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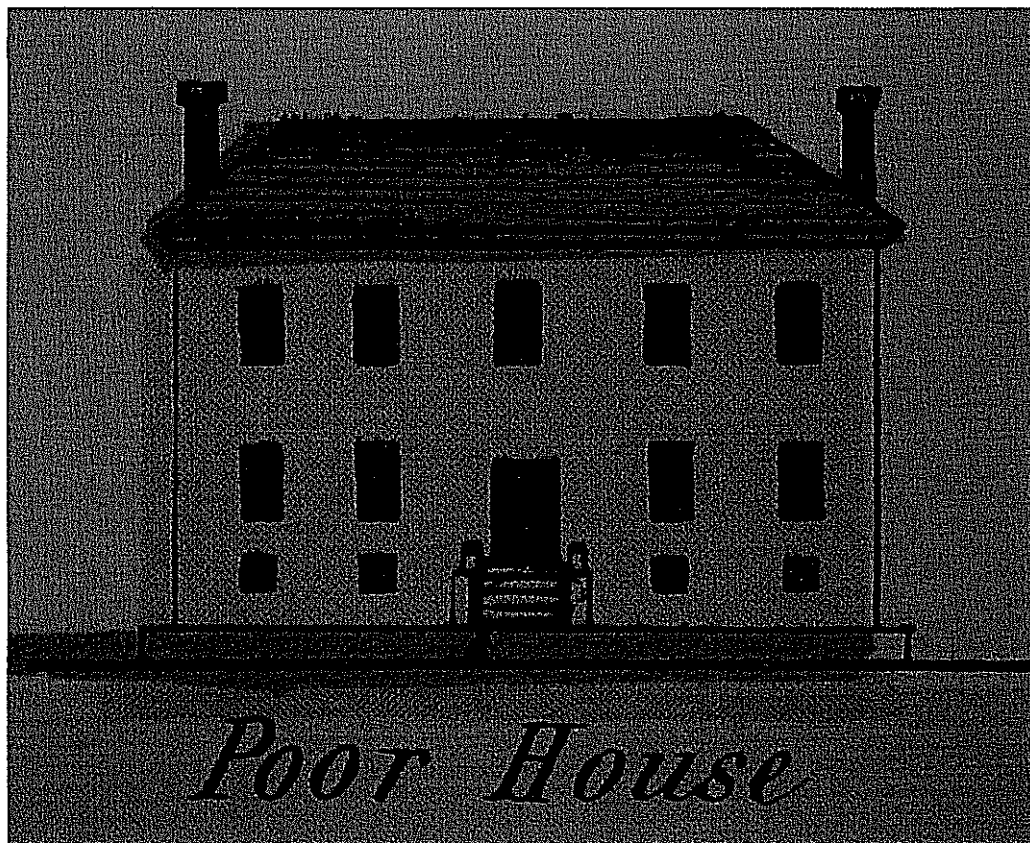
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Cellulose Nitrate Plastic (Celluloid) in Archaeological Assemblages: Identification and Care

Megan E. Springate

Invented in the mid-19th century, cellulose nitrate is commonly regarded as the earliest synthetic polymer or plastic. As increasing numbers of historical sites dating from the mid-1800s are excavated, cellulose nitrate objects are more frequently found in archaeological assemblages. The inherent instability of cellulose nitrate makes proper handling, storage, and display conditions vital to the longevity of recovered objects. In this paper, the composition, manufacture, and means of identifying cellulose nitrate are summarized. The processes of degradation and means of slowing those processes are elaborated, as well.

Inventé au milieu du XIX^e siècle, le nitrate de cellulose est considéré comme le plus ancien polymère synthétique, ou plastique. À mesure qu'on fouille des sites historiques datant du milieu des années 1800, on trouve de plus en plus fréquemment des objets en nitrate de cellulose dans des assemblages archéologiques. À cause de l'instabilité inhérente du nitrate de cellulose, de bonnes conditions de manipula-

Introduction

The earliest synthetic plastics, including Celluloid and Bakelite, have been in existence for almost a century and a half. As a result, they are found with increasing frequency in archaeological assemblages. Unfortunately, there has not been a corresponding increase in the archaeological literature regarding these substances—their composition, manufacture, means of identification, processes of degradation, and how best to store them to prevent deterioration. This paper will focus on the earliest synthetic plastic, cellulose nitrate.

Also known as nitrocellulose, trade names for this plastic include Celluloid, Collodion, Pyralin, Pyroxylin, Xylonite, HMG, Parkesine, Fabrikoid, Viscoloid, Ivoride and French Ivory (Clydesdale 1982; Katz 1986: 19; Morgan 1991: 21; Williams 1997a). It can be found in many forms, depending on the amount of nitrogen present, in items ranging from gun powders to photographic films to fabrics to the focus of this paper, plastic objects.

Used in explosives and photographic films from the 1840s, cellulose nitrate was first made into a plastic in 1856 by Birmingham inventor Alexander Parkes using a solvent casting process. Samples of the resulting Parkesine,

which is generally accepted to be the first plastic, were displayed at the 1862 International Exhibition. Celluloid, a less flammable cellulose nitrate plastic than Parkesine, made with a camphor plasticizer, was first registered in the United States by Hyatt in 1872; in 1877, the British Xylonite company was established to manufacture Celluloid in Britain (Katz 1986: 19; Morgan 1991: 21; Mossman 1993: 26; Williams 1997a).

Until about 1920, cellulose nitrate was the only commonly available colorless, transparent plastic (Williams 1997a); it was also easily dyed, and the range of colors possible was virtually unlimited (Morgan 1991: 21). In fact, cellulose nitrate has been used as a convincing imitation of ivory, tortoiseshell, bone, horn, mother-of-pearl, coral, and leather. Objects made from cellulose nitrate included: combs, dresser ware, boxes, toys, cutlery handles, jewelry, drafting set-squares, drawing templates, spectacle frames, buttons, and toilet seats (FIG. 1) (Katz 1986: 19; Williams 1997a). The versatility, low cost, and world-wide availability of cellulose nitrate made it one of the most widely used plastics for almost 100 years. Still in production, cellulose nitrate has been surpassed in popularity by other more stable plastics (Fenn 1994: 46; Williams 1997a).

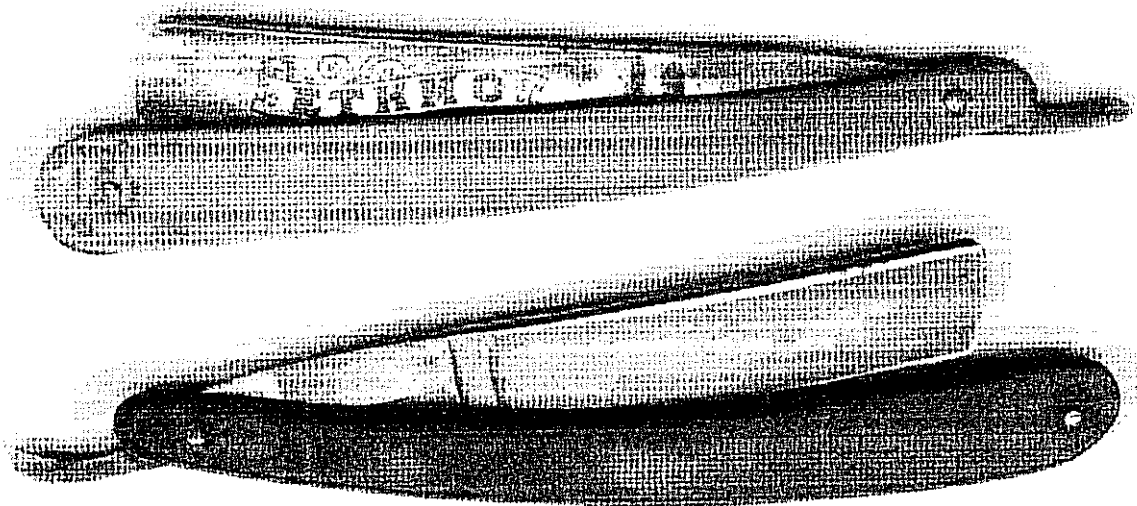


Figure 1. Celluloid handled straight razors. Deterioration is causing darkening and crazing (not visible). The bottom razor has a dark-brown handle. Note the whitish blooms, indicating deterioration. (From the author's collection)

The Chemistry of Cellulose Nitrate

Cellulose nitrate does not have a fixed chemical formula; rather, it is "a polynitrate ester of the natural polysaccharide, cellulose" (Selwitz 1988: 1). This semi-synthetic or chemically modified natural polymer is created when cellulose in the form of cotton or wood pulp is reacted with nitric acid (Clydesdale 1982; Morgan 1991: 21). During this reaction, some hydroxyl ($-OH$) groups of each glucose unit in the cellulose are replaced by nitrate ($-ONO_2$) groups. The number and position of these groups varies, which is why there is no definitive chemical formula.

The amount of nitration dictates both the form and the stability of cellulose nitrate: plastics and lacquers contain 10.5 to 11.5 percent nitrogen; lacquers, films, and sheets contain between 11.5 and 12.3 percent nitrogen; while explosives and gun powders contain 12.4 to 13.5 percent nitrogen (Williams 1997a). Fully

nitrated cellulose, known as guncotton, is used as both an explosive and a propellant (Gillespie et al 1989: 1096). The reactive sites of cellulose nitrate are the nitrate groups (Williams 1997a).

During the manufacture of cellulose nitrate plastic, plasticizers such as camphor and castor oil are added. These plasticizers are relatively involatile substances which separate the molecules of individual polymers. This weakens the inter-molecular bonds and allows the long molecular chains of the plastic to move relative to one another. Cellulose nitrate on its own is a hard, brittle plastic at ordinary temperatures; with a plasticizer, it becomes more resilient and easier to work (The Conservation Unit 1987: 43-44).

Manufacturing Processes

As cellulose nitrate plastic could not easily be molded into objects, thin sheets were sliced

from blocks of material. Parallel lines or scratches caused by the cutting blade can often be seen on the surfaces of cellulose nitrate objects, especially when examining unfinished surfaces with a 10X magnifying lens (Morgan 1991: 21; Williamson 1992: 4). Objects were then formed from these thin sheets by thermoforming or blow molding.

In the thermoforming process, the thin sheets of cellulose nitrate were heated using an oven, hot water or hot oil bath, or the use of infra-red or dielectric heating. These plastic sheets were then shaped by bending or forcing them into a mold using a vacuum, air pressure, or a matched tool in a process similar to press molding (Morgan 1991: 47).

Blow molding involved the clamping together of two warmed sheets of cellulose nitrate between mold faces. Air was then blown between the sheets, forcing them into the mold. In some cases, plaster was used to fill the resulting hollow to give the objects more weight (Morgan 1991: 47). Ping pong balls were manufactured for almost one hundred years using this blow molding process (Williamson 1992: 5).

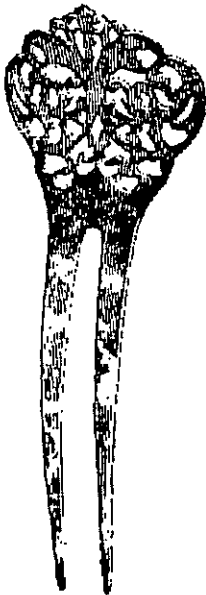


Figure 2. Celloid was often used to make convincing tortoiseshell imitations for items such as hairhair combs. (Image from Grafton 1994:2)

Identification of Cellulose Nitrate

When dealing with collections of plastics, it is crucial that they be properly identified so that the appropriate cleaning, stabilization, and storage measures may be observed. Infrared spectroscopy is by far the most accurate means to identify cellulose nitrate; however, this method may not always be accessible. Following are some other observations and tests to aid in the identification of cellulose nitrate.

Visual Appearance

While cellulose nitrate was the earliest clear plastic, later polymers such as cellulose acetate, plasticized poly (vinyl chloride), poly (methyl methacrylate), polystyrene and polyester are all now commonly used to produce clear materials. Neither is the presence of a high gloss sufficient to distinguish cellulose nitrate. Other plastics, including poly (methyl methacrylate), other cellulose, polystyrene and polished casein may also have glossy finishes (Morgan 1991: 36).

The most convincing imitations of ivory are made of cellulose nitrate. While the plain color of ivory can be imitated using many other plastics, only cellulose nitrate can be manufactured to have a grain, color, and weight almost identical to ivory. Imitation tortoiseshell is likely to be either casein or cellulose nitrate, which has a greater brilliance and clarity than both casein and natural tortoiseshell (FIG. 2) (Morgan 1991: 36; Williamson 1992: 4).

Under low power magnification (such as that provided by a 10X hand-held loupe), one may see the distinctive weathering pattern of celluloid nitrate; consisting of a series of conchoidal fractures forming a checked pattern.

Odor

When gently warmed, by either rubbing or washing in warm water, a slight camphor smell may be released (Morgan 1991: 37). The lack of a camphor smell does not preclude the test sample from being cellulose nitrate, as many other plasticizers were used during manufacture.

Physical Tests

Because of similarities to many other plastics, neither the specific gravity (1.3 to 1.4) nor the placement on the Barcol hardness scale (around 70) are sufficient to identify cellulose nitrate (Morgan 1991: 39–40).

Chemical Tests

Although testing for the presence of nitrogen is possible, this is not sufficient to identify cellulose nitrate as there are a number of other polymers which also contain nitrogen. These include nitrile rubber, polyurethane, casein, melamine-formaldehyde, nylon, and urea-formaldehyde (Saunders 1966: 22).

The pH of the plastic fumes may be determined by heating a small sample in a test tube (a fine emery paper may be used to remove a sample from an unobtrusive area). A piece of moist litmus paper is then held in the mouth of the test tube. The presence of acidic fumes (i.e., a pH between 1 and 4) suggests that the plastic may be cellulose nitrate. Note, however, that cellulose acetate, polyurethane, polyester, and poly (vinyl chloride) also give off acidic fumes upon heating (Morgan 1991: 37; Williamson 1992: 7–8).

A small sample of the plastic (again, a fine emery paper may be used, and this method is preferred over testing the object directly) may be heat tested, using extreme caution as cellulose nitrate is extremely flammable. Positive observations for this test include the following: the material burns very quickly and continues to burn after it is removed from the flame; the plastic burns with a yellow color; and a camphor odor may be noticed (Saunders 1966: 18).

Although the above mentioned tests and observations may all be used to suggest the presence of cellulose nitrate, the diphenylamine spot test is the best chemical method to identify this polymer (Williams 1997a). A full description of the diphenylamine spot test can be found in Appendix A.

Deterioration

The progression of cellulose nitrate deterioration is typical of most polymers. Specifically, a long period of deterioration where little change is visible is followed by rapidly accel-

erating degradation. Thus, it is crucial to recognize the early stages of deterioration, so that the process may be slowed (Morgan 1992: 1).

The reactive sites of cellulose nitrate are the nitrate groups themselves. During degradation, the liberated oxides of nitrogen, including nitrous oxide and nitric oxide, may react with atmospheric moisture to form acids such as nitric acid. It is the presence of the resulting acidic conditions which further accelerates degradation, eventually causing the main polymer chain to break (Morgan 1991: 21–22; Williams 1997a).

Five stages of deterioration have been described for cellulose nitrate film. The same progression can be expected for cellulose nitrate objects, albeit at a slower rate, due to the lower concentration of nitrogen. These stages include progressive yellowing (to dark brown), checking and crizzling, the formation of bubbles or foam on the surface, and embrittlement and shrinkage (FIG. 3). All of these stages are accompanied by the foul odor of nitrogen oxide gases (Williams 1997a). A misty haze-type bloom with an acidic "taste" is one of the earliest signs of cellulose nitrate deterioration (Williamson 1992: 4). These visual changes are accompanied by an associated decrease in auto-ignition temperature, which is the lowest temperature at which an object will self-ignite without a direct heat source. Undegraded cellulose nitrate auto-ignites at about 325°F (150°C); in the last stages of deterioration, when all that is left is a powdery or foamy mass, the self-ignition temperature of cellulose nitrate can be as low as 125°F (50°C)—a temperature easily reached near light bulbs, heat sources, and in unventilated storage areas in summer months (Williams 1997a). Deteriorated cellulose nitrate objects are extremely fragile, and may even break under their own weight.

If allowed to build up, the products of cellulose nitrate deterioration can result in what is known as an antagonistic synergistic effect, also known as "bad neighbors." In these situations, the close proximity of one material (in this case, cellulose nitrate) induces or accelerates the degradation of another, such as the corrosion of metals, and the embrittlement and discoloration of organics (Morgan 1991: 15; Williams 1997a). The following are brief

CARVERS.



No. 14748. Celloid handle Carvers. Blades of best steel, finely finished; a strong and neat design. Set consists of knife, fork and steel to match.
 Length of blade, inches, 8 9 10
 Price, per set, \$2.30 2.50 2.65



No. 14749. Grained celloid handle Carvers, with difficulty distinguished from ivory, which it will outlast. Blades of best steel, finely finished. Pair consists of knife and fork.
 Length of blade, inches, 6 9 10
 Price, per pair, \$2.40 2.60 2.80
 Steel to match, extra, .60 .60 .60



No. 14750. Celloid handle Carvers, with German silver ferrule. A carver with best steel blade and every merit of beauty and finish. Pair consists of knife and fork.
 Length of blade, inches, 8 9 10
 Price, per pair, \$2.85 3.15 3.45
 Steel to match, .75 .75 .75

Figure 3. Celloid-handled knives from the 1897 Sears and Roebuck catalogue (Israel 1993:108)

descriptions of conditions leading to the chemical alteration and deterioration of cellulose nitrate.

Inherent Vice

This category includes effects of manufacturing which play a role in deterioration. Cellulose nitrate is, itself, an unstable polymer. While careful preparation of cellulose nitrate and careful fabrication of objects can reduce the rate of decay, there is currently no effective means of completely stopping the deterioration process (Williams 1997a).

Cellulose nitrate manufactured with a high nitrogen content (usually over 13 percent), which is primarily used for explosives or gun powders, is very unstable, and can easily explode if subjected to heat, friction, or shock. Objects made of cellulose nitrate plastic (usually having a nitrogen content of 12 percent or less) are not this explosive; they are, however, extremely flammable (Williams 1997a).

The percentage of nitrogen present is not the sole cause of deterioration; the form of the object also plays a role. In the case of thin

items, such as photographic films, the nitrogen oxide gases quickly diffuse out of the object and may be vented away. In the case of thicker object such as cutlery handles, however, the diffusion of these gases out of the object is slower. Cellulose nitrate deterioration is autocatalytic. That is, the acids created by the degradation process encourage further deterioration. As a result, in thicker objects, where the nitrogen oxide gases and acids are trapped within the object longer, there is more opportunity for them to catalyze even further deterioration (Williams 1997a). This process of autocatalyzation results in visible internal cracks which spread rapidly throughout the object (Williamson 1992: 5). The heat created by this exothermic reaction may cause the object to spontaneously ignite (Williams 1997a).

Plasticizers, such as camphor, are not necessarily tightly bound within the structure of the plastic. Thus, over time, they are lost through sublimation, resulting in a loss of lustre, distortion, embrittlement, and an object which is easily soiled (Morgan 1991: 23; Williamson 1992: 4).

Environmental Conditions

Light, heat, and a high relative humidity encourage deterioration of cellulose nitrate. The degradation process is also accelerated by the presence of acidity, alkalinity, or certain metals which may be found as impurities in the plastic itself, or as component parts of an object (Morgan 1991: 21).

Ultraviolet light is particularly harmful as it tends to break the cellulose polymer backbone, weakening the plastic. As a result, objects discolor and yellow, weaken, embrittle, craze, crack, or break. Once this deterioration process has begun, it will continue even in the dark (Williams 1997a). Heat also encourages the deterioration and weakening of cellulose nitrate.

All moisture, including that present as a result of a high relative humidity, is detrimental to cellulose nitrate products, because it readily combines with nitrogen gases produced during cellulose nitrate deterioration, forming harmful nitric acid (Williams 1997a). The presence of this acid encourages further deterioration.

Biological Degradation

Although based on cellulose, nitrocellulose is not generally subject to biological attack (Morgan 1991: 23).

Handling

While undeteriorated cellulose nitrate is quite resilient and robust, in a degraded condition it must be handled with caution. Vibrations, such as those encountered during transportation, and direct physical shock (i.e., dropping an object) can result in the disintegration of unstable cellulose nitrate.

Arresting and Preventing Deterioration

Once begun, the deterioration of cellulose nitrate cannot be stopped. It is, however, possible to slow down the reactions of degrading materials, and to protect undegraded objects. Ventilation and the exclusion of light are the most important factors in maintaining stability (Morgan 1991: 22). Also, due to the detrimental effects that the products of deterioration can have on other objects, degrading cel-

lulose nitrate objects should be isolated and stored in a ventilated and fire-proof area (Williams 1997a).

Ventilation

Good ventilation is crucial to lengthening the life of cellulose nitrate, since it removes nitrogen oxide gases from the vicinity of the objects. Objects in storage should be loosely packed to encourage air circulation, and there should be at least one complete air change per day. The vented air contains harmful gases and should not be allowed to circulate to other areas of a collection (Morgan 1991: 22; Williams 1997a). Note that oxygen-free storage of cellulose nitrate materials is not recommended—containment of these items in an oxygen-free enclosure with no ventilation will accelerate deterioration (Williams 1997b).

Light

To prevent light damage, cellulose nitrate should not be exposed to sunlight or illuminated strongly. All ultraviolet rays, particularly those from fluorescent lighting and the sun, should be screened out with ultraviolet filters. Cellulose nitrate should be considered particularly vulnerable to light and exposed to no more than 50 lux (Morgan 1991: 16; Williams 1997a).

Relative Humidity

Because atmospheric moisture is a major factor in deterioration, cellulose nitrate objects should be kept in an environment with a relative humidity below 40 percent (Morgan 1991: 10, 22).

Temperature

Cellulose nitrate should be stored below 68°F (20°C), with a temperature of 50°F (10°C) being preferable. The relatively low auto-ignition point of degraded cellulose nitrate means that temperatures should never be permitted to rise above 85°F or 30°C (Morgan 1991: 22; Williams 1997a). When moving objects to and from cold storage, they must slowly be acclimatized to the new environment so that condensation of water vapor and thermal stresses are avoided (Williams 1997a).

If a refrigerator is to be used to keep cellulose nitrate objects cool, be certain that a high relative humidity is not produced during the refrigeration cycle, as is the case in some frost-free models (Williams 1997a). Note that if the humidity and ventilation of the storage area cannot be controlled, then the storage of cellulose nitrate below room temperature is not recommended (Morgan 1991: 22).

Other Considerations

Cellulose nitrate must not be allowed to come into contact with buffered papers or other alkaline materials. This includes acid free papers which contain calcium carbonate (i.e., Woolfitt's "super acid free" paper). While alkalinity encourages the degradation of cellulose nitrate, deliquescent nitrate salts may also form on the object (Dignard 1994: 3).

Polishes, waxes, and other film-forming materials are often found on the surface of cellulose nitrate objects. These coatings encourage degradation by trapping deterioration products, such as nitric acid, against the object. A conservator familiar with cellulose nitrate should be consulted regarding the proper removal of these coatings.

If repairs are required, avoid solvent-based adhesives. The solvents will cause deterioration of the cellulose nitrate, and the joins are likely to remain weak and liable to fail. In general, it is best to avoid repairs unless absolutely necessary, and a conservator familiar with cellulose nitrate should be consulted. Solvents should also not be employed to "de-water" these items during cleaning, as they may dissolve the plasticizers, causing damage. When using any adhesives, the proper safety procedures should be observed; consult the appropriate Material Data Safety Sheet, available from the manufacturer or supplier.

Note that nail polish and Acryloid B-72, often used to label artifacts, also contain solvents which are damaging to cellulose nitrate. A first indication of damage is the appearance of crazing under the label. Water-based materials, such as clear acrylics, are better choices for labeling cellulose nitrate. Use as little water as possible in the mixture, since water also causes deterioration (Derrick and Stulik 1993: 180).

When storing objects made of cellulose nitrate, it is advisable to prevent contact between the plastic and any metals, especially copper; this may be accomplished by using an inert barrier film such as Mylar. If possible, the disassembly of any thick sections is also recommended, to allow for the greater rate of release of deterioration products (Morgan 1991: 22).

Washing

Cellulose nitrate objects should be cleaned periodically to remove surface dirt accumulated during handling and storage, as well as to remove any degradation products that may have formed. Other than gentle surface dusting with a soft brush, cleaning should only be done by a conservator familiar with the plastic.

Monitoring

Regular monitoring of cellulose nitrate collections for early signs of deterioration is the best means of preventing damage to large portions of the collection. In some cases, preventive treatments or storage decisions may be carried out in order to slow down the rate of decomposition, while in other instances greatly deteriorated objects may have to be isolated from the collection in order to prevent either combustion or the catalyzation of deterioration in other objects (Morgan 1991: 10; Williams 1997a). Indicator cards, such as those manufactured by 3M, are available that measure atmospheric pollutants and compounds off-gassed from materials during deterioration. These may be a helpful addition to a monitoring program.

Conclusion

Objects made of cellulose nitrate, as well as other early plastics, are increasingly making their way into archaeological assemblages and collections. When one considers the immense impact of plastics on society, the value of these early examples becomes apparent. While we may think of plastics as permanent substances that never break down in landfills, early plastics such as Celluloid and other varieties of cel-

lulose nitrate are inherently unstable and are very susceptible to their surroundings.

The deterioration of these early plastics is inevitable; however, precautions in their care and handling can slow this process considerably. The best preventive measures include a regular monitoring and cleaning schedule to isolate any badly deteriorated objects, and storage/display in a low relative humidity (less than 40 percent), low light (no UV, and no more than 50 lux), and low temperature (between 50°F–68°F, or 10°C–20°C) environment with lots of ventilation (at least one full air change per day).

Acknowledgments

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Appendix: The Diphenylamine Spot Test For Cellulose Nitrate (from Williams 1994)

The Reagent

Slowly add 90 ml of concentrated sulphuric acid to 10 ml of water while constantly stirring. Add this 90 percent sulphuric acid, in small portions and while stirring constantly, to 0.5 g of diphenylamine. Use extreme caution; this reaction is very exothermic. Have lots of water, particularly running water, nearby to flood any spills.

This solution is very corrosive. It may be stored for several years and is effective even after it becomes slightly blue or brown. Store this solution in glass bottles labeled "0.5 percent Diphenylamine in 90 percent Sulphuric Acid; Corrosive." Be certain to use stoppers which are resistant to 90 percent sulphuric acid (i.e., not paper, cork, rubber, or metal foil).

The Procedure

From an unobtrusive area of the object, take a tiny chip or scraping or use fine emery paper. The total sample need not be larger than a pin head, as the test is extremely sensitive. Place the sample on a glass surface or on a white glazed porcelain spot plate. Using a pipette or eye dropper, place a single drop of the reagent onto the sample. If the sample quickly stains a blue-violet color which diffuses into the test drop, the presence of cellulose nitrate is indicated. If there is no color change, or other colors such as orange, yellow, brown, or green appear, the absence of cellulose nitrate is indicated.

Cautions

For reliable results, the object to be tested must be clean. Any dust or oozing plasticizer on the surface of an object, or embedded in surface cracks, may give a false positive for the presence of cellulose nitrate. Cross-contamination is also a concern due to the highly sensitive nature of the test—a pipette which has accidentally come into contact with a cellulose nitrate object prior to testing can also give a false positive if used on a non-cellulose nitrate object. The diphenylamine test should never be used directly on the surface of an object, due to the potential of marking or discoloration (Coxon 1993: 404). False results are possible when materials, such as pigments containing chromates (yellow, orange, or green), or coatings containing ester gums, copal, and other natural resins, are present (Williams 1994: 2).

Notes

Other published diphenylamine spot test "recipes" call for varying proportions of components in creating the reagent (see, for example, Coxon 1993, who calls for a 5.0 percent solution). Tests conducted by the Canadian Conservation Institute using the 0.5 percent solution described above indicate that it is effective; 30 samples of objects, coatings, and adhesives were selected. Each sample was tested using the diphenylamine test, as well as

tested using the diphenylamine test, as well as examined using infra-red spectroscopy (IR). All samples that were shown through IR to contain cellulose nitrate gave positive spot test results; all those shown not to contain cellulose nitrate tested negative. There were no problems with contamination (Williams 1994: 2).

Materials required to conduct the diphenylamine test are available from standard chemical suppliers.

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