Ecological Technology for Leather and Furskin Dry Cleaning and Restoration

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Abstract

The use of tetrachloroethylene (PERC) as solvent for degreasing of sheepskins and dry cleaning of furskins and leather articles is worldwide spread as an efficient process. Almost 90% of dry cleaning services are based on the use of PERC, a carcinogenic solvent, involved in ozone depletion process. The alternatives to PERC take into consideration the use of liquid CO_2 or decamethylcyclopentasiloxane, commercially known as D5, a solvent commonly used in cosmetic products and practically devoid of toxicity. The study of decamethylcyclopentasiloxane as alternative solvent for leather and furskins dry cleaning was performed by experimenting in a dry cleaning equipment designed for both D5 and PERC use. The technology for furskin and leather articles dry cleaning was developed and the main results confirmed the advantages of D5 in comparison to PERC use: the color parameters improvements (intensity, brightness), the dimension preservation (shrinkage temperature increasing), the softness restoration and improvement even in the case of very old items, and the odour elimination. The dry cleaning risks for materials processed with unknown technologies were diminished, as well as the need of the after dry cleaning restoration of leather and furskin items. A micro and non destructive assessment system was proposed for leather and furskins articles based on shrinkage temperature assessment on fiber (MHT), softness (Softmeter) and color measurements (Data color colorimeter).

Keywords: dry cleaning, solvent degreasing, PERC, decamethylcyclopentasiloxane, furskins, sheepskin garments.

Introduction

Wearing leather articles means that they are exposed to a series of degradation factors such as: dirt, light, humidity, temperature, and mechanical stress, requiring cleaning and reconditioning steps (www.fenice.com). Sustainability of leather articles became increasingly important with the introduction of global environmental protection concept, with the increasing interest in consumer health and with the shift towards consumption of low-maintenance long-term use products.

The dry cleaning process was discovered in 1825 in France, when a worker in a lighting lamp cleaning factory accidentally spilled the content of a lamp, a petroleum-based solvent, on a dirty table cloth. When the table cloth dried, the spots were gone and a new industry emerged. The new method was called “dry”

because it used kerosene, as opposed to the "wet" one which used water. The rapid development of dry cleaning shops was arrested by the fact that solvents used were highly flammable, often causing fires putting neighbours at risk.

Throughout the years, attempts were made to remove the odour of solvents and fire hazards. In the 1900s chlorinated hydrocarbons were discovered and synthesized. These non-inflammable solvents were quickly tried in dry cleaning shops. The first one used, carbon tetrachloride, was very toxic and had a corrosive effect on metals and clothes. In 1950, carbon tetrachloride was replaced by tetrachloroethylene, better known as perchloroethylene (PERC, C_2Cl_4).

Between 1920 and 1950 the Stoddard solvent was the most frequently used in the dry cleaning industry, a blend of C_5-C_{12} containing 10-20% alkyl aromatic compounds. But over time, regulations have imposed increasingly high temperatures for the flammability point of the solvent and reduction of aromatic compound content.

DF2000, discovered in 1994, is an aliphatic hydrocarbon, which does not contain aromatic compounds and its flammability point is 64°C; EcoSolv is made of isoparaffins and its flammability point is 62°C;

Hydroclene Fluid is a mixture of normal, iso- and cyclo-paraffins, and its flammability point is 63°C.

An important issue related to the use of petroleum-based solvents is biodegradability. Bacteria introduced in the cleaning system by the cleaned clothes or by the water used feed on solvents, detergents, oils, fatty acids and cause unpleasant odours. In order to prevent this problem, bactericide use is mandatory.

Rynex, produced in 1999, is a mixture of aliphatic propylene-glycol ethers. The currently used product is called Rynex 3 and contains only dipropylene glycol tert-butyl ether. Its flammability point is higher than 93°C. Solvair is a process using a mixture of solvents (dipropylene glycol normal-butyl ether) for washing and carbon dioxide for rinsing.

Liquid carbon dioxide, used as solvent in dry cleaning, is non-toxic, non-flammable and does not contaminate the environment (Foppe B. de Walle, 2005). At room temperature, carbon dioxide is a gas, but it can be liquefied at high pressure. Dry-cleaning machines using liquid carbon dioxide have high costs, as they are built to comply with norms for systems operating under high pressures, carbon dioxide reaching a pressure of 55 bar. Identification of efficient and ecologic degreasing solvents is reported in the most recent research works (Terrado 2011).

Today 90% of dry cleaning shops use PERC, a very little flammable colourless liquid, with a characteristic odour. Although the fire hazard has decreased, in case of exposure to high temperatures, perchloroethylene decomposes to HCl and carbon chlorides. Hydrochloric acid causes dermatitis, light sensitivity, and phosgene gases, used as chemical weapons in World War II, destroy the respiratory system. Exposure to PERC, even during short periods, may cause liver and kidney diseases, fatigue, nose and eye irritation and it has been classified as carcinogenic air pollutant.

PERC enters the human body through the air we breathe, through food or contaminated water and it remains stored in fatty tissue. Medical problems have been reported in persons living in the same buildings or near dry cleaning shops. The new machines used in dry cleaning significantly reduce health risks but, even if PERC is recycled, toxins remain inside clothes, affecting the health of children and sensitive persons. Dry cleaning operations in Europe release more than 70.000 tonnes of PERC per year in

the environment. The EU Detective on Volatile Organic Compounds (VOC) has major restrictions on the use of chlorinated hydrocarbons.

In the U.S. a recent rule prohibits the use of perchloroethylene in dry cleaning starting from 2020 (Jacobs Engineering 2004).

To protect the quality, colour, size and lifetime of clothing, manufacturers often recommend dry cleaning of clothes. Water swells the fibers, especially natural ones, and during drying, agitation changes product size due to stretching and compression of natural fibers, leading to a reduction of the product size.

Studies have shown that 50-70% of clothing whose label recommends dry cleaning, including leather, suede and wool, can be cleaned using water. Eco-labelled biodegradable detergents are used in wet cleaning. Water temperature, degree of agitation, the moisture content should be monitored and supervised to size change, dye migration and destruction of clothing shape. Stain removal is very important before the actual cleaning and can be performed with enzymes, peptides or other detergents. Wet cleaning, however, is a process that consumes a lot of water, requires highly trained personnel and causes more damage to clothes than other methods, therefore it is a risky method that requires intensive and expensive skilled labour.

Decamethylcyclopentasiloxane was used as solvent for the first time in 1999 and its flammability point is 77°C.

Silicones, also called siloxanes, are substances used in everyday life. Silicones are chemically inert substances. Depending on their molecular weight, they can be oils or highly viscous liquids (Fig. 1). They are used in chemical, cosmetics and medicine industries.

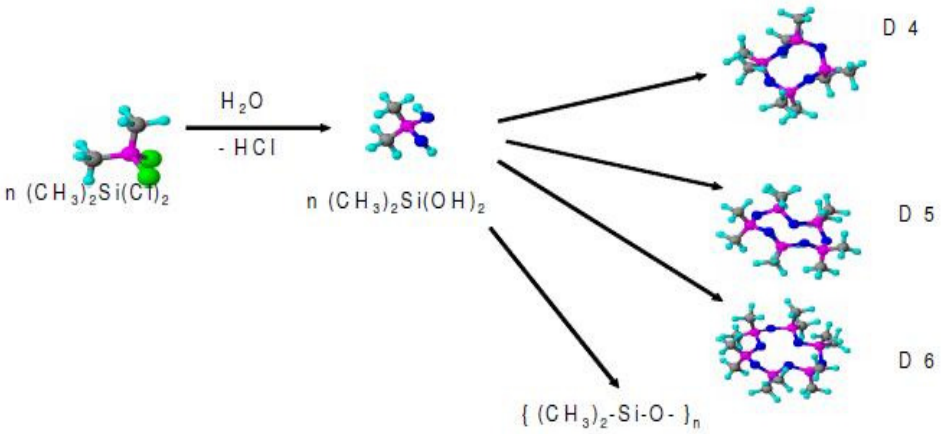


Figure 1: Siloxanes with various molecular weights and polymerization degrees

Decamethylcyclopentasiloxane (D5) is used as dry cleaning solvent, which upon decomposition generates carbon dioxide, water and sand, and is not toxic or pollutant.

As a result of studies on dry cleaning using D5, it was reported that this technology leads to obtaining soft clothes, with pleasant odour and bright and clear colours.

These studies have shown that in textile products, D5 cleaning system achieved a cleaning performance comparable to PERC in removing stains, preserving colour intensity and maintaining the original appearance of clothes (Seiter 2004). Cleaning leather and fur articles with PERC leads, in many cases, to size and colour change, degreasing, staining due to dissolution of adhesives and requires significant post-cleaning treatment (Inatsugi 2008).

In the context of declining purchasing power and consumption of luxury items, the cleaning services market may reach a share of 24% of the population resorting to dry cleaning services per month.

The influence of D5 solvent on leathers and furs is little known, an issue that this paper addresses in detail below.

Materials and Methods

Materials studied in order to assess performance of dry cleaning using D5 solvent have varied significantly in terms of structure and processing: beige and denim dyed sheepskins, blue dyed polar fox fur, 2 used mink and sheep fur coats in 2 colours (beige and brown).

Dry cleaning was performed using the Euromac machine (NOVA 40, Italy). Characteristics of D5 solvent (Cyclopentasiloxane,2,2,4,4,6,6,8,8,10,10-decamethyl-) are: Molecular formula-$C_{10}H_{30}O_5Si_5$, Molecular wt.: 370, Density: 0.958 g cm^{-3}, Melting point: -44 °C, Boiling Point: 210°C, Vicosity: 3.74 cP.

Two types of dry cleaning technologies were tested: variant 1, consisting in washing with water and detergent followed by cleaning with D5 and variant 2, consisting in cleaning with D5 only, under the technological conditions recommended by the manufacturer (www.cyclosiloxane.eu).

The quality of cleaning and its influence on the colour, softness and size of various materials tested were assessed using micro-destructive and non-destructive methods by means of: Datacolor Check II Instrument with color management software interface (Datacolor), ST300 *softness* tester (MSA Engineering Systems, Ltd) according to EN ISO 17235:2002, MHT (Micro Hot Table system, Caloris SA) and Digital Shrinkage temperature apparatus (Giuliani Technology) according to ISO 3380. The presence of D5 solvent after cleaning furs was assessed by SEM-EDAX electron microscopy (FEI Quanta 200). Contact angle was determined for the surface of tested leathers and furs using VGA Optima XE (AST Products USA). Correlation of characteristics obtained by means of non-destructive and micro-destructive methods were compared with classic, destructive analyses: extractable matter content (EN ISO 4048) and tear load measurement (EN ISO 3377-1).

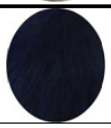
Results and Discussion

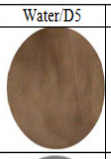
Color assessment of dry cleaned furskins and leathers

The dry cleaned furskins and leathers present restored colours as compared with the initial state of leather or furskin items (Table 1). The dry cleaned items with D5 (V2) are more intensely coloured and brighter as compared with water/D5 cleaned items (V1) and initial state, before dry cleaning (0) (Fig.1-9). The different behaviour, meaning lighter color with preserving of wriggled finishing appearance as in initial

state was recorded in the case of denim leathers (Fig. 6). In general, the colour of leathers and furs intensifies and becomes brighter in the case of cleaning using D5 only, and becomes lighter and loses some of its brightness when using water and D5. Water proves to be an excellent solvent, but it is too polar for dyes, which leads to dye elimination and loss of brightness.

Table 1- Furskins and leather samples before and after dry cleaning with water/D5 and D5

Leather / furskin sample	Treatment		
	Initial state	Water/D5	D5
Mink furskin coat			
Sheepskin coat			
Polar blue dyed fox			

Leather / furskin sample	Treatment		
	Initial state	Water/D5	D5
Sheepskin beige leather			
Sheepskin denim leather			

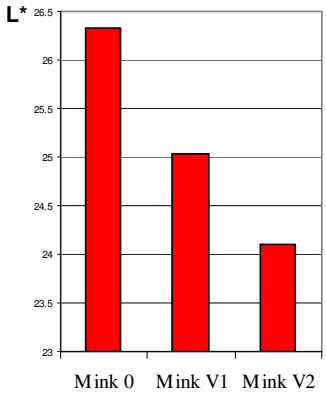


Fig. 1-Mink coat colour lightness

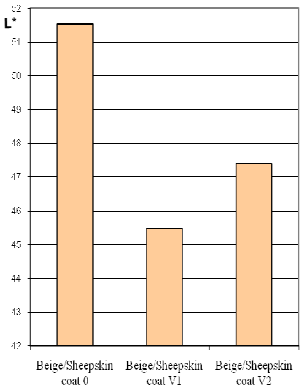


Fig. 2- Sheepskin coat lightness: beige side

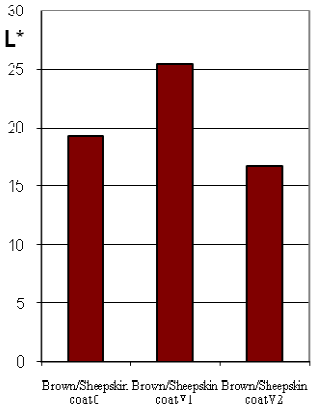


Fig. 3- Sheepskin coat lightness: brown side

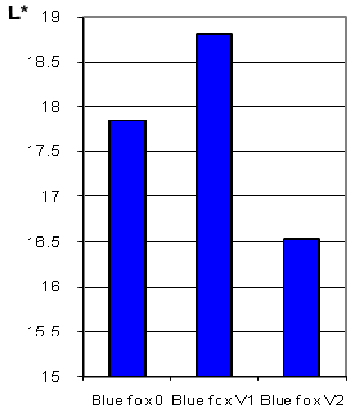


Fig. 4- Blue fox lightness

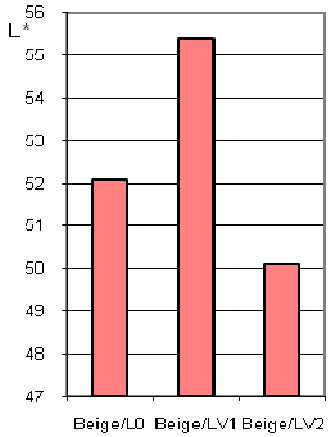


Fig.5- Beige leather lightness

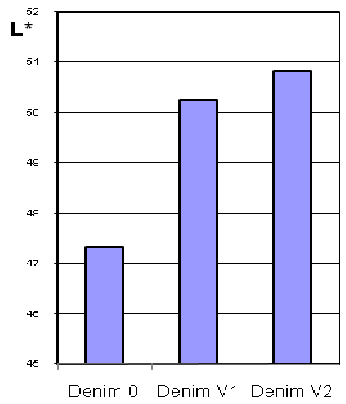


Fig. 6- Denim leather lightness

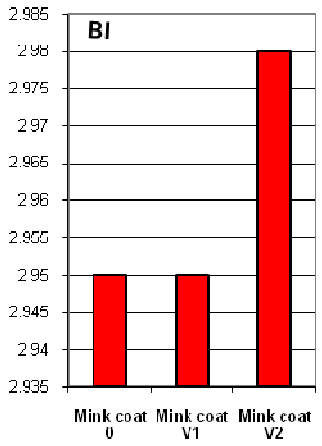


Fig. 7-Mink colour brightness

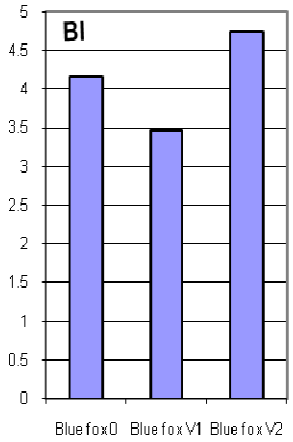


Fig. 8-Blue fox colour brightness

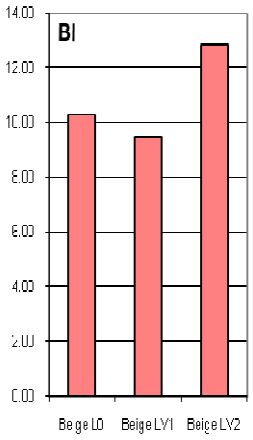


Fig. 9-Beige leather brightness

Softness assessment of dry cleaned furskins

In all cases cleaning leads to an improvement in fur softness (Fig.10-12), and the known effects of water as cleaning solvent are annihilated by the silicone solvent which does not allow structural elements to stick to one another and does not lead to structure hardening. Although the extractable matter content is reduced, dermis softness is improved. A slight increase of extractable substances from hair and wool may explain the higher brightness when using D5 solvent (Fig.13-15).

An increase in shrinkage temperature of dermis cleaned with D5 (Fig. 16, 17) and an increase in tear strength (Fig. 18, 19) suggests an interfibrillary deposit and improvement in shrinkage resistance along with softness improvement, also confirmed by identifying silicon by EDAX spectroscopy in the dermis structure (Fig. 20, 21). Investigations performed have shown that in the case of old fur coats, with lower shrinkage temperatures, hydrothermal resistance is

substantially improved after cleaning, which confirms the restoration effect of cleaning using D5 solvent.

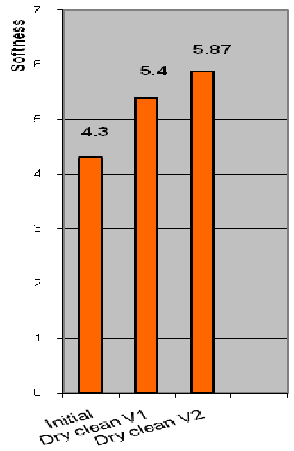


Fig. 10- Blue fox softness

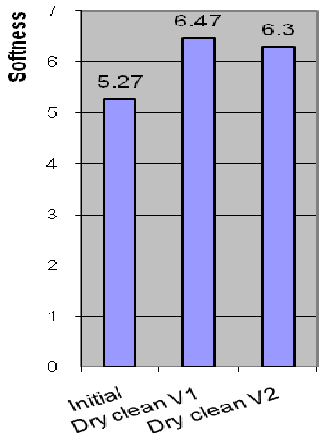


Fig. 11- Sheepskin coat softness

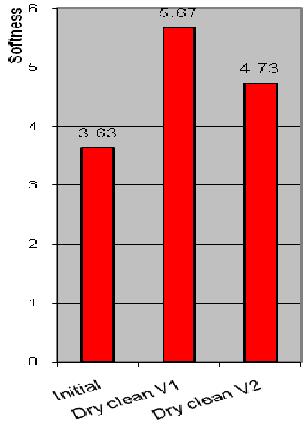


Fig.12- Mink coat softness

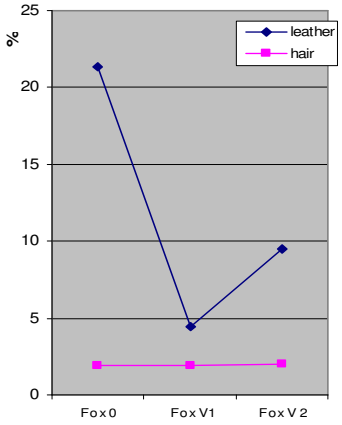


Fig.13- Blue fox fat content

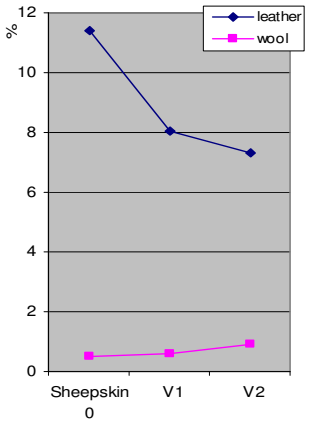


Fig.14- Sheepskin coat fat content

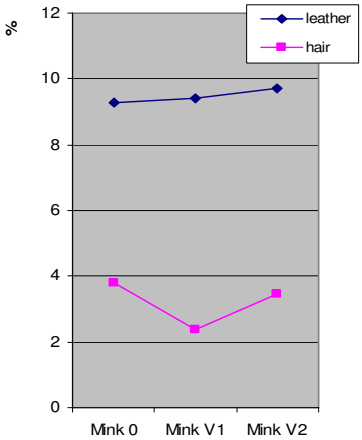


Fig.15- Mink coat fat content

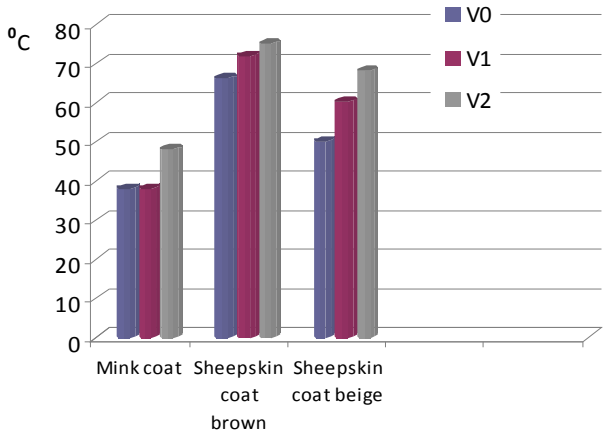


Fig.16- Shrinkage temperature of old coats

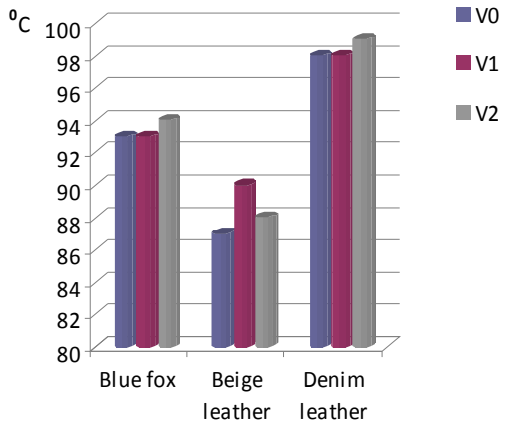


Fig.17- Shrinkage temperature of fox skin and leathers

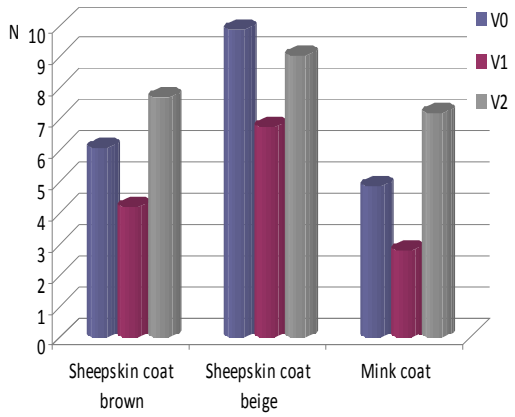


Fig.18- Tear load for sheepskin and mink coats

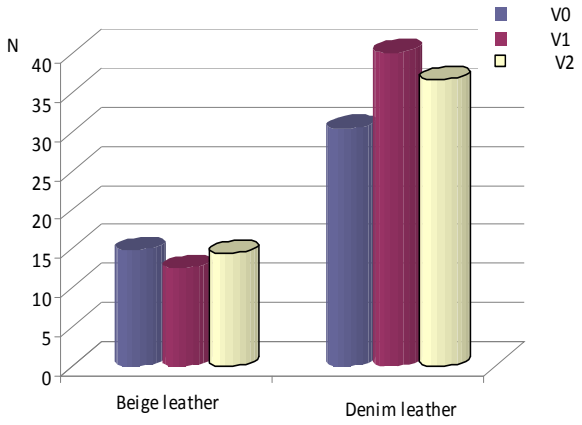


Fig. 19- Tear load for beige and denim leathers

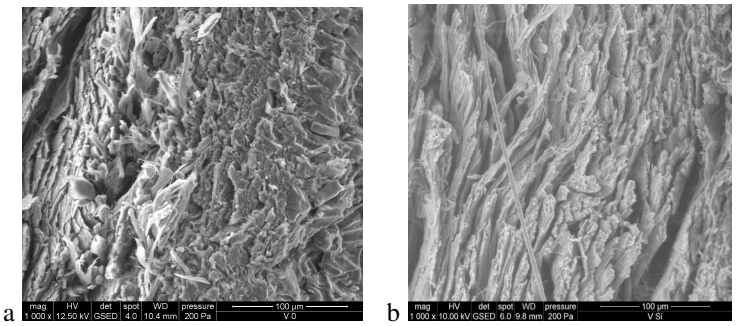


Fig.20- SEM image of dermis structure before (a) and after dry cleaning (b)

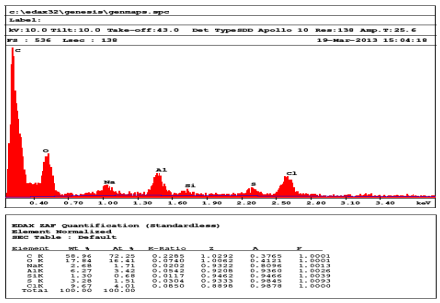


Fig.21- EDAX identification of Si in dermis structure

Surface properties assessment of dry cleaned furskins and leathers

The improvement of surface properties for dry cleaned furskins and leathers can add value to the new method based on D5 solvent. Contact angle measurements (Table 2) proved to add hydrophobicity to the dry cleaned surfaces of leathers and furskins (Fig.22-25), very probably due to the siloxane solvent. The results suggest that the wearing of furskins and leather articles cleaned with D5 solvent will protect them from hydrophilic soils.

Table 2 - Contact angle of furskins and leather surfaces dry cleaned with D5

Samples	Contact angle, (^{0}) Water	
	Before cleaning	After dry cleaning with D5
Mink coat	67.4	88.3
Beige sheepskin	57.9	76.8
Brown sheepskin	112.7	115.6
Blue fox	67.4	88.3
Beige leather	119.5	127.5
Denim leather	69.7	79.0

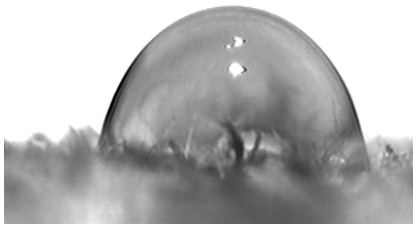


Fig. 22. Contact angle of water drop on mink leather

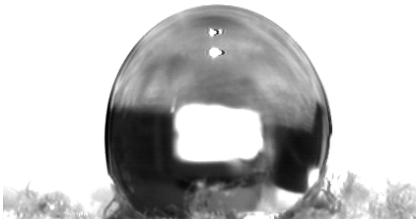


Fig. 23.Contact angle of water drop on dry cleaned mink leather

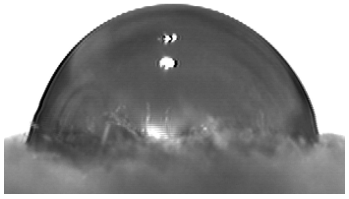


Fig.24. Contact angle of water drop on denim leather

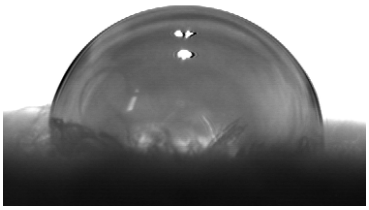


Fig.25. Contact angle of water drop on dry cleaned denim leather

Conclusion

Dry cleaning using decamethylcyclopentasiloxane (D5) is an eco-friendly alternative providing leather and fur articles with durability and non-toxicity during wear. Colour, softness and brightness of items cleaned with D5 are restored and do not require subsequent re-dyeing processes. Assessment based on micro-destructive analysis (MHT) and non-destructive analysis (softness, colour) provides the required information for evaluation before and after cleaning articles to be subjected to dry cleaning.

Acknowledgement

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