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METALLIC ACCESSORIES ON ETHNOGRAPHIC TEXTILES DETERIORATION PROBLEMS

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Abstract

The Ethnographic Museum of Moldavia within 'Moldova' National Museum Complex of Iași detains a valuable collection of ethnographical objects, mainly from Moldavia area. This study aims the determination of metallic accessories by XRF spectrophotometry in order to identify the metals used on ethnographic textiles and their impact on the deterioration processes to which these are subjected. The metals identified in the decoration elements on ethnographical textiles were silver, alloys of copper or iron, sometimes showing a noble metal coating. Some of these metals proved to be implied in the deterioration processes, appearing as coloured spots on the fabrics. The information gathered in this study is important for establishing the preservation strategy of the ethnographical textiles.

Keywords: metallic accessories, XRF spectrophotometry, deterioration processes, preservation strategy

1. Introduction

An ethnographic object can be dated according to the type of cloth, the embroidery thread and colouring. The oldest embroideries are made on linen or hemp cloths [1, 2]. Metallic threads have been used in textiles decoration for thousands of years.

The earliest metals used were gold strips, later these strips were wound around a fibrous core for more flexibility [3, 4]. Silver, copper or copper based alloys, sometimes covered with a precious metal layer, have been largely used from the late medieval and Renaissance period until the XIXth century [3]. Since the beginning of the XXth century, new materials have been introduced, such as man-made fibres and aluminium [5, 6]. In the Romanian folk art embroidery and stitching are applied on linen, cotton or, more rarely, on hemp cloths, using wool

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threads – 'arnici' (twisted cotton in one thread, dyed in various colours), spool, silk, sequins, metallic threads, etc. [1, 2] (Figure 1).

Figure 1. Ethnographic pieces decorated with metallic accessories.

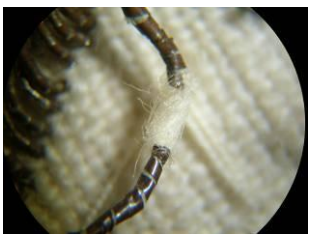


Figure 2. Detail core threads cloth.

(a) (b) (c)

Figure 3. Gold and silver threads: (a) no. inv. 78, (b) no. inv. 2198, (c) no. inv. 4967.

Making peasant fabric is one of the oldest and most complex occupations. After ornamentation of animal skins, through various embroidery and even stitches, as mats weaving or other fiber products – on the surface on which appears also decorative elements – appeared textile pieces, becoming more diversified and closely related to those objects functionality [1]. Canvas type, nature of embroidery thread or the colour can give an indication of the realization period of an ethnographic piece. The oldest embroidery is worked on linen or hemp canvas [2]. The utilization of metallic thread to decorate textiles is mentioned in the Old Testament for pieces dating from centuries XII-XIII B.C [3]. Oldest wires were actually thin strips of precious metals (gold, silver), cut from a metal sheet obtained by tapping. Subsequently, in order to achieve more flexibility, the metallic band (filé or lamina) is wrapped around an organic material core (silk, linen, wool, or even parchment, paper and horse hair).

In medieval times appear the silver or plated silver-copper alloy threads. [5]. Threads and beads (most often copper) were used in decorating Romanian ethnographic textiles, especially after the first half of the nineteenth century [7, 8]. This explains the presence of numerous museum collections of nineteenth-century textile pieces embroidered with metallic thread and/or sparkles and the appearance of chemical dyes of various foreigners that started bringing all kinds of materials from other countries [9]. Since the XXth century new materials have been introduced for decorating textiles: chemical fibres or plastics, often eloxated [6].

The metallic thread in the form of tape is wrapped on an organic material support, that can easily be cellulosics (paper, textile) or proteics (skin, parchment etc.) [4, 5, 10]. The literature describes several methods of obtaining these kinds of threads [5, 11].

The spangles, used since the sixteenth century, are made from small sectioned thread discs, flattened between rollers [11], by cutting the metal foil [12], referring to the round sequins, these were made from a spiraled wire, cut down one side to produce individual links which were then beaten flat [10, p. 234] These sequins are usually not perfectly circular and have an indent on one edge where the butt join runs through to the stitching hole [10].

In order to characterize the metal accessories used in textiles decorating a series of non-destructive investigation methods are available, such as optic microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX). These methods are applied for determining the chemical composition, identification of the fabrication technology or for detection of the reasons of corrosion processes of these accessories [11, p. 73; 12, 13]. Complex metal threads made from both strips of metal and metal wire in XVIIth century embroidery have been revealed by radiography: the central thread appeared to have a solid core that was produced by the overlapping of two separate wrapped threads [10, p. 154].

Metal threads used in both textiles decoration and embroidery were investigated extensively, often using energy dispersive X-ray fluorescence spectroscopy [14-16].

2. Experimental

The paper aimed at determining the composition of metallic accessories (threads, sequins) on ethnographic textiles and identifying the corrosion products, in order to determine a possible connection with the state of conservation of the items. Some textiles, used for interior design, and traditional clothing from different ethnographical regions – Bassarabia, northern Moldavia, Central Plateau of Moldavia and Vrancea, dating in XIX-XX centuries, richly decorated with various metallic accessories (sequins, threads), were investigated. Initially, the items have been examined by optical microscopy, using an Olympus SZ60 microscope, in order to establish the manufacturing technique used for the metallic accessories.

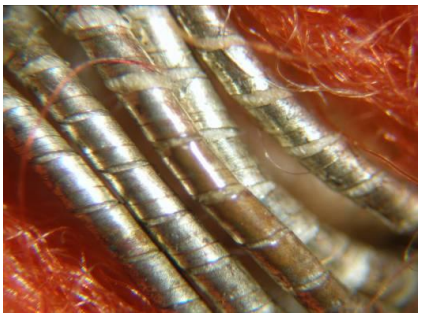
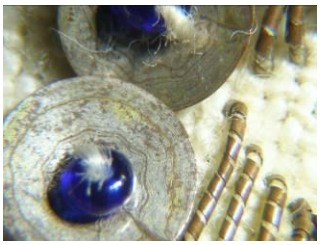
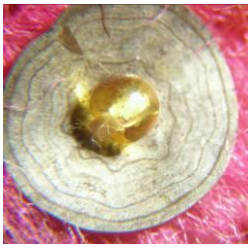


Figure 4. Silver thread (silver-copper) (no. inv. 2191).

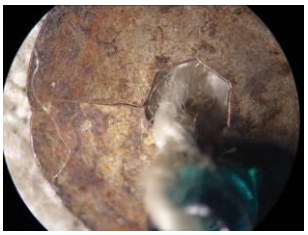


(a)



(b)

(c)



(d)

Figure 5. Sequins: (a) no. inv. 2189, (b) no. inv. 2191, (c) no. inv. 8171, (d) no. inv. 2671).

Table 1. Composition of the metallic thread (XRF).

Base metal	Film coat.	Characteristic elements (XRF)%					Metal accessory analyzed	Name of the ethnographic piece (no. inv) Location	Dating (century)
		Cu	Zn	Fe	Pb	Ag			
Copper (Pb, Zn)	-	99	0.53				Golden thread	Woman shirt (8455) Negrileşti – Vrancea	XX
		98					Golden thread	Handkerchief (2189) Negrileşti – Vrancea	XIX
	Silver	98				1.1	Silver thread		
		98.2				1	Silver thread	Headdress (3232) Negrileşti – Vrancea	XIX
		98			0.8	1	Silver thread	Woman shirt (78) Basarabia	XIX
		96	1.3			1.6	Silver thread	Woman shirt (80) Basarabia	XIX
		96.4				2.4	Silver thread	Woman shirt (4550) Tulnici – Vrancea	XX
		98				1.76	Silver thread	Skirt 2307) Iaşi	XX
		98				1.93	Silver thread	Skirt (4689) Negrileşti – Vrancea	XX
		98.7				0.95	Silver thread	Skirt (9352) Neamţ	XX
	Brass	96	3				Golden thread	Woman shirt (80) Basarabia	XIX
		97	1.6		0.8		Golden thread	Woman shirt (126) Basarabia	XIX
		98	1.2				Golden thread	Woman shirt (4585) Negrileşti – Vrancea	XX
		97	1.2				Golden thread	Handkerchief (4673) Păulești – Vrancea	XX
		97	2.4				Golden thread	Skirt (2307) Iaşi	XX
Copper with Lead (Zn, Fe)	-	96		0.6	2.3		Silver thread	Woman shirt (126) Basarabia	XIX
		83			10		Silver thread	Woman shirt (2198) Negrileşti – Vrancea	XIX
		93.5			2.4		Silver thread		
		97			1.3		Silver thread	Woman shirt (8455) Negrileşti – Vrancea	XX
		93.4	1		1.6		Silver thread		
		96.5	0.6		2.2		Silver thread	Handkerchief (4563) Negrileşti – Vrancea	XX
		96			2		Golden thread	Handkerchief (4697) Tulnici – Vrancea	XX
	Silver	96.5			1.1	0.99	Silver thread	Handkerchief (2191) Negrileşti – Vrancea	XIX
		94			4.2	1	Silver thread	Woman shirt (126) Basarabia	XIX
		96			1.7	1	Silver thread	Handkerchief (4564) Negrileşti – Vrancea	XX
		83	3.7	2.4	10.4	traces	Silver thread	Handkerchief (4673) Păulești – Vrancea	XX
		95	1		3.2	traces	Silver thread		
		96			1	1	Silver thread	Handkerchief (4697) Tulnici – Vrancea	XX
		96			1	0.98	Silver thread	Woman shirt (4549) Negrileşti – Vrancea	XX
		97.5			0.16	1.1		Woman shirt (8455) Negrileşti – Vrancea	XX
		94			1.6	1.27	Silver thread	Woman shirt (9984) Câmpuri – Vrancea	XX
	Brass	89	3.4	1	6.3		Golden thread	Woman shirt (78) Basarabia	XIX
		96	1		2		Golden thread	Woman shirt (2198) Negrileşti – Vrancea	XIX
		997	11.3		11.64		Golden thread	Woman shirt (2199) Negrileşti – Vrancea	XIX
		93	3.6		2.7		Golden thread	Handkerchief (4564) Negrileşti – Vrancea	XX
		92,7	1.8		3.4		Golden thread	Woman shirt (4549) Negrileşti – Vrancea	XX
		97	1		1		Golden thread	Woman shirt (8455) Negrileşti – Vrancea	XX
		95	1.3		1.1		Golden thread	Woman shirt (9984) Câmpuri – Vrancea	XX

Table 2. Composition sequins (XRF).

Base metal	Film coating	Characteristic elements (XRF)%						Metal accessory analyzed	Name of the ethnographic piece (no. inv) Location	Dating (century)
		Cu	Zn	Fe	Pb	Ag	Ni			
Copper (Pb, Zn)	-	100						silvery sequins	Handkerchief (4563) Negrileşti – Vrancea	XX
		94.8						gold sequins	Woman shirt (11511) Şipote – Iaşi	XX
	Brass	97.6	2.15					gold sequins	Male shirt (6260) Bosia – Iaşi	XIX
	Silver	98	1			traces		silvery sequins	Handkerchief (2191) Negrileşti – Vrancea	XIX
		98.2				1		silvery sequins	Handkerchief (3232) Negrileşti – Vrancea	XIX
		88,.5						silvery sequins	Woman shirt (4343) Munteni – Vaslui	XX
		99				1		silvery sequins	Woman shirt (8455) Negrileşti – Vrancea	XX
	Nickel	99			0.15		0.18	silvery sequins	Handkerchief (4571) Negrileşti – Vrancea	XX
		99.8					0.11	silvery sequins	Woman shirt (11511) Şipote – Iaşi	XX
Copper with Lead	-	97			1.6			silvery sequins	Handkerchief (2671) Fălticeni – Suceava	XX
		94.8			3.6			silvery sequins	Handkerchief (4564) Negrileşti – Vrancea	XX
		94			4.67			silvery sequins	Woman shirt (5177) Mădârjac – Iaşi	XX
		92.6			7.4			silvery sequins	Handkerchief (4563) Negrileşti – Vrancea	XX
	Silver	94			4.5	0.6		silvery sequins	Handkerchief (4682) Negrileşti – Vrancea	XX
		93			4.5	0.7		silvery sequins	Woman shirt (5177) Mădârjac – Iaşi	XX
		89			9.5	0.7		silvery sequins	Woman shirt (5241) Vama – Suceava	XX
	Brass	89.1	1.7		9.18			gold sequins	Woman shirt (2198) Negrileşti – Vrancea	XIX
		94	2		4			gold sequins	Handkerchief (5048) Popeşti – Iaşi	XIX
		90	5	1	1			gold sequins	Handkerchief (8171) Hârtop – Suceava	XIX
Brass	-	80	3.5	2.8	12		0.18	gold sequins	Handkerchief (2191) Negrileşti – Vrancea	XIX
		63	9	6	20			gold sequins	Handkerchief (2189) Negrileşti – Vrancea	XIX
		81	3.8	3	9			gold sequins	Handkerchief (8171) Hârtop – Suceava	XIX
		72	5	4.4	12			gold sequins	Woman shirt (4549) Negrileşti – Vrancea	XX
		87	2.3	1	8			gold sequins	Handkerchief (4564) Negrileşti – Vrancea	XX
Iron	-	1	3.6	22	24			silvery sequins	Handkerchief (2671) Fălticeni – Suceava	XX
	Brass	50	19	29				gold sequins	Woman shirt (2876) Ibăneşti – Botoşani	XX
		54	15.5	29				gold sequins		
	Nickel			84			15	silvery sequins	Woman shirt (3122) Crăcăoani – Neamţ	XIX
				75.6			24	silvery sequins	Woman shirt (2876) Ibăneşti – Botoşani	XX
			2.3	85	8.3		2.5	silvery sequins	Handkerchief (2671) Fălticeni – Suceava	XX
			12	66	15		1.7	silvery sequins	Handkerchief (2481) Rădăuţi – Suceava	XX
	Nickel/ Copper	26.4		38			20	silvery sequins	Handkerchief (2608) Fălticeni – Suceava	XX
Zinc (Fe, Pb)	-	2	79	3	13.8			silvery sequins	Woman shirt (2876) Ibăneşti – Botoşani	XX
		10	79		10			silvery sequins	Handkerchief (7755) Fălticeni – Suceava	XIX
		3	72	2	17			silvery sequins		

Subsequently, the X-ray fluorescence spectrometry (XRF) analysis was applied, by using an Innov-X Systems Alpha Series hand-held apparatus, equipped with a W anticathode X-ray tube, working at 35kV and 40μA and Si(PIN) detector, thermoelectrically cooled. The semi-quantitative analysis was carried out using Analytical Mode soft for heavy matrices, the excitation time being set at 30 seconds.

2.1. Optical microscopy

By optical microscopy it was possible to clarify the technique used to realize the ornamental metallic threads. All studied threads are made of thin metal strips wrapped around a core yarn, usually cotton (Figure 2) or, sometimes, fine wool, as mentioned in the literature [6]. The core yarn was often painted in different colours according to the colour of the metallic thread. Microscopic study also revealed the presence of a gold or silver coating, with double role: decorative and protective over base metal (Figure 3).

Table 3. Identification of corrosion products (XRF).

Name, date, location	Analyzed area	Characteristic elements (XRF), ppm				
		Fe	Cu	Zn	Cr	Mn
Woman shirt XIXth century Crăcăoani – Neamț	Textile (1)	728	143	276	43	144
	Textile (2)	897	-	147	-	218
	Stain I (3)	5061	-	177	65	-
	Stain II (4)	10712	-	263	74	-
Woman shirt XIXth century Ibăneşti – Botoşani	Textile (5)	782	-	83	5	129
	Textile (6)	749	-	105	42	157
	Stain (7)	997	221	293	2215	122
	Stain II (8)	890	259	198	1947	164

Figure 6. Analysed areas from Table3.

For many pieces the film coating is strongly affected by functional wear, being kept only on small portions of areas less exposed (Figure 4).

Regarding sequins, microscopy revealed details of the realization technique that has been used, of film coating structural features and specific aspects of processes of deterioration.

Microscopic images for most of sequins are suggestive of craft making technique similar to that described in the literature (Figure 5). Sequins have a specific indent of the obtaining way by flattening a spiral wire, moreover, on the surface can be observed concentric circles from individual strands compacted by tapping and the attachment hole is not perfectly centred. Another group of beads are those obtained by stamping, perfectly round and into the clamp, centre, has a hexagonal shape (Figure 5d). It can be said that these are industrial accessories and may be assigned to a more recent period – after 1900.

2. 2. Composition analysis for metal accessories

XRF analysis carried out in situ on different clothing and interior design textiles from nineteenth and twentieth centuries belonging to the Ethnographic Museum of Moldavia, revealed the following characteristics of metallic accessories (Tables 1-3, Figure 6).

3. Results and discussion

Information from the literature on metal components used in decorating ethnographic pieces is sporadic and incomplete.

In a large study that aimed composition and obtaining technique of metallic threads, the copper ones are classified as follows: gilded copper, silvered copper, copper and then silver plated, brass, copper thread coated with brass and others based on copper identified at textiles from XIX-XX centuries. Within these main groups, different manufacturing techniques and methods of identifying studied threads have been treated separately [5].

In the analyzed metal accessories of the ethnographic pieces, belonging to the Ethnographic Museum of Moldavia collection, were identified the following types of metals:

- silver plated copper or brass thread;
- copper wire with lead (1-10%), zinc and iron as impurities film coating: silver or brass;
- brass thread with lead and iron, plated with silver or zinc;
- copper sparkles, lead and zinc contaminated, silvered or nickel plated;
- copper sequins with lead (1-11%), silvered or brass plated;
- sequins of brass with iron and lead;
- sequins of iron nickel plated or brass;
- sequins of zinc.

Composition analysis revealed certain characteristics in making textiles with metal accessories. Regarding metallic thread used in decorative embroidery, it appears that during the end of the XIXth century and early XXth century copper wire silvered or brass dominated, to achieve the desired colour variety. This applies to Bessarabia, ethnographic Vrancea area, Northern Moldova and Moldavian Central Plateau.

Other types of alloys used in making decorative metallic threads are based on copper with lead added in different concentrations. Regarding film coating for gold wires was used the metal itself or brass, while for the silvery wire was used routinely silver. A third type of alloy identified in metallic wires is represented by a type of brass containing a high concentration of lead (up to 24%) and iron (up to 18%), used as such for gold wires or coated with silver or zinc, for silver wires.

The wide variety of alloys used for decorative threads and sequins found on pieces from Negrileşti–Vrancea lead to the conclusion that there is an important craft in this area. We can assume that the mentioned pieces could be assigned to the same craftsmen, or could indicate a handicraft workshop producing metal threads.

Regarding the metal used to make the sequins, it has been identified a large variety of compositions: copper, brass with lead and iron, iron, and zinc. For film coating were determined silver, brass, nickel, copper-nickel alloy, zinc.

Metallic wires and sequins from XIXth–early XXth century are preferentially silvered. During the XXth century there was a more frequent use of less noble metal: brass, nickel, zinc. The information gained allows the placing in time of the undated parts.

The method used allows rapid and nondestructive determination of the composition of metal accessories, but presents some difficulties in interpretation for pieces with multiple coatings such as sequins made of Fe-Pb-Zn alloy coppered, then nickel plated.

By analyzing coloured spots on ethnographic textiles has been identified a high concentration of elements such as Fe, Cu, Zn from metal accessories and colorants used for dyeing threads used in decorating (Cr) with an important role in accelerating the deterioration of the cellulose, especially in the case of an improper microclimate.

4. Conclusions

The preference for cheap and easy workable metals, as copper based alloys, is evident. For decorative purposes, in the XX century, these metals were covered with golden or silvery layers, made of brass or silver, but also of zinc or nickel. Sequins of iron or zinc are dating from the same period of time. In the XIXth–early XXth centuries, covering layers for the metallic accessories were preferentially of silver, while in XXth century less noble metal have been used, such as brass, nickel and zinc.

Electrolytic copper (100% copper) was identified for one item, indicating the XXth century as the period of production.

The elements identified in the coloured stain on the textiles, especially Fe and Cu, have an important impact on the deterioration of cellulose support.

XRF method allows a rapid and non-invasive identification of the composition of metallic accessories on ethnographic textiles. All the information acquired gives us the possibility to place in time the undated pieces.

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