

The yellowing problem: Causes and possible technical solutions

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Light-coloured leather, especially leather with a white finish, falls within the category of materials used mainly for luxury and high-end products. For this type of article, the uniformity of colour and appearance of the overall surface are fundamental requirements demanded by major national and international fashion and luxury brands. This study aims to give an overview of all the main advanced diagnostic tools for identifying the causes of yellowing, with a view to offer manufacturers and users possible ideas for developing strategies to resolve and/or minimise the problem of yellowing.

One of the most common and undesirable defects of this light-coloured leather is alteration in colour, with particular reference to localised or widespread yellowing effects on the surface of the material.

Numerous factors may cause this type of defect, depending on the complexity of the matrix and the variability of the traditional or innovative production processes used, such as the intrinsic fragility, photosensitivity and thermo-sensitivity of the finishing polymers, the chemical instability of some components of the finishing pigments, the presence of photosensitive chemical additives, the migration of the leather components or assembly components of the products (greases, fillers, plasticisers, glues, etc.), as well as the indirect contribution of environmental and thermo-climatic factors capable of negatively impacting the performance of the material.

The yellowing defect is divided into various types:

Yellowing induced by light or UV radiation:

This phenomenon occurs by the action of direct light and only on the parts exposed to light.

The evaluation method is sunlight exposure or Xenotest for a few hours, generally from 24 to 72 hours; the difference between the exposed yellowed part and the unaltered part protected from the exposure is then evaluated. The main cause of this type of yellowing is the poor light fastness of some leather components:

- Finishes
- Resins

- Natural and synthetic tannins
- Fats (if the photo-oxidation products are yellow)

Yellowing not induced by light:

This phenomenon is not related to exposure to light and also occurs in the dark. The evaluation method is the ageing test with dry heat and wet heat (tropical test). The main causes are migration, oxidative phenomena, hydrolysis, thermal degradation of some leather components such as:

- Dyes or colouring components of other substances
- Pigments
- Finishes
- Additives (plasticisers, antioxidants, optical brighteners, crosslinkers)
- Fat substances (with high degree of unsaturation)

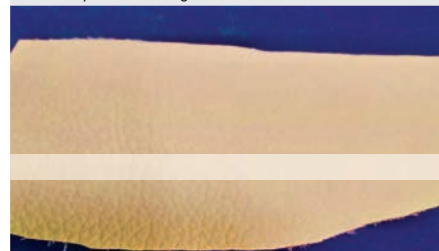
Irreversible yellowing:

This phenomenon is not related to exposure to light and is generally caused by migration or thermal-oxidative degradation. Fatliquors and finishing solvents often act as vehicles for the migration of the substances that cause surface yellowing.

Reversible yellowing:

This phenomenon disappears after exposure to light or UV (Figure 1) rays because the components that come to the surface are destroyed by photochemical action. If the leather is brought back to the dark, the yellowing reappears and then disappears again with the action of light. With the repeating of these cycles several times, the defect may completely disappear since the whole compound that caused

Figure 1: Disappearance of the yellow colour after exposure to light.



the yellowing is destroyed.

Yellowing on manufactured products

The action of the temperature during the manufacturing of the product, the ironing or “shaping” operations of the finished article sometimes require the use of hot air or modelling moulds that can exceed temperatures of 180°C. Most leather components degrade at such high temperatures, producing yellowing effects. It may also be caused by migration of coloured components contained in adhesives or coupled materials (fabrics, bonded leather, other materials).

Phenolic yellowing

This phenomenon is caused by the migration of phenolic compounds (e.g. butylated hydroxytoluene BHT), used as antioxidants and added to plastic materials, oils and waxes to counteract the effects of time. The phenolic compounds react with nitrous compounds present in the air (vehicle exhaust gases, boiler fumes). The products of this reaction are yellow. This type of yellowing occurs especially during storage or on items displayed in windows or in particularly polluted environments.



Figure 2: FTIR-ATR Spectrum of aliphatic polyurethane.

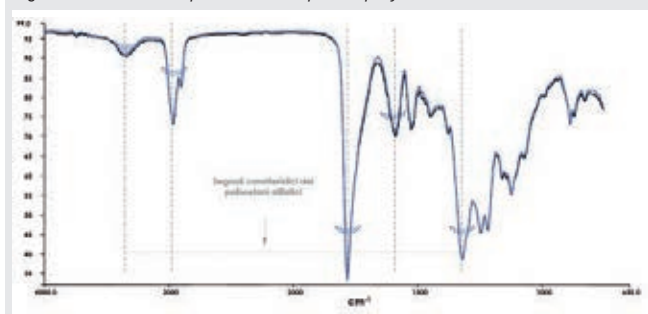
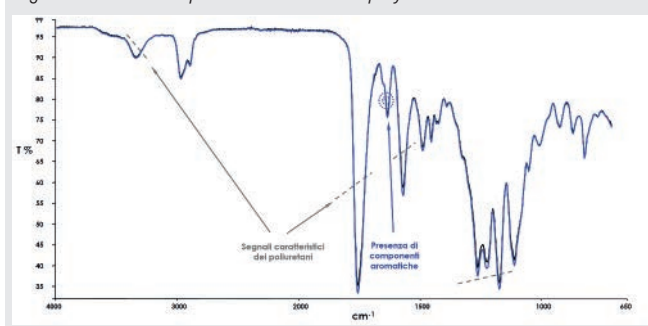


Figure 3: FTIR-ATR spectrum of Aromatic polyurethane.



Yellowing of nitrocellulose finishes

Nitrocellulose based fibres can be effected by degradation phenomena, in particular under thermo-climatic conditions, but also due to exposure to UV rays if they come into contact with amino groups present, for example in polyaziridine (polyethyleneimine), which is a crosslinker used in polyurethanes, or with another component used in the processing of polyurethanes as a catalyst, such as diazobicyclooctane (DABCO). These components can evaporate, decomposing the nitrocellulose and producing a yellow/brown coloration.

Yellowing of polyurethane finishes

Aliphatic polyurethanes, (Figure 2) unlike those made with aromatic components, have a good resistance to yellowing.

Polyurethanes with aromatic components (Figure 3) have a greater reactivity and a greater tendency to degrade because of environmental conditions, leading to problems of colour alteration (yellowing/browning).

Figure 4: Defective test specimen / non-defective test specimen.



It is important to point out that the degradation phenomena that only effects the surface finishing layer are different from the phenomena of migration of components inside the leather due to the fact that the variation in colour, which can be seen on the tested

sample and also following the laboratory tests carried out to evaluate the appearance of the defect, is homogeneous over the entire surface (Figure 4) and not localised or distributed in spots as in the case of migration of components inside the leather.

Each case of yellowing requires a specific analytical/study

approach. The Leather Research Institute over the years has handled numerous cases based on requests from the sector (tanneries, leather users, etc.).

Below are the most representative cases of the issue:

Case no. 1

Sample: White leather with yellowing located in the central area and the release of an unpleasant smell.

Analytical tests

- Ageing tests (UNI EN ISO 17228) Non-defective test specimens

Results

Yellowing of the leather is evident on the flesh side and on the grain side.

Chemical analysis to evaluate self-oxidising phenomena of the fatty substances:

- Determination of the content of fatty substances (extraction with methylene chloride)

Results

17.4% stained area

14.4% unstained area

- Determination of the iodine number (index of the degree of saturation)

Results

72 fatty substances extracted from the stained area

93 fatty substances extracted from the unstained area

Final opinion

Yellowing was caused by a chemical reaction between the fatty substances present in the hides and the hot air used to dry them. In fact, when the hides were placed in the pile after drying, conditions occurred such to promote a further reaction of the fatty substances, which was aided and/or influenced by a higher temperature in the centre of the pile of hides. The oxidative chemical reaction between the oxygen in the air and the unsaturated fatty substances lead to the intermediate formation of hydroperoxides with subsequent transformation into aldehydic compounds, which are responsible, among other things, for the unpleasant odour.

Case no. 2

Sample: White sofa upholstery with yellowing stains (Figure 5) located on one of the sewn pieces (Figure 6).

Analytical tests

- Artificial light exposure test (Xenotest method according to UNI EN ISO 105-B02).

Results

Defective piece: Disappearance of the yellowing

Non-defective piece: No alteration

- Ageing tests:

Defective piece: Yellowing after 72 hrs at 60°C and 80% r.h.

Non-defective piece: No alteration

- Microscopic examination

A visual inspection of the manufactured product showed a difference in the coloration of the leather (of the various sewn pieces) on the flesh side. This lead us to believe that different types of leather were used to make the product (Figure 7 &



Figure 5: Defective area.

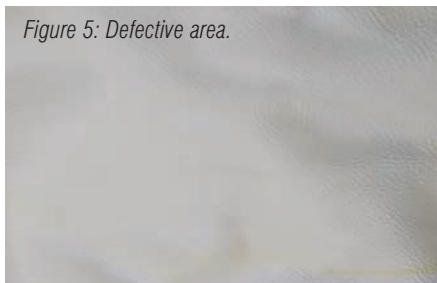
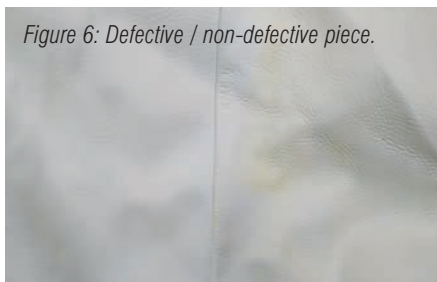
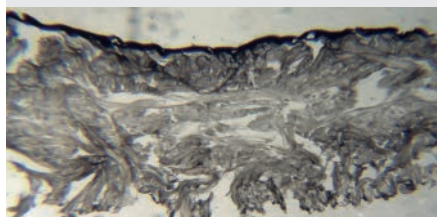
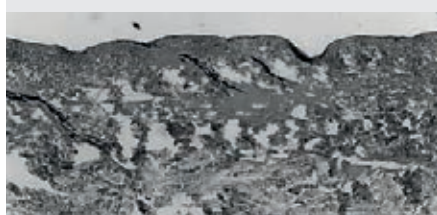


Figure 6: Defective / non-defective piece.

Figure 7: Optical microscopic examination of a 30 μ section of non-defective leather. The test sample is finished crust.Figure 8: Optical microscopic examination of a 30 μ section of defective leather. The test sample is finished buffalo leather.

8).

- Determination of the content of fatty substances (extraction with methylene chloride)

Results

- 10.5% piece of stained leather
- 2.7% piece of unstained leather

Final opinion

In the same period, there were several similar cases of yellowing that were found to have common origins, these being buffalo hides, with the amount of fatty substances rather high for this type of article (upholstery). It was concluded that the high fatty substances content present in buffalo hides (natural fat) could have caused the phenomena of migration towards the surface layer with consequent yellowing of the finish.

Case no. 3

Samples: Heel of a shoe covered in yellowed leather, glue, leather of reference (not yellowed).

Analytical examination

- Artificial light exposure test (Xenotest).

Results

Non-defective leather: no alteration

- Ageing tests with dry heat (80°C for 48 hrs) and wet heat (60°C and 80 % r.h. for 72 hrs).

Non-defective leather: no alteration

- Steam exposure tests of various solvents on the flesh side (hexane, ethanol, acetone)

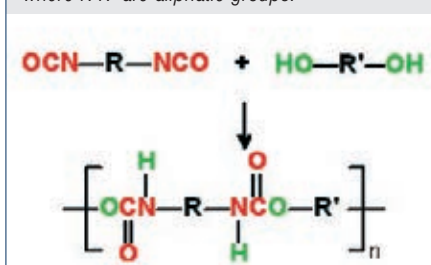
Non-defective leather: no alteration

- Ageing tests at 70°C for 72 hrs

Glue + leather appearance of yellowing

- FT-IR ATR analysis of the leather surface polyurethane finishing with aliphatic components (Table 1).

Table 1: Example of synthesis of a polyurethane where R R' are aliphatic groups.

**Technical opinion**

Aliphatic polyurethanes, unlike those made with aromatic components, have a good resistance to yellowing, as confirmed by the ageing tests to which the leather was subjected. The defect found on the article can be attributed to the use of assembly materials, with particular reference to the adhesive, possibly favoured by particular process conditions (e.g. high temperatures). In many cases, the defect is attributable to coloured components present in the active part of the adhesive, in particular solvent-based adhesives, where the solvent generally acts as a concave cause, fostering migration.

Another type of yellowing occurs in the form of small yellow, orange or pink stains and can sometimes be interpreted as the instability or degradation of dyes and pigments.

The GC-MS analysis of samples taken from the finished surfaces with a swab soaked in hexane and a mixture of acetone-toluene in a ratio of 1:1 showed

the presence of a component belonging to the class of carotenoids in the defective areas.

This substance is also known as lycopersene, which represents the dehydrogenated analogue of lycopene, which, in nature, is a precursor. The defect may also be caused by the use of other carotenoids not identifiable by methodological-instrumental limits, or by degradation processes already taking place.

Carotenoids in general can be used as pigments or as antioxidants in combination with other known antioxidants, such as tocopherol and BHT (butylated hydroxytoluene). The use of antioxidants as a finishing agent is rather common.

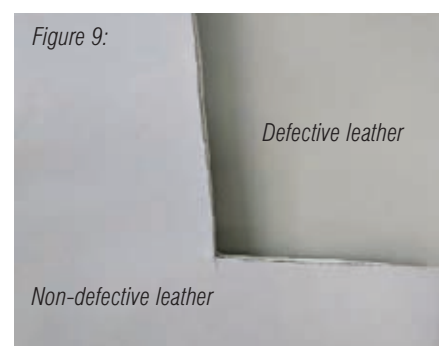
The phenomenon is quite singular, since the antioxidants commonly used in the tanning sector have the very purpose of improving some of their performances, including resistance to the action of UV rays and to protect white leather from yellowing. These substances separate and migrate towards the surface because they are weakly bonded to the fibrous structure of the leather. A microanalysis with X-ray probe of the surfaces of the samples revealed the presence of titanium and silicon, elements normally found on white leather. Titanium dioxide is a well-known catalyst capable of degrading numerous organic compounds when activated by UV radiation.

The interaction of titanium with carotenoids, already in itself not very stable to light, involves the reversibility of the phenomenon resulting in the finish "returning" to its initial colour due to the effect of energy from light sources.

Case no. 4

Samples: Yellowed piece of leather assembled for a car plus a piece of non-defective leather of the same batch not assembled (Figure 9).

Figure 9:





Analytical tests

- Artificial light ageing test (UNI EN ISO 105-B02 method)

Results

Defective leather: Disappearance of colouring

Non-defective leather: No alteration

- Dry and moist heat ageing test (UNI EN ISO 17228 procedure)

Results

Defective leather: No alteration

Non-defective leather: No alteration

- Determination of the fat content (extraction with methylene chloride)

Results

10.0% piece of stained leather

- FT-IR examination in ATR of the surface layer of yellowed areas.

Figure 10: Microscopic examination of a 30 μ section of defective leather. The examination revealed the presence of material inside the canals of the hair follicles.

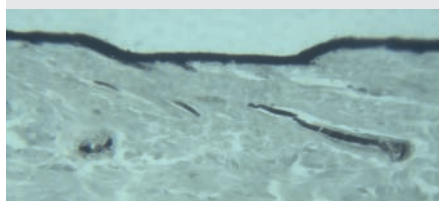


Figure 11: Microscopic examination of a 30 μ section of non-defective leather. The examination did not reveal the presence of material inside the canals of the hair follicles.



Results

No component detected with respect to the non-defective areas.

The presence of an unknown material inside the follicles (Figure 10) leads to the hypothesis of a migration phenomenon of some substances towards the surface of the leather. Although the content of fatty substances is high for the type of leather in question, no fatty substances have been identified on the yellowed surface. The scanning electron microscopic examination with relative X-ray probe microanalysis revealed another interesting parameter, namely a considerable difference in titanium content between the surfaces of the defective leather (Figure 12) and that of the non-defective leather of reference (Figure 13).

Figure 12: Microanalysis of defective leather (yellowed).

Spectrum	C	O	Si	Ti
Spectrum 1	65.67	24.97	7.45	1.90
Spectrum 2	75.13	19.99	3.86	1.02
Spectrum 3	64.99	25.75	7.11	2.15
Mean	68.60	23.57	6.14	1.69

Figure 13: Microanalysis of non-defective leather.

Spectrum	C	O	Si	Ti
Spectrum 1	66.92	26.43	6.11	0.54
Spectrum 2	64.46	27.82	7.29	0.43
Spectrum 3	68.70	24.74	6.13	0.43
Mean	66.70	26.33	6.51	0.47

Figure 14: Microanalysis of defective leather (yellowed) after removal of the top layer.

Spectrum	C	O	Si	Ca	Ti
Spectrum 1	63.40	25.45	1.92	1.81	7.42
Spectrum 2	59.36	26.69	2.23	0.14	11.58
Spectrum 3	63.97	23.68	2.20	0.13	10.02
Mean	62.24	25.27	2.12	0.69	9.67

Figure 15: Microanalysis of non-defective sample after removal of the top layer.

Spectrum	C	O	Si	Ti
Spectrum 1	72.74	24.02	0.73	1.96
Spectrum 2	72.70	24.13	0.58	1.91
Spectrum 3	71.37	23.85	0.87	3.18
Mean	72.27	4.00	0.73	2.35

Figure 12: Microanalysis of defective leather (yellowed).

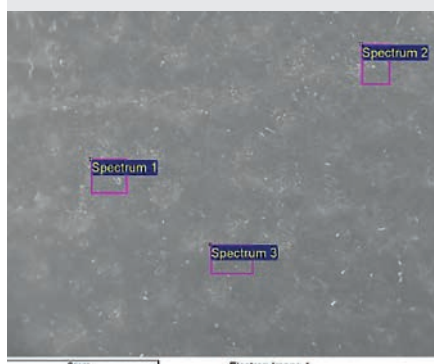


Figure 14: Microanalysis of defective leather (yellowed) after removal of the top layer.

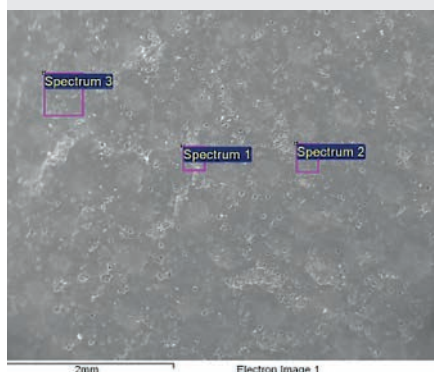


Figure 13: Microanalysis of non-defective leather.

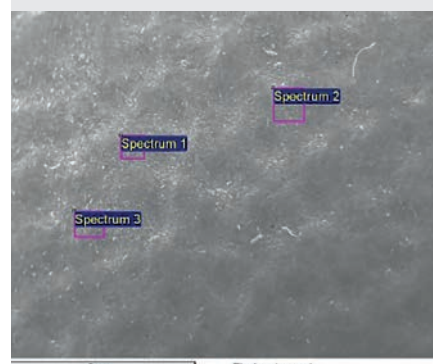
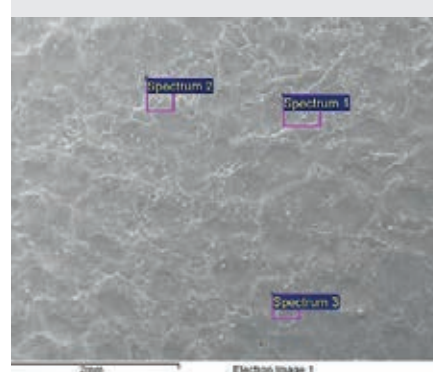


Figure 15: Microanalysis of non-defective sample after removal of the top layer.





The surfaces of the samples were examined with an X-ray probe after removal of part of the top finishing layer and it was found that the titanium content increased considerably in the underlying finishing layers (*Figure 14 & 15*).

The total content of titanium in the leather determined after digestion of the sample and reading with ICP Plasma (UNI EN ISO 17072-2 method) was equal to 0.8%.

The total titanium value in the leather is quite high compared to what is normally found, which suggests that the high concentration of titanium detected on the surface may have been accentuated by the further migration of this element from within the leather towards the surface. The results of the tests suggest that the yellowing can be attributed to the presence of too much titanium which, under certain conditions that have yet to be clarified or associated with other substances, may lead to colour changes. The disappearance of the defect with exposure to light confirms the self-cleaning action of titanium when subjected to light energy.

Technical aspects related to “exudation/migration” phenomena on leather: Primary Causes

The expulsion of “incompatible” molecules towards the surface of the leather (interface of contact with the air), causing “exudation,” is attributable to chemical components:

- with low molecular weight (as order of magnitude up to triglycerides, Mw < 500-1000, size 2.5nm)
- with prevalently non-polar structure, not retained by active components inside the leather of an ionic/polar nature and as such having less affinity for collagen

The inner part of the leather, and probably each fibre, can be assimilated to a cylindrical electrical conductor, which creates an electrostatic field that is incompatible and thermodynamically “repulsive” for any components not having a charge and therefore not bonded to the fibre.

Such as:

Fatty substances

Not equipped with substantive properties for the fibre.

Pigments

“Carotene” type pigments present also in natural fat as components of the food diet (grains and fodder).

Dyes

“Mixtures” of different dyes and colorants, whose components, if not properly dyed, may move differentially over time in the section as in a chromatographic migration/separation.

Plasticisers

Finishing substances added as “polymeric flexibilisers”.

By-products

Degradation or impurities of the same polymeric materials as the finish; or other functional auxiliaries, even intentionally added.

The driving force of these phenomena is obviously the chemical-physical affinity (“polar with polar, non-polar with non-polar, electrostatic with electrostatic of opposite sign”). That is, the same principle of “spontaneity” that leads to the known head/tail orientation of surfactant molecules on the surface of a polar liquid medium such as water, with their non-polar tails turned in the “air” phase, obviously

considered “non-polar”, placed in contact with the aqueous medium. In short, there are two immiscible phases present at the same time:

air (non-polar) and water (polar)

Phases that in the case of the “leather” system become:

- air limiting the product
- the entire interlacing matrix of the fibres that makes up the leather product

Time and temperature foster these widespread phenomena.

Secondary Causes

The migration/diffusion effect of these substances towards the surface is fostered by the presence of other components, which act as a semi-fluid vehicle/transport means, such as a lubricant with dual action of solubilisation/dispersion and mobilisation/sliding due to their intrinsic plastic consistency.

Possible remedies

When the yellowing occurs as an accumulation of substances on the surface, it can be removed with appropriate solvents. Generally the most suitable are dichloromethane, toluene, hexane, ethyl-alcohol and acetone.

However, when the yellowing is incorporated in the top layer, very little can be done.

Removing the stain is easier when the substance tends to crystallise by isolating itself from the support, such as for example in the case of fatty efflorescence and when the substance has a low molecular weight (e.g. dyes).

The degree of coverage of the finishing layer is also fundamental, i.e. whether the migrated substance can pass through it or remains embedded inside.

Technical opinion

Leather processing is a long and complex series of operations which involve the use of numerous chemical products, often necessary to increase the versatility of the articles.

The resistances to be met must be carefully evaluated and products capable of offering a good degree of safety must be selected. Therefore, it is recommended to:

- Reduce the use of fats with high presence of double bonds
- Reduce the use of polyurethane refinishing products with aromatic groups
- Use pigments and dyes that are resistant to light and critical environmental conditions
- Do not combine the components present in polyurethanes with leather finished with nitrocellulose
- Do not use adhesives with a tendency to yellow
- Do not use high temperatures
- Carry out dry and moist heat ageing tests and light exposure tests to check for any tendency towards yellowing. The eventual disappearance of yellowing in the light can be used to eliminate the defect definitively with appropriate dark/light cycles where possible.

In any case, the appearance of the defect can be reduced by identifying the type of yellowing and then eliminating the possible causes. ☺