THE DEGRADATION OF POLYESTER POLYURETHANE: PRELIMINARY STUDY OF 1960s FOAM-LAMINATED DRESSES
Doon Lovett and Dinah Eastop

ABSTRACT
Four 1960s dresses that form part of the costume collection at the Museum of London (UK) are made from a laminated fabric, which consists of a layer of foam sandwiched between two knitted fabrics. As the foam deteriorates, it breaks up into small particles that escape through the knitted fabric, as dust. The foam was identified as one of two types of polyurethane (PUR) polyester polyurethane or PUR(ES). The foam dust was found to be acidic and accelerated corrosion tests confirmed volatile organic acids as end-products of PUR(ES) foam breakdown. Accelerated aging tests, performed on samples of new PUR(ES) in a variety of environmental conditions, suggest that hydrolysis rather than oxidation is the dominant mechanism for deterioration and that the rate is slowed at low relative humidity. The authors suggest that objects containing PUR(ES) should be stored at low relative humidity and away from acid-sensitive items, and emphasize the importance of correct identification of this synthetic material in museum collections.

INTRODUCTION
While the active conservation treatment of sculptures made from polyurethane (PUR) has been reported [1, 2], the conservation problems of mass-produced, foam-laminated dresses from the 1960s, once commonplace, are not widely recognized [3]. This paper reports on four such dresses belonging to the costume collection of the Museum of London. The unusual foam interlining was investigated to determine its identity, condition, and factors involved in its deterioration. The information is collated to make recommendations for the care of garments containing polyurethane foam in other collections.

The four dresses (Fig. 1) are made from a laminate consisting of a layer of foam between two knitted fabrics (Plate 42). Following their acquisition in the late 1960s and early 1970s, the dresses were hung in storage until 1977 when, because the foam interlining was deteriorating, they were stored horizontally in boxes. The foam layer continued to deteriorate, breaking up into small particles that escape as dust through the knitted fabric.

PUR has been available commercially as foam since 1957 and foam-backed and foam-laminated fabrics appeared soon after. Their commercial success was due to their ability to give inferior materials, as well as promoting the breakdown process of sensitive items, and emphasizing the importance of correct identification of this synthetic material in museum collections.

The main pathways of degradation for all forms of polyurethane are oxidation and hydrolysis, although opinions differ as to which factor is dominant for polyester and polyester polyurethanes. Wilks [11] states that polyester PUR is more resistant to hydrolysis than polyester PUR, and Keneghan believes that oxidation is the significant pathway for both groups [12]. Williams thinks that PUR(ES) foams are broken down predominantly by hydrolysis while PUR(ET) is more sensitive to oxidation, but that ‘polyol oxidation requires the presence of moisture’. Also, there are a few ether bonds in PUR(ES) that are susceptible to oxidation, but their relative contribution is unclear [13]. Irrespective of the specific pathways, the absorbed energy results in changes in the chemistry and structure of the polymer molecule. These changes explain the physical changes observed in aging plastics: discoloration, brittleness and weakness. The state of the foam in the dresses was recorded using both simple observation and instrumental analysis.

Determining the physical state of the foam
To document the small amount of residual foam and lamination within the dresses, the transparency or opacity of the fabrics was assessed by placing the fabric on a light-box [14]. It was possible to detect areas of residual foam, some of which was loose and still trapped within the two knitted fabrics. In some areas, there was evidence of foam still attached to the outer layer. These areas were not as dense as the areas of loose foam, which tended to drift as the dress was moved. The remaining lamination could be detected by feeling the slight increase in thickness of the fabric, which was also slightly spongy.

An approximate percentage of residual foam was ascribed to each dress: yellow <5%, cream 10-20%, brown 5-10% and blue 40%. The colour of the foam from the four dresses varied from orange to black but it was not possible to determine whether this was the original colour or a result of degradation.

Determining the chemical state of the foam
Hydrolytic breakdown of PUR(ES) produces small volatile acidic molecules that encourage further breakdown of the parent polymer. Experimental work confirmed that the foam dust is acidic, and the results of a modified Oddy test [15] indicated that volatile organic acids were being released [3]. Although these compounds have not been identified, it is known that they will initiate or accelerate the rate of degradation in neighbouring sensitive materials, as well as promoting the breakdown process in the foam itself. This has implications for the protective conservation of objects that are stored near foam-containing items.

THE RELATIVE IMPORTANCE OF TWO AGENTS OF DETERIORATION
An experiment was devised to determine the significance of the two deterioration pathways of PUR(ES). Accelerated aging was

![Fig. 2 Foam structure. (a) The gas structural element (GSE): a dodecahedron that forms the repeating unit in any foam network, whether it is a plastic foam, bubble bath, or flexible foam sheeting. (b) Photomicrograph of a piece of new polyester polyurethane flexible foam: the pentagonal faces of the dodecahedron can be seen. (c) Magnified image of the foam dust that has been lost from the cream dress: the fragments of the struts, or ribs, of the polymer network can be identified. © Lovett, 2003](image1)

![Fig. 3 FTIR analysis of the foam from the yellow dress (performed by Dr Brenda Keneghan, V&A Museum, London). The lower trace is the spectrum for a reference sample of PUR(ES). There are characteristic absorption bands at 1740-1680 cm⁻¹ (carbon C=O) and at 1187, 1128 and 1064 cm⁻¹ (ester C–O–C), which indicates that this particular foam is a polyurethane derived from a polyester, PUR(ES). Although, macroscopically, the samples of foam from the four dresses were different in colour and texture, they were all identified by FTIR spectroscopy as PUR(ES).](image2)

Physical characteristics
Foam, whether it is in a bubble bath, a rigid insulating material or a thin flexible sheet within a laminate, is a three-dimensional network that has two components: the polymer that forms the ribs or struts of the network and the gas that fills the voids. The discrete repeating unit of foam resembles an old-fashioned football: a pentagonal-faced dodecahedron called the gas structural element (GSE) (Fig. 2a) [7].

With age, the three-dimensional network fails and the solid component breaks up. Figure 2c shows foam dust that has been lost from one of the dresses; fragments of the ribs or struts of the GSE are evident. As the polymer has aged, it has become brittle and discoloured. Initially, additional physical forces are needed to cause fracture of the structure, but a point is reached when this happens spontaneously (Plate 43).

Chemical characteristics
Any synthetic polymer can be made into a foam. They will all exhibit the typical pattern seen in Figure 2a, so it is not possible to identify the specific polymer by its morphology [8]. Simple tests may help in the identification of synthetic polymers, but they usually involve destructive sampling and may not give a definitive answer [9]. One certain means of identifying a plastic polymer is Fourier-transform infrared (FTIR) spectroscopy,
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The four dresses (Fig. 1) are made from a laminate consisting of a layer of foam between two knitted fabrics (Plate 42). Following their acquisition in the late 1960s and early 1970s, the dresses were hung in storage until 1977 when, because the foam interlinings were deteriorating, they were stored horizontally. The foam layer continued to deteriorate, breaking up into small particles that escape as dust through the knitted fabric. PUR has been available commercially as foam since 1957 and foam-backed and foam-laminated fabrics appeared soon after. Their commercial success was due to their ability to give inferior fabrics the characteristics of more expensive and more costly textiles [4]. While the upper end of the market achieved the fashionable 1960s silhouette by using high-quality thick fabrics, designs were ‘widely plagiarised, often in crude copies, machine-made in cheap, foam-backed fabrics’ [5]. In design terms, the dresses are typical of the era with a characteristic stiff, flared silhouette and topstitching. They are important examples of an innovative material and a fabrication technique that were brought together for the mass-production of relatively cheap garments. PUR foam revolutionized the upholstery industry and the motor trade, as well as being widely used in automotive and interlining. In these forms it is present in museum collections in clothing, footwear, accessories and seating, as well as in works of art.

FOAM CHARACTERIZATION

In each dress, the thicker outer knit, made from acrylic or acrylic/wool blends, is uppermost and the finer lining knit forms the bottom layer of the ‘sandwich’. Between these two knitted fabrics lie the remains of the foam layer. Foam particles can be seen caught in the fabric, as they break up into dust. This layer now measures 0.25-0.5 mm but may originally have been thicker, since foam sheets were commonly produced in thicknesses between 1.5 and 4 mm [6].

Fig. 1 One of the four foam-laminated dresses that formed the starting point of this research © Lovett, 2003

Physical characteristics

Foam, whether it is in a bubble bath, a rigid insulating material or a thin flexible sheet within a laminate, is a three-dimensional network that has two components: the polymer that forms the ribs or struts of the network and the gas that fills the voids. The discrete repeating unit of foam resembles an old-fashioned football: a pentagonal-faced dodecahedron called the gas structural element (GSE) (Fig. 2a) [7].

With age, the three-dimensional network fails and the solid component breaks up. Figure 2c shows foam dust that has been lost from one of the dresses; fragments of the ribs or struts of the GSE are evident. As the polymer has aged, it has become brittle and discolored. Initially, additional physical forces are needed to cause fracture of the structure, but a point is reached when this happens spontaneously (Plate 43).

Chemical characteristics

Any synthetic polymer can be made into a foam. They will all exhibit the typical pattern seen in Figure 2a, so it is not possible to identify the specific polymer by its morphology [8]. Simple tests may help in the identification of synthetic polymers, but they usually involve destructive sampling and may not give a definitive answer [9]. One certain means of identifying a plastic polymer is Fourier-transform infrared (FTIR) spectroscopy, although this is a destructive sampling technique, the sample size is very small [10]. The foam layer in the dresses sheds dust, making sampling easy.

Fig. 2 Foam structure. (a) The gas structural element (GSE): a dodecahedron that forms the repeating unit in any foam network, whether it is a plastic polymer, bubble bath, or flexible foam sheeting. (b) Photomicrograph of a piece of new polyester polyurethane flexible foam: the pentagonal faces of the dodecahedrons can be seen. © Lovett, 2003

Researching the history of textile laminates suggested that the foam in the dresses was made from polyurethane. This is a heterogeneous class of polymers, commercially available since the early 1950s, characterized by a area linkage that is formed by the addition polymerization of a polycyanurate and a polyol. There are two main subdivisions that are based on whether a polyol, PUR(ET), or an ester polyol, PUR(ES). These two subsets have different properties and, importantly for their preservation, degrade differently.

Samples were taken from each of the dresses and analysed using FTIR spectroscopy. The spectrum for the yellow dress is shown in Figure 3. It shows absorption bands at wavelengths 1740-1680 cm⁻¹ (carbonyl C=O) and 1187, 1128 and 1064 cm⁻¹ (C–O–C), which indicates that this particular foam is a polyurethane derived from a polyester, PUR(ES). Although, macroscopically, the samples of foam from the four dresses were different in colour and texture, they were all identified by FTIR spectroscopy as PUR(ES).

THE PROCESS OF DETERIORATION

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THE RELATIVE IMPORTANCE OF TWO AGENTS OF DETERIORATION

An experiment was devised to determine the significance of the two deterioration pathways of PUR(ES). Accelerated aging was
Samples were placed in plastic bags, impermeable to oxygen, at variable oxygen levels of relative humidity and oxygen concentration, and carried out on samples of new PUR(ES) foam under varying conditions. The reliability of tensile strength testing at the end of the experiment [16]. The experiment was conducted in a laboratory dried out at 70°C.

Volatile oxygen
Samples were placed in plastic bags, impermeable to oxygen, at three different oxygen concentrations:

<table>
<thead>
<tr>
<th>Type</th>
<th>Oxygen Concentration (%)</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Unaged</td>
<td>&gt;0.01</td>
<td>Control sample</td>
</tr>
<tr>
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<td>Sample in bag with one sachet of Agentless ZPS (200 ml) and one Ageless Eye #4 indicator tablet. The sample was double-bagged, that is, the bag was placed within another, also containing a sachet and indicator tablet [17].</td>
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Table 1 Results of tensile strength measurements on samples of PUR(ES) foam after aging in a variety of humidity and oxygen concentrations

<table>
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<tr>
<th>Condition</th>
<th>Break Load (N)</th>
<th>Maximum Extension (%)</th>
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<tbody>
<tr>
<td>Unaged</td>
<td>3.79 ± 0.15</td>
<td>154 ± 8</td>
</tr>
<tr>
<td>Anoxic</td>
<td>0.00 ± 0.00</td>
<td>367 ± 10</td>
</tr>
<tr>
<td>Sealed</td>
<td>4.45 ± 0.30</td>
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Note: The average of each group of three samples is given, along with the standard deviation. The breaking load measured in Newtons and the maximum extension as a percentage of the starting length. The samples at 100% humidity have been ascribed values of zero because they all ruptured spontaneously.

The tensile strength of the PUR(ES) samples, apart from the unaged samples, that is, an equivalent of 20 years aging has not altered their strength or elasticity. Although there has been no impairment of the mechanical properties of these samples, they are acidic and have started to discolor.

RECOMMENDATIONS

Using the information collated from a variety of sources, including the experimental work described above, it is possible to make a number of general recommendations for the care of PUR-containing artifacts, as well as specific recommendations for the foams.

- The most important factor for the preservation of modern objects is to establish the identity of their component materials on acquisition. For items containing foam, the polymer must be identified; if it is PUR, it is important to determine whether it is based on an ether or ester polyol. For PUR to be reliably identifiable, an instrumental analytical method is recommended. A sample the size of a pinhead is sufficient, and analysis costs very little. The results will help the institution in an accessible and searchable format.

- Documentation should also include archival-standard images, as deterioration of the PUR foam is inevitable, even if a protective coating is used. Once the foam has been lost from the dresses, all that will survive is the documented image and, for a while, some foam that is lost in a test-tube. It is recommended that these dresses should be recorded by a professional photographer.

- If the item is a work of art or has been made by a specific designer, a recent working party has recommended that the artist’s conceptual and future intent for the piece be recorded. These views can be incorporated into the decision-making model devised to assist professionals dealing with the restoration and conservation of modern art. In the case of these dresses, the designer could not be identified.

- The other items identified are in a similar condition, with brittle and weak foam that is being lost as dust. When modern and popular has become historic and rare, as well as a challenge for the care and management of museum collections.

ACKNOWLEDGEMENTS

The author is indebted to: Dr Brenda Keney, Dr Paul Gasiule, Dr David King, Dr Scott Williams, and colleagues at the Museum of London, the Department of Engineering, University of Southampton and the Textile Conservation Centre.

MATERIALS


Ageless Oxgen Absorbers: Mitsubishi Gas Chemical Co. Inc., www.mgc.co.jp

Novasina (Division of Axat AG): www.novasina.ch

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The tensile strength of the PUR(ES) samples, apart from the unaged samples, that is, an equivalent of 20 years aging has not altered their strength or elasticity. Although there has been no impairment of the mechanical properties of these samples, they are acidic and have started to discolor.

RECOMMENDATIONS

Using the information collated from a variety of sources, including the experimental work described above, it is possible to make a number of general recommendations for the care of PUR-containing artifacts, as well as specific recommendations for the foams.

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carried out on samples of new PUR(ES) foam under varying levels of relative humidity and oxygen concentration, and degradation was measured quantitatively by tensile strength readings. Samples were cut from a sheet of new white PUR(ES) foam, 7 mm thick (supplied by Dr David King). Three ‘doughnut’ shaped pieces of foam were used for each variable, to improve the reliability of tensile strength testing at the end of the experiment [16]. The experiment was conducted in a laboratory drying oven at 70°C.

### Variable oxygen

Samples were placed in plastic bags, impermeable to oxygen, at three different oxygen concentrations:

1. Atmospheric (O₂ content 20%): sample in bag, unsealed
2. Sealed (O₂ content 20% and decreasing): sample in bag, sealed
3. Anoxic (O₂ <0.01%): sample in bag with one sachet of Ageless ZPU (200 ml) and one Ageless Eye indicator tablet. The sample was double-bagged, that is, the bag was placed within another, also containing a sachet and indicator tablet [17].

### Variable humidity

Samples were placed in glass hybridization beakers. The relative humidity (RH) was measured with a cobalt chloride humidity indicator tablet [17]. The sample was double-bagged, that is, the bag was placed within another, also containing a sachet and indicator tablet.

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<th>Breaking load (average in Newtons)</th>
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</tr>
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<tbody>
<tr>
<td></td>
<td>Result</td>
<td>Std dev</td>
</tr>
<tr>
<td>Unaged</td>
<td>3.79</td>
<td>0.24</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>3.06</td>
<td>0.12</td>
</tr>
<tr>
<td>Sealed</td>
<td>4.5</td>
<td>0.03</td>
</tr>
<tr>
<td>Anoxic</td>
<td>4.2</td>
<td>0.14</td>
</tr>
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**Note:** The average of each group of three samples is given, along with the standard deviation, for the breaking load measured in Newtons and the maximum extension in percent of the starting length. The samples at 100% humidity have been ascribed values of zero because they all dropped spontaneously.

The tensile strength of the PUR(ES) samples, apart from the three high-humidity samples that had ruptured spontaneously, was tested using an Instron Universal Testing System IX. The results are summarised in Table 1. The unaged foam samples broke under an average load of 3.79 N, their length having extended by 34.7% at maximum strain. Observations were made on the samples aged at low and medium RH. Comparable values were recorded for the sealed and atmospheric samples. The samples that were aged in an anoxic environment broke under a much smaller load, 0.38 N, and extended by only 77% before rupture. The samples that were aged in 100% humidity were ascribed values of zero.

### Discussion

PUR(ES) aged at 100% RH was the most deteriorated sample, as shown by the spontaneous rupture of the fabric in the foam samples. This agrees with Williams [18] who said that hydrolysis is the predominant pathway by which PUR(ES) deteriorates. The samples aged in atmospheric RH were more discoloured than the samples kept at low RH, and more so than those at any oxygen concentration. Hydrolytic breakdown in the PUR(ES) foam, initiated by high humidity, must be much more significant at low humidities and more significant than oxidative breakdown, producing more chromophores and explaining the colour change visible in the samples.

The samples of foam aged in the anoxic environment were found to be unexpectedly weak when tested for tensile strength. If oxidative breakdown is the only mechanism for PUR(ES), it might be expected that the samples aged in anoxic environment would be less deteriorated (that is, have higher tensile strength) than those aged under atmospheric oxygen. However, if the oxidative mechanism is not significant, then all three sets of samples would be expected to be equally degraded, which is not the case. This result may be attributable to Ageless ZPU, which was used in the experiment. The supplier’s catalogue recommends that if ‘high humidity adversely affects the artefacts’, Ageless RP-K should be used, but the project budget did not allow the purchase of the expensive product to prevent the accumulation of acidic breakdown products [20].

### CONCLUSION

Although these dresses can no longer be displayed as examples of 1960s fashion, it could be argued that they have no further museum use, it is strongly recommended that they should remain as part of the Museum of London’s collection for study, as they appear to be four of only six dresses of this once popular type identified in UK collections.

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### MATERIALS

Agelox Oxygen Absorbers: Mitsubishi Gas Chemical Co. Inc., www.mgc.co.jp
Novasina (Division of Axair AG): www.novasina.ch
Inston Corporation: www.inston.com

### REFERENCES

LIVING ARTIST, LIVING ARTWORK? THE PROBLEM OF FADED COLOUR PHOTOGRAPHS IN THE WORK OF GER VAN ELK

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ABSTRACT

Current conservation ethics, based on the preservation of authentic material, are of little importance to an artist like Ger van Elk, to whom the conceptual message is more important than its material realization. This is illustrated by a recent conservation project in which the artist was involved and was not consulted. The background of an art-historical survey of the meaning of the artist’s work in relation to the materials and techniques used. When preventive conservation fails and the museum seeks a solution in cooperation with the artist, the end result might be an authorized copy but what is left of the artistic value? Since photographic materials have their own characteristics, and often show the effects of time, an alternative form of conservation treatment is proposed with respect to the original material. Coloured light is used as a ‘rotocycling medium’ to enhance a severely discoloured photograph which forms part of Rosequartz, a sculpture by Ger Van Elk from 1979.

INTRODUCTION

Brightly lit exhibition spaces and unsuitable storage facilities alter most artworks in which colour photographs are incorporated, as in the paintings and sculptural installations ofGer van Elk (b. Amsterdam, 1941). The artist’s own solution, as carried out recently to reproduce photographs which are nearly 30 years old and often painted or hand-manipulated, using the latest digital imaging techniques – raises questions about authenticity, patina, the meaning of materials and the artist’s intention, then and now. The conservator of modern art thus not only faces the challenge of solving problems relating to possible discrepancies between the meaning of the artwork, its original appearance and its current condition, but also has to act as a mediator between the artist and art history.

PHOTOGRAPHIC MATERIAL MATTERS

Photography is often considered an immaterial, impersonal and therefore an ‘objective’ medium. This suited conceptual artists, in particular, since they wanted to suppress all personal touches in their work. Although Ger van Elk cannot be considered a true conceptual artist, his work may be looked at against this background. He considers photography mainly as a practical means of realizing his ideas. He has stated that the photograph in itself has no artistic value; it is the image that counts. This is why replacement of discoloured photographs in his work seems justified, and is generally assumed to be the solution to this problem.

Patina

This practice must be looked at critically, however, even when it is the artist himself who proposes reprinting the photographs. The photographic material in which the image exists, and in which the artistic idea is originally visualized, carries specific qualities that are characteristic of a certain era. Size, format, the type of surface and the colour range are all properties that vary over the years. The way photographs alter can also be related to a printing process or a certain manufacturer. These characteristics generate a secondary meaning in a photograph, apart from the image: one that is embedded in time and thus in art history. So even discoloured photographs should be regarded as ‘patina’.

Choice of materials

Furthermore, the look of a photograph is related to the artist, who chooses the brand, the surface quality, the paper, and the photographic process available at the time. Ger van Elk chose his materials carefully. In the 1970s he preferred Kodak’s chromogenic prints to Cibachrome’s silver dye-bleach prints, which are based on a totally different printing process. He disliked the harsh colours, the unnatural, vivid red and the slick and smooth surface that characterized Cibachrome at that time. The chromogenic prints that Van Elk chose often had a silkscreened surface, typical of many photographs in the early 1970s. Photographs with this finish were less vulnerable to scratches than glossy paper and this suited his unconventional use of photographs in sculpture and installation. This kind of surface also formed a good base to paint on.

Artistic freedom

The various optical characteristics can prove the authenticity of a ‘vintage print’ — a print contemporaneous with the negative, processed either by the artist, an assistant or the photographic laboratory, but at least with the artist’s final approval. Ger Van Elk recently printed some of his negatives from more than 30 years ago. He explained that he never got round to printing them at the time they were made, due to lack of money. The new prints do not have any of the characteristics of the early 1970s, nor will they show any discoloration. This challenges our notion of authenticity. A 30-year-old Ger Van Elk with whiskers and wearing ‘bell-bottom’ trousers is shown in a large, colourful Cibachrome print which has the characteristics of the beginning of the twenty-first century. The artist does not mind the discrepancy between the image and the material used. He simply signed the work with two dates: one for the concept and one for the print. This illustrates the freedom of the artist. But when the artist wants to reprint or reproduce discoloured photographs in a work which is in a museum collection, must the conservator of modern art go along with him?

CHANGED ARTWORKS: RECENT CONSERVATION HISTORY

In two works by Ger van Elk from the early 1970s, the painted colour photographs had discoloured so badly that the artist suggested that the museum should reproduce them.

From the 1970s to the 1990s

C’est mon qui fait la musique (1973, 60 x 120 cm, Stedelijk Museum, Amsterdam, A25269) is an airbrushed photo-collage which shows the artist playing the piano, while his tailcoat straightens and the grand piano bends backwards, perfectly following the profile of the triangular wooden frame. The colour in the photographs of this popular artwork has shifted so badly that the airbrushed parts now stand out, which destroys the magical appearance of the manipulated image (Fig. 1). The discolouration reveals the techniques used, whereas the strength of the artwork should derive from the supposed realism of the image. This work had lost its meaning and so a solution needed to be found. Reproduction was considered the best way to solve the problem. Because the original negatives were missing, the artwork was scanned as a whole. The discoloured areas of the photographs were manipulated using digital imaging techniques, as a result of which the airbrushed areas ‘disappeared’. When the image had been digitized, the artist decided to erase the seams in