Patent and laminated leather: the role of crucial parameters in the damage of fashion goods.

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Abstract: In the last years, due to the growing trend of the fashion industry, a significant increase in the production of patent and laminated leather is found. In spite of the commercial success reached by this kind of items, tanners are involved even more in technical or legal problems, joined to the presence of some peculiar defects of the goods, especially if they cause a loss of image of big brands. This is due to the typical chemical and mechanical features of patent or laminated leather, often showing a tendency to damage.

The aim of the work was the clarification of the mechanisms causing and/or worsening these defects. It was carried out by the monitoring of some technical parameters for 50 cases of damage on leather or items. The investigated parameters were: the chemical nature of the finishing material; its mechanical resistance; the amount and the type of fats in the leather (and/or on its surface); the amount and the type of solvents in the leather and in other materials used to assemble the goods; the amount and the type of other substances in the leather (and/or on its surface), as hydrocarbons, surfactants, plasticisers and so on; the temperature, both as ageing and as process factor.

Furthermore, as an upcoming development of the investigation, we are going to consider other parameters, as the finishing thickness and the base coat features. The study, based on the utilisation of dedicated instrumental techniques (AT-IR, SEM, GC-MS), allowed to have a good understanding of the crucial role of some features to afford the damages. Finally it resulted useful to the tanners, since it could provide them the right tools to solve the technical problems on the items, and/or clarify their eventual responsibility, on the damage occurred, rather than the ones of the other actors of the productive chain.

Key words: patent leather; laminated leather; leather defects; technical masteries; legal issues

1 Introduction

The most famous fashion brands, in the last years, especially in the last two ones, made an extensive utilization of patent and laminated leather. Although this kind of items have been utilised also in the past, it is necessary to point out that the materials utilised for the finishing are affected, over the years, by continual changes of their chemical composition and of their mechanical properties, according to the growing developments reached by materials technology, with particular reference to the polymeric branch. At the beginning, for example, patent and laminated finishings were released, with oils and with gold or silver thin

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coatings respectively, today they are mainly released with polymeric or more sophisticated polymeric/metallic films. Therefore, the resolution of technical problems due to the damage of these two kinds of finishing, needs dedicated studies and continual updates.

2 Experimental

2.1 Materials and Methods

Concerning patent leather, 25 cases of damage on leather and items have been analysed. Each case included more samples (104), provided to SSIP for the resolution of technical masteries and consisting in both damaged and not damaged patent leather, beyond semi-finished leather samples and chemicals.

As many laminated cases were studied (25), including finished leather samples, both damaged and not damaged, semi-finished leather samples, chemicals and metallised transfer films, in the gross amount of 102 samples. In both patent and laminated leather cases, some known brands were involved.

The following physical tests were carried out on finished samples:

1. Colour fastness to to-and-fro rubbing, according to UNI EN ISO 11640 (on laminated samples only)
2. Adhesion of finish, according to UNI EN ISO 11644 (on patent samples only)
3. Flexing endurance, according to UNI EN ISO 5402 (on patent samples only)
4. Artificial ageing by heat or by heat and elevated humidity, according to UNI EN ISO 17228
5. Conditioning by solvents, through migration from flesh side to grain side of the leather and through straight contact with leather surface.

Furthermore, tests from 1 to 3 have been repeated also after the carrying out of tests 4 and 5 have, in order to evaluate solvent and temperature effects on mechanical properties of finishing, where temperature effects are meant either as ageing and as process features (for example the process utilised to applying finishing itself or the process of manufacturing of leather items, as shoes, bags and so on), depending on the applied conditions.

The chemical analysis of the soluble substances in dicloromethane has been carried out too, either on patent and laminated samples, according to UNI EN ISO 4048, in order to evaluate the effects of this parameter on producing damages on finishing.

2.2Instrumental Characterization

Finally, the following instrumental methods for samples characterization have been utilised:

- § Optical microscopy for the surface an for examination of the cross section of the leather;
- § Scanning Electron Microscopy (SEM) equipped with an X-ray probe for the microanalysis of the surface;
- § ATR-IR for the characterization of the chemical nature of finishing;
- § Gas Chromatography with FID detector and equipped with a special column for the characterization of the chemical nature of the fats of leather samples;

- GC-MS for the characterization of hydrocarbons and plasticisers;
- GC-MS equipped with a Purge & Trap sampling system for the characterization of volatile substances of the samples.

3 Results and discussion

3.1 Patent Leather

3.1.1 Defect and surface characterization

Among the examined cases the 76 % resulted affected by a defect consisting in a connection of fracture and detach (loss of adhesion) of finishing. The remaining 24 % was affected by defects consisting in stains and particular changing in finishing layer morphology (particularly for the presence of some “bumps” and “holes” in the upper finishing layer). Since this two last defect resulted originated strictly by the intrinsic properties of the upper finishing layer and the basecoat rather than by the leather or by assembling processes, our attention was mainly focused on the more interesting cases of samples affected by fracture and detach of finishing. For these samples the surface analysis provided the following results:

- In about the 90 % of the analysed cases, finishing (upper layer) was characterised by aromatic polyurethanes (it is necessary to point out that these kind of material was found both for defected and not defected samples) (figure 1 and 2);
- In the remaining 10 %, finishing (upper layer) was aliphatic polyurethanes based;
- The basecoat characterization was carried out only for damaged samples, where the separation from topcoat was possible: mainly aliphatic polyurethanes and more rarely polyacrylates were found.

3.1.2 Study on the parameters involved in the defect formation phenomenon

Phenomenological studies on patent leather shown that, for the most part of the analysed cases, the defect on finished items, characterised, as already highlight, by a composite nature, due to the simultaneous presence detach and fracture of finishing, was originate by a sum of causes, in which more than one parameter were involved. Anyway the statistical treatment of information obtained, provided the following results:

- The main parameter (for number of cases in which it was found and degree of influence on phenomenon) that resulted to have influence on defect, to a degree of about 40 %, was the content of fats in the leather (more exactly substances soluble in dicloromethane), depending on their nature and composition rather than on their amount, mainly due to their influence on adhesion properties of finishing; long chain esters (esters of fatty acid with fatty alcohols) and aliphatic hydrocarbons, whose detaching properties are already known, resulted the most involved substances in the processes causing the patent items damage;
- Another crucial parameter, to a degree of about 27 %, resulted the intrinsic properties of finishing, not meant strictly as its chemical composition, since it was the same both for defected and not

defected samples, but joined to possible differences in molecular weigh of polymers or functionalising degree with consequent differences mechanical properties, further than to thickness or to applying process errors;

- Then, to a degree of about 17 %, a further crucial parameter identified, was the influence of solvents, mainly deriving from assembling operations of finished items (as solvents deriving from adhesives utilised); more rarely solvents deriving from leather and from an insufficient drying of finishing was found;
- Finally, for the remaining 16 % of examined cases, other factors were found, as the presence of a large amount of plasticisers in the finishing polymers and consequent migration of this substances under the topcoat (between basecoat and the upper finishing layer), further than the mechanical characteristics of basecoat.

Temperature effects needed a separated treatment. About this parameter, for the examined cases, the main temperature effects were registered for samples whose damage resulted affected by fats and hydrocarbons content in the leather. High temperatures (100°) on these samples resulted improve the mechanical behaviour of damaged samples. On the other hand, high temperatures made the mechanical behaviour of not damaged samples worse.

The hypothesis putted forward on the possible reasons of these experimental results guess, beyond eventual chemical-physical effects on polymeric films, temperature-induced (as further reticulation and so on), a correlation between fatty matter migration and temperatures effects on mechanical properties: in other terms, where hydrocarbons and fats were found between basecoat and the upper finishing layer, a further, possible temperature induced migration of these substances on the topcoat surface, should have allowed a better adhesion between basecoat and upper layers; on the other hand, where any migration phenomenon had not begun at all, temperature should have activated it, producing possible deposition of fatty material between the layers, with possible worsening of adhesion.

Finally, in figures from 3 to 5, an interesting example is reported, in order to better clarify the role of fats and hydrocarbons on patent items damage. It could be synthesized as follow:

- two samples “A” and “B” had the same finishing polymer as upper layer (figure 3);
- sample “A” shown worse mechanical properties, compared with sample “B”, especially concerning adhesion (1,0 vs. 2,5 N/cm);
- sample “A” was characterised by a slightly lower content of soluble substances in dicloromethane, compared with sample “B” (14 % vs. 15 %); furthermore, dicloromethane extract of sample “A”, contained a larger amount of hydrocarbons and waxes, compared with the one of sample “B” (figure 4); the same hydrocarbons and waxes was found between the basecoat and the upper finishing layer of sample “A” (figure 5).

These substances, therefore, results the main parameter able to have influence on the coming out defect.

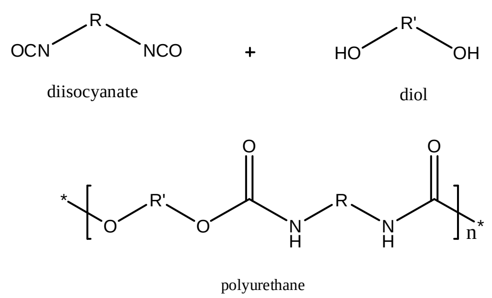


Fig. 1 Polyurethane formation

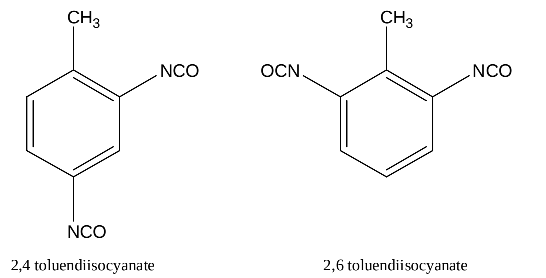


Fig. 2 Diisocyanates usually utilised for aromatic polyurethanes production

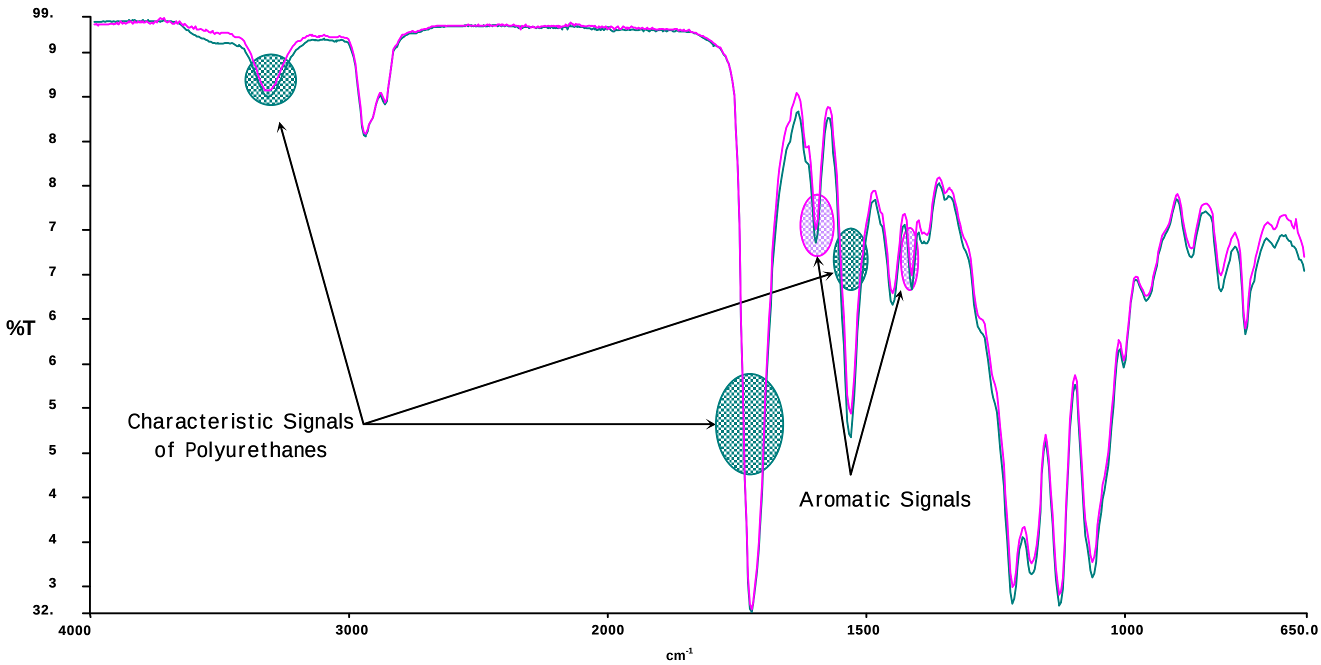


Fig. 3 IR spectra overlap of the surfaces of samples "A" (green) and "B" (pink)

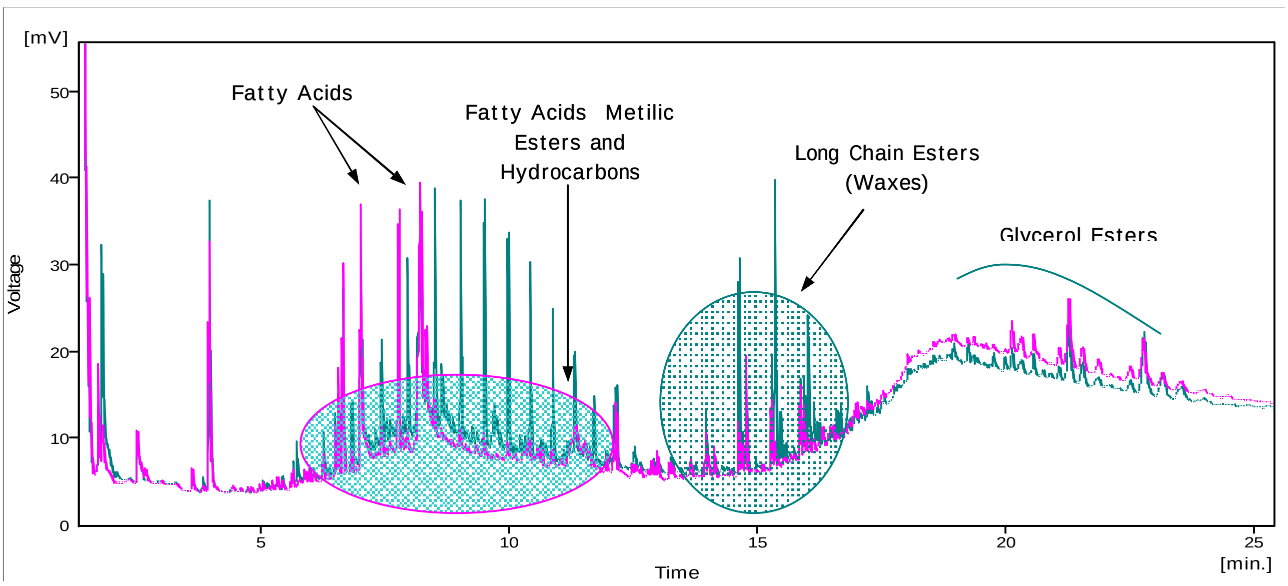


Fig. 4 Gas-chromatographic profiles overlap of the dicloromethane extracts of samples "A" (green) and "B" (pink)

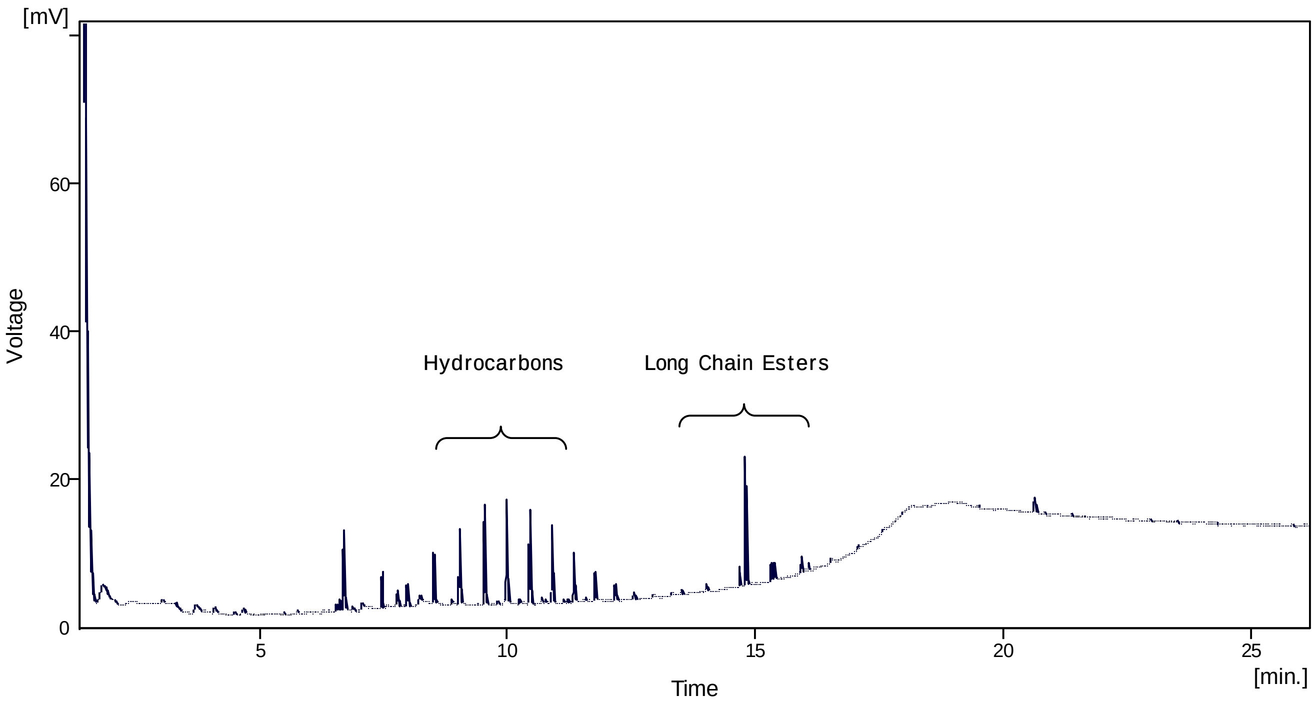


Fig. 5 Gas-chromatographic profile of the material taken from the interface between the basecoat and the upper finishing layer of the sample "A"

3.2 Laminated Leather

3.2.1 Defect and surface characterization

All the analysed samples were affected by "delamination", i.e. the removal of the coloured layer from surface and consequent coming out of the metallic, silver coloured underlying layer. In the most damaged samples this defect was associated to local removal of the whole transfer film and consequent coming out of the leather surface.

As shown by AT-IR analysis, combined with SEM microscopy equipped with X-ray probe, all the transfer films (ten samples) were characterised by three tin layers: a support film, silver coloured, that is brought into contact with the grain side of the leather, mainly aluminium or polymer/aluminium based; a coloured layer that provides characteristic surface effects (gold, platinum, bronze and so on), where pigments have been dispersed in a nitrocellulose film; a final layer of PET (polyethylene terephthalate) that will be removed during the application (usually by thermoadhesion at 90-100°C for few minutes under a traditional press).

The investigations on leather samples and assembled items surface provided the following results:

- in almost all the analysed cases, (92 %), spectroscopic examination of the sample surface shown that the characteristic coloured layer, as already found for the only transfer films, was nitrocellulose based (figure 6), both for damaged and not damaged samples;

- for the remaining cases (8 %), surfaces were characterised by the presence of polyurethanes and polyurethanes/silicones based polymeric surface layer. For these samples a better mechanical behaviour was found, compared with the one exhibited by nitrocellulose based laminated items.

3.2.2 Study on the parameters involved in the defect formation phenomenon

Phenomenological studies on laminated leather provided the following information:

- the main parameter that resulted to have influence on defect, to a degree of about 65 %, was the content of solvents in the damaged samples, with particular reference to some polar organic ones, as esteric and ketonic derivates, further than alcoholic and finally aromatic ones, as toluene and p-xilene, most of them are typical solvents or diluents for nitrocellulose, but, in the examined cases, they were found in the assembling materials of finished items and in semi-finished leather too. In particular, if the different solvent contributes are considered separately, the main influence on defect was assigned to solvents deriving from assembling operations (adhesives, textile fabrics and so on), to a degree of about 40 %. Solvents deriving from semi-finished leather resulted to engrave to a degree of about 17 %. Finally, solvents deriving from other chemicals directly added to the surface of finished items resulted to engrave to a degree of about 8 %. The first two classes of solvents were correlated to migration phenomena;
- the intrinsic properties of finishing, with reference to the fragility of the nitrocellulose layer in which the surface colour was dispersed, resulted to have influence on damage, to a degree of 20 %;
- fats and hydrocarbons, in this case, resulted to have a lower influence on defect, compared with the patent leather case, that was estimated to be of about 10 %;
- other factors had an influence on defect of about 5 %, with reference to the presence, on finished items surface, of other substances besides the ones whose effect was already discussed, as surfactants.

Temperature resulted to have a significant influence on damage, as ageing tests (both with and without high humidity) demonstrated. This parameter was tightly correlated to migration, as factor able to activate or accelerate these phenomena, as the fact that, temperature had more negative influence (in terms of increase of damage) on the items whose solvent content was higher, demonstrated.

Finally in order to highlight the different role of crucial parameters as solvents, fats and hydrocarbon on laminated items damage, compared to the one on patent items, an example of an analysed case was reported in figures 7 and 8. It could be synthesized as follow:

- three samples “C” , “D” and “E” had the same finishing polymer as upper layer;
- sample “C” shown better mechanical properties, compared with sample “D” and “E”, as resulted by the different effects on the surface produced by the colour fastness to to-and-fro rubbing test;
- sample “C” was characterised by an higher content of soluble substances in dicloromethane, compared with sample “D” and “E”, furthermore its dicloromethane extract contained a larger

amount of hydrocarbons and waxes, compared with the other two ones (but, in this case these substances had no influence on the mechanical properties of finishing);

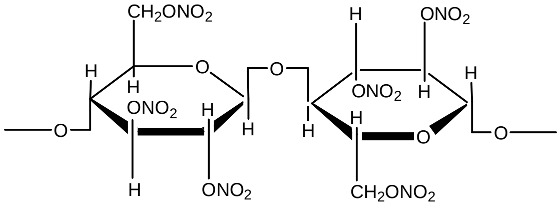
- for sample "C" a lower content of polar organic solvents was found, while, for the samples "D" and "E" a large amount of these substances was found. Furthermore, for these two last samples, ageing condition applied (50°C for 24 hours and 90 % of humidity) resulted to engrave the damage.

Therefore, in this case, solvents and their possible thermo-climatic induced migration on the surface, resulted the main parameter able to have influence on the coming out defect.

4 Conclusions

Either for patent and laminated samples an interesting correlation between their typical defects insurgence and some crucial parameters was found. The presence in the patent leather of large amount of aliphatic hydrocarbons (as possible consequence of paraffin utilize in fatliquoring chemicals), besides of long chain esters (as possible consequence of a large utilize of waxes), resulted to be the main factor able to influence the phenomenon cause of the defect of detach and detach accompanied by fracture of finishing, for these kind of items; the presence in laminated samples of a large amount of solvents, with particular reference to the ketonic and esteric ones, resulted to be the main factor able to activate or to worsen the typical delamination defect of these items. Temperature resulted to have influence in either kind of finishing, but bigger effects were registered for laminated leather; in this case, the increase of temperature produced a significant worsening of the mechanical properties of finishing, especially for those items characterised by a high solvent content (as the assembled items, were the most of solvents derived from adhesives or other assembling stuff). So this parameter has been tightly correlated to migration phenomena. This result was very important to clarify all those cases in which items were produced without any defect, and their only ageing determined the characteristic delamination of the surface.

The results obtained may afford a significant tool to tanneries involved in legal question on these concerns, in order to clarify their eventual role or in order to improve the quality of their production; in particular, for the examined cases, the tanning process resulted have more influence on patent leather defects insurgence, while for the most of laminated samples examined, tanning process didn't result the main cause of items damage.



Nitrocellulose

Fig. 6 Chemical structure of nitrocellulose

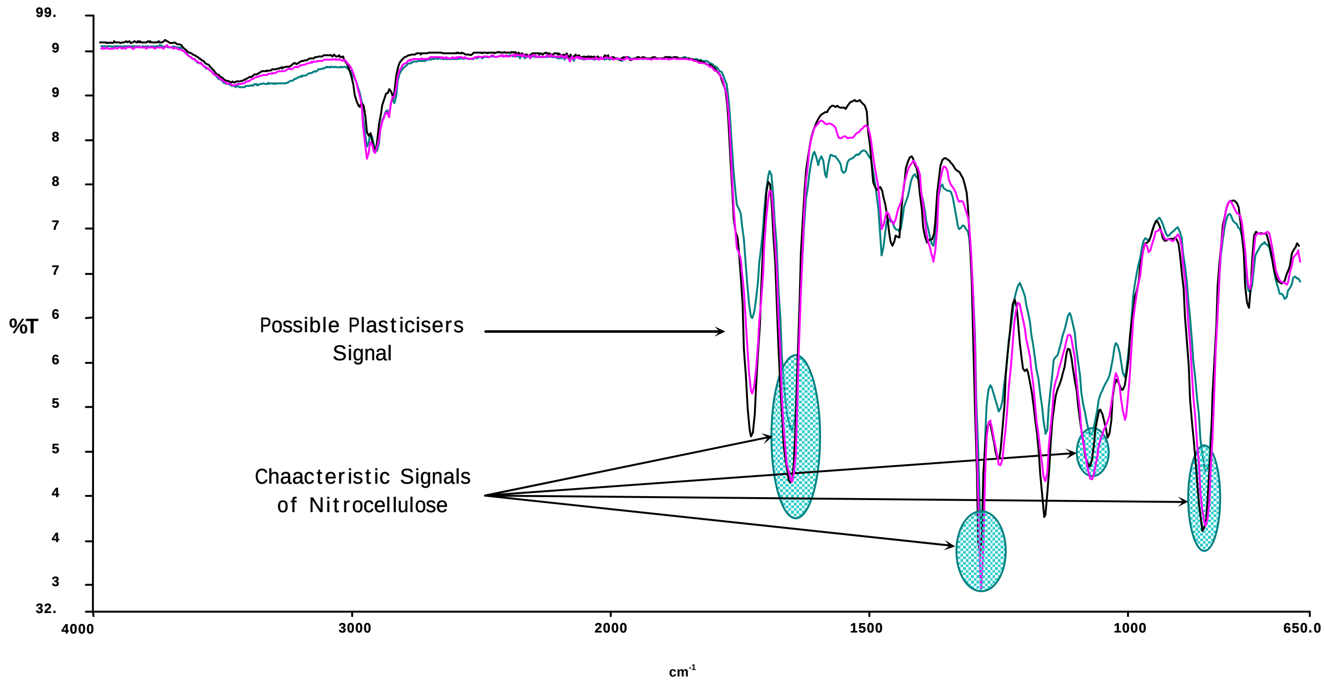


Fig. 7 IR spectra overlap of surfaces of samples “C” (green), “D” (pink) and “E” (black)

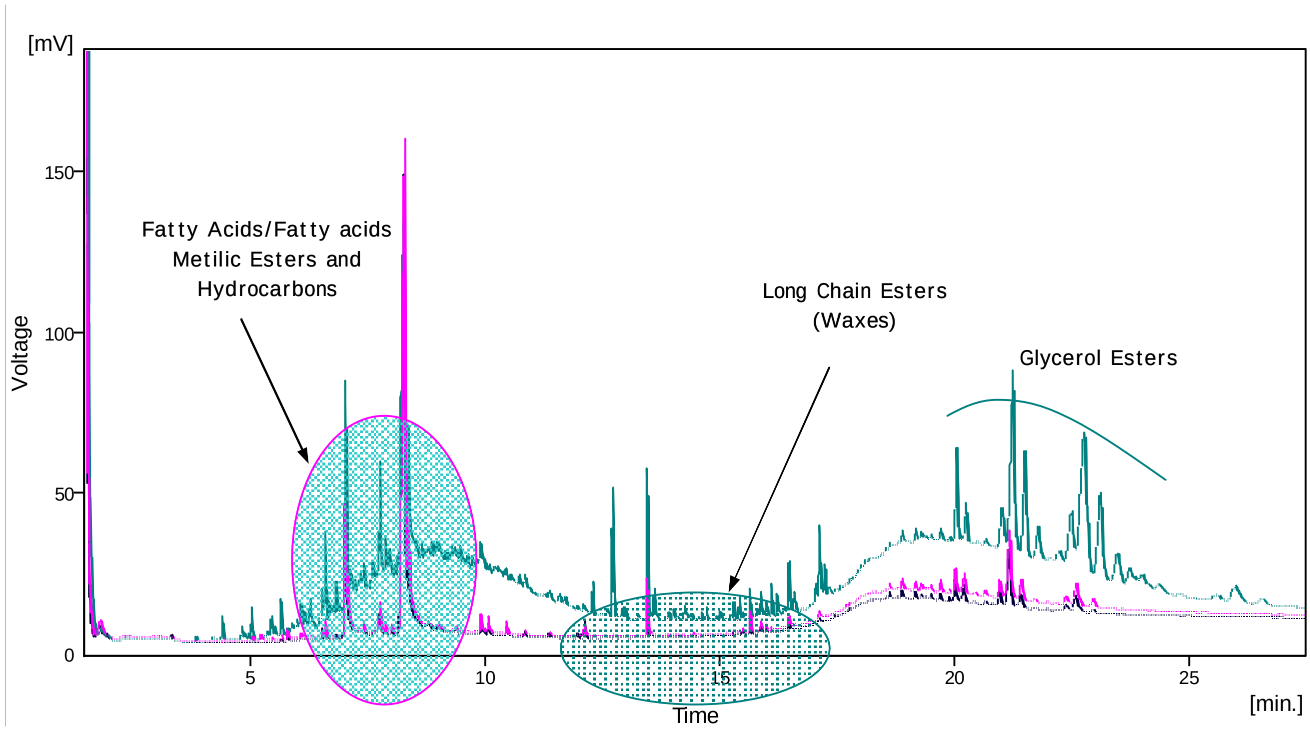


Fig. 8 Gas-chromatographic profiles overlap of the dicloromethane extracts of samples “C” (green) and “D” (pink) and “E” (black)

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