NEW FRONTIERS OF ADVANCED DIAGNOSTICS AND NON-DESTRUCTIVE TESTING FOR QUALITY CONTROL IN THE TANNING INDUSTRY

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Abstract. Leather is one of the most representative materials of the leading sectors of world markets, such as fashion and luxury, interior design, automotive, thanks to its excellent properties able to guarantee its high quality.

Although material of natural origin, leather undergoes numerous substantial transformations during the production process, which, together with its anisotropy and with the increasing use of a wide range of novel sustainable tanning systems, sometimes makes some defects unpredictable.

This work describes how some specific instrumental detection techniques are able to provide information regarding the possible causes of defects, also revealing the specific phase of the tanning process potentially responsible for the problem; particularly, the study emphasizes the effectiveness of techniques such as ATR-IR (Attenuated Total Reflection Infrared) Spectroscopy, Scanning Electron Microscope (SEM)-X-Ray Probe, Gas Chromatography-Mass Spectrometry (GC-MS), DSC/TGA (Differential Scanning Calorimetry/ Thermogravimetric Analysis) in identifying the causes of stains, chromatic or morphological alterations, cracks and detachment of the finishing.

Furthermore, in order to guarantee increasingly predictive and non-invasive approaches, Non-Destructive Testing (NDT) systems have been considered for their use in the quality control of tanning productions, with particular reference to the use of optical Interferometric Techniques, laser based, such as the Electronic Speckle Pattern Interferometry (ESPI), and of Computer Vision techniques, based on the acquisition and processing of signals and images at different wavelengths, from visible to infrared.

The possibility of using robotic systems specifically designed for the scanning of online products, through non-destructive and automated approaches, was also evaluated thanks to the increasingly widespread use of deep learning approaches, where these technological developments will certainly benefit the production chain to achieve ever higher standards of quality of leather products.

***Keywords*: Leather Defects; Advanced Diagnostics; Non-Destructive Testing; Quality Control; Novel Detection Techniques; Automated Approaches; Robotic Systems; Deep Learning.**

1 Introduction

There are numerous defects that can affect leather articles, and that can concern purely aesthetic aspects or can affect structural and performance features; sometimes, the causes underlying them can be complex, multiple, and simultaneously capable of compete to the onset of the defect. It should also be added that the progressive use of innovative tanning systems with low environmental impact, and with a consequent radical change in the production process, currently makes it more difficult to predict the type of defects that may affect the final articles.

On the other hand, the use of appropriate investigation tools can allow identifying the elements able to determine the problem, such as possible errors in the individual phases of the tanning process, rather than storage or assembly errors of the leather items.

Early diagnosis can also avoid possible negative repercussions for producers in economic and image terms, especially due to the possibility of onset of "hidden defects", macroscopically visible even after a long time and, in some cases, when the article it is already commercialized.

This work firstly provides an overview of the use of the main destructive and non-destructive diagnostic techniques, which have been found to be crucial for the analysis of a wide range of cases of defects on leather and leather items, as well as for the identification of the causes determining them, with the possibility of providing suitable activities for the prevention and minimization of critical issues.

The work also provides an overview of additional non-destructive and automated control tools, which can be effectively used for the early identification of defects[1,9], and definitely to ensure the quality of new generation leather products.

The main diagnostic techniques used in the first part of the work were:

- Attenuated Total Reflection Infrared Spectrometery (ATR-IR)
- Optical microscopy (OM)/ Phase-contrast microscopy (PCM)
- Scanning Electron Microscope equipped with X-Ray Probe (SEM-X-Ray Probe)
- Differential Scanning Calorimetry/ Thermogravimetric Analysis (DSC/TGA)
- Gas chromatography-mass spectrometry (GC-MS) equipped with autosampler for VOC analysis

<u>ATR-IR (Attenuated Total Reflection Infrared) Spectroscopy</u>

This technique is a non-destructive approach is based on the combination of IR spectroscopy with reflection theories, allowing the spectroscopic analysis of surfaces and is particularly efficient for the recognition of functional groups of natural and synthetic polymers.
The frequency range used is 4000-600 cm^{-1} and falls in the mid-infrared region).
The technique has numerous advantages, such as:

- Direct analysis of solids.
- High quality of the spectra for qualitative analysis.
- Small sample surface required for analysis.
- Non-destructive analysis.
- Short sample preparation times.
- Spectra independent of the sample thickness.
- High reproducibility.
- Wide variety of analysable samples (polymers, fibers, pastes, powders, suspensions, etc).

In terms of the use of the technique in the tanning sector, this is particularly efficient for the characterization of finishing polymers, for the recognition of some organic molecules, such as some plasticizers and fats, for the recognition of some anions and functional groups related to use of organic substances functionalized in chemicals, as well as for investigations on collagen and its possible modifications, following degradation phenomena.

Optical microscopy (OM)/ Phase-contrast microscopy (PCM)

Optical microscopy, which involves the use of light with a wavelength from near infrared to ultraviolet, covering the entire visible spectrum, is an indispensable approach for the observation and study of leather samples of different origins and intended use, thanks to the possibility of being able to investigate the morphological conformation, the distribution of the constituents, the fibrous microstructure, the chemical-physical characteristics; The optical reflected light microscope or stereomicroscope represents a useful tool for a first cognitive investigation and is a non-destructive approach, through which it is possible to obtain information on the morphology and on the three-dimensional surface structure; the phase contrast optical microscope exploits the phenomenon of light interference and uses a system capable of converting the differences in the refractive index into a difference in brightness; through this approach it is possible to obtain detailed information on the structural characteristics of the leather section.

Scanning Electron Microscope equipped with X-Ray Probe (SEM-X-Ray Probe)

The technique utilized is based on the electron-sample interactions and allows to reach information about the sample including external morphology and chemical composition. More in detail, The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of a given specimen. The signals deriving from electron-sample interactions reveal information about the sample. These signals include secondary electrons, backscattered electrons (BSE), photons (characteristic X-rays), visible light, and heat.
Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples, while backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples, for example for rapid phase discrimination. X-rays are useful for microanalysis; their generation is produced by inelastic collisions of the incident electrons with electrons in discrete shells of the sample atoms.
Concerning leather defects investigations, the technique is potentially effective for both surface morphological/ topographic analysis and for microanalysis of the chemical composition of the surface.

Differential Scanning Calorimetry/ Thermogravimetric Analysis (DSC/TGA)

Thermal analysis allows to study the chemical-physical transformations undergone by the material during a heat treatment.
The “Thermogravimetric Analysis” (TGA) is a technique used to determine the mass variations of the sample in a controlled atmosphere as a function of temperature and time. Its usefulness is limited to transformations involving mass variations.
Scanning Calorimetry (DSC) is a thermal method in which the difference between the heat flows in the substance and in a reference is measured as a function of the sample temperature while both are subjected to a controlled temperature program.
In the tanning sector, the technique is particularly promising for investigations on the structure and technical features of leather and finishing polymers, allowing to analyse very small amounts of samples.

Gas chromatography-mass spectrometry (GC-MS) equipped with autosampler for VOC analysis

Chromatographic approaches are chemical-physical methods of separation of analytes mixtures based on the different affinity of each substance with two different phases, a stationary phase and a mobile phase, with which the mixture is put into contact. The sample is introduced into the mobile phase, wich will transport it inside the chromatographic system. By sliding the mobile phase over or stationary phase, competitive balances are established between the two phases and the substances that make up the mixture: therefore, the components of the sample enter the chromatographic system together but exit separately. When the mobile phase is a gas, the technique is called gas chromatography.
One of the most used gas chromatographic systems for the most transversal applications is Gas chromatography-mass spectrometry, used to study liquid, gaseous or solid samples; in thi approach, once the components leave the GC column, they are ionized and fragmented by the mass spectrometer using electron or chemical ionization sources; then ions are separated based on their different mass-to-charge (m/z) ratios. When a complex sample is separated by GC-MS, it will produce many different peaks in the gas chromatogram and each peak generates a unique mass spectrum used for compound identification. In that way, using extensive libraries of mass spectra, unknown compounds and target analytes can be identified and quantified.
In the tanning sector, many organic analytes potentially responsible for leather problems can be identified (antioxidants, plasticizers, hydrocarbons, etc.).
It is also possible to use a sampling system of the Purge and Trap type. It consists of the gas chromatographic analysis of the substances extracted from an inert gas, pre-concentrated in an adsorbent trap and cryogenically focused. This sampling system allows to determine volatile substances of particular interest in the tanning sector, which can provide useful information on the origin of specific defects.

Novel Non-Destructive Testing

Non-destructive testing (NDT) methods are defined as a set of technologies to verify processes and products in accordance with suitable quality control requirements. Any NDT method should preferably guarantee some important technical prerequisites, such as non-invasiveness and the ability to perform non-contact full-field measurements. There is a wide variety of NDTs used in very different sectors. However, NDTs relate more to industrial processes and products. Examples of applications include checking the integrity of materials and components, measuring geometrical properties, detecting and assessing damage and defects or even monitoring process parameters, where some novel approaches will be shown for applications in the tanning sector in monitoring defects and quality features of leathers.

2 Materials and methods

90 cases of defects were analysed: each case concerned leather and/or leather articles of different origin and for different intended uses (furniture, automotive, footwear, clothing, leather goods); more in detail: 30 cases for Furniture; 30 cases for Footwear; 10 cases for Leather Goods; 10 cases for Clothing; 10 cases for Automotive. Where deemed necessary, chemical products used in the production process were also analysed, as well as products and materials other than leather used to assemble the finished articles (adhesives, fabrics, synthetic linings).

The samples were analyzed with the following instruments:

- *Spectrum One ATR-IR (Attenuated Total Reflection Infrared)* Spectrometer (Frequency range: 4000-600 cm^{-1}).
- *Wild Heerbrugg* Stereoscope equipped with *OPTIKA* Room B3 Digital Camera.
- *Zeiss - Phoni 3* - Optcal Microscope (0.01 - 1 mm - Resolving power: 0,001 mm).
- *Zeiss EVO MA10* Scanning Electron Microscope (Magnification: 10x - 200,000x Resolving power: 2µm) equipped with *INCA X-act ENERGY-250XT* detector.
- Gas-chromatograph *TRACE 1300-THERMO SCIENTIFIC* coupled to a *TSQ 9000-THERMO SCIENTIFIC* mass spectrometer detector and equipped with *ATOM XYZ-TELEDYNE TEKMAR* autosampler for analysis of volatiles on solid and liquid samples.
- *STDQ600 TA* Instrument for DSC/TGA (Differential Scanning Calorimetry/Thermogravimetric Analysis equipped with a *THERMOSTARTM* Mass Spectrometer.
- *Electronic Speckle Pattern Interferometry System* (Laser 0.5W, wavelength 532nm) - *KA Associates, Coventry, Storrs, CT* (USA)

3 Results and Discussion

3.1 Main diagnostic techniques for defects detection

The 90 cases of defects were analysed using the main diagnostic approaches used to search for the causes of leather problems [2,3,4,5,6,7,8]. The cases investigated were chosen in such a way as to have a case history as representative as possible of all the main categories of defects found on the leather, as can be seen from table 1, showing an overview of the type of defects found and their incidence by category of article and their overall impact.

TYPE OF DEFECT		INCIDENCE OF THE DEFECTS BY TYPE OF LEATHER INTENDED USE [% incidence]					INCIDENCE BY TYPE OF DEFECT FOR 90 TOTAL CASES [% incidence]
		FURNITURE (30 CASES)	FOOTWEAR (30 CASES)	LEATHER GOODS (10 CASES)	CLOTHING (10 CASES)	AUTOMOTIVE (10 CASES)	
STAINS	STAINS from metals	23,3	3,3	0,0	0,0	10,0	10,0
	STAINS from organic substances	6,7	10,0	30,0	10,0	0,0	10,0
	STAINS from soaps	6,7	10,0	0,0	0,0	10,0	6,7
	STAINS from saline repousse	0,0	10,0	0,0	10,0	10,0	5,6
	STAINS from fatty repousse	0,0	6,7	30,0	40,0	0,0	10,0
	STAINS from microbial attacks	0,0	6,7	30,0	20,0	0,0	7,8
DIFFUSED CHROMATIC ALTERATIONS	Yellowing	26,7	0,0	0,0	0,0	20,0	11,1
	Other alterations	16,7	3,3	0,0	0,0	0,0	6,7
LACK OF DYEING HOMOGENEITY INSIDE THE LEATHER SECTION		6,7	3,3	0,0	0,0	10,0	4,4
DETACHMENT OF THE FINISHING		6,7	26,7	0,0	0,0	20,0	13,3
MORPHOLOGICAL DEFECTS AND CRACKS IN THE FINISHING		6,7	13,3	0,0	0,0	20,0	8,9
LOW MECHANICAL RESISTANCE		0,0	6,7	10,0	20,0	0,0	5,6

Tab. 1. Incidence of defects by analysed cases

The main techniques most commonly used to characterize defects and identify their causes, for each defect category, are shown in table 2. As shown in the table, and as a result of previous works, the resolution of individual cases required the simultaneous use of more than a diagnostic technique, even if some of these have proved to be decisive for characterizing specific critical issues.

TYPE OF DEFECT		% INCIDENCE BY TYPE OF DEFECT FOR 90 TOTAL CASES	MAIN DIAGNOSTIC TECHNIQUES
STAINS	STAINS from metals	10,0	SEM-X-Ray Probe
	STAINS from organic substances	10,0	GC-MS/ATR-IR
	STAINS from soaps	6,7	SEM-X-Ray Probe/GC-MS
	STAINS from saline repousse	5,6	SEM-X-Ray Probe/ATR-IR
	STAINS from fatty repousse	10,0	GC-MS/ATR-IR
	STAINS from microbial attacks	7,8	SEM/OM/GC-MS
DIFFUSED CHROMATIC ALTERATIONS	Yellowing	11,1	ATR-IR/GC-MS/SEM-X-Ray Probe
	Other alterations	6,7	GC-MS/SEM-X-Ray Probe/ATR-IR
LACK OF DYEING HOMOGENEITY INSIDE THE LEATHER SECTION		4,4	SEM-X-Ray Probe/PCM
DETACHMENT OF THE FINISHING		13,3	ATR-IR/GC-MS/OM/PCM
MORPHOLOGICAL DEFECTS AND CRACKS IN THE FINISHING		8,9	PCM/OM/DSC-TGA/ATR-IR
LOW MECHANICAL RESISTANCE		5,6	PCM/OM/DSC-TGA

Tab. 2. Main techniques vs type of defects

The main contribution of each of these techniques in the characterization of defects and in the identification of their causes will be discussed in the following**.**

3.1.1 The role of ATR-IR (Attenuated Total Reflection Infrared) Spectroscopy

As found from the examination of the cases covered by this study and from previous works [2,3,4,5,8,13], the technique was mainly used to solve problems related to finishing, in relation to critical issues related to mechanical, chemical and chemical-physical finishing fragility. Examples are represented by cases in which the fragility towards some chemical agents, deriving from the leather or from the assembly materials migrated in the finishing, has determined the damage of some articles, due to the chemical nature of the finishing. For example, figure 1 shows the overlap of spectroscopic profiles of samples that have exhibited a different behaviour towards these agents: the profile of the damaged sample is specifically found to be characteristic of nitrocellulose-based finishes, more sensitive to the action of organic-polar solvents, compared to finishes based on polyurethanes.
More in detail, Figure 1, shows that the blue profile is typical of polyurethanes, given the presence of the following typical signals**:**

- Stretching vibration -NH at 3300 cm^{-1}
- Stretching vibration -C=O a 1720-1726 cm^{-1} (amide I)
- Bending vibration -NH at 1530 cm^{-1} (amide II)

The green profile is typical of nitrocelluloses, given the presence of the following typical signals:

- Two strong signals of symmetrical and asymmetrical stretching vibrations of $-NO_2$, at 1640-1650 cm^{-1} and 1275-1278 cm^{-1}
- Stretching vibration of -C–O, of glucopyranose ring at 1070 cm^{-1}
- Stretching vibration of $-O-NO_2$, at 840 cm^{-1}

Other cases have shown that both finishes consisting of nitrocellulose have shown a different behaviour to the action of protic solvents, due to the different nitration degree of nitrocelluloses, identified by the different intensity of the signals relating to the $-NO_2$ groups.

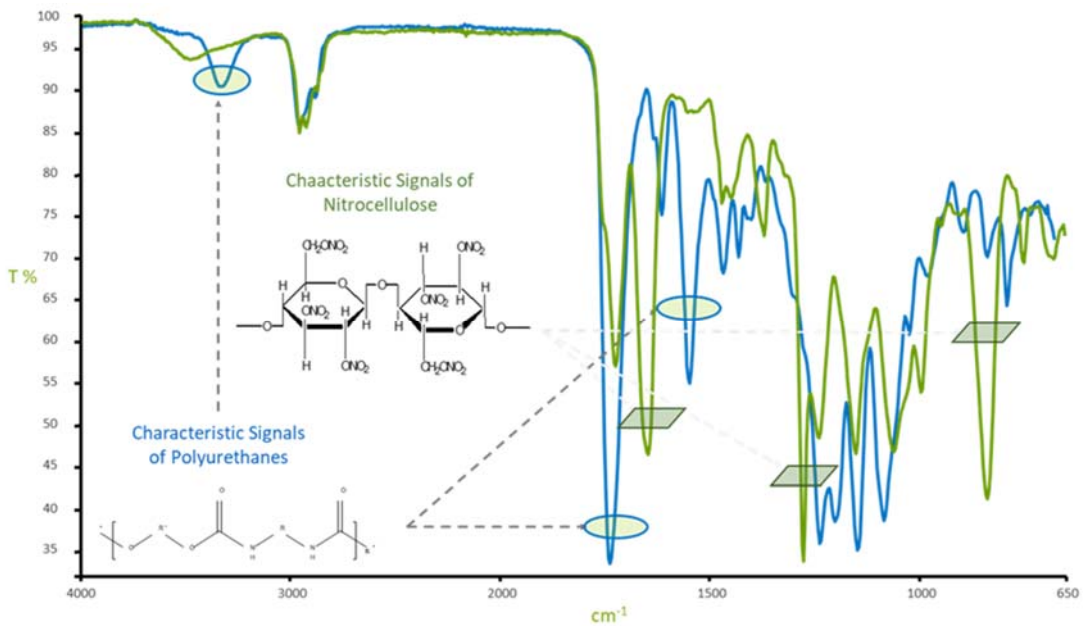

Fig. 1. IR spectra overlap of the surface of finished leather samples with two different polymers

The technique has also been effectively used to study cases of defects related to surface yellowing and related to the use of aromatic polyurethanes in finishing (Fig. 2), where the tendency to yellowing of these categories of polymers under given conditions of thermo-climatic aging (exposure to light and heat) is known[8,11,12].

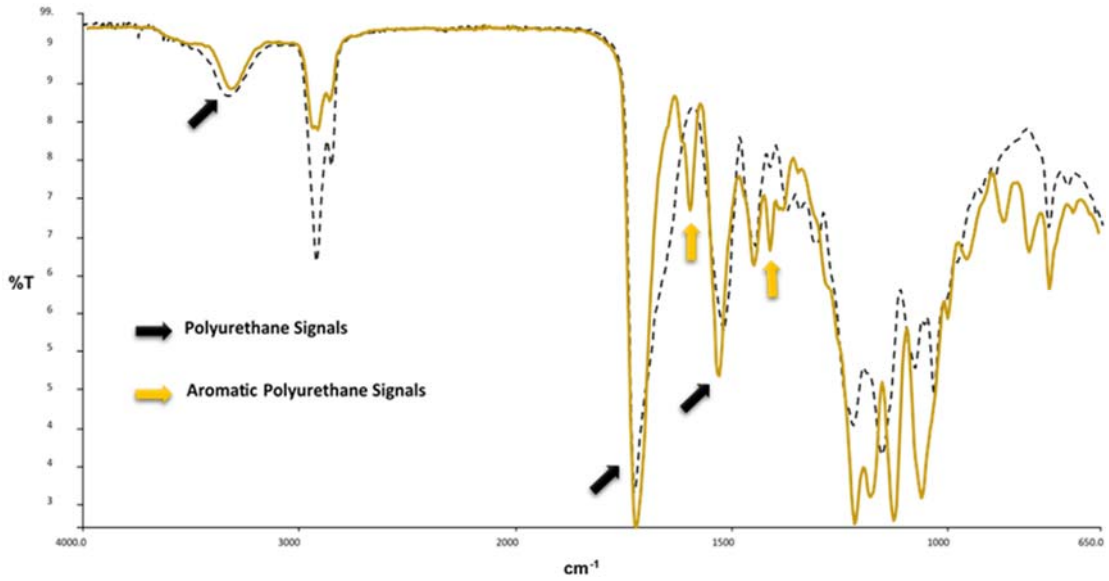

Fig. 2. IR spectra overlap of the topcoat of defective (yellow) and not defective (black) samples.

3.1.2 The role of Optical microscopy (OM)/ Phase-contrast microscopy (PCM)

Stereomicroscopy was proved to be generally effective for all preliminary surface analysis, in order to have some initial clues on the possible origin of defects, mainly concerning grain and finishing damage (Fig. 3).

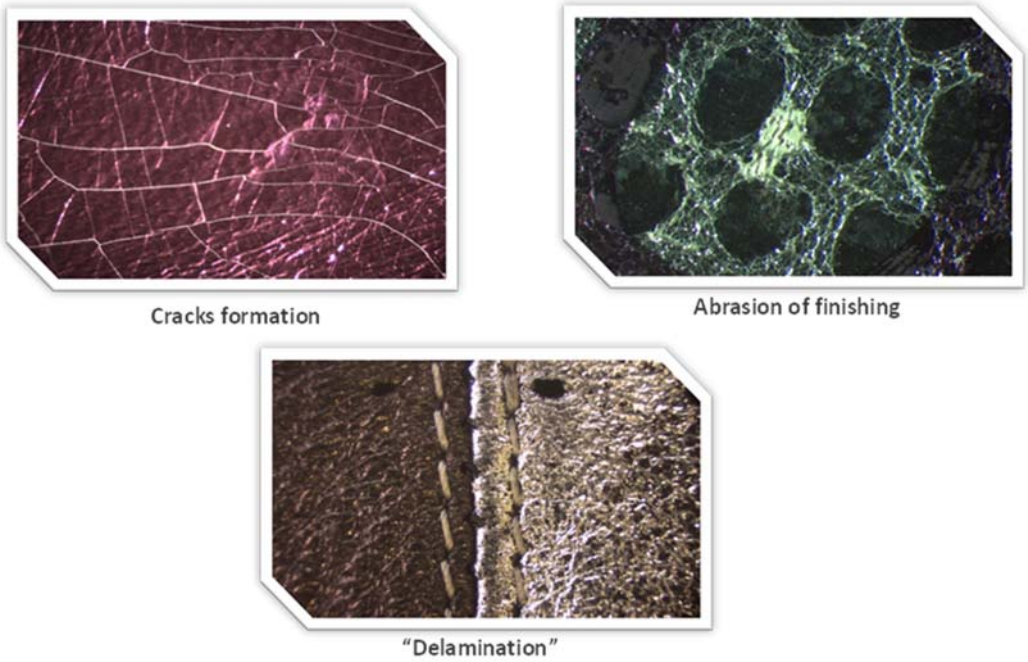

Fig. 3. Images obtained from the stereomicroscope of the surface of defective samples

The use of Phase-contrast microscopy (PCM) for investigating the possible causes of mechanical-structural finishing defects, through the examination of the leather section was then proved to be very decisive (Fig. 4).

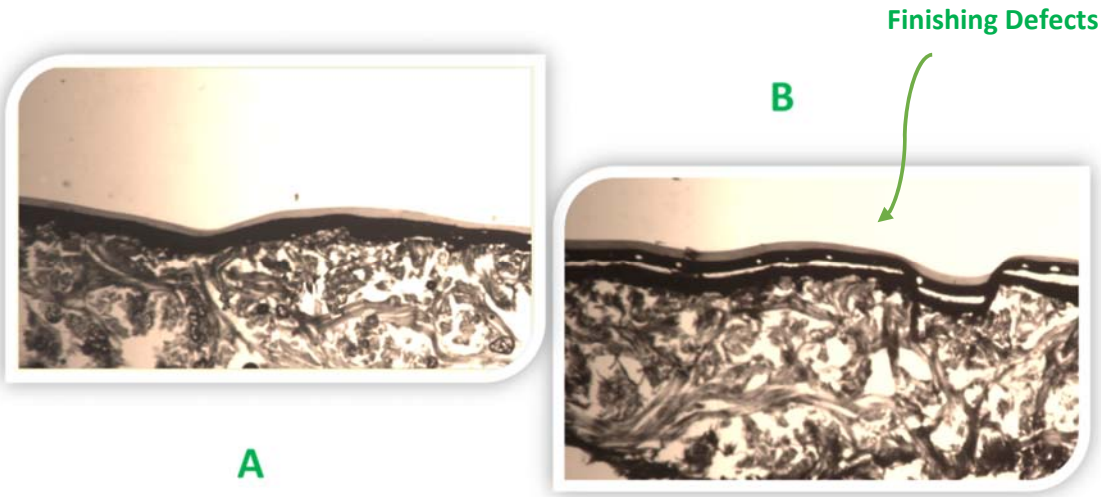

Fig. 4. Images obtained by the phase contrast microscope,
of the section of two samples of patent leather (not deteriorated - A; deteriorated - B)

This technique can also provide the first clues on possible causes of defects related to process errors, allowing to identify the presence in section of hair residues, blood residues and leaks in the structural characteristics of the leather fibres.

3.1.3 The role of Scanning Electron Microscope equipped with X-Ray Probe (SEM-X-Ray Probe)

This technique has proved to be one of the most useful and transversal for the study of leather defects, almost always proving crucial for the understanding of the possible causes and phenomena underlying the origin of the critical Issues[6].
Concerning the morphological and topographical analysis, the technique allowed the investigation of the crystalline, rather than amorphous morphological features of deposits, suggesting their possible nature (saline, fatty, organic, etc.) (Fig. 5).
Beside the study of defects, morphological analysis allowed the characterization of animal species, when it has not been possible by optical microscopy, that was in all those cases in which the leather surface was heavily damaged or in slightly grounded leathers, where grain design was hardly recognizable.
Finally, the topographic analysis of leather surface was proved to be suitable for finished leathers affected by peculiar defects, due to the presence of bumps, holes, bubbles folds and halos.

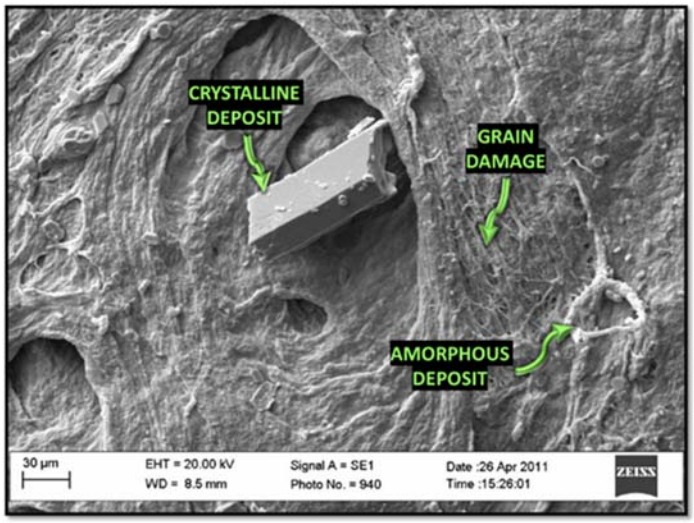

Fig. 5. SEM morphological analysis of leather defects

SEM analysis was also fundamental for the study of defects caused by microorganisms: there are in fact many microorganisms that can cause damage to the leather; the typology and the amount of microorganisms found, resulted to vary according to some environmental factors, as pH, temperature, water activity, concentration of biocides and so on. As found also in previous studies (ref), microorganisms found on leather belong both to *Prokaryota* (as *bacteria*) and to *Eukaryota* domain (as *moulds* and *yeasts*, from *Fungi* kingdom). However, the most commonly encountered microorganisms was proved to be wide set of *fungi* were found, with particular reference to *moulds*. They are recognizable through peculiar spores, as the moulds belonging to *Ascomycetes* class, with particular reference to the ones from genus *Penicillium* and *Aspergillus*. Most of these can be found in pickled, wet-blue and finished leather, resulting to be resistant at high temperatures and to have a quick growth in presence of an high humidity degree. These *moulds* differ by colour as much as by appearance; normally ones from genus *Penicillium* are glassy or velvet looking and are green or blue coloured, while the ones from genus *Aspergillus* form yellow or black stains, where SEM analysis resulted to be effective for the recognition of both genus (Fig. 6). Most of stains produced by moulds formations on leather among all the tanning process resulted to be blue, gray or black coloured. The blue formations have been normally identified as *Penicillium glaucum*, the gray ones as *Mucor mucedo*, while the black ones have been classified as *Aspergillus niger*.

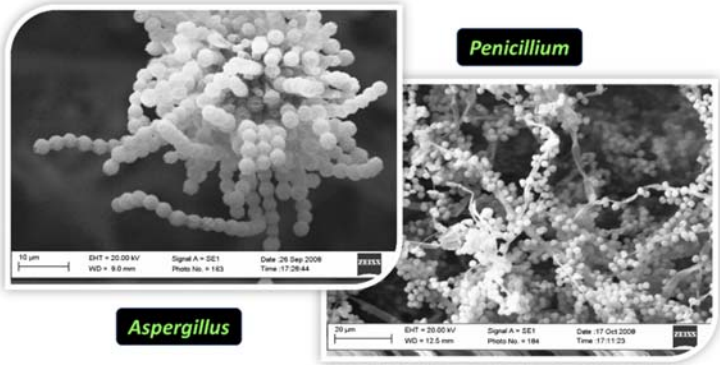

Fig. 6. SEM study of defects caused by microorganisms

When other techniques are coupled to the SEM analysis, such as GC-MS, it is also possible to get clues to the state of degradation of the leather, which suggests the exposure of the articles to climatic conditions favourable to the development of microorganisms, and it is also possible to obtain information on the biocides used in the process, whose quantity and type, can play a certain role in fostering microbiological attacks in leather articles.

Finally, SEM-Microanalysis, was found to be one of the most effective and crucial technique, particularly to study the possible origin and causes of metal-based defects; during the tanning process, there are many metals that can come into contact with the leather, both accidentally and due to their use often foreseen in the processing, where they can be involved in leather defects, when able to determine:

- coloured spots on the leather surface, of different size and appearance, sometimes in combination with deposits;
- non-homogeneity in the dye distribution, both on the surface and across the leather section.

These main types of defects are generally due to formation mechanisms which can be:

- direct type, through the formation of coloured metal compounds (for example oxides, sulphides, etc., of metals such as lead, copper and iron or coloured compounds deriving from interactions of some metals such as iron and magnesium with vegetable tanning agents, as well as from more complex interactions between metal and organic substances, which can occur at the finishing level);
- indirect type, in the event that metals (commonly chromium and calcium) are involved in the formation of compounds that can produce a non-homogeneous absorption of tannery chemical products, with particular reference to the fattening and dyeing phases. In some cases, these mechanisms can be complex and difficult to identify.

Figure 7 shows some metal-based defects investigated by SEM-Microanalysis.

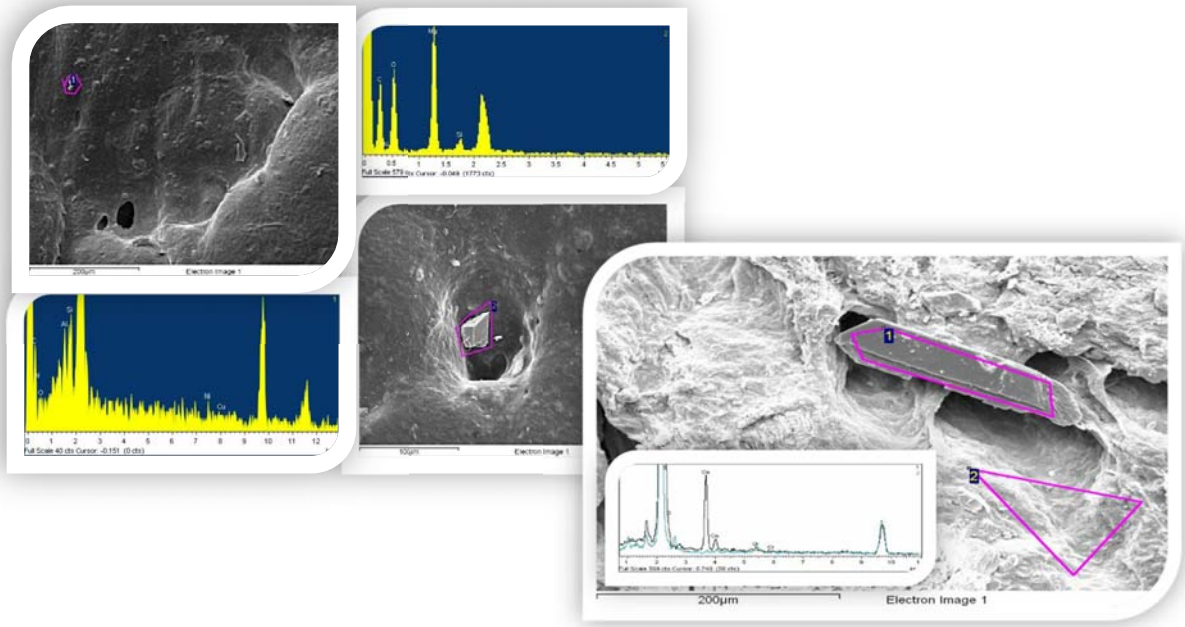

Fig. 7. SEM-Microanalysis of metal based-defects

3.1.4 The role of Differential Scanning Calorimetry/ Thermogravimetric Analysis (DSC/TGA)

This technique was proved to be effective both for studying defects related to possible critical issues of finishing polymers, and defects related to structural issues of the components of the leather, such as collagen itself, when stabilized in a non-effective way.

With reference to the defects of finishing polymers, the knowledge of the degree of crystallinity of the polymers, the determination of the glass transition temperature, and more generally of the parameters correlated to their chemical, structural and consequently performance characteristics, has represented a crucial tool for the comparative study of finishes and for the design of improved and innovative solutions (Fig. 8).

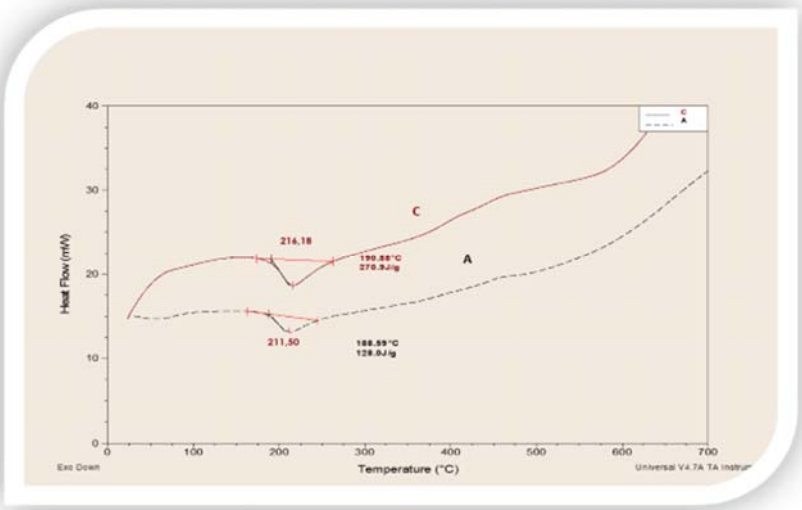

Fig. 8. DSC study of two finishing samples based on nitrocellulose characterized by a different degree of nitration

These diagnostic approaches have also proved to be potentially strategic for the characterization of possible defects related to the thermal resistance of new generations of leathers, particularly in relation to the possibility of carrying out comparative studies of thermal stability of leather processed with different types of tanning agents; these studies complete and enrich the macroscopically obtained information by determining the shrinkage temperature of the leathers (according to UNI EN ISO 3380: 2015); more in detail, differential scanning calorimetry (DSC) allows to study the enthalpy changes associated with the denaturation of collagen, of which contraction represents the macroscopic manifestation. These changes are associated with other chemical and mechanical characteristics of the material, as a result of the breaking of non-covalent bonds that stabilize the collagen with the increase in temperature.

3.1.5 The role of Gas chromatography-mass spectrometry (GC-MS) equipped with autosampler for VOC analysis

The use of Gas chromatography-mass spectrometry (GC-MS) was proved to be particularly effective in all those cases of defects caused by organic substances; more in detail, many stains or diffused chromatic alterations resulted to be related to the migration of organic pigments or fatty substances, directly involved in the formation of defects; furthermore, other organic substances, such as antioxidants, plasticizers, fats, biocides, whose presence was revealed with this technique, were involved in the defects, through more indirect and more complex mechanisms.

Moreover, when combined with autosampler for VOC analysis, this technique allowed to reach also Very crucial information for the resolution of some cases of defects; in more detail, the analysis of VOCs made it possible to identify two main classes of compounds capable of providing clues to the origins of specific critical issues:

- aldehydes, ketones, furans, sulphur compounds, which can provide indications on the state of degradation of the organic components of the leather, such as fats, in order to clarify the possible contribution of thermo-climatic aging conditions on the onset of defects related to degradative phenomena of leather, finishing or involved in the development of microorganisms;

- solvents deriving from leather, such as production residues or deriving from assembly materials, in order to identify the causes of degradation of some components of the finishing sensitive to the action of these solvents (Fig. 9).

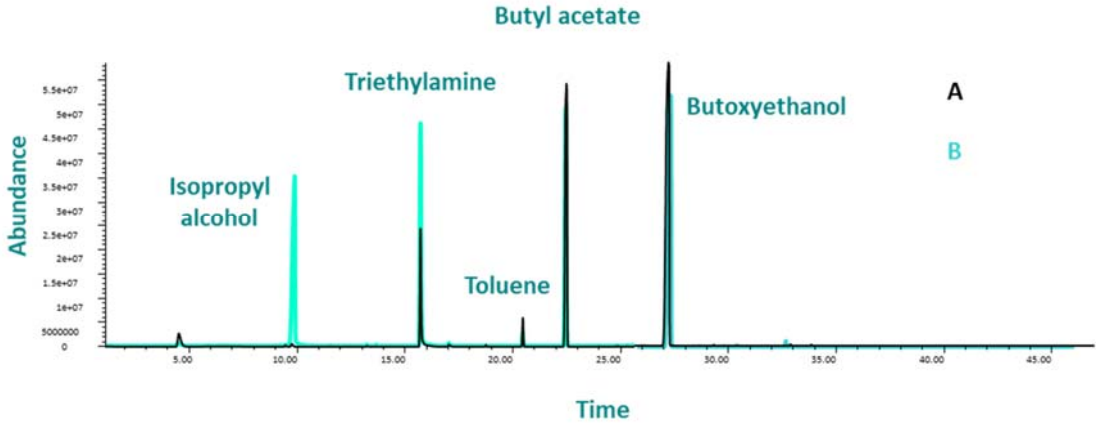

Fig. 9. VOC comparative analysis for the evaluation of residual solvents in two different samples

3.2 Main Novel Non-Destructive Testing for the detection of leather defects

Different NDT methods have been developed to meet different needs [14], some of which have proved suitable for the timely analysis of leather defects. Among many others, optical interferometric techniques — using lasers — have found use in the testing of various types of composite materials and textiles. This type of technology, thanks above all to the evolution of sensors, the improvement of calculation capacities and the increased efficiency and compactness of laser sources, offers the possibility of real-time control and monitoring in full field on articulated surfaces such as those made of leather objects. Interferometric techniques are based on the interference phenomenon and, in particular, on the so-called 'speckle'. Speckle — which gives its name to one of the most widely used techniques [15], Electronic Speckle Pattern Interferometry (ESPI) — is a phenomenon based on the coherence of the light used (i.e. the laser), which when striking a rough surface, makes a random phase jump without losing its coherence. This generates an interference effect that can be constructive or destructive, resulting in images composed of dark and bright 'dots'. This dot pattern is used to detect surface variations with a sensitivity below the wavelength of the laser used (i.e. in the visible range of a few hundred nm). The basic scheme of the optical setup is shown in figure 10.

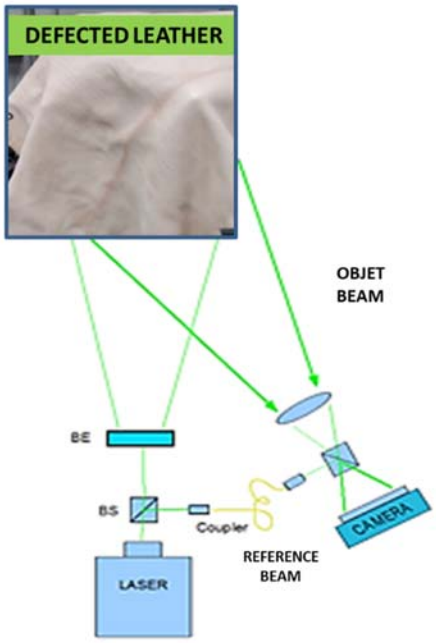

Fig. 10. Basic scheme of the optical setup of a speckle system

If the object to be examined is subjected to adverse conditions, e.g. through heating, it changes its geometric properties and consequently the way it reflects light, i.e. its speckle. The digital comparison of the different speckles leads to the creation of an image showing a series of overlapped fringes on the screen of the surface being examined. By observing the shape and direction of the fringes, it is possible to highlight surface inconsistencies caused by damage such as cuts or incisions, leather discolouration, scratches or curling. An example of an evaluation of a piece of leather (right) is shown in the figure 11, where from the processed image of the fringes (left) it is possible to highlight the presence of barely visible scratches and cuts on the surface of the leather.

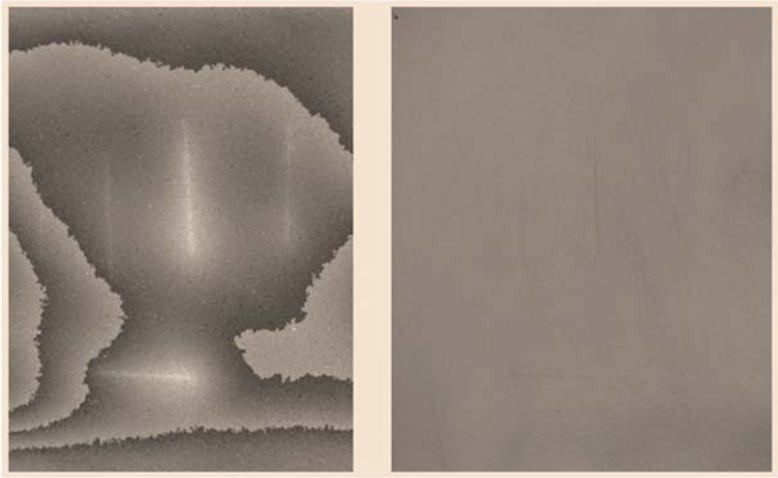

Fig. 11. NDT of a slightly defective leather sample

In addition to techniques based on interferometry, there are also computer vision techniques, which are based on the scanning and processing signals and images at different wavelengths, from the visible to the infrared (NIR, SWIR etc.). More generally, a computer vision system is a set of hardware and software used to equip a machine with functions that are typical of human vision. The hardware used for two-dimensional imaging involves the use of cameras, based on CCD or CMOS sensors, which can be a) linear, scanning a single line at a time but also able to scan a large number of lines per second and with photosensitive elements that tend to be large, but which require an auxiliary external movement and trigger system to form a 2D image; b) frame, directly scanning a two-dimensional (2D) image and operating at slower speeds than linear cameras and with pixel dimensions that can also be particularly small. Cameras can scan a variable number of channels: one for monochrome cameras, three for colour cameras (Red, Green, Blue), many more for multi-spectral or hyperspectral cameras. Depending on their sensitivity to different wavelengths, the channels may cover the visible spectrum, the infrared (near or far) or wide frequency ranges as in hyperspectral techniques, which associate each of the many channels with a specific, very narrow band of wavelengths. The choice of sensor type depends on the type of behaviour or defect you wish to detect and the conditions under which the images can be captured. In the tanning industry, but also in all industrial applications, it is necessary to make the data acquisition and processing operations in line, so robotic systems specifically designed for handling, scanning and analysing products in line are often used. These systems include automated guided vehicles (AGVs), which can operate autonomously to move sensors and N-degree-of-freedom robotic arms, i.e. they can be used to handle products and to position sensors so that even very large areas can be inspected.

Finally, at the software level, a vision system must be able to analyse the acquired data in order to extract relevant information, in this case, the presence and possible characterisation of a defect. Historically, image analysis has been carried out by defining, extracting and identifying particular distinguishing features of a product in order to analyse colour configurations, surface structure or otherwise homogeneous and non-homogeneous regions of the image. Once the features have been extracted, a classification algorithm can recognise which areas of the image are defective or not, based on the numerical values of the extracted features. In this context, in recent years, the advent of deep learning techniques [10,16], a family of artificial intelligence models that are particularly effective for image analysis, has made it possible to tackle classification problems (and therefore also NDTs) with a new approach based on artificial and data-driven neural networks, thanks to the ability of these models to learn from the data autonomously which are the best features to extract. These models are generally trained in a supervised manner on so-called labelled datasets, i.e. with images for which the defect or no defect classification is known and available a priori. Under appropriate conditions, these algorithms are able to generalise what they have learnt and thus recognise and characterise defects even when required to process new (in-line) images that were never seen in the training phase. This feature is particularly important in applications, such as NDT of leather, in which the intrinsic variability of the material, of natural origin, makes constructing an exhaustive case history of the types of defects and their possible manifestations extremely complex. In this case, having algorithms capable of autonomously constructing sufficiently general representations of both the defect-free material and the different classes of anomalies constitutes a powerful tool for solving NDT problems.

4 Conclusion

The use of advanced diagnostic techniques considered, mainly non-destructive or based on the use of small amounts of samples, allows to obtain crucial information for understanding the phenomena capable of originating the most disparate leather defects; specifically, the use, also conjugated of spectroscopic methods, of specific gas-chromatographic techniques, of optical and electronic microscopy approaches and of systems for thermal analysis, allows to identify errors and critical issues deriving from the specific phases of the production process, in order to plane improvement actions and designing more efficient and innovative solutions to guarantee product quality.

Moreover, it is possible to act in a preventive and predictive manner through the increasing use of NDT technologies and automated approaches for the in line control of production: interferometric optical techniques, and more generally computer vision techniques, are suitable for fast inspections and were found to be consistent with future trends in NDT technologies, which will see the development of automated non-destructive testing in the coming years thanks to the increasingly widespread use of artificial intelligence (deep learning) and robots. The tanning industry and the production chain can certainly benefit from these technological developments in order to achieve ever higher standards of quality and functionality of products that use leather.

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