CCI Notes

15/3

Display and Storage of Museum Objects Containing Cellulose **Nitrate**

Introduction

Cellulose nitrate, often called nitrocellulose, has been used in photography since the 1840s (Hager 1983), in explosives since 1845 (Roff et al. 1971), and in moulded plastic objects since about 1870 (Dubois 1943). It was distributed under various trade names including Celluloid, Collodion, Gun Cotton, Pyralin, Pyroxylin, and Xylonite. The variety of objects made from cellulose nitrate includes cutlery handles (French ivory and ivory-like substitutes), drafting set-squares and drawing templates, toys and dolls, photographic film, eyeglass frames, protective and decorative lacquers, and many other cosmetic, toiletry, and household items ranging from buttons to toilet seats.

The conservation literature on cellulose nitrate deals mainly with the preservation of nitrate photographs (e.g., Calhoun 1953; Hager 1983) and the deterioration of adhesives (Koob 1982; Shashoua, Bradley and Daniels 1992). Selwitz (1988) discusses cellulose nitrate used as an adhesive for ceramics and as a lacquer for metals. Johnson (1976) describes many products and applications found in museums. This Note addresses the neglected subject of the degradation, preservation, and storage of larger three-dimensional cellulose nitrate objects.

Unfilled, unpigmented, and undegraded cellulose nitrate is colourless and transparent. For about 50 years, until about 1920, it was the only lightcoloured transparent or translucent plastic commonly available. Objects with these physical characteristics that were acquired or manufactured before this period are probably made of cellulose nitrate. Although objects are still made from this material, cellulose nitrate has been largely replaced by other, more stable plastics.

Cellulose nitrate is made by nitration processes that replace varying amounts of hydroxyl groups of cellulose with nitrate groups. Nitrogen content (degree of nitration) affects the physical and chemical properties of the plastic. Table 1 shows the types of products that can be made from cellulose nitrate stock of different nitrogen contents.

Table 1 Nitrogen Content in Different **Types of Products**

Product Group	Nitrogen Content (%)
plastics, lacquers	10.5 - 11.5
lacquers, films, sheets	11.5 - 12.3
explosives, gun powders	12.4 - 13.5



The stability of cellulose nitrate is strongly influenced by the amount of nitrogen present in it: the greater the nitrogen content, the more unstable the product. While some cellulose nitrate products with high nitrogen content (typically greater than 13%) will explode if subjected to heat, friction, or shock, objects and films with lower nitrogen contents (usually less than 12%) are not explosive. They are extremely flammable, however, and because of this they require special attention. All of these products, regardless of their nitrogen content, can be detected by the Diphenylamine Spot Test (see CCI Notes 17/2, The Diphenylamine Spot Test for Cellulose Nitrate in Museum Objects).

Degradation of Cellulose Nitrate

A detailed discussion of degradation of cellulose nitrate at ambient and elevated temperatures is given by Selwitz (1988).

Cellulose nitrate degrades to produce acidic and oxidizing nitrogen oxide gases (including nitrous oxide, nitric oxide, and nitrogen dioxide). In closed drawers, cabinets, and display cases with restricted ventilation, high concentrations of these gases build up that can corrode metals, embrittle and discolour organic materials, and accelerate the degradation of objects. In photographic film and in objects of thin cross-section, the problem is far less acute because the gases diffuse out of the object quickly and can be vented away. For objects of thick cross-section, diffusion is much slower. The gases are trapped in the object for longer periods and have a greater chance to catalyze degradation. A vicious circle forms: faster decomposition increases the concentrations of nitrogen oxide gases, which in turn increase the rate of decomposition. The concomitant heating of the object can cause spontaneous ignition.

Although care in preparation of the cellulose nitrate and in fabrication of objects can reduce the rate of decay, no effective method has been found

to completely stop it. Five stages in the degradation of photographic film have been described (Cummings et al. 1950), including progressive yellowing (to dark brown), formation of bubbles or foam, embrittlement and shrinkage of the film, and degradation into a powdery or foamy mass. These changes are accompanied by foul odours from nitrogen oxide gases. The same progression of decay can be expected for any cellulose nitrate object, but at a much slower rate for three-dimensional objects because they are made from less highly nitrated material than is film.

These changes are accompanied by progressive decreases in auto-ignition temperature, the lowest temperature at which an object will self-ignite without a direct heat source (spontaneous combustion). Fresh, undegraded cellulose nitrate auto-ignites at 150°C (paper ignites at 315°C to 370°C). The powdery or foamy mass of cellulose nitrate in the last stages of decomposition can auto-ignite at temperatures as low as 50°C. This temperature can easily be reached near light bulbs, radiators, and other heating equipment, or in unventilated buildings and attics during hot summers. This accounts for spontaneous combustion in film repositories.

Reports of spontaneous ignition of cellulose nitrate are restricted to collections of photographic motion picture and x-ray film in poorly ventilated, densely packed, bulk storage deposits, where the sequence of events described above has been implicated. Incidents of spontaneous combustion under less dense and well-ventilated conditions, such as in collections where film is interleaved with paper or where the objects are spaced loosely on shelves, have not been reported.

To identify and solve the problems in photograph repositories, many studies were done during the 1950s and 1960s on the unstable, highly nitrated film base material. Storage recommendations arising from these studies are more stringent than those required

for the majority of museum objects. The underlying principles for those recommendations are, however, a useful guide for the storage of all cellulose nitrate objects.

Recommendations for Storage

Segregation and Ventilation

Although cellulose nitrate objects are very flammable, they are unlikely to explode or to spontaneously combust when stored under normal museum conditions. This is especially true of objects that do not exhibit the extreme state of decay described above. Cellulose nitrate objects do, however, undergo constant and unrelenting degradation at varying rates with the release of noxious, corrosive, acidic, oxidizing gases. To prevent the destructive reaction of these gases with adjacent materials, especially metals or organics, all cellulose nitrate objects should be segregated into a separate ventilated and fire-proof storage area.

Cellulose nitrate objects should not be enclosed, but should be stored loosely enough to allow air to circulate freely and to vent any decomposition gases. There should be at least one air change per day to prevent the build up of fumes. Vented air must not be circulated to other parts of the collection.

Environmental Conditions

Light, heat, and high relative humidity all accelerate cellulose nitrate degradation. Effects from these environmental factors should be minimized under appropriate storage conditions. The conservation literature gives little guidance for objects other than photographic materials.

For still camera negatives comprising only a few kilos of cellulose nitrate, with ample storage space for individual items, environmental conditions of 10°C and RH of 40% to 50% have been recommended (Calhoun 1953). Low temperature and RH are recognized as being more stabilizing for cellulose nitrate but are unsuitable for photographic emulsions without

taking special precautions (Haynes 1981). For museum objects, refrigeration or cold storage at RH below 50% should be considered. Household refrigerators can be used if they are chosen very carefully. Some models of frost-free refrigerators produce very high RH during their refrigeration cycle and must be avoided. Wilhelm (1978) has discussed this problem and has given some recommendations. Objects moved to and from such cold storage environments must be slowly acclimatized to each new set of conditions. Condensation of atmospheric water and thermal stresses must be avoided. In any case, temperatures must never be allowed to exceed 30°C. (As mentioned above, some severely degraded cellulose nitrate motion picture film has been shown to ignite spontaneously at 50°C.)

Cellulose nitrate yellows when exposed to radiation between 360 nm and 400 nm (Parkins 1957). Once started, this process continues even in the dark. Light of greater energy (ultraviolet light with a wavelength of less than 360 nm) tends to break the cellulose polymer backbone, reducing the strength of the cellulose nitrate plastic. Coatings discolour and crack; objects weaken and embrittle, then craze, crack, or break; and adhesives fail. To prevent this damage, do not expose cellulose nitrate objects to sunlight or illuminate them too strongly by other light sources. These should be considered as particularly vulnerable objects and should not be exposed to light levels above 50 lux (Macleod 1978).

Monitoring Program

The most important storage activity is to monitor the collection. Establish a schedule to examine and record the condition of the objects regularly. Although cellulose nitrate is extremely flammable, there are no reports of fires where there has been constant monitoring. Only in unmonitored motion picture and x-ray film repositories have problems occurred. As cellulose nitrate degrades, it undergoes a variety of changes in appearance that signal its state of decay.

Objects that are decaying must be treated at once with the measures described above. Decomposition can be slowed but not reversed. If decomposition is too far advanced, the objects cannot be saved. In the final stages of decay, objects are too hazardous to the rest of the collection to justify retaining them. Such objects should therefore be disposed of, after ensuring that sufficient documentation of the objects exists. In this state, the object is probably in such poor condition that it is useless for museum applications.

Fire Prevention

Because cellulose nitrate is so flammable in comparison to most other museum objects, special fire prevention measures and fireproof storage areas should be considered. The fire hazard of cellulose nitrate is similar to that of other common highly flammable materials such as gasoline and solvents. It should be stored and handled in the same way. Relatively undegraded cellulose nitrate poses no more of a fire hazard than do these other materials.

Conclusion

Cellulose nitrate is a very flammable material and must be isolated from heat and ignition sources. The primary hazard of cellulose nitrate objects in the museum context is not their propensity to ignite spontaneously or to explode, but rather their production of corrosive, acidic, oxidizing gases as they degrade. Therefore, cellulose nitrate objects should be isolated from the rest of the collection.

Any storage or display program should strive to reduce light exposure, temperature, and RH, because all of these environmental factors increase rates of degradation. Ventilation should be provided to remove all fumes produced during degradation.

A monitoring program should be established to detect physical changes in objects that indicate the advancing and accelerating decomposition of the objects, with correspondingly increased hazardous properties. If

decomposition is too far advanced, the object cannot be saved. The object must be removed from the collection and be disposed of (or be given very special attention in special isolated storage). Ensure that sufficient documentation of the object exists before it is disposed of.

If these recommendations are followed, it should be possible to store and display cellulose nitrate objects safely without fear of catastrophic fires or other damage to the rest of the collection as a result of their deterioration. There is no need to discard and destroy objects indiscriminately simply because they are made of cellulose nitrate.

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