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## Glossy surfaces – Abstract year 1

#### Introduction

The Glossy Surfaces project, composed by an international consortium of museums – Museu do Design e da Moda (MUDE, Portugal), Mode Museum (MoMu, Belgium) and The Metropolitan Museum of Art (MET, USA) – as well as scientific partners – Department of Conservation and Restoration from NOVA School of Science and Technology (Portugal) and Centexbel (Belgium)-seeks conservation solutions for thermoplastic polyurethane (TPU) coatings in fashion collections. As important research has already been conducted on PUR foams, our focus will only be on TPU coatings (often found in 20th and 21st century imitation leathers and coated fabrics). This material appears in most contemporary fashion and design collections, but is often not recognized or is mistaken for plasticised polyvinyl chloride (PVC-P). Prone to inherent vice, there are currently no accepted treatments for this material beyond preventive conservation measures, and identifying the material takes sophisticated technology, like Fourier transform infrared (FTIR) spectroscopy techniques and often sampling..

This multi-year project will progress in stages. The first year's focus is on analysis of objects held in important fashion collections and creating a benchmark.

The use of plastics has evolved during the last century and the presence of synthetic polymers is unmistakably present in fashion collections and museums. By the 1960s, synthetic materials like imitation leathers and impermeable fabrics became popular, and shiny coated surfaces have grown in popularity ever since because of the enormous aesthetic and functional possibilities of the material. Despite the fact that these materials are so commonly used by designers, from a conservation point of view, the short lifespan and the broad range of aging characteristics of synthetic polymers are challenging for the preservation of this material. Conserving plastics poses demanding challenges, since thousands of different polymers can be used for the production of plastics, complicated by the presence of plasticisers, stabilisers, colorants, fillers, coatings, and different kinds of production. The lifespan of plastics is short and it is the task of conservators now to extend it. Plastics are significant cultural artifacts present in many museum collections, so their conservation cannot be ignored. This project thus investigates new ways to prolong the lifespan of the plastics cultural heritage. While there are many plastics that present problems in museum collections, this consortium has chosen to give its full attention to TPU-ester coated fashion objects, which are significantly present in modern and contemporary fashion collections.

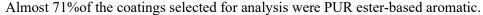
Starting from the second half of the  $20^{th}$  century, many polyurethane coated garments and accessories show signs of degradation such as peeling, blooming, stickiness, and powdering. Sometimes these degradation signs are showing very soon after the production of the material. The lifespan of a newly produced TPU coating varies from 1 to 5 years .

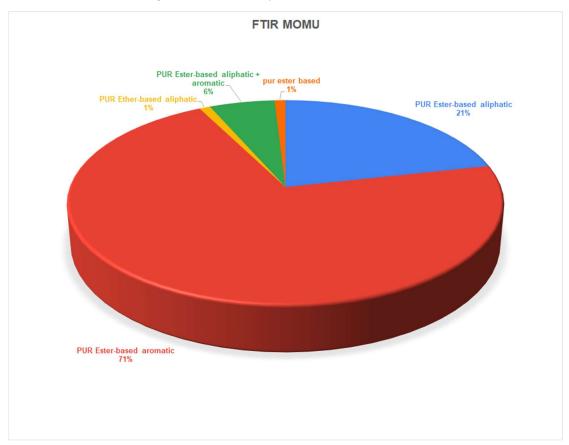


## **Status Questions & Analysis**

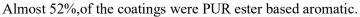
In the first year of this project, the three partners did preliminary analysis of the coated objects from their collections. This gave more insights into how many coated objects in the collections are TPU. MoMu analysed 202 coated objects from its collection using micro ATR FTIR. The Met analysed 90 objects mostly using portable External Reflectance- FTIR (ER-FTIR) and MUDE analysed 21 objects using micro ATR FTIR. We were expecting most of them to be either PVC-P or TPU ester coatings. It was surprising to see that other materials were also discovered at MET and MoMu, for example cellulose nitrate, polyacrylate, polyester, silicone, and polycarbonate. Although these different materials were identified, the entire focus of this project is the TPU ester based coating as mentioned before since this material represents the largest portion of TPU coatings analysed.

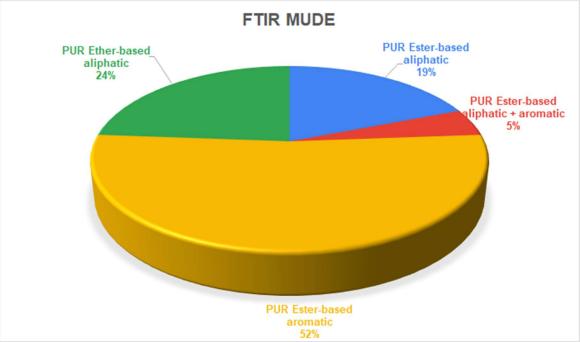
#### <u>MoMu</u>





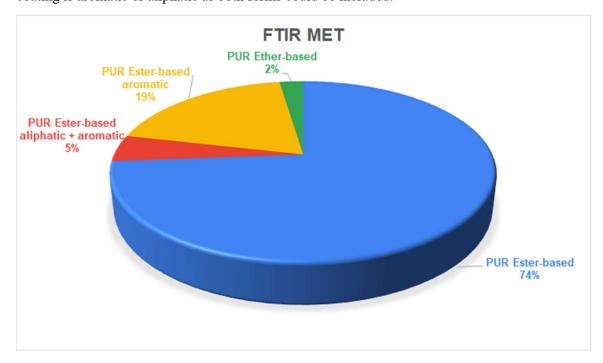
#### **MUDE**





#### The MET

Most of the coatings were PUR ester-based aromatic; almost 19%. However 74% was not determined to be either aromatic or aliphatic. Since most objects where analyzed before the start of the project, this was not specifically taken in account. Even by the use of FTIR, It is not always very clear if a coating is aromatic or aliphatic as both forms could be included.



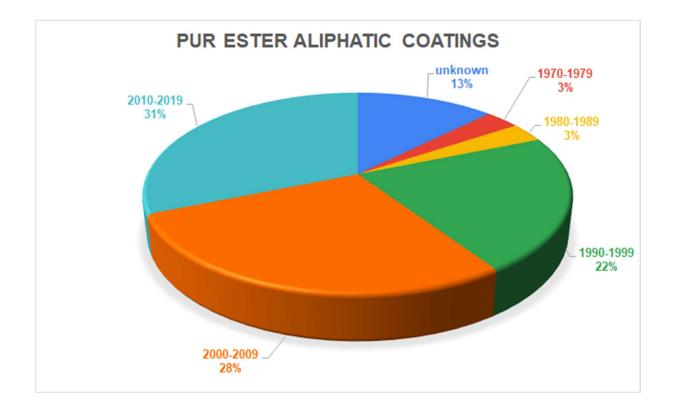
Concluding that these results clearly show that most of the coatings in the three collections are PUR ester-based. Most of them are aromatic. PUR ether-coated objects are not very common.

#### PUR ester aliphatic coatings

According to preliminary condition assessment of the collections, the most common types of damage for **PUR ester aliphatic coatings** are:

- tackiness
- peeling
- micro cracks
- discoloration
- blooming (rare)

The analysed PUR ester aliphatic coatings date from 1970 to 2019. In all of our collections starting from the 1990s, these coatings are more common.

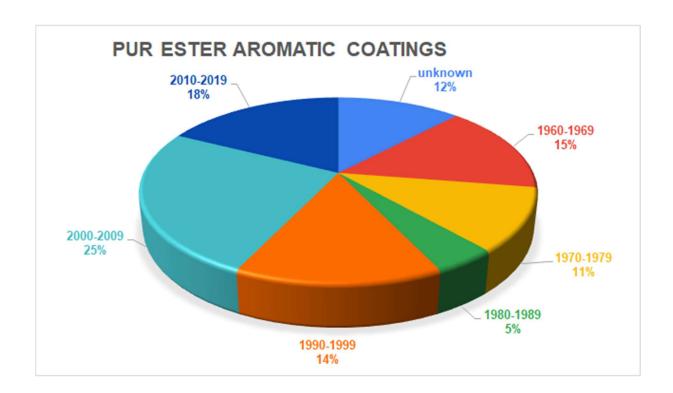


#### PUR ester aromatic coatings

The most common types of damage for PUR ester aromatic coatings are:

- blooming
- gloss change
- discoloration
- micro cracks
- powdering
- peeling
- tackiness (rare)

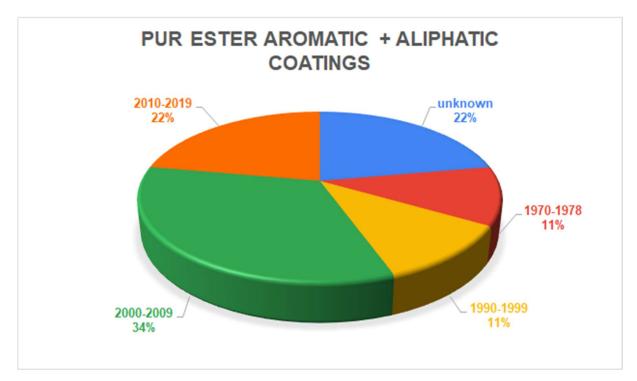
For the aromatic type of ester coatings there is not really a specific difference visible between time periods. Based on this study of these three museums' collections, , this type of coating is used through all decades from the 1960s to present day.



#### PUR ester aromatic + aliphatic coatings

The most common types of damage for the mixture of **PUR ester aromatic** + **aliphatic coatings** are:

- blooming
- micro cracks
- tackiness
- peeling
- cracks



Similar to PUR ester aromatic coatings, the mixed coating of PUR ester aromatic + aliphatic also cannot be linked to a specific time period, but exists in examples dating from the 1960s - present day.

#### Conclusion findings year 1

Our initial findings indicate that if we compare condition issues for aromatic and aliphatic coatings, aliphatic coatings tend to be sticky while aromatic coatings tend to start blooming. However, there are a few aromatic coatings out of this first analysis that also seem to be sticky. It might be possible that the condition of tackiness starts before blooming occurs, although at this point the evidence is inconclusive. This is among the issues that will be looked at in the next two years of research.

The substrate was also analysed in addition to the coating as an essential part of the research. It is the substrate that will often co-determine how fast the degradation process will go. Textiles are very hygroscopic, so for example a cotton will swell more severely when humidity is high than a polyester substrate. The more the fabric shrinks and swells, the more tension there will be put on the coating.

The most common types of substrate are:

- Leather
- Silk
- Polyester
- Cotton
- Cellulose nitrate
- Polyamide
- Polyamide + polyester

Out of this large selection of analysed objects, each museum chose 15 collection objects to work on, covering all the decades under consideration.

## What is Polyurethane

Otto Bayer discovered polyurethane in 1937 by chance. It was only ten years later that polyurethane was manufactured into customized materials. Polyurethanes are formed by the reaction of a diol (alcohol with two reactive hydroxyl groups) or a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polyfunctional isocyanate (with more than two reactive sides) in the presence of suitable catalysts and additives.

Polyurethane is well known as the most difficult polymer to conserve as the hydrogen bonding makes it very unstable and sensitive to natural aging processes, as well as its soft domain (composed by the polyol component) which is more prone to the interaction of deterioration agents. However, this material has been very popular in the fashion industry since the 1960s – 1970s because of its customizability and broad functional, and aesthetic characteristics.

Polyurethanes are very diverse, versatile, and have different applications. They can be rigid, soft, foam, elastic, matte, or glossy. They are known as the first polymeric materials that have rubber elasticity and thermoplastic properties, which t is, of course, very much appreciated in a fashion industry looking to offer choice to customers. TPU coatings can be custom-made with desired properties, for example, they can make clothing waterproof yet breathable, abrasion and stain resistant, as well as washable. Because of all these possibilities it is very difficult to conserve objects with PUR, which makes conducting research for a standard conservation solution very challenging.

PUR is a group of plastics with different compositions and a very large variety of applications. In museums they occur in different forms:

- Cellular materials including flexible and rigid foams
- Films
- Surface coatings and adhesives
- Elastomers: Fibres, soft and hard rubber

The most commonly used techniques for producing coated fabrics for fashion are calendaring, solution applications, and reactive coatings. These different types of applications make the material even more complex, because of the unlimited possibilities in composition, shine, thickness, type of substrate, ...

The unlimited chemical and physical diversity of the material makes understanding polyurethane's morphology crucial for understanding its properties and long term behaviour. For preventive conservation, this is very important, as without proper knowledge of a material's composition, it is impossible to work out guidelines for preventive conservation.

In phase 2 of the glossy surfaces project coatings will be created in function of aging tests. More information on the used techniques will follow further out of this stage.



During the decades there have been several commercial trade names for PUR products. A table of PUR Trade names was made by Susana França de Sá and can be found in image 1.

An example of a commercial trade name is Corfam, developed by DuPont as an example of a popular polyurethane-based leather. It was a three-ply laminate synthetic leather composed of a polyurethane reinforced with a polyester fibre base and a top coat of urethane copolymer<sup>1</sup>.

According to an article written by Debra Hughes at the Hagley Museum, Corfam is an excellent example of a synthetic product that did not live up to its expectations over time for DuPont. Corfam was created in the late 1950s. It was a material created to look like leather with a high shiny gloss surface which resembled patent leather. Corfam was mainly used for the production of dress shoes as well as other kinds of articles such as purses. From 1964 to 1969, 7.5 million pairs of Corfam shoes were sold, but after that the market declined for several reasons including the popularity of vinyl shoes. The fact that Corfam did not breathe and did not stretch, numerous consumer complaints, so in 1971 the production stopped. <sup>2</sup>

Fashion designers of the 1960s and 1970s known to work in modern materials include André Courrèges, Paco Rabanne, Emilio Pucci and Pierre Cardin. André Courrèges in particular made use of polyurethane artificial leathers. In the collection of MUDE, The MET and MoMu polyurethane artificial leathers from Courrèges can be found, and will be studied in this project.

The use of coatings to provide a glossy finish was also common in the 1970s, as has been confirmed by Susana França de Sá in her PhD. "When leather goods required glossy finishes, polyurethane was also an option. One example was patented in 1972 by E.I DuPont de Nemours and Company (Hodge & Patsis, 1972:n.p). Although prior art methods were offering coatings for these purposes, most of them were non-porous, failed on flexibility, scuff resistance (crack and loose shine), and presented surface tack (Hodge & Patsis, 1972). To fulfil this need, chemists from DuPont patented a coating based on blends of TPU, PVC and poly siloxane, resulting in a microporous layer showing water vapour permeability and glossy appearance (Hodge&Patsis, 1972). "<sup>3</sup>

## **Degradation of Polyurethanes**

Fashion designers frequently do not consider the lifespan of a material, but they choose material for its properties and design. Clothing is designed to last only for a short time, and then typically gets thrown away or handed down. Since fashion is always changing, people adapt their choice of clothing constantly.

Fashion that ends up into museum collections can come from many different sources and its individual history can alter the deterioration behaviour. An object can be bought straight from the designer and have never been worn. It can also be a donation and, if this is the case, the object has had a history when it might have been exposed to cold, warmth, rain, tension, cleaning processes, and any other number of conditions All of these factors will of course accelerate the degradation process of polymers severely.



<sup>&</sup>lt;sup>1</sup> What does the future hold for polyurethane fashion and design? Conservation studies regarding the 1960s and 1970s objects from the MUDE collection. Susana Catarina Dias França de Sá.P 76.

<sup>&</sup>lt;sup>2</sup> https://www.hagley.org/librarynews/museum-collectionthe-short-life-dupont%E2%80%99s-corfam

<sup>&</sup>lt;sup>3</sup> What does the future hold for polyurethane fashion and design? Conservation studies regarding the 1960s and 1970s objects from the MUDE collection. Susana Catarina Dias França de Sá.P 65.

The most common agents of degradation are **light** - which causes the shortening of polymer chains and/or cross-linking between chains - **oxygen**, **moisture**, **additives** such as fillers or plasticizers from within the plastic itself, and **mechanical stress**, for example the parts of a jacket that are under pressure when wearing it, or mounted on a bust or mannequin. The substrate supporting the coating itself also plays a very big role in the route of degradation. For example a cotton substrate is very sensitive to humidity and will likely cause more tension between the substrate and the coating.

Within the class of polymers there are two important families – The ester based polyurethanes are more sensitive to hydrolysis and thermal ageing. Ether bases are more resistant to hydrolysis, but more sensitive to photo oxidation. In both cases, degradation will alter the object and result in a loss of its chemical, physical and mechanical properties. An object can become unrecognizable, unstable and eventually fall apart.

The most common forms of degradation that have been established are:

**Blooming**: Whitish deposits that can evolve to a more crystalline appearance over time, coming out from the superficial coating layer This white bloom is commonly identified as adipic acid, which is formed by the reaction of the polyester based polyol with water (moisture).

**Peeling**: the coating comes loose from the substrate. The most common types of substrate are cotton, silk, polyester and leather.

**Stickiness**: Substrate showing an adhering surface due to the migration of additives and/or degradation of constituent materials. Commonly found in aliphatic polyurethane coatings.

**Flaking**: Cracking and loss of adhesion of the coating, due to hydrolysis of the polyester polyurethane. The flaking is worsened by the presence of a flexible substrate (e.g. knit) Commonly found in early ester-based and aromatic polyurethane coatings

**Cracks**: Breaks crossing the entire coating due to an increased brittleness of the material. Commonly found in ester-based and aromatic polyurethane coatings

The type of degradation depends heavily on the period of the object, the kind of substrate and the conditions the object has been exposed to. Understanding the material and knowing its entire composition is fundamental. Anoxic conditions, with low temperature in the dark with an RH of 45-55% are showing a lot of promise as a preventive measurement for long term storage.

#### **Preventive conservation**

If we look at polyurethanes in general it is a fact that this material continues to degrade even under the standard climate conditions in Museum storage (as noticed in our collections and also reported in the survey by the respondents). While most materials seem to benefit from an environment of 18 -21 °C and 45 - 55% RH, these conditions are ineffective in retarding polyurethane deterioration, making a uniform storage environment insufficient for collections including this material. Since polyurethane is sensitive to oxidation, a solution could be to seal these objects in an enclosure, however this is not a very practical solution if the objects are to be displayed. The use of a scavenger, lfor example Ageless, could help to reduce the oxygen concentration to 0,01%.MoMu has stored one object from f its collection in this manner since 2012. It is fair to say that to the present the condition of this object has been stabilized. However, anoxia is a very expensive storage method and it is uncertain how long it can postpone the degradation process. The object remains very fragile even in this package and at present it is still not possible to consolidate the coating or put the jacket back on display.

With the available preventive conservation measures it is possible to extend objects' lives without active interference. For this optimal storage, darkness, good ventilation, and freedom from stress is essential<sup>4</sup> for all types of plastics. Conservation literature indicates that promising preventive measures for long term storage of Polyurethanes are a low temperature (not lower than 10°C), anoxic, dark environment with an RH of 45 -55%. All chemical reactions slow down at low temperatures, so low temperature storage will presumably slow down all decay reactions. We must take into account that reducing the temperature below 10°C might cause other physical damages such as shrinkage, stiffening and condensation. A lower RH, of 30% might also be better for the preservation of polyurethane Ester. However, given that most storage spaces contain a variety of objects other than those including polyurethane ester materials, a compromise addressing the needs of all types of materials is in order.

In the PhD<sup>5</sup> written by Susana França de Sá, several storage methods have been tested. The most problematic type of storage was open storage. Anoxia clearly was the better option.

Further research for this topic is crucial and clearly more testing is needed regarding the aging behaviour of TPU coated objects. What we already know is that through the decades there is a difference in the aging pattern of the TPU ester coatings. Of course the evolution of the production of TPU coatings plays a very big role in this process. Several types of materials are now no longer in use in the production process because of health and environmental concerns. There are also differences between the aging of aromatic and aliphatic coatings. The possibility of mixtures of aromatic and aliphatic coatings presents even more challenging difficulties.

<sup>&</sup>lt;sup>4</sup> Friederike Waentig. Plastics in Art. Germany, 2008. P127.

<sup>&</sup>lt;sup>5</sup> What does the future hold for polyurethane fashion and design?Conservation studies regarding the 1960s and 1970s objects from the MUDE collection. Susana Catarina Dias França de Sá.

In the PhD of Susana França de Sá<sup>6</sup> a natural ageing experiment in the dark (12 months, 45-55%RH) has been carried out with unaged and naturally aged references of PUR Foam and TPU film in four selected environments:open air at room temperature, sealed enclosures at room temperature, and with and without oxygen atlow temperature (11-13°C). It was concluded that open air storage is to be considered the least desirable condition for the preservation of ester based TPU films and that ester based TPU films are more stable than PUR foams even in open air.

Taking this result into consideration, one can already see that the choices now made for displaying fashion exhibitions in open air will always hasten the degradation process. (Susana de Sá) 'To the current knowledge, after degradation starts, damage is irreversible and only consolidation and/or stabilisation may be considered to preserve the original materiality of the object; although, in some cases, even these hypotheses are not realistic. In addition to these drawbacks, even in controlled environmental conditions PUR continues to degrade and in the near future, the exhibition of these objects is at risk.'

We face an enormous challenge in the conservation of TPU not only in storage but also for exhibitions. Of course we want to show our collections to the public, but at what cost?

<sup>&</sup>lt;sup>6</sup> What does the future hold for polyurethane fashion and design?Conservation studies regarding the 1960s and 1970s objects from the MUDE collection. Susana Catarina Dias França de Sá. P 186-187.



# **Images**

Image 1

Table 1.3 Commercial trade names of PUR products available between the 1940s—1970s

PUR form	Trade name	Company	Reference
Rubber	I-rubber or I-Gummi	Bayer	(Meckel et al., 1996: 16; Prisacariu, 2011: 1)
	Vulkollan	Bayer	(Bayer et al., 1950 as cited in Hill et al., 1956: 927)
	Vulcaprene	ICI	(Harper et al., 1948 as cited in Hill et al., 1956: 927
	Adiprene	DuPont	(Hill et al., 1956)
	Chemigum SL	Goodyear Tire & Rubber Co.	(Seeger et al., 1953 as cited in Hill et al., 1956: 927
Fibres	Perlon U	Bayer	(Szycher, 1988: 298; Szycher, 2013: 1)
	Igamid U	Bayer	(Szycher, 1988: 298; Szycher, 2013: 1)
	Spanzelle	Courtaulds	(Lushington, 1967: 75)
	Fiber K	DuPont	(Carraher, 2013: 287)
	Lycra	DuPont	(Lushington, 1967: 131)
	Elura	Chemstrand	(Lushington, 1967: 131)
Coating or leatherlike product	Estane	B.F. Goodrich	(Meckel et al., 1996: 16; Prisacariu, 2011: 2)
	Desmopan	Bayer	(Meckel <i>et al.</i> , 1996: 16; Prisacariu, 2011: 2; Verg, 1988: 394; Schneider, 2013: 56)
	Texin	Mobay	(Meckel et al., 1996: 16; Prisacariu, 2011: 2)
	Pellethane	Upjohn	(Meckel et al., 1996: 16; Prisacariu, 2011: 2)
	Elastollan	Elastogran	(Meckel et al., 1996: 16; Prisacariu, 2011: 2)
	Corfam	DuPont	(Lushington, 1967: 134; Fenichell, 1997: 281)
Foams	Troporit M	Bayer	(Szycher, 1988: 298)
	Bayflex	Bayer	(Schneider, 2013: 56)
	Baydur	Bayer	(Schneider, 2013: 57)
	Moltopren	Bayer	(Bayer, 1971: 138)

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<sup>&</sup>lt;sup>7</sup> What does the future hold for polyurethane fashion and design?Conservation studies regarding the 1960s and 1970s objects from the MUDE collection. Susana Catarina Dias França de Sá.P 47.

#### Literature list

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