The Corrosion of Metal Accessories In Contact With Leather

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1. Introduction

In the production of leather goods, metal accessories are used as decorative or functional elements to connect, for example, different parts of the product.

During the use of the leather artefact, corrosion and oxidation processes could occur on metal accessories, determining the reduction in the commercial value of the item for customers. The corrosion or oxidation often occurs in transit, especially after shipping from overseas, and their effects become evident only when they reach the destination. This is one of the most common causes of disputes between leather goods manufacturers, tanneries and metal accessories suppliers that accuse each other about the responsibility.

The aim of this work is the determination of those leather characteristics that can contribute to the corrosion phenomenon of metal accessories. The scope is to verify whether or not leathers have an influence on the corrosion or oxidation process. For this purpose, different metal accessories with different surface anticorrosive treatments were analyzed under different conditions. The physical evaluation was associated with the chemical determination of some substances in leather with "corrosive" properties; in particular the presence of chlorides and sulphates were analyzed. Finally, because acidic environments favor the oxidation of the metal species, the study was completed by evaluating the pH of leather.

The secondary objective of this work is the definition of a standard procedure to verify whether the corrosion of an accessory is due to the contact with the leather or to their low corrosion resistance.

2. Materials and methods

Twelve different leather samples were analyzed. In table 1 is reported a summary of their characteristics and their final use:

Sample ID	Type	Tanning	Finishing	Colour	Destination
LC 1	Ovine nappa	Chrome	Aniline	Dark blue	Address book
LC 2	Ovine nappa	Chrome	Wax	Pink	Woman handbag
LC 3	Bovine crust	Chrome	Pigmented	Brown	Watchstrap
LC 4	Bovine nappa	Chrome	Aniline	Black	Man bag
LV 5	Bovine	Vegetable	Pigmented	Brown	Watchstrap
LC 7	Ovine crust	Chrome	None	Blue	Woman Bag
LC 8	Ovine	Chrome	Aniline	Blue	Woman Bag
LV 9	Bovine	Vegetable	Pigmented	Brown	Suitcase
LC 10	Bovine nappa	Chrome	Pigmented	Blue	Watchstrap
LC 11	Ovine split leather	Chrome	Patented	Grey	Woman handbag
LV 12	Bovine crust	Vegetable	Pigmented	Violet	Woman handbag
LVC 13	Bovine	Vegetable/Chrome	Aniline	Brown	Woman handbag

Table 1: Characteristics of leather sample analyzed

The pH of aqueous extract of leathers was determined in accordance with EN ISO 4045. The same aqueous extracts were analyzed to quantify the presence of chlorides and sulphates in the samples.

Chlorides were determined using a direct titration with silver nitrate in a slightly basic environment according to IRSA-CNR 2003-4090 method A1.
Sulphates were determined using a colorimetric method according to IRSA-CNR 4140 method B.

About the accessories, two different base metals (zamac and iron) plated with brass and nickel (protected and not protected with zapon painting) were analyzed. In table 2 is reported the summary of the characteristics of the fifteen metal accessories under investigation:

Metal Accessory ID	Type	Base Metal	Finishing / Effect	Protection
BPZ 1	Snap hook	Zamac	Brass-plated	Zapon painting
NPZ 2	Buckle	Zamac	Nickel-plated	Zapon painting
BZ 3	Ring	Zamac	Brass-plated	None
NZ 4	Ring	Zamac	Nickel-plated	None
BZ 7	Zip puller	Zamac	Brass-plated	None
BI 9	Bag Stud	Iron	Brass-plated	None
BZ 10	Ring locker	Zamac	Brass-plated	None
BZ 11	Rectangular Buckle	Zamac	Brass-plated	None
NZ 12	Rectangular Buckle	Zamac	Nickel-plated	None
BI 15	Purse feet	Iron	Brass-plated	None
NI 16	Purse feet	Iron	Nickel-plated	None
BI 17	Wire ring	Iron	Brass-plated	None
NI 18	Wire ring	Iron	Nickel-plated	None
NI 19	Rectangular wire ring	Iron	Nickel-plated	None
BI 20	Key ring	Iron	Brass-plated	None

Table 2: Characteristics of metal accessories analyzed

The corrosion/oxidation resistance of metal accessories was assessed under different conditions. The first series of tests was carried out to simulate the effects of the environment (dry oxidation or corrosion by humidity) by:

- artificial ageing by heat (7 days at 50°C),
- artificial ageing by heat and elevated humidity (7 days at 50°C and 95% R.H.).

In the second series of tests, the corrosion resistance of metal accessories to different solutions was analyzed placing the sample in a piece of cotton wool wetted with:

- 30 g/L sodium chloride solution according to EN ISO 22775 method 2,
- the aqueous extract of chrome tanned leather LC 1,
- the aqueous extract of vegetable tanned leather LV 12.

In the test with aqueous extract of leather was followed the same procedure indicated in EN ISO 22775 by replacing the salt water solution.
Finally to reproduce the effects of leather and environment on metal accessories during the use or shipping, metal accessories were placed on leather samples and subjected to:

- artificial ageing by heat on dry leather (3 days at 50°C),
- artificial ageing by heat and elevated humidity on dry leather (1 day at 50°C and 95% R.H.),
- artificial ageing by heat and elevated humidity on wet leather (1 day at 50°C and 95% R.H.).

3. Results and Discussion

3.1 Chemical tests on leather samples

In table 3 are reported the chemical parameters assessed on the leather samples under investigation:

Sample ID	Leather sample description	pH (U.pH)	ΔpH (U.pH)	Chlorides (mg/kg)	Sulphates (mg/kg)
LC 1	Chrome tanned ovine nappa col. dark blue	3,74	0,44	515	1.559
LC 2	Chrome tanned ovine nappa col. pink	3,97	0,46	370	1.217
LC 3	Chrome tanned bovine crust col. brown	3,96	0,32	296	783
LC 4	Chrome tanned bovine nappa col. black	3,77	0,46	1.329	2.024
LV 5	Vegetable tanned bovine col. brown	3,95	0,41	0	1.346
LC 7	Chrome tanned ovine crust col. blue	3,60	0,36	664	936
LC 8	Chrome tanned ovine col. blue	3,92	0,28	1.181	1.040
LV 9	Vegetable tanned bovine col. brown	4,02	-	8.414	1.518
LC 10	Chrome tanned bovine nappa col. blue	3,59	0,48	590	615
LC 11	Chrome tanned ovine split leather col. grey	3,80	0,48	0	198
LV 12	Vegetable tanned bovine crust col. violet	3,44	0,67	9.743	1.217
LVC 13	Vegetable/Chrome tanned bovine col. brown	3,40	0,55	1.476	3.884

Table 3: Chemical determinations on leather samples

The results show that the maximum content of chlorides is referred to vegetable tanned leathers LV 9 and LV 12.

3.2 Ageing test on metal accessories

In table 4 the results of corrosion/oxidation related to the ageing tests on metal accessories are reported. The data show that environmental factors (humidity and presence of oxygen) did not cause rusting or changes on all the metal accessories under investigation (protected and not, iron and zamac, brass and nickel plated). Only a slight discolouration in terms of browning and loss of gloss of some brass plated accessories was observed.

Accessory ID	Description	Heat ageing (50°C - 7 days)	Humidity ageing (50°C/95% RH - 7 days)
BPZ 1	Snap hook – Protected Zamac Brass-plated	5	5
NPZ 2	Buckle - Protected Zamac Nickel-plated	5	5
BZ 3	Ring - Zamac Brass-plated	5	4
NZ 4	Ring - Zamac Nickel-plated	5	5
BI 9	Bag Stud – Iron Brass-plated	5	5
BZ 10	Ring locker - Zamac Brass-plated	5	5
BZ 11	Rectangular Buckle - Zamac Brass-plated	5	4
NZ 12	Rectangular Buckle - Zamac Nickel-plated	5	5
BI 15	Purse feet - Iron Brass-plated	5	4-5
NI 16	Purse feet - Iron Nickel-plated	5	5
BI 17	Wire ring - Iron Brass-plated	5	5
NI 18	Wire ring - Iron Nickel-plated	5	5
NI 19	Rectangular wire ring - Iron Nickel-plated	5	5
BI 20	Key ring – Iron Brass-plated	5	4

Table 4: Results of ageing tests on metal accessories (scale for assessment corrosion/oxidation according to EN ISO 22775: 5 = No change, 4 = Slight uniform change, 3 Slight patchy change or slight rusting, 2 = Marked change or noticeable rusting, 1 = Very marked change, discolouration or rusting)

3.3 Corrosion tests on metal accessories according to EN ISO 22775

In table 5 are reported the results of corrosion tests in accordance with EN ISO 22775. The tests were carried out wrapping the metal accessories with a piece of cotton lawn saturated with salt water solution (30 g/L), aqueous extracts of sample LC 1 and LV 12 (representative of chrome and vegetable tanned leathers). The damage of metal coatings was assessed after 24 hours in room temperature using the grading scale as reported in EN ISO 22775. Any staining of cotton lawn was recorded too.

The aim of these tests is the definition of corrosion properties in aqueous environment (low concentration of oxygen) with the presence of corrosive substances.

Accessory ID	Type	Salt water solution		Aqueous extract LC 1		Aqueous extract LV 12	
		Grade	Staining	Grade	Staining	Grade	Staining
BPZ 1	Snap hook - Protected Zamac Brass-plated	5	None	5	None	5	None
NPZ 2	Buckle - Protected Zamac Nickel-plated	5	None	5	None	5	None
BZ 3	Ring - Zamac Brass-plated	3-4	None	5	None	3-4	Light orange
NZ 4	Ring - Zamac Nickel-plated	5	None	5	None	3-4	Light orange
BZ 7	Zip Puller - Zamac Brass-plated	5	None	5	None	3	None
BI 9	Bag Stud - Iron Brass-plated	3-4	None	5	None	4	Orange
BZ 10	Ring locker - Zamac Brass-plated	5	None	5	None	3	Light orange
BZ 11	Rectangular Buckle - Zamac Brass	4	None	4	None	3-4	Dark orange
NZ 12	Rectangular Buckle - Zamac Nickel-plated	5	None	5	None	2	Dark orange
BI 15	Purse feet - Iron Brass-plated	4-3	Dark orange	4	Orange	4-3	Dark gray / orange
NI 16	Purse feet - Iron Nickel-plated	5	Dark orange	5	Orange	5	Dark gray / orange
BI 17	Wire ring - Iron Brass-plated	2-3	Dark orange	5	Light orange	5	Dark gray
NI 18	Wire ring - Iron Nickel-plated	2-3	Orange	2-3	Orange	3-4	Dark gray / orange
NI 19	Rectangular wire ring - Iron Nickel-plated	2	Dark orange	4-3	Light orange	4-3	Dark gray / orange
BI 20	Key ring - Iron Brass-plated	2-3	Dark orange	5	None	4-5	Light orange

Table 5: Results of corrosion/oxidation tests (scale for assessment corrosion/oxidation according to EN ISO 22775: 5 = No change, 4 = Slight uniform change, 3 Slight patchy change or slight rusting, 2 = Marked change or noticeable rusting, 1 = Very marked change, discolouration or rusting)

No damages or coating changes were observed on protected zamac samples. For zamac brass-plated accessories:

a) no relevant damages were observed using the chrome tanned aqueous extract LC 1,
b) the damages using salt solution and vegetable tanned aqueous extract of vegetable tanned leather LV 12 were similar excluding two cases where the corrosion due to water extract was more evident (BZ 10 and BZ 11).

For zamac nickel plated accessories, no rusting or discoloration was observed in all the tests, excluding that carried out on sample NZ 12 using the water extract of vegetable tanned leather LV 12 (Figure 1). In all zamac accessories described, the corrosion/discoloration observed was related to the formation of a orange/dark red compound. The staining on cotton wool (where present) was in the same colouration. However all the damages were not so evident, excluding the test on NZ 12

Figure 1: Corrosion of sample NZ 12 using aqueous extract of vegetable tanned leather LV 12

For the iron plated accessories (brass and nickel plated) only localized effects were observed; the most evident corrosion/discoloration was observed using salt solution.

3.4 Ageing tests on metal accessories placed on dry or wet leathers

In table 6 are reported the results of ageing tests carried out placing the metal accessories on the flesh side of leather sample and conditioning the composite specimen by heat and heat and elevated humidity. While in the previous tests the corrosion properties were analyzed on metal accessories alone, the aim of these series of tests is simulating the effects of the environment (eg. shipping or use) on metal accessories applied on leather for leather goods. As previously specified, in the ageing by heat the metal accessories were tested only on dry leather, while in the conditioning by elevated humidity they were tested on dry and wet leather. The ageing was carried out choosing three different chrome tanned leathers and two vegetable tanned leathers with different concentration of chlorides and sulphates.

Access. ID	Type	Ageing on dry LC 1	Ageing on wet LC 1	Ageing on dry LC 4	Ageing on wet LC 4	Ageing on dry LC 11	Ageing on wet LC 11
BPZ 1	Snap hook - Protected Zamac B-P	5	5	5	5	5	5
NPZ 2	Buckle - Protected Zamac N-P	4-5	4	4	4	4	4
BZ 3	Ring - Zamac B-P	3-4	3	-	-	-	-
NZ 4	Ring - Zamac N-P	4	3-4		-	-	-
BZ 7	Zip Puller - Zamac B-P	3	1-2	3-4	2-3	3	2-3
BI 9	Bag Stud – Iron B-P	4	2	4-5	2	3	2-3
BZ 10	Ring locker - Zamac B-P	3	2	3	2-3	3-4	2-3
BZ 11	Rectangular Buckle - Zamac B-P	3-4	3	-	-	4	4
NZ 12	Rectangular Buckle - Zamac N-P	3-4	3-4	-	-	3	2
BI 15	Purse feet - Iron B-P	3	2-3	4	2	3-4	2
NI 16	Purse feet - Iron N-P	3-4	2	3	1-2	2-3	1-2
BI 17	Wire ring - Iron B-P	4	2-3	4-3	2-3	2	2-3
NI 18	Wire ring - Iron N-P	4	1-2	5	1	2	2
NI 19	Rectangular wire ring - Iron N-P	3	2	4-3	2	2-3	2
BI 20	Key ring - Iron B-P	3-4	2	3	2	3-4	4

Table 6a: Results of ageing tests carried out placing the metal accessories on chrome tanned leather samples at elevated humidity (scale for assessment corrosion/oxidation according to EN ISO 22775: 5 = No change, 4 = Slight uniform change, 3 Slight patchy change or slight rusting, 2 = Marked change or noticeable rusting, 1 = Very marked change, discolouration or rusting)

Access. ID	Type	Ageing on dry LV 5	Ageing on wet LV 5	Ageing on dry LV 12	Ageing on wet LV 12
BPZ 1	Snap hook - Protected Zamac B-P	5	5	5	5
NPZ 2	Buckle - Protected Zamac N-P	4	4	4	2
BZ 3	Ring - Zamac B-P	-	-	3	2-3
NZ 4	Ring - Zamac N-P	-	-	3	2-3
BZ 7	Zip Puller - Zamac B-P	2-3	2-3	2	2
BI 9	Bag Stud – Iron B-P	2-3	3-4	3-4	3-4
BZ 10	Ring locker - Zamac B-P	2-3	2-3	1-2	1-2
BZ 11	Rectangular Buckle - Zamac B-P	-	-	3	3
NZ 12	Rectangular Buckle - Zamac N-P	-	-	3-4	3-4
BI 15	Purse feet - Iron B-P	3-4	2-3	3-4	3
NI 16	Purse feet - Iron N-P	2-3	2	4-3	2-3
BI 17	Wire ring - Iron B-P	2-3	2	3-4	3
NI 18	Wire ring - Iron N-P	2	1-2	4-5	3
NI 19	Rectangular wire ring - Iron N-P	3	1	4	3-2
BI 20	Key ring - Iron B-P	3-4	2	2	1-2

Table 6b: Results of ageing tests carried out placing the metal accessories on vegetable tanned leather samples at elevated humidity (scale for assessment corrosion/oxidation according to EN ISO 22775: 5 = No change, 4 = Slight uniform change, 3 Slight patchy change or slight rusting, 2 = Marked change or noticeable rusting, 1 = Very marked change, discolouration or rusting)

The ageing in dry conditions did not determine any noticeable rusting or discolouration of metal coatings for all the test pieces.

In the ageing by elevated humidity many accessories showed evident or marked signs of corrosion, oxidation or discolouration. For protected zamac accessories, no coating changes were found. Only in the case of vegetable tanned leather LV 12 placed on wetted leather was observed a marked discoloration of the surface of NPZ 2 (Figure 2).

Figure 2: Corrosion of sample NPZ 2 on wet vegetable tanned leather LV 12

For zamac brass plated accessories, surface changes where observed for both kind of tests (dry and wet leather). The worst behaviour was found for metal accessories on vegetable tanned leather LV 12 (maximum value of chloride) and in the wet test on chrome tanned leather LC 1 (Figure 3). In all the cases the surface damage was related to a dark red/brown compound.


(a)

(b)

Figure 3: Corrosion of sample: (a) BZ 7 on wet chrome tanned leather LC 1, (b) BZ 7 on dry and wet vegetable tanned leather LV12

For zamac nickel plated accessories no relevant changes were found in all the test. Only testing accessory NZ 12 with chrome tanned leather LC 11 a marked rusting was observed. As reported in table 3, this sample has no chlorides a very low content of sulphates.

For iron accessories the behaviour of accessories was more interlocutory. In quite all cases, as expected, the wet tests determined more evident damages than in dry one, but not clear matches were found between the content of chlorides and sulphates of samples with the surface damage of metal accessories. For example, considering the wire ring BI 17 and NI 18, no marked rusting was observed in contact with sample LV 12 (vegetable tanned leather with greatest value of chlorides) in dry or wet conditions, while very marked or total rusting of coatings were found testing the same accessories on sample LV 5 (vegetable leather with no chlorides), sample LC 1 (chrome tanned leather with an average concentration of chlorides and sulphates) and sample LC 11 (chrome tanned leather with no chlorides and a very low concentration of sulphates.

An aspect that is common to all the metal accessories is: samples in contact with leather having a great concentration of chlorides present a localized rusting (where present) while for all the other leather samples the formation of a layer of powdery oxide green colour.

4. Conclusions

The results of the analysis carried out on metal accessories show that there is not a clear match between the damage of coating and the chloride and sulphate content, even if is evident that high concentrations of chlorides contribute in the development of corrosion process.

In all the cases examined, the corrosion related to leather properties occurs only in presence of humidity an oxygen. No damages occur in dry environment and placing the accessories on dry leather. When leather is wetted or in a high humidity environment, the solubilization of substances having corrosive properties (anions) determines a local attack of the metal that develops in a spread surface damage due to the joint action of the atmospheric oxygen.

It is evident that the presence of chlorides and sulphates is not a sufficient condition to activate the oxidation and corrosion processes. In some cases, in fact, evident damages of metal accessories surface were observed where the chlorides and sulphates content was practically negligible.

An important aspect to underline is that no corrosion or oxidation occurs when the metal accessories are exposed in an environment reach of chloride and sulphates (in vapour phase). The damages are evident only when the items are in contact with a leather sample in a "not dry" environment.

For the consideration exposed above, a suitable test method for the corrosion properties of accessories in contact with leather should forecast the contact of the elements in a high humidity environment for a maximum time of 24 hours. Testing the items on wet leather, is probably a extreme condition, so it will preferable the leather in dry conditions
The future studies will be focused on the other substances present in leather and on their effective interaction with the different metal coatings.

5. References

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