A study of sequins on a Cantonese opera stage curtain

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ABSTRACT Objects associated with Chinese Cantonese opera form one of the major collections of the Hong Kong Heritage Museum. The sequins on one of the Cantonese opera stage curtains are disintegrating seriously; the curtain itself was used as a backdrop during the performance of the opera. In order to understand the possible causes for this degradation and hopefully to devise the proper strategies for remedial treatment and storage, the composition of the sequins was studied using a variety of analytical techniques including Fourier transform infrared spectroscopy (FTIR), x-ray fluorescence (XRF) spectroscopy and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX). The analyses were carried out on broken sequins that had become detached from the curtain. The results indicated that cellulose nitrate, silver and gelatin were present. As there was little information about the fabrication and the past history of the stage curtain, the complete mechanism for its degradation could not be deduced. It is believed, however, that the deterioration of the sequins was due to the presence of unstable cellulose nitrate and had been accelerated by the unfavourable environment in which the curtain had been stored. Preventive measures were adopted to retard the deterioration rate of the sequins while considering other long-term preservation strategies.

Keywords: sequins, Cantonese opera, cellulose nitrate, gelatin, vibrational spectroscopy, energy-dispersive x-ray (EDX) spectroscopy

Introduction

Cantonese opera (also known as Guangdong drama) is one of the major forms of Chinese opera in southern China. The art had become popular by the end of the Ming dynasty (1368–1644) and is well received in the Guangdong and Guangxi provinces as well as in Hong Kong. Cantonese opera is a traditional Chinese art form that involves music, singing, martial arts, acrobatics and acting, to depict the country's history, traditions, culture and philosophies. To promote this art form in Hong Kong, the Hong Kong Heritage Museum has set up a Cantonese Opera Heritage Hall (exhibition gallery) to display objects associated with the opera. The range of artefacts is diverse, including opera costumes, headdresses and accessories, musical instruments, librettos and scripts, wooden trunks for costumes, wooden weapons, etc. Within this collection, a large proportion of the textile artefacts, including costumes and curtains, are sequined. When worn on stage, the sequined costumes were designed to produce a glittering effect under the stage lighting. One sequined Cantonese opera stage curtain was noted to have serious problems with the condition of its sequins when it was recently accepted into the collection. This phenomenon had not been observed on similar textiles decorated with sequins.

The Cantonese opera stage curtain

This particular stage curtain was made in the period 1940 to 1950. It measures 228 cm in height and 174 cm in width. The curtain has a hanging sleeve at the top and is comprised of two layers. The base layer is made of two pieces which can be drawn to either side from the centre. On top of the base curtain, there are two side-flaps with tassels. The curtain was intended to be hung on stage as a backdrop during the performance. It is densely decorated with disc-shaped sequins of 5 mm diameter. The non-iridescent side of each sequin is sewn onto the fabric with the iridescent side facing outwards. The sequins formed a dragon pattern in the middle portion of the curtain. A total of six colours of sequins was observed on the stage curtain, namely, bright pink, purple pink, light pink, gold, purple and black. The purple and black sequins were used on the hanging sleeve and the eye of the dragon pattern respectively, and were found in smaller numbers than the other colours. The base fabric of the curtain itself is made of a rayon/silk blend, lined with rayon at the back while the two side-flaps are made of cotton. As more sequins were used on the two side-flaps, a stronger fabric (cotton) was required for the lining (instead of rayon and silk) to bear this additional weight (Fig. 1).

Condition of the stage curtain

The stage curtain is structurally sound but suffers from loss of sequins in various areas. It is torn around the middle area of pink fabric and slightly split along the edges. The sequins are very brittle and many are lost each time the curtain is handled. The sequins exhibit various degrees of deterioration including surface crazing, blistering, disintegration, shattering and sticking together; some powdery substances

Figure 1 Cantonese opera stage curtain

were observed on their surface. The sequins in the worst condition were found in the following locations:

- The upper part near the name of the performer;
- The two side-flaps especially near the bottom;
- Around the dragon tail and head;
- The circle around the dragon pattern in the middle of the pink fabric;
- The bottom portion of pink fabric.

As can be seen in Figure 1, the pattern of loss of sequins appears to be symmetrical, which suggests that it may have been folded in the past and exposed to unfavourable storage conditions. The curtain also has pink and brown stains in numerous areas, but not limited to those areas sewn with sequins. Stains are also seen on the back of the lining where there are no sequins. Such staining is apparently caused as a result of colour transferring from the sequins when the curtain was folded for storage.

Cellulose nitrate

Cellulose nitrate is formed by the reaction of cellulose ($C_6H_7O_2(OH_3)_x$) and nitric acid (HNO_3) in the presence of sulphuric acid (H_2SO_4) (Reilly 1991). Sulphuric acid is added to control the rate and extent of the reaction. Nitrate groups replace the hydroxyl groups of the cellulose; the extent of nitration affects the physical properties of the resultant cellulose nitrate.(1)

$(C_6H_7O_2\ (OH_3)_x) + 3HONO_2 + H_2SO_4 \rightarrow (C_6H_7O_2\ (ONO_2)_3)_x + 3H_2O + H_2SO_4$ Reaction (1)

Figure 2 Condition of a degraded sequin

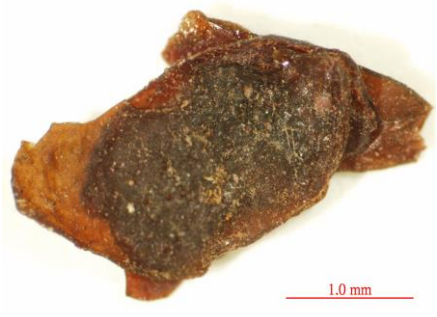

Figure 3 Condition of a degraded sequin(changed to amber in colour)

The greater the nitrogen content, the more unstable the cellulose nitrate (Williams 1994a;

Stewart et al. 1995). Cellulose nitrate deteriorates as a result of thermal, chemical and photochemical reactions. The O-NO bonds cleave and produce the NO_2 radical, followed by chain scission or ring opening when exposed to ultraviolet (uv) radiation (Selwitz 1998). Nitrogen dioxide will be formed as the major degradation product. In the presence of moisture, nitrogen dioxide (NO_2) reacts to form nitrous acid (HNO_2) and nitric acid(HNO_3).

$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$ Reaction (2)

These acids further accelerate the degradation of the material, acting as catalysts for the cleavage of the nitrate group and also attacking the polymer in general by breaking it down into shorter chain fragments (Fig. 4).

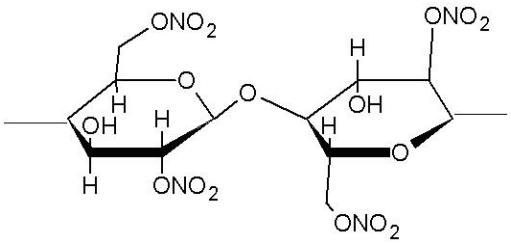

Figure 4 Cellulose nitrate

Analytical techniques

The compositions of the sequins were studied using various analytical techniques and chemical tests in order to identify the possible causes of their degradation.

Fourier transform infrared spectroscopy (FTIR)

FTIR is a tool for identifying the types of chemical bonds in a molecule by producing an infrared (IR) absorption spectrum. When IR radiation interacts with a sample, radiation of the same frequency as that of inter-atomic bond vibrations is absorbed. Every molecule will have its own characteristic IR spectrum, akin to a fingerprint, which corresponds to the specific types of bonds found within it; hence the nature of the molecule can be deduced. Attenuated total reflectance (ATR) is one of the sampling methods available to use with the technique. The sample is placed in contact with a crystal of high refractive index, where total internal reflection will occur along the crystal–sample interface. The IR beam enters the crystal and is internally reflected along the length of sample; it interacts with the surface of the sample through a phenomenon known as the evanescent wave effect, before leaving the crystal and being recorded by a detector.

x-ray fluorescence spectroscopy (XRF)

XRF is a non-destructive analytical technique used to provide information on the elemental composition of materials.
When a sample is irradiated with x-rays, radiation can either be absorbed by the component atoms or scattered through the material. If the energy of an x-ray is sufficient, an electron from the inner shells will be ejected to give rise to an unstable state. An electron from the outer shell will then drop down to fill this vacancy, losing its excess energy as an x-ray of characteristic frequency. Each element has a unique set of energy levels and as a result the energies of x-ray fluorescence are specific to the elemental composition of the material in question.

Scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM–EDX)

SEM–EDX can also give an elemental analysis of the sample. The surface of the sample is scanned using a beam of high energy electrons. The incident electrons will give rise to different types of emitted particles or radiation depending on the type of interaction between the electron beam and the sample. Secondary electrons and backscattered electrons emitted from the sample may be captured to yield high magnification images of the sample surface. Furthermore, the electron beam on the sample will also generate other signals, such as x-rays with characteristic energies, in a similar manner to the XRF technique. With a built-in energy-dispersive x-ray (EDX) spectrometer, the elemental composition of sample can be identified from the x-ray spectrum.

Experimental method and results: analytical techniques

Light microscopy

When the sequins were examined under the stereomicroscope, it was noticed that they were composed of three layers. The top layer was the iridescent surface (with colorant); the middle layer was shiny and appeared to be metallic; the base material was a gelatin-like substance. The iridescent surfaces were readily soluble in acetone, revealing the metallic layer below. The

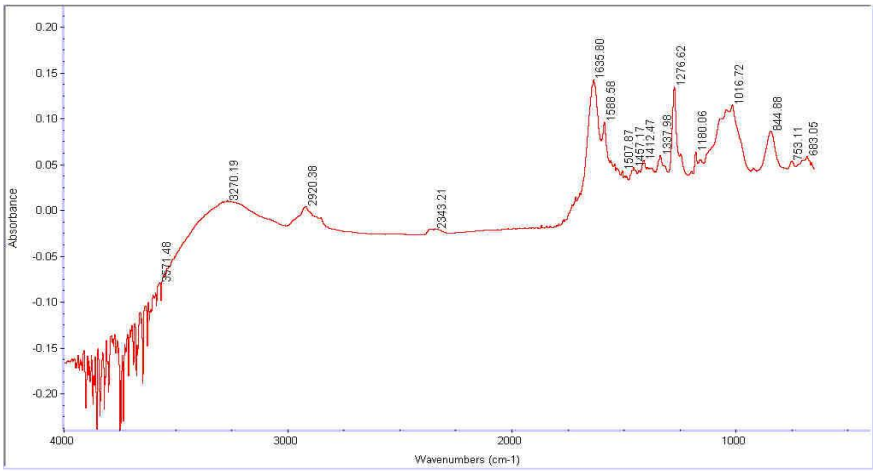

Figure 5 FTIR spectrum of a pink sequin (iridescent side)

colour of the base substrate ranged from pale yellow to light brown and amber. This layer dissolved in water to form a jelly-like substance and was readily soluble in hot water.

Fourier transform infrared spectroscopy (FTIR)

The sequins were analyzed using a Nicolet Nexus 470 FTIR spectrometer and ATR was employed as the sampling technique. The spectra were recorded over the range 4,000–400 cm^{-1}, with a resolution of 0.5 cm^{-1}, averaging the data over 64 scans. Sequins of various colours were analyzed by FTIR and the results summarised in Tables 1 and 2. The spectra indicate that cellulose nitrate is present in the sequins. The peaks at 1,636 and 1,277 cm^{-1} correspond to N-O stretching, 1,017 cm^{-1} is assigned to C-O bending and 845 cm^{-1} to N-O bending. The additional peaks observed from the spectrum at around 3,269, 1,500–1,550 and 1,440–1,460 cm^{-1} suggest the presence of an amide group (Derrick et al. 1999). From spectra of the base material (using a sequin from which the colorant and the metallic layer had been scraped off) it appears that the peak near 1,540 cm^{-1} is due to C-N and N-H vibrations, and C-H bending near 1,450 cm^{-1} which suggests a high possibility that this layer contains gelatin.

As some of the sequins were so highly degraded and discoloured as to appear amber, only the substrate could readily be observed by light microscopy. The FTIR spectrum of the degraded sequins shows the peaks at 1,613, 1,316, 1,015 and 760 cm^{-1}, which are likely to arise from the presence of oxalate. The peak at 1,277 cm^{-1} is absent, which suggests that the N-O bond is not present in the degraded material. (Fig. 5)

Table 1 Principal peaks from FTIR spectrum of the iridescent sides of sequins.

Sequin	Wavenumber (cm^{-1})
Pink	3,270; 2,920; 1,636; 1,589; 1,338; 1,277; 1,016; 845
Light pink	3,246; 2,921; 1,637; 1,277; 1,061; 845
Purple pink	3,253; 2,923; 1,636; 1,541; 1,457; 1,277; 1,016; 845
Yellow	1,639; 1,278; 1,033; 833; 695
Purple	3,269; 1,639; 1,278; 1,017; 846
The surface where the colorant and middle layer were scraped off (base material)	1,628; 1,541; 1,448; 1,332; 1,236; 1,079

Table 2 Principal peaks from FTIR spectrum of the non-iridescent side of sequins.

Sequin	Wavenumber (cm^{-1})
Pink	3,270; 2,920; 1,637; 1,589; 1,412; 1,276; 1,016; 844
Light pink	3,225; 2,921; 1,636; 1,276; 1,016; 842
Purple pink	3,269; 2,923; 1,636; 1,541; 1,457; 1,277; 1,015; 846
Yellow	1,639; 1,278; 1,005; 839
Purple	1,636; 1,276; 1,015; 843
The surface where the exterior layer of the base of sequin was scraped off (base material)	3,291; 1,653; 1,636; 1,559; 1,540; 1,457; 1,279

XRF

The analysis on the sequins was conducted with a SEA 200 XRF spectrometer, using measurement conditions of 50 kv for 600 seconds, with a 5 mm collimator. Using this equipment, which can detect elements from sodium to uranium, silver was detected in the sequins.

SEM-EDX

The sequins were analyzed by SEM-EDX using a Quanta F 200, in order to detect the possible elemental composition of sequins at different stages of deterioration, including those elements of lower atomic number which cannot be detected by XRF. The elemental analysis suggests the presence of carbon, oxygen, nitrogen, silver, sulphur, calcium and chlorine in the sequins. For the badly degraded sequins, however, nitrogen, silver and sulphur are absent (Fig. 6).

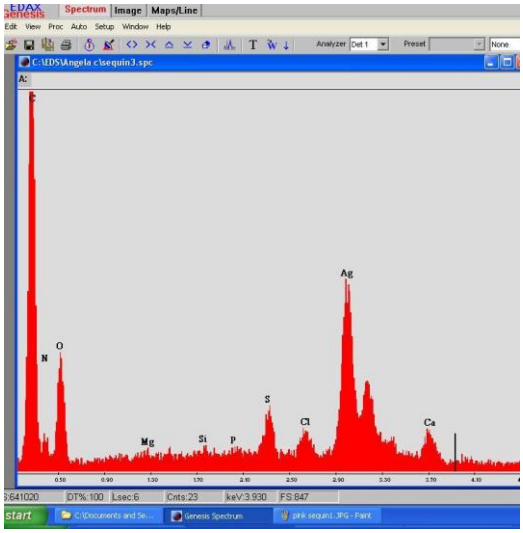

Figure 6 SEM-EDX spectrum of a light pink sequin

Experimental method and results: chemical tests

Diphenylamine spot test

The diphenylamine spot test was used to confirm the presence of cellulose nitrate in the sequins. A solution of 0.5% diphenylamine in 90% sulphuric acid was employed as the reagent; this reagent is highly corrosive. Sulphuric acid reacts with the cellulose nitrate to liberate nitrogen oxide. The diphenylamine is then oxidised by the nitrogen oxide to form a quinoid-type blue dye. As a result, if cellulose nitrate is present, a blue-violet colour will develop (Williams 1994b).

The sequin was placed on a microscopic slide and a drop of reagent was added. A blue colour developed on the sequin within seconds, confirming the presence of cellulose nitrate.

Ehrlich's reagent test

This test is commonly used to identify the gelatin in photographic emulsion, and requires the following solutions:

- 4-dimethylaminobenzaldehyde (5 g) dissolved in 100 cm^3 propan-1-ol
- 0.01 M copper sulphate solution
- (20 vol) hydroxide peroxide solution which must be freshly prepared
- 2M sulphuric acid
- 4 M sodium hydroxide solution

If gelatin is present, a pink coloration will develop. The sequin showed a positive result for this test.

Discussion

The analyses and chemical tests carried out on the sequins indicate that cellulose nitrate, gelatin and silver are present. Trace amounts of elements such as calcium, sulphur and chlorine are also detected. The signs of degradation of the sequins, such as blistering, disintegration, browning, etc, are similar to those recorded in the literature for cellulose nitrate degradation (Blank 1990; Derrick et al. 1993; Matsumura et al. 2002). It is well known that cellulose nitrate is unstable and will degrade over time, therefore the overall deterioration of the sequins may be a direct result of cellulose nitrate deterioration. The rate of degradation of cellulose nitrate-based materials depends on the composition of the material (additives, stabilisers, etc.) as well as its past storage history.

Degradation of sequins

Cellulose nitrate is prone to degrade under unfavourable environmental conditions, such as high temperature, high humidity and exposure to sunlight. Gelatin is also very susceptible to damage in the presence of moisture. As this Cantonese opera stage curtain was used frequently in performances, it is not unreasonable to deduce that it had been stored inappropriately in the past and subjected to unfavourable environments of high and possibly fluctuating humidity, high temperature and poor ventilation, resulting in the rapid deterioration of the sequins. The contaminants introduced during the manufacturing process and the additives used in the fabrication of the cellulose nitrate are also likely to have contributed to this degradation. As noted in the SEM–EDX analysis, calcium, sulphur and chlorine are present. Calcium may have come from the additives or stabilisers of cellulose nitrate, whereas sulphur and chlorine

may be trace elements left after either the fabrication process of the cellulose nitrate or from the colorants.

The FTIR spectra of the badly degraded sequins are different from the less heavily degraded ones. The nitrate bond of the cellulose nitrate breaks down during deterioration and degradation products in the form of oxalate may result. The badly degraded sequins contain no cellulose nitrate at all. The presence of silver (Ag), as detected by both XRF and SEM–EDX, could originate from the reflective surface of the sequins. Nitrogen dioxide, released by the degradation of cellulose nitrate, is known to react with the very fine silver particles, such as those found on the surface of the sequins.

$$2NO_2 + Ag \rightarrow NO + AgNO_3 \qquad \text{Reaction (3)}$$

$$2HNO_3 + 2Ag \rightarrow AgNO_3 + AgNO_2 + H_2O \qquad \text{Reaction (4)}$$

Furthermore, the corrosive acidic gas formed in reaction (2) will attack the fabric itself.

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \qquad \text{Reaction (2)}$$

Evidence of such damage is particularly noticeable in the middle portion of the pink curtain where there is a peach-like pattern. This area is seriously torn and stained brown in colour.

Preservation strategies

The early detection of cellulose nitrate and the adoption of appropriate strategies can help to slow down the overall deterioration of the object and minimise further damage (Sutcliffe and Jenkins 2003). Following the detection of the unstable cellulose nitrate, pH indicator paper such as Cresol red (o-cresolsulphonephthalein) can be employed as a monitoring tool for the emission of the acidic nitrogen dioxide (Fenn 1995). A thorough evaluation of the application method and concentration of pH indicator dyes can be found in the literature (Matsumura et al. 2002).

Further research is required to more fully understand the constituents and compositions of historical sequins, and the preventive approaches required to slow down the extent of their deterioration. In the interim, the stage curtain is currently stored in an acid-free archival box under a controlled and stable museum environment, maintained at 23 ℃ and 60% RH.

Conclusions

The composition of the sequins under investigation is different from those of modern sequins, which are usually made of polyvinyl chloride as a base material. The core substrate of the sequins from the curtain was found to be gelatin with the additional presence of silver and cellulose nitrate. The presence of cellulose nitrate might be the root cause of the severe deterioration of the curtain. As no effective stabilising method is yet available to halt the degradation of cellulose nitrate materials, preventive measures are currently being adopted in order to slow down the overall deterioration of the sequins. A long-term storage and treatment strategy for the stage curtain will be drawn up after further research when, hopefully, the physical and chemical properties of the sequins are better understood.

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