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Determination of oxidation parameters of fatliquored leather by DSC

A.M. Manich*, S. Cuadros, J. Cot, J. Carilla, A. Marsal

Ecothechnologies Department and Laboratory of Thermal Analysis, Instituto de Investigaciones Químicas y Ambientales de Barcelona, Consejo Superior de Investigaciones Científicas, Jordi Girona 18-26, 08034 Barcelona, Spain

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Abstract

The oxidation of a number of fatliquoring formulations, of different iodine index, derived from fish oil, rapeseed oil, neatsfoot oil, lecithin, paraffin, sulphited and sulphated variants was studied. The formulations included dispersing agents, stabilizers and/or anti-oxidants. Sheepskins were treated with fatliquoring agents at 5% of fatty matter. The oxidation of the fatliquoring formulations and the fatliquored skins was studied by non-isothermal differential scanning calorimetry (DSC). The onset thermoxidation temperature and the enthalpy of the thermoxidation peak located between 195 and 265 °C were determined and then related to the different fatliquoring standard formulations. The skins were subjected to ageing treatments using UV radiation and temperature. The fall in the denaturation temperature of the skin due to ageing was related to the oxidability of the fatliquoring agent.

Keywords: Thermoxidation; Fatliquor; Leather; Non-isothermal DSC; Ageing

1. Introduction

Leather is a biomaterial (skin) made of collagen fibrous protein, which has been industrially modified and transformed in order to avoid its putrefaction [1]. After being tanned with trivalent chromium salts a complete stabilization is achieved: the resistance against water absorption increases and the tanned material cannot undergo putrefaction, swelling, or drying off to an inflexible solid mass. Fatliquoring is necessary to confer the final mechanical, aesthetic and handle characteristics of leather [2].

The reaction of oxygen with lipids involves free radical initiation, propagation and termination, and its kinetics has been investigated for years. Experiments based on analytical methods (determination of peroxide concentrations) or on volumetric methods (measurement of rate of oxygen consumption) have been carried out on oxidation of lipids and other natural and synthetic products. Given that the oxidation is an exothermal process, measurements of enthalpy by means of calorimetry can be applied to determine oxidative stabilities [3]. The enthalpy involved in the exothermal process of oxidation can be measured by differential scanning calorimetry (DSC) as well as the oxidative stability.

Atmospheric oxygen is the most ubiquitous and economically important oxidising agent in many chemical processes including those of the tanning industry. However, autoxidation is an undesirable process since rubber, plastics, fuel oil, fat and fatliquored materials such as tanned fatliquored leather may undergo autoxidative deterioration or rancification [4]. The free-radical chain oxidation reaction of fats and other oxidizable substrates is catalysed by light, transition metal ions or water molecules, and is propagated by free hydroperoxy radicals [4]. In the tanning industry, the catalysing effect of the transition metal ions on the oxidation of unsaturated fats is well-known. It has been reported that stacks of leather have burst into flames when piled up under moist and warm conditions [5].

Analysis of hide fat has not yet been standardised or even informally customized in the tanning industry [6]. Consequently a variety of techniques and procedures are employed, from simple visual examination through stringent quality

* Corresponding author. Tel.: +34 934006154; fax: +34 932045904.
E-mail address: ambeco@cid.csic.es (A.M. Manich).

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monitoring via sampling and extraction protocols. The analytical procedures are based on the works of Porter, who studied the oxidation of numerous oils on tanned hide powders [7] using Mackey's method [8]: This method is based on the mixture of oil and tanned hide powder, which is heated at 97 °C while a controlled air flow is forced through the mixture. Given that the oxidation is an exothermal reaction, the time required to reach the maximum temperature is used to determine the oxidability of the oils.

The potential for oxidation, often related to insaturation in fats, has long been of interest to tanners as a matter of descriptive analytical data on the fats and oils employed in the industry. References to the iodine number [9] have been a common feature of oil quality requirement. Nevertheless, no new methods, apart from Mackey's, have been developed to test the oxidability of fatliquored leathers. Fat content in the tanned state is a critical quality control assessment and process control indicator. Fat values from the tanned-state reveal just how well degreasing has been accomplished and also whether a more vigorous and/or additional treatment is needed [5]. Thereafter, tanned hides are subjected to fatliquoring in order to obtain the most suitable properties for the final application of the leather.

The oxidation of fatliquored leathers starts with that of the fatliquoring agent or with the oxidation of natural fat that was not completely eliminated. Subsequently, the propagation phase, during which the products of decomposition react with all the oxidable substances contained in the skin, takes place. One of the ways of assessing oxidative ageing of the skin is to determine the change undergone by diverse parameters after ageing. The most prominent of these include: skin-yellowing, odour, change in values of tear resistance and tensile strength, fall in the shrinkage temperature and skin contraction [10] despite the fact the tests are very time-consuming and that the sample size required is large. The shrinkage temperature is the value at which the denaturation of collagen in leather takes place when the sample is soaked in water. This temperature is macroscopically detected by a sudden contraction in the leather and it has been used as a way of controlling the performance of the tanning process [1]. The oxidation of the collagen molecule, leads to a decrease on the denaturation temperature.

Given that autoxidation of fats, fatty acids and lipids is an exothermal process, the methods of thermal analysis are useful for studying thermostability, thermoxidation and autoxidation by isothermal experiments or non-isothermal experiments at a constant heating rate [11]. DSC has been used for monitoring the oxidation of heated oils [12]. There is good correlation between DSC method and other standard chemical methods. DSC offers an alternative for monitoring oxidation because it saves time, requires small samples with minimal preparation, and needs no chemicals.

DSC has also been applied to autoxidation kinetics of saturated and unsaturated fatty acids and their esters [13,14]. The oxidation course was monitored by DSC to determine the oxidative stability of these fat components under conditions of industrial processing and exploitation. The start of oxidation was dependent on the number of double bonds in the carbon chain and constitutes useful values to assess anti-oxidant activity [15].

Isothermal DSC experiments are rather time-consuming and are usually carried out under high oxygen pressure (PDSC). In contrast, non-isothermal DSC experiments are much faster and may yield more information not only about the first step of oxidation (observed in conventional isothermal methods), but also about further steps of oxidation from a single run. In conclusion, this experiment shows that the onset of the thermoxidation process may be a very useful value to determine the effects of additives, such as pro- and anti-oxidants [16].

The authors used DSC to determine the onset temperature of oxidation of diverse fatliquoring agents applied to bovine hides in an earlier paper [17]. DSC curves of hides treated with 10% fatliquoring agents from rapeseed oil and its variants sulphated and stabilized with anti-oxidant; dehydrogenated and sulphited fish oil; lecithin with dispersing anti-oxidant and emulsifying agent and sulphonated or sulphochlorinated paraffin were obtained. Hide samples were press-cut and tested in an oxygen atmosphere. The initial reactions of oxidation, which took place above 160 °C, were identified by the changes in the slope of the curve prior to the exothermal peak of substrate oxidation, which always occurred above 240 °C.

This study seeks to employ DSC to determine oxidation parameters of sheepskin samples treated with 5% of fatliquoring formulations as alternative to the classical very time-consuming Mackey's method.

2. Materials and methods

The fatliquoring formulations were based on crude and sulphited fish oil, crude and sulphited neatsfoot oil, lecithin, sulphated base and chlorated paraffin. Vitamin E and Tara extract were added to the fish oil as anti-oxidants. The sulphitation of fish oil was carried out in two different ways. The Hanus method [9] was employed to determine the iodine index of the fatliquoring agents. The fatliquoring is the application of an oil-in-water emulsion, which is subsequently induced to break, thus depositing a film of fatty matter over the collagen fibre structure of the tanned leather. The type of interaction between the fatliquor and the collagen network depends on the chemical nature of the several raw and chemically modified oils and surface-active agents. The sulphited and sulphated fractions are attracted by leather through ionic bonds. The free fatty acids may produce coordinated unions with the metallic tanning agents. The sulphochlorinated paraffins are able to form covalent unions with the non-dissociated amidic groups of collagen [18].

The fatliquoring agents were all of commercial type used by the tanning industry and the procedure of fatliquoring was also the standard process used by the tanning industry [19].

The oxidation temperature of the fatliquoring agents and fatliquored skin samples, which were press-cut or ground, was determined using a Mettler–Toledo differential scanning calorimeter (DSC 20) in an oxygen atmosphere with a flow of 100 ml/min. The ground samples underwent a temperature increase from 30 to 350 °C and the press-cut samples were subjected to a temperature variation from 30 to 275 °C with a heating speed of 10 °C/min using an open aluminium pan of 40 μl.

A Mettler–Toledo differential calorimeter (DSC 821 E) with a 40 μl closed aluminium pan was employed to determine the denaturation temperature of the skin. This determination was carried out with skin samples saturated with water. Once the samples were totally immersed in a vessel with water; the excess water was eliminated with filter paper. The test was carried out with a temperature programme from 20 to 120 °C at 5 °C/min.

The ageing tests were as follows: ground samples were subjected to UV radiation in a Suntest CPS$^+$ instrument for 48 h with a radiation of 450 W/m^2 and a temperature of 40 °C. Oxidation and denaturation temperatures of the aged samples were also determined. The press-cut samples underwent a thermal ageing test in an oven at 100 °C for 24 h to induce oxidation of the fatliquoring agent according to the ageing method 6B of the IULTCS Standard [20]. Subsequently, the denaturation temperature of the skin was determined again.

3. Results

3.1. Fatliquoring agents

The non-isothermal DSC was employed to assess the thermoxidation phenomena of the fatliquoring agents. Likewise, iodine indexes were also determined. The results are summarized as follows:

- *Crude fish oil*: iodine index 102. Oxidation commences at 121.25 °C. After a period of stabilization, a second oxidation takes place at 224.1 °C until total oxidation is produced.
- *Sulphited fish oil I*: iodine index 66. The break of the emulsion is observed above 100 °C. Oxidation of the product commences at 223.8 °C.
- *Sulphited fish oil II*: iodine index 69. The break of the emulsion is also observed above 100 °C. Oxidation of the product commences at 251.7 °C.
- *Crude neatsfoot oil*: iodine index 83. Oxidation commences at 158.8 °C whereas the final oxidation of the product starts above 240 °C (both temperatures are somewhat higher than those observed for crude fish oil).
- *Sulphited neatsfoot oil*: iodine index 54. After the break of emulsion above 100 °C, oxidation commences at 216.6 °C with a maximum around 240.8 °C whereas the final oxidation commences at 249.4 °C.
- *Lecithin*: iodine index 58. After the break of emulsion above 100 °C, oxidation is observed at 220 °C. The final oxidation is initiated at 260.6 °C.
- *Sulphated base*: iodine index 35. Oxidation occurs at 218.9 °C after the break of emulsion above 100 °C, whereas the second oxidation takes place at 247.2 °C.
- *Chlorinated paraffin*: iodine index 10. Break of emulsion is also observed near 100 °C. Although oxidation cannot be clearly identified, a number of changes in the slope of the baseline may be observed at 139.9 and 185.1 °C with a moderate peak at 229.2 °C. In contrast to the other fatliquoring agents, no significant final exothermal of oxidation is observed.

3.2. Fatliquored skin: ground samples

We determined in duplicate the oxidation and denaturation temperatures of the original samples and those subjected to ageing by UV radiation. The onset temperature of oxidation was determined from the DSC curve. Given that this oxidation can start before the oxidation of the substrate, the first exothermal peak may be attributed to either a first oxidation of the fatliquoring agent or to the oxidation of the substrate altered by this agent. This oxidation always was detected between 195 and 265 °C. Above 265 °C the final oxidation of the collagen substrated was produced. Consequently to assess the intensity of the oxidation effect due to fatliquoring,

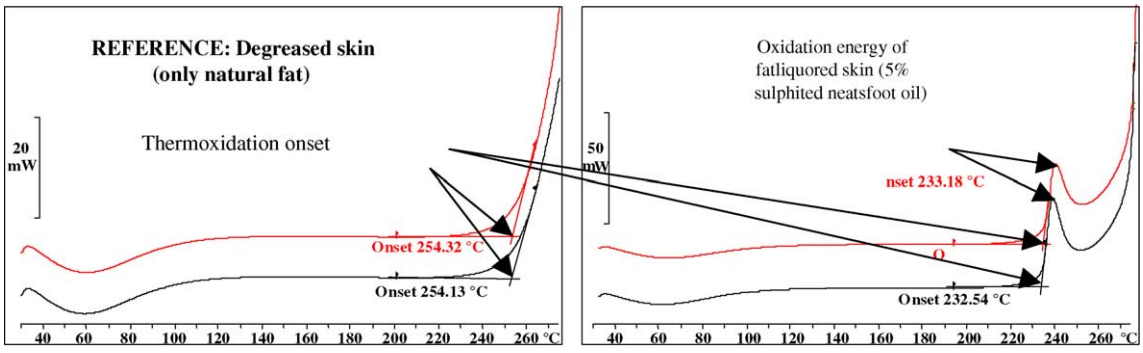

Fig. 1. DSC oxidation curves of the degreased skin taken as reference that contains only natural fat, and those of the sulphited neatsfoot oil 5% fatliquored skins. The oxidation peak due to fatliquoring is detected below 265 °C.

Table 1
Onset temperature of oxidation (OT_{ox}), Oxidation energy between 195 and 265 °C (E_{ox}) and denaturation temperature (T_d) of the ground samples before and after (OT_{ox}', $E_{ox'}$ and T_d', respectively) being subjected to ageing treatment with UV radiation

Fatliquoring agent	OT_{ox} (°C)	OT_{ox}' (°C)	E_{ox} (J/g)	E_{ox}' (J/g)	T_d (°C)	T_d' (°C)
Crude fish oil	234.5	225.7	492.6	482.3	96.0	98.4
	226.9	225.7	476.5	471.9	97.7	98.4
	238.1	226.4	439.9	435.5	97.2	97.0
	238.3	226.9	441.1	431.6	96.8	97.0
Sulphited fish oil 1	238.5	229.9	647.4	578.8	96.4	96.6
	237.8	228.4	614.7	582.2	97.0	98.8
Sulphited fish oil 2	254.8	250.8	194.2	168.2	96.6	98.0
	255.3	251.7	184.7	189.3	96.9	97.8
Crude neatsfoot oil	216.2	216.2	418.5	348.9	98.5	95.9
	216.8	210.0	428.7	329.0	97.3	95.4
Sulphited neatsfoot oil	233.5	230.1	455.0	400.7	103.0	102.2
	233.1	230.6	408.4	396.3	101.9	101.8
Lecithin	245.9	247.7	311.3	287.9	95.4	95.0
	245.5	247.9	302.6	305.0	91.9	94.0
Sulphated base	243.6	242.6	285.7	284.8	90.2	89.9
	241.6	242.8	287.5	286.7	90.0	94.3
Chlorated paraffin	255.2	257.1	199.4	201.2	92.7	93.2
	259.0	269.7	188.1	287.9	84.4	94.1

the exothermal enthalpy of the DSC curve between 195 and 265 °C was measured (Fig. 1).

The determination of the denaturation temperature is not very accurate given that the structure of the collagen is altered by the grinding operation. Table 1 shows the results of the oxidation temperature, the oxidation energy and the denaturation temperature before and after ageing treatment by UV radiation.

3.3. Fatliquored skin: press-cut samples

Tests were carried out in duplicate on the press-cut samples that were subjected to the same test of oxidation temperature determination. Table 2 shows the onset temperature of oxidation and also the oxidation energy determined from the DSC curve between 195 and 265 °C. Fig. 1 shows the DSC oxidation curves of the degreased skin taken as reference that contains only natural fat, and those of the sulphited neatsfoot oil fatliquored skin. The denaturation temperature was determined from the original samples and from samples subjected to thermal ageing in an oven at 100 °C for 24 h [20].

4. Discussion

4.1. Influence of sample preparation (ground/press-cut) on the determination of the thermoxidation onset temperature and the oxidation energy

A regression analysis between the oxidation parameters of the original samples revealed a negative correlation between the onset thermoxidation temperature and the oxidation energy released between 195 and 265 °C. The oxidation energy was higher in the case of the press-cut samples (correlation coefficients −0.605 and −0.792, respectively). The correlation between the onset temperature of oxidation of the ground and press-cut samples was very high ($r = 0.900$) as was the correlation between the oxidation energies ($r = 0.905$) (see Fig. 2). It may be observed that both values were, in general, higher for the press-cut samples. There was also a significant correlation between the denaturation temperature of the ground and press-cut skins ($r = 0.672$). The measurement of the denaturation temperature on the ground samples was less accurate than that of the press-cut samples due to the unclear peak shape of the former.

4.2. Influence of ageing on the oxidation parameters of fatliquored skin

Variance analysis [21] was employed to determine the influence of the type of fatliquoring agent, treatment of ageing and its possible interaction on the oxidation parameters of the ground samples of fatliquored skin. A very significant influence of fatliquoring agent and ageing (significance level

Table 2
Onset temperature of oxidation (OT_{ox}), Oxidation energy between 195 and 265 °C (E_{ox}) of press-cut samples and denaturation temperature of the press-cut samples before (T_d) and after (T_d') thermal ageing, and decrease in denaturation temperature (DT_d) due to ageing

Fatliquoring agent	OT_{ox} (°C)	E_{ox} (J/g)	T_d (°C)	T_d' (°C)	DT_d (%)
Degreased skin (natural fat) – reference NF	254.3, 254.1	228.6, 222.6	101.7, 101.9	94.3, 95.3	7.3, 6.5
Crude fish oil 1 (F1)	246.5, 246.4	330.1, 324.6	106.0, 106.0	93.3, 92.6	12.6, 12.0
Crude fish oil 1 plus Vitamin E (F1 + E)	239.2, 239.6	337.8, 344.7	106.0, 105.9	96.2, 93.3	11.9, 9.3
Crude fish oil 1 plus Tara extract (F1 + T)	273.8, 273.3	269.9, 265.6	105.4, 105.6	96.7, 96.9	8.2, 8.3
Crude fish oil 2 (F2)	239.5, 240.9	514.9, 494.9	104.2, 104.1	94.9, 95.4	8.9, 8.4
Sulphited fish oil 1 (SF1)	238.1, 238.6	722.8, 694.7	103.8, 103.6	96.8, 95.0	6.7, 8.3
Sulphited fish oil 2 (SF2)	274.4, 274.6	311.6, 246.2	104.4, 104.8	97.9, 99.1	6.3, 5.4
Crude neatsfoot oil (N)	217.9, 221.5	538.1, 446.5	105.3, 105.8	98.0, 97.8	7.5, 7.3
Sulphited neatsfoot oil (SN)	233.9, 232.5	641.7, 666.0	106.2, 106.5	98.7, 97.8	7.0, 8.2
Lecithin (L)	269.9, 269.9	351.1, 338.0	105.1, 105.3	94.2, 92.9	10.4, 11.8
Sulphated base (SB)	272.2, 272.3	289.0, 297.1	103.5, 103.3	98.4, 98.3	4.9, 4.8
Chlorated paraffin (CP)	269.3, 272.4	267.9, 244.7	103.6, 103.6	98.9, 99.2	4.5, 4.0

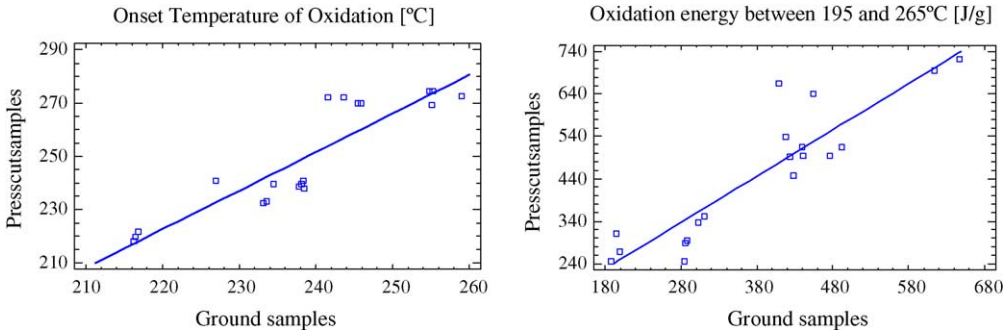

Fig. 2. Influence of sample preparation on the determination of oxidation temperature and oxidation energy released between 195 and 265 °C.

5%) on the thermoxidation onset temperature was observed. Ageing led to a fall in the thermoxidation onset temperature although interaction with the fatliquoring agent indicated that ageing did not affect the different fatliquoring agents in the same way. Fig. 3 shows that the lowest thermoxidation temperatures correspond to crude neatsfoot oil and fish oil whereas the highest temperatures correspond to sulphited fish oil and chlorinated paraffin. Ageing also lowered the oxidation temperature of fish oil and of one sulphited variant, whereas the effect of ageing was negligible in the case of the other variants. Ageing had the opposite effect in the case of chlorated paraffin. The oxidation energy and the denaturation temperature were not affected by ageing or by its interaction with fatliquoring agents. These parameters were only influenced by the fatliquoring agents.

By contrast, in the case of the press-cut samples, we observed that thermal ageing treatment in an oven at 100 °C for 24 h exerted a significant influence on the denaturation temperature. Significant interactions with the fatliquoring agent were produced with the result that the fall in the denaturation temperature was more marked in accordance with the type of the fatliquoring agent. The results are shown in Fig. 4.

The denaturation temperature of the aged press-cut samples fatliquored with crude fish oil and lecithin underwent a bigger fall than the samples treated with other agents. The regression analysis between the iodine index and the decrease in the denaturation temperature after ageing shows that there is a very significant relationship between these variables (at 0.1% level) with a correlation coefficient of 0.68. Fig. 5 shows that the higher the iodine index (the insaturation level of the fatliquor), the higher the decrease induced by ageing to the denaturation temperature.

4.3. Monitoring the thermostability of the press-cut fatliquored samples through the thermoxidability parameters obtained by non-isothermal DSC testing

If the experimental results are plotted as a function of the onset temperature of thermoxidation, the oxidation energy released between 195 and 265 °C and the fall in the denatu-

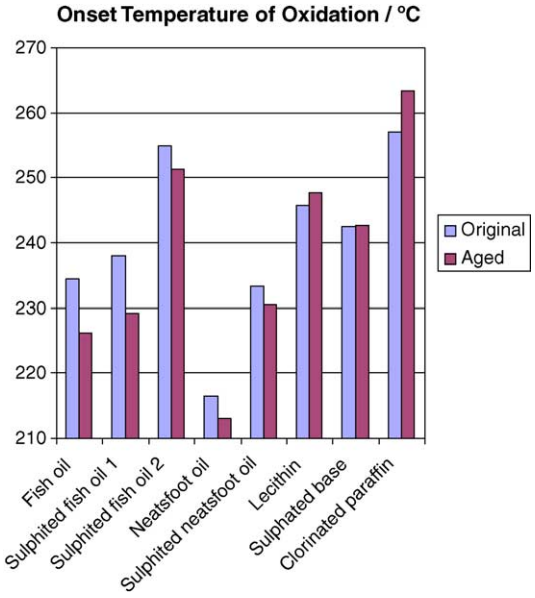

Fig. 3. Onset temperature of thermoxidation in ground samples with/without UV ageing treatment as a function of the type of fatliquoring agent.

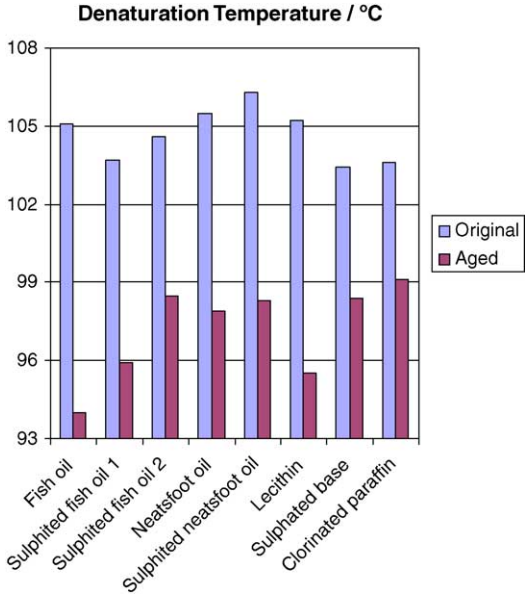

Fig. 4. Denaturation temperature of press-cut samples with/without thermal ageing as a function of the type of fatliquoring agent.

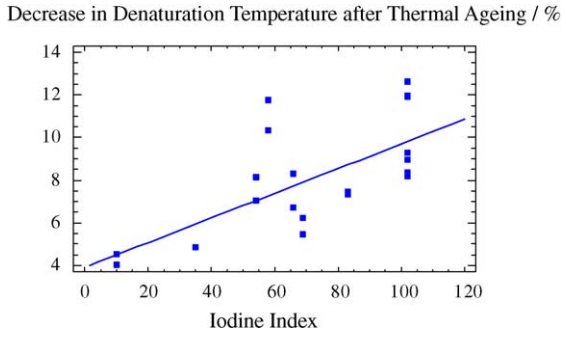

Fig. 5. Relationship between the iodine index of the fatliquoring and the decrease induced by ageing on the denaturation temperature.

ration temperature after thermal ageing of the press-cut samples, the graph in Fig. 6 is obtained. The 'reference' sample containing only natural fat presents an onset temperature of thermoxidation, which is somewhat above 250 °C and an oxidation energy of 220 J/g. The samples fatliquored with crude fish oil, a variant of sulphited fish oil, crude and sulphited neatsfoot oil yield onset temperatures of thermoxidation that are lower, and oxidation energies that are higher. The samples treated with fish oil plus Tara, a variant of sulphited fish oil, lecithin, sulphated base and chlorated paraffin present thermoxidation onset temperatures that are higher than that of the 'reference' sample (with only natural fat). In all these cases, the oxidation energies are low and it seems that the oxidation of these fatliquoring agents takes place at the same time as that of skin collagen. In order to differentiate between this group of fatliquoring agents, the fall in the denaturation temperature due to thermal ageing should be considered. Lecithin led to the biggest fall in the denaturation temperature, followed by fish oil plus Tara, the second variant of sulphited oil, sulphated base, and chlorinated paraffin.

The three variables have been used to derive discriminating functions [21] in order to classify the type of fatliquor applied to the skin. All three variables were highly significant (at 0% level) being the onset temperature of thermoxidation the variable which accounts for most of the differences between

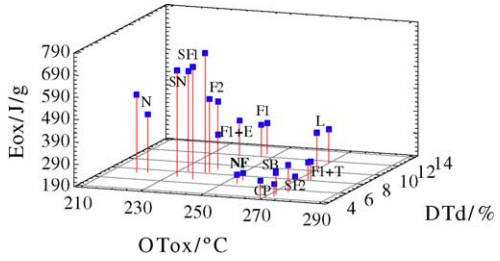

Fig. 6. Graph of press-cut samples of sheepskins treated with different fatliquoring agents classified in accordance with the onset temperature of oxidation OT_{ox}, the oxidation energy released between 195 and 265 °C E_{ox} and the decrease in the denaturation temperature DTd after thermal ageing. NF: non-fatliquored samples; F1: fish oil 1; F1 + E: fish oil 1 + Vitamin E; F1 + T: fish oil 1 + Tara; F2: fish oil 2; SF1: sulphited fish oil 1; SF2: sulphited fish oil 2; N: neatsfoot oil; SN: sulphited neatsfoot oil; L: lecithin; SB: sulphated base; CP: chlorinated paraffin.

the fatliquoring agents (93.5%), followed by the oxidation energy which accounts for the 5% of the differences between the fatliquoring agents and the decrease in the denaturation temperature that accounts just for the 1.5% of differences between the groups. Consequently the onset temperature of thermoxidation seems to be the most reliable parameter in order to evaluate the oxidability of the fatliquored leather samples, followed by the oxidation energy released between 195 and 265 °C.

5. Conclusions

- The non-isothermal DSC gives a fast and reliable method of testing the oxidability of the press-cut fatliquored leather samples, through the determination of the onset temperature of thermoxidation and the oxidation energy released between 195 and 265 °C.
- In order to discriminate between fatliquored samples with similar values of thermoxidation onset temperature and oxidation energy, it should be useful to determine the decrease on the denaturation temperature after submitting the sample to thermal ageing 24 h at 100 °C.
- The effectiveness of this method in contrast with the classical long time-consuming methods is based on its appreciable timesaving and the use of small samples with minimal preparation that enables to obtain a fast and reliable assessment of the oxidability of the fatliquored leathers.
- The method has probed to be sensitive to the lowest levels of fatliquoring used in the tanning industry (5%).
- The oxidability determined by non-isothermal DSC of the different fatliquoring agents are in accordance with the relative oxidability assessed by the industrial experience acquired by the tanning industry.

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