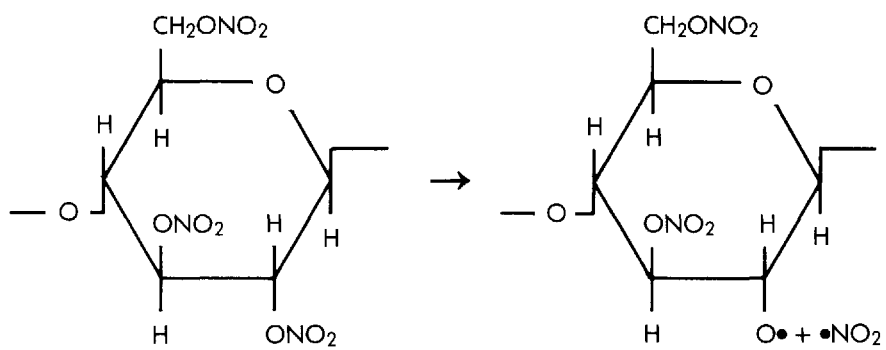
These findings are perhaps best explained by a mechanism where initial scission occurs by cleavage, in the nitrate group, of the bond between the nitrogen and the oxygen bound to the ring (Adams and Bawn 1949:494). Consideration of the strengths of covalent bonds in organic molecules finds that the oxygen-nitrogen bond at 36-40 kilocalories is the weakest by far of all those listed for nonradical species. In contrast, the breakdown on the other side of the oxygen requires 79 kilocalories while carbon carbon and carbon hydrogen bonds require 80-100 kilocalories.



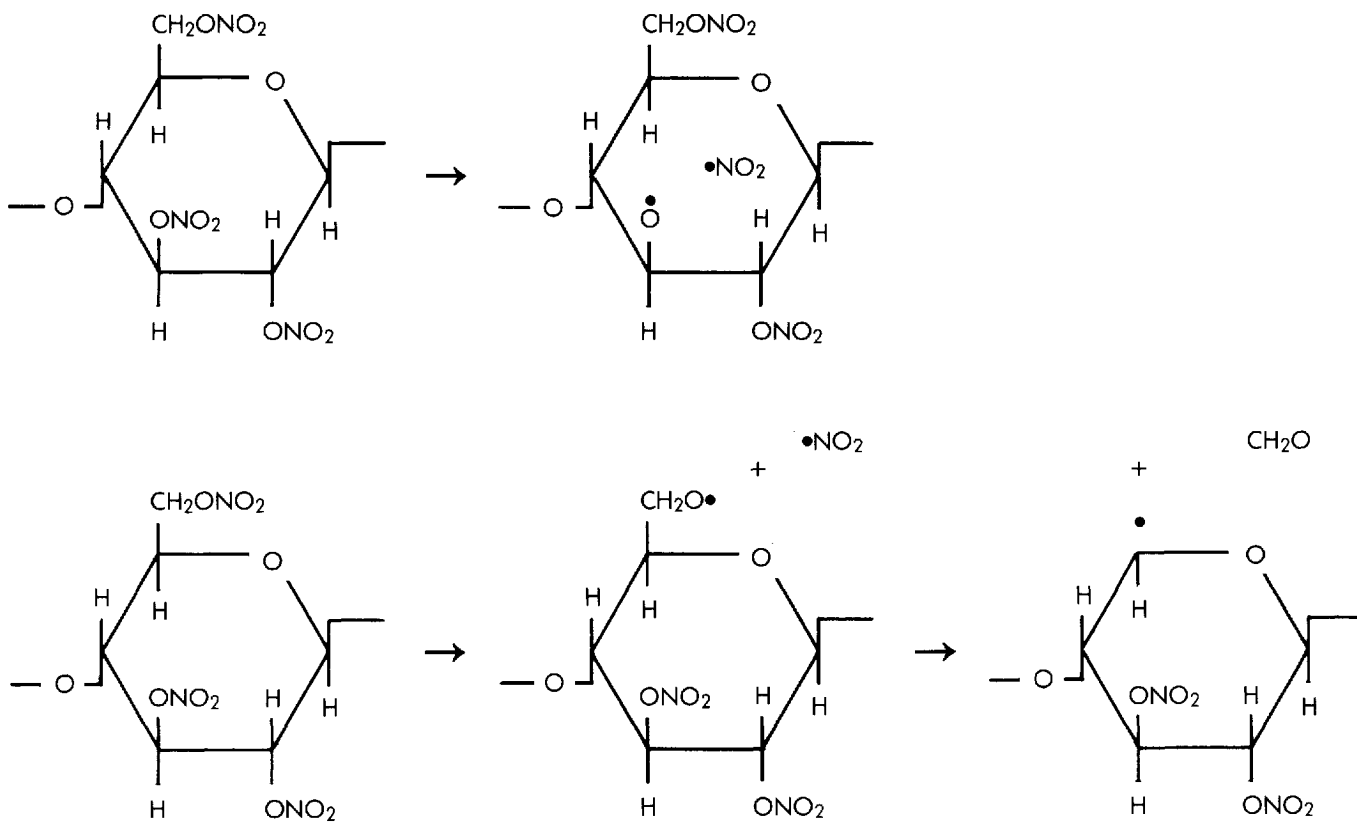
Studies comparing the stability of the three different nitrate groups consistently show that the primary nitrate is the most stable to both hydrolytic and thermal cleavage (Gelertner 1956:1260-4). Wu (1980:74-9) finds that for hydrolysis the primary nitrate group, at the number 6 carbon, is more stable by a factor of 3 than the secondary nitrate group on the 2 position, which in turn is twice as stable as the secondary nitrate group on the 3 position. Leider and Pane show that a similar order of stability exists between primary and secondary esters during thermal decomposition. They have also found that trinitrated rings are much more prone to this mode of decomposition than dinitrated glucoside rings (Leider and Pane 1986; Leider and Seaton 1979). Their studies indicate that in a typical adhesive-grade cellulose nitrate with a degree of substitution of 2.3 there exist 50% trinitrated rings, 34% dinitrated rings, 16% mononitration, and no rings without nitration. Thus, initial bond scission in this polymer molecule at 135°C will most likely occur in a trinitrated ring at the nitrate group on a secondary carbon and between the oxygen attached to the ring and the adjacent nitrogen. As the temperature is increased and more energy is pumped into the molecule, however, decomposition becomes more randomized and breakdown occurs increasingly at the primary carbon nitrate grouping, which leads to the formation of formaldehyde (Fig. 5).

Figure 5. Upper temperatures decomposition pathways

Favored Pathway 120-135°C



Competing Pathways 135-200°C



Low Temperature

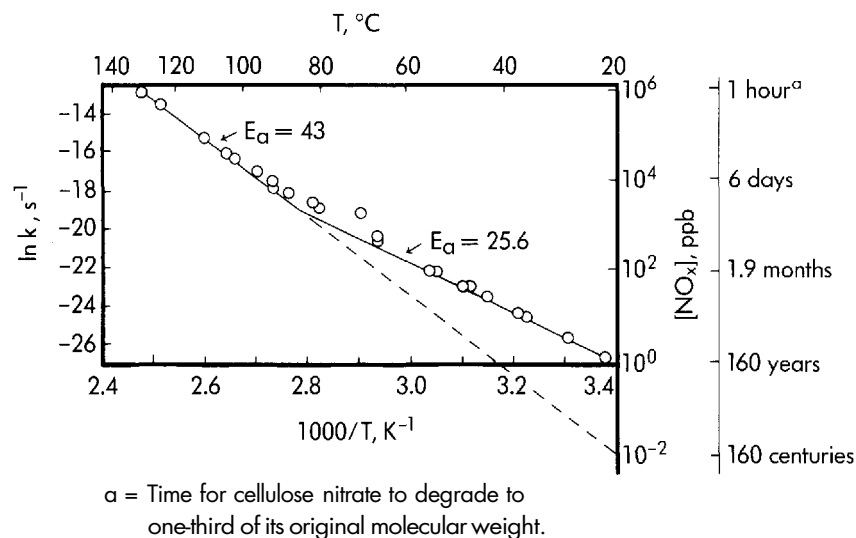
An important consideration for the use of cellulose nitrate in conservation is its uncatalyzed rate of decomposition under ambient conditions. Will and others show that the activation energy for the thermal decomposition in the range of 120° to 180°C is 46 Kcal per mole. With the aid of the standard Arrhenius equation, one can calculate the decomposition rate at any temperature. A calculation based on this value, the formation of 0.86 milligrams of nitrogen per hour per gram of cellulose nitrate at 135°C, and the effect of the degree of substitution suggests the formation of about 1 milligram of nitrogen in the breakdown products per gram of cellulose nitrate per 15,000 years at 25°C.

It is far more desirable, however, to have this value actually determined at room temperature. Within the last 10 years, techniques have evolved that permit the detection and analysis of the extremely small chemical changes that occur as conditions approach ambient. A considerable amount of work has been done at the Lawrence Livermore National Laboratories over the last several years on cellulose nitrate stability at lower temperatures. Cellulose nitrate is used as the binder in the rocket propellant PBX-9404 and was found to be the component of greatest instability in the formulation. The studies at Livermore were concerned with the degradation of molecular weight and loss of nitrate ester in adhesive grade material (12% nitrogen), primarily in the range of 80-120°C, with some measurements done at temperatures as low as 50°C (Leider and Pane 1986; Leider and Seaton 1979).

Work done at Rensselaer by Arthur Fontijn under contract to Livermore uses chemiluminescence procedures that measure NO_x (NO_x is a mixture of NO and NO₂) in nitrogen at concentrations down to 10 parts per trillion. This procedure permits studies on cellulose nitrate to be done at temperatures as low as 20°C. In this work, the flow methodology devised by Will 80 years previously was used, and essentially only the NO_x off-gas analysis procedure was changed. The results of a series of runs made with 6.2 grams of cellulose nitrate containing 12% nitrogen (Will uses 2.5 grams of 13.5% nitrogen content) are shown in Figure 6 as an Arrhenius plot covering the temperature range of 20-135°C. The first order rate coefficients are calculated as moles of NO_x given off per submole of nitrated glucose anhydride unit, which for 12% nitrogen has a molecular weight of 264. The figure provided by Fontijn also very conveniently plots parts per billion of NO_x formed per second versus temperature. In Figure 6 there is added to the graph published by Fontijn an ordinate that provides the amount of time it would take for 1 gram of cellulose nitrate to form approximately 1 milligram of nitrogen as a function of temperature. This is a more readily followed descriptor of what is happening and makes possible simple, direct comparison with Will's work. The experimental points yield a nonlinear Arrhenius plot, which, however, can be resolved into two straight lines corresponding to an activation energy of 25.6 Kcal per mole below 80°C and 43

Kcal per mole above 100°C. The first value is in excellent agreement with the recent work of Leider at 50-80°C using molecular weight and nitrate ester analyses, while the higher temperature value agrees well with results obtained by Will and many others. Thus Fontijn's work corresponds to the formation of 0.76 milligram of nitrogen per gram of cellulose nitrate (12% N) per hour at 135°C, while Will found 0.86 milligram of nitrogen per gram of cellulose nitrate (13% N) under otherwise similar conditions.

Figure 6. Effect of temperature on decomposition



The lower activation energy that prevails over the lower temperature range means that a different reaction mechanism predominates under milder conditions and indicates a mechanism that is much less temperature dependent. The falloff in decomposition rate as the reaction is carried out at lower temperatures is not as great as would be predicted from the upper temperature activation energy. Calculation of this decomposition rate at 25°C based on 26 Kcal per mole provides a value that is 100 times higher, i.e., instead of 1 milligram of nitrogen per gram of cellulose nitrate every 15,000 years there is formed 1 milligram every 150 years. This still very low value for the spontaneous decomposition under ambient conditions was obtained both by direct measurement and by calculation from studies made at somewhat higher temperatures.

The mechanism for the inherent thermal decomposition above 100°C was previously described as involving cleavage of oxygen nitrogen bonds of secondary nitrate groups. The literature on this decomposition is extensive. The lower temperature spontaneous decomposition is not as well understood. Perhaps the most helpful information on providing a mechanism is the finding that the rate of molecular weight degradation correlates well with the rate of conversion of nitrate esters to nitrogen oxide and provides the same activation energy. Thus, chain scissions are occurring apace with nitrate breakoff. The nitrate groups, however, are not in a linear backbone, but on glucoside

rings. Loss of nitrogen functionality and even ring opening under these very mild conditions should not be the direct cause of chain cleavage even when both are occurring at the same rate. It seems more likely that a different phenomenon is causing these two actions to occur at the same time. It is suggested that in the natural bond vibrations of a ring containing three nitrate ester groups a state will occur with infrequent regularity but with sufficient energy to cause the relatively unstable ring to come apart. Whether instantaneously or in very fast concerted reactions, the atoms of the ring fly apart and are released as gases. The polymer is degraded and nitrogen oxides are evolved.

There is a general feeling in the recent literature that spontaneous decomposition of pure cellulose nitrate is an inherent property occurring at a fast enough reaction rate to defeat any effort to make a relatively stable product (Koob 1982:31-4). It may not be possible to make a polymer with the desired longer-term stability, but these studies suggest that this would result from an inability to eliminate decomposition due to hydrolytic, radiation, and secondary breakdown mechanisms rather than from the kinetics of the spontaneous instability of the polymer.

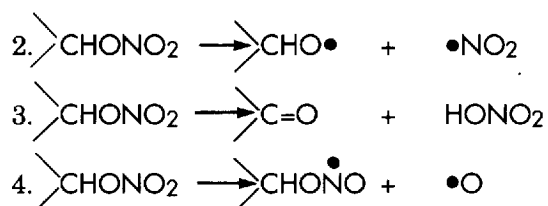
Decomposition by Ultraviolet Radiation

It has been known for many years that cellulose nitrate is susceptible to photochemical degradation. As early as 1867 it was noticed that highly nitrated cellulose exposed to strong light underwent discoloration from water white through yellow to brown, a gradual loss of important physical properties, and ultimately, complete degradation. In view of the determination that inherent thermal decomposition is very low and apparently a negligible contributor to the instability of cellulose nitrate observed at room temperature, it becomes important to evaluate and understand the impact of photochemical degradation under ambient conditions. Many workers report that even the diffuse light of the laboratory in time seriously degrades cellulose nitrate, particularly when it is in solution, but there has been little or no theoretical work done under these low-quanta conditions (Miles 1955:253).

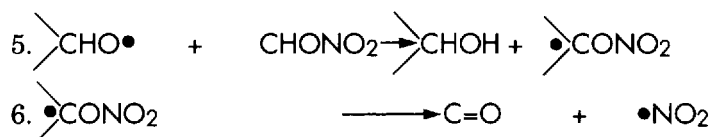
Basic research on the photochemistry of cellulose nitrate was much slower in coming than thermal studies partly because there was little interest from those doing work on explosive propellants and partly because defining and reproducing light energy is much more difficult than doing thermal studies. Interest in this problem picked up with the increasing use of this polymer in lacquer finishes after 1930. What appears to be landmark work was done by G.G. Jones in 1935 and is described in some detail in Miles's book, *Nitrocellulose* (1955). Unfortunately, the references on Jones's work (1933) are difficult to obtain.

Jones was able to show that in the violet to far-ultraviolet range (4100 to 2000 Å), the absorption curve of any cellulose nitrate containing from 10.9% to 14.1% nitrogen is continuous and rises without a maximum, although the shape of the curve suggests that there is an absorption band with its summit at about 2200 Å. He also found that in the near UV (3500 Å), the hydroxyls are more absorbent than the nitrate groups, but for the shorter wavelengths this is reversed. Relationships between the light flux, quantum efficiency, and viscosity change were developed in equation form. Jones determined molecular weight changes from viscosity measurements and nitrogen content for cellulose nitrates irradiated at different wavelength groupings, i.e., 4078 and 4079 Å (visible violet); 3633, 3654, and 3650 Å (near ultraviolet); 3136 and 3120, 2536 Å (far ultraviolet). The outstanding feature of these results, for which there appears to be no explanation in the literature, is the dependence of the nature of the reaction on the frequency of the radiation. Short wavelengths cause mainly viscosity changes without much loss of nitrogen, and longer wavelengths, loss of nitrogen with little change in viscosity.

A convenient explanation for Jones's findings is that the two mechanisms occurring in ultraviolet induced decomposition of cellulose nitrate are essentially the same two modes of breakdown that occur thermally. The nitrogen loss with little viscosity change, induced by longer wavelengths, occurs by a nitrate ester cleavage, which is the mechanism used to explain the 46 Kcal activation, upper temperature range, and thermal decomposition. Model studies with simple alkyl nitrates show that there are three primary processes occurring in the near ultraviolet (Philips 1950:165):



The first is favored. Reaction then proceeds sequentially in the following manner:



This mechanism provides for loss of nitrogen but does not involve chain scission. However, at shorter wavelengths, deeper into the ultraviolet range, viscosity drops with little change in nitrogen. This is exactly the basis Leizer uses to formulate the ring disintegration mechanism for spontaneous decompositions at lower temperatures. The loss of one entire ring, in a chain of several hundred rings, divides the average molecular weight in half. However, all elements, carbon and hydrogen as well as oxygen and

nitrogen, are eliminated in about the same ratios that exist in the parent polymer and it can be shown that the nitrogen content in the residuum will be essentially unchanged.

More recent work by Clark and Stephens (1982:182-93) involves irradiating solid cellulose nitrate with ultraviolet of 2900 Å and measuring the surface changes in the outermost few tens of Angstroms by X-ray photoelectron spectroscopy (ESCA; Clark and Stephens 1982:182-93). This procedure provides information about changes in carbon, nitrogen, and oxygen ratios with time. The rationale is that in solar radiation exposure the loss of nitrogen oxides is the main reaction rather than viscosity changes and they preferred to study the changing elemental nature of decomposing materials rather than examine the released gases.

Their principal finding is that radiation causes a faster loss of nitrogen from cellulose nitrate with a D.S. of 1.9 than material with a D.S. of 2.6. This is attributed to the lower nitrate ester polymer having more sulfate esters, which could act as photoinitiators. A better explanation is one more in keeping with the previous discussion. The polymer with a D.S. of 1.9 contains mostly dinitrated glucose anhydride rings. The ester dissociation mechanism predominates and this causes ESCA-determined N/C ratios to fall. The ring disintegration mechanism can occur only in rings containing three nitrate esters and cellulose nitrate with a D.S. of 2.6 consists primarily of trinitrated rings. In this mechanism there is little change in residual nitrogen content. Their findings provide support for the two different modes of photochemically induced cellulose nitrate decomposition.

Even more recent work on the photodegradation of cellulose nitrate is reported by Hon and Gui (1986:299-310). Unfortunately, the work cited was done with the broad spectrum of wavelengths provided by a high-pressure quartz mercury vapor lamp. The spectral distribution contained wavelengths from 2224 Å in the far ultraviolet to 13073 Å in the infrared, a situation that precludes learning about the effect of wavelengths on reaction type. Most of the energy was concentrated in the infrared and the visible, although about a quarter of the radiant energy was at 3130 Å or lower. Exposures in air and vacuum over 48 hours gave roughly parallel decreases in molecular weight. There were irregularities in the falloff of molecular weight in the first hours, particularly in the presence of air, which suggested some initial oxygen-induced crosslinking. In addition, loss of nitrogen occurred during irradiation both in vacuum and in air. The polymer contained 11.79% nitrogen and approximately equal amounts of di- and trinitrated rings. The occurrence of mechanisms yielding both a diminution in molecular weight and decrease in nitrogen content would be expected. Almost complete loss of UV absorption below 270 nanometers in the very early stages and a surprising increase in nitrogen content during intermediate stages of exposure are

explained by Hon and Gui as further evidence of intermolecular bridging.

This crosslinking, which is induced by oxygen and involves nitrate groups in the bridging, occurs with the formation of a carbonyl type chromophore that absorbs at 290 nanometers. On continued exposure past 18 hours, the molecular structure that provides the crosslinking is degraded and eliminated and a new chromophoric group showing at 253 nanometers is generated. Little structural correlation is provided in the publication and more work is needed to confirm and interpret these interesting findings.

Mechanisms of Primary Decomposition

Low temperature studies provide a basis for redefining cellulose nitrate decomposition into three different mechanisms. The first is conventional acid-catalyzed ester cleavage. The second involves a nitrogen-oxygen bond cleavage as described in Figure 4. This is the predominant mode of thermal decomposition above 100°C, or when the molecule is irradiated with visible and near UV light and its occurrence is not dependent on the number of nitrate ester groups on the ring. Both of these decomposition pathways are supported extensively in the chemical literature. The third mechanism is much more speculative and arises from findings of unique events under special conditions. These include a different activation energy for thermal breakdown at lower temperatures and regimes where molecular weight changes rapidly but nitrogen content does not. This breakdown occurs photochemically in the far ultraviolet where nitrate ester groups absorb and not in the near ultraviolet where they do not. In any event, it occurs only on rings bearing three nitrate groups, a situation that cannot be explained by the other two mechanisms, and so at least one more has to be invoked. The data best fit a very improbable spontaneous coming apart of one entire nitrated glucoside ring within the polysaccharide chain. Therefore, the primary mechanisms for cellulose nitrate decomposition are: (1) acid catalyzed ester cleavage, (2) homolytic scission of the nitrogen-oxygen bond, and (3) ring disintegration.

Secondary Modes of Decomposition

Since it is not possible to eliminate or suppress all the primary mechanisms, the question of secondary reactions must be considered. At the very least, the slow thermal mechanisms provide traces of nitrogen oxides that will accumulate with time. The autocatalytic effect of this buildup needs to be studied and defined. Barsha writing on the decomposition of explosive-grade cellulose nitrate, states

It is apparent from the results of many investigations on the mechanism of decomposition of nitrocellulose that this decomposition takes place in two stages. In the first stage, the reaction is relatively slow; in the second stage, the initial decomposition products react with the nitrocellulose, and the reaction becomes autocatalytic and therefore accelerates rapidly. If the products of decomposition in the first stage are removed as rapidly as possible (for example, by a stabilizer), the reactions of the second stage are prevented, and the decomposition is held down to a relatively slow rate (1954:724-30).

Just what he means concerning the chemistry of nitrogen oxide buildup and interaction with residual polymer is not clear. The Barsha references go back to the 1920s, and researchers at that time did not have the technology to do the low-temperature studies that were needed to evaluate the basic chemistry of the two stages.

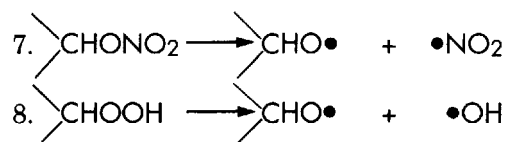
Fontijn, in his work using chemiluminescence to study the decomposition of cellulose nitrate at room temperature, provides valuable insight on secondary mechanisms through his findings that NO and NO₂ are both formed in the decomposition occurring at room temperature. He further found that the more rapidly decomposition products were removed from the polymer (e.g., by going to lower pressures), the higher the NO₂/NO ratio became, and thus showed that NO is a secondary and not a primary breakdown product of the polymer. He also showed that the addition of traces of NO₂ to the nitrogen stream passing over cellulose nitrate at ambient conditions led to the formation of significant amounts of NO and further demonstrated that this resulted from NO₂ reduction and not enhanced cellulose nitrate decomposition. The fact that NO₂ was observed to have an autocatalytic effect on cellulose nitrate decomposition in extended time storage tests at the Frankford Arsenal in 1973 was deemed not inconsistent with this conclusion because of a large difference in time scale. Fontijn found that below 80°C, addition of 1% carbon dioxide or N₂O to the nitrogen stream had no effect on NO or NO₂ production rates, nor did replacing the nitrogen with argon, helium, or oxygen have any effect. Increased cellulose nitrate decomposition was found to be caused by oxygen in long-term tests that were made at temperatures over 90°C. Carbon dioxide, nitrogen, nitrous oxide, and oxygen were found to be secondary product gases in long-term decompositions at mild temperatures.

More recently, Hon and Tang (1988:73-6) have claimed that films of cellulose nitrate (Hercules RS 1/2, N=11.5%) lose about 5% of their nitrogen content on standing in air at ambient temperatures in the dark over 144 hours. They describe this process as a slow denitration brought about by the presence of oxygen. However, their data also show that this loss of nitrogen actually occurs within 30 hours and thereafter, at least for the next 114 hours, there is no further change in nitrogen content. This behavior is more characteristic of a thin film holding about 5% of a volatile nitrogen additive that is gradually lost as vapor over a 30-hour period. This is consistent with their findings that

reagents such as ferric and ferrous compounds, phenol, and lignin fail to exert any effect on this nitrogen loss. Also the failure to find a change in molecular weight over this period indicates that no measureable ring disintegration was occurring.

In real use situations, where there is no effective removal either by sweeping with an inert gas or by using vacuum, decomposition products accumulate. As NO_2 builds up, it can react with itself and N_2O_4 is found in decomposition studies at higher temperatures where the off gas is a mixture of NO_2 and N_2O_4 . NO_2 reacts primarily with the polymer and, as a common factor in polluted atmospheres, the chemistry of NO_2 has been studied in some detail (Rånby and Radek 1975). The extended organic chemistry of its reaction with cellulose nitrate is, however, virtually unexplored.

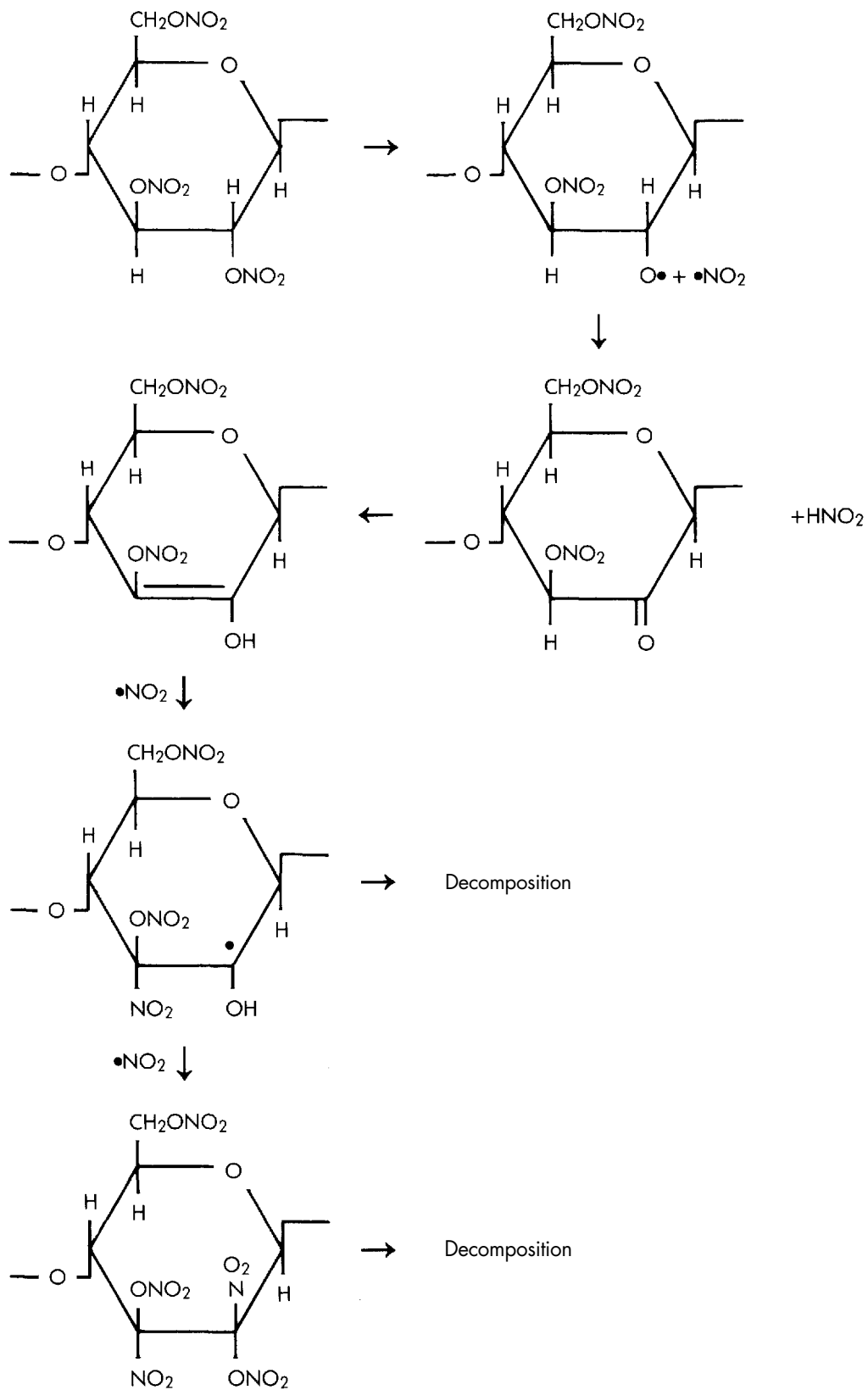
Decomposition of a nitrate ester at elevated temperatures is, in many respects, similar to the breakdown of an organic hydroperoxide. Both initially go through homolytic cleavage between heteroatoms to form oxy radicals.



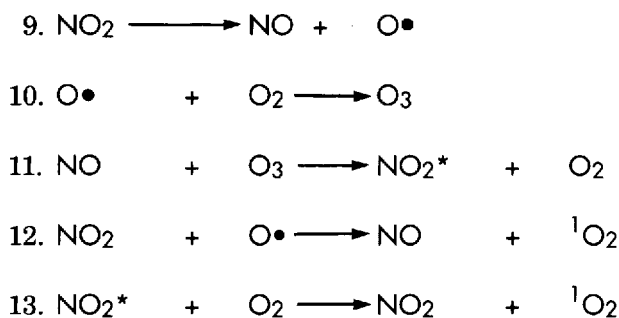
The oxy radicals in each case give both ketone and alcohol in a ratio that depends to a large extent on the availability of protons in the environment. Ketone may be the minor product in the cellulose nitrate system but there is evidence that further decomposition goes through the ketone and not the hydroxyl group. Ketones generally exist in tautomeric equilibrium with an unsaturated, enolic isomer and in a cellulose nitrate ring this configuration probably predominates. Olefinic molecules are reaction sinks for reactive species like ozone and nitrogen oxides. Addition occurs rapidly to form highly oxidized, reactive, and unstable species that readily undergo decomposition.

The nature of secondary reactions at ambient temperatures is more speculative. Little is known about the chemistry that is occurring under conditions where ring disintegration is the predominant reaction. It is known that NO_2 is an initial decomposition product and is rather easily converted to NO . Oxygen in the short term does not enhance decomposition. The work of Hon and Gui (1986:299-310) supports the idea that a ketone can be formed. By taking these facts into account a mechanism of secondary decomposition can be formulated as shown in Figure 7. An initially formed oxy radical (Structure A in Fig. 7) converts to a cyclic ketone; this conversion step may be the source of NO formation. The keto-enol structure is relatively stable but in the presence of NO and NO_2 addition reactions occur. These lead to products that contain multinitrated rings, D and E, with dinitrated carbons. These are structures that should be highly susceptible to ring disintegration. Therefore, trinitrated rings can be expected to be less stable than dinitrated rings by secondary modes of decomposition at ambient conditions.

Figure 7.
Pathways of secondary
decomposition



There is additional enhancement of secondary modes of decomposition by ultraviolet. Photolysis gives NO and atomic oxygen and, in the presence of molecular oxygen, the reactions indicated in equations 9 to 13 can occur:



In particular the reaction between ozone and NO is highly exothermic and leads to electronically excited NO_2^* . The destructive effect of this reactant is well known (Jellinek 1971; Jellinek and Chaudher 1972). Thus, the effect of UV radiation is to enhance markedly the decomposition caused by secondary reactions particularly where the radiation takes place in the presence of oxygen. Lawton and Nason (1944:1128-30) show this experimentally in their study on the effect of UV light on cellulose nitrate stability. Figure 8 indicates what happens to the viscosities of solution of samples of cellulose nitrate that are: (a) kept dark; (b) exposed to UV under nitrogen, and (c) exposed to UV in air for 200 hours. Clearly the additional presence of oxygen dramatically accelerates the light-induced decomposition.

Figure 8.
The effect of UV light on cellulose nitrate stability

Condition	Relative Viscosity		Intrinsic Viscosity	
	Start	Finish	Start	Finish
a. Dark, air	1.266	1.258	1.187	1.031
b. UV, N_2	1.268	1.231	1.179	1.148
c. UV, air	1.270	1.031	1.195	0.153

Primary processes appear to be slow and allow a tolerable period of stability; ultimately, secondary processes are destructive. There is, however, an initial time period when secondary reactions are also slow and polymer integrity is essentially maintained. There is a need, therefore, to know and understand how quickly secondary rates increase as products accumulate and how far the polymer can go into the secondary decomposition time period—once this is added on to the primary decomposition time period—and still maintain critical properties. There are two methods that should be used to accomplish this end. One basic approach to arriving at a better understanding of at least the preliminary phases of the secondary chemistry is to use ultrasensitive analytical procedures that can measure very small changes under ambient conditions in short periods of time. Thus the work of Fontijn using chemiluminescence would be expanded to

explore the region between his work, where he found NO₂ went to NO without enhanced cellulose nitrate decomposition, and the work at the Frankford Arsenal where, over longer periods of time, NO₂ did have such an effect (Apatoff and Norwitz 1973).

The other is to examine old, authentic examples of cellulose nitrate and determine how various formulations have fared under typical usage conditions over long periods of time. In this case, it is necessary to know as much as possible about the original composition and then use conventional analytical processes to determine the change.

Analysis of 50-year-old cellulose nitrate sheets used by Walt Disney as cartoon covers was carried out in a collaboration between the Getty Conservation Institute and the Lawrence Livermore National Laboratories. A typical 5-millimeter thick, 12-by 18-inch sheet was strong and flexible, with a pale yellow tint save for an essentially colorless border 7/16 inch in width. This border was formed after the cover sheet had been mounted on an original cartoon cell of the same size with the aid of clear tape. Analyses carried out on samples of the clear border and yellow interior are shown in Figure 9.

Figure 9.
Comparison of protected and unprotected sections of a 50-year-old cellulose nitrate sheet

Material	Protected	Unprotected	
Date	1937	1937	1935
Appearance	Clear	yellow	yellow
Thickness	5 mil	5 mil	5 mil
Location	border	interior	interior
MW _N	194,000	136,000	145,000
MW _W	67,300	43,700	51,000
Yellowness Index			
ASTMD1925-69T	3.95	13.8	
Nitrogen, %	9.85	9.28	8.23
Substitution (C ₁₃ NMR)			
6-Mono-	.217	.176	.201
6,3-Di-	.233	.293	.295
6,2-Di-	.290	.373	.390
Tri-	.260	.158	.115

It has not been possible to determine with certainty the original composition and manufacturing source of this material. Up until 1947, both Eastman Kodak and Ansco produced a nitrate film—generally a polymer containing 12% nitrogen in a blend with 20% plasticizer—with both phthalates and aryl phosphates used as the plasticizer. The plasticizer in the Disney sheets was shown by gas chromatography not to be dibutyl phthalate or dioctyl phthalate. It provided a peak in the chromatogram that was much broader than those given by the reference phthalates. The peak occurred between the peaks for dibutyl and dioctyl phthalate, which indicates that the plasticizer was relatively volatile, and significant loss could be expected over the time periods under consideration. The 9.80% nitrogen

value at the rim is close to what might be calculated for material that is little changed and contains 20% plasticizer, an indication that the clear tape played a role in deterring plasticizer loss and filtering out most of the destructive ultraviolet radiation—including radiation in the near-ultraviolet region. Analysis reveals a drop in nitrogen content to 9.28% from border to internal sample, even though diluent plasticizer had been lost from the latter region. This considerably reduced nitrogen content indicates that bond dissociation due to exposure to near-ultraviolet radiation occurred in the interior but not in the protected border. (Ring disintegration was not a factor in this degradation.) The molecular weight in the internal section was 70% of the molecular weight in the border region, a drop modest enough to indicate that relatively little breakdown occurred by chain scission. Kinetics developed by Fontijn suggest that less than 0.33% loss of nitrogen should occur by thermal mechanisms over a 50-year period.

The primary mechanism of degradation of this material, therefore, appears to be bond dissociation caused by irradiation in the near-ultraviolet region. The distribution of ring substitution types was made on clear (border) and yellow (internal) samples using C_{13} NMR procedures (Fig. 9). Comparison between the samples indicates that the change between the clear and yellow tinted material was caused primarily by trisubstituted rings going to disubstituted rings. Again the C-6 nitrate bond appears to be much stronger than the C-2 bond, which is slightly stronger than the C-3 bond.

Some interesting conclusions can be made. The binding tape appears to have quite effective barrier properties. It seems likely that the stability of the cellulose nitrate sheet could be improved through the use of heavier plasticizers, such as ditridecyl phthalate. Phthalates of higher alcohols exhibit notably better permanence qualities than dioctyl and dibutyl phthalates and, although more expensive, the former have been commercially significant for the past 30 years.

It is the common experience to find cellulose nitrate photographic film (generally stored in canisters) that is far more colored—yellowish and even brown—brittle, cracked, and with a pungent acid odor than the samples noted above. The aged sheet material we examined had none of the general appearance associated with decomposing photographic film. On occasion, it is possible to find photographic film, such as negatives and movie reels over 50 to 60 years old, which shows no signs of extensive decomposition and is relatively flexible and clear. The differing levels of stability are often blamed on uncertainties and variations in the effectiveness of the cleanout of acid in the original production of the cellulose nitrate. That, however, is not the cause of the extensive decomposition of old photographic film. Rather, the decomposition has resulted from unsuccessful attempts to build stability into the material by adding soluble bases, which, over time, have had a greater tendency to cause a

complex, catalytic degradation than to effect neutralization of slowly released acids. When products such as the described lacquer and sheeting were manufactured without such bases, they held up for well over a 50-year period. The barrier properties of the binding tape suggest that when cellulose nitrate is used as an adhesive for ceramics, which inhibits loss of plasticizer and exposure to radiation, it should perform for much longer periods of time.

Cellulose Nitrate Stability at Ambient Conditions

Discussion has thus far focused on the fundamental and theoretical causes of cellulose nitrate breakdown. In this chapter we will examine issues of practical importance for the conservator attendant upon this breakdown. In particular, we will consider how the polymer behaves when it is used in applications of interest to the conservator, then examine the properties of stability and the problems of instability under ambient conditions and, finally, suggest what might be done to achieve results of greater permanence.

Historically, important improvements in making a more stable and usable cellulose nitrate have been preceded by research that has advanced basic knowledge of the chemistry of this material. In recent years remarkable advances in instrumental analysis have provided the methodology to do low-temperature studies leading to research that has given us a more complete picture of behavior under ambient conditions. In earlier work, qualitative or quantitative determination of stability was done at severe conditions by measuring decomposition temperatures or analyzing breakdown products. High temperatures or intense ultraviolet radiation were needed in order to get rapid, measurable change. Relative stabilities were compared and improvement in durability was noted, but extrapolation to behavior at room temperature was tenuous.

New referee work using chemiluminescence was done by a procedure that is capable of finding one part of NO_x in 10 trillion parts of nitrogen and one can now determine in minutes what happens to cellulose nitrate as it sits in a stream of nitrogen at 20°C (Leider and Seaton 1979). The methodology is not simple, but it is well defined for anyone interested in working at this relatively low temperature. More importantly, it has been shown that results obtained between 50° to 80°C generally correlate with room temperature behavior, and in this modestly higher temperature range, reactions are fast enough so that other, much simpler analytical procedures can be used. Specifically, this relates to molecular weight determination by viscometry and gel permeation chromatography, and nitrate group analysis by infrared absorption spectrometry.

With this foundation we can go on to consider ways in which better performance under ambient conditions and improved room temperature stability can be achieved. There are three general approaches to achieving a more stable cellulose nitrate. The first is to provide an inherently better material. This might be done by defining a molecular structure that has

greater stability or by finding a better cleanup process for removing destructive impurities. The second approach is to understand the limits of stability of cellulose nitrate to various inevitable forces and with this knowledge use the material appropriately. The third is to find additives that will protect and extend the life of the polymer.

The discussion that follows will explore cellulose nitrate stability at ambient conditions in a general way, will further examine structure stability considerations, and will suggest a synthesis to achieve a cellulose nitrate of unique molecular configuration that theoretically, at least, should have a much improved stability. There will also be general discussion on the effects of acid impurities, heat, radiation and secondary decomposition in the context of mild, real use conditions.

Structural Factors for a More Stable Cellulose Nitrate

It is generally recognized that as the number of nitrate groups increases, cellulose nitrate becomes less stable. A sufficient number of groups are needed, however, to create the polarity required for adhesion and film formation and for solubility in plasticizers and solvents. A polymer molecule with exactly two nitrate groups on each anhydroglucose ring (11.1% nitrogen, D.S. = 2.0) should retain these properties, while the lack of trinitrated rings would eliminate the fast mechanism for thermal decomposition at lower temperatures, i.e., ring disintegration. Figure 5 shows how a polymer that contains mostly more highly nitrated rings, 50% trinitrated and 34% dinitrated, behaves at various temperatures.

While the line plotted in Figure 5 has been analyzed to show that two different decomposition mechanisms are occurring, it represents, in fact, the sum of the rates by both mechanisms. The contribution of dissociation to the overall rate at low temperatures is small, just as, at higher temperatures, the contribution of ring disintegration becomes small. If all the trinitrated rings were converted to dinitrated rings, i.e., to a polymer having 84% dinitrated rings and no completely esterified rings, then a much lower rate of decomposition would be expected at lower temperatures. In Figure 5 the linear extension to 20°C of the 43 Kcal activation energy bond dissociation plot indicates that the remaining decomposition, were it based solely on bond dissociation, would be about 100th of the rate of a more typical polymer. This extrapolation is based on the dissociation of nitrate groups in both dinitrated and trinitrated rings. Removal of the trinitrated rings can be expected to lead to an even greater fall off in decomposition rate than that shown by the dotted 23 Kcal line.

There are two reasons for this. First, the polymer with 84% dinitrated rings would have 20% fewer nitrate groups than a polymer with 50% trinitrates and 34% dinitrates, and would probably have nitrates on more stable ring positions. Second, just as partial rate factors based on ring position are not independent of the degree of substitution in acid-catalyzed hydrolysis, so, too, in the nitrate bond dissociation reaction it is likely that partial rate factors are a function of the number of nitrate esters in the ring. The rate of nitrate dissociation on a given position in a trinitrated ring will be higher than dissociation from the same position on a dinitrated ring. Support for this comes from work by Leider and Pane (1986) of studies on the differences in stability between the nitrate ester positions on the ring. They used high resolution Fourier transform nuclear magnetic resonance to distinguish between the C₂, C₃, and C₆ positions. It was found that, upon aging cellulose nitrate (D.S. = 2.21) at 110°C for up to 15 days, the C₆ ester concentration remained unchanged while the nitrate group at the 2 position decomposed twice as fast as the nitrate group at the 3 position. These results contrast with relative rates of ester cleavage by acid hydrolysis at 25°C where reaction at the 3 carbon goes twice as fast as reaction at the 2 position, which in turn proceeds three times as rapidly as hydrolysis at the anomeric carbon. They also showed that the decomposition was predominantly by the bond dissociation mechanism. The contribution by ring disintegration was probably under 15%. Leider and Pane did not consider how the degree of substitution would effect bond dissociation at a given position. However, by comparing buildup and falloff rates for ester positions on the different ring structures and using the overall relative rates generated in this work, relative partial bond dissociation rate factors can be calculated. For the overall period, it appears that for the 2-nitrate position the ratio of rates between tri- and dinitrate ring is 1.4 and for the 3-nitrate position the ratio is 1.1. We have postulated that decomposition induced by ultraviolet radiation involves the same reaction mechanisms that occur thermally, i.e., dissociation and ring disintegration. Therefore, by all primary modes of decomposition—acid-catalyzed, thermal, and exposure to ultraviolet radiation—trinitrated rings lead more rapidly to decomposition than dinitrated rings. Elimination of trinitrated rings might be expected to lead to a 200-fold or better improvement in the stability of cellulose nitrate used as an adhesive or a lacquer.

Unfortunately the preparation of a nitrated cellulose with exactly two nitrate esters on each and every ring cannot be achieved by direct nitration. Well before a D.S. of 2.0 is reached, random esterification provides substantial numbers of trinitrated rings as well as di-, mono- and unnitrated units. Dinitration can be obtained by going to a sufficiently high degree of nitration—to insure that the molecule contains essentially only dinitrated and trinitrated rings—and thereafter selectively removing one nitro group *only* from those rings containing three groups. Denitration

has generally been done through the use of basic reagents. In general, base will remove nitrate groups by a saponification reaction that is many times faster than acid hydrolysis. This reaction, however, is very complex and invariably gives an extensive and broad mixture of cleavage and oxidation products. Under reducing conditions this complex breakdown is less likely to occur.

A unique and selective removal by a basic system of a single, specific nitrate group was discovered by Segall and Purves (1952:860-71; Falconer and Purves 1957). They found that when cellulose nitrate (D.S. = 2.9) was dissolved in pyridine at room temperature, the solvent had sufficient basicity to remove quickly the nitrate ester from the 2 position. The initial product was mostly (90%) the expected 3,6-dinitrate-2-hydroxyl ring polymer, but a small amount of 2-position ketone (8-10%) was also formed. Degradation proceeded rapidly however, and in two days 60% of the cellulose nitrate was decomposed. This decomposition apparently involved a mechanism going through the ketone, for when the reaction was carried out in pyridine containing a large excess of hydroxylamine, the ketone was replaced by a ketoxime and a very stable product was formed in 98% yield. The small amount of ketone was stabilized as the oxime.

The pyridine hydroxylamine work shows that the concept of selective denitration will provide a stable polydinitrate. This approach, however, is not a practical synthetic procedure for a number of reasons. The best way to achieve selective denitration is probably by reductive cleavage with hydrogen gas using a nickel or noble metal catalyst. Heterogeneous hydrogenolysis with a palladium on calcium carbonate catalyst has been shown to return nitrate esters of mono- and diglucosides to parent sugars quickly and quantitatively (Kunn 1946:1761-2). It has been amply demonstrated that nitrate groups are removed from the different positions of the anhydroglucose ring at different rates and great progress has been made in recent years toward designing noble metal complexes as catalysts to obtain remarkably selective hydrogenations (Onopchenko et al. 1984:265). A research program to develop a hydrogenation system that will selectively pluck off only the nitrate group on the 2 position of trinitrated rings has a good probability of success.

Avoidance of Acid Catalyzed Ester Cleavage

When Will did his study showing that there was an inherent thermal decomposition underlying cellulose nitrate instability, he was able to do so by first eliminating all destructive acidic impurities as a source of breakdown. He showed that there was a variety of procedures that could be used, most of which are well within the capabilities of normal chemical plant facilities.

For example, Will found that acid-free material was obtained by boiling it in water for 70 hours or by heating it in water at 144°C for 4 hours. Today's typical industrial purification is described as a series of boiling and washing treatments in water of controlled pH to remove retained acid and decompose and remove unstable products. The actual procedures used by Hercules and others are trade secrets but the work of Fontijn and Leider suggests that the material manufactured today is acid free. Both researchers did thermal decomposition studies on material obtained directly from Hercules and found thermal decomposition rates at 135°C to be essentially the same as the rates obtained by Will with his purified samples.

This fact indicates that present manufacturing processes invest sufficient effort in washing and purification procedures so that acid sulfate catalyzed cleavage is eliminated as a source of instability. Acid-free cellulose nitrate is achievable and this mode of primary polymer decomposition should not be a concern. There is, nonetheless, a need for some caution on this question. Koob (1982), working with plasticized cellulose nitrate samples from a number of manufacturers, found traces of acid when material dissolved in acetone was precipitated with water. He also found differences in a property known as "explosion point" among different adhesive formulations. The explosion point of a properly stabilized cellulose nitrate occurs at 183-186°C. Koob, however, found that the presence of acid impurities in different commercial samples of cellulose nitrate caused variations in the explosion point ranging from 150° to 178°C. These results could also be due to unremoved plasticizers and additives, the use of off-specification material in adhesive formulations, or less than perfect cleanup procedures.

Something better than explosion point, therefore, is needed to screen for acid-generated instability, and thermogravimetric analysis may be a suitable replacement. This instrumental procedure automatically supplies a slow constant rate of temperature increase to the sample while measuring the weight at each temperature. A reproducible record of thermal behavior can thereby be obtained. A comparison of this plot against a plot of an authentic acid-free sample should provide much more information on the effect of acid impurities than a comparison of explosion points. In addition, TGA could yield information on solvent content and plasticizer volatility. The TGA of a material that decomposes exothermally is not without problems, but these appear to have been solved by a quasi-isothermal heating technique described by Paulik and coworkers (1977:383-90).

Thermal Cleavage

The decomposition that occurs in the absence of catalysts or other outside influences is a temperature-dependent phenomenon that is very slow. At 25°C there is a 0.67 milligram loss of NO_x,

as nitrogen, per gram of polymer per century. For a cellulose nitrate with a typical, initial molecular weight of 100,000, this would be 67 molecular weight units or the loss of about two rings via the ring disintegration mechanism over this period. The molecular weight of the polymer fragments would then be expected to drop into a range between 20,000 and 50,000, values that should still leave a material of good bonding strength after a period of 100 years. Additional extended periods of degradation would lead to molecular weights too low to maintain needed adhesion.

Ultraviolet Degradation

In certain applications, and specifically in coatings, the contribution of ultraviolet-induced decomposition as a primary cause of molecular breakdown is very important. The isolation and evaluation of this primary effect is, however, much more difficult than with the comparable hydrolytic or thermal primary contributions. In adhesive, propellant binder, and other dark applications, the primary thermal effect proceeds for some time until breakdown products accumulate. Thereafter, an autocatalytic process begins, which can be very rapid. Photochemical decomposition is more complicated because radiation not only invokes primary decomposition, but also activates the breakdown products to higher energy states and may even cause the autocatalytic phase to begin almost immediately.

The work of Lawton and Nason that demonstrates this process has been mentioned. They show that when a film of cellulose nitrate is exposed to an S-1 type sunlamp in air, there is an immediate and rapid drop in polymer molecular weight as measured by relative and intrinsic viscosities of the product in solution. There is no indication of an induction period. In a separate experiment, similar exposure—first under nitrogen and then under oxygen—yielded a very slow degradation in the first phase and a much faster breakdown under oxygen. The authors assert that ultraviolet degradation occurs only in the presence of oxygen, and the slow decomposition is due to traces of oxygen as an impurity. The evidence from other studies indicates, however, that oxygen is not involved in primary mechanisms of cellulose nitrate decomposition.

Two primary ultraviolet decomposition pathways have been suggested that are comparable to the two thermal decomposition mechanisms, and all these are independent of the presence of oxygen. In the Lawton study, the use of an S-1 sunlamp suggests exposure to the much longer visible and near-visible violet frequencies that would cause breakdown by the bond dissociation mechanism. The slow degradation under nitrogen would therefore either be due solely to primary, ultraviolet-induced bond dissociation, or to the sum of this primary decomposition and some degradation by secondary

mechanisms caused by the presence of traces of oxygen. The rapid drop in viscosity in air results from the much larger contribution by this latter factor brought about by the relatively high oxygen concentration.

Consider the following three scenarios where cellulose nitrate is exposed to: (1) oxygen, but not to ultraviolet radiation; (2) ultraviolet radiation, but not to oxygen; and (3) both to oxygen and ultraviolet radiation. In the first case, the decomposition will occur by the low temperature ring disintegration mechanism at a very slow rate. As Fontijn and others have shown, oxygen below 90°C has no effect on this reaction. In the second case, we can add radiation-induced primary decomposition to the thermal decomposition. This radiation-induced decomposition is most probably much faster than the thermal rate, which depends only on the temperature and has been rather well defined. The radiation rate, however, will depend on both the intensity and the frequencies of the radiation. This is an important area for study since much is alluded to, but very little is known about, the photochemical effect of low-level, diffuse light. In the presence of both light and oxygen the autocatalytic decomposition brought on by secondary reactions is quickly added to the two primary modes of breakdown and, in fact, overwhelms them, resulting in a relatively fast decomposition.

The development of formulations to provide major improvements in the stability of cellulose nitrate containing coatings has to deal with both of these factors. There has been little or no work on the combined effect of oxygen and ultraviolet radiation on cellulose nitrate decomposition beyond the study done by Lawton and Nason (1944:1128), and the scope of that effort was limited. In view of the large dollar volume of cellulose nitrate going into commercial lacquers and coatings, the lack of research and basic understanding is surprising. There is an important need for more fundamental studies on the effect of the interaction of oxygen, light frequency, and light intensity on cellulose nitrate stability.

The Use of Cellulose Nitrate as an Adhesive for Ceramics

The principal concern when cellulose nitrate is used as an adhesive is lifetime. This is also an important consideration when this polymer is used as a coating. Coatings, however, are relatively easily removed and reapplied when obvious signs of aging suggest the need. To do this every 15 to 25 years is not unduly burdensome for conservators. In contrast, the process of reconstructing a large pottery piece from many fragments is a much more time-consuming and expensive process.

It is not uncommon for a conservator rebuilding a ceramic antiquity to take months to achieve a product with perfect alignment. There is usually a need to dismantle parts of the construction a number of times in order to obtain the most satisfactory positioning of pieces. The task of replacing an adhesive, because it is failing or for other reasons, in a reconstructed ceramic antiquity—and especially for large collections—is not one likely to be approached with relish by conservators. In any case, it is usually undertaken for reasons other than to replace an aging polymer before the object collapses. The higher investment in replacing an adhesive suggests that the polymer should provide for a longer period of stability than is usually required in coatings. This is a matter that does not seem to have been addressed to any extent, either from the point of view of museum practice or in the large volume of scientific inquiry that has gone into the use of these materials for these purposes.

A lifetime of 400 years for preservation is often cited as being desirable; others have suggested that any treatment ought not to be redone more than once in the working lifetime of a conservator. Thus the time span under consideration is from 40 to 400 years. The evidence now available for a properly stabilized cellulose nitrate suggests a lifetime of probably more than 25 years but not more than 200 years. In view of Feller's (1976) criterion of 100 years for the lifetime of a top-grade coating and the greater difficulty of replacing an adhesive, it may be stated that a period of stability of 200 to 400 years is more appropriate for adhesives. In order to answer the question of how this can be achieved there is a need, particularly for art conservation, to put the understanding of the aging and longevity of adhesives on a more scientific basis.

Research on improving cellulose stability is more properly the study of cellulose nitrate plasticizer blends than of the

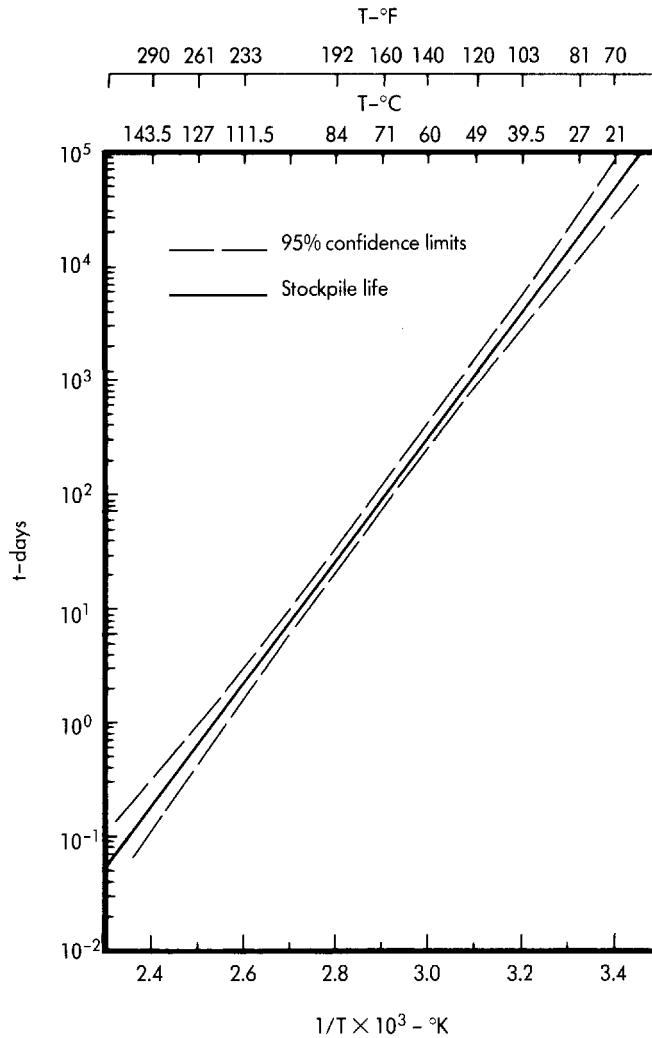
polymer itself, since the polymer is hard and brittle and the incorporation of plasticizer is essential. Concern has to be directed to the reversibility, degradation, tensile strength, and adhesive properties of blends rather than to these same properties of pure cellulose nitrate. The end of the lifetime of an adhesive arrives when degradation has taken blend strength to the point where it can no longer hold the reconstructed piece together. A value greater than zero has to be defined as a minimally acceptable bonding strength, and some measurement of this value appropriate to the manner in which failing constructions come apart, perhaps lap shear strength, must be chosen. The lifetime of the adhesive blend therefore becomes the span of time under ambient conditions between the preparation of the glued joint and the time when the joint's bonding strength falls below the accepted minimum value.

The chemical and physical properties of the plasticizer will impact on the stability and aging of the cellulose nitrate formulation. Workers at the Lawrence Livermore National Laboratory have shown that through the use of appropriate stabilizing additives the expected stockpile lifetime of cellulose nitrate can be brought to about 150 years. This is shown in Figure 10. Lifetime is plotted as days for 10% decomposition of PBX-9404, a blend of cellulose nitrate and diphenylamine, as a function of temperature. Figure 10 shows that the mid-range value for the decomposition at 70°C is approximately 55,000 days or 150 years. In the PBX formulation, the inevitably formed nitrogen oxides that arise from spontaneous thermal decomposition are removed before they can react with the parent cellulose nitrate. When this is done, the secondary autocatalytic reactions are thwarted and only the very slow spontaneous reaction remains. In the case of cellulose nitrate used as a binding polymer for high explosives, this has been done effectively by the addition of aromatic amines. Diphenylamine has been found to be the most efficient NO₂ trap in this group of compounds.

Unfortunately, aromatic ester plasticizers—not amine stabilizers—are used in commercial-grade cellulose nitrate adhesives. In formulating to market the most cost-effective plasticizer, the cheapest possible materials with adequate efficiency as plasticizers, are generally used, a criterion that has usually resulted in diisooctyl or di(2-ethylhexyl) phthalate being used as plasticizer. Phthalate esters, however, have little capacity for binding nitrogen oxides. Inasmuch as an extensive screening effort was made to find diphenylamine, 150 years probably represents the upper limit of a time range over which cellulose nitrate can be protected.

Plasticizers are materials that improve the processability of less tractable materials and most commonly they are moderately viscous liquids with low volatilities and pour points and with appropriate molecular functionality to provide solubility with the polymer being plasticized. One of the earliest applications of a plasticizer was the use of about two parts of cellulose nitrate

Figure 10.
Stockpile life as a function of
temperature for PBX-9404



Based on 10% decomposition of the nitrocellulose with no acceleration or inhibition from other materials.

with up to one part of camphor, a blend that provided a processable composition known as celluloid. Camphor, 1,7,7-trimethylbicyclo(2,2,1)hepta-2-one, is a nine-carbon cyclic ketone that melts at $179^\circ C$, sublimates at $209^\circ C$, and has a relatively high volatility for a plasticizer. Mixtures of camphor and cellulose nitrate powders, molded by heat and pressure, form celluloid, an important industrial commodity that was fabricated into substitutes for horn, ivory, bone, etc. Celluloid loses camphor at a very slow rate and after 30 to 40 years reaches a composition where the amount of camphor remains at a constant 15% level. Shortly before World War II, camphor was replaced by triphenyl and tricresyl phosphates. The use of phthalates, particularly dibutyl phthalate, as plasticizers began in the early 1920s, al-

Figure 11.
Plasticizers for cellulose nitrate

Plasticizer	Concn, phr	Tensile strength, psi	Elonga- tion %	Flexi- bility ^{a,b}	Water permeability ^c %
<u>0.5-Second cellulose nitrate^a</u>					
none		8550	6	30	100
camphor	25	6550	5	27	89
	50	5400	6	22	84
	75	4650	4	14	96
dibutyl phthalate	25	5050	5	25	36
	50	2640	4	10	65
	75	412	8	3	
N-ethyl-o,p-toluene- sulfonamide	25	6050	7	22	31
	50	2340	11	16	63
	75	440	36		96
o,p-toluene sulfonamide	25	6640	8	27	60
Santolite ^d MHP	25	6550	2	7	51
<u>30-40 Second cellulose nitrate^b</u>					
2-butoxyethyl stearate	100	2200	58	38,400	
oil-modified sebacic acid alkyd	100	5300	56	13,000	
diisopentyl phthalate	900	3600	36	8,200	
2-butoxyethyl oleate	100	3200	51	7,650	
nonoxydizing alkyd	100	3700	70	7,300	
2-ethoxyethyl ricinoleate	100	3100	70	6,500	
nonoxidizing alkyd	100	4100	37	6,000	
raw castor oil	100	3100	53	5,800	
dioctyl phthalate	100	3800	60	2,800	
methyl isopentyl phthalate	100	3500	56	2,200	
phenyl diglycol carbonate	100	4900	35	2,100	
tricresyl phosphate	100	2800	65	1,700	
butyl acetyl ricinoleate	100	2800	73	1,200	
sebacic acid alkyd	100	4800	92	700	
sebacic acid alkyd	100	3400	62	600	
diethylene glycol monolaurate	100	3000	61	530	
2-methoxyethyl acetyl ricinoleate	100	2700	82	480	
fractionated linseed oil	100	6600	12	480	
tributyl aconitate	100	2300	92	350	
trioctyl phosphate	100	2100	79	240	
low-mw polystyrene	100	7100	6	230	
triethylene glycol di-2-ethylhexoate	100	2400	96	1501	
mixed cresyl phenyl phosphate	100	3400	67	too soft	
butoxyethyl diglycol carbonate	100	3400	70	too soft	
acetyl tributyl citrate	100	2700	74	too soft	
triethylene glycol dipelargonate	100	2400	93	too soft	
dioctyl phenyl phosphate	100	1900	104	too soft	
dibutyl phthalate	100	1900	90	too soft	
poly(ethylene glycol) di-2-ethylhexoate	100	1700	92	too soft	
triethylene glycol di-2-ethylbutyrate	100	1300	67	too soft	
dibutyl sebacate	100	1600	105	too soft	

^a The RS 0.5-sec. cellulose nitrate (12% nitrogen) solvent-cast film had a thickness of 1.0-1.5 mil for tensile and permeability tests and 2.5-3.2 for flexibility (Schopper folds, ASTM D 643) (129).

^b The 30-40 sec. cellulose nitrate film had a thickness of 2.7-4.3 mil. Flexibility is MIT flexibility (number of double folds, ASTM D 2176-63T) (128).

^c Water permeability is based on the unmodified resin = 100%

^d Trademark Monsanto Co.

though di(2-ethylhexyl)phthalate, now the principal plasticizer used (and the cheapest available), was not patented until 1933.

Essentially all of the commercially available plasticizers have been used with cellulose nitrate and, in general, their compatibility with this polymer is very good (Fig. 11; Hercules Powder Co. 1965; Modern Plastics Encyclopedia 1980:699-709, 1968: 466-90; Crowley 1966:269). The plasticizers probably all function as stabilizers to some extent, although this is an area where there is little information available in the literature. The phthalates would be expected to be relatively poor stabilizers because the carboxyl substituents deactivate the benzene ring toward reacting with nitrogen oxides. Aromatic amines, phenols, and olefins are good NO_x absorbers. The first two types have activated aromatic rings that remove NO_x via ring substitution. Amines have an additional capacity for taking up NO_x through attack on the amine nitrogen. Amines are not, however, used as plasticizers because of their reactivity, their tendency towards color formation, and their relatively high price.

It is likely that organic compounds can be developed that both plasticize and absorb NO₂. Some of these compounds can therefore be expected to provide adhesive formulations that give constructions of better longevity than are obtained with present commercial cellulose nitrate-based cements. This approach to providing the best adhesive for ceramics has several shortcomings. A program for developing better formulations and then demonstrating longevity would be expensive and take a long time. Even if this were accomplished, it would be difficult to convince any manufacturer to offer a material into a market that is potentially very small. Most users of cellulose nitrate glues are not interested in the unusually long lifetimes sought in conservation; the volumes used as an adhesive for all museum work where a premium would be paid for stability is probably under 100 gallons a year. The most serious concern, however, is that the best possible product is, for reasons previously developed, unlikely to provide a sufficiently long lifetime, certainly not the 200 years that has been offered as a requirement. On the other hand, collapse of ceramics joined by cellulose nitrate over the past several decades may not be as imminent as some concerned conservators have suggested.

A more feasible suggestion might involve improving the working properties of acrylic polymers such as Acryloid B-72, rather than increasing the stability of cellulose nitrate. B-72 is a commercial product produced by Rohm and Haas that is a copolymer of methyl acrylate and ethyl methacrylate. While it was primarily developed to be applied as a coating, it is highly regarded by conservators for many uses, including adhesive applications. Both acrylic polymers and cellulose nitrate would avoid light-induced and oxidative decomposition when used as an adhesive for opaque objects. Acrylic polymers do not, however, undergo the slow, inherent decomposition that occurs with cellulose nitrate, at least not within a comparable time frame.

Much longer lifetimes in ceramic constructions with acrylic polymers can therefore be expected.

Despite its drawbacks, cellulose nitrate has several working properties that appeal to many conservators. It is liked for its reversibility, quick drying, and for the fact that plastic polymer blends are commercially available in squeeze tubes providing for convenience and less waste. Moreover, the polymer is not thermosetting, and spills are cleaned up without difficulty. The gel-like adhesive has a good working consistency and reaches a desirable tackiness relatively easily, and it does not penetrate. Its proponents cite the unique and critical ability of cellulose nitrate formulations to give thin, tight, strong bonds that they claim are not attainable with B-72.

Other conservators argue that the properties mentioned above can also be obtained in formulations with acrylic polymers. Many of the suggested differences are, however, subjective and disputable. Squeeze tubes containing acrylic adhesive formulations are not available but Koob (1986:7-14) has shown how they can be prepared in the conservator's laboratory. He has also shown how to formulate to avoid stringiness, low tack, poor adhesion, and slowness in setting.

Formulations described by Koob may lead to joints that are too thick for some conservators, but this should be correctable by changes in the polymer or modifications in formulation. Cellulose nitrate is structurally quite a different polymer than B-72. It is a relatively low molecular weight material; the molecular weight of Hercules RS 1/2 grade is only 23,000. Owing to extensive intramolecular hydrogen bonding the material, however, behaves like a very high molecular weight polymer in solution. Interestingly, a completely nitrated cellulose (D.S. = 3.0) that cannot cross bond in this manner provides solutions of much lower viscosity than one that is partially nitrated. Typically, adhesives grade cellulose nitrate is about two-thirds substituted (D.S. = 2.0). B-72, in contrast, provides relatively thin solutions at equivalent concentrations. To get to useful viscosities, quite high concentrations are required. Koob (1986:7-14) used 50 weight % acetone solutions (87% w/v) to get a proper thickness and that included the use of 0.1% fumed silica as a thickening agent. By contrast, cellulose nitrate systems may be 1/5 to 1/10 of this concentration, a condition that leaves much less polymer to be accommodated in making a tight bond.

There are several possible ways to get a workable gel with an acrylic polymer that has a lower concentration of adhesive. One is to use a much higher molecular weight polymer that provides higher viscosities at lower concentrations. B-72 comes in only one molecular weight grade, but others in the Rohm and Haas Acryloid series, notably B-48N and B-50, provide significantly higher viscosities at equivalent concentrations. For example, a 40% solution of B-72 in acetone at 25°C has a viscosity of only 200 cps while B-50 has a viscosity of 1,800 cps and B-48N at 45% solids has a viscosity of 1,740 cps. These latter

materials are methyl methacrylate copolymers. Viscosity can also be manipulated by using thickeners like silica gel, selecting appropriate solvents, or by using a mixture of B-72 and higher molecular-weight polyacrylates in the event that higher molecular weight polymers were too brittle.

Cellulose nitrate does indeed have many desirable applications. Nevertheless, the serious questions surrounding its long-term stability as an adhesive for archaeological and antiquities ceramics suggest that conservators learn to replace cellulose nitrate with other, more stable materials such as acrylic polymers.

The Use of Cellulose Nitrate as a Metals Coating

Introduction

The major application for cellulose nitrate is in coatings. Here, too, there are a number of desirable properties, e.g., ease of application, adhesion, optical qualities, and others that make its use attractive in spite of concerns with instability. In contrast to usage in adhesives and as a binder, cellulose nitrate as a coating will have an unavoidable exposure to light and oxygen and will be, therefore, subject to decomposition both by photochemical degradation of polymer bonds and by accelerated attack of radiation activated nitrogen oxides in the presence of oxygen. (This chemistry is shown on page 29 of Chapter 3.) Despite these liabilities, the commercial use of cellulose nitrate is surprisingly large. In 1978, about 75% of the wood furniture finishes manufactured in the United States were based on cellulose nitrate; in West Germany this figure was 65%.

The use of cellulose nitrate in coatings is made possible by recognizing the limitations on where it can be employed and on how long these formulations will hold up. In general, lacquers based on cellulose nitrate are used indoors, out of sunlight, and for a modest number of years, i.e., well within the expected lifetime of the polymer. For outdoor applications, the life expectancy of cellulose nitrate has been increased by the use of pigments and stabilizers. Nevertheless, the lifetimes of cellulose nitrate-based coatings are generally shorter than when products of this polymer are used as an adhesive. Reliable documentation on precisely how long such coatings do last remains to be established. Cellulose nitrate cast into films and kept out of bright light, for instance, appear to have held up quite well for over 60 years.

The use of cellulose nitrate as a coating in conservation is directed primarily to the protection of silver and other tarnishable metal art objects, i.e., those made of copper, iron, paktong, alloys of brass, bronze, etc. Plenderleith and Werner (1971) generally recommend Frigilene, a proprietary form of cellulose nitrate, for the protection of silver. Don Heller (1983:57-64), Objects Conservator of the Winterthur Museum, has been a very strong advocate of the use of cellulose nitrate for the coating of metal objects. This application in conservation can be seen as a special area of usage within cellulose nitrate coatings technology although most of the same general concerns apply, i.e., stability problems; unique properties; selection of appropriate coresins, sol-

vents, and plasticizers, among others. There are, however, aspects unique to conservation which, for the most part, deal with achieving extended lifetime. Cellulose nitrate formulations for commercial use as coatings for wood, leather, paper, etc., are widely and extensively described in the literature. The combination of a smaller market and the special longevity needs in conservation has resulted, however, in suppliers developing proprietary, undisclosed formulations. The most popular commercial coatings for protecting metals, such as Frigilene and Agateen, are generally marketed as product lines with a variety of formulations, several of which usually contain stabilizers. The composition and loading of these additives has not, however, been disclosed. Without documentation, it is not possible to know how much improvement in stability has been achieved.

Compositions

Cellulose nitrate-based lacquers generally consist of four non-volatile components: the nitrate polymer, plasticizers, resins, and pigments. An excellent discussion of the selection, use, and interactions of these components and solvents is provided in books by Henry Payne (1977) and Eugene Hamilton and Lawrence W. Early (1972). Examples of formulations for various applications are given in Figure 12. Very often it is convenient to use a mixture of cellulose nitrates in order to obtain a desired viscosity. The compatibility of most commercial plasticizers with this polymer is very good. Diisooctyl phthalate and di(2-ethylhexyl)phthalate are the most widely used plasticizers, primarily because they are the cheapest. For most commercial applications phthalate esters are satisfactory, but if one is trying to design a formulation with the longest possible lifetime there are potentially much better plasticizers than dibutyl and dioctyl phthalates.

Resins are used primarily as extenders that can increase the solids content at spray viscosities without hurting other properties. Depending on application they can also promote better depth, gloss, and adhesion. Cellulose nitrate is remarkable with respect to the wide range of oligomeric and polymeric types that it is compatible with, a characteristic that permits the design of formulations for a broad variety of applications. Alkyd resins are most commonly used for these lacquers. Alkyds are low molecular weight polyesters formed from alcohols such as glycols, glycerin, and pentaerythritol and acids such as phthalic, lauric, adipic, and linoleic. When polyunsaturated acids (such as linoleic) are employed in this process, the products are known as "oxidizing" alkyds. The oxidizing alkyds are less frequently used in cellulose nitrate lacquers for two reasons: Their additional film-forming capacity is not needed, and their use often leads to lifting. Among other resins used in the lacquers are those derived from natural sources. These include shellac, dammar, and maleic anhydride modified rosins and synthetics such as

urea and melamine formaldehyde condensates, polyacrylates, epoxy resins, and poly(vinyl acetate).

Pigments are an important component in many commercial lacquers. These materials impart color and opacity but also protect the cellulose nitrate (and any other film-forming polymers) from degradation caused by ultraviolet radiation. Clear lacquers that are supplied for coating metals, of course, do not contain pigments. The composition of these products and their content of materials that might stabilize the cellulose nitrate is not information generally available in the open literature. There is an example of a metals coating formulation, described by Payne (1977) that consists of 22% cellulose nitrate, 68% alkyd resins, 5% dewaxed shellac, and 4% dibutyl phthalate. This may be a suitable composition for coating metal novelty goods, but it is far from an optimum formula for long life and stability. The presence of alkyd resins—particularly an oxidizing alkyd—and the relatively volatile dibutyl phthalate is detrimental. Moreover,

Figure 12.
Cellulose nitrate lacquer
formulations (dry basis)

Nitrocellulose Type	%	Polymer Type	%	Plasticizer Type	%	Other Type	%	Application Type	Reference
Unspecified	55	Polymethyl methacrylate	25	Diocetyl phthalate (DOP)	20	UV stabilizer hydroxybenzophenone type cyasorb UV-24	1	Aircraft metal coating	H.C. Su, <i>Analyt. Chem.</i> 1967, 39(8):947-53
RS1/4	40	Nondrying alkyd resin	50	DOP	10	—	—	Wood furniture top-coat	
RS1/2	11	Acrylic, ester polymer	49	Butyl benzyl phthalate	15	TiO ₂ Chrome green	24.2 0.8	Exterior metal	
RS1/2	77	Acrylonitrile butadiene rubber	6	Butyl rinoleate	14	Siloxane	3	Bowling alley finish	U.S. 3,402,507
Unspecified	20	Acrylic polymer acrylic A	74	Dibutyl phthalate	5	Zinc malcate	1	Stabilized lacquer	J.P. 79, 145, 736 CA 92: 130727C
DHX3-5,8-15	49	Dammar	34	Dibutyl phthalate	17			Aerosol for wood finish	
RS1/2	52	Acryloid B-82	24	DOP	22			Military lacquer	H.L. Payne, <i>Org. Coating Tech.</i>
RS1/2	30	Acryloid C-1	40	Dibutyl sebacate	30			Fabric base coat	H.L. Payne, <i>Org. Coating Tech.</i>
RS1/2	30	Non-oxidizing alkyd	60	Unspecified	5			Automobile lacquer	H.L. Payne, <i>Org. Coating Tech.</i>
		Melamine formaldehyde resin	5						

there is no mention made of UV absorbers, organic stabilizers, or the use of finely ground sodium or calcium carbonate to provide longevity.

Before 1920, cellulose nitrate lacquers were primarily used for coating bronze and silver. Only high molecular weight, high viscosity-grade polymer was available, and the low solids content solutions were usable only where thin films were suitable.

Special Properties

Solvent Release

Cellulose nitrate-based coatings are favored over others in many applications because of the ease and speed of their application. There are several possible ways to get film formation during the application of a lacquer, e.g., vinyl polymerization (polyesters), condensation polymerization (amines, acids), addition polymerization (isocyanates), or by the use of systems that harden merely by solvent evaporation, such as those based on cellulose nitrate. The control and speed of this last approach gives it a big advantage over *in situ* polymerization systems. Additionally, the extremely facile solvent release of cellulose nitrate makes it a more satisfactory material than other polymers such as acrylates and poly(vinyl acetate) when these are applied from solvent. This ability to cause rapid solvent release extends to blends with other polymers. Cellulose nitrate, therefore, enjoys a unique position among polymers in that finishes made with it air dry faster than those made with any other film former. Cellulose nitrate finishes dry to a dust free condition in a few minutes. Even in complex formulation, this polymer enhances rapid solvent release and drying. Other approaches to rapid drying have appeared, such as the use of baking synthetics and these alternatives have displaced cellulose nitrate in many applications, one example being automobile coatings. Cellulose nitrate is highly regarded, however, where the substrate can not take higher temperatures and rapid drying and certain appearance properties are desired.

In commercial usage, quick solvent release means shorter drying times, more efficient use of facilities, lower costs, and bigger profits. For use in conservation, a different set of advantages accrue. Heller (1983:57-64) points out that when using acrylic polymers, such as B-72, to coat silver objects, the solvent evaporates slowly, spraying is very difficult, and the coating has a tendency to run and not level. He claims that the length of drying time, both during application and afterward, renders the use of B-72 impractical. During application, the lengthy drying time prohibits handling the object and, therefore, makes difficult its immediate relocation or installation in the collection. Afterwards, the coating remains soft and susceptible to fingerprints or lint from cloth. De Witte (1973-74:140-52) compared poly(vinyl acetate), acrylate polymers, and cellulose nitrate for coating silver and noted that poly(vinyl acetate) released solvent even more slowly than the acrylates. A short survey of conservators at

several locations in the United States found agreement with the opinions of Heller. Cellulose nitrate was favored for good leveling qualities, ease and reliability of application, quick drying, and lack of color. Comments on the use of acrylic polymers for the same purpose were that B-67 tended to have color and that B-72 did not level, dried slowly, and picked up dust. B-44 was better than B-72 for appearance and drying, but was not as good as cellulose nitrate. One conservator preferred B-44 or B-72 as a coating for archaeological fieldwork where preservation, rather than appearance, was important.

Appearance

A second property of cellulose nitrate that has won it acclaim is in the quality of the appearance of its coatings. Conservators who use it feel that it provides a brighter, clearer coating than other polymers. One respondent to our survey said that she had found no other polymer, neither acrylates nor poly(vinyl acetate), that provide the unique, bright appearance of cellulose nitrate. Another compared it with coatings made with B-72 and found that it gave a clearer, less polymeric coating. Heller states that:

The clarity of Agateen No. 27 is evidenced by a group of seven silver objects that were on display for a three-year period and were viewed by hundreds of people, most of whom were museum professionals. Five were coated with Agateen No.27 and two were not coated at all. In that time, not one person guessed correctly which were coated and which were not. We were satisfied that we had what we considered an excellent coating for our collection objects (1983).

Similarly high marks are won by cellulose nitrate for the appearance of its wood coatings, where it is particularly commended for the degree to which it emphasizes natural wood patterns.

Other Properties

A number of other properties of importance for silver coatings are described in a study by De Witte (1973-74:140-52). He measured and compared the following properties of films that were prepared from a variety of methacrylates, poly(vinyl acetates), and cellulose nitrates: (1) permeability to water and hydrogen sulfide, (2) hardness, (3) distensibility, (4) abrasion resistance, (5) adhesion, and (6) elasticity. The methacrylates included Incralac (a mixture of B-44 and benzotriazole), B-72, B-66, Plexisol 709, Acryfilm, and Titacryl. The poly(vinyl acetates) were Union Carbides AYAT, AYAF, and AYAA and the cellulose nitrates were Frigilene, Ercolene, and material from Mobil Oil. Description of the methodology used in each of the tests is quite complete. Results are summarized in Figure 13. Permeabilities were measured using Payne permeability cups. Since, as De Witte points out, the tarnish mechanism involves the interaction of oxygen and H₂S to form sulfur and then the reaction of sulfur with silver, it would probably have been more useful to have measured oxygen rather than water transmission

through the polymer films. Permeabilities of H₂S through cellulose nitrate and poly(vinyl alcohol) are comparable, but passage is much higher through polymethacrylates. Distensibility, or stretchability, was determined using bending mandrels. The distensibility of all new films was very good except for several of the polymethacrylates, although after aging, distensibility disappeared completely for all films. Hardness was determined before and after aging by pencil tests and by the Clemen hardness tester. The films generally were similar in hardness although the polymethacrylates were best. Abrasion resistance was measured by rubbing a 1 centimeter square carbide abrasion paper, weighted with 300 grams over the film and noting how many times it had to be moved back and forth before breakthrough occurred. The polymethacrylates were exceptionally good, the acetates were good before aging, but the cellulose nitrate films were poor. Adhesion was measured by a crosscut adhesion test. Cuts 1 millimeter apart were made through the film to form 100 squares. Each square was 1 millimeter on a side. The number of squares that remained intact was a measure of adhesion. In this test cellulose nitrate was very good. The poly(vinyl acetates) and the polymethacrylates, except for B-72, were poor. Elasticity of the films was measured by means of a variable impact tester. In this test, a 1 kilogram weight is dropped from varying heights and the drop height where the film first shows cracking is recorded. Except for Frigilene, the results were not very good. Overall it appears that cellulose nitrate has poorer resistance to abrasion than the other films; is comparable in H₂S permeability, distensibility, and hardness; and much better in adhesion and elasticity.

Figure 13.
Summary of evaluation results on various coatings for silver

Coating Type:	Acrylates	PVA	Cellulose Nitrate
Adhesion:	varied poorest	varied	very good
Solvent Retention:	poor		
Elasticity:	poor	poor	best
Distensibility:	all new films were good except B66 and Acryfilm; all aged films failed		
Hardness:	films were similar, acrylates were best		
Abrasion:	very good	good	poor
Aging:	slight yellowing, Paraloids poorest	held up the best	all very yellow and damaged
Reversibility after aging:	Paraloids good, others poor	good	poor

The same factors are also important in commercial coatings. The weakness in abrasion-resistant properties may be a major reason for incorporating alkyd or other resins in lacquer formulations. The resins generally are not film formers but they

contribute substantially to durability. Adhesion is a very important coating property and the excellence of cellulose nitrate in this regard is important in its widespread use.

Stability

The critical, and most controversial, property of cellulose nitrate is its stability. In earlier sections, this report looked at stability in terms of degradation and molecular breakdown. Discussions of stability in coatings, for example in the article by De Witte (1973-74), also raised questions of yellowing and reversibility. In the De Witte studies, all films went through 16 daily 30° to 90°C temperature cyclings and five 30% to 100% relative humidity cyclings while being exposed to a xenon arc. In addition, they were put in a deep freeze at -18°C during intervening weekends. Total exposure to the arc was 183 hours, which caused a No. 6 blue wool standard to fade. This would be equivalent to 100 to 150 years on a museum wall without taking into account the effects of temperature and humidity extremes. After this exposure, all the cellulose nitrates were very yellow and damaged. Frigilene and Ercolene had peeled off in many places. In addition, these compounds were no longer soluble in the organic solvents used to prepare the films, but required dimethylformamide for removal. The acrylics showed some aging, but the poly(vinyl acetate) films were only slightly damaged and still had a good gloss.

Unfortunately, while these tests show that vinyl polymers are much more resistant to temperature, moisture, and ultraviolet radiation, severely applied, they provide no information on the lifetime of cellulose nitrate coatings on silver artifacts in a museum environment. There is, for example, a significant amount of time that polymer is at 90°C (194°F). Examination of Figure 4 shows that when cellulose nitrate is heated to this temperature, the prevailing thermal ring decomposition mechanism switches to a faster nitrate group dissociation and the formation of decomposition products and secondary modes of decomposition are greatly accelerated. In addition, surges in humidity combined with this temperature will cause even more hydrolytic, acid-catalyzed ester cleavage. This process describes an environment causing modes of decomposition these polymers would not experience when used as a coating for fine metals. In fact, these conditions are selectively destructive for cellulose nitrate. De Witte's model for accelerated aging has to be seen as unrealistic for predicting the ability of coatings on silver to provide protection against tarnishing under ambient conditions.

While there have been no aging studies that would predict or suggest the upper limit to the lifetime of these coatings, there are reports from conservators on their experiences that establish lower limits. Stambolov (1966) describes procedures for cleaning and coating silver objects. At the time of

writing the article, he had shown that pieces covered by Frigilene and then kept under museum conditions possessed very good stability against tarnishing after a four-year period as evidenced by test samples. Treatment was completely reversible. Heller (1983) reports on objects in the Winterthur collection that were lacquered with Agateen and showed no signs of deterioration after six years. He had personal objects coated with Agateen last as long as 15 years in the adverse environmental conditions of his home. He cites studies where coatings have held up for 28 years. Other conservators have seen coated pieces of good appearance that are 30 to 40 years old. Unfortunately, in considering the best available commercial formulations, we are dealing with materials of unknown composition and uncertain longevity. The lifetime of a well-stabilized coating, designed for use in conservation, might be from 30 to 160 years in a museum environment. The determination of precisely how long this period could be is complex and involves not only polymer stability under ambient conditions but the nature of sulfur content in the environment and the relationship of hydrogen sulfide permeability and film integrity over time.

The long-term stability of cellulose nitrate when used as a coating can be expected to be poorer than when it is used as an adhesive. But as Meryl Johnson points out, "Silver gets cleaned too often for a coating to have time to deteriorate" (1976:66-75). The much greater ease of applying and removing the polymer for this use and the exceptional solvent release and appearance properties recommend it for metals conservation until a superior coating can be found. The commercial formulations described by Heller appear adequate, but conservator should have more information on their composition and should also have available simple quality control procedures to insure suitable performance.

Appendix:

Proprietary Materials Cited in the Text

<u>Proprietary Name</u>	<u>Composition</u>	<u>Source</u>
AcryFilm	Acrylic polymer	Levis, Belgium
Acryloid B-72	Acrylic copolymer	Rohm and Haas, U.S.
Agateen	Cellulose nitrate	Agate Lacquer Manufacturing Co., U.S.
AYAF	Poly(vinyl acetate)	Union Carbide, U.S.
AYAP	Poly(vinyl acetate)	Union Carbide, U.S.
AYAT	Poly(vinyl acetate)	Union Carbide, U.S.
Duco Cement	Cellulose nitrate	Du Pont, U.S.
DuroFix	Cellulose nitrate	Rawplug Co., England
Ecolene	Cellulose nitrate	W. Corning, England
Frigilene	Cellulose nitrate	W. Corning, England
HMG	Cellulose nitrate	H. Marcel Guest, England
Inobaldc	Acrylic polymer, benzotoidzole	Stanchem Inc. U.S.
Plexisol	Acrylic polymer	Röem and Haas, Germany
Titacryl	Acrylic polymer	Pigment Minereau, Belgium

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Index

A

abrasion resistance 4,53-54
Acryfilm 53,57
acrylate polymers 52
acrylic polymer 4,45,51,57
Acryloid B-72 3,45-46,53-54,57
adhesion 53-54
adhesive 3-4,41
 theory 2
Agateen 50,53,56,57
alkyd resins 50,51,54
amines, aromatic 45
Anso 30
appearance 53
archaeological uses 3
autocatalytic reactions 42
automobile coatings 52

B

B-44 53
B-76 53
B-72 3,46,53-54
Balsa 3
birefringence properties 3
bonding strength 42
brass 49
bronze 4,49,52

C

camphor 1,43
cartoon covers (Walt Disney) 30
celluloid 1,3,43
cellulose nitrate, properties of 10
ceramics 3-6,41,45,47
 restoration 3
chemiluminescence 20,26,29,33
chromatography 33
clay 5
Clemen hardness tester 54
coatings 49,53-56
 automobile 52
 metals 4
commercial applications
 history 2
contamination, iron 11
copper 49
crosslinking 24
cuneiform tablets 5

D

damar 2
decomposition
 hydrolytic 15
 photochemical 22-25
 primary 25
 ring 55
 secondary 25-32
 thermal 17-21
decomposition mechanism 21,
 24-26,34-35
degree of polymerization (D.P.) 9
degree of substitution (D.S.) 9
denitration 35-36
di(2-ethylhexyl)phthalate 43,50
diphenylamine 42
Disney 6,30
distensibility 53
Duco cement 3-4,57
durability 7
Durofix 3-4,57

E

earthenware 3
Eastman Kodak 30
elasticity 53
enamel 4
Ercolene 4,53,55,57
ESCA 7
ester groups, distribution 11,30
explosion point 37
explosives 1,9,15,42
extenders 50

F

film 6,30-31,38,52,54,56
formaldehyde 18
Frigilene 4,49-50,53-55,57

G

gel permeation chromatography 33
Gettons and Stout collection 6
glass 3-4
 Samerthrace 5
gloss 50, 55
Guardsman Chemical Company 11
gun cotton 1

- H**
hardness 53
Harvard University Art Museum 6
Hercules Incorporated 9-11,37
 RS grade 9
HMG 3-4,57
hydrogen sulfide permeability 56
hydrogenolysis, heterogeneous 36
hydrolysis, degree of 12,35
hydrolytic decomposition 16
- I**
Incralac 4,53
infrared absorption spectrometry 33
infrared spectrum 6
iron 4,11,49
 contamination 11
ivory, comb of St. Cuthbert 4
- L**
Lackfilm method 4-5
lacquers 1,51
lap shear strength 42
Lawrence Livermore National
 Laboratory 20,30,42
leveling qualities 52
lifetime 42,55
- M**
magnetic resonance analysis 11
marble, removing stains 5
mastic 2
metals coating 4
modes of decomposition
 primary 25
 secondary 25
molecular structure 1,12-13
molecular weight 1,9,31,33,37-38
museum environment 55
- N**
nitrate group analysis 33
nitrate esters distribution 9,35
NOx absorbers 45
- O**
optical qualities 2
- P**
paktong 49
Payne permeability cups 53
permeability
 hydrogen sulfide 53
 to water 53
- pigments 50-51
plasticizer 3,30,42,45,50
Plexisol 709 53,57
polarity 2
Polychrome Chemicals
 Corporation 9
polydinitrate, stable 36
polyketones 2
poly(methyl methacrylate) 3,51
poly(vinyl acetate) 3,52-55,57
porcelain 3-4
pottery 3,41
printing inks 1,11
propellants 1,20
purification 11
- Q**
quasi-isothermal heating
 technique 37
- R**
resins 50
reversibility 2-3
ring decomposition 55
ring disintegration 21,23,34-35
rocket propellant (PBX-9404) 20
- S**
silver 4,52-53,55
Societe Nationale des Poudres et
 Explosifs 9
solubility 2
solvent loss 3
solvent release 52,56
spontaneous decomposition 21,
 23-24
spray viscosities 50
squeeze tubes 46
stability 2,7,29,35,55
stabilizers 4,5,42,45
structural factors 34
sulfate esters 15
sunlight 9-10
- T**
tarnish mechanism 53,55
testing procedures 11
thermal decomposition 17,20,25,
 37-38,55
 mechanism 18
 rate of decomposition 17
thermogravimetric analysis 37
tile 3
Titacryl 53,57
tricresyl phosphates 43

U

ultraviolet radiation 22-23,29-30,
35

Union Carbide 53,57

V

variable impact tester 54

viscometry 7,33

W

Walt Disney cartoon cells 6

Winterthur Museum 49,56

wood coatings 11,53

wood furniture finishes 49

X

X-ray photoelectron spectroscopy
23

Y

yellowing 6-7,11,55

yellowness index 30

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