ADVANCED DIAGNOSTICS AND INNOVATIVE SOLUTIONS FOR LEATHER DEFECTS: THE PROBLEM OF YELLOWING

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Abstract. Providing peculiar enhanced features to leather items is a factor of primary importance for the marketing of high-end articles; although the tanning production is oriented to satisfy a wide market range, it is mainly in the "high end" and "premium luxury" categories that the quality properties of the material are more expressed, indeed. And it is particularly on this market segment that the main current challenges have been focalized, according to the growing requirement of technological innovation, sustainability and product quality. The light-coloured leathers, with particular reference to the white items, belongs to the category of materials designed especially for the luxury market. For this type of articles, the uniformity of the colour and the agreeableness of the overall surface appearance are crucial requirements for the most of international fashion and luxury brands. One of the most common and undesirable defects of this type of article is the alteration of the colour, with particular reference to the localized or diffused effects of yellowing of the surface of the material. There are several causes able to contribute to the production of this type of defects, due to the complexity of the matrix and to the variability of traditional or innovative production processes used: from the intrinsic fragility, photosensitivity and thermo-sensitivity of the finishing polymers, to the chemical instability of some components of the finishing pigments, further than the presence of photosensitive chemical additives, the migration of skin components or assembly components of the manufactured articles (fats, fillers, plasticizers, glues, etc.), up to the indirect contribution of environmental and thermo-climatic factors able to affect negatively the performance of the material. SSIP, which has always been involved in research and consulting activities for the leather industry with regards to defect monitoring, through this work, would offer an overview of all the main tools for advanced diagnostics (with particular reference to Scanning Electronic Microscopy and to chromatographic and spectroscopic methods) aimed to the identification of the causes of yellowing, beside to explore innovative solutions for the development of strategies for the resolution and/or minimization of the problem of yellowing. The technical solutions will include innovative tanning processes, innovative finishing methods, and leather surface treatments carried out in order to provide a sensible attenuation of surface absorption of IR and UV-visible radiation.

1 Introduction

The progress achieved in the field of tanning technology, have largely reduced the risk of the formation of many defects on the manufactured leather articles. However, there are some persistent issues affecting the tanning industry. More in detail, in many of the leather articles, particularly in those destined for a high-end market, frequently characterized by a light colour, the problematic of yellowing, where present, is particularly evident.

The most common causes of yellowing are known in literature [6,7,8,9], however the phenomenon generally appears to be rather complex, for the following main reasons:

- In addition to the common components inside the leather and the finishing, other substances used as additives can cause the defect;
- In some cases, the substances derive from assembly materials used for the production of the finished articles;
- More than one chemical component may be involved in the problem;
- Some chemical agents are of environmental origin;
- Other environmental/external factors can be involved in causing the problem (such as exposure to light or heat of the samples);

- The defect may originate from a set of previous direct and indirect factors that combine to cause the problem;
- The problem may arise after the article is marketed, as it does not appear immediately, thus falling within the hidden defects.

An overview of the main causes able to determine the problem is shown in Figure 1 below.

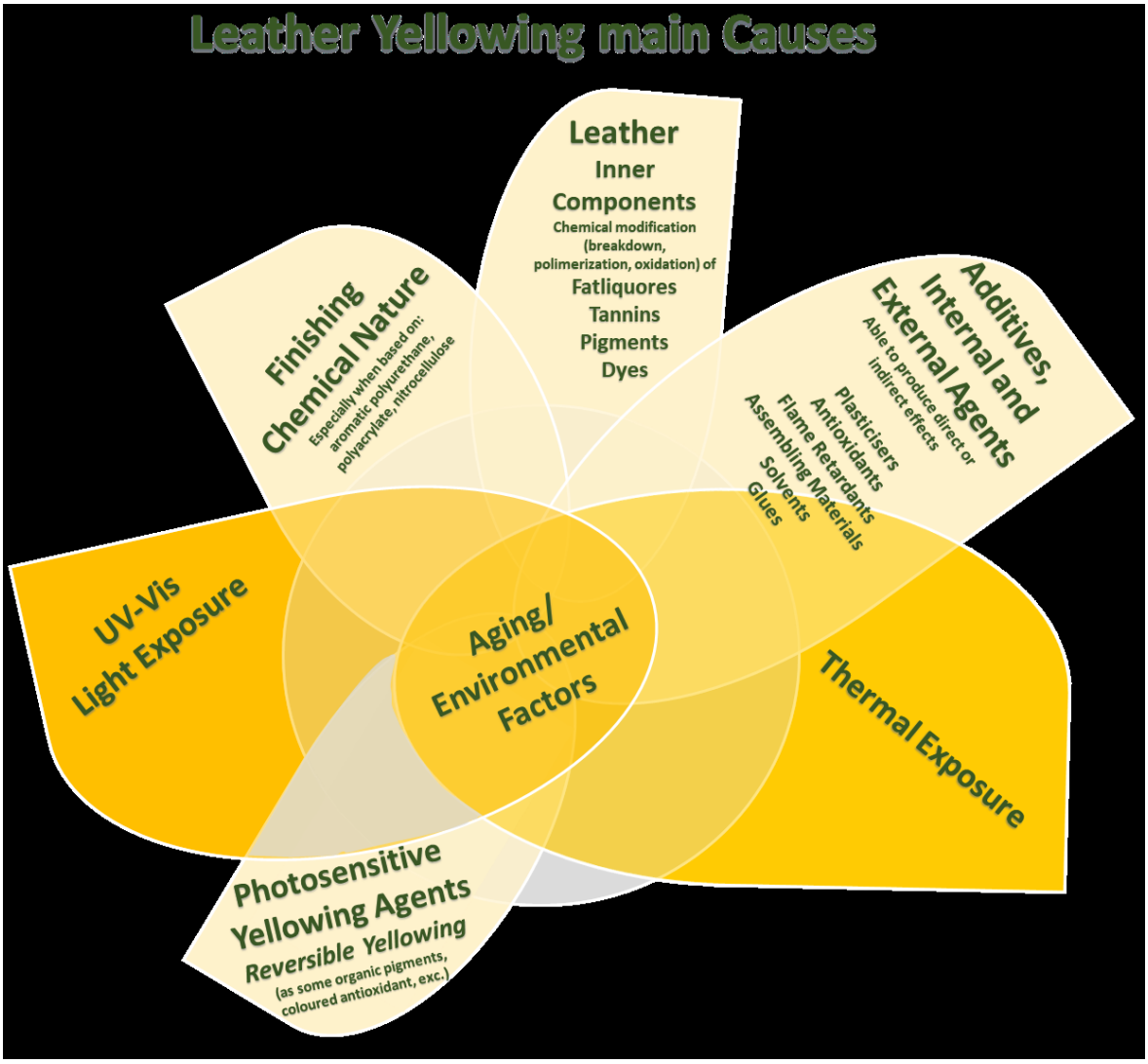

Fig. 1. The different main factors able to promote leather yellowing.

As shown in the figure, among the most common causes of yellowing, there may be the chemical nature of the finishing[5]: particularly, due to the presence of photo and/or thermosensitive polymers, as well as to chemically labile polymers which, in the presence of certain environmental conditions or atmospheric agents, may be passible of oxidative or hydrolytic degradations. Examples are constituted by nitrocellulose-based finishes, some polyacrylates and aromatic polyurethanes.

Other "physiological" causes of yellowing are related to degradation phenomena affecting fatty substances, due to the animal's natural fats or to fatliquors used during the production process; it is known, in fact, that many oils and fats, particularly rich in unsaturations, following to aging, or exposure to thermo-oxidative or photo-oxidative degradation factors, can produce degradation products characterized by a yellow-brown colour.

Further components physiologically passable of yellowing are some dyes and pigments; generally the leathers are dyed using a mix of these components, some of which may have a different resistance

to light; for example, some yellow azo-dyes exhibit better resistance to light, compared to those of red or blue colour, and therefore, following exposure to light, the yellow colour may be prevalent[6].

Natural and synthetic tannins can also be involved in the problem, mainly due to photo-oxidative mechanisms.

Also the possible interaction between chemical agents used in the tanning process (retanning, fatliquors, dyes, etc.) can play a crucial role in the problem. Furthermore, other chemical agents used as additives, or deriving from the assembly materials (plasticizers, fillers, and some same antioxidants, and phenolic-based components, sometimes used to stabilize some of tanning chemicals, solvents, adhesives), can determine the problematic, directly (if they themselves or their products of degradation or reaction with atmospheric agents are yellow), or indirectly, by promoting the passage of coloured components to the surface.

In any case, the environmental exposure factors can determine the conditions to foster the problem, either by promoting the degradation of the yellowing agents, or by promoting the migration of coloured components on the leather surface. Also, some atmospheric agents, such as nitrogen oxides, can contribute by reacting with active components of the leather, determining the problem (as in the case of some reactive dyes).

To increase the complexity of the scene, some yellowing phenomena are reversible: this is the case, for example, of some coloured substances, mainly organic, rising to the surface, following migratory phenomena, in the presence of particular thermo-climatic conditions, where they are photosensitive, and therefore degraded by exposure of the articles to light (UV-Vis).

Other types of yellowing are reversible depending on the pH (like some phenolic products, which give yellow adducts in an alkaline environment and colourless in an acid environment).

In this work, 32 cases of yellowing were considered, as a result of research and consultancy activities, carried out for leather producers and users, for different destination uses of the material. The investigations carried out offered a widely comprehensive overview of the problem where the causes were identified in a very targeted way, sometimes only thanks to the use of advanced diagnostic tools.

In the following sessions, a framework of technical-analytical approaches and strategies to identify the cause or causes of the problem will be offered. The issue of resolution and prevention of defects will also be addressed, where necessary, also through innovative approaches, which will be explored and developed to respond in a targeted manner to this type of problem.

2 Materials and methods

32 cases of yellowing were investigated, by analysis of leather and leather articles of different origin (bovine, ovine, caprine) for different uses (furniture, automotive, footwear, leather goods). 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:

- *Heraeus Industrietecnik Alpha LM* Xenotest
- *Binder FD 115* Heating Chamber
- *Pegasil – Zipor EL-83* Veslic Machine.
- *Atlas/SFTS B.V.* Martindale Abrasion Machine.
- *HP GC System/6890 - HP/5973 Mass Selective* Chromatograph equipped with a Purge & Trap *O.I.Analytical 4660* Sampler.
- *DANI GC1000* Gas-Chromatograph - Flame Ionization Detyector.
- *Spectrum One ATR-IR* Spectrometer.
- *Zeiss EVO MA10* Scanning Electron Microscope equipped with a *INCA X-act* detector.

3 Results and Discussion

3.1 Technical and diagnostic approach

The approach used to identify the possible causes of the problem involved the use of adequate investigation strategies, starting from the simplest methods for merceological analysis, to pass to the execution of leather performance evaluation tests, to finally arrive at more sophisticated instrumental analytical techniques, where the cause of the defect was found to be more difficult to identify.

The initial product analysis of the samples started from a careful observation of the defect and was based on the following general considerations:

- the presence of yellowing both on the flesh side and on the grain side of the articles, in general, suggests that internal leather components can be migrated, such as fatty substances, and also suggests that the problem is not solely attributable to finishing; on the other side, if the yellowing, or the tendency to yellowing, even after specific aging tests, is observed only on the finished grain side surface, it would be advisable to focus the subsequent investigations mainly on the finishing;
- the particular location of the defect in a finished article also suggests other important elements for the investigation: if the yellowing is present only in the areas exposed to the environment, and not in the hidden ones (for example, below the seams, in assembled artifacts), this data suggests that the problem may have arisen following phenomena affected by the presence of light or atmospheric agents (such as in cases of photo-oxidative yellowing); if the problem is found, in the finished articles, in correspondence of gluing areas, it is possible to assume the involvement of the glues or other assembly materials; if, within a sample assembled with leather cuttings of different animal origin, the yellowing or the tendency to yellowing, even after specific aging tests, is observed only for some clippings, this finding suggests that the defect may be related to the nature of the leather used.

During the merceological analysis, the visual examination was sometimes supported by optical microscopy techniques, both through stereomicroscope analysis and through the phase contrast optical microscope, where it was necessary to observe the cross section of defective leather samples. For further details on the morphological features of the samples, the Scanning Electron Microscopy (SEM) was also used.

The product analysis of defective and non-defective samples was also repeated after performing tests to evaluate the performance of the material and to simulate aging after exposition to light, to heat and to the action of external agents. The mainly performed tests were:

- Artificial light exposure test (Xenotest method, according to UNI EN ISO 105-B02), from 24 to 72 hours;
- Artificial aging to heat and artificial aging to heat and humidity, according to the UNI EN ISO 17228 - 6C and 7B method (72 hours aging at 60 °C - 96 hours aging at 50 °C and 90% R.H);
- Colour fastness to rubbing, according to the UNI EN ISO 11640 method (before and after aging tests);
- Colour fastness to migration into plasticized PVC, according to the UNI EN ISO 15701 method (before and after aging tests);
- Exposure to solvent vapors and buffering with solvent soaked pad (internal method SSIP MI-PF 001 - 2008).

As chemical tests the determination of matter soluble in dichloromethane was performed, according to the UNI EN ISO 4048 method.

The merceological analysis of the samples surface was also supported by infrared spectroscopy, particularly by ATR-IR spectroscopy, a technique that allows to analyse the surface of solid state samples; this technique resulted particularly useful for identifying the chemical nature of the finishing and for assessing whether the problem was related to this. In general, the technique was also used to advance hypothesis on the possible chemical nature of surface organic substances (other than finishing, such as plasticizers, fats, phenols, adhesives, etc.).

Where the first investigations led to the hypothesis that the problem could depend on fats (high content of matter soluble in dichloromethane, yellowing also present on the flesh side, easy removal of the color by solvent), we proceeded with an in-depth study of their chemical nature: the degree of unsaturation was estimated using the determination of the Iodine Value; sometimes in-depth instrumental chromatographic analysis was necessary, through the use of GC-MS (Gas Chromatography - Mass Spectrometry) techniques, also used for the identification of other organic agents potentially involved in the defect and GC-FID (Gas Chromatography - Flame Ionization Detyector).

More in detail, the second of the aforementioned techniques proved to be particularly useful for the speciation of all the fatty substances contained in the organic extracts of the leather, in the colored patinas taken by buffering the surface with dicoloromethane or other organic solvents, as well as in the organic fraction of fatliquoring chemicals subjected to liquid-liquid separation; the overlap of the chromatograms allowed us to attribute the possible cause of the problem to chemicals rather than to the natural fats of the skin.

For further details on the chemical nature of substances with a predominantly inorganic base, the surface microanalysis of the samples was carried out using SEM-EDX (Scanning Electron Microscopy - Energy Dispersive X-ray Analysis).

Finally, to identify possible volatile substances involved in the defect (directly or indirectly, such as solvents, as agents capable of solubilizing and foster the migration of colored substances), the GC-MS technique (Gas-Chromatography - Mass Spectroscopy Detector/Purge & Trap sampler) was used; this last technique was also used to identify substances correlated to the degradation of the organic components of the leather, with particular reference to the degradation of fats (such as aldehydes, ketones, furans), as a consequence of a possible state of aging of the sample in correspondence with the defect.

3.2 Technical results

The survey on the 32 cases of yellowing was carried out on leather samples, leather goods and chemical products analyzed during the technical consultancy on the problem, about 44% of which related to defects in upholstery leather (14 cases out of 32), in reason for the greater use of white/light colors for the production of furniture items, and the remaining cases concerning defects in leather for footwear, automotive and leather goods. The overall survey has produced interesting results, the most relevant of which will be discussed in this section.

First, regardless of the intended use of the leathers, the main cause of yellowing was found to be correlated to the nature of the finishing (14 cases); in particular, a significant frequency has been found in the use of aromatic polyurethanes in the external finishing layer for defective samples (Figure 2). In all these samples analysed, an increase in the defect due to exposure to heat was found (especially to dry heat) and/or to light.

The second factor resulted involved in the onset of the defect was correlated with the presence of substances inside the matrix of the material (8 cases), with particular reference to fats; in the majority of the cases examined, the quantity of fats was found to be greater for the defective samples, which also presented a type of fats with a high degree of unsaturation. Regarding the origin of the fats, the instrumental tests carried out, as described in the previous paragraph, have shown that a crucial role was determined by the nature of the fatliquoring products used. However, in one case, the possible correlation of the defect to the natural fats of the skin was found; the case

concerned an article for furniture, consisting of assembled leathers of different origin (Figure 3): the non-defective parts, of calf, were characterized by a content of soluble matter in dichloromethane of 2.7%, while the defective parts, made of buffalo (processed by the same tannery), were characterized by a content of soluble matter in dichloromethane of 10.5%. Therefore, in this case, the particularly fatty nature of buffalo skins has been related to the onset of the defect.

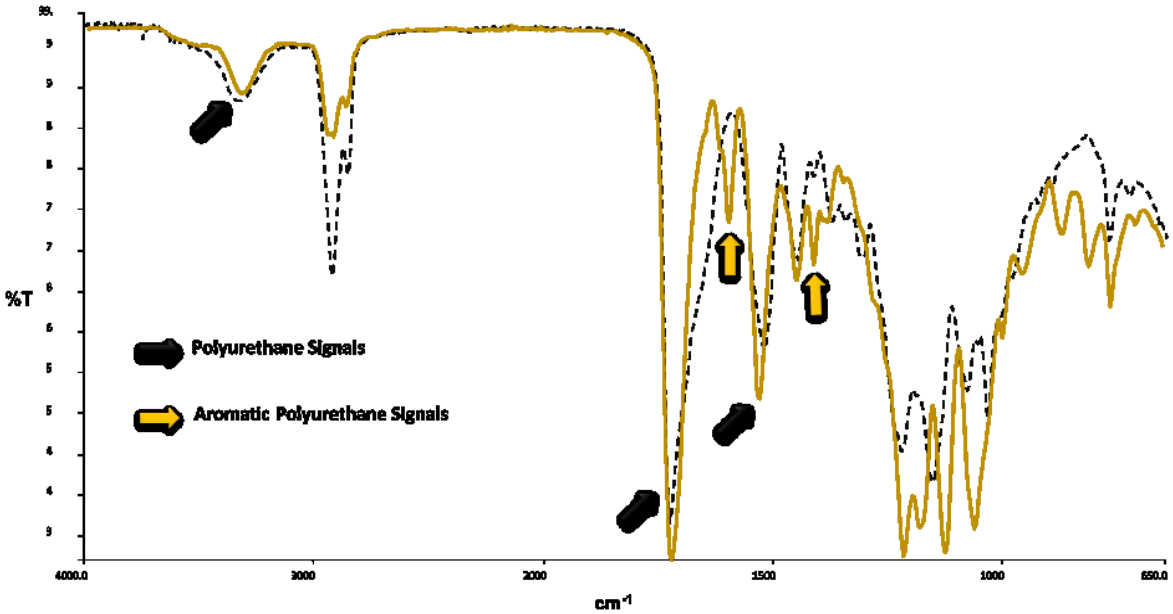

Fig. 2. IR spectra overlap of the topcoat of defective (yellow) and not defective (black) samples.

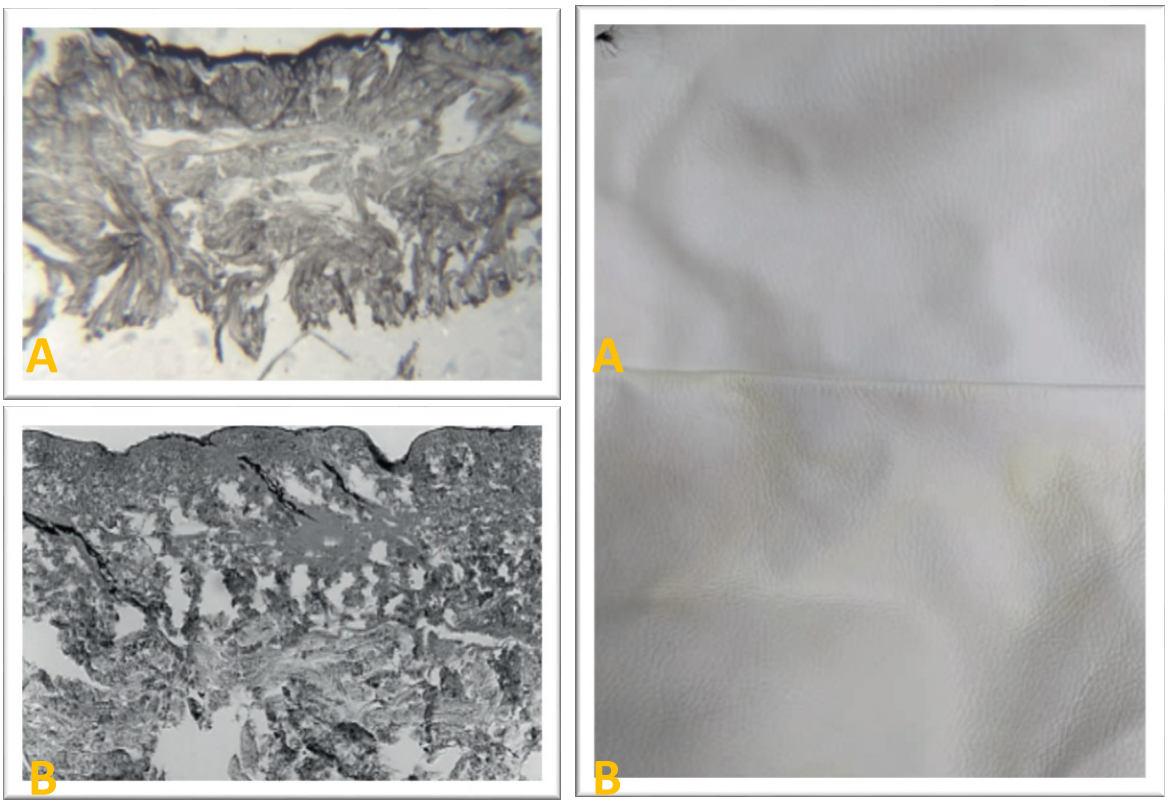

Fig. 3. A: cross section and surface of a not defective calf leather; B: cross section and surface of a defective buffalo leather.

In the remaining 10 cases, the problem was related to additives used in the production process (plasticizers, antioxidants), as well as with external agents deriving from the assembly materials (adhesives, solvents, coloured fabrics).

Particularly interesting, in this sense, was the survey on the yellowing of an article for leather goods, due to the association of the problem with more than one external agent. In this item the defective parts were affected by the presence of acrylic glues on the surface (Figure 4).

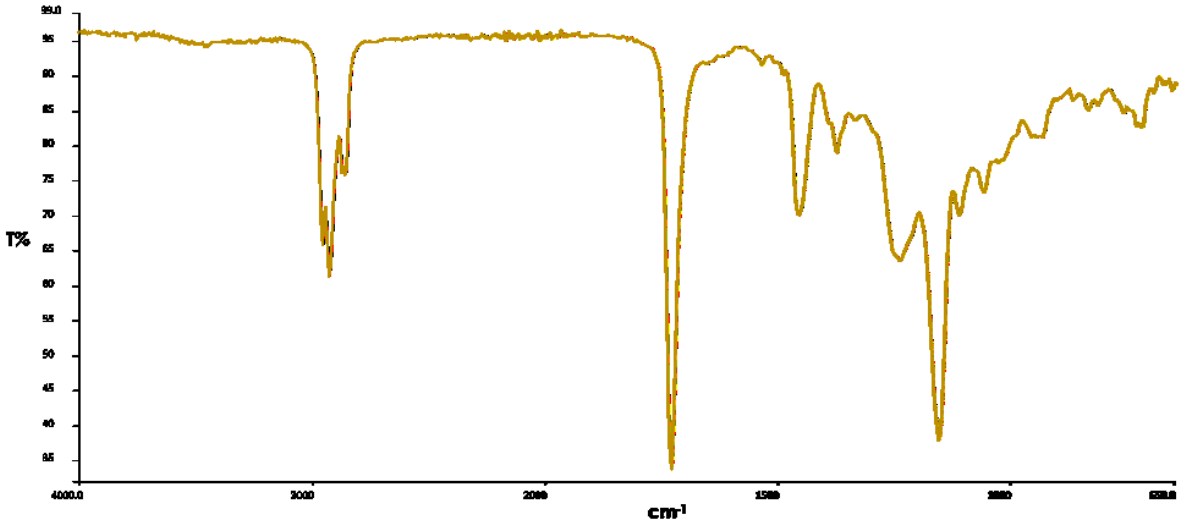

Fig. 4. IR Spectrum of the glue found on the sample: spectroscopic profile compatible with a polyacrylate

These substances, due to their own nature, are potentially able to produce the complained yellowish colour. However, in the specific case, the glue was also present in non-defective areas of the assembled product. Therefore, the mere presence of the glue did not justify the onset of the problem. On the other hand, an in-depth visive analysis of the sample provided more clues, highlighting that, in correspondence with the defect, there was also a regenerated leather reinforcement lining (absent in the areas without defects). The artificial aging tests (60 °C for 72 hours), as well as the ironing test, led to the onset of a yellowish colouring in not defective areas and to an increase in the yellowing in the defective ones. We then proceeded with the determination of the volatile substances of two specimens, using the Purge & Trap - GC-MS technique (Gas-Chromatography - Mass Spectroscopy Detector/Purge & Trap sampler):

A. defective/yellowed specimen containing all the materials (leather, glue and lining);
B. non-yellowed specimen in which the reinforcing lining was absent.

The result of this investigation is reported in Tables 1 and 2, and shows that:

- in both specimens the presence of volatile substances with solvent action was identified, as well as substances of other nature, such as hydrocarbons, fatty substances and respective degradation products;
- a higher percentage of hydrocarbons and chlorinated hydrocarbons was found in the defected area (substances whose migration tendency is known).

The investigations carried out and the results obtained led in this case to hypothesize that the problem was connected to a combined action of substances with a tendency to yellowing (glues) and substances able to foster the passage of the glue from the flesh side to the grain side of the item. The use of any high temperatures to assemble the artefact was considered, according to the experimental results, a factor potentially capable of contributing to the onset of the problem.

Tab. 1. Gas-chromatographic determination of the volatile substances in the not defective sample (A)

SUBSTANCE	T_R (MIN)	CAS N.	QUALITY%	AREA%
Acetone	12,3	000067-64-1	90	12,86
Hexane	14,5	000110-54-3	91	3,33
Pentanal	21,2	000110-62-3	78	1,84
Tetrachloroethylene	25,2	000127-18-4	52	0,87
4-Pentenal	29,9	002100-17-6	56	1,77
Oxirane, (bromomethyl)-	30,3	003132-64-7	50	1,91
Benzene, 1,3,5-trimethyl-	33,1	000108-67-8	27	0,97
1H-Pyrrole, 2,5-dihydro-1-nitroso-	33,7	010552-94-0	50	2,66
1-Hexanol, 2-ethyl-	34,6	000104-76-7	59	27,00
3'-Amino-6-methoxyaurone	36,0	077764-95-5	49	1,07
2-Nonenal, (Z)-	37,2	060784-31-8	90	6,22
3-Methylheptyl acetate	37,9	072218-58-7	58	12,36
Butane, 1-chloro-2-methyl-	38,3	000616-13-7	59	3,47
2-Nonynoic acid	39,5	001846-70-4	72	2,14
2-Octenal, (E)-	40,2	002548-87-0	59	3,41
1-Pentene, 5-chloro-	41,0	000928-50-7	43	3,73
1,2-Hydrazinedicarboxylic acid, di	42,5	004114-28-7	52	1,60
2-Pentenal, 2-ethyl-	42,6	003491-57-4	43	2,83
1-Pentanol, 2-methyl-	43,2	000105-30-6	91	7,10
Nonane, 2-methyl-	44,0	000871-83-0	92	2,86

Tab. 2. Gas-chromatographic determination of the volatile substances in the defective sample (B)

SUBSTANCE	T_R (MIN)	CAS N.	QUALITY%	AREA%
Acetone	12,3	000067-64-1	9	1,63
2-Butene, (E)-	14,6	000624-64-6	64	4,68
Ethane, 1,1-diethoxy-	20,3	000105-57-7	64	6,26
Propane	21,2	000074-98-6	40	1,38
Benzaldehyde, 2-methyl-	23,8	000529-20-4	78	1,97
Tetrachloroethylene	25,2	000127-18-4	99	4,79
1H-Pyrrole, 2,5-dihydro-1-nitroso-	25,8	010552-94-0	90	9,03
Benzene, 1,2-dimethyl-	28,2	000095-47-6	50	2,24
Propene	29,9	000115-07-1	53	3,40
Carbonic acid, diethyl ester	30,3	000105-58-8	53	4,99
2,4-Nonadienal	32,3	006750-03-4	53	1,52
Benzene, 1,2,4-trimethyl-	33,1	000095-63-6	50	3,48
4-Pentenal	33,7	002100-17-6	64	3,29
Cyclopropane, 1,1'-ethenylidenebis	33,8	000822-93-5	59	2,30
Butane, 1-chloro-2-methyl-	34,6	000616-13-7	91	16,51
Butane, 1-(ethenyloxy)-	37,2	000111-34-2	47	5,29
3-Methylheptyl acetate	37,9	072218-58-7	93	10,29
2-Penten-1-ol, (Z)-	38,3	001576-95-0	94	1,62
3-Hexenal, (Z)-	39,5	006789-80-6	64	0,97
3-Hepten-1-ol	40,2	010606-47-0	38	3,32
1-Pentene, 5-chloro-	41,0	000928-50-7	47	3,04
Hexanoic acid, butyl ester	41,7	000626-82-4	95	1,00
6-Oxabicyclo[3,1,0]hexane	42,5	000285-67-6	96	1,89
Nonane	43,2	000111-84-2	50	3,72
Cyclopentaneundecanoic acid	44,0	006053-49-2	20	1,39

With regard to the possible involvement of plasticizers, we report the case of a leather sample for footwear where, as in the previous case, the execution of the first tests described in paragraph 3.1 had not provided sufficient elements to advance hypothesis on the origin of the problem and therefore a an in-depth investigation was necessary through specific instrumental techniques; in particular, considering that the yellowing agent resulted to be soluble in ethanol, the gas-

chromatographic analysis was performed of an extract in ethanol from the sample, using the GC-MS technique (Gas-Chromatography - Mass Spectroscopy Detector). The gas-chromatographic profile obtained for the extract is reported in Figure 5, showing that the most intense signal is the one characterized by a tR (retention time) of 33.37 min, identified as "2-Ethylhexyl diphenyl phosphate ", CAS: 1241-94-7. This substance is used as a plasticizer-flame retardant, insoluble in water which, as commercialized substance, is characterized by a pale yellow color (as reported in the technical sheets). Therefore, a possible involvement of this substance in the onset of the problem has been hypothesized, both for the coloration of the identified substance itself, and for the tendency to migration/transport of other substances, notoriously exhibited by plasticizers.

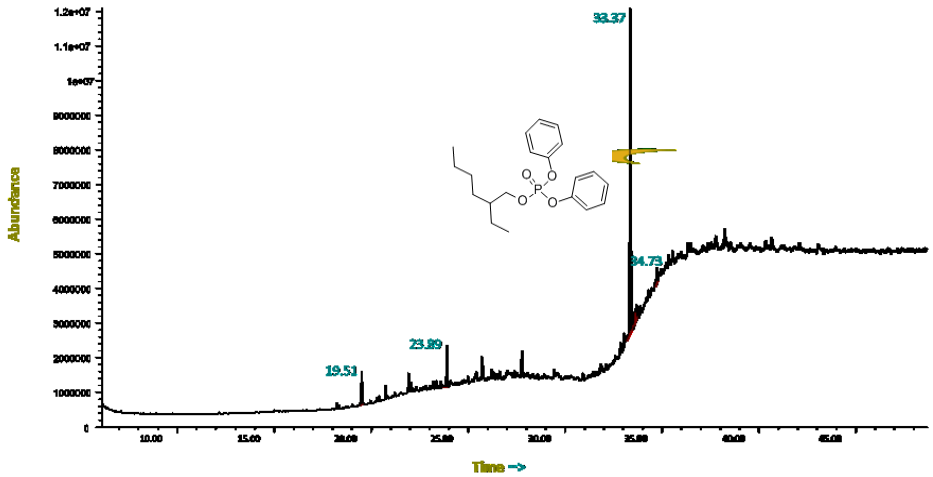

Fig. 5. Gas-chromatographic profile of the organic extract of the defective sample (leather for footwear)

Similarly, in-depth analysis was required, with the same technique, for the characterization of organic extracts (in 1: 1 acetone/dichloromethane mixture) of a leather sample for automotive with reversible defect following the exposure to light. The results obtained, for both its yellowed and not yellowed parts, are reported in Figure 6, and show that for the yellowed parts of the sample only, the presence of "2,2'-Methylenebis (6-tert-butyl-4-methylphenol) was found at a t_R of 14.885 min ", CAS: 119-47-1.

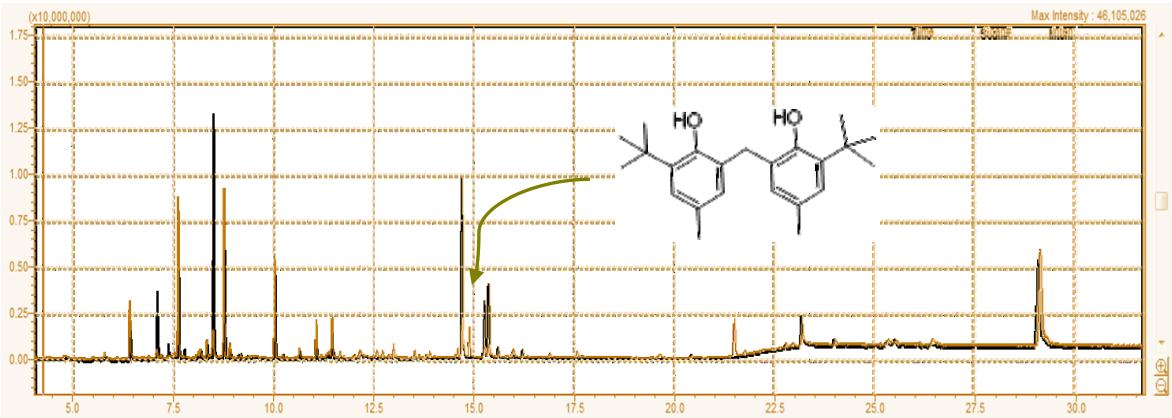

Fig. 6. Overlap of the gas-chromatographic profiles of the organic extract of the defective (yellow) and not defective parts (black) of the sample (leather for automotive)

This substance is used as an antioxidant and the technical data sheets report that the pure product is a white powder, which is slightly yellowish when exposed to air for a long time.

The sometimes controversial role of antioxidants, normally used just as stabilizers, but resulted instead potentially to be involved in the problems of alteration of the colouring, has already been discussed in previous works [3,2]; in the specific case, it has been hypothesized that the air reactivity of the antioxidant, migrated due to particular thermo-climatic conditions, may have contributed to the onset of the defect.
Finally, the in-depth investigation with the GC-MS technique was necessary to characterize the organic extracts (in a 1: 1 mixture acetone/dichloromethane) of a leather sample for furniture, where the other tests did not provide exhaustive and clarifying results on the possible origin of the defect. The results obtained in this case have shown the presence, in correspondence of the only defective parts, of 2-Octyl-2H-isothiazol-3-one, CAS: 26530-20-1, t_R of 10.535 min, whose structure is reported in Figure 7.

Fig. 7. 2-Octyl-2H-isothiazol-3-one

This substance is known to be used as a fungicide for the preservation of leather and has a yellow colortation (Light Yellow Oil, Yellow solid or clear dark amber liquid). The reactivity of this agent corresponds to that of an isothiocyanate, reacting particularly with amines, aldehydes, alcohols, alkaline metals, ketones, mercaptans, strong oxidants, hydrides, phenols and peroxides.

Also in this case, the problem was related to the migration of this agent to the surface, where the substance may have caused the problem, either directly (because of the colour exhibited) or indirectly (due to its reactivity).

3.3 Possible technical solutions

Since the most frequent cause of yellowing was found to be correlated to the chemical, intrinsic nature of the finishing, devices in this sense by the producers, can contribute to minimizing the problem. It would be particularly advisable, specifically, to avoid the use of aromatic polyurethanes in the outermost layer of the finishing of articles with light colours: although polyurethane polymers are known for their excellent mechanical and technological properties, presenting, overall, a high mechanical strength, on the other hand, it is known in fact that polyurethanes with aromatic components have a low resistance to light; alternatives can be constituted by aliphatic polyurethanes, for example starting from hexamethylenediisocyanate (HDI) or from trimethylamethylenediisocyanate (TMDI), or alternatively using mixed isocyanurates. In general, it may be appropriate to use adequate crosslinkers to increase the durability of the finishing polymers to hydrolysis [11].

For problems of yellowing due to fats, the results obtained suggest, first of all, that it would be advisable to avoid using as raw materials skins characterized by a high fat content for the production of light coloured leather articles, while other measures concern the moderate use of fatliquors, where synthetic products should preferably be used, even if more environmentally friendly alternatives currently appear on the market, which include the use of fatliquors based on specially modified vegetable oils, able to provide high performance in heat and light fastness, which is comparable to synthetic products [10].

In general, and for all other cases, sector studies have shown that the use of stabilizers (such as UV absorbers, radical scavengers and an appropriate use of antioxidants) can significantly improve the light resistance of dyed and crust leathers [9].

However, in consideration of some limitations that traditional stabilizing agents can exhibit, SSIP is evaluating, together with some partners, the use of nanostructured TiO_2, appropriately doped or associated with SiO_2, to foster the shift of absorption towards the region of visible and improve its self-cleaning functions [1,4].

4 Conclusion

The investigations carried out showed that the problem of yellowing can be caused by disparate factors, revealing a significant complexity of the phenomena potentially involved, and therefore requiring advanced diagnostic tools to identify some yellowing agents. However, some traditionally known causes of yellowing have been confirmed to be those that have the greatest impact on the problem: the most frequent cause of yellowing has in fact been found to be related to the chemical nature of the finishing. The use of aromatic polyurethanes in defected samples has been particularly frequent. The presence of fatty substances with a high level of unsaturation also proved to be a crucial factor in the onset of the problem.

In all the other cases, a more complex dynamic was found of the phenomena underlying the defect, instead, where the simultaneous responsibility for several factors was hypothesized, with particular reference to the factors of thermal and thermo-oxidative aging, associated to phenomena of migration and reactivity of potentially yellowing agents, used as auxiliaries or present in assembly materials. Examples in this sense refer to adhesives, plasticizers, antioxidants and fungicides, whose presence was found transversally in the defective samples, regardless of the nature of the skin of origin and of the intended use of the material.

Problem minimization strategies were also explored, which will be further developed later, including the possible use of applied nanotechnologies.

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