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STRATEGIES FOR THE CONSERVATION OF CELLULOSE ACETATE ARTWORKS – A CASE STUDY OF TWO PLASTIC BOOKS

Keywords: plastic objects, cellulose acetate (CA), poly (methyl methacrylate) PMMA, plasticizer, Lourdes Castro, artist book, flattening

ABSTRACT

Two artist's books made of cellulose acetate by Lourdes Castro were studied in order to more fully characterise the materials of which they are composed, assess their condition and find an appropriate treatment methodology. The books are similar in materials, but different in their condition. One is in a fairly good preservation state, while the other presents severe deformation and shrinkage due to chemical and physical deterioration. Both pieces need urgent treatment and a preventive conservation plan. Samples taken from one of the books and original spare sheets kept by the artist were analysed by Fourier transform infrared (FTIR) spectroscopy and pyrolysis gas chromatography-mass spectrometry (pyGCMS). The results revealed the plastic types and plasticizers used in the formulation. A treatment methodology for flattening the deformed cellulose acetate sheets is being developed.

RÉSUMÉ

Deux livres d'artistes en acétate de cellulose créés par Lourdes Castro ont été étudiés afin de caractériser l'intégralité des matériaux qui le composent, d'évaluer leur condition et de déterminer la méthodologie de traitement appropriée. Similaires du point de vue des matériaux, les livres diffèrent quant à leur état. L'un se trouve dans un état de conservation relativement bon, tandis que l'autre présente de sévères déformations et un rétrécissement dus à une dégradation physique et chimique. Les deux exemplaires ont besoin d'un traitement de restauration urgent et d'un plan de conservation préventive. Des échantillons prélevés sur l'un des livres et sur des feuilles d'origine conservées par l'artiste

INTRODUCTION

Two plastic books made in the 1960s by Lourdes Castro (born 1930) were studied. Castro is a Portuguese artist that frequently uses plastic materials in her pieces. Born on the island of Madeira, she studied painting at the Fine Arts Academy in Lisbon and in 1958 moved to Paris, where she lived for 25 years. The artist currently lives and works in Madeira.

Throughout her life, Lourdes Castro intensively explored the theme of shadows, depicting people, flowers and different objects by their silhouettes and outlines. From 1964 onwards, the artist began to use plastic materials, such as polymethylmethacrylate (PMMA) and cellulose acetate (CA). These materials helped her to achieve the transparency and lack of texture she was looking for, since they are as "immaterial" as the shadows, in the artist's own words (Castro 2010). The different coloring, cutting and superimposition of the plane plastic sheets allowed the artist to achieve several aesthetic effects.

The two artist's books are entitled *Ombres tranparentes* (transparent shadows) and belong to a series of 30 equal pieces made in the artist's studio in Paris, in 1967. Each book measures 30 × 28.5 × 2 cm and contains 25 CA sheets. In an interview with the artist, she recalled using Rhodoïd®, a French trademark of CA, which was sold in Paris in transparent and opaque sheets of different thickness (Castro 2010).

Some of the book's sheets are transparent and others are strongly coloured, having different visual effects due to matt and glossy finishing (Figure 1). The designs were made using a silkscreen technique, while the cuttings were made manually by a pyrographic method. All the sheets and the two covers were assembled with a metal spiral. Book B retained its original and rigid PMMA box, which was made by a manufacturer, in order to get a better finish (Castro 2010). She kept some original CA sheets that remained after completing this book series, which were also analyzed during this research.

Both books are stored at a contemporary art museum in Oporto (Museu de Serralves), but present very different conditions as a result of the type of environment in which they were kept. Book A is in a fairly good state of preservation, although some of the sheets have begun to show mechanical distortion because it has been stored in an open environment. Book B is

ont été analysés par spectroscopie infrarouge à transformée de Fourier et chromatographie en phase gazeuse à pyrolyse couplée à la spectrométrie de masse. Les résultats ont révélé les types de plastiques et les plastifiants utilisés dans la formulation. Une méthodologie de traitement pour aplanir les feuilles d'acétate de cellulose déformées est en cours de développement.

RESUMEN

Se estudiaron dos libros artísticos de acetato de celulosa hechos por Lourdes Castro para caracterizar más a fondo los materiales de los que estaba compuesto, evaluar su estado de conservación y encontrar una metodología de tratamiento adecuada. Los libros se parecen en la composición de los materiales, pero tienen distintos estados de conservación. Uno está bastante bien preservado, mientras que el otro presenta deformaciones severas y se ha encogido debido al deterioro químico y físico. Ambos objetos necesitan tratamiento urgente y un plan de conservación preventiva. Se utilizó espectroscopía infrarroja de transformada de Fourier (IRTF) y cromatografía gaseosa por pirólisis acoplada a espectrometría de masas (pyGCMS) para analizar muestras de uno de los libros y hojas sueltas originales guardadas por el artista. Los resultados revelaron los tipos de plástico y plastificantes utilizados en la formulación. Se está desarrollando una metodología para el tratamiento que permita aplanar las hojas deformadas de acetato de celulosa.

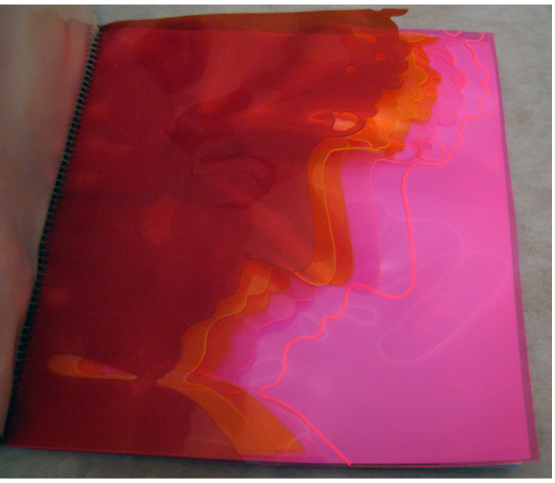


Figure 1
Detail of colored and cut CA sheets in book A

much more degraded and is now considered a total loss by the artist and museum (Figure 2). Its severe deterioration is due to being stored in a closed environment in its original PMMA box (Figure 3). The CA material exuded acidic vapors, which accelerated the degradation.

Book B presents serious physical and chemical damage, such as:

- accentuated distortion and shrinkage of the material caused by the loss of plasticizers (Figure 2)
- the presence of a liquid – probably a mixture of acetic acid and plasticizers or other additives – between the sheets. In some areas, this liquid has a gelatinous consistency
- offset of the ink on the silkscreen impression in some sheets
- corrosion of the metal spiral, caused by the acidity released by the CA (Figure 3)
- brittleness, cracks and losses on the cover of the book and on the Plexiglass/Perspex box.

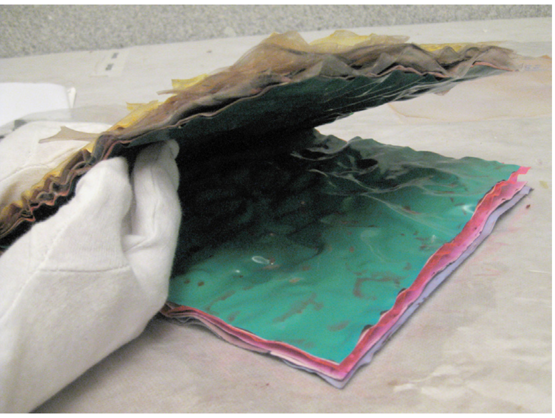
CELLULOSE ACETATE

Production and properties

Cellulose acetate (CA) is an ester of cellulose and is formed by substituting a certain percentage of the hydroxyl groups present in cellulose with acetate groups (Edge et al. 1988). Cellulose sheets and thin film production started in 1937 and continues today. Cellulosic film can be produced either solvent-cast or extruded (Yarsley 1964). Utilizing a specialized casting technology, it can be produced as thin as 14 µm to 500 µm, available as transparent sheets, matt and semi-matt finishes and in colours. Typical properties of cellulose acetate film are: outstanding clarity and gloss in clear film form, with low haze, near-zero birefringence, non-oriented cast film, high water vapour transmission rate, good tensile strength and elongation, with low tear strength, good printability and compatibility with adhesives and good "write-on" characteristics (Yarsley 1964). Specific properties of CA are a slight tendency to cold flow, a high water absorption (1– 2.8% at 24 h immersion, ASTM D256-38) and a Rockwell M hardness of -25 to + 75(ASTM D229-39).

Degradation

The major disadvantage of CA is its dimensional instability due to changes in ambient temperature and humidity. High water absorption leads to dimensional changes which cause warping. The dimensional changes that take place are related to the water absorption and the type and amount of plasticiser used (Delmonte and Asselin 1944). Extensive studies have been performed on the degradation and degradation factors of CA (Edge et al. 1988). Deterioration of cellulose acetate upon ageing has been shown to be a photochemical and chemical (hydrolysis) process, which is catalysed by ultraviolet radiation, light, moisture and the presence of oxygen. Symptoms of degradation include distortion (warping), weeping, shrinkage, odour and blooming. The so called 'vinegar syndrome', in which acetic acid is given off by degradation of CA, is the result of hydrolysis. Hydrolysis causes acetyl groups to be lost from the polymer chains and react with water to form acetic acid (Edge et al. 1988). As CA degrades, it loses plasticizer, which leads to shrinkage and warping of the material.



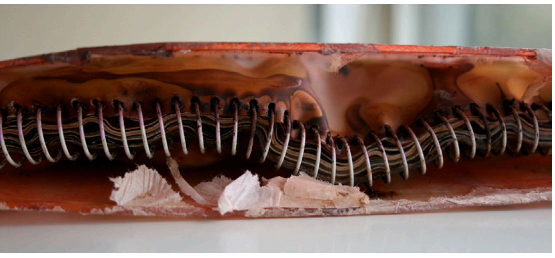


Figure 2
Photograph of book B showing the deformed CA sheets

Figure 3
Detail of book B inside its original PMMA box

Migration of plasticizer

Plasticizer migration is caused by re-arrangement of CA polymer chains on degradation which reduces space for plasticizers. Cellulose acetate often contains up to 40 percent of several plasticizers of which some are used to increase flexibility (such as di-ethylphthalate, di-ethylhexyl phthalate or dibutylphtalate) of the rather rigid cellulose acetate. Others are used both as flame retardants and plasticizers (triphenyl phosphate). Migrating or evaporating of plasticizer produces shrinkage, warping and embrittlement. The rate of loss of plasticizer depends upon the concentration of plasticizer present in the surrounding environment (Mossman 2008). Ageing studies revealed that upon ageing a rapid loss of plasticizer occurred, followed by a more gradual loss, tending towards constant plasticizer content (Yarsley et al. 1964, Pullen et al. 1988, Allen et al. 1992).

A typical formulation for casting cellulose acetate clear sheets (52–54 percent of acetate groups) is cellulose acetate (100 parts by weight), dimethyl phtalate (23 parts by weight), triphenyl phosphate (7 parts by weight), acetone (50 parts by weight), methylated spirits (10 parts by weight) and benzene (10 parts by weight). This formulation dates from the 1960s, when all these solvents were in use, since their use is currently restricted (Yarsley et al. 1964).

EXPERIMENTAL

Samples and techniques

FTIR

The spare sheets from the artist studio, referred to as samples D (Table 1), and the nine samples from book B, referred to as samples A (Table 1 and 2), were analysed by Fourier transform infrared spectroscopy (FTIR). Spectra were recorded from 4000 to 600 cm^{-1}, over 40 scans at a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum 1000 FTIR Reflectance accessory (ATR, Graseby spectrometer combined with a Golden Gate single Reflection Diamond Attenuated Total Specac, sample size 0.6 mm^2).

Pyrolysis GCMS

The pyrolysis unit used was a modified GSG Curie point pyrolyser on a Thermo Quest 8000^{top} Gas Chromatograph – Voyager^{plus} Mass Spectrometer combination. The pyrolysis unit was directly coupled to a SLB5 ms (Supelco) column with a length of 20 meters, an internal diameter of 0.18 mm

Table 1

Spare samples from the artist's studio, condition and composition

Sample	Thickness (µ)	Description	Condition	Identification after FTIR analysis
D,3,4,5,6	255	Transparent sheet	Warped, white bloom	CA + plasticizer
D 3,4,5,6 White bloom		Solid material	Brittle white surface bloom	Plasticizer (triphenyl phosphate
A9 back cover	500	White translucent sheet	Warped	CA + plasticizer
Transparent part	255	Transparent sheet with blue lines	Warped	CA
Blue lines		Transparent sheet with blue lines		Alkyd paint , TiO_2,
D14 glossy side	255	White sheet, not transparent	Warped	CA + plasticizer
D 14 matt side	255	White sheet, not transparent	Warped	CA + plasticizer
D 14 white side	255	White sheet, not transparent	Warped	CA
D 15	255	Green sheet, transparent	Warped	
D 16 glossy side	300	Light green sheet, not transparent	Warped	CA + plasticizer
D 17 white paint	285	White sheet with white paint		$CaCO_3$, $BaSO_4$, white pigment
D 17 yellowed part on white sheet	290	White sheet with white paint		Alkyd paint
D 18	255	Red sheet, transparent	Warped	CA + plasticizer
D 19	255	Yellow sheet, transparent	Warped	CA + plasticizer
D 21 +22 = A6	255	Pink sheet, transparent	Warped, deformed	CA + plasticizer
No label Glossy side	255	White sheet, painted figure	Warped	CA + plasticizer
No label Matt side	255	White sheet, painted figure	Warped	CA + plasticizer
D 24 = A7		Coloured sheet Havana verao 1967, Blue painted part	Warped	CA
D 24 = A7	495	Coloured sheet Havana verao 1967. Transparent part	Warped	CA
D 24 = A7		Coloured sheet Havana verao 1967. White part	Warped	Alkyd paint
D 24-22 matt side	255	White sheet	Warped	Alkyd paint
D 24-22 glossy side	255	White sheet	Warped	CA

Table 2

Samples from book B

Sample number	Description	Identification after FTIR analysis
A1	Cover of the book, transparent plastic, rigid and brittle	CA + plasticizer
A2	Sheet no.1, transparent (more yellow in book A), brittle, yellow leaf design	CA + plasticizer
A3	Sheet no. 2, matt, opaque, whitish/yellowed	CA + plasticizer
A4	Sheet no.5, transparent	CA + plasticizer
A5	Sheet no. 9, grey, matt. The sample was collected from an area with black material detaching. Yellow liquid deposit on the sheet	CA + plasticizer
A6	Sheet no. 22, pink, transparent, glossy	CA + plasticizer
A7	Sheet no. 24, impressed on both sides, whitish, more blue in book A (change of colour)	CA + plasticizer
A8	External box that evolves the piece. Rigid and hard	PMMA
A9	Isolated sheet, similar to the back cover of the book. Matt on one side and glossy on the other side. Blue letters printed	CA

and a film thickness of 0.18 µm. Helium was used as the carrier with a constant flow of 0.8 ml/min. The pyrolysis temperature was 740°C and the temperature of the pyrolysis unit was 290°C. The GC temperature programme was initially 35°C, maintained for 1 min, subsequently heated at a rate of 13°C per minute to 310°C, maintained for 2 minutes. The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 250°C; the temperature of the ion source was 220°C. Mass spectra were recorded from 30 until 600 amu at a speed of 7 scans per second.

RESULTS

FTIR analysis showed that all samples of book B and spare sheets (Tables 1 and 2) provided by the artist (except one) presented absorption bands of cellulose acetate at wavelengths of 3454 cm^{-1} (hydroxyl C-OH stretch), weak absorption at 2940 cm^{-1} (CH_2, CH_3), strong carbonyl absorption at 1732 cm^{-1} (carbonyl C=O), CH_3 deformation at 1367 cm^{-1} and strong absorption at 1215, 1161 and 1030 cm^{-1} (ester C-O-C stretching).

The presence of plasticizer triphenyl phosphate is shown by the presence of absorption bands at 1594, 1491 cm^{-1}, 1260, 1193, 1165 cm^{-1} and 1013, 964 cm^{-1} and 761 and 691 cm^{-1} (Figure 4).

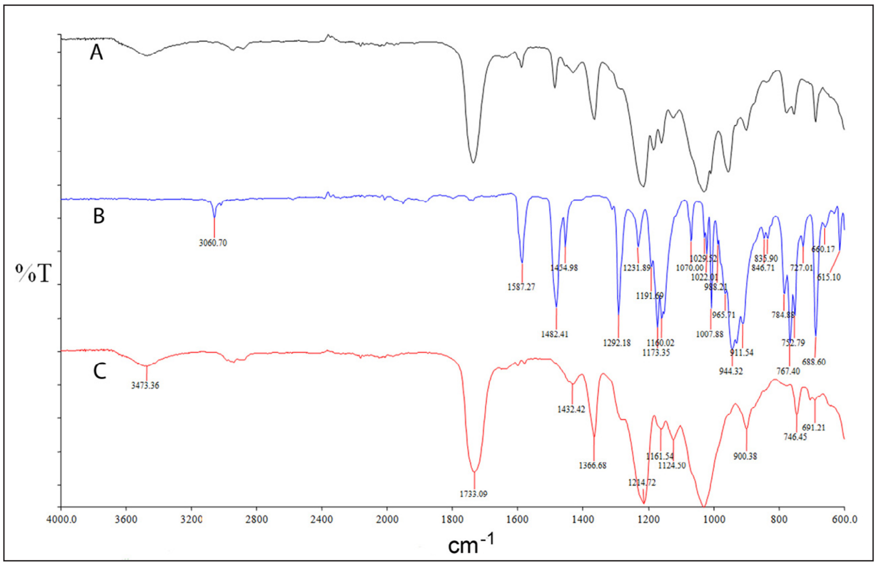


Figure 4

FTIR spectrum of CA and plasticizers. A: sample D 3, 4, 5, 6 of the transparent sheet corresponds to CA and triphenyl phosphate; B: sample D 3, 4, 5, 6 of the solid plasticizer corresponds to triphenyl phosphate; C: CA sheet (not aged)

At ageing, an increasing intensity of hydroxyl absorption at 3332 cm-1 in the infrared spectra of samples was observed, showing that the CA sheets have deacetylated (Figure 6). A decrease in C=O absorption at 1732 cm^{-1} and a shift of the carbonyl band to lower frequency was noticed. Also at ageing, CA is transformed more and more into cellulosic compounds with absorption bands between 1200- 950 cm^{-1}.

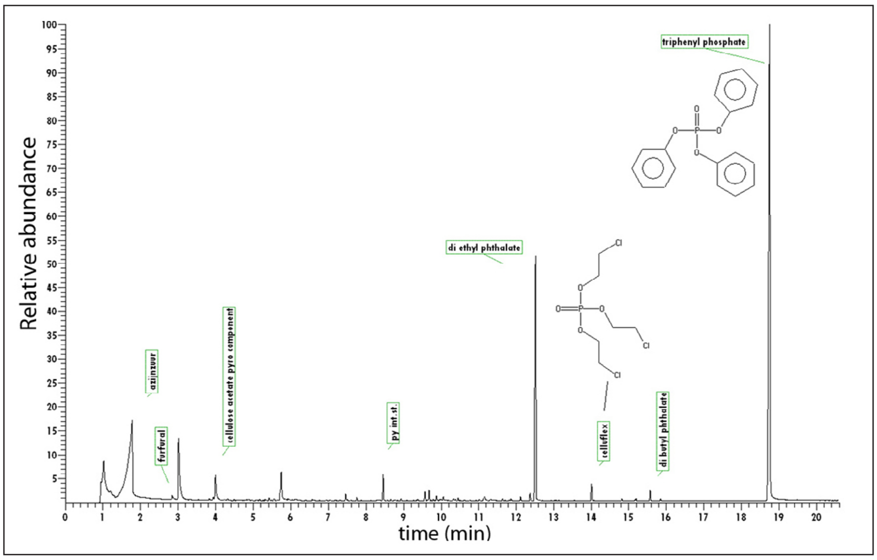


Figure 5
Chromatogram of the PY-GCMS analysis of sample D 3, 4, 5, 6. The white surface bloom on the sheet is triphenyl phosphate and the sheet consists of cellulose acetate. The plasticizers diethyl phthalate and dibutyl phthalate are also present

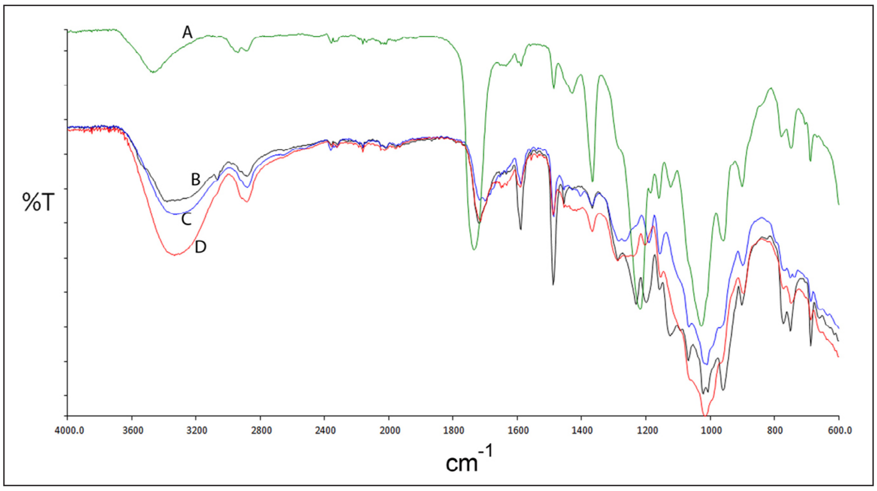


Figure 6
FTIR spectrum of samples A9, A4, A3 and A6 of book B. A: Sample A9; B: Sample A4; C: Sample A3; D: Sample A6

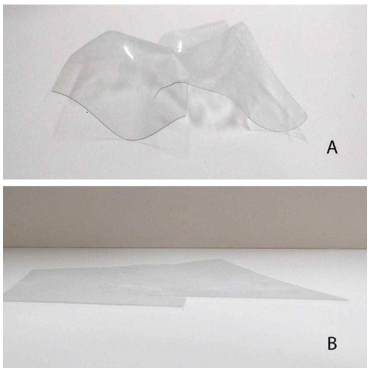


Figure 7
Gilding press (50-250°C), Karl Krause, Leipzig, used to flatten test CA sheets

Figure 8
Flattening test of CA sheets. A: before treatment; B: after treatment

FLATTENING WARPED CA SHEETS

In order to recover the books appearance and flatten the CA sheets, a treatment methodology using temperature and pressure is being developed. Test sheets of 120 microns have been flattened (Figures 7 and 8) using the gilding press at the book conservation studio in the Rijksmuseum. For a 120 micron thick test sheet, a temperature of 70°C for 30 seconds was used and flattening was achieved. Temperature under the press was measured using liquid crystal flexible thermometers from LCR Hallcrest.

Temperature of the gilding press could not be uniformly regulated; therefore, the use of a laminator was also tested at a temperature of 85°C for 10 seconds. A good result with the laminator was acquired because a warped CA was flattened and remained flat. However, when a sheet of heavily warped degraded CA showing solid plasticiser on the surface was flattened, plasticizer was pressed out as a fluid on both surfaces. This plasticizer could be removed using white spirit and a cotton swab. The plasticizer was identified using FTIR and PY-GCMS analyses as triphenylphosphate (TPP). Thiphenylphosphate has a melting point of 48.5°C and a boiling point of 245°C, is insoluble in water and is used as a plasticizer and flame-retardant. A moderate warped CA sheet could be flattened totally. However, after flattening a heavily degraded warped CA sheet, some folding returned. Research into the best temperature and duration of pressure is ongoing on degraded and non-degraded CA test sheets and flattening will be monitored in the long term.

CONCLUSION

Details of composition could be established from the analyses of the spare CA sheets obtained from the artist's studio and the degrading sheets from one of the books, using FTIR and pyrolysis GCMS. Understanding the behaviour and performance of the degraded CA sheets is based on the outcome of research from the past 20 years.

To get insight into the amount of plasticizer content and about the condition of the cellulose acetate sheets of the books of the artist Lourdes Castro, research into the ageing behaviour of cellulose acetate sheets has started. Therefore, reference CA sheets are artificially aged and this research is currently in progress. The condition of the artificially aged sheets will be correlated with the condition of the spare sheets provided by the artist, sheets of book A and book B, in a process of ongoing research.

The flattening of CA is currently ongoing and the promising results so far will be further tested on dummies resembling the sheet of the two books. All aspects of the two books and the spare sheet from the artist's studio and their context will be discussed with the artist and the owner of the books before a decision is made on how to restore them.

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MATERIALS LIST

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