Study on Dry Cleaning with Decamethylcyclopentasiloxane as Ecological Alternative for Leathers and Furskins

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The study of using a new solvent, decamethylcyclopentasiloxane, for dry cleaning of natural leather and fur articles, has shown improvements regarding: maintaining or increasing colour intensity and brightness of dermis and hair, increasing softness and hydrophobicity of the dermis substrate, provided that the two substrates have been efficiently degreased. The correlation of non-destructive (colorimetry, softness measurement, contact angle), micro-destructive (SEM, EDAX, MHT) and destructive (fat content, tear strength) analysis has proven that the effects of decamethylcyclopentasiloxane are due to its deposition in the dermis structure or on the hair surface, after cleaning, improving their structure without the known disadvantages of tetrachloroethene (discolouration, hardening, toxicity, increased soil affinity).

Keywords: dry cleaning, solvent degreasing, decamethylcyclopentasiloxane

Today 90% of dry cleaning shops use tetrachloroethene, a very little flammable colourless liquid, with a characteristic odour, able to decompose to the hydrochloric acid and carbon chlorides at high temperature. Exposure to tetrachloroethene, even during short periods, may cause liver and kidney diseases, fatigue, nose and eye irritation and it has been classified as carcinogenic air pollutant [1].

Tetrachloroethene enters the human body through the air we breath, through food or contaminated water and it remains stored in fatty tissue. Medical problems have been reported on persons living in the same buildings or near dry cleaning shops. The new machines [2] used in dry cleaning significantly reduce health risks but, even if tetrachloroethene 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 tetrachloroethene per year in the environment and in USA a recent rule prohibits the use of tetrachloroethene in dry cleaning starting from 2020 [3].

Decamethylcyclopentasiloxane, a silicone class substance, used as solvent for the first time in 1999, has the flammability point at 77°C and is neither toxic nor pollutant.

The studies [4] have shown that in textile products, decamethylcyclopentasiloxane cleaning system achieved a cleaning performance comparable to tetrachloroethene in removing stains, preserving colour intensity and maintaining the original appearance of clothes. Cleaning leather and fur articles with tetrachloroethene leads, in many cases, to size [5] and colour change, overdegreasing and staining due to dissolution of adhesives and requires significant post-cleaning treatment. Identification of efficient and ecologic degreasing solvents is reported in the most recent research works [6]. The influence of decamethylcyclopentasiloxane solvent on leather and fur dry cleaning is unknown, an issue that this paper addresses in detail.

Experimental part

Materials and methods

Materials studied in order to assess performance of dry cleaning using decamethylcyclopentasiloxane solvent have varied significantly (table 1) in terms of structure and processing: beige and denim dyed sheepskins, blue dyed polar fox fur, 2 old mink and sheep fur coats in 2 colours (beige and brown).

Leather/furskin sample	Treatment		
	Initial state	Water/ decamethylcyclopenta-siloxane	Decamethylcyclopenta-siloxane
Mink furskin coat	Mink 0	Mink V1	Mink V2
Sheepskin coat	Beige sheepskin coat 0	Beige sheepskin coat V1	Beige sheepskin coat V2
Sheepskin coat	Brown sheepskin coat 0	Brown sheepskin coat V1	Brown sheepskin coat V2
Polar blue dyed fox	Blue fox 0	Blue fox V1	Blue fox V2
Sheepskin beige leather	Beige L0	Beige LV1	Beige LV2
Denim leather	Denim 0	Denim V1	Denim V2

Table 1
FURSKINS AND LEATHER SAMPLES BEFORE AND AFTER DRY CLEANING WITH WATER/ DECAMETHYLCYCLOPENTASILOXANE AND DECAMETHYLCYCLOPENTASILOXANE

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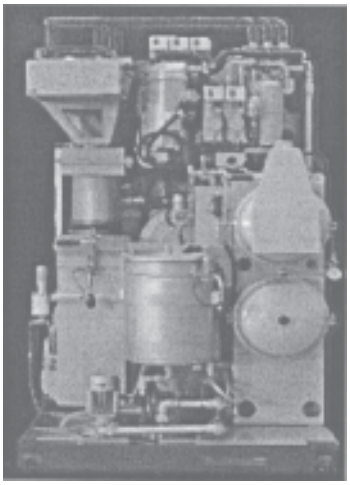

Fig.1. Dry cleaning machine

Dry cleaning was performed at industrial level with the Euromac machine (NOVA 40, Italy, fig.1) and decamethylcyclopentasiloxaneas solvent (D5).

The main characteristics of decamethylcyclopentasiloxane (cyclopentasiloxane, 2,2,4,4,6,6,8,8,10,10-decamethyldecamethylcyclopenta-siloxane) solvent 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 decamethylcyclopentasiloxane and variant **2**, consisting in cleaning with decamethylcyclopentasiloxane only, using the technologies presented in table 2.

The quality of cleaning and its influence on the colour, softness and size of various tested materials were assessed using micro-destructive and non-destructive methods by means of: Datacolor Check II Instrument with colour management software interface (Datacolor), ST300 *softness* tester (MSA Engineering Systems, Ltd) according to EN ISO 17235, MHT (Micro Hot Table system, Caloris SA [7]) and Digital Shrinkage temperature apparatus (Giuliani Technology) according to ISO 3380. The presence of decamethylcyclopentasiloxane 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) with the final aim of identification of post-cleaning wearing behaviour. Characteristics obtained by means of non-destructive and micro-destructive methods were compared with those of classic, destructive analyses: extractable matter content (EN ISO 4048) and tear load measurement (EN ISO 3377-1). The target of non-destructive analyses was the development of a scientific method for the dry cleaning shops in order to evaluate leather and furskin articles before dry cleaning, as a tool for diminishing damage after dry cleaning.

Table 2
DRY CLEANING TECHNOLOGY BASED ON DECAMETHYLCYCLOPENTASILOXANE SOLVENT

Washing (V1)
H_2O – 600% (% with respect to leather or furskins weight);
1% nonionic detergent
temperature – 20°C;
duration– 15 min;
running – 14 min with 25 rot/min.
Draining
Drying
Machine washing with mechanical filter
50% D5;
running-20 sec with 40 rot/min.
Dry cleaning preparing(V1 and V2)
200% D5;
temperature— 20°C;
running-10 sec with 40 rot/min.
Mechanical filter cleaning with solvent and detergent add
running-10 sec with 40 rot/min;
1% non-ionic detergent.
Solvent heating
temperature— 28°C;
running-30 sec with 40 rot/min.
Dry cleaning with leather/furskins load
running-7 min with 40 rot/min on sense invertors.
Solvent download
running-45 sec with 40 rot/min.
Press out
running-5 min with 300 rot/min;
running-5 min with 300 rot/min.
Drying
temperature—under 80°C;
duration– 80 min.

Results and discussions

Colour assessment of dry cleaned fuskins and leathers

The dry cleaned furskins and leathers present preserved or restored colours as compared with the initial state of leather or furskin items. The assessment of color intensity (L*) and brightness (BI) was performed on hair or wool cover for furskins and on dermis for leathers (table 3).

The items dry cleaned with decamethylcyclopentasiloxane (V2) are more intensely coloured and brighter as compared with water/decamethylcyclopentasiloxane cleaned items (V1) and initial state, before dry cleaning (0). The different behaviour, meaning lighter color with preservation of wriggled finishing appearance as in initial state was recorded in the case of denim leathers. In general, the colour of leathers and furs intensifies and becomes brighter in the case of cleaning using decamethylcyclopentasiloxane only, and becomes lighter and loses some of its brightness when using water and decamethylcyclopentasiloxane. Water proves to be an excellent solvent, but it is too polar for dyes, which leads to dye elimination and loss of brightness.

Softness assessment of dry cleaned furskins

In all cases cleaning improves the softness for furskins (table 4), the known effects of water as cleaning solvent are annihilated by the silicone solvent, which does not allow structural elements to stick together and does not lead to structure hardening as water or tetrachloroethene do.

The extractable matter content is substantially reduced by 16.9-11.8% for blue fox, by 3.36-4.1% for sheepskin fur coat and dermis softness is improved. A slight increase of extractable substances from wool (by 0.4%) may explain the higher brightness when using decamethylcyclopentasiloxane solvent (fig. 2-4).

The possibility of replacing natural fat with decamethylcyclopentasiloxane solvent was also proved by EDAX identification of Si on hair surface at the level of 0.26% wt (fig.5).

An increase in shrinkage temperature of dermis cleaned with decamethylcyclopentasiloxane (fig. 6, 7) and also, an increase in tear strength (fig. 8, 9) suggests an interfibrillary deposit of solvent with effect on improved splitting of fibril structure.

Sample	L*	BI
Mink 0	26.32	1.95
Mink V1	25.04	2.95
Mink V2	24.11	2.98
Beige sheepskin coat 0	51.52	9.41
Beige sheepskin coat V1	45.5	10.72
Beige sheepskin coat V2	47.4	11.37
Brown sheepskin coat 0	19.22	1.58
Brown sheepskin coat V1	19.22	1.22
Brown sheepskin coat V2	16.69	2.49
Blue fox 0	18.80	4.16
Blue fox V1	18.54	3.46
Blue fox V2	17.84	4.73
Beige L0	52.08	10.31
Beige LV1	55.38	9.48
Beige LV2	50.1	12.88
Denim 0	47.33	12.77
Denim V1	50.24	15.24
Denim V2	50.84	15.66

Table 3
LEATHER AND FURSKINS LIGHTNESS AND BRIGHTNESS BEFORE AND AFTER DRY CLEANING

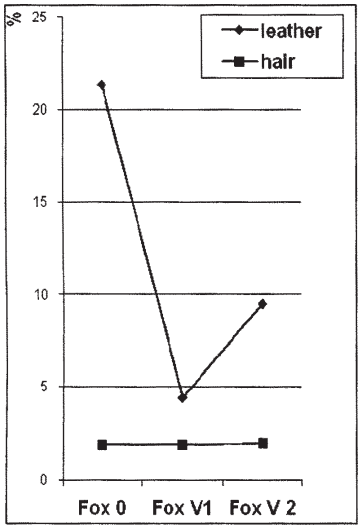

Fig.2. Blue fox fat content

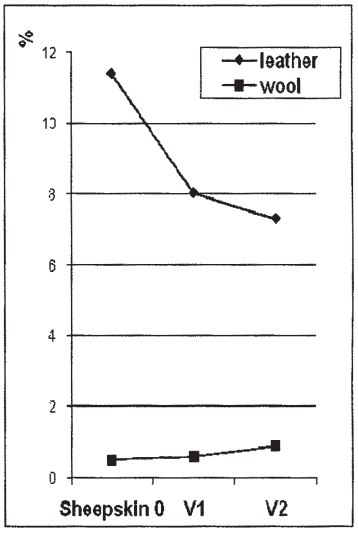

Fig.3. Sheepskin fat content

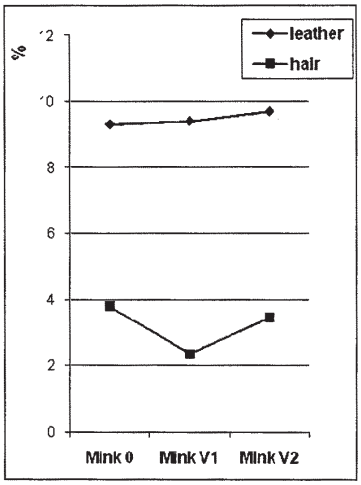

Fig.4. Mink fat content

Table 4
THE INFLUENCE OF DECAMETHYLCYCLOPENTASILOXANE BASED DRY CLEANING METHODS ON LEATHER AND FURSKINS SOFTNESS

Stage of chemical treatment	Softness		
	Blue fox	Sheepskin	Mink
Initial	4.30	5.27	3.63
Dry cleaned V1	5.40	6.47	5.67
Dry cleaned V2	5.87	6.3	4.73

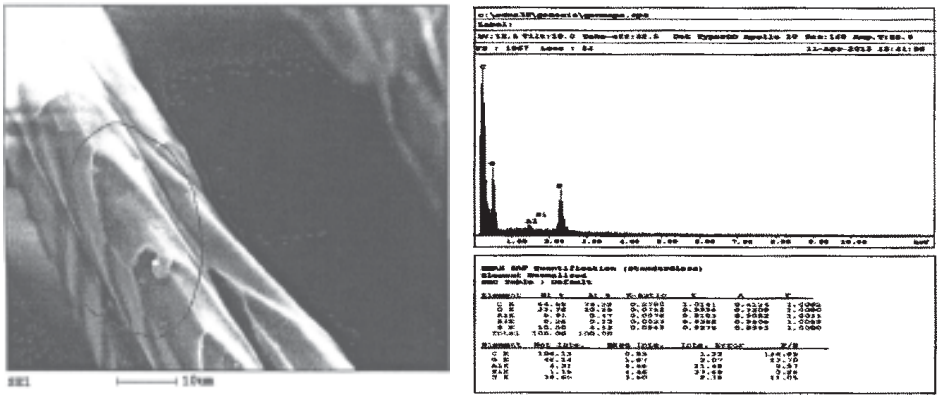

Fig. 5. EDAX identification of Si on the surface of blue fox hair

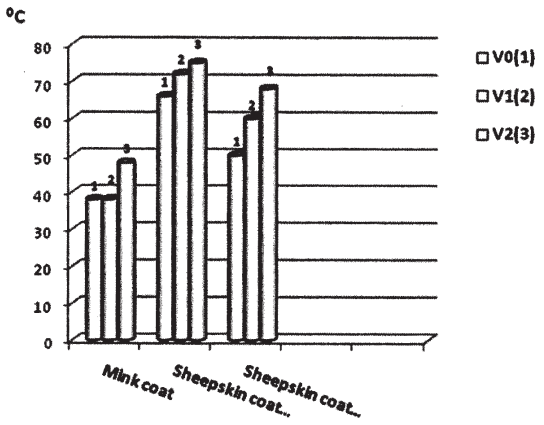

Fig.6. Shrinkage temperature of old coats

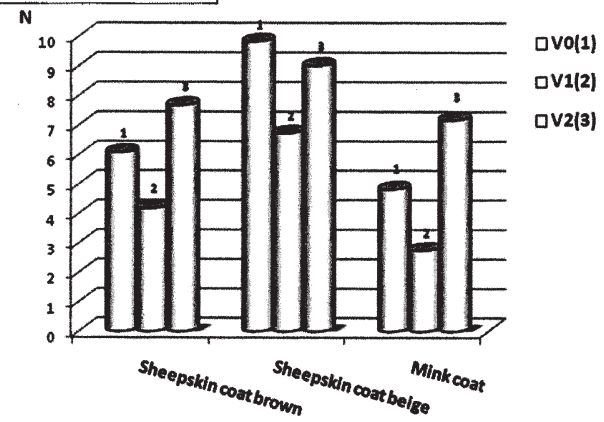

Fig.8. Tear load for sheepskin and mink coats

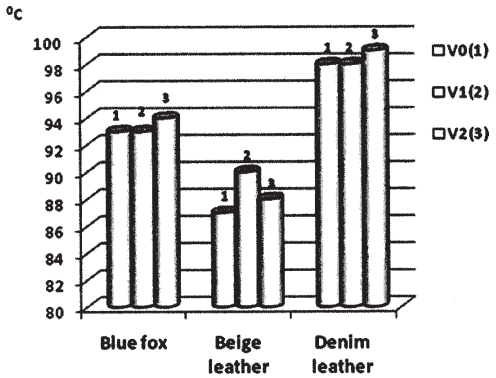

Fig.7. Shrinkage temperature of fox skin and leathers

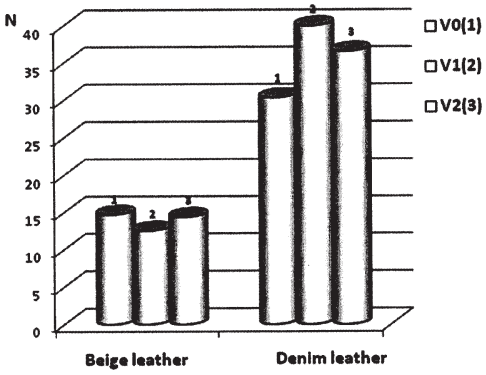

Fig. 9. Tear load for beige and denim leathers

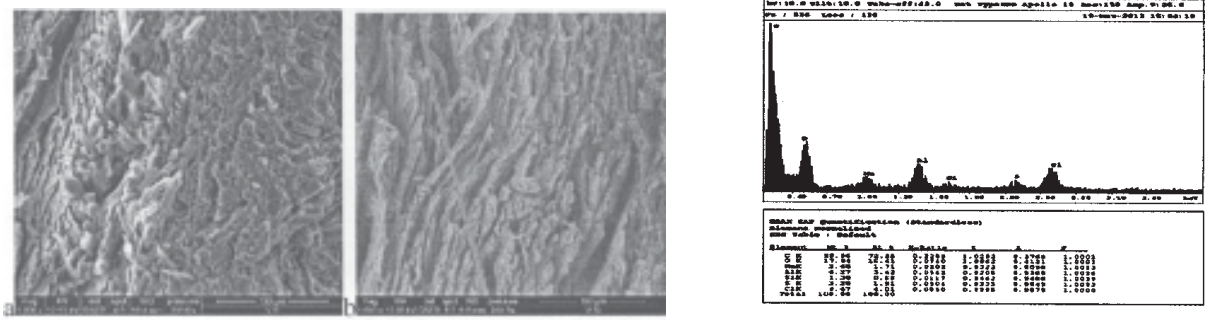

Fig.10. SEM-EDAX analyze of dermis structure before (a) and after dry cleaning (b) with identification of Si in dermis structure after decamethylcyclopentasiloxane dry cleaning (b)

Investigations performed have shown that in the case of old fur coats, with lower shrinkage temperatures, hydrothermal resistance is improved by 10^0C for the mink coat, by 6-9^0C for brown sheepskin and by 10-18^0C for beige sheepskin after dry cleaning, which confirms the restoration effect of dry cleaning using decamethylcyclopentasiloxane solvent. The leathers and furskins with high shrinkage temperatures are not influenced by decamethylcyclopentasiloxane dry cleaning.

The effect on the new structured material after dry cleaning is the improvement in shrinkage resistance along with softness increase, also confirmed by identifying silicon by EDAX spectroscopy in the dermis structure (fig. 10). The concentration of Si in dermis cross section was at the level of 1.30% wt.

Table 5
CONTACT ANGLE OF FURSKINS AND LEATHER SURFACES DRY CLEANED WITH DECAMETHYLCYCLOPENTASILOXANE

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

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 decamethylcyclopentasiloxane solvent. Contact angle measurements (table 5) proved hydrophobicity of the dry cleaned surfaces of leathers and furskins, due to the siloxane solvent [8]. The analyses proved that wearing of furskins and leather articles cleaned with decamethylcyclopentasiloxane solvent will protect them from hydrophilic soils and improve their quality.

Conclusions

Dry cleaning using decamethylcyclopentasiloxane is a new eco-friendly alternative as compared to tetrachloroethene based dry cleaning, providing leather and fur articles with durability and non-toxicity during wear. Colour lightness and brightness, softness, tear resistance of items cleaned with decamethylcyclopentasiloxane are improved or preserved as compared with initial state. The quality improvement of leather and furskins dry cleaned with decamethylcyclopentasiloxanesolvent is proved by its deposition in dermis structure and on wool/hair surface with effect on tear strength, shrinkage temperature and surface angle increasing.

Assessment based on micro-destructive analysis (MHT) and non-destructive analysis (softness, chromatic parameters) provides the required information for evaluation before and after cleaning articles to be subjected to dry cleaning.

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References

1. PETER WATT, Tetrachloroethene, Concise International Chemical Assessment Document 68, World Health Organization, Geneva, 2006.
2. FOPPE B., DEN OTTER W. A.J.L., Demonstration pilot scale testing of textile dry cleaning with sub/supercritical carbon dioxide, LIFE Project Number LIFE00 ENV/NL/000797, 2005.
3. *** Jacobs Engineering, Viable alternative to perchloretylene in dry cleaning-Jacobs Engineering, Pasadena, California, USA, December 2004.
4. SEITER, M., Textile cleaning in Cyclosiloxane D5/Green Earth solvent-Chemische Fabrik Kreussler&Co.GmbH, November 2004.
5. INATSUGI,T., SATO, K., NAKAMURA, M., NAKANO, H., YAMAMOTO, T., Decrease in leather water resistance due to dry cleaning, Magazine of the Japanese Leather Chemists Association: Leather Science, 54 (2), p. 90-97, 2008.
6. TERRADO, R., VAN MIERLO,M., MARGINET,X., Degreasing process based on the use of DME, XXXI IULTCS Congress, Valencia (Spain) - September 27th-30th, Paper E55, 2011.
7. PLAVAN,V., GIURGINCA, M., BUDRUGEAC, P., VILSAN, M., MIU, L., Rev. Chim. (Bucharest), **61**, 7, 2010, p.627
8. NAVIGLIO, B., CALVANESE, G., FLORIO, C., CARACCIOLO, D., SCOTTI, M., L'impermeabilizzazione del cuoio: caratteristiche e prestazioni dei trattamenti di idro e oleorepellenza, Cuoio Pelli Materie Concianti, 87 (2/3), p. 83-94, 2011

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