Ge-conservación
Conservação | Conservation

Facing new challenges in the conservation of the boots of former Valencia Club de Fútbol player Gaizka Mendieta

Rosario Llamas-Pacheco

Abstract: The article presents the restoration process carried out on the boots of former Valencia Club de Fúbtol player Gaizka Mendieta. The boots have become an object of socio-cultural relevance, as they were donated to the Club by the player. These boots are more than twenty years old and are made of kangaroo leather. The sole is made up of two layers: the first, thicker, of Phylon (ethylene-vinyl acetate), and the second, thinner and lighter, of thermoplastic polyurethane elastomer (TPU).

The condition of the sole was extremely unstable, since, due to hydrolysis, the polyurethane had degraded, generating a very accentuated film of whitish crystals. On the other hand, the rubber studs of the football boots were in an extremely high state of degradation and loss. Moreover, the whole assembly was deformed, dirty and poorly adhered. The article describes in detail the materials and techniques used in the restoration, being one of the few dedicated to this problem.

Keywords: football boots, restoration process, Gaizka Mendieta, TPU, Phylon

Afrontando nuevos retos en la conservación de las botas del ex jugador del Valencia Club de Fútbol Gaizka Mendieta

Resumen: El artículo presenta el proceso de restauración llevado a cabo en las botas del ex jugador del Valencia Club de Fúbtol Gaizka Mendieta. Las botas se han convertido en un objeto de relevancia sociocultural ya que fueron donadas al Club por el jugador. Las botas tienen más de veinte años y están fabricadas en piel de canguro. La suela está compuesta por dos capas: la primera, más gruesa, de Phylon (etilvinilacetato), y la segunda, más fina y ligera, de elastómero de poliuretano termoplástico (TPU).

El estado de la suela era extremadamente inestable, ya que, debido a la hidrólisis, el poliuretano se había degradado generando una película muy acentuada de cristales blanquecinos. Además, los tacos de goma de las botas de fútbol se encontraban en un estado de degradación y pérdida extremadamente elevado. Por otra parte, todo el conjunto estaba deformado, sucio y mal adherido. El artículo describe detalladamente los materiales y técnicas utilizados en la restauración, siendo uno de los pocos dedicados a este problema.

Palabras clave: botas de fútbol, proceso de restauración, Gaizka Mendieta, TPU, Phylon

Enfrentando novos desafios na conservação das botas do antigo jogador do Valencia Club de Fútbol, Gaizka Mendieta

Resumo: O artigo apresenta o processo de restauro realizado nas botas do antigo jogador do Valencia Club de Fútbol, Gaizka Mendieta. As botas tornaram-se um objeto de relevância sócio-cultural, uma vez que foram doadas ao clube pelo jogador. Estas botas têm mais de vinte anos e são feitas de pele de canguru. A sola é composta por duas camadas: a primeira, mais espessa, de Phylon (etileno e acetato de vinilo), e a segunda, mais fina e mais leve, de elastómero de poliuretano termoplástico (TPU). O estado da sola era extremamente instável, uma vez que, devido à hidrólise, o poliuretano tinha-se degradado, gerando uma película de cristais esbranquiçados muito acentuada. Além disso, os pitões de borracha das botas de futebol estavam em estado extremamente avançado de degradação e perda. Todo o conjunto estava deformado, sujo e mal aderido. O artigo descreve em detalhe os materiais e técnicas utilizados no restauro, sendo um dos poucos dedicados a este problema.

Palavras-chave: botas de futebol, processo de restauro, Gaizka Mendieta, TPU, Phylon

Introduction

Valencia Club de Fútbol is a Spanish first division football team. In nineteen ninety-nine they won the Spanish "Copa del Rey" championship, thanks in part to a goal scored by the player Gaizka Mendieta. The goal became hugely popular, and the player ended up giving the boots he was wearing in that match to the football club. From that moment on, the boots became a valuable object, symbolically charged and, of course, worthy of being kept, according to a wide social sector [1].

However, as the years went by, the condition of the boots deteriorated, so the Club requested their restoration from the University Institute of Heritage Restoration of the Universitat Politècnica de València. In 2020, the restoration was undertaken, on the understanding that the object had become part of the cultural heritage of Valencian society.

This work presents the study of football boots from both a technical and material point of view. It also demonstrates the need for the exhibition and storage of new types of heritage objects, which are part of the cultural fabric and identity of the community.

For this reason, the constituent materials of the boots, their method of construction, their evolution over time and the assumption of new values as an entity are analysed. Finally, the process of intervention carried out on them is presented, as well as a concrete proposal for preventive conservation.

Research aim

The main objective of this research is to show how an object that initially had no heritage value whatsoever has become part of the Valencian popular imagination. This object is widely known and valued as a symbolic and conceptual element (Llamas 2020). Although our entity "football boots" does not have an artistic character, it would be constituted, in the same way, by a material plane (the one that degrades); a biographical plane (the one that studies its evolution over time); and the imaginary plane (the one that gathers the affections that the community has contributed to it until it configures its current essence as a valuable object).

The study is intended to serve as a guide for conservators of this type of heritage objects, on which there is little scientific literature. Therefore, an analysis of the three mentioned levels is presented. The sum of these three areas constitutes the consistency of our object, which must be known before applying any decision-making model. What is important about the article is that it provides a novel study describing the manufacturing processes; the materials used; the degradation mechanisms and the restoration processes carried out.

State of the art

The object analysed is made up of various types of materials, both of natural and synthetic origin. The behaviour of these materials as a whole has not been studied before, so it is necessary to analyse each of them separately and then specify what their degradation process has been. It is also necessary to see how this has affected the surrounding materials.

Thus, the article describes how certain football boots have been restored after having acquired a series of cultural values.

On the other hand, the materials that showed the greatest deterioration were the leather of the upper, the polyurethane of the sole and the rubber of the studs. There are many studies that can be found on the restoration of leather in artistic objects, but in general, these are objects in which the leather is highly degraded by the passage of time. In our specific case, kangaroo leather was used for the boots, which is one of the best performing leathers for this use, but even so, it was already showing a certain amount of drying and deformation.

Leather in good condition exchanges water with the environment in which it is found, according to variations in relative humidity. This mechanical behaviour is specific, natural and has no conservation implications. However, the degradation of leather leads to the denaturation of collagen. This phenomenon is not visible to the naked eye. In this sense, water is the main agent of deterioration of the fibrillar structures of leather.

Regarding the behaviour of degraded leather, it should be noted that, "leather objects with different degrees of deterioration have different hydrodynamic properties in relation to their degree of deterioration, establishing a specific desorption curve". Thus, leather will react to changes in humidity in such a way that: the greater its initial degradation, the greater the deformation it will undergo (González 2005: 80-87). In the case of Gaizka Mendieta's boots, the leather, being in good condition, continues to behave well to changes in humidity.

In addition, leather loses elasticity and becomes deformed over time. As to how to solve this problem, Vergara (2002) recommends the use of lubricants to soften the leather, when it is necessary to eliminate deformations and discourages the use of aqueous solutions for this purpose. Aqueous solutions can produce stains, contractions, and physical changes in leather objects.

On the other hand, as regards the final protections of leather, Vergara (2002) advises the use of microcrystalline waxes.

This is not an article that focuses solely on the degradation of polyurethane. Polyurethane is only one of the materials presents. However, knowledge of the behaviour of this material is necessary to understand the state of conservation of the boots.

The behaviour of foamed polyurethane has been referenced in several scientific investigations (Pellezi et al. 2014:255-261; Lattuati et al. 2011: 4498-4508). Where, after different natural and artificial ageing tests, it has been found that polyurethane degradation occurs by scission and cross-linking of the polymer chain, both for the polyurethane ester family and for the polyurethane ether family. According to the study by Pellezzi et al. (2014: 255-261), the degradation of polyurethane esters coincides with the previous literature, having determined that, in a humid atmosphere, and by ATR-FTIR, hydrolysis of the polyol fraction of the polyurethane is detected.

Lovett and Eastop (2004:100-104), for their part, aged several polyethylene samples at varying amounts of oxygen and different RH, showing that RH affected more than oxidation in the case of PUR (ES). In this regard, they made some important recommendations regarding preservation. Thus, it is necessary to identify at an early stage the type of plastic of our objects; the degradation of PUR is inevitable even in good conditions; it is necessary to properly document our objects; each family of polyurethane degrades by different ways; it is advisable to keep the RH low to slow down hydrolysis as long as other materials are not affected; it is necessary to store PUR in isolation as it emits acid compounds; it is not advisable to store in closed boxes; it is advisable to adapt and cushion the supports so as not to produce stresses on the objects...

Lattuati et al. (2011: 4498-4508) also confirm hydrolysis as the degradation mechanism of PUR (ES) and note that the main compounds produced during degradation after natural or artificial ageing were alcohol and some acidic raw materials. The presence of these compounds would be indicative of degradation.

On the other hand, Brydson (1999), explains the ageing of vulcanised rubbers, which is produced by autocatalytic radical processes (breaking of bonds and chain scission), favoured by high temperatures. During these processes, sulphur oxides are emitted.

In addition, exposure of rubber to light causes a rapid degradation of its surface resistance. "This is thought to be due to the formation of sulphuric acid through the oxidation of the rubber-sulphur complex". The sulphuric acid transpires, forming droplets on the surface of the polymer, and eventually a stage is reached where the droplets coalesce to form a continuous conductive film.

Materials and Methods. General description of the constituent materials of the boots and their method of manufacture.

— *Materials used in the boots*

The restoration work began with the organoleptic study of the different materials. The initial analysis of the boots was carried out using macro-photography with visible and ultraviolet light. Samples of the different materials were also observed, as well as the different surfaces of the object. A digital video microscope MOD. AM4113 T-FVW of CTS was used. The samples were also analysed using a Leica S8 APO stereo microscope with a Leica DFC camera.

To better understand how a football boot is made, we will start by briefly describing the parts that are usually present.

In relation to the materials, when we talk about the cutting material, we are referring to the material mainly used to make the boot. In general terms, in the upper rear part of the boots, we find the reinforcement or buttress; in the lower rear part, we find the heel buttress; in the upper (upper part of the shoe) we find the laces, and under it, we find the tongue; finally, the midsole, the sole and the studs [Figure 1] are found in the lower part of the shoe.

Kelme® is the brand that produced our boots, and has specified the materials used in this particular model (García 2007). Therefore, we can describe the materials used and the technology employed in the manufacture of the boots. Kelme® is a sports footwear brand based in the city of Elche (Spain) [2]. Our boots have been identified as the "milenia" model from 1999; therefore, they are twenty-four years old at this point.

As for the materials used in its production, we will begin by describing the one used as the cutting material, which in our case is kangaroo leather (Olaso et. al 2016). This type of leather is one of the most resistant leathers available. Kangaroo leather can be laminated in thin layers that maintain a high tensile strength, above other types of leather. Kangaroo leather is remarkably light and, at the same time, extraordinarily strong, due to its anatomical structure. The fibre bundles are evenly oriented and parallel to the surface. Moreover, it contains no sweat glands and the elastin, the protein that gives it its elasticity, is evenly distributed throughout the thickness of the skin. All these properties result in its excellent performance.

On the other hand, the insoles of the boots are made with a fabric called Cambrelle® Lining (García 2007), also currently supplied by various manufacturers for the manufacture of different types of footwear. This lining, which may have different weights, is a non-woven fabric made of 100% polyamide, whose main characteristics are its high absorption and easy drying and its high resistance to abrasion.

The boots are also equipped with Flexotex (García 2007), a brand created in 1989. These insoles are designed to allow greater forefoot flexion.

Furthermore, the boots have a synthetic midsole, made of a material called Phylon (Sărăndan et. al. 2020; Promjun and Sahachaisaeree 2021). This material is, nowadays, one of the most used in the production of sports footwear and has the objective of absorbing vertical impacts. Phylon is obtained from the compression, in a mould, and at elevated temperatures, of beads of EVA (ethylene vinyl acetate), a thermoplastic polymer made up of repeated units of ethylene and vinyl acetate. This process is repeated twice, resulting, after cooling, in a material that is even lighter than EVA. This lightness can reduce the weight of the shoes largely, which is why it is a very desirable material for sports footwear manufacturers.

Our sole is made of PU (polyurethane) (Rolaniec 2005). Polyurethanes used in footwear production are non-porous, rigid (as is the case) and have a high density. Polyurethane is a polymer obtained from hydroxylated bases combined with diisocyanates. Thermoplastic polyurethanes are those that flow with heat (Oosten et al. 2011) and are used in the manufacture of shoe soles (McPoil 2000). TPU (thermoplastic polyurethane elastomer), which is used in soles for its mechanical properties, can be soft and flexible or very hard, as in the case of our boots [Figure 2].

Two types of studs, aluminium and rubber reinforce the underside of the sole. The aluminium studs are screwed directly to the sole, while the rubber studs have been bonded into small cavities that have the exact shape of each of the studs.

Rubber is the generic name given to vulcanised natural rubber. The vulcanisation process involves heating natural rubber in the presence of sulphur, so that it becomes harder and more resistant (Brydson 1999). Vulcanisation, obtained in 1839, includes cross-linking processes, whereby parallel polymer chains are joined together by sulphur (Shashoua 2008). Cross-linking strengthens the rubber, changes its physical properties, and turns the polymer into a large molecule.

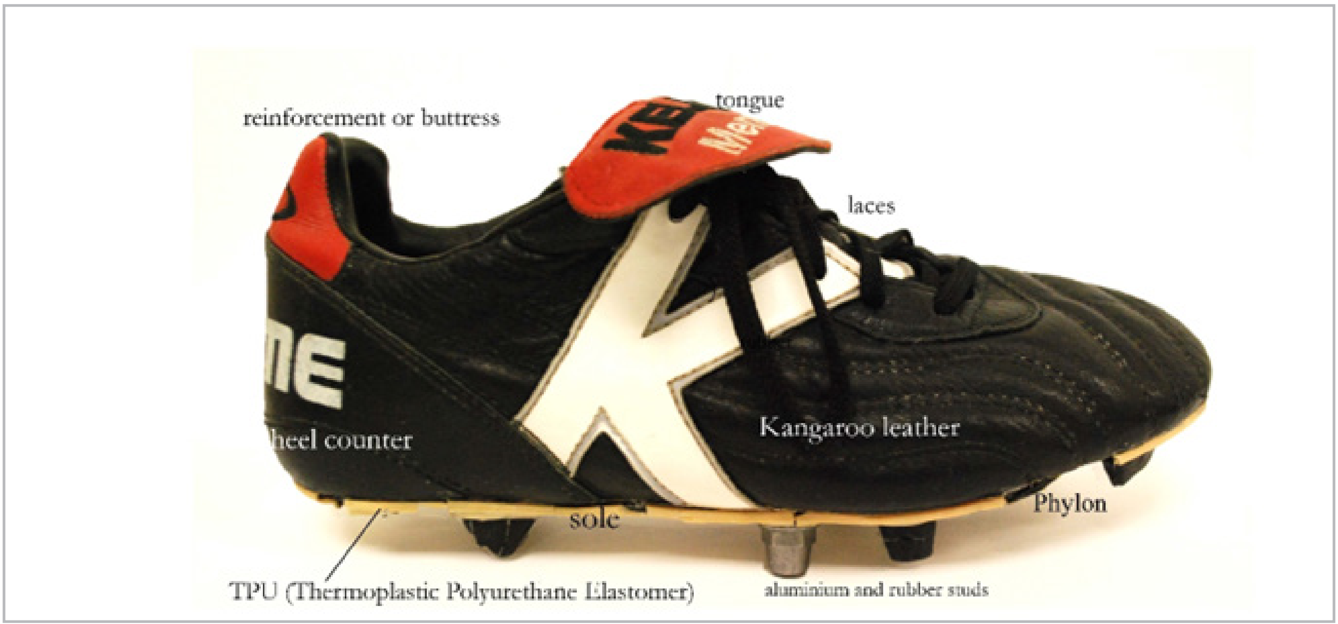

Figura 1.- Parts of Gaizka Mendieta's boots

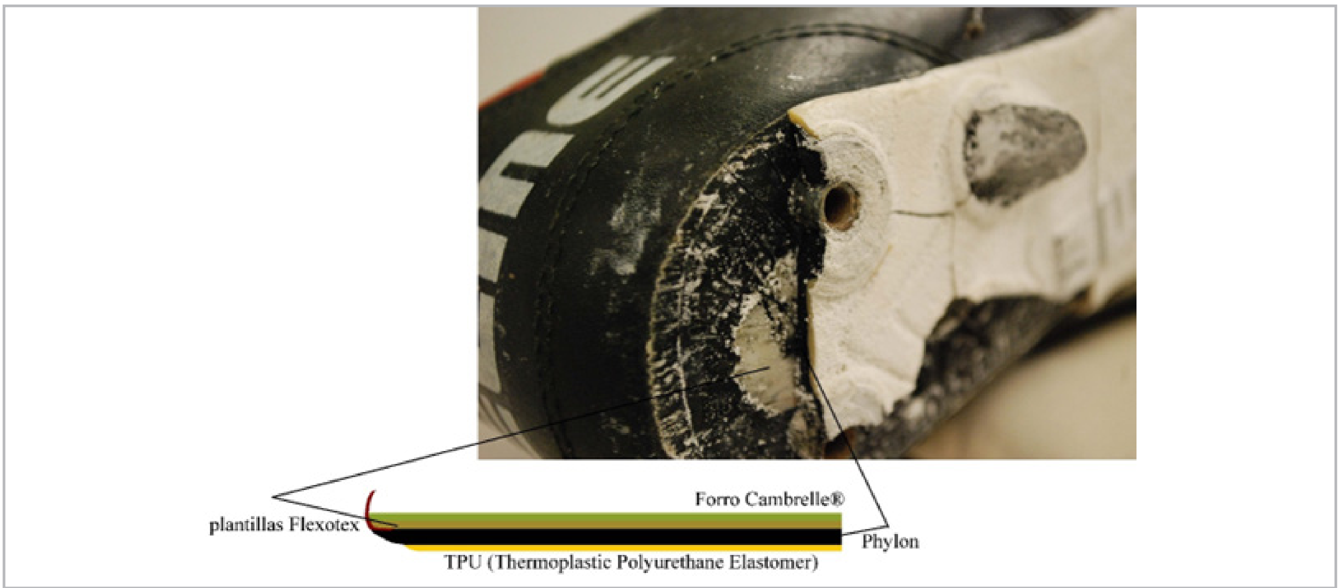

Figure 2.- Materials that make up the sole and midsole of boots.

— *Boot manufacturing method*

Once we have explained the materials we found, we will go on to explain the production process.

As for the design, the boots are made of black leather, but the flap turns red on the outside and is embroidered with the Kelme® shoe brand and the surname of the footballer Mendieta. The letter "K" has been placed on the reinforcement and the Kelme® brand name on the heel counter. In addition, the sides of the boots are reinforced with a piece of white leather in the shape of a "K" adapted to the lateral space.

In general, the boots are built on an inner sole. The leather rotates and adheres externally to this rigid sole thanks to a layer of glue.

Overall, customised boots, as is the case here, are produced on the last of the foot of the footballer in question. The first step in the manufacturing process would be the cutting of the leather, then all the parts that make up the shell (upper part of the boot) are sewn together, and the back of the boot is placed on a last at elevated temperature. By placing the back of the boot on the hot last and then applying cold, the leather hardens strongly and begins to shape the shoe. The excess leather is then folded over and sanded to adhere it to the bottom of the boot (midsole) (Promjun and Sahachaisaeree 2021; Motawi 2021; Olaso 2015).

Degradation processes

We will start by describing the situation of the object as a whole. In this respect, both boots were in an extremely unstable state. In general, the common pathologies that affect many cultural objects were observed: generalised deformation, surface dirt, changes in the appearance of the skin... Although, obviously, the action of the usual agents of deterioration (light, humidity, temperature) had acted in a specific way on each of the materials that make up the ensemble [Figure 3].

Figure 3.- General photographs of the boots, in visible light, before starting the intervention. Photograph: own authorship.

As for the kangaroo skin, it was in a good condition, not cracked, although it was somewhat dry and dirty. In the refining process, after the skins have been tanned, pigments and oils are usually added to the skins. With the passage of time, the effect of these oils diminishes, producing, as in this case, a certain dullness due to dryness. On the other hand, the surface dirt consisted of adhering greasy dust and large white particles on the surface from the sole.

The polyester laces that make up the laces were in good condition, but also showed surface dirt. [Figure 4]

In addition, both boots were found to contain newspaper balls inserted to maintain their original shape. Also, found inside were several aluminium studs that had become detached and had been stored. On the inside, the lining and the insoles were dirty, but in good condition.

However, the lower part of the boots showed an advanced state of degradation. In fact, the boots had to be transported on a polypropylene tray because they could not stand upright and parts of the sole, midsole and studs were coming off.

Regarding the Phylon midsole, it should be noted that, after so many years, its consistency was good, with no cohesion failure at any point [Figure 5]. However, the main problem of the right boot, in relation to adhesion, was the adhesive failure between the Phylon and the leftover leather of the shell. In fact, serious detachments had occurred, leaving this leather exposed.

In part, this process is also due to the mechanical force exerted by the TPU, which is becoming less flexible, on the sole as a whole. Due to the increased stiffness, the outer TPU layer cracked and the Phylon cracked, leading to adhesive failure and material loss.

The result was the detachment of large areas of the sole, a generalized loss of adhesion of the Phylon to the insoles and, in short, a considerable risk of loss in the event of any movement.

Figure 4.- Macro and microphotographs with visible light. Microscopic detail of the kangaroo leather, of the area of the footballer's name, at the turn of the tongue, and of the general condition of the laces. Before the intervention. Photograph: own authorship

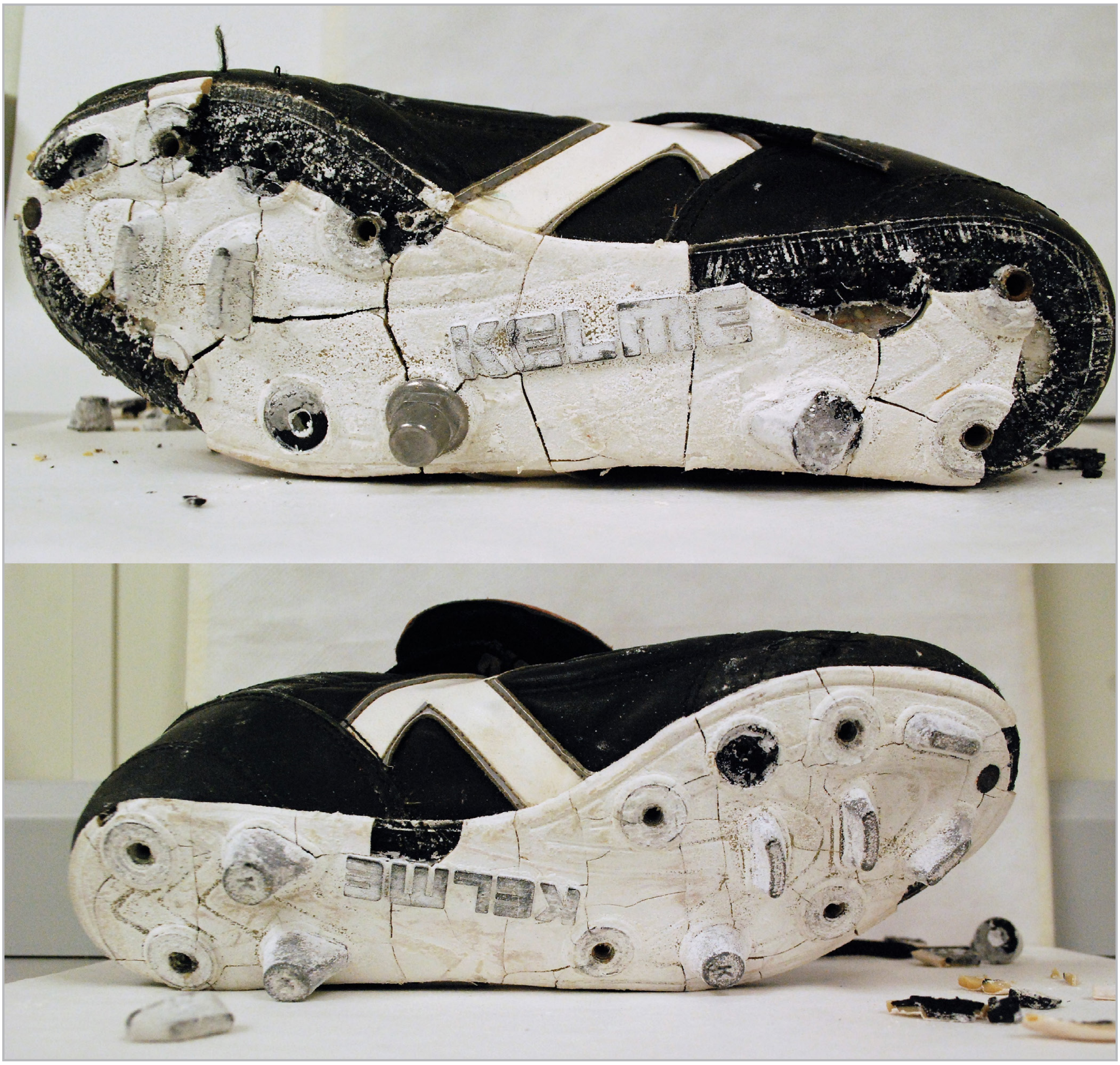

Figure 5.- Photographs of the soles of the boots before starting the intervention. Visible light. The whitish appearance produced by the particles of the thermoplastic polyurethane degradation product or by plasticiser migration can be seen. Also visible are the large areas where the sole has been lost due to widespread adhesive failure. Photograph: own authorship.

To summarize: the adhesion between the TPU (light-colored and thin layer) and the Phylon (black and thick layer) is perfect, while the adhesive failure occurred between the Phylon and the base of the insoles, which are partially covered with leather.

On the other hand, and looking at the boots as a whole, it should be added that several of the studs, both metallic and rubber, were missing.

Finally, it is worth mentioning the abundant presence of whitish agglomerations that had spread all over the surface of the sole, which could be plasticiser migration or chemical deterioration product. Thus, we are faced with a case of crystalline blooming (Krieg et.al 2022). These whitish crystals could be either adipic acid or also an adipate. It is not possible to say for sure since infrared spectroscopy was not performed. Adipic acid is a reagent in polyurethane chemistry, so it would not be an additive. However, if they were adipates, the presence of these crystals on the surface could be due to the loss of plasticizer. [Figure 6].

Adipic acid is produced from a mixture of cyclohexanone and cyclohexanol called KA oil. KA oil is oxidised with nitric acid to give adipic acid, with the resulting environmental problem. Most of this acid is used to produce nylon and for the production of polyurethane (Yumei L. et al. 2024)

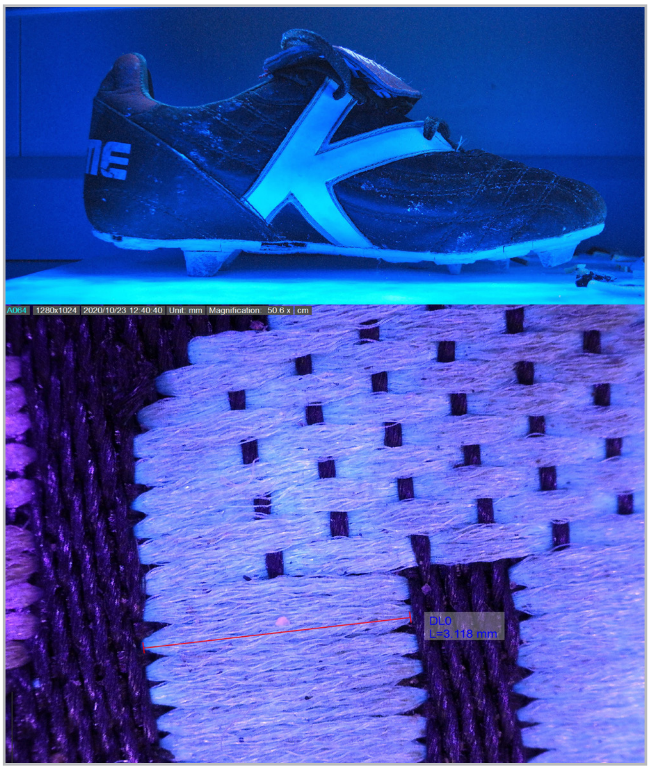

Figure 6.- Photograph of the right boot and microphotography of the area of the embroidery with ultraviolet light before the intervention process. In the image above, we can see the deposited surface dirt and the crystals scattered all over the surface. The image below shows a detail of the embroidered area of the footballer's name. Photograph: own authorship.

For their part PU undergoes significant physical degradation due to hydrolysis. In general, this chemical process is a reaction between a water molecule and another macromolecule, whereby the water molecule breaks one or more chemical bonds of the macromolecule, attaching its atoms to the macromolecule. This process causes the disintegration of the material (Brydson 1999).

Polyurethanes based on polyester diols tend to be the most commonly used in the production of shoe soles and are precisely those with the lowest strength. The conditions of high relative humidity accelerate the degradation processes by hydrolysis. In addition, agents such as light, ultraviolet radiation, oxygen, temperature, solvents, etc. affect this type of materials.

When the stratigraphy of the sole is studied under the microscope, several distinct layers are observed. Firstly, the widest, black one, which corresponds to the Phylon. Next, with a perfect adhesive bond to the previous one, a first phase of polyurethane of a homogeneous yellowish color can be observed. Above this phase begins a second phase in the polyurethane layer, slightly lighter in color and less thick, where the beginning of degradation is observed [Figures 7 and 8]. Finally, on the surface, a layer of white crystals is observed, which is easily removed.

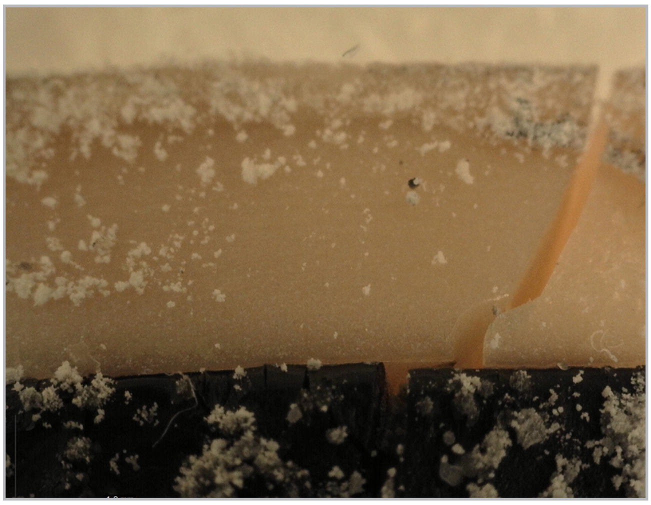

Figure 7.- Photomicrograph with visible light of one of the cracks through the polyurethane reaching the Phylon. Photograph: own authorship.

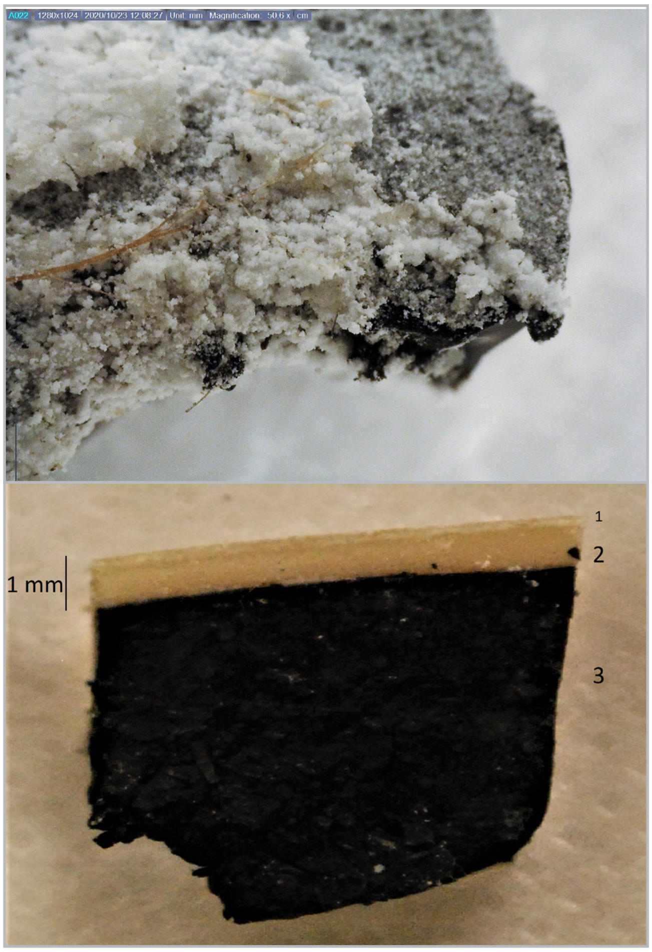

Figure 8.- At the top: micrograph of crystals. The lower part shows a stratigraphy of a clean sole area. For this reason, no whitish residue is visible. The image stands out because it shows the perfect adhesive bond between the polyurethane and the Phylon. With number one, a thinner, lighter layer is also visible where the degradation of the polyurethane begins. Next, with number two, a darker layer of polyurethane in a better state of conservation, and with number three, the Phylon in perfect condition. Photograph: own authorship.

Constituent materials	Degradation processes	Pathologies present in the boots
Cutting material: kangaroo leather	Loss of effect of oils used in production process	Matt and dryness. Stiffness, surface dirt, greasy pink stains, whitish deposits.
String (polyester)	In good condition	Deformation and surface dirt
Aluminium studs	In good condition	Surface soiling. Loss of most of the studs
Vulcanised natural rubber studs	Ageing due to autocatalytic processes of radical type (breaking of bonds and chain scission), favoured by elevated temperatures. Emission of sulphur oxides.	Largest brittleness, breakage with handling. Occasional loss of several studs.
Cambrel® lining, 100% polyamide fabric	In good condition	Surface dirt. De-adhesion in some areas
Flexotex® midsole	In good condition	Adhesive failure with the Phylon midsole.
Phylon midsole (ethylene-vinyl acetate)	Material in good condition	Adhesive failure with the leather adhered on the back of the insole and with the Flexotex insole itself. Cracs.
TPU outsole (Thermoplastic Polyurethane Elastomer)	Degradation by hydrolysis	Deep cracks that reach the insole. Stiffness, yellowing. Presence of a uniform layer of white crystals on surface (plasticiser migration or chemical deterioration product)
General condition	In general, the object could not be handled manually due to the risk of losing the rubber studs and part of the sole. There was widespread deformation and great instability. There were noticeable whitish sole deposits on all surfaces of the boots. There had been loss of the studs. Parts of the sole had been lost. Many fragments were already detached	

Table 1.- Summary of the degradation processes suffered by the materials and alterations found.

Results and discussion. Restoration treatments

— *Boot carcass treatment*

The intervention process was conducted in the laboratories of the University Institute of Heritage Restoration of the Polytechnic University of Valencia. First, we began by removing, by mechanical means and controlled suction, the solid deposits from the surface, both whitish crystals and solid particles of surface dirt.

The boots were then unlaced so that the leather could be cleaned. This cleaning was conducted with Velvesil PlusTM, a product manufactured by Momentive [3] which has been classified as non-hazardous to health and the environment. It is a product in gel form, colourless, with a relative density of 0.959 g/cm3, soluble in aromatic substances and highly stable [Figure. 9].

Figure 9.- Detail photograph with visible light during the cleaning process of the kangaroo skin with Velvesil PlusTM. Photograph: own authorship

Specifically, it is a gel based on a cross-linked siloxane containing a silicone solvent, cyclomenticone D5. Velvesil PlusTM gel is used to clean water-sensitive works, localising the cleaning effect only on the surface. It must be removed dry and then the removal of the gel is completed with the solvent cyclomethicone D5 (Decamenthylcyclopentasiloxane) [4] [5]. [6].

In the case of the boots, the procedure described above was followed.

The cords were cleaned by immersion in an aqueous solution composed of distilled and deionised water and Teepol® at a concentration of 0.3%, a neutral detergent based on a mixture of sodium lauryl ether sulphate and dodecylbenzene sulphonic acid. The soap was then rinsed off by several baths in distilled and deionised water. Finally, the cords were ironed to restore the first shape.

In turn, to recover the shape of the boot, and after the cleaning process of the leather, which gave it some elasticity, the boot was ironed at a low temperature, which eliminated many of the deformations present.

In addition, the aluminium studs that were found inside the boot were screwed back on and the lacing was re-done, just as it was at the start of the intervention.

As a protective coating, a light layer of microcrystalline wax was applied to the leather, using a cotton swab. This wax is a product consisting of a mixture of saturated hydrocarbons with linear and branched chains obtained from petroleum refining. It is a very resistant and flexible wax and does not yellow due to its chemical inertness. Moreover, due to its high melting point (76-80ºC) it does not soften at room temperature, so it does not absorb surface dirt. [7].

— *Treatment of the sole*

The entire sole was covered with a whitish powdery coating that flaked off to the touch. This pathology was very intense and widespread, giving the sole a lighter shade than the real one (Oosten 2022). Removal of this white layer revealed yellowing of the TPU.

The cleaning process started with a vacuuming of the loose particles of the TPU deterioration product or plasticiser migration, carried out with the help of a soft brush. However, at some points the suction could have dislodged some of the sole plates that were poorly adhered to the insole, so it was necessary to re-bond them using Beva O.F. D-8-S diluted in distilled and deionized water in a ratio (60:40). Beva O.F® D-8-S consists mainly of ethylene vinyl acetate (EVA). This is the same material as Phylon, which had to adhere to the stencil [Figure 8]. It is this affinity that determined the selection of this film-forming substance.

Once the stability and good adherence of the whole sole has been checked, we continue with a deeper mechanical cleaning. This was again carried out with a brush and gentle suction. This process was not sufficient to completely remove the whitish layer, so we continued the cleaning with the same method that had been used to clean the leather of the carcass (Velvesil PlusTM) (Cremonesi 2016). This method acts only on the surface and does not provide moisture that could have accentuated the degradation of the polyurethane. We consider this aspect particularly important, as the application of moisture is especially discouraged in this case.

On the other hand, the rubber studs that had become detached were consolidated, i.e., impregnated in their

Adhesive	Compound	Solubility	Concentration	Effective
Acryl Me	Microemulsion acrylic copolymer (30 nm particles) Recommended for consolidations	Aqueous	10% in H2O dt	No
			40% in H2O dt	No
Elvacite 2044	Particularly elastic consolidant. Acrylic resin based on POLI(MMA/nBMA)	Acetone, methyl ethyl ketone, diacetone alcohol	8%	Yes
			40%	Yes
Aquazol	Poly(2-ethoxy-2-oxazoline)	Aqueous Polar solvents	2.5 %	No
			30%	No
Polyvinyl Alcohol	Polyvinyl alcohol	Aqueous	3%	No
			6%	No

Table 2.- Summary table of the tests conducted with distinct types of synthetic resins for the consolidation and adhesion of the studs.

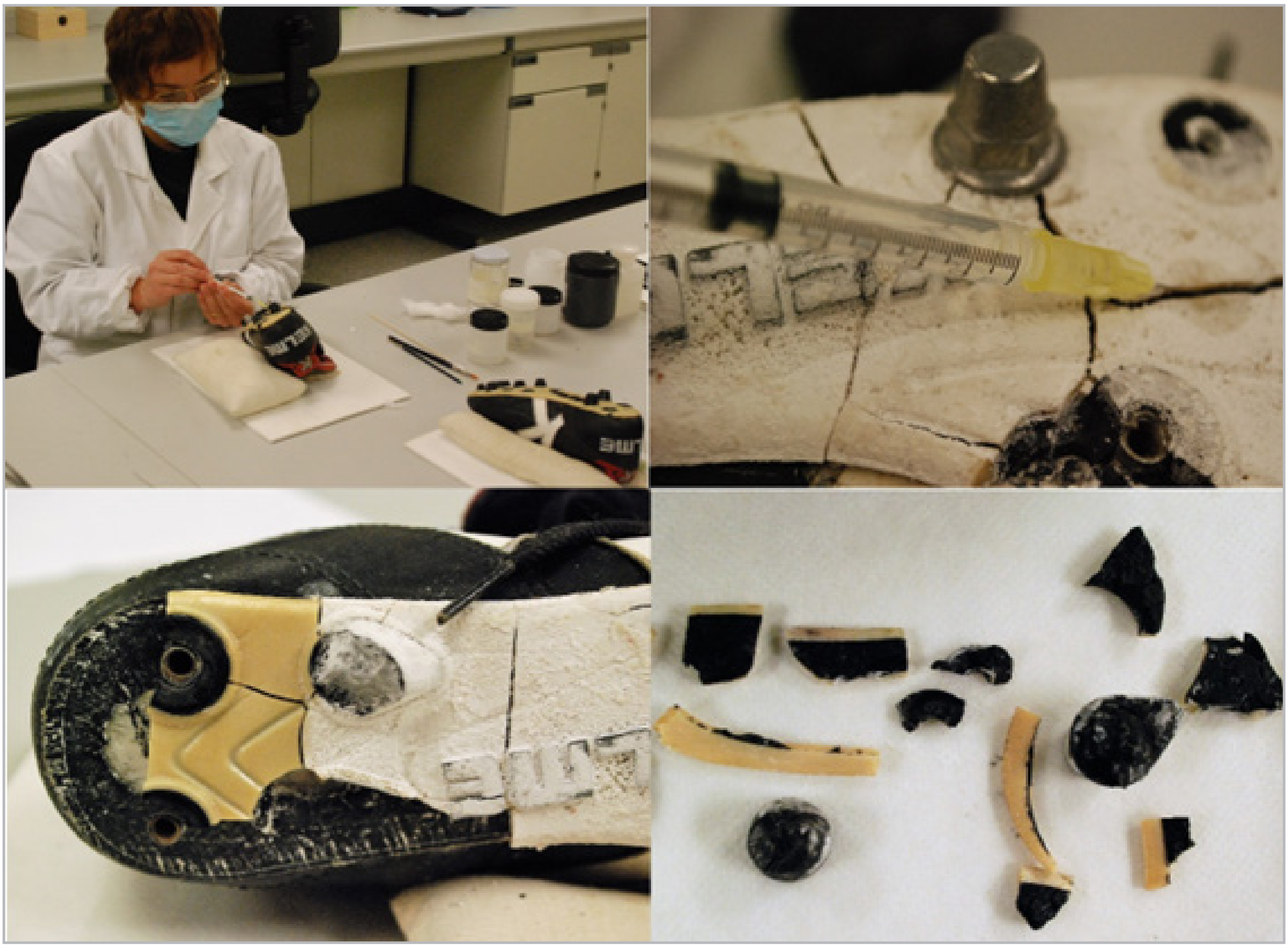

Figure 10.- During the process of adhesion and consolidation of the detached fragments. Photograph: Salvador Muñoz and Rosario Llamas.

thickness with a film-forming substance that gave them back their consistency, in this case Elvacite 2044, a polymer based on methyl methacrylate and n-butyl methacrylate, was used. Also, the parts that had become detached from the soles were adhered with this acrylic resin, at a higher concentration [Figure 10]. Before selecting this adhesive, several tests were conducted, checking manually, after drying, the compressive strength of the rubber plugs in the case of consolidation and the tensile strength in the case of adhesion of the parts.

Preventive conservation

Degraded plastics are extremely fragile. In this regard, some recommendations for handling can be given. Suitable trays should be used for transport. In addition, they should be placed on rigid surfaces cushioned with inert materials, avoiding vibrations. The boots should not be in contact with solvents or cleaners. Surface cleaning treatments should always be carried out by a restorer (preferably by suction or with a soft, dry cloth). On the other hand, handling should be done with nitrile gloves.

Figure 11.- Photographs with visible light of the soles after the intervention process. Photograph: own authorship.

Figure 12.- General photographs of the boots after the intervention process. Visible light. Photograph: own authorship.

It can produce sulphur oxides during the degradation process and is therefore considered a hazardous plastic. For this reason, it should not be stored together with other types of plastics.

The most common are sulfur dioxide and nitrogen dioxide, as well as organic and inorganic acids such as acetic, formic, nitric, nitrous, hydrochloric, sulfuric, etc. The possibility of these contaminants accumulating when the objects are in open spaces is not a cause for concern. However, when stored in airtight containers, the action of these volatile compounds can be detrimental. Moreover, rising temperatures increase the rate and speed of these emissions.

In our case, polyurethane, even in museum conditions, is an emitter of polluting volatile compounds. To slow down this process, the boots should be stored and exposed (given the impossibility of differentiating between storage and exposure conditions in this case) at a temperature between 17-20°C and a RH between 45-50%.

A-D strips (Liébana 2021) can be used to check for the presence of volatile compounds inside the display case or container. If so, zeolites or activated carbon should be considered to retain these contaminants.

On the other hand, an increase in ambient RH causes an increase in the humidity present in synthetic plastics. For this reason, they swell and become more flexible, but chemical degradation by hydrolysis is facilitated. Thus, a low RH is preferable, which is not common in the city of Valencia. Lovett and Eastop (2004) aged several polyurethane samples at different oxygen and relative humidity conditions, demonstrating that PUR(ES) degrades primarily by hydrolysis and should therefore be stored at low RH.

Finally, as in the case of most cultural goods, when they are exposed, low intensity lighting should be used, not exceeding 50 lux and filtering ultraviolet radiation. In addition, it is preferable to store the boots in the dark. This should be managed by the museum.

Conclusions

What makes an object valuable and what determines that it should be preserved? The boots that are the object of this restoration arrive at the Restoration Institute of the Universitat Politècnica de València because they had already acquired socio-cultural values and affectivities that made them worthy of being conserved. The values complete the consistency, form part of the biographical plane of the object and determine its identity.

In this case, the intervention consisted of restoring their stability, studying their mode of manufacture and the materials used in their production. Once restored, the boots have largely recovered their original appearance. The leather is clean, supple and protected [Figures 11 and 12]. Likewise, the adherence of the sole to the insole has been reinforced and all the detached fragments have been glued. At times, this process has led to a significant recovery of the sole, as these fragments have been put back together as if they were a puzzle.

The passage of time has left its mark on the object (deformation, surface dirt...) But the phenomenon of hydrolysis is the cause of the poor condition of the outer layer of the sole, which is made of polyurethane. In any case, the rigidity of the polyurethane, acquired over time, has led to the appearance of serious cracks and subsequent detachments.

Also important is the poor condition of the vulcanized rubber that makes up the rubber studs, which disintegrated to the touch.

Finally, it is concluded that proper preventive maintenance can slow down the degradation of the boot as a whole, but the TPU, even with it, will continue to degrade.

Notes

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[2] Ver página oficial Kelme®, https://kelme.com/es/

[3] Momentive: Geles de Silicona. https://www.momentive.com/es-mx/brands/velvesil

[4] CTS. "Velvesil Plus. Descripción del producto". https://www.ctseurope.com/es/scheda-prodotto.php?id=4001

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Author/s

Rosario Llamas-Pacheco
rllamas@crbc.upv.es
Departamento de Conservación y Restauración de Bienes Culturales. Universitat Politècnica de València
https://orcid.org/0000-0002-1238-1555

La Prof. Dra. Rosario Llamas Pacheco es Catedrática en el Departamento de Conservación y Restauración de Bienes Culturales de la Universitat Politècnica de València. Es miembro del Instituto Universitario de Restauración del Patrimonio, del cual ha sido subdirectora. Ha impartido clase en varias universidades. Ha sido directora tanto del Máster Oficial, como del Programa de Doctorado en Conservación y Restauración de Bienes Culturales de la Universitat Politècnica de València.Cuenta con una gran cantidad de publicaciones, tanto de tipo docente como investigador. Ha publicado en las revistas nacionales e internacionales más prestigiosas, y ha participado en gran cantidad de eventos relativos a la conservación y restauración del arte contemporáneo. Ha sido la investigadora responsable de diferentes proyectos de investigación.

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