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COMPLEX PROCESSING OF METALLISED FABRICS BY ELECTROLYSIS

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metallised fabric, electrochemical technology, copper and silver cathodic coating, nitrided polyamide degradation products, oligomers, rubber compounds, electrochemical kinetics

Abstract: *The paper provides the need and economic efficiency of recycling metallised fabrics lost their functional properties. We selected the recycling options to ensure the total recovery of the fabrics containing metallic and polyamide yarns. We proposed the electrochemical technology involving cathodic separation of recyclable metals in the form of coatings firmly adhered to the surface of the cathode as the main method of metal threads recycling. By the experiments, there is a degradation of polyamide yarns and subsequently nitration in nitric acid as a result of preliminary operations before the electrolysis. Also we proposed a method for the utilisation of the resulting nitrated polyamide degradation products, providing them as oligomers for general purpose rubber compounds. The results agree with the possibility of obtaining a brilliant silver cathode precipitate strongly adherent to the surface of the cathode made of the nitroxide electrolyte. Obtained kinetic rules of electrochemical process of cathodic deposition of recycled metals indicate the presence of significant polarization at the initial moment of time during the discharge process of silver and copper cations.*

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Introduction

Metallised fabrics include fabrics made of metallised threads, or the metallisation of the fabric is achieved by ion-plasma atomisation [1]. Metallised fabrics obtained by ion-plasma atomisation are not of practical interest for electrochemical combined processing due to their low electrical conductivity. Fabrics produced using metallic and metallic threads can be recycled using electrochemical technologies [2]. This class of fabrics includes brocade fabrics and fabrics with a metallic laminette yarn.

Brocade is a heavy fabric with patterns made with laminette yarns of gold, silver or their alloys [3]. Brocade is used for sewing church vestments, shoulder knots for military dress uniforms and for making electrically conductive equipment for sports fencing. Church vestments and shoulder knots have long operating life, while fencing equipment fails after in general a year

of use because the specific electrical resistance of the material fencing gear made of becomes more than 5 Ohm-m [4]. Mainly, it is due to oxidation of the metallic brocade threads through the athletes' activity, competitions (temperature fluctuations) and mechanical damage (frequent contact with the opponent's weapon) [5].

Today, the substandard fencing gear is piling up in sport institutions or acts like household garbage, as it is not accepted for recycling.

Main body

According to the Russian Fencing Federation [6], about 18 thousand square metres of electrically conductive metallised fabric is produced annually in the form of electrically conductive sports fencing gear.

Fig. 1 shows a diagram of the annual formation (in %) of oxidised electrically conductive metallised sportswear from Federal Districts of Russia.

Analysis of the data presented in the diagram allows to conclude that practically one third of oxidised electrically conductive metallised sports fabrics is from the Central Federal District (6,000 m^2), which emphasises the relevance of the issue related to complex extraction of non-ferrous metals from metallised fabrics by electrochemical method.

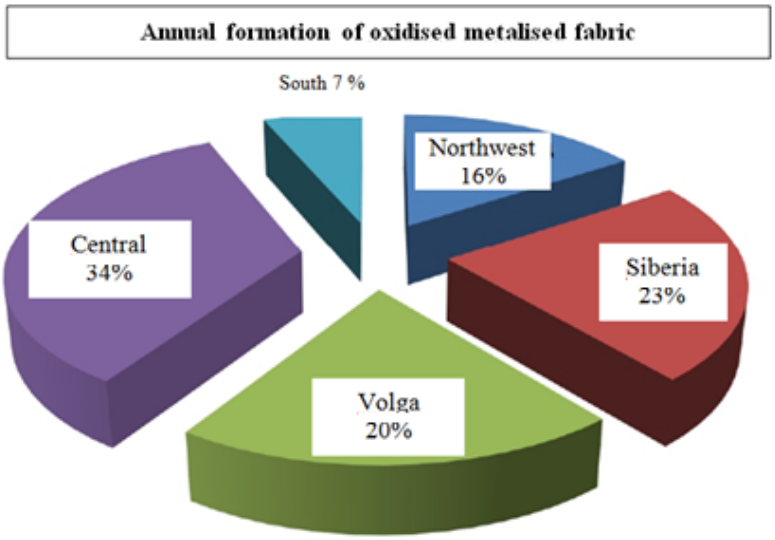


Fig. 1. Diagram of the annual formation (in %) of oxidised electrically conductive metallised sportswear from Federal Districts of Russia

The base of the electrically conductive fencing fabric is a polyamide yarn with 0.1 mm copper laminette yarn coated with a silver coating up to 5 μm (Fig. 2).

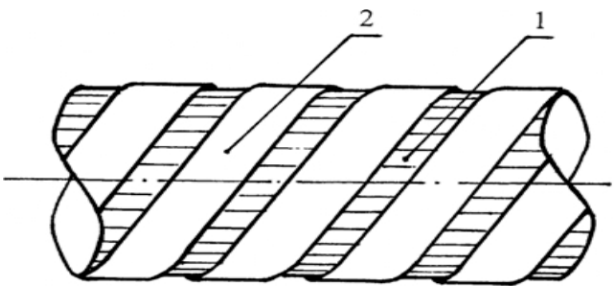


Fig. 2. Structure of the metallic laminette yarn: 1 - polyamide textile yarn; 2 - metallic yarn

The weight of 1 m^2 of metallised fabric is 180-190 g. The cross-section of fabric is 84.76% and the cross-link density is 15.24%. According to [7], the electrical conductivity of the fabric is provided by a metallic laminette yarn with a synthetic core. The synthetic core consists of 45.4 tex polyamide

yarn. The metallic laminette yarn is made of copper and entirely coated with silver, which predetermines the further technology of extracting these metals from the metallized fabric.

Table 1 shows the financial and economic balance of a metallic laminette yarn with a polyamide synthetic core.

Table 1. The financial and economic balance of a metallic laminette yarn with a polyamide synthetic core

№	Composition of metallic brocade thread	% wt.	1 g metal price on 1 May 2022
1	Metallic laminette yarn	100	-
2	Copper laminette yarn	75.3	0,585 RUB
3	Silver coating	4.7	52,89 RUB
4	Polyamide yarn	20	-

By Table 1, the cost-effectiveness of silver recovery is more than 5 times higher compared to copper one, so the technology was chosen to recover both silver and copper.

It is known [8] that silver coating does not oxidize when heated up to 960 °C. Silver does not react with oxygen, water, alkaline solutions, hydrochloric and diluted sulphuric acids, but dissolves in concentrated nitric acid.

$$Ag + 2HNO_3(\text{concentrated}) = AgNO_3 + NO_2 + H_2O$$

Copper reacts readily with nitric acid of any concentration:

- with concentrated nitric acid:

$$Cu + 4HNO_{3(\text{concentrated})} = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

- with diluted nitric acid:

$$3Cu + 8HNO_{3(\text{diluted})} = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Therefore, burning out the organic substrate (polyamide yarn) will not produce silver and copper oxides.

Copper oxides in contact with sulphuric acid transfer Cu^{2+} ions into solution, in order [9] to obtain pure copper by electrolysis.

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$
$$Cu^{2+} + 2\bar{e} \rightarrow Cu^{\circ}$$

Fig. 3 shows the following technological scheme for the electrochemical extraction of metals from metallised fabrics.

Metallised fabric that does not meet the electrical resistivity requirements of the application is placed in concentrated nitric acid for 5-10 seconds. During this period, the silver coating dissolves and the polyamide yarn is degraded. The destructed polyamide yarn is collected and removed from the nitric acid and then washed with water distilled from the acid and silver ions Ag^+. Wash water and degradation products are collected for further processing.

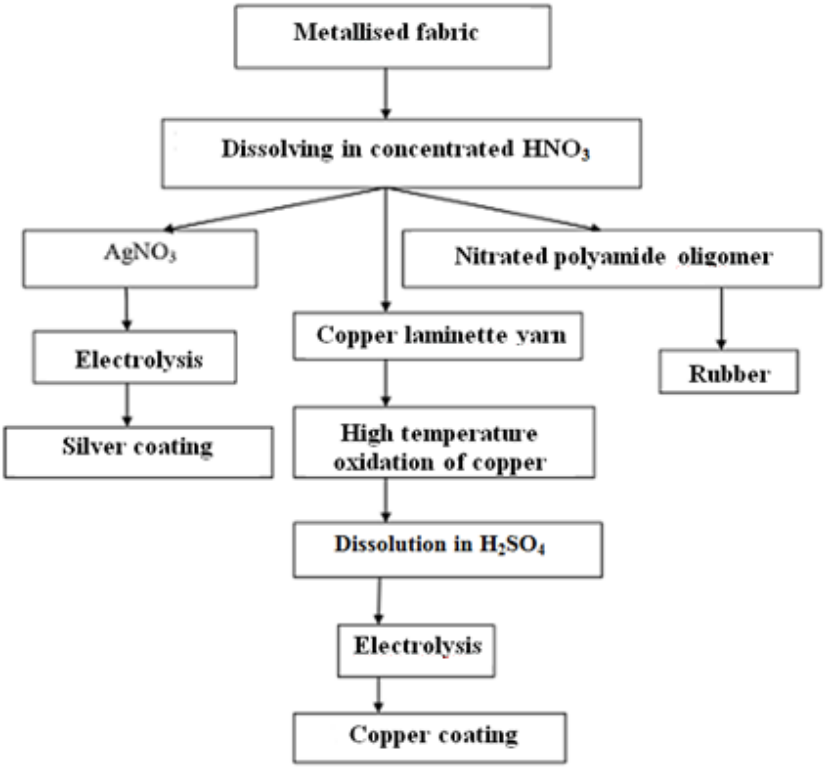
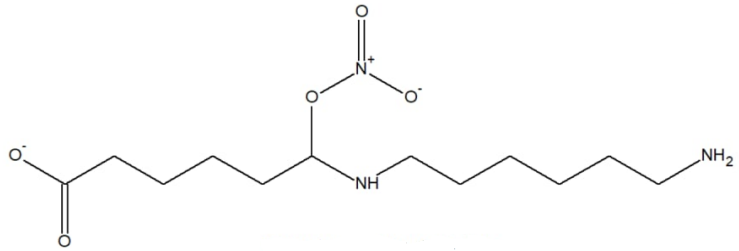


Fig. 3. Technological scheme for the electrochemical extraction of metals from metallised fabrics

The polyamide yarn degradation products are nitrated aliphatic oligomers —6-[(6-aminohexyl) amino]-6-(nitroxy)hexanoates, which is consistent with the infrared spectroscopy data of the original and degraded polyamide yarn shown in Fig. 4. IR spectra of polyamide and nitrated polyamide degradation products were obtained on a Perkin Elmer RX-1 FT-IR spectrophotometer



6-[(6-aminohexyl) amino]-6-(nitroxy)hexanoate

In the infrared spectra of polyamide and nitrated polyamide degradation products (Fig. 4) an absorption band of 3295 and 3327 $см^{-1}$ characteristic of NH group and an absorption band of 2930 and 2937 $см^{-1}$ characteristic of CH_2 were found. The presence of absorption bands 1708–1733 $см^{-1}$ in both spectra indicates the presence of the C=O group. The difference in the IR spectra is that the nitrated polyamide degradation products have absorption bands 1616 $см^{-1}$ characteristic of asymmetric NO_2 vibrations and absorption bands 1277 $см^{-1}$ characteristic of symmetric NO_2 vibrations.

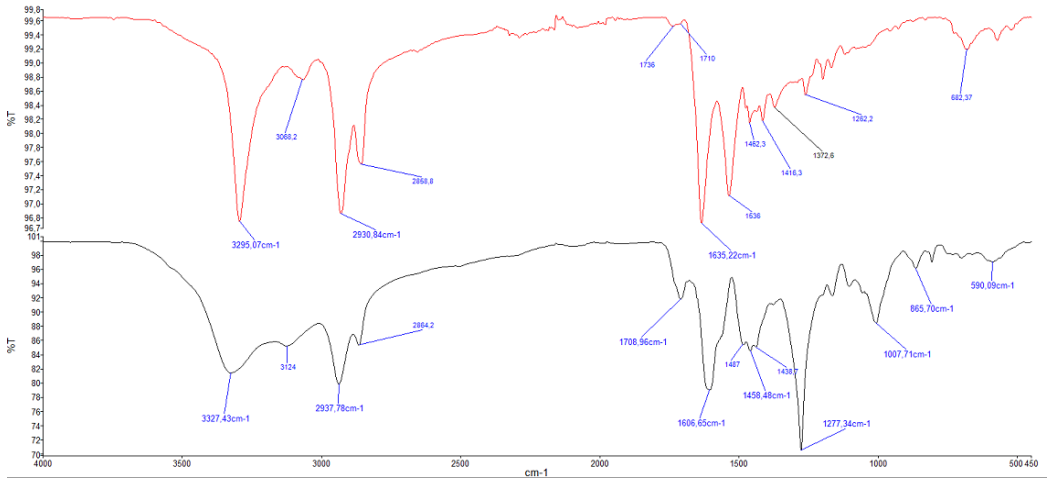


Fig. 4. IR spectra of the polyamide (lower graph) and the degraded polyamide yarns (upper graph)

The spectra (Fig. 5) obtained by proton nuclear magnetic resonance (NMR H1) confirm the nitration, the signal at 4.5 ppm (chemical shift) is identical to the hydrogen next to the nitro group.

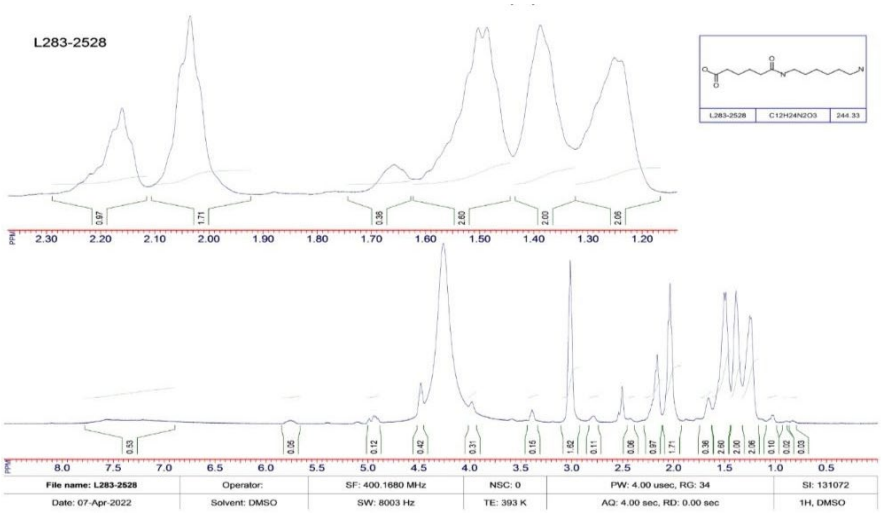


Fig. 5. NMR spectroscopy of a degraded polyamide yarn

Similar degradation products of polyamide yarn (nylon 6) are known to be used in biomedical chemistry as an enzyme degrading the by-product of nylon-6 of carboxyesterase with a beta-lactamase fold [10-12]. L.A. Tikhomirov studied the interaction of degradation products of nylon-6 resulting from heat treatment with butadiene-nitrile rubber [13]. In this work, the obtained nitrated aliphatic oligomers from polyamide yarn degradation products were used in the formulations of general purpose rubber compounds according to the methods presented in [14]. Rubber mixtures based on natural rubber: original and with the addition of nitrided aliphatic oligomers from the degradation products of polyamide yarn were made on heating rollers PD 320 160/160 with roller friction 1:1,08 for 15 minutes.

Table 2 shows the comparative properties of a rubber compound based on natural rubber: original and with the addition of nitrated aliphatic oligomers from polyamide yarn degradation products.

Table 2. The comparative properties of a rubber compound based on natural rubber: original and with the addition of nitrated aliphatic oligomers from polyamide yarn degradation products.

Formula and indicator names	Per 100 wt. parts of rubber	
Natural rubber	100.0	100.00
Nitrated aliphatic oligomers from polyamide yarn degradation products	-	5.00
Sulphur	2.00	2.00
Mercaptobenzthiazole	0.65	0.65
Tetramethylthiuramdisulphide	0.30	0.30
Zinc oxide	15.00	15.00
Stearic acid	2.00	2.00
Rubber properties (151 °C·15 min)		
f_r, MPa	19.75	19.02
ε_r, %	820	850
θ, %	9.6	11.7

Symbols:
f_r - conditional tensile strength;
ε_r - breaking elongation
θ - conditional persistent elongation

Comparative properties of rubber, presented in Table 2, show that with the introduction of nitrated aliphatic oligomers from degradation products of polyamide yarn into the formulation of rubber compounds based on natural rubber, the elastic strength properties of the studied rubber samples under tension are almost the same, which is very important for the consumer properties of general purpose rubber compounds.

In order to avoid formation of a large amount of dark crystalline precipitate on the anode [15, 16] due to anodic oxidation of oxygen the saturation of the electrolyte with silver was conducted by chemical dissolution of the silver coating in concentrated nitric acid. Concentrated sulphuric acid was also added to the electrolyte to prevent the formation of nitrogen oxides.

The proposed technology avoids the opportunity of mixing of cathodic and anodic precipitation inherent to the refining process, as a cathodic silver-bearing precipitate is formed, which is tightly bound to the surface of the cathode.

In order to select optimum conditions for silver cathode precipitation the polarisation curve of silver cathode precipitation from nitric acid test electrolyte was obtained (Fig. 6) using platinum electrodes in galvanostatic mode.

By data obtained, the initial moment of time (at $i \rightarrow 0$) there is a significant polarisation of the electrode $\Delta\varphi$ = 230 mV, caused by the presence of polyamide yarn degradation products and dissolution of the released silver cathode. The course of the polarisation curve takes the form of the Taffel dependence ($\eta = a + b\lg i$) only with co-deposition of Ag и Ag_2SO_4, cathodically, i.e. with increasing current density (i). The analysis of the polarisation curve allows the selection of the following conditions for the silver-bearing cathode precipitation:

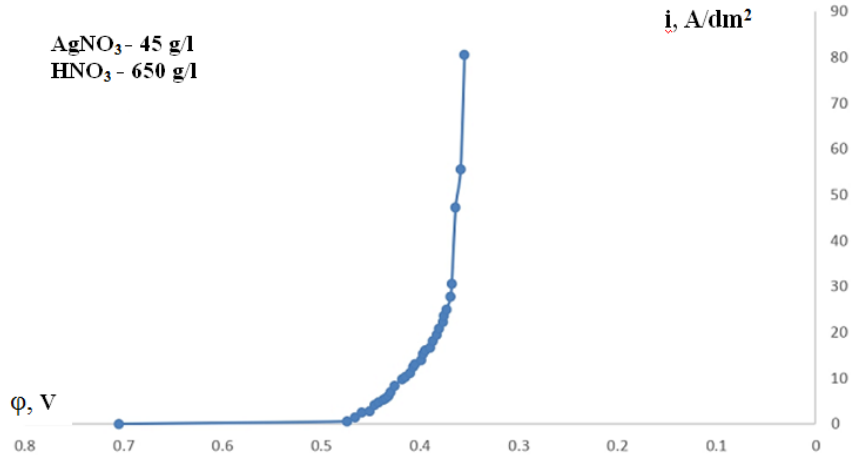


Fig. 6. Polarisation curve of the cathodic precipitation of a silver-bearing precipitate from a nitroxide test electrolyte

Electrodes: platinum.

Temperature: $T = (40\pm3)$ °C.

Current density: $i = 35\text{-}90$ A/dm^2.

Stirring: none.

The structure of the silver-containing cathode precipitate was investigated by X-ray diffractometry on an ARL X'TRA X-ray diffractometer (see Fig. 6):

1. Platinum (Pt) with cubic structure (peaks 1) and unit cell parameters $a = b = c = 3.9237$ Å, at angles: $\alpha = \beta = \gamma = 90^0$;

2. Silver (Ag) with cubic structure (peaks 2) and unit cell parameters $a = b = c = 4.0855$ Å, at angles: $\alpha = \beta = \gamma = 90^0$;

3. Silver sulphate (Ag_2SO_4) with orthorhombic structure (peaks 3) and unit cell parameters: $a = 10.269$ Å, $b = 12.706$ Å, $c = 5.8181$ Å at angles: $\alpha = \beta = \gamma = 90^0$.

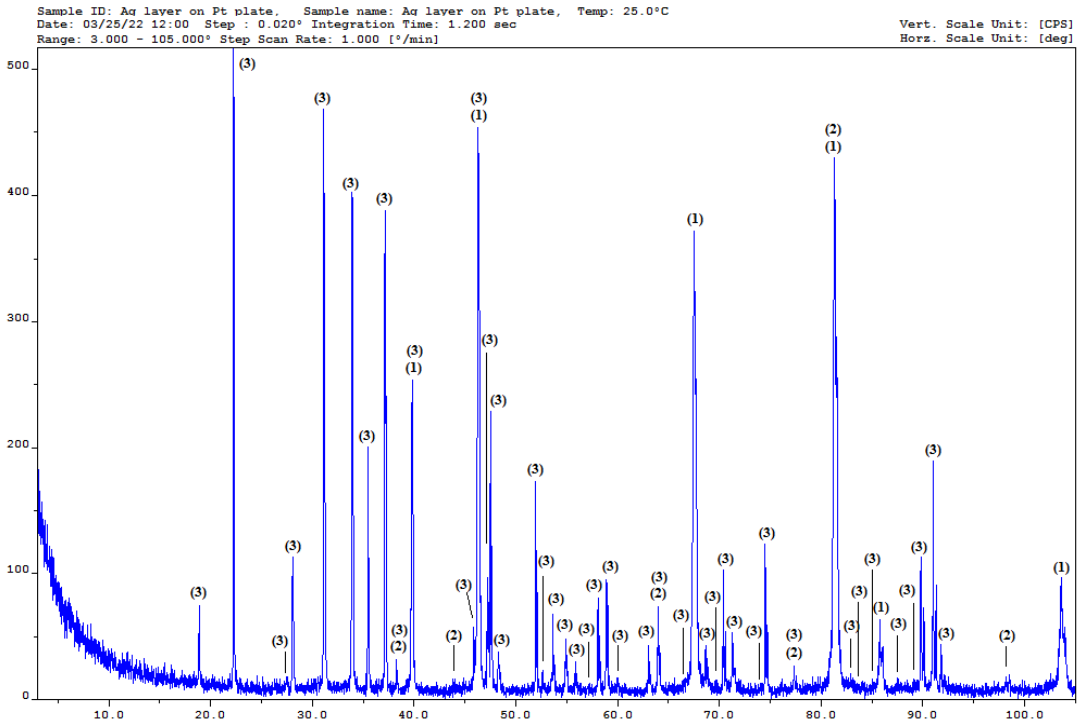


Fig. 7. Diffractograms of silver coating on platinum

In this coating (Fig. 7) no degradation products of the polyamide yarn were detected, but these products were present in the electrolyte. When challenging the electrolyte with the additional introduction of saturated KCl under conditions of cathodic coating deposition parameters

According to Table 3, the main product of the sedimentation was 6-[(6-aminohexyl) amino]-6-(nitroxy)hexanoate potassium and insoluble sulphates, with the exception of silver sulphate.

In order to optimize conditions of cathode copper precipitation polarization curves were obtained in galvanostatic mode of cathode copper extraction from sulphuric acid experimental and standard electrolyte (Fig. 8) using copper plates as anode, steel electrodes served as cathodes.

The composition of the experimental electrolyte was prepared from copper oxides, which were obtained by calcining at 650 °C for 120 minutes of copper laminette yarns and dissolved in concentrated sulphuric acid.

The concentration of Cu^{2+} ions in the experimental electrolyte determined by iodometric method [17] was 68.43 g/l, the sulphuric acid for dissolving copper oxides had a density of 1.82 g/cm^3.

Composition of standard electrolyte: Cu^{2+} - 70 g/l; SO_4^{2} - 70 g/l.

Table 3. Elemental energy dispersive analysis of the anode product

	1_1		1_2		2_1		2_2	
Element	Wt %	At %	Wt %	At %	Wt %	At %	Wt %	At %
C K	13.3 ± 0.68	24.5	16.7 ± 0.67	28.46	13.4 ± 0.79	24.7	16 ± 0.61	26.8
O K	29.3 ± 0.92	40.4	35.1 ± 1.03	44.94	27.7 ± 0.94	38.49	38.7 ± 1.02	48.6
NaK	0.52 ± 0.12	0.5	0.48 ± 0.14	0.43	0.49 ± 0.14	0.47	1.4 ± 0.16	1.23
AlK	0.95 ± 0.14	0.78	0.95 ± 0.15	0.72	0.26 ± 0.13	0.21	0.42 ± 0.12	0.31
S K	18.3 ± 0.49	12.6	7.67 ± 0.35	4.9	24.8 ± 0.60	17.19	6.48 ± 0.31	4.06
ClK	0.32 ± 0.16	0.2	0.77 ± 0.19	0.45	0.24 ± 0.17	0.15	0.6 ± 0.17	0.34
K K	37.3 ± 0.92	21.1	38.4 ± 0.96	20.1	33.1 ± 0.91	18.79	36.4 ± 0.91	18.7
Total	100	100	100	100	100	100	100	100

Element	Inte. Error	Inte. Error	Inte. Error	Inte. Error
C K	2.56	2	3	1.91
O K	1.58	1.47	1.7	1.32
NaK	11.8	14.4	14	5.55
AlK	7.25	8.06	25	14.1
S K	1.34	2.28	1.2	2.41
ClK	24.6	12.4	36	13.8
K K	1.23	1.25	1.4	1.25

The polarisation curve of cathodic copper release from standard sulphuric acid electrolyte (see Fig. 8) fully coincides with the graphical interpretation of the general equation of polarisation curve for one-step discharge-ionization reaction (Tafel's formula).

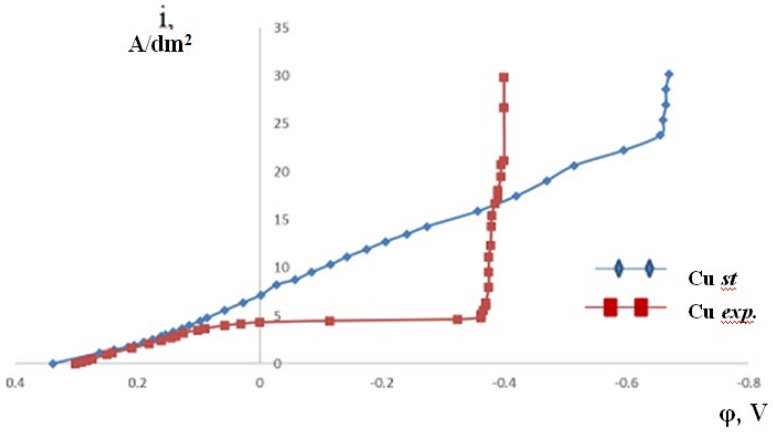


Fig. 8. Polarisation curves of cathodic separation of copper from sulphuric acid test and standard electrolytes

When concentrated sulphuric acid is used as the electrolyte at low values of current density (i) a polarisation of the cathodic process $\Delta\varphi$ = 480 mV is observed, caused by the low electrolyte conductivity and dissolution of the released cathode copper. Leveling of polarisation-related processes occurs at current densities above 5 A/dm^2.

Kinetic relations revealed by the study of polarization curve of copper recovery from the experimental electrolyte allow to choose the following conditions of cathode precipitate recovery: i = 25-90 A/dm^2 and T = (20±3) °C.

Analysis of the structure of the cathode copper precipitate performed by X-ray diffractometry (Fig. 9) showed the presence of:

1. Copper (Cu) - cubic structure (peaks 1) and unit cell parameters: $a = b = c$ = 3.62465 Å at angles $\alpha = \beta = \gamma = 90^0$;

2. Ferrite (α-Fe) - volumetrically centred cubic structure (peaks 2) and unit cell parameters: $a = b = c$ = 2.8664 Å at angles $\alpha = \beta = \gamma = 90^0$.

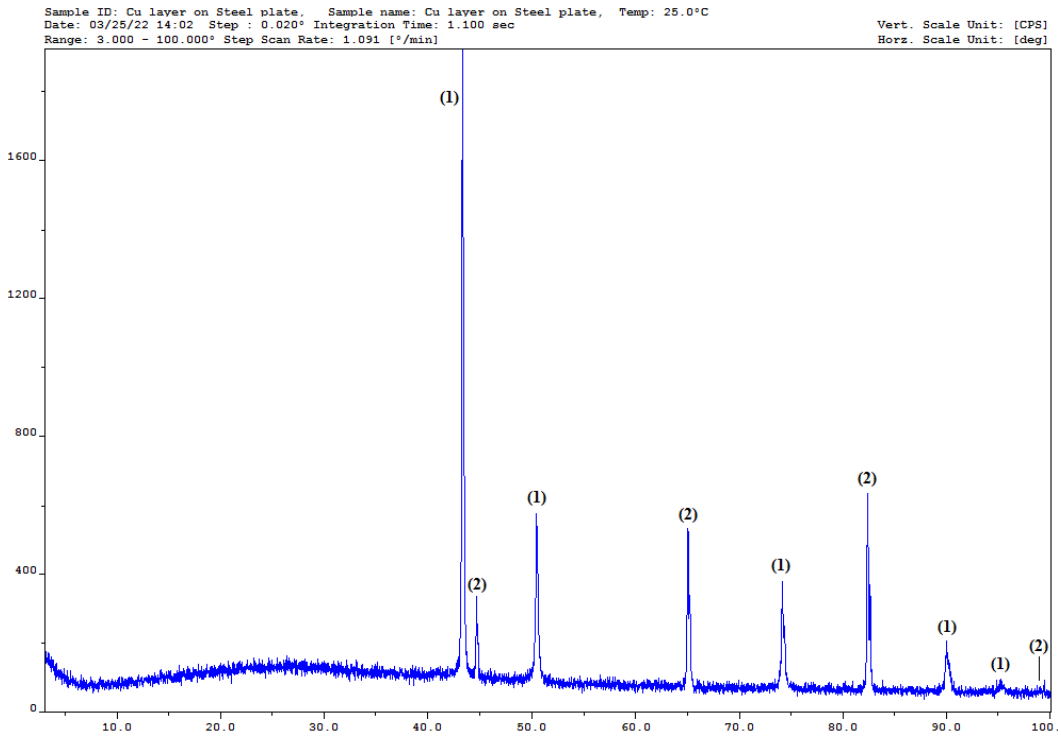


Fig. 9. Diffractograms of copper coating on steel

Conclusions

Thus we provide the need and economic efficiency of recycling metallised fabrics lost their functional properties. We selected the recycling options to ensure the total recovery of the fabrics containing metallic and polyamide yarns. We proposed the electrochemical technology involving cathodic separation of recyclable metals in the form of coatings firmly adhered to the surface of the cathode as the main method of metal threads recycling . By the experiments, there is a degradation of polyamide yarns and subsequently nitration in nitric acid as a result of preliminary operations before the electrolysis. Also we proposed a method for the utilisation of the resulting nitrated polyamide degradation products, providing them as oligomers for general purpose rubber compounds. The results agree with the possibility of obtaining a brilliant silver cathode precipitate strongly adherent to the surface of the cathode made of the nitroxide electrolyte. Obtained kinetic rules of electrochemical process of cathodic deposition of recycled metals indicate the presence of significant polarization at the initial moment of time during the discharge process of silver and copper cations.

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