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Figure 4. *UV-visible spectra for raw linseed oil, MBL, TBL 1h and TBL 4h.*

Figure 5. *SEC chromatograms. The molecular mass values for linear polystyrene are indicated.*

The UV-visible spectra of the MBL, Figure 4, shows a slight increase in the absorption at longer wavelengths attributed to conjugated sequences as compared to the raw oil. A significantly larger increase is observed already after heating the TBL for one hour. Four hours of heating results in another substantial increase in absorption at longer wavelengths indicating an increase in both the number and the length of conjugated systems.

As seen in Figure 5 a continuous build up of material with higher molecular mass is observed for the TBL's. After only 1h of heating the raw oil has been polymerized to a much higher degree than the MBL which shows only a minor MW increase. Four hours heating results in a considerable amount of material with high molar mass while about 35% of the raw oil still remain unreacted.

Analyzing by ICP-OES showed no detectable amount of Cu (< 10 ppm) while the Pb content was about 0.3 % after 4 hours of heating of the TBL and about 0.2 % up to 3 hours of heating time. The remaining part of the Pb was either lost as metallic Pb in the reactor or remaining as Pb containing compounds in the milky precipitated part of the reaction mixture.

Discussion

The appearance of a milky bottom layer was the first indication of a possible good agreement between our laboratory produced TBL and the experiences of the senior craftsmen. The viscosity of the TBL 4h seems to be a little bit higher and the brownish color a bit stronger than reported, however. These deviations may be due to somewhat larger air exposure caused by an increased surface to volume ratio for the smaller amounts used in our laboratory experiments.

The major changes taking place when linseed oil is heated at high temperatures to body or more specific, to polymerize, has been the subject of many studies up to the 1960-ies. Extensive reviews on the main mechanisms are given in references (5, 9, 10, 11, 12). Generally, we have two dominant reaction types. One is a free radical chain reaction involving oxygen, which in its detail is extremely complex already at ambient temperature (13). Even for a saturated polymer like polyethylene the oxidation reactions necessary to explain the structural changes taking place at elevated temperatures are numerous (14).

For linseed oil the free radical reactions on the one hand bring about the formation of volatile products like water, carbon dioxide and a complicated mixture of organic compounds which opens the way for molecular enlargement by radical recombination or addition to olefinic groups. But more importantly these reactions also lead to the transformation of the isolated olefinic groups initially present to conjugated sequences. At 250° C these conjugated sequences may then undergo Diels Alder -type of addition with another unsaturated fatty acid. The reaction may take place both within and between triglyceride molecules (intra- or inter molecularly) the latter reaction only leads to increase in molecular mass.

Our infrared and UV-visible results, Figures 3 and 4, are in close agreement with the above general scheme. Isolated olefinic groups disappear while the conjugated cis, trans- and trans, trans- conjugated bands increase in the infrared spectra. The formation of even longer sequences is evidenced by the long absorption wavelengths in the UV-visible spectra for the TBL's.

The SEC-analysis shows that substantial molecular enlargement occurs, with there still remaining an appreciable amount of unreacted linseed oil left in the sample even after 4h of heating at 250° C.

The molar masses indicated in Figure 5 were obtained by calibration with linear polystyrene. In our opinion they should be in the same order of magnitude as for the polymerized product. The reason is that the molar mass indicated from the polystyrene calibration is close to 900 g / mole for our triglyceride monomer, while a calculated average molar mass based on our fatty acid distribution indicates a molar mass close to 875 g /mole.
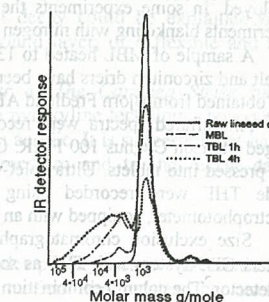

It can be seen that TBL 1h contains molecules with molar mass above 10,000 g/mole corresponding to more than 10 triglyceride units while TBL 4h may contain polymer molecules with more than 40 triglycerides. Such large molecules have not previously been reported in polymerized linseed oil. This is in good agreement with the marked viscosity increase observed, however, as the presence of only minor amounts of material in this molecular mass range will give rise to a substantial viscosity increase.

The MBL shows only a minor amount of enlarged material, the largest molecules corresponding approximately to tetramers and consequently a barely noticeable increase in viscosity.

The description of drying oil films as a log jam in which a relatively small proportion of highly developed polymer holds enmeshed a relatively large proportion of liquid oils in a low state of polymerization (11) fits well with the favorable characteristics of our 15 months old film shown in Figure 2. Neither the gloss nor the resilience demonstrated can be reached with the commercially available products of today. The probable main reason for this is the presence of "primary" or surface-drying catalysts like cobalt influencing the hydroperoxide decomposition. Although such driers catalyze the formation of cross-linked films, they unfortunately also catalyze postdrying embrittlement reactions (5)

Secondary or through driers such as lead present in the TBL's work mainly by other mechanisms, of which the ability to form co-ordination-type complexes with polar groups (10) seems most probable to us.

The excellent aging properties observed in many old paint layers are in accordance with a linseed oil based product cross-linking and cracking very slowly whilst retaining low molecular mass fractions which have a plasticization effect that retain the resilience of the painted layers.

Conclusions

Our traditionally reacted linseed oil shows distinct differences with respect to the products available commercially today. Most prominently they contain a low content of molecular sizes greater than 40 repeating units and an appreciable amount of unreacted linseed oil and secondary driers only. The properties are close to those described by the senior craftsmen interviewed.

Cleaning with solvents may be detrimental to the original paint layers, as there is an obvious risk that low molecular mass components are extracted.

Our next step will be to work in the 100 L scale using a copper metal reactor and evaluate the products both by applying in different fields of conservation and expose the resulting painted films to different methods of accelerated aging. This work will be supported by the Swedish Central Board of National Antiquities.

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THE PHYSICAL PROPERTIES OF PHOTOGRAPHIC FILM POLYMERS SUBJECTED TO COLD STORAGE ENVIRONMENTS

Charles S. Tumosa, Mark McCormick-Goodhart and Marion F. Mecklenburg

Smithsonian Center for Materials Research and Education, MRC 534, Washington DC 20560

Introduction

The long term preservation of photographic materials must of necessity involve the effects of light, relative humidity (RH) and temperature. Storage of film in the dark is almost axiomatic while the setting of RH and temperature for storage has been subject to some discussion. Previous research has described the benefits and trade-offs between RH and temperature (1). From this research it is clear that any long term storage of photographic materials would benefit more from temperature control strategies than by RH control strategies. For the cold temperature strategy for storage to work, the following questions needed to be answered. What is the dimensional change associated with lowering the temperature, what are the stresses developed, do these stresses affect the film and finally, how often can the films be cycled through temperature changes?

Experimental

Photographic film stock was used for the testing the dimensional changes with temperature. The cellulose triacetate was of recent origin while the nitrocellulose was taken from a 50 year old film. The measurements were taken with tensile testers as described previously (2).

Results

The dimensional changes associated with lowering the temperature of nitrocellulose and cellulose triacetate were determined down to -40 C. The total dimensional changes in the film stock at 50% RH from ambient to -40 never reached a value of 0.004 for these polymers which would be significant if the films were completely restrained, i.e. yield would likely occur. Similar curves were developed at other RH. Figure 1 shows the data for these materials and illustrates the close matching of physical properties for these materials.
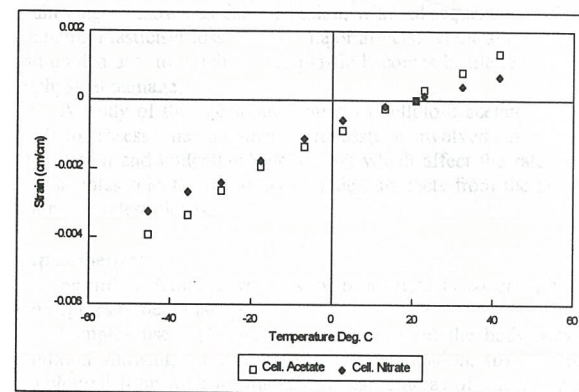

Figure 1. The dimensional changes of cellulose triacetate and nitrocellulose film stock from +40 to -40 C. at 50% RH.

Similar measurements for gelatin have been made and reported elsewhere (1,2) and indicate a yield point of 0.004 or greater.

If the assumption is made that one or more layers in the photographic material are fully restrained, then as the film is cooled, stresses should be developed. Figure 2 shows the development of stress in specimens of cellulose triacetate as the temperature is dropped. Stress development in the restrained films would not exceed 600 PSI which corresponds to a uniaxial strain considerably less than that required to cause plastic deformation in cellulose triacetate (i.e 1600 PSI or a strain >0.004). Nitrocellulose film stock will also develop stresses less than 600 PSI on cooling to -20 C. Its yield point is also >0.004. The film stock would also be able to sustain higher stress levels in a biaxial system.
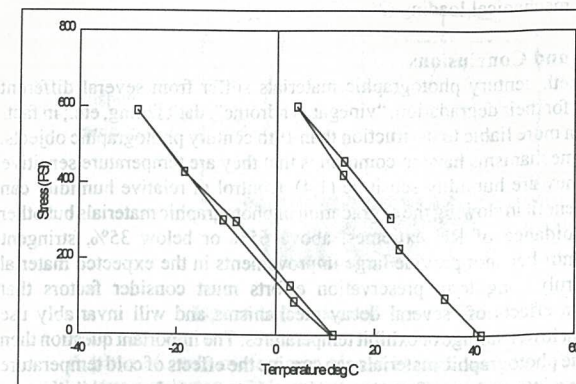

Figure 2. Stress development in cellulose triacetate films as the temperature is decreased.
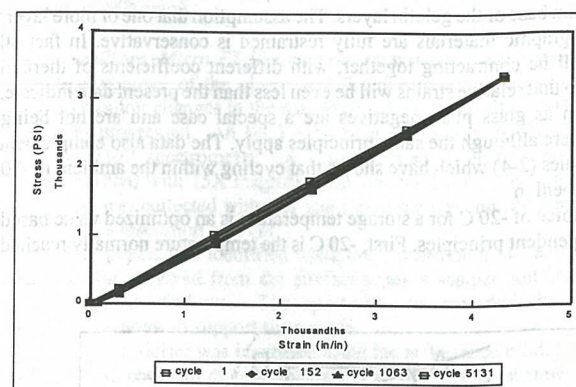

Figure 3. The unload compliance tests for nitrocellulose showing a series of stress-strain curves at various times during 5131 cycles to a strain value of 0.0044.
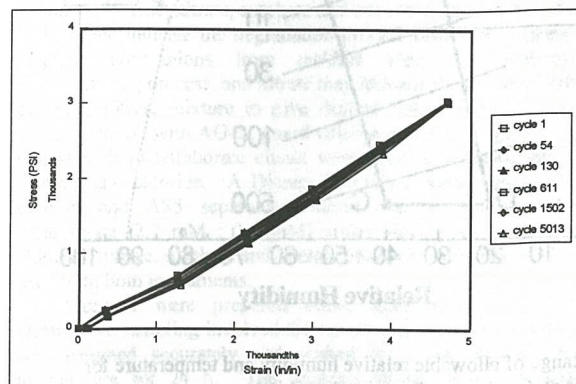

Figure 4. The unload compliance tests for gelatin showing a series of stress-strain curves at various times during 5013 cycles to a strain value of 0.0048.

The number of times that the photographic materials can be cycled from ambient to cold temperatures also needs to be determined for an adequate storage strategy. If the strain values remain below the yield point, it follows that there would be no deformation regardless of the number of times the materials was cycled. Figures 3 and 4 show the mechanical cycling of nitrocellulose film and gelatin for over 5000 cycles. No plastic deformation was observed. It is also interesting to note that the stress-strain curve for gelatin is a non-linear elastic system. Similar studies have also been done on cellulose triacetate. Within these

strain ranges there is no evidence for strain hardening or damage. Mechanical cycling was used because of the demonstrated equivalence of environmental loading and mechanical loading (3).

Discussion and Conclusions

Twentieth century photographic materials suffer from several different mechanisms for their degradation, "vinegar syndrome", dark fading, etc.; in fact, they are often more liable to destruction than 19th century photographic objects. What these mechanisms have in common is that they are temperature sensitive more than they are humidity sensitive (1,4). Control of relative humidity can have some benefit in slowing the degradation of photographic materials but other than the avoidance of RH extremes, above 65% or below 35%, stringent humidity control cannot provide large improvements in the expected material lifetimes. Truly long term preservation efforts must consider factors that minimize the effects of several decay mechanisms and will invariably use strategies that lower storage or exhibit temperatures. The important question then is whether the photographic materials can survive the effects of cold temperature and of cycling into and out of storage environments for study or exhibition.

The data presented here indicate that the dimensional change induced by lowering the temperature to that of a single stage freezer, i.e. -20 C, is considerably less than that which would induce plastic deformation in either the polymeric film base or the gelatin layers. The assumption that one or more layers in the photographic materials are fully restrained is conservative. In fact all materials will be contracting together, with different coefficients of thermal expansion, so that relative strains will be even less than the present data indicate. Objects such as glass plate negatives are a special case and are not being considered here although the same principles apply. The data also complement previous studies (2-4) which have shown that cycling within the ambient to -20 C region is benign.

The choice of -20 C for a storage temperature is an optimized value based on two independent principles. First, -20 C is the temperature normally reached
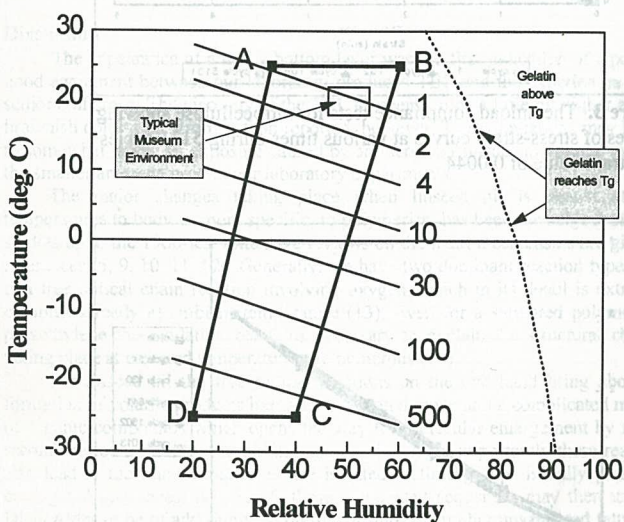

Figure 5. Range of allowable relative humidity and temperature for photographic materials containing a gelatin binder.

in commercial freezers and the lowest temperature that is reached before more expensive two stage compressor systems are needed. Second, if the collection is used to any extent during the year, then the time-out-of-storage becomes important and further improvement in stability brought about by storage temperatures below -20 C becomes limited (1).

The data described above and similar data for other materials allows certain conclusions to be drawn. As a practical matter photographic materials typically contain a gelatin image bearing layer adhered to various substrates (e.g., polyester, triacetate, glass, paper). The chemically and physically safe environment for these common types can be summarized in a simple plot such as figure 5. This figure shows the boundaries of RH and temperature, A, B, C,

and D, which represent the limits of safe storage and exhibition. A is 35% RH, B is 65% RH both at 25 C, while C is 40% RH and D is 20% RH both at -25 C.

The benefits of a preservation strategy which utilizes lowering the RH, i.e. moving horizontally on the graph, has a maximum effect of only increasing the expected life by a factor of 2 to 4. A strategy of lowering the temperature to subzero values, i.e. moving vertically on the chart, has a much more profound impact. The contour lines going through 2, 4, 10, 30, 100 etc. denote the improvement in expected lifetimes compared to a room temperature environment of 21 C/50%RH by allowing progressively lower storage temperatures.

Hazards do exist with any storage or user environment that causes the glass transition temperature of gelatin (as indicated in the graph) to be exceeded. Procedures should be used to ensure that cold stored objects are returned to room temperature in such a way that the microclimate at the surface of the object does not condense water or otherwise exceed the recommended RH limits.

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PROBING THE FACTORS WHICH CONTROL DEGRADATION IN MUSEUM COLLECTIONS OF CELLULOSE ACETATE ARTIFACTS

Jane Ballany[1], David Littlejohn[1], Richard A. Pethrick[1], Anita Quye[2]

[1]Department of Pure and Applied Chemistry, University of Strathclyde 295 Cathedral Street, GLASGOW, G1 1XL, UK.

[2]National Museums of Scotland, Chambers Street EDINBURGH, EH1 1JF, UK.

Introduction

Plastics have had an increasing influence on human activity since the early years of the 20th century and as such are becoming an increasingly important part of museum collections. However, a large number of artefacts in these collections are showing various signs of degradation. The synthetic plastics, including cellulose acetate, from the first half of the century are especially sensitive to these problems and therefore, investigation into the causes of degradation is essential.

Cellulose acetate was first discovered in 1865 by Schutzenberger, when he heated cotton wool and acetic acid to 140 °C in a sealed tube[1]. Manufacturing processes in the 1920's - 1940's were slightly more sophisticated, using lower temperatures and sulphuric acid as a catalyst. Acetic anhydride also replaced acetic acid as the acetylating agent, owing to its better efficiency. Furthermore, the use of pressurised vessels in recent years has reduced the manufacturing time from several days to hours. Although sulphuric acid is a useful catalyst, incomplete washing of the product can result in some of the acid being trapped within the plastic, which may be a source of degradation, as occurs in certain cellulose nitrate artefacts[2].

Conservators have observed that certain cellulose acetate artefacts are showing signs of warping, crazing and shrinkage accompanied by a strong smell of acetic acid and a sticky surface. Discolouration is also a major problem especially with dolls. Previous studies on cellulose acetate films[3,4,5] have shown the degradation processes to involve deacetylation, hydrolysis and plasticiser loss. Deacetylation produces acetic acid vapours which cause further problems, as the trapped acid will catalyse hydrolysis of C-O bonds in the polymer backbone. This hydrolysis causes a reduction in the polymer chain length, known as chain scission, with subsequent reduction in polymer strength. Plasticiser loss has two major affects: a) the surface becomes sticky and unpleasant to touch; b) the plastic becomes brittle and more susceptible to physical damage.

A study of the accelerated aging of cellulose acetate samples has been used to assess the dominant process(es) involved in cellulose acetate degradation and understand the factors which affect the rate of degradation. The samples selected for study included artefacts from the period 1940 - 70 and modern test pieces.

Experimental

Samples. Samples were taken from artefacts covering a range of ages and degrees of degradation.

Samples used: (1) doll from 1940's - (a) the body was in excellent condition showing no visible signs of degradation, (b) the leg was badly discoloured from pink to orange with large areas of crazing and cracks, the surface was also blistering. (2) tortoiseshell effect comb manufactured in 1946, this comb was in good condition with only a few small areas of crazing. (3) tortoiseshell effect comb manufactured in 1967, this comb was in excellent condition showing no visible signs of degradation. (4) tortoiseshell effect hair slide manufactured in 1967, this piece was also in excellent condition. (5) modern cellulose acetate manufactured in 1996, this piece was a transparent test piece from Courtaulds Chemicals and was used as the 'control sample'.

Samples were cut into pieces approximately 4 cm x 5 cm, weighed and suspended from the lid of a small dessicator (volume about 950 mL), using polystyrene strips and small pieces of 'blu-tac'. A saturated solution of a particular salt was placed in the well of the dessicator to control relative humidity (RH). The dessicators were exposed to temperatures of 35 °C, 50 °C and 70 °C in ovens and the relative humidities in the dessicators were controlled at 12% (lithium chloride), 55% (magnesium nitrate) and 75% (sodium chloride).
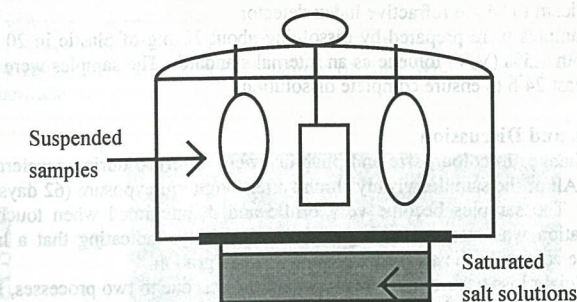

Figure 1. Accelerated aging apparatus

A piece of each artefact was placed in each dessicator resulting in six samples per dessicator. This meant that each artefact was exposed to all temperatures and relative humidities. The experiments at 70 °C were stopped after 62 days exposure, this was due to the extreme degradation of the samples. The experiments at 50 °C and 35 °C are still being conducted (in excess of 150 days).

Analyses. *Micro FT-IR spectroscopy* was used to confirm the identity of the base polymer of the plastic and the plasticiser before testing began and also to monitor changes in the magnitude of the ratio of the O-H to C=O peaks as aging progressed. An MCTA Nicplan microscope was used coupled to a Nicolet 510P spectrometer. A Cassegrainian Reflechromat objective lens (SpectraTech) with 15X magnification was used for collecting spectra. Each spectrum was collected with 128 scans over the wavenumber range 4000 - 600 cm^{-1} with a resolution of 8 cm^{-1}. The spectra was recorded in the transmission mode. About 1 mg of sample was removed from the artefact using a scalpel and crushed between two diamond windows. The spectrum was recorded through only one diamond window to support the sample.

The plastic was identified using the reflectance mode. A cotton wool swab moistened with dichloromethane was wiped several times over a 2 cm^2 area of the artefact surface. The plasticiser was extracted from the swab into 2 mL of dichloromethane, which was then evaporated to a small volume. This was transferred onto a gold mirror and evaporated to dryness and an IR spectrum recorded.

Ion chromatography was used to investigate the presence acetate, formate, chloride, nitrate, sulphate and oxalate in the plastic. Acetate, formate and oxalate indicate the degradation process involved in aging; chloride and sulphate are anions from residual chemicals remaining from the manufacturing process, and nitrate may indicate the use of a cellulose acetate - cellulose nitrate mixture to give desired colour effects. A Dionex 4000I chromatograph with AG4A guard column and AS4A separator column and a 6 mM sodium tetraborate eluant were used to separate and detect acetate, formate and chloride. A Dionex DX-100 chromatograph with AG5 guard column and AS5 separator column and sodium carbonate : sodium bicarbonate (2.2 mM : 2.8 mM) eluant were used to separate and detect chloride, nitrate, sulphate and oxalate. Suppressed conductivity detection was used with both instruments.

Samples were prepared either destructively or non-destructively. Destructive sampling involved the removal of about 50 mg of material, which was weighed accurately and soaked in 5 mL distilled water at room temperature for 24 h. The aqueous extract was then analysed by ion chromatography. Non-destructive sampling involved a cotton wool swab, moistened with distilled water being wiped twenty times over a 2 cm^2 area of the artefact. The cotton wool swab was soaked in 5 mL distilled water for 10 minutes; the extract was then analysed by ion chromatography. In both procedures the levels of anions present were quantified, in concentrations of mg g^{-1} for the destructive method and as mg mL^{-1} for the non-destructive method.

Gel Permeation Chromatography (GPC) was used to monitor changes in the molar mass distribution of the polymer in an artefact during accelerated aging. The apparatus used was a Pye Unicam PU 4003 pump in conjunction with a Pye Unicam PU 4003 controller. A tetrahydrofuran (HPLC grade) (THF) eluant was passed through two GPC columns (type 10^{4}Å and 500Å in