sustainable chemistry

MDPI

Article

Use of Antioxidants to Reduce Chromium (VI) Formation during the Leather Tanning Process

Omar Salmi, Alessandro Molinelli, Simone Gelosa, Alessandro Sacchetti, Filippo Rossi and Maurizio Masi *

Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milan, Italy; omar.salmi@polimi.it (O.S.); alessandro.molinelli@polimi.it (A.M.); simone.gelosa@polimi.it (S.G.); alessandro.sacchetti@polimi.it (A.S.); filippo.rossi@polimi.it (F.R.)

* Correspondence: maurizio.masi@polimi.it; Tel.: +39-022-399-3131

Abstract: For a long time, the leather industry has considered the chromium tanning process to be the easiest and fastest way to treat raw hides and transform them into valuable products. In the last few decades, increasing attention has been paid to the potential oxidation of the trivalent chromium in tanned leather. This happens for many reasons, such as the quality of the tanning agent or the adoption of good manufacturing practices. Anyway, the main problem, which is difficult to solve, is the sensibility of the free residual chromium tanned leather, which is high enough for possible harmful activity. Given this scenario, this work proposes a solution to decrease hexavalent chromium formation by using antioxidants during the leather tanning process. In this regard, a screening work was started, to find the worst-case scenario for trivalent chromium oxidation. To do this, commercial tanning products were employed, especially fatliquoring agents, which, in some cases, are the main source that could easily react with ROS (Reactive Oxygen Species) to drive chromium oxidation. After the determination of conditions, different groups of common antioxidants were tested to analyse the antioxidation performances and their possible use in the chromium-based tanning process. The results underline the efficient action of the antioxidants studied, paving the way for some interesting perspectives to limit the drawbacks of chromium tanned leather.

Keywords: chromium (III) oxidizing; antioxidants; fatliquoring agents; chromium tanning; leather

Citation: Salmi, O.; Molinelli, A.; Gelosa, S.; Sacchetti, A.; Rossi, F.; Masi, M. Use of Antioxidants to Reduce Chromium (VI) Formation during the Leather Tanning Process. *Sustain. Chem.* **2024**, *5*, 244–257. https://doi.org/10.3390/suschem5030016

Academic Editor: Florent Allais

Received: 26 July 2024
Revised: 28 August 2024
Accepted: 2 September 2024
Published: 5 September 2024

1. Introduction

For a very long time, leather has represented a highly valuable product for several reasons. Thanks to its features and quality, it has found applications in the clothes industry, which still remains one of the most important industrial sectors. Despite the ancient use of this product, nowadays, it is present in the industrial sector, thanks to its sustainable nature, which tends to follow the current trend of the fashion market. In this regard, leather can be considered a material that conforms to sustainable politics, since it meets the circular economy standards, being strongly connected to the meat industry [1]. Indeed, it is obtained as a waste product from slaughterhouses, and after several operations, it becomes a highly valuable and stable material. This is why, over and above other aspects, leather constitutes a potential sustainable product [2]. The process of transforming raw putrescible hides into a durable, stable, versatile, and high-quality product such as leather is called tanning. It is structured in several steps, with different procedures and harmful chemicals used downstream. These chemicals could, indeed, contribute to environmental pollution [3] as well as giving rise to human health issues and energy/material loss [4].

In this regard, a representative class of chemicals used in the leather tanning process is chromium-based compounds, e.g., basic chromium sulphate. Chromium is a transition metal, presenting different oxidation states. In the tanning process, chromium salts are commonly used, characterized by a trivalent oxidation state, and they are not subjected to

oxidation state changes during storage conditions [5]. Nowadays, the use of chromium represents the most efficient method for tanning raw hides to obtain stable high-quality leather [6]. Other alternatives are possible, such as vegetal tannins or aldehydes, which can be more or less sustainable with respect to chromium, but their lower efficiency determines their very low use (10%) with respect to chromium tanning [7]. These are the reasons why it is important to discuss and find new solutions for this kind of market, which is very difficult to avoid but important to control and develop with a sustainable focus.

As a matter of fact, chromium is able to complex with the collagen present inside the raw skin, resulting in a stable bond. During the tanning process, through the pickling process, complex interactions take place with the trivalent chromium through the free electron lone pair belonging to the carboxylic oxygen of collagen side chemical groups of amino acids, i.e., aspartate and glutamate. These available electrons are able to fill the free orbitals of trivalent chromium [8], making a coordination complex characterized by hexagonal geometry [9]. In solution, the basic chromium complexes can form polymeric oxides, a process known as olation [10]. The basic chromium salts in dimeric form increase the tanning stability and the leather quality.

Despite the storage conditions being unproblematic for chromium-based compounds, stability problems arise during exposure to external oxidizing conditions, such as drying, light exposure [11], high temperature, as well as the action of oxidizing chemicals. All of these factors could slowly alter the oxidation state of trivalent chromium during the time, forming hexavalent chromium, which is a well-known cancerogenic and irritating substance [12]. Evidence in the literature points out the electrochemical stability of trivalent chromium and that its oxidation state can only be modified by external factors [13]. Moreover, an acidic environment can hinder chromium oxidation better than alkaline conditions. Irradiation, in terms of both UV-visible exposure and heat, acts as a catalyst for this oxidation reaction [14]. Also, the use of fatliquoring agents during leather tanning can induce chromium oxidation. However, these compounds are indispensable for leather processing [11] to ensure leather quality, in terms of improved softness, wear resistance, tear resistance, and porosity [15]. These substances should come from four different origins: petrol, fish, vegetal, or animal fats. These last ones are characterized by a high presence of fatty acids, possibly with a high content of unsaturated fatty acids. Their main action is to prevent collagen fibre collapse caused by the water removal by drying, acting as lubricants [16]. At the same time, due to their physico-chemical properties, they could easily bring hydroperoxides, free radicals, and other reactive species to the double bond, provoking the oxidation of trivalent to hexavalent chromium [17]. This oxidation reaction potentially happens in an uncontrolled way only to the residual unbounded chromium inside the tanned leather, which is more susceptible to oxidation rather than complexed chromium [18]. As a matter of fact, a solution to slow down or hinder the oxidation process is strongly needed. In the scientific literature, there are already some indirect approaches, as the inhibition of fatliquoring agent oxidation [19], but different procedures are required to find versatile methods.

Considering the previous observations, the aim of this work is to find a suitable strategy to tackle the induced trivalent chromium oxidation in the leather industrial scenario, without a major concentration on fatliquor [20]. From this perspective, the idea is to use antioxidants to inhibit the formation of hexavalent chromium, both during the tanning process and during the whole life cycle of the tanned leather, similar to other molecules already known but with a different experimental approach [21]. Screening of the most known antioxidants is performed to compare the antioxidant performances applied to the currently used commercial materials for the leather tanning process; to do so, the conditions are optimized to better understand the role of the most critical components used during leather tanning. High chromium quantities and different fatliquoring agents are studied in combination. Subsequently, the best antioxidants are selected, between the already suggested ones, e.g., ascorbic acid [22] or vegetal tannins, and a new class of antioxidants, motor oil ones, characterized by imparting important stability to oxidation. The proposed

study poses a basis to improve leather processing, looking for a not-yet-used strategy to increase the safety of leather processing and by keeping leather quality unchanged. The comparison analysis permits us to check the effect and compare the behaviour of notorious antioxidants on leather to promote their use in this peculiar sector.

2. Materials and Methods

2.1. Materials

Commercial fatliquoring agents used are as follows (composition declared in safety sheets):

Keoil SK 042: sodium dodecyl sulphate 10–20% (Kemas s.r.l., Santa Croce sull'Arno, Italy). Lipsol MSW: dodecane 2.5–10% + 2-methylpentan-2, 4-diol 2.5–10% (Schill + Seilacher GmbH, Böblingen, Germany). Riveroil TIS: sulphonate esters, polyglycol ethers, fish oil derivates and alkanediols; Riveroil LSW: H_2SO_4 + mono-C12-18-alkyl esters, ammonium salts 10–25%; Riveroil GLH: isotridecanol ethoxylate 0.9–2.8% + NH_3 0.9–2.8% (all from River Chimica Industriale S.p.A., Ponte a Egola, San Miniato, Italy). Truposist D: 2-butoxyethanol <15% + distilled petrol <20% + disodium sulphosuccinate and dodecyl <5% (Trumpler Italia s.r.l., Santa Croce sull'Arno, Italy).

Tanning agents used are as follows:

Chromic sulphate: $Cr_2(SO_4)_3 \times nH_2O$, MW = 392.18 g/mol (Carlo Erba Reagents, Val de Reuil, France). Cromo F-D: $Cr(OH)SO_4$ + Na_2SO_4 > 75% (River Chimica Industriale S.p.A., Ponte a Egola, San Miniato, Italy). Chromosal B: $Cr(OH)SO_4$ 100% (Lanxess Deutschland GmbH, Leverkusen, Germany).

Antioxidant screening involved the following:

Tara powder: milled Peruvian carob (*Tara peruviana*) (Silvachimica s.r.l., San Michele Mondovì, Italy). 4,4′-methylenebis (2,6-di-tert-butylphenol): $C_{29}H_{44}O_2$, MW = 424.66 g/mol, for synthesis; 4,4′-thiobis(2-tert-butyl-5-methylphenol): $C_{22}H_{30}O_2S$, MW = 358.54 g/mol, for synthesis; L-ascorbic acid: $C_6H_8O_6$, MW = 176.12 g/mol, ≥99.0%, crystalline; Tetraethylenepentamine: $C_8H_{24}N_5$, MW = 189.30 g/mol, technical grade (all from Merck KGaA, Darmstadt, Germany). Hydroil: natural polyphenols condensed (Workem s.r.l., Santa Croce sull'Arno, Italy). 2,6-di-tert-butylphenol: $C_{14}H_{22}O$, MW = 206.32 g/mol, >98% (Fluka, Switzerland). DL-α-tocopherol: $C_{29}H_{50}O_2$, MW = 430.71 g/mol, >96.0% (Tokyo Chemical Industry Co., Tokyo, Japan). 2,2,6,6-tetramethylpiperidinoxy free radical, TEMPO, $C_9H_{18}NO$, MW = 156.25 g/mol, 99% (Fluorochem Ltd., Hadfield, UK).

Potassium dichromate: ≥99.0%, $K_2Cr_2O_7$, MW = 294.19 g/mol; starch soluble GR for analysis: $(C_6H_{10}O_5)_n$; 1,5-diphenylcarbazide: ≥98.0%, $C_{13}H_{14}N_4O$, MW = 242.28 g/mol; sodium thiosulphate: ≥99%, $Na_2S_2O_3$, MW = 158.11 g/mol; isooctane: ≥99.0%, C_8H_{18}, MW = 114.23 g/mol; nitric acid: >68%, HNO_3, MW = 63.01 g/mol; d-chloroform: 99.8%, $CDCl_3$, MW = 120.38 g/mol; dichloromethane (DCM): ≥99.8%, CH_2Cl_2, MW = 84.93 g/mol; ethyl acetate: ≥99.5%, $C_4H_8O_2$, MW = 88.11 g/mol; butanol: ≥99.8%, $C_4H_{10}O$, MW = 74.12 g/mol (all purchased from Merck KGaA, Darmstadt, Germany). Sulfuric acid: ≥96%, H_2SO_4, MW = 98.08 g/mol (Carlo Erba Reagents, Val de Reuil, France). Potassium iodide: ≥99.5%, KI, MW = 166.00 g/mol (Carlo Erba, divisione chimica industriale, Milano, Italy). Acetone: ≥99.5%, C_3H_6O, MW = 58.08 g/mol (Carlo Erba Reagents, Val de Reuil, France). Glacial acetic acid: ≥99%, $C_2H_4O_2$, MW = 60.05 g/mol (Fisher Scientific UK, Loughborough, UK).

2.2. Methods

This study is divided into two steps: the first aims to develop a model to reproduce the worst operating conditions by using a highly oxidant system, measured by BS EN ISO 3960:2017 [23] and NMR analysis. The second step involves a screening procedure of several antioxidants by testing their performances with the hard conditions selected before. The hexavalent chromium quantification method was developed by the CNR (National Research Centre) and IRSA (Water Research Institute), two Italian national research centres,

and it relies on the spectrophotometric detections of Cr(VI) by means of diphenylcarbazide (DPC) redox [24].

2.2.1. Fatty Acid Peroxide Determination

This assay was inspired by the BS EN ISO 3960:2017, where 5 g and 10 g of sample were used according to the two possibilities to study if the peroxide number grade is not previously known. The principle is based on iodide titration by starch indicator using sodium thiosulphate [23]. This makes it possible to determine the number of oxidized double bonds by oxidation of KI to I_2. Next, Nuclear Magnetic Resonance was used as a tool for alkene carbon determinations (C sp^2) in ^{1}H-NMR and ^{13}C-NMR [25]. The NMR tube was prepared by using one drop of sample diluted in 1 mL of deuterated solvent. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer operating at a 500 MHz proton frequency, with 16 or 1024 acquisitions and samples prepared in $CDCl_3$.

2.2.2. Hexavalent Chromium Determination

The determination of Cr(VI) was performed through a spectrophotometric analysis by means of diphenylcarbazide [24]. It consists of a principle similar to BS EN ISO 17075-1 [26]: diphenylcarbazide (DPC) is oxidized by the hexavalent chromium and becomes diphenylcarbazone (DPCA), detectable on the UV spectrophotometer. So, through an evaluation of the absorbance due to this last molecule, with a calibration line, it is possible to conduct a quantitative analysis of the hexavalent chromium. The instrument used is a V-600 Series UV-vis spectrophotometer from JASCO (Cremella, Italy). The detection was performed at 540 nm wavelength, with a range between 0.1 and 1 mg/L Cr(VI). The quantity of Cr(VI) was evaluated on the liquid sample according to the procedure, and each datum is the average of three measurements. In previous studies, it was common to quantify Cr(VI) at 350 nm, but this procedure is indicated for a higher concentration of metal. For a lower range, the official normative at 540 nm is indicated [27].

2.2.3. Other Analysis

ICP-OES OPTIMA 8300 (PerkinElmer, Shelton, CT, USA) was used to quantify the number of metals on the tanning agents, through a destructive test after a previous oxidation and strong acidic digestion (by HNO_3 and H_2SO_4). Yttrium was used as the internal standard. The pH measurements were performed using a lab pH meter (HI98191, Hanna Instruments, Villafranca Padovana, Italy) with a standard error of 0.04. The analytical balance used has an error of 0.0001, so the experiments were conducted by this weight uncertainty.

2.2.4. Antioxidant Screening

The evaluation of the antioxidant performances was carried out in multi-well plates with 12 positions. The amount of tanning agent was around 0.75 mg (corresponding to the amount of 0.258 g/mL of chromium available for oxidation), 1.35 mL of water (0.466 g/mL) and 0.8 mL of fatliquoring agent (0.276 g/mL) [28]. In case of antioxidant-containing samples, 0.1 mL of Hydroil, 0.03 g Tara powder and 0.02 g ascorbic acid were used [29]; all these substances are already known in leather processing. In case of the other new materials, 0.04 g was used, which is quite high as a value but was chosen to control and extremize the effects. The ingredients were added after weighing by spatula or syringe. An issue derived from this procedure was the presence of some interfering materials: fats and organic antioxidants are inside the analysed system and they can change the results of the DPC action [30]. The samples were, therefore, extracted through liquid–liquid extraction using a separating funnel and organic solvents, such as butanol, ethyl acetate (previous wash) and methylene chloride (DCM, for the final washes). The extraction was repeated a maximum of 4 times (3 + 1). Different chemicals were used to ensure the efficient extraction of hydrophobic substances: ethyl acetate and DCM for Riveroil-containing products, butanol and DCM for Keoil ones. This different treatment was decided on after a comparative study of which could be the most solubilizing agent. For this experiment,

filter membrane of 0.45 µm (Durapore, Italy) was used for ensuring the absence of particles that can compromise the UV spectrophotometer analysis.

Different reaction conditions were tried and divided into steps. After a first part of the experiment by stirring in plate (room temperature or 50 °C), the experiment was stopped, purified by extraction/filtration, and then UV analysis was performed. The time between the extraction and UV analysis changes as aging processes improve. Samples were conserved in closed volumetric flasks, under cover of light to avoid uncontrolled oxidation.

For each antioxidant, 4 trials were performed: two with the oxidation sensible agent (water + tanning agent + fatliquoring agent + antioxidant), one without them (water + tanning agent + antioxidant), and another final one without chromium (water + antioxidant). The first trials show the versatility of the antioxidant candidate, the middle trial shows the result of a simple interaction, while the final trial shows the extent of the measuring error due to some interfering actions.

3. Results and Discussion

With the aim of finding the most useful and efficient antioxidant, capable of reducing the oxidation process of Cr(III) to Cr(VI), a preliminary selection of the most suitable conditions for the experiments was carried out. For that, several analyses were conducted to establish which fatliquoring agents represented the most satisfying to determine the worst-case conditions for hexavalent chromium formation during leather tanning.

3.1. Determination of Peroxides

The aim of this study was to determine the potential oxidation properties associated with different commercial fatliquoring agents. The official normative BS EN ISO 3960:2017 for peroxide determination was employed, as reported in Section 2.1 [23]. This is employed for the study and characterization of fatty acids via the determination of the peroxide number. It is based on a colour change happening during iodide titration. As a first commercial fatliquoring agent, Riveroil TIS was studied. This is interesting due to the presence of fish-derived compounds, which characterize the product with several double bonds [31]. The analysis of this product was slightly problematic due to the poor solubility, which produces a light milky mixture in solvents. This resulted in a difficulty in the detection of the point of colour changes, which should have happened with a blue formation after the addition of starch during iodometric titration. For this reason, Lipsol MSW was analysed as an alternative fatliquoring agent, as it should be less problematic. In this case, a surfactant was added in the analysis to increase the solubility, such as sodium dodecyl sulphate or sodium octadecyl sulphate [32]. Heating until 30 °C and stirring did not change the results. For this reason, another quantification method was employed for peroxide determination.

3.2. NMR Analysis

^{1}H and ^{13}C-NMR analysis can reveal unsaturated hydrogens and carbons. As the fatliquoring agents tested are commercial products, the mixture of substances is not completely known. For this reason, we decided to use this method to only evaluate how many olefinic hydrogens/carbons are in the mixture. Alkene hydrogens are characterized by a chemical shift within the range of 4.5–7.5 ppm, while the unsaturated part of the compounds is usually present in the spectral region between 110 and 130 ppm in ^{13}C-NMR. Furthermore, we expected a higher signal intensity due to the decreased probability of finding carbon isotopes compared to hydrogen [33]. The evaluation was performed by comparing the integral of the standard presence of the alkyl peaks at 1.26 ppm and the integral of the single peak of unsaturation at 5.3 ppm in the case of ^{1}H-NMR. Similar criteria were applied for ^{13}C-NMR, where the reference alkyl peak is at 77 ppm, while the unsaturated region peak is found at 130 ppm. The NMR analysis is collected in Table 1 and spectra are reported in Figures S1–S12.

Table 1. NMR analysis on fatliquoring samples for characterization in terms of olefinic regions, at 5.3 ppm in ^{1}H-NMR and 130 ppm in ^{13}C-NMR. The numbers represent the integral ratio between unsaturation and reference alkyl peak. The higher the ratio of NMR peaks, the higher the amount of unsaturated regions.

Fatliquoring Agents	^{1}H-NMR	^{13}C-NMR
Keoil SK 042	0.07	0.15
Riveroil TIS	0.11	0.05
Lipsol MSW	0.04	0.07
Truposist D	0.02	0.01
Riveroil LSW	0.01	<0.01
Riveroil GLH	<0.01	<0.01

These results reveal a realistic picture of the samples, without relevant interfering substances, as in the case of the ISO test. Anyway, these results ensured an interesting starting point for the selection of the most potential oxidant substances. In fact, for the next steps, the first four substances were used, as they showed the presence of unsaturated carbon–carbon bonds. This evaluation also makes it possible to have a concrete result and demonstrates the validity of the NMR data.

3.3. UV Analysis

After the selection of the potential fatliquoring agents, which can cause oxidation by means of the analyses reported above, a quantitative analysis for the determination of hexavalent chromium was performed. The method relies on the spectrophotometric evaluation of hexavalent chromium using diphenylcarbazide, which is able to generate a complex with Cr(VI) characterized by an absorption peak at a wavelength of 540 nm. As the method includes the use of diluted H_2SO_4, the UV analyses were performed against a reference constituted by water and H_2SO_4 as a blank [24]. As declared in the normative method, the variance between different labs is in the order of 5%, and this error could increase in the presence of other competitors such as vanadium or other oxidating agents.

The experiment was carried out using a multi-well plate to ensure efficient and easy control of the reactions. The idea was to create a model situation, which replicates the conditions of unbonded chromium in the tanning process without using the hides. Therefore, the quantities used reproduced a real case in extremely harsh conditions. In the specific case of chromium, its amount was selected based on the worst case of the process, i.e., after tanning without the basification step, which improves chromium binding to the tanned leather, stabilizing the chromium complex with collagen. Regarding water, the amounts employed correspond to the one present inside leather, while the fatliquoring agent quantity was selected considering the average used in tanneries. In Figure 1, the calibration line in the concentration range between 0.1 and 1 mg/L is reported, experimentally evaluated by following the procedure reported in the CNR-IRSA method.

The first part of this study was focused on the chromium sources to validate the result of the oxidized metal detection method. Then, the screening of tanning and fatliquoring agents was started for an accurate selection of the reagents of interest. Lastly, after the reagents and reaction condition determinations, a comparative analysis of the antioxidant performances was carried out.

All the data in this study are summarised in Tables 2 and 3. The reaction time takes into account the time used for mixing the samples, plus the time within the sample collection after the liquid–liquid extraction and the UV analysis. This is to check for the effects of the ageing period, added time that could increase the oxidation, after extraction and without DPC addition yet.

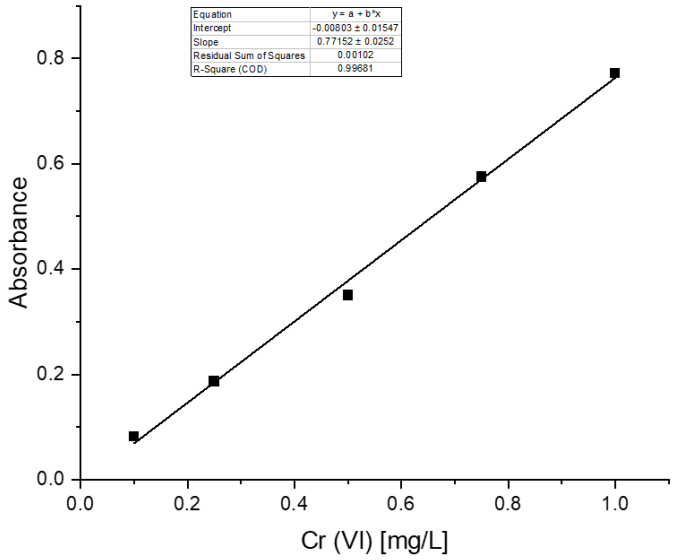

Figure 1. Calibration line for the DPC-Cr VI detection method.

Table 2. Blank test for studying chromium and test validation. In case of the first experiment, an excess of chromium was used for checking its behaviour in a supersaturated solution.

Substance	Conditions of Reaction		Cr(III) Starting (g/L)	Cr(VI) Final (mg/L)
	Time	Temperature		
Cromo FD	6 h	rt	555.6	5.1 ± 0.5
Cromo FD	48 h	50 °C	7.5	1.4 ± 0.1
Cromo FD	120 h	rt	7.5	0.65 ± 0.06
Cromo FD	24 h	rt	7.5	0.65 ± 0.06
Cromo FD	6 h	rt	7	0.64 ± 0.06
Cromo FD	24 h + 72 h	rt	7.5	0.60 ± 0.06
Cromo FD	72 h + 24 h	rt	7.5	0.57 ± 0.06
$Cr_2(SO_4)_3$	6 h	rt	7.5	0.37 ± 0.04
$Cr_2(SO_4)_3$	6 h	rt	4.75	0.2 ± 0.02
Chromosal B	-	rt	0.28 (?)	0.14 ± 0.01

Table 3. Comparison test for checking the sensibility to oxidation of reagents. Trials were conducted at room temperature for five days.

Water	Chromium Source	Fatliquoring Agent	Cr(VI) Concentration (mg/L)
No	Cromo FD	Keoil SK 042	1.2 ± 0.1
No	Cromo FD	Lipsol MSW	0.94 ± 0.09
No	Cromo FD	Riveroil TIS	0.79 ± 0.08
No	Chromosal B	Keoil SK 042	0.77 ± 0.08
Yes	Cromo FD	Riveroil TIS	0.73 ± 0.07
Yes	Cromo FD	-	0.65 ± 0.06
Yes	Cromo FD	Keoil SK 042	0.57 ± 0.06
No	Chromosal B	Lipsol MSW	0.56 ±0.06
Yes	Cromo FD	Lipsol MSW	0.51 ± 0.05
No	Cromo FD	Truposist D	0.48 ± 0.05
Yes	Cromo FD	Truposist D	0.47 ± 0.05
Yes	Chromosal B	Truposist D	0.47 ± 0.05
No	Chromosal B	Truposist D	0.42 ± 0.04
Yes	Chromosal B	-	0.37 ± 0.04
Yes	Chromosal B	Lipsol MSW	0.37 ± 0.04
Yes	Chromosal B	Riveroil TIS	0.37 ± 0.04
Yes	Chromosal B	Keoil SK 042	0.36 ± 0.04
No	Chromosal B	Riveroil TIS	0.28 ± 0.03

3.3.1. Chromium Behaviour

As already stated, trivalent chromium is characterized by high stability. Water has a negative influence on chromium oxidation as it acts as a dilutant for the oxidative agents synthetized in situ. In addition, it shows oxidation-inhibiting behaviour [34]. The DPC colorimetric revelation system [30] has many limitations, such as the difficulty in measuring replication, continuing complexation of chromium in water that changes the UV results and the relative turbidity of the solutions [35]. Another problem of the experimental procedure is represented by the possible aggregation of solid materials due to the high concentration and poor solubility of some substances in the mixture. One interesting point was the presence of interfering substances, and it was already demonstrated that trivalent chromium itself is partially detectable by using this method [35]. To demonstrate this relevant activity, samples with a high concentration of chromium (III) were prepared in water. Their behaviour was analysed under different conditions, and the result was explicated according to the CNR-IRSA norm [24]. To prepare the samples for UV analysis, liquid–liquid extractions to eliminate possible lipophilic contaminants were carried out twice in ethyl acetate and twice in DCM.

It is interesting to see how the results in Table 2 reflect what was expected. Indeed, by increasing the reagent amount (trivalent chromium), the detected concentration of hexavalent chromium revealed a higher error. Another aspect concerns the effect of temperature [34]: a higher temperature increases the quantity of the oxidized metal [36]. The expected situation is the content of impurities in Cromo FD compared to chromium sulphate that could oxidize or contain interfering agents [37]. The last entry in Table 2 comes from the literature [35], but it was not possible to estimate/extrapolate the reaction time. However, this value can be helpful for a deep understanding of the other data. The replication of data in the 7 g/L zone shows the accuracy of the results.

3.3.2. Agent Selection

After all the preliminary studies, a first screening was performed on the fatliquoring agents previously selected to select the most oxidation-sensitive one, which was used later in the other analyses. The samples were prepared, as reported in the Section 2.2, and the separation of hydrophobic interfering compounds was carried out using ethyl acetate/DCM extractions [38]. This phase aimed to explain Cr(III)'s response under conditions different from those of the agents previously examined. The results are reported in Table 3.

These results demonstrate many different points:

- Water shows an inhibiting action on chromium oxidation. Indeed, all the samples showing a high concentration of Cr(VI) detected were prepared in the absence of water.
- Cromo FD has more sensitivity to oxidation than Chromosal B for various reasons, which are more fully investigated below.
- The results of NMR spectra agree with the results of this analysis. Indeed, on average, the most effective substances acting on chromium oxidation are Riveroil TIS and Keoil SK 042, thanks to the higher presence of unsaturation.

For the reasons described above, all the following tests with the antioxidant agents were conducted by using the following compounds: Cromo FD as a chromium source; Riveroil TIS or Keoil SK 042 as fatliquoring agents. However, before analysing the samples with the addition of the antioxidants, some analyses were performed on the chromium source.

The results reported in Figure 2 show that Cromo FD tend to give a higher oxidation rate than Chromosal B, according to the previous partial result before extrapolation.

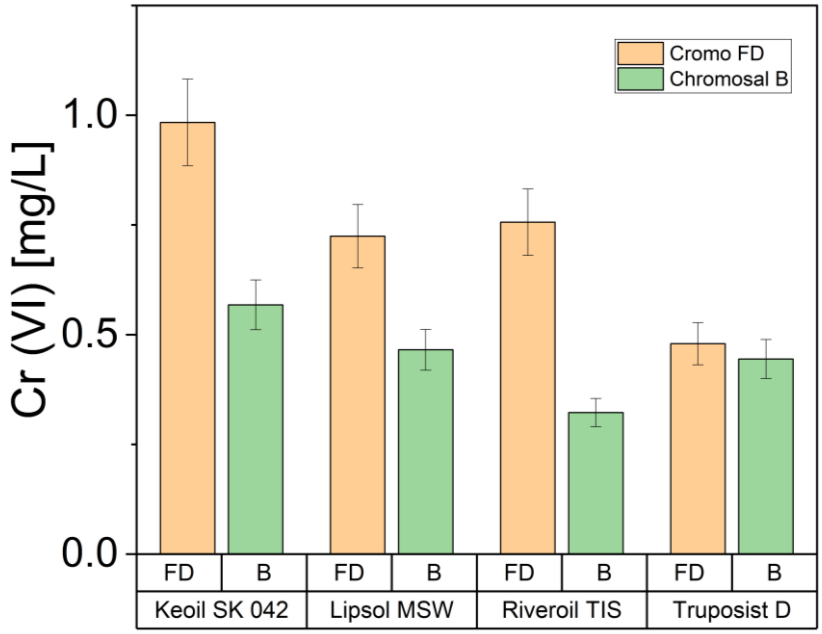

Figure 2. Comparison of tanning agents in hexavalent chromium formation and focalization about versatility for different fatliquoring agents.

The reason of this behaviour could be associated with the different hydrolysis mechanisms in water and to the concentration of Cr [39]. Indeed, when chromium basic sulphate was mixed with water, it became a triprotic acid and ensured acidic conditions [40]. As is known, a lower pH enhances the chromium stability, resulting in a higher amount of trivalent chromium present in the mixture. For this reason, a comparison of the two chromium sources was performed. The main focus was given to the pH of the two tanning agents and to the amount of chromium effectively present in the two products.

From the results of the analyses reported in Table 4, Chromosal B contains a slightly higher amount of chromium, and it is characterized by a lower pH than Cromo FD. This can be attributed to its higher stability and lower sensitivity to chromium oxidation than Cromo FD.

Table 4. Cromo FD vs. Chromosal B pH and metal content comparison. The pH was measured in a solution 80 g/L, with an instrumental error of 0.04. The ICP-OES refers to the amount of chromium, evaluated in grams under 100 g of total powder. The error in this last measurement is in the order of 0.5.

Technique	Cromo FD	Chromosal B	Difference
pH meter	3.8	2.1	1.7
ICP-OES [g/100 g]	16.8 ± 0.5	18.5 ± 0.5	1.7

3.3.3. Antioxidant Evaluation

After a complete characterization and discussion of the reagents, a comparative study between many chemicals recognized for their antioxidant activity was carried out. They were tested under different temperature and time conditions to find the most versatile substance, acting as an inhibitor of Cr(VI) formation. The detailed quantities used for each sample are as described in the Methods. A summary of the results is shown in a histogram in Figure 3. For the sake of completeness, the specific conditions and detailed results are available in the Supplementary Data (Table S1).

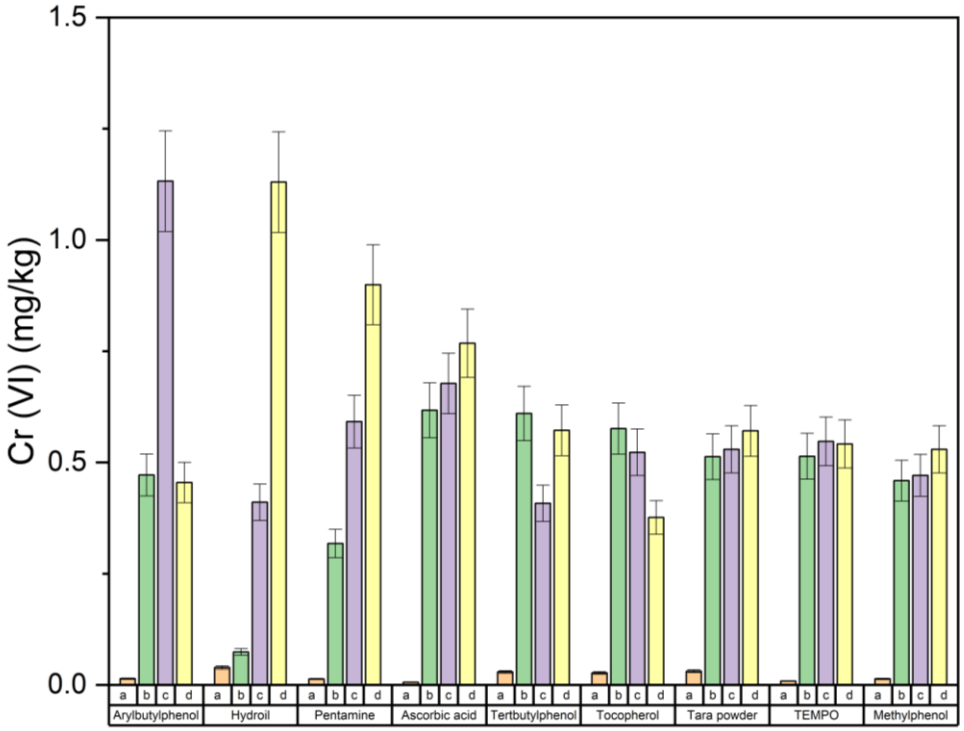

Figure 3. Summary of results for a facilitated comparison. The antioxidant name indicates only the category, and letters/colours mean different conditions: a columns for trials without chromium; b columns for blank trials; c columns for Keoil trials and d columns for Riveroil trials.

The blank error evaluation without chromium was essential for a correct evaluation of the measurement; this is due to turbidity, coloration or interactions, as already described before. In the case of the average concentration of Cr(VI) found at the end of the process, it is achieved by fatliquoring, and it is important for knowing whether or not the substance is ideal for chromium protection. The versatility of the different antioxidants is evaluated based on the difference between hexavalent chromium made based on fatliquoring agents. The lower this value, the greater the versatility. A high delta value means less interest in using an effective antioxidant as a pure substance. Anyway, if an antioxidant has good effectiveness with only one fatliquoring substance, it could be used in a mixture with another one better as another oxidation-sensitive agent. Finally, as the DPC assay is the official one, it is important to check the error due to the interaction with antioxidants that could influence their actions with oxidative radicals, explained as an increase in Cr(VI). At the same time, an increase in other substances could lead to interaction with DPC or UV rays.

Evaluating the results shows that the most efficient antioxidant for the considered criteria is TEMPO, followed by: 4,4′-thiobis(2-tert-butyl-5-methylphenol), tocopherol, 2,6-di-tert-butylphenol, Tara powder and ascorbic acid.

TEMPO has an uncommon regeneration mechanism that explains the strong antioxidant characteristics in various fields and conditions [41]. It is the only SET (Single-Electron Transfer) substance used, and, due to its great stability as a radical, it could easily protect chromium [42] for a long time.

4,4′-thiobis(2-tert-butyl-5-methylphenol) and 2,6-di-tert-butylphenol come from the same field (motor oil antioxidants) and have a similar mechanism [43]. They are bulky phenols, and, thanks to that, their HAT (Hydrogen Atom Transfer) mechanism makes the tanning agent stable over time [44].

For tocopherol, the mechanism is similar. Thanks to HAT and good mobility with other substituents, the aromatic alcohol could lose a hydrogen atom without any great loss of stability [45].

In the case of Tara powder and ascorbic acid, both are HAT antioxidants but with a different principle of stability that is already well known. They are used in the leather field, but our interest was in their comparison and finding a new more efficient way because they represent some problems. In the case of Tara, it is used as a vegetal tanning agent, and the final leather is characterized by compactness and firmness [46]. This is a problem if particularly soft leather is desired, and this substance could change the results. In the case of ascorbic acid, in this evaluation, it appears to be quite a good antioxidant; the main problem lies in its degradation over time. Anyway, this is a material with efficient short-term characteristics, so it could be used for a mixture formulation [47].

The results for the others show that they are not acceptable as substances for this use under these particular conditions and assay.

In case of Hydroil, it is an interesting tanning agent, based on OOMWW (Olive Oil Mill Wastewater) [48]. This is a source of antioxidants and tannins, but in these experiments, it cannot explain its activity as an antioxidant agent [49], probably due to the hard operating conditions (7500 mg/L Cr free). Furthermore, the extraction was quite difficult, possibly due to the presence of other substances that should interact with fatliquoring and organic solvents under these conditions.

4,4′-methylenebis (2,6-di-tert-butylphenol) and tetraethylenepentamine came from the group of motor oil antioxidants [50], but they did not have any particular effects and are chemicals from different sub-groups. The former is a hindered phenol, but it has more hydrophobic parts, and it is possible that its hard solubilization stops at all its interactions with the protection of chromium. In the case of amine, we tried to analyse and use this molecule, which is commonly much more efficient as an antioxidant at high temperature to detect a new possible chemical category [51]. However, the results are not relevant, and it will be shelved for the next steps.

4. Conclusions

It was possible to improve knowledge about the stability of the main tanning agents used for leather. Anyway, chromium, with all its problems, rests as the most used product, thanks to practicability and a low treatment time, incomparable leather characteristics and simple application. Furthermore, it is used by 90% of worldwide leather industries, and it is not possible to shift rapidly to other tanning products that are less problematic. For this reason, for sustainability improvements for workers, customers and nature, we decided to find a possible solution for this problematic chemical agent.

After many trials and analyses, we established the category of chemicals, which could be the one for developing a series of new solutions to deal with the main problem of hexavalent chromium. TEMPO, 4,4′-thiobis(2-tert-butyl-5-methylphenol), tocopherol and 2,6-di-tert-butylphenol are selected as new substances to be implemented in the leather tanning process. Despite the similarity of the evaluation amount (Figure 3), the interest in these compounds is to find an efficient replacement for ascorbic acid and tara tannin.

According to the SDGs (Sustainable Development Goals), one of the priorities is caring for people's health and finding a new way for continuing to tan leather, while, at the same time, eliminating the possibility of causing health problems, which is a very serious challenge in terms of common sustainable development.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/suschem5030016/s1, Figure S1: ^{1}H-NMR Keoil SK 042; Figure S2: ^{13}C-NMR Keoil SK 042; Figure S3: ^{1}H-NMR Riveroil TIS; Figure S4: ^{13}C-NMR Riveroil TIS; Figure S5: ^{1}H-NMR Truposist D; Figure S6: ^{13}C-NMR Truposist D; Figure S7: ^{1}H-NMR Lipsol MSW; Figure S8: ^{13}C-NMR Lipsol MSW; Figure S9: ^{1}H-NMR Riveroil LSW; Figure S10: ^{13}C-NMR Riveroil LSW; Figure S11: ^{1}H-NMR Riveroil GLH; Figure S12: ^{13}C-NMR Riveroil GLH; Table S1: Complete data recorded for the antioxidant assay. The sum in the first column corresponds to the reaction period and to the time between the stopping/analysing.

Author Contributions: Conceptualization, M.M. and A.S.; methodology, O.S. and S.G.; software, O.S.; formal analysis, O.S. and S.G.; investigation, A.M.; resources, S.G., F.R. and A.S.; data curation, O.S. and S.G.; writing—original draft preparation, O.S.; writing—review and editing, F.R., A.S., O.S. and A.M.; visualization, O.S.; supervision, M.M.; project administration, M.M.; funding acquisition, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Lineapelle s.r.l., the PON "Ricerca e Innovazione" 2014–2020, Asse IV "Istruzione e Ricerca per il recupero" Azione IV.5 "Dottorati su tematiche green" and MICS (Made in Italy Circolare e Sostenibile), financed by European Union—NextGenerationEU (National Recovery and Resilience Plan (PNRR)—mission 4 component 2, investment 1.3—D.D. 1551.11-10-2022, PE00000004) fund.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available upon request.

Acknowledgments: The authors would like to thank Elisabetta Scaglia (Lineapelle) and Giacomo Pacchi (BCN Concerie) for their support and interest in this topic.

Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Ellen MacArthur Foundation. What Is a Circular Economy. Circular Economy Introduction. Available online: https://www.ellenmacarthurfoundation.org/topics/circular-economy-introduction/overview (accessed on 18 April 2024).
2. Omoloso, O.; Mortimer, K.; Wise, W.R.; Jraisat, L. Sustainability research in the leather industry: A critical review of progress and opportunities for future research. *J. Clean. Prod.* **2021**, *285*, 125441. [CrossRef]
3. Dixit, S.; Yadav, A.; Dwivedi, P.D.; Das, M. Toxic hazards of leather industry and technologies to combat threat: A review. *J. Clean. Prod.* **2015**, *87*, 39–49. [CrossRef]
4. Joseph, K.; Nithya, N. Material flows in the life cycle of leather. *J. Clean. Prod.* **2009**, *17*, 676–682. [CrossRef]
5. Torras, J.; Buj, I.; Rovira, M.; de Pablo, J. Chromium recovery from exhausted baths generated in plating processes and its reuse in the tanning industry. *J. Hazard Mater.* **2012**, *209–210*, 343–347. [CrossRef]
6. Karanam, S.B.; Raji, P.; Selvarani, J.A.; Samrot, A.V.; Pazhayakath, T.M.J.; Appalaraju, V.V.S.S. Leather Processing, Its Effects on Environment and Alternatives of Chrome Tanning. *Int. J. Adv. Res. Eng. Technol.* **2019**, *10*, 69–79.
7. Thyssen, J.P.; Jensen, P.; Carlsen, B.C.; Engkilde, K.; Menné, T.; Johansen, J.D. The prevalence of chromium allergy in Denmark is currently increasing as a result of leather exposure. *Br. J. Dermatol.* **2009**, *161*, 1288–1293. [CrossRef] [PubMed]
8. Han, W.; Zeng, Y.; Zhang, W. A Further Investigation on Collagen-Cr(III) Interaction at Molecular Level. *J. Am. Leather Chem. Assoc.* **2016**, *111*, 101–106.
9. Fathima, N.N.; Baias, M.; Blumich, B.; Ramasami, T. Structure and dynamics of water in native and tanned collagen fibers: Effect of crosslinking. *Int. J. Biol. Macromol.* **2010**, *47*, 590–596. [CrossRef] [PubMed]
10. Ding, Y.Q.; Chen, C.L.; Li, T.D.; Cheng, J.Y.; Zhang, H.Y. Effects of Chromium-olation Length on Crosslinking Effects Investigated by Molecular Dynamics Simulation. *Soft Mater.* **2015**, *13*, 24–31. [CrossRef]
11. Fontaine, M.; Clement, Y.; Blanc, N.; Demesmay, C. Hexavalent chromium release from leather over time natural ageing vs accelerated ageing according to a multivariate approach. *J. Hazard Mater.* **2019**, *368*, 811–818. [CrossRef] [PubMed]
12. Holmes, A.L.; Wise, S.S.; Wise, J.P., Sr. Carcinogenicity of hexavalent chromium. *Indian J. Med. Res.* **2008**, *128*, 353–372.
13. Wadhawan, A.R.; Stone, A.T.; Bouwer, E.J. Biogeochemical Controls on Hexavalent Chromium Formation in Estuarine Sediments. *Environ. Sci. Technol.* **2013**, *15*, 8220–8228. [CrossRef] [PubMed]
14. Arellano-Sánchez, M.G.; Devouge-Boyer, C.; Hubert-Roux, M.; Afonso, C.; Mignot, M. Chromium Determination in Leather and Other Matrices: A Review. *Crit. Rev. Anal. Chem.* **2022**, *52*, 1537–1556. [CrossRef]
15. Zhang, Y.; Wang, L. Recent Research Progress on Leather Fatliquoring Agents. *Polym. Plast. Technol. Eng.* **2009**, *48*, 285–291. [CrossRef]
16. Measuring the moisture content of wet-blue. In *Leather International*; Business Trade Media International: London, UK, 2007.
17. Xu, T.; Jiang, X.; Tang, Y.; Zeng, Y.; Zhang, W.; Shi, B. Oxidation of trivalent chromium induced by unsaturated oils: A pathway for hexavalent chromium formation in soil. *J. Hazard Mater.* **2021**, *405*, 124699. [CrossRef]
18. Shen, Y.; Ma, J.; Fan, Q.; Gao, D.; Yao, H. Strategical development of chrome-free tanning agent by integrating layered double hydroxide with starch derivatives. *Carbohydr. Polym.* **2023**, *304*, 120511. [CrossRef]
19. Batema, G.; von Behr, D.; van Driesten, S. Preventing chromium VI—Smit & Zoon. In *Leather International*; Business Trade Media International: London, UK, 2016.

20. Udkhiyati, M.; Rachmawati, L. Comparison the Effect of Using Different Fatliqour to the Formation of Chromium (VI) in Leather Production. *Mater. Sci. Forum* **2019**, *948*, 217–220. [CrossRef]
21. Compte, I.; Torras, Q.; Izquierdo, F.; Cuadros, R.; Bacardit, A. Use of Long-Chain Synthetic Phenolic Antioxidants to Produce Chromium-Tanned Leather without Risk of Hexavalent Chromium Formation. *J. Am. Leather Chem. Assoc.* **2023**, *118*, 439–449.
22. TFL Ledertechnik GmbH and Co KG. Leather Treatment and Agent. CN Patent 101316938A, 27 November 2006.
23. *BS EN ISO 3960:2017*; Animal and Vegetable Fats and Oils. Determination of Peroxide Value. Iodometric (Visual) Endpoint Determination. British Standard European Standard International Organization for Standardization: Geneva, Switzerland, 2017.
24. Tiwari, A.K.; Orioli, S.; De Maio, M. Assessment of groundwater geochemistry and diffusion of hexavalent chromium contamination in an industrial town of Italy. *J. Contam. Hydrol.* **2019**, *225*, 103503. [CrossRef]
25. Hama, J.R.; Fitzsimmons-Thoss, V. Determination of Unsaturated Fatty Acids Composition in Walnut (*Juglans regia* L.) Oil Using NMR Spectroscopy. *Food Anal. Methods* **2022**, *15*, 1226–1236. [CrossRef]
26. *BS EN ISO 17075-1:2017*; Chemical Determination of Chromium(VI) Content in Leather—Part 1: Colorimetric Method. British Standard European Standard International Organization for Standardization: Geneva, Switzerland, 2017.
27. Sanchez-Hachair, A.; Hofmann, A. Hexavalent chromium quantification in solution: Comparing direct UV–visible spectrometry with 1,5-diphenylcarbazide colorimetry. *Comptes Rendus Chim.* **2018**, *21*, 890–896. [CrossRef]
28. Bajza, Z.; Vinkovic Vrcek, I. Fatliquoring agent and drying temperature effects on leather properties. *J. Mater. Sci.* **2001**, *36*, 5265–5270.
29. Eyizi, V.; Tontul, I.; Türker, S. Effect of variety, drying methods and drying temperature on physical and chemical properties of hawthorn leather. *J. Food Meas. Charact.* **2020**, *14*, 3263–3269. [CrossRef]
30. Lace, A.; Ryan, D.; Bowkett, M.; Cleary, J. Chromium Monitoring in Water by Colorimetry Using Optimised 1,5-Diphenylcarbazide Method. *Int. J. Environ. Res. Public Health* **2019**, *16*, 1803. [CrossRef]
31. Wąsowska, I.; Maia, M.R.G.; Niedźwiedzka, K.M.; Czauderna, M.; Ramalho Ribeiro, J.M.C.; Devillard, E.; Shingfield, K.J.; Wallace, R.J. Influence of fish oil on ruminal biohydrogenation of C18 unsaturated fatty acids. *Br. J. Nutr.* **2006**, *95*, 1199–1211. [CrossRef]
32. Domínguez, H. Self-Aggregation of the SDS Surfactant at a Solid–Liquid Interface. *J. Phys. Chem. B* **2007**, *111*, 4054–4059. [CrossRef] [PubMed]
33. Adams, R.W.; Aguilar, J.A.; Atkinson, K.D.; Cowley, M.J.; Elliott, P.I.P.; Duckett, S.B.; Green, G.G.R.; Khazal, I.G.; López-Serrano, J.; Williamson, D.C. Reversible Interactions with para-Hydrogen Enhance NMR Sensitivity by Polarization Transfer. *Science* **2009**, *323*, 1708–1711. [CrossRef]
34. Mathiason, F.; Lidén, C.; Hedberg, Y.S. Chromium released from leather—II: The importance of environmental parameters. *Contact Dermat.* **2015**, *72*, 275–285. [CrossRef]
35. Davis, S.J.; Wise, W.R.; Recchia, S.; Spinazzè, A.; Masi, M. The Evaluation of the Detection of Cr(VI) in Leather. *Analytica* **2021**, *3*, 1–13. [CrossRef]
36. Hauber, C.; Buljan, J. *Formation, Prevention & Determination of Cr(VI) in Leather*; United Nations Industrial Development Organization: Vienna, Austria, 2000.
37. Pettine, M.; Capri, S. Removal of humic matter interference in the determination of Cr(VI) in soil extracts by the diphenylcarbazide method. *Anal. Chim. Acta* **2005**, *540*, 239–246. [CrossRef]
38. Hron, W.T.; Menahan, L.A. A sensitive method for the determination of free fatty acids in plasma. *J. Lipid Res.* **1981**, *22*, 377–381. [CrossRef]
39. McNeill, L.; McLean, J. State of the Science of Hexavalent Chromium in Drinking Water. *Water Res. Found.* **2012**, *44*, 1–35.
40. Zhitkovich, A. Chromium in Drinking Water: Sources, Metabolism, and Cancer Risksacquosa. *Chem. Res. Toxicol.* **2011**, *24*, 1617–1629. [CrossRef] [PubMed]
41. Pierre, G.; Punta, C.; Delattre, C.; Melone, L.; Dubessay, P.; Fiorati, A.; Pastori, N.; Galante, Y.M.; Michaud, P. TEMPO-mediated oxidation of polysaccharides: An ongoing story. *Carbohydr. Polym.* **2017**, *165*, 71–85. [CrossRef] [PubMed]
42. Li, Q.; Zeng, R.; Han, B.; Li, J. Single-Electron Transfer Reactions Enabled by N-Heterocyclic Carbene Organocatalysis. *Chem. A Eur. J.* **2021**, *27*, 3238–3250. [CrossRef]
43. Knapp, G.; Orloff, H. Improved Lube Oil Antioxidants. *Ind. Eng. Chem.* **1961**, *53*, 63–66. [CrossRef]
44. Foti, M.C. Antioxidant properties of phenols. *J. Pharm. Pharmacol.* **2010**, *59*, 1673–1685. [CrossRef]
45. Sachdeva, M.; Karan, M.; Singh, T.; Dhingra, S. Oxidants and Antioxidants in Complementary and Alternative Medicine: A Review. *Spatula DD Peer Rev. J. Complement. Med. Drug Discov.* **2014**, *4*, 1–16. [CrossRef]
46. Madhan, B.; Aravindhan, R.; Ranjithakumar, N.; Venkiah, V.; Raghava Rao, J.; Unni Nair, B. Combination tanning based on tara: An attempt to make chrome-free garment leather. *J. Am. Leather Chem. Assoc.* **2007**, *102*, 198–204.
47. Devikavathi, G.; Suresh, S.; Rose, C.; Muralidharan, C. Prevention of carcinogenic Cr(VI) formation in leather—A three pronged approach for leather products. *Indian J. Chem. Technol.* **2014**, *21*, 7–13.
48. Franceschi, M.; Pacchi, G.; Maraviglia, M. Use of Olive Mill Waste Waters in the Leather Tanning Industry. European Patent 3494237B1, 3 August 2017.
49. Azaizeh, H.; Halahlih, F.; Najami, N.; Brunner, D.; Faulstich, M.; Tafesh, A. Antioxidant activity of phenolic fractions in olive mill wastewater. *Food Chem.* **2012**, *134*, 2226–2234. [CrossRef] [PubMed]

50. Kupareva, A.; Mäki-Arvela, P.; Grénman, H.; Eränen, K.; Sjöholm, R.; Reunanen, M.; Murzin, D.Y. Chemical Characterization of Lube Oils. *Energy Fuels* **2013**, *27*, 27–34. [CrossRef]
51. Moktadir, M.A.; Ahmadi, H.B.; Sultana, R.; Zohra, F.T.; Liou, J.J.H.; Rezaei, J. Circular economy practices in the leather industry: A practical step towards sustainable development. *J. Clean. Prod.* **2020**, *251*, 119737. [CrossRef]