MINERAOLOGICAL AND CHEMICAL ANALYSIS OF THE HISTORIC OBJCTS FOUND IN THE KATYN GRAVES AND DEVELOPMENT OF TECHNOLOGY PREVENTING THEIR FUTURE DESTRUCTION

Badania mineralogiczno-chemiczne obiektów historycznych znalezionych w grobach Katyńskich i technologia ich zabezpieczenia przed zniszczeniem

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Summary

Mineralogical and chemical analyses of the historic objects found in the Katyn graves have been done. The analyses were aimed at identifying processes leading to destruction of the historic objects and at development of technology preventing their further destruction. Analyses with the use of digital and scanning (electron) microscopes as well as chemical EDS analyses were carried out.

Observations showed that the examined objects undergo several processes of different degree of intensity. The main process observed in the examined objects (their plastic parts) is a kind of recrystallization, that is polymer's structure ordering. Fragments of the polymer shrink, which results in formation of systems of fractures leading to the destruction of the material. Besides, the examined materials undergo condensation of polymers (ageing of polymer),

oxidation and migration of foreign substances into the structure of the examined objects.

Research results and information about celluloid, ebonite and resin (toothbrush) show that the best way to protect the relics is vacuum packaging in transparent plastic bags.

Introduction

Materials surrounding us vary in structure, physical, mechanical and chemical properties. By plastic we understand materials, whose basic ingredients are synthetic or modified polymers. Plastics can be obtained from pure polymers or modified polymers by adding different auxiliary substances such as fillers, pigments, dyes, plasticizers, stabilizers etc. (Hyla 1984, Pielichowski & Puszyński 1998).

History of development of the world plastic industry started in 1850-1875 when celluloid was first produced in the USA on industrial scale. Starting the synthetic rubber production in Germany in 1915 was a great achievement in the history of plastic industry development. The following years brought more and more diversified development of plastic production in the aspect of type and quantity (Hyla 1984).

The aim of the examination was to identify the material from which the objects found in the Katyn graves were made.

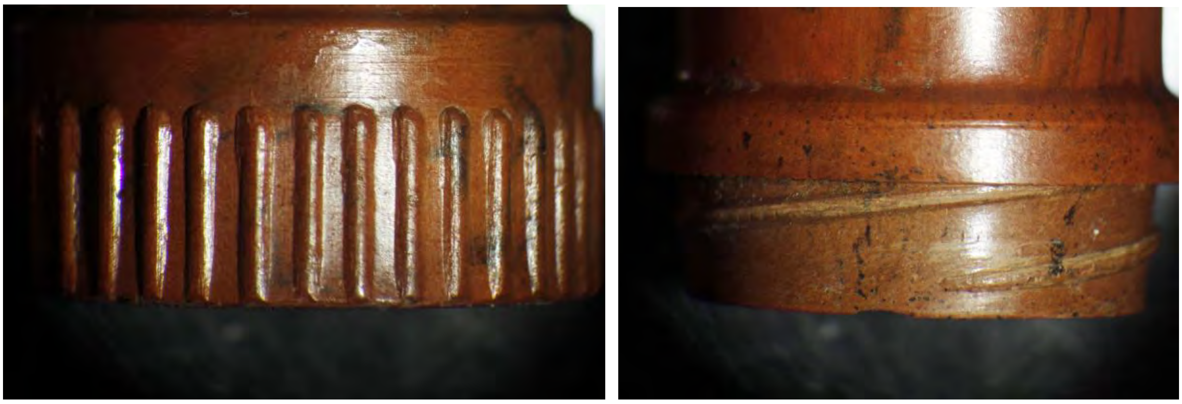
The aim of the research was also to show if the examined objects were influenced by the difficult conditions in which they remained over the years. Besides, the final effect of the research was to develop the technology preventing further destruction of the found objects.

Materials and methodology

Table 1. The list of the objects from graves at Katyn selected for study.

Lp.	Object	Number	Comments
1.	Toothbrush case	853/M	2 parts
2.	Comb	858/2/M	
3.	Toothbrush	848/31/M	5 fragments
4.	Fragment of a soapbox	774/M	the upper part
5.	Glasses	90/CH	
6.	Razor	BN 1179	
7.	Pocket knife	870/9/M	

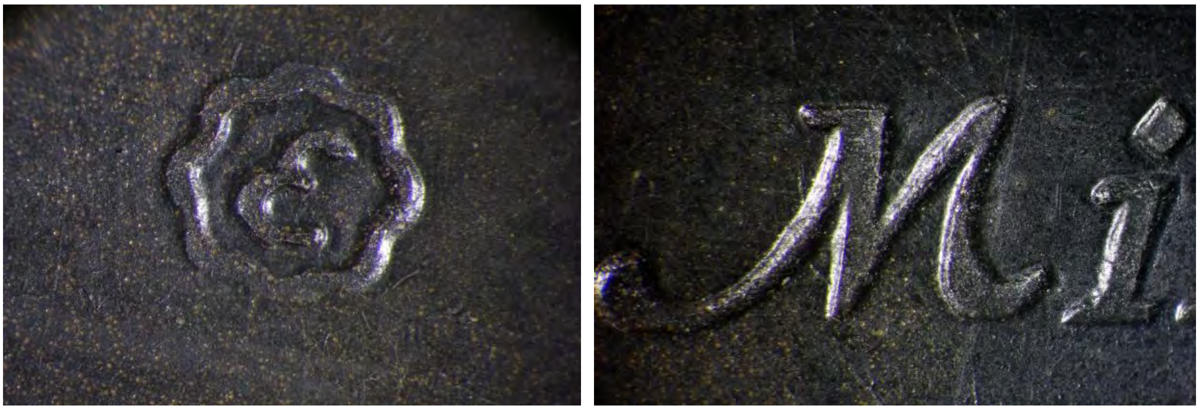
Picture 1. Macroscopic picture of a toothbrush case (Sample 1).



A **B**

Picture 2. A – the insets on the cap of toothbrush.
B – thread of the twisted case. Material – dyed celluloid (Sample 1).

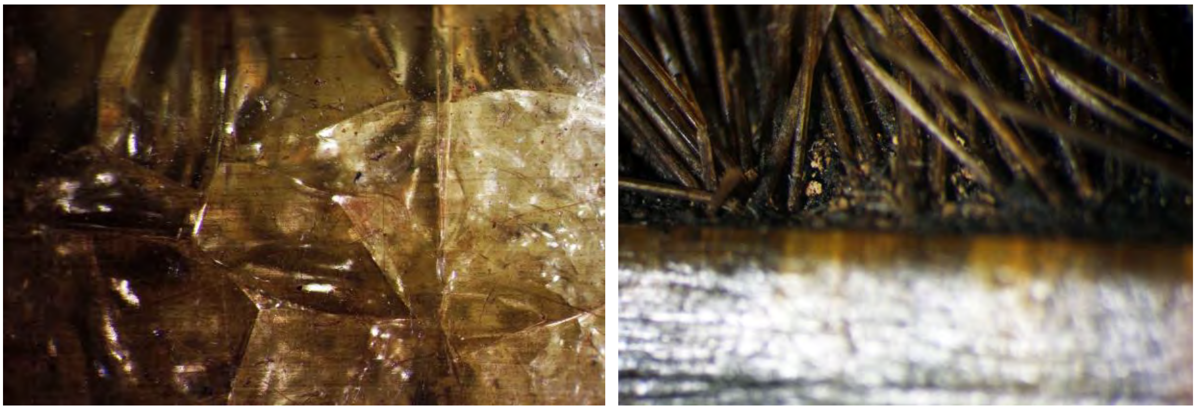
Picture 3. Macroscopic picture of the comb (Sample 2).



A **B**

Picture 4. A - symbol of the comb - before the word Minerva.
B - the initial letters of the inscription Minerva. Material - black ebonite (Sample 2).

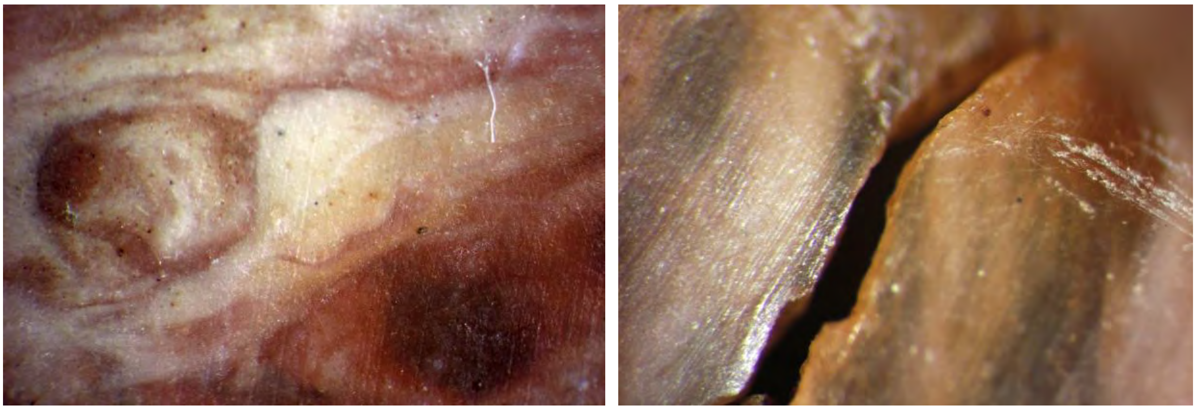
Picture 5. Macroscopic picture of the examined parts of the brush (Sample 3).



A **B**

Picture 6. A – the cracked structure of the brush handle.
B – eroded and deformed hair of the toothbrush stuck in the polymer. Material - resin (Sample 3).

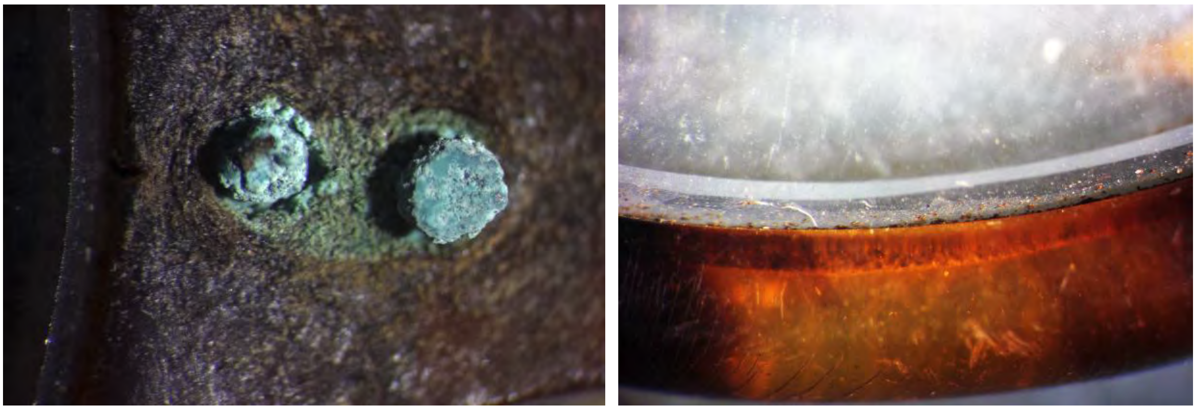
Picture 7. Macroscopic picture of the soap dish piece (Sample 4).



A **B**

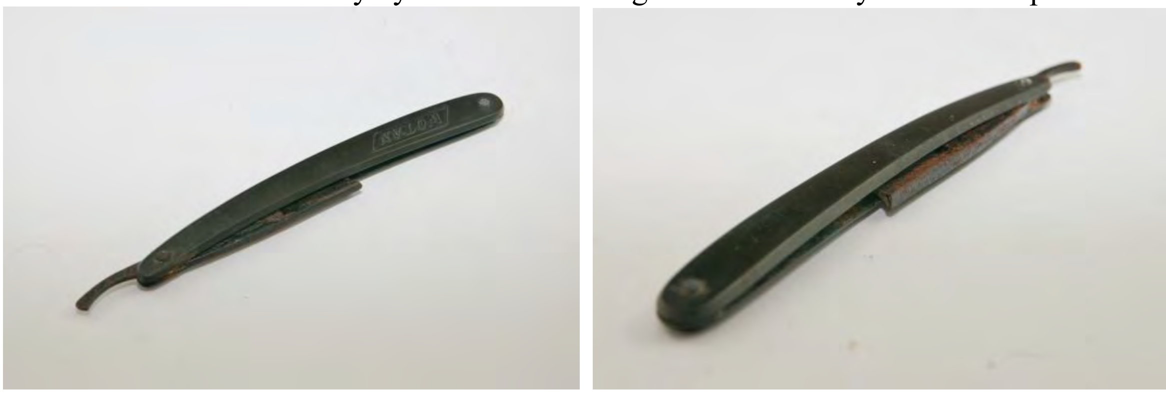
Picture 8. A – the structure of dyed celluloid.
B - crack within the celluloid of the direction complies with arrangement of its structure. Material - dyed celluloid (Sample 4).

Picture 9. Macroscopic image of the examined glasses (Sample 5).

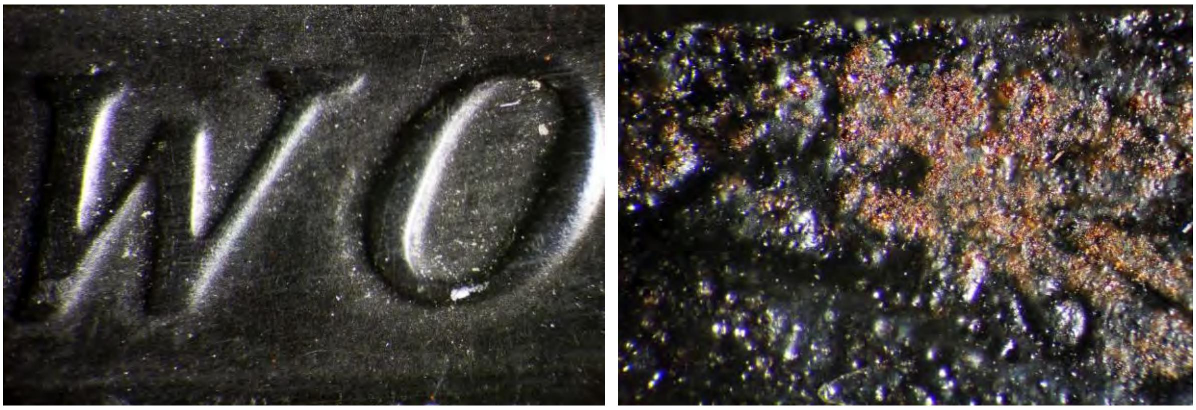


A **B**

Picture 10. A - oxidized copper rivets from eyeglasses hinge.
B - the contact of differently dyed celluloid with glasses covered by destruction process.



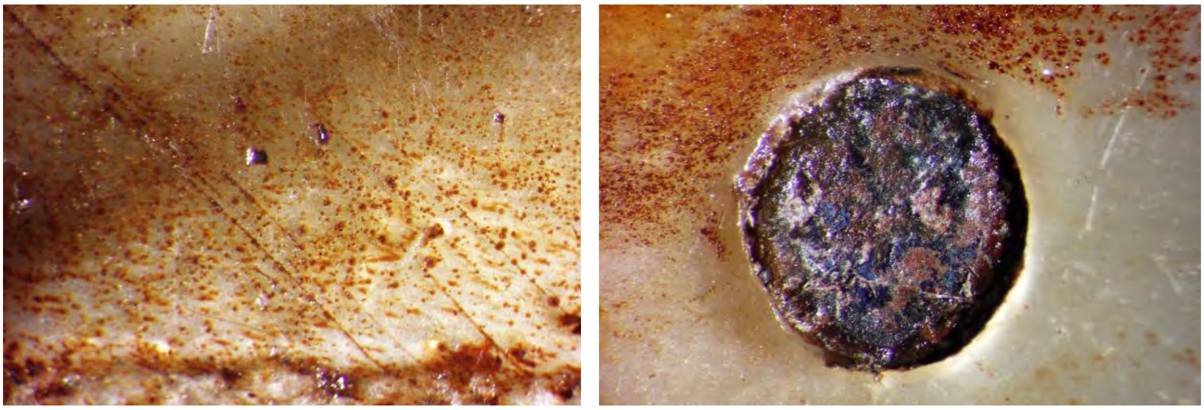
Picture 11. Macroscopic image of a razor (Sample 6).



A **B**

Picture 12. A - the initial letters of the inscription WOTAN pressed the razor.
B - oxidized iron compounds coating the razor blade. Razor holder - Black ebonite (Sample 6).

Picture 13. Macroscopic picture of the pocket knife (Sample 7).



A **B**

Picture 14. A – the area of the pocket knife made of celluloid covered with the secondary concentrations of iron oxide arising from the corrosion of the knife blade.
B - the axis of the blade pocket knife. Currently, they are oxidized copper compounds (azurite - blue spots). Originally there were bronze copper - tin. Holder - dyed celluloid (Sample 7).

The analyses carried out with the use of the digital microscope were non-destructive (non-invasive) and involved observation of the plastics' morphology and details on their surface. The observed phenomena were photographed and became the basis of selection of samples for further research. The American INTERPLAY microscope was used in the research.

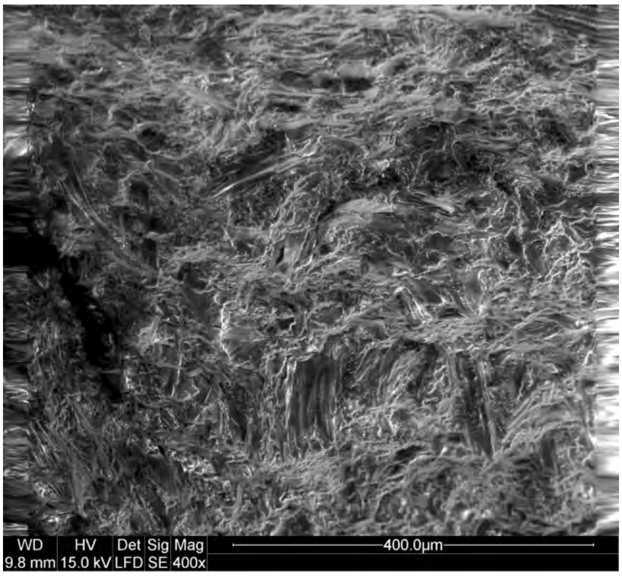
Scanning microscopy was used to observe the details of the morphology of the plastics, from which elements of the examined objects were made. A Japanese JEOL 549 microscope was used. Observations were carried out within the magnification range 500 – 2000x. The phenomena occurring in the samples were photographed. The research was used to distinguish areas in which chemical analyses of samples were carried out with the use of the EDS method (Energy Dispersive Spectroscopy).

Chemical analyses with the use of the EDS method were carried out in the JEOL540 microscope. Local and surface analyses of the distinguished areas were done to identify the admixtures including dyeing additives used to dye the plastic parts of the relics.

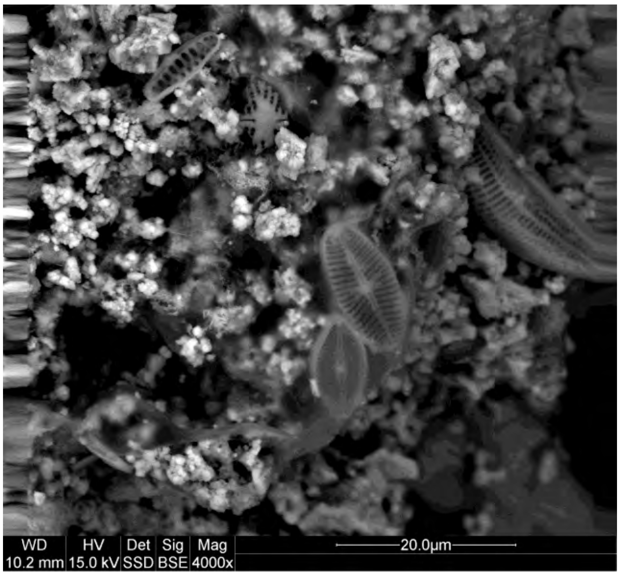
Results

Sample 1. Toothbrush case. Dyed celluloid.

The analyses with the use of the scanning microscope enabled to observe celluloid structure and morphology. The damaged structure of the material was found mainly in the area of fractures (Picture 15). Unicellular algae -diatoms as well small secondary calcite crystals were also observed in the microscopic image (Picture 16). The EDS chemical analyses of celluloid indicate that it can contain traces of zinc, magnesium and titanium (Fig. 1 – 2).



Picture 15. Morphology of damaged surface of the celluloid. Magnification by the scale (Sample 1).



Picture 16. Microscopic picture of celluloid, damaged structure observed in the cracks. There are visible diatoms and minor secondary calcite crystals. Magnification by the scale (Sample 1).

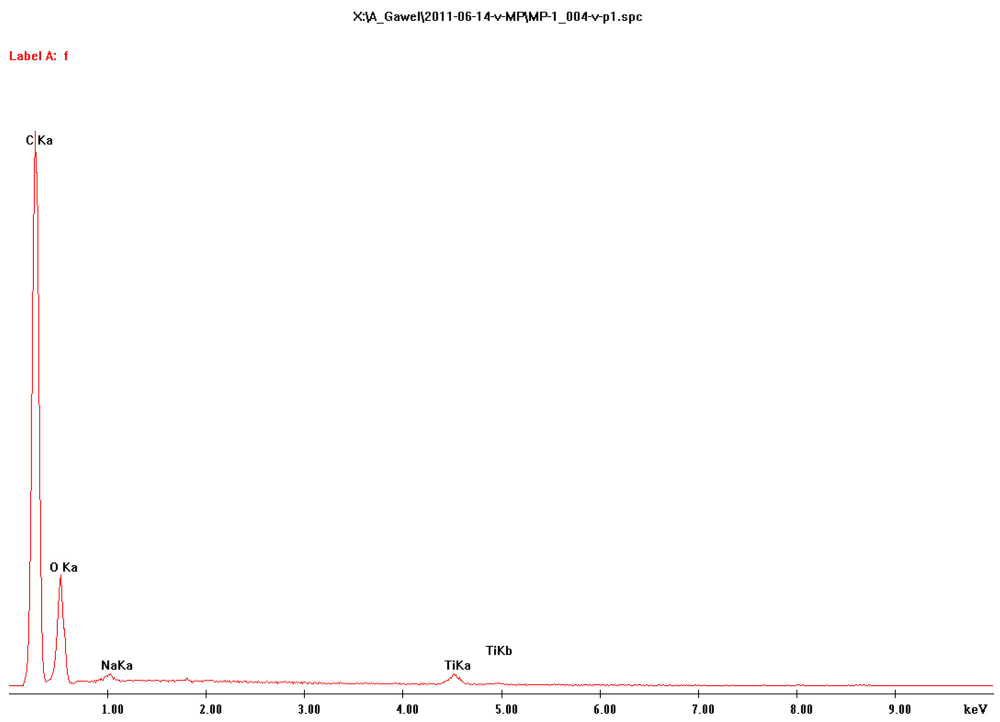


Figure 1. EDS spectrum of celluloid (Sample 1).

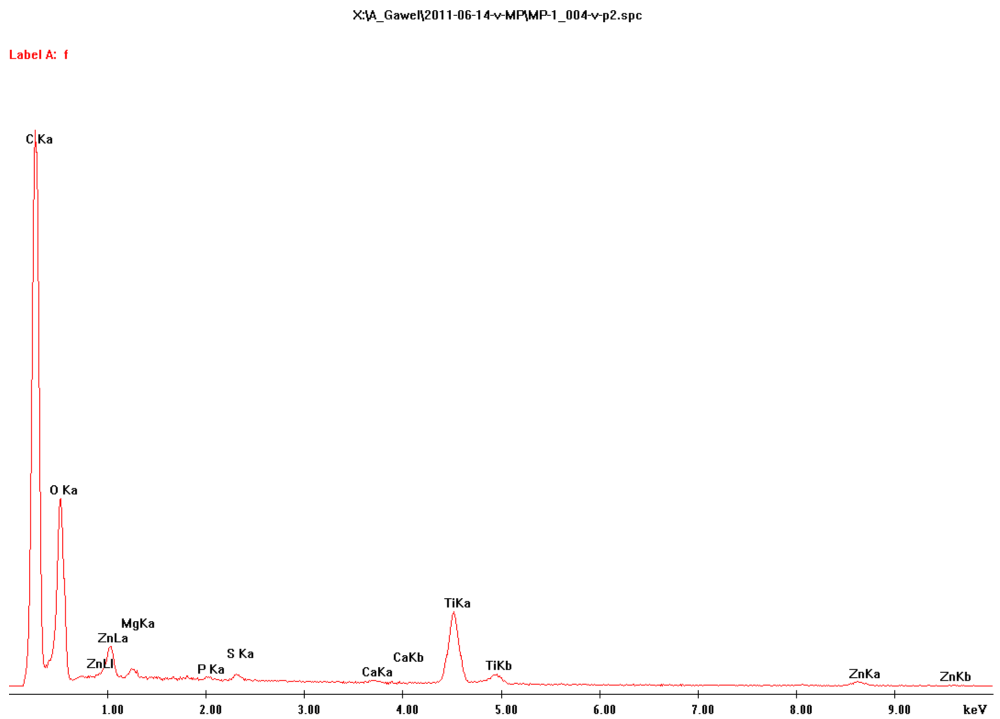
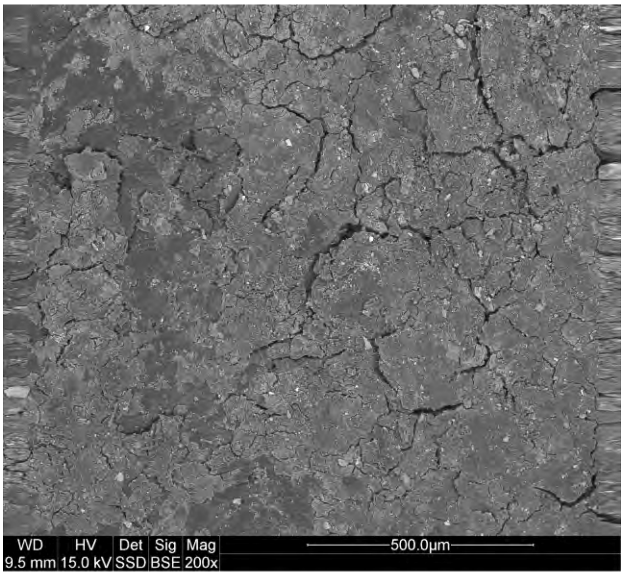


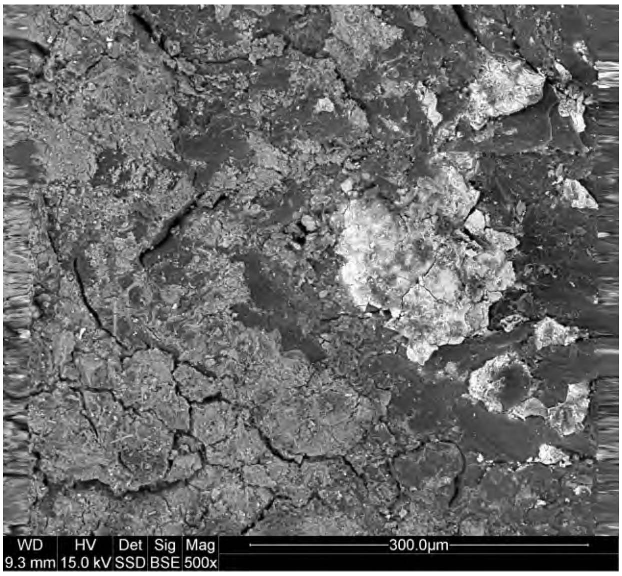
Figure 2. EDS spectrum of surface of celluloid containing traces of zinc, magnesium, titanium (Sample 1).

Sample 2. Comb. Black ebonite.

Ebonite was the building material of the analyzed comb and observations carried out with the use of the scanning microscope indicate that the material has a damaged surface (Picture 17). Moreover, research shows that the material was partially oxidized (Photography 18). The EDS chemical analyses inform that ebonite could be enriched in iron (Fig. 3), as well as in other chemical elements such as aluminium, silicon, sulphur and others (Fig. 4).



Picture 17. Morphology of the damaged surface of the ebonite. Magnification by the scale (Sample 2).



Picture 18. A thin layer of oxidized ebonite covering the surfaces of the comb. Magnification by the scale (Sample 2).

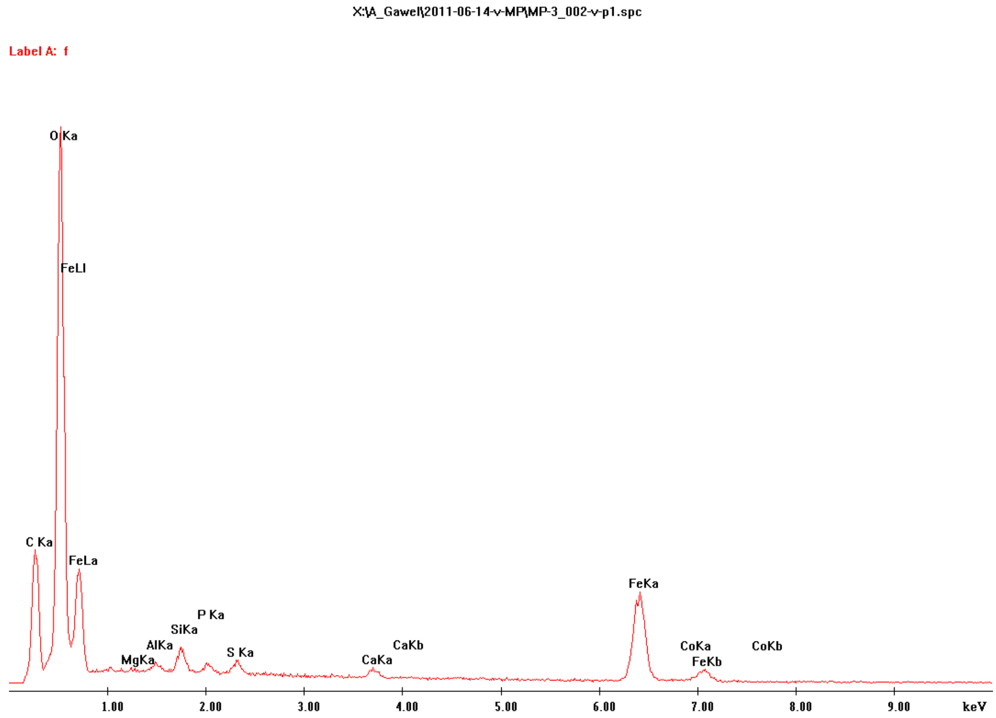


Figure 3. EDS spectrum of plastic enriched in iron (Sample 2).

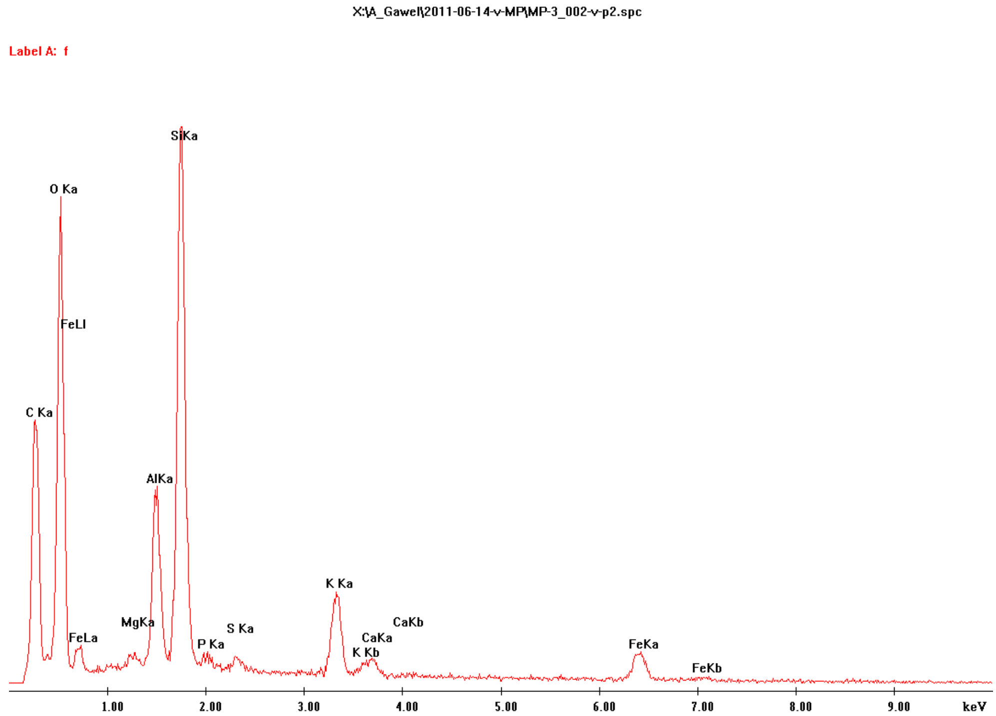
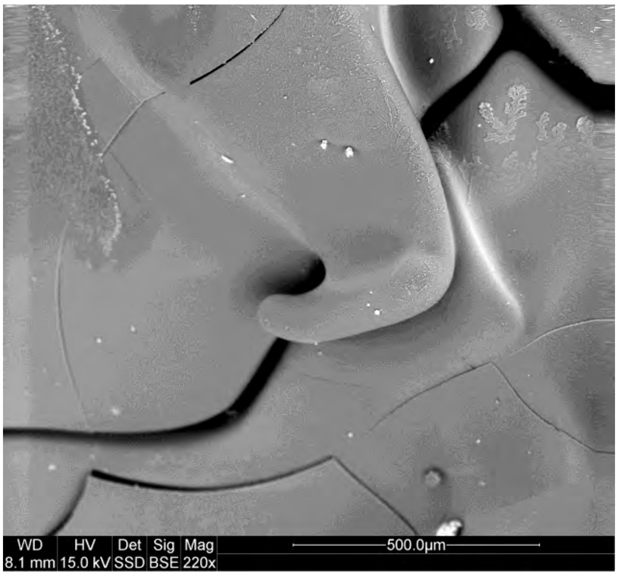
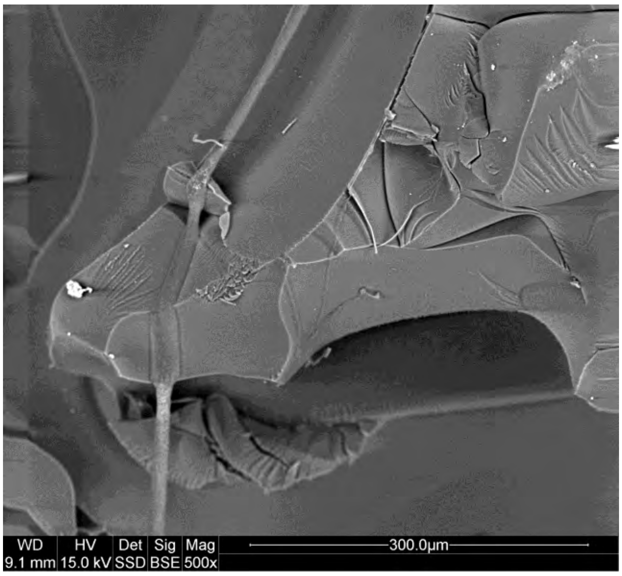


Figure 4. EDS spectrum of the object enriched in aluminum, silicon, sulphur and other elements (Sample 2).

Sample 3. Toothbrush. Pressed resin made of two parts overlaying each other.



Picture 19. Microscopic image of fractured surface of the resin covered by the aging process and polymerization. Magnification by the scale (Sample 3).



Picture 20. Irregular cracks of polymerized (aging) resin with a typical non-directional passes. Cracks are places of penetration of secondary substances into the object (Sample 3).

The analyses carried out with the use of the scanning microscope enabled to observe the resin from which the toothbrush was made. The microscopic image showed systems of irregular fractures on the surface of the resin which underwent the process of ageing and polymerization (Picture 19). Also systems of irregular fractures of polymerizing (ageing) resin with characteristic non-directional orientation (Picture 20) were observed. The EDS chemical analyses show composition of the unchanged resin (Fig. 5).

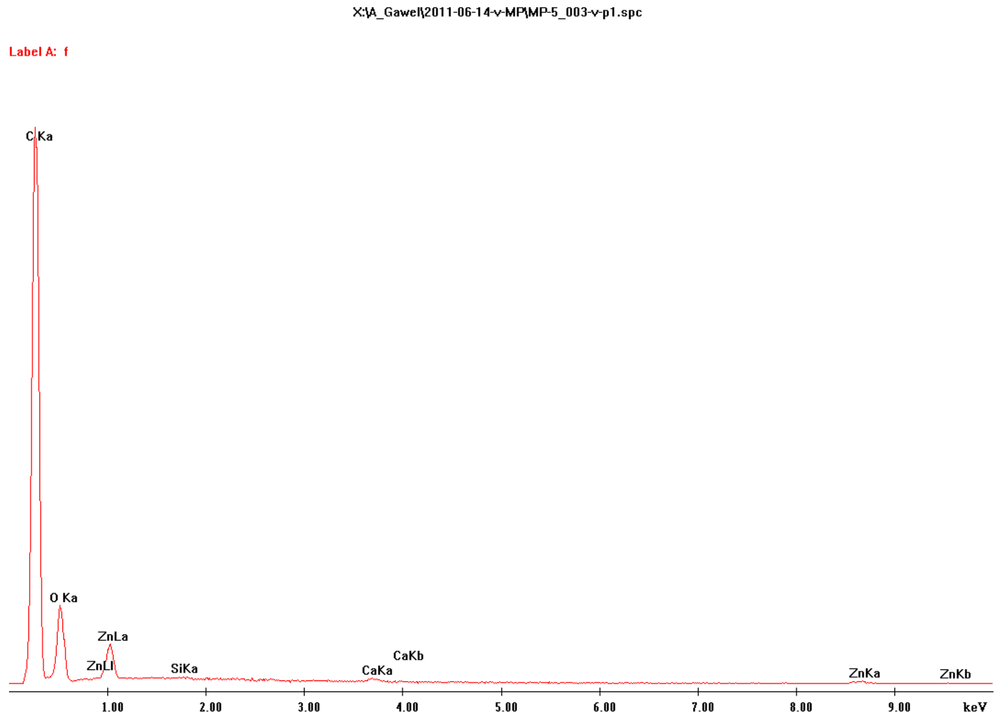
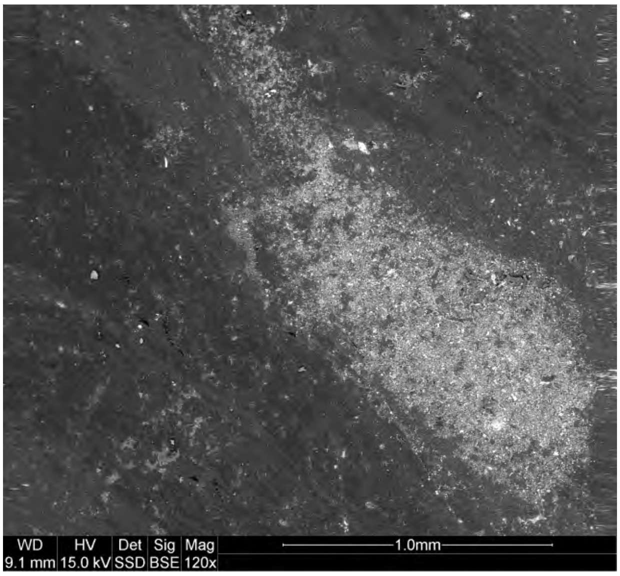


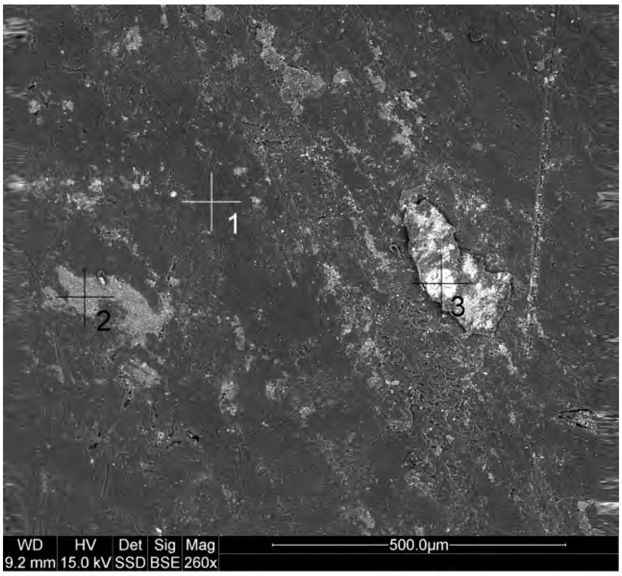
Figure 5. EDS spectrum of "pure" i.e. natural , not modified resin (Sample 3).

Sample 4. Fragment of a soapbox. Dyed celluloid.

The analyses with the use of the scanning microscope enabled to observe structure and morphology of the celluloid, from which the soapbox was made. The microscopic image shows secondary substances formed on the soapbox (Picture 21, 22). The EDS chemical analyses show that they are zinc and copper phosphates. Phosphorus probably comes from the bones of the victims, whereas copper and zinc from the metal elements of uniforms (Fig. 6). Additionally, calcium, sulphur, chlorine and other peaks are visible in the energy spectrum.



Picture 21. The morphology of the soapbox surface observed at low magnifications. Visible spots on a dark background of celluloid are secondary substances forming on the soapbox. Magnification by the scale (Sample 4).



Picture 22. Microscopic picture of secondary substances present on the celluloid surface.
1 - celluloid 2, 3 - bright spots of zinc and copper phosphate. Phosphorus is bone origin of the murdered, copper and zinc from metal uniforms. Magnification by the scale (Sample 4).

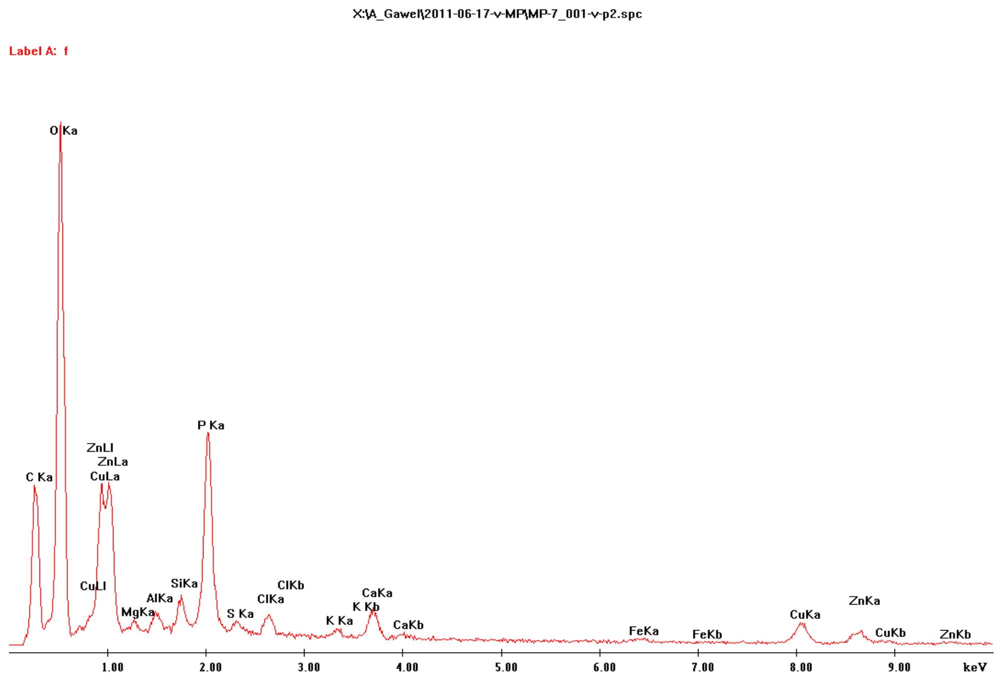
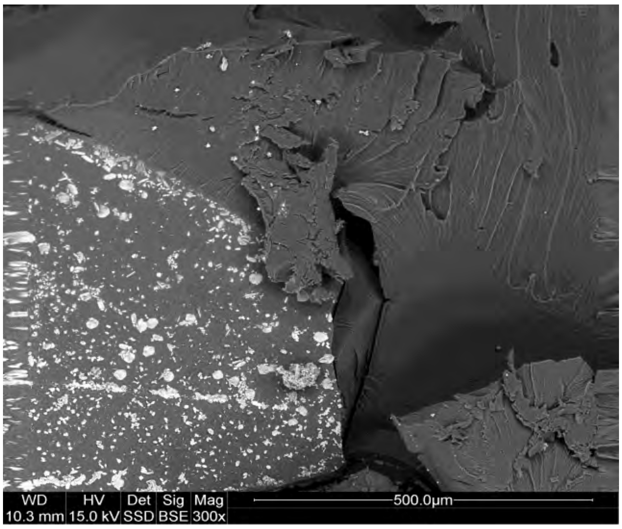


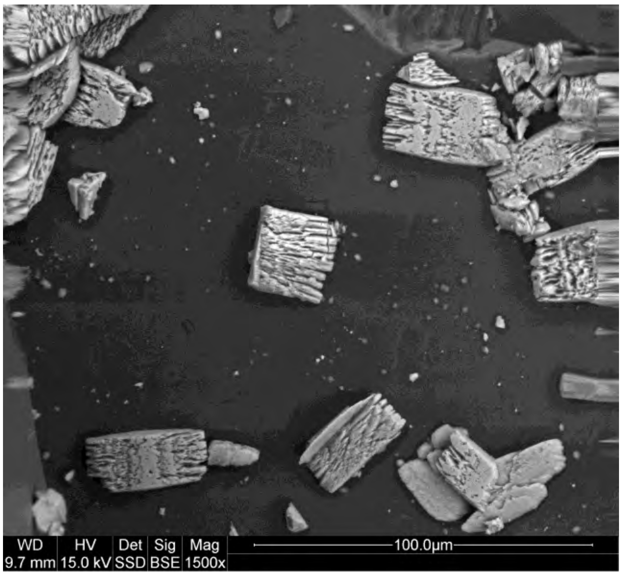
Figure 6. EDS spectrum of celluloid of the soapbox enriched in phosphorus of bone origin . In addition, the EDS spectrum shows the presence of zinc, calcium, sulphur, chlorine and others. (Sample 4).

Sample 5. Glasses. Dyed celluloid.

The analyses carried out with the use of the scanning microscope enabled to observe morphology of the dyed celluloid, from which the examined glasses were made. Microscopic images show that the surface of the analyzed celluloid is partially damaged (Fig. 23). Also the image shows parts of the celluloid undergoing heavy destruction, whose symptoms are precipitates of bright concentration (Fig. 23). Moreover, the scanning microscope enabled to observe secondary aggregates, that cover the celluloid glasses in some parts (Fig. 24). The EDS chemical analyses show that it is celluloid enriched in zinc absorbed by the celluloid structure form the environment (Fig. 8).



Picture 23. Morphology of celluloid near the hinge of the glasses. There are two types of celluloid surface – smooth - undamaged and destroyed. Party of celluloid covered by strong process of destruction manifests as a light concentration. Magnification by the scale (Sample 5).



Picture 24. Microscopic picture of secondary aggregates covering celluloid of the eye glasses. EDS analysis indicates that this is a celluloid enriched in zinc absorbed by the celluloid structure from the environment. Magnification by the scale (Sample 5).

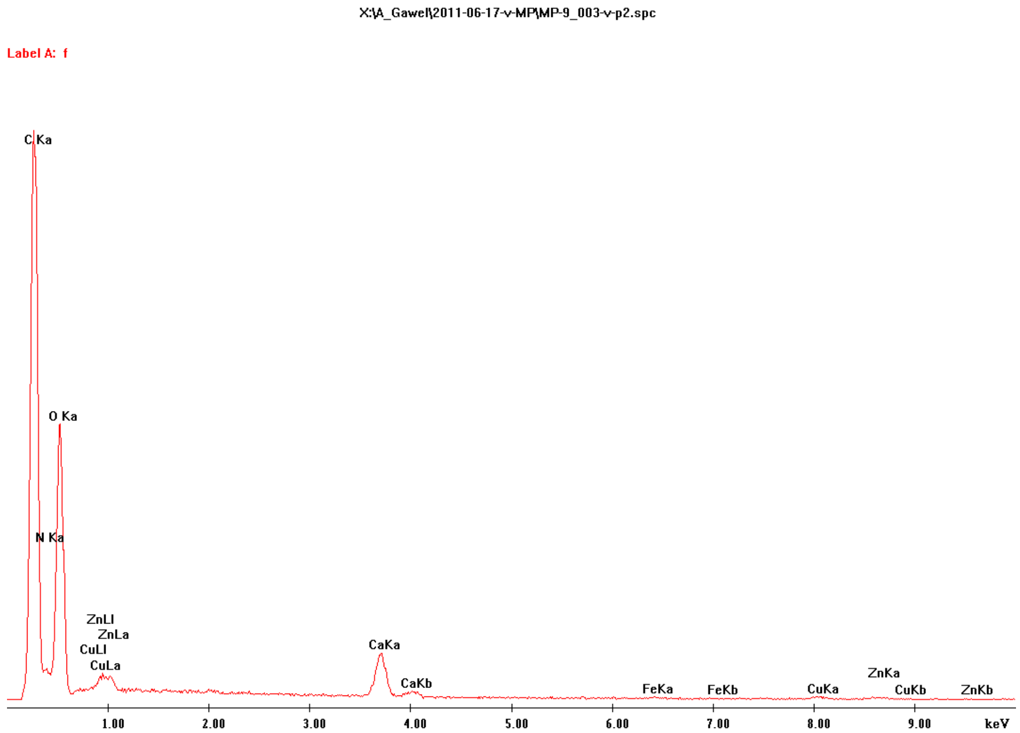


Figure 7. EDS spectrum of unchanged celluloid (Sample 5).

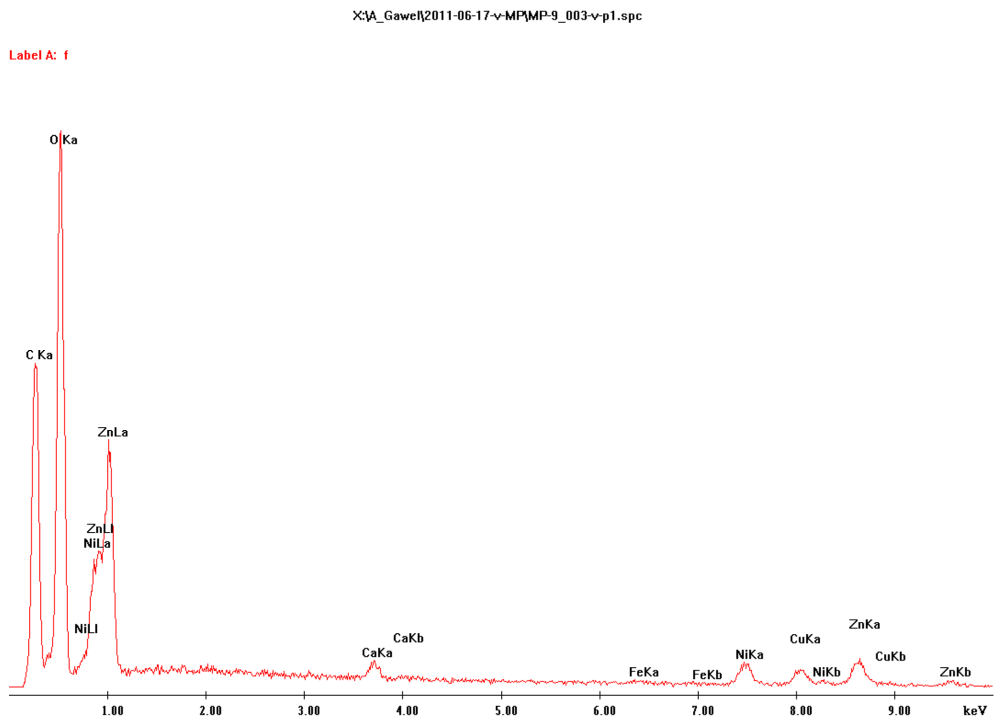
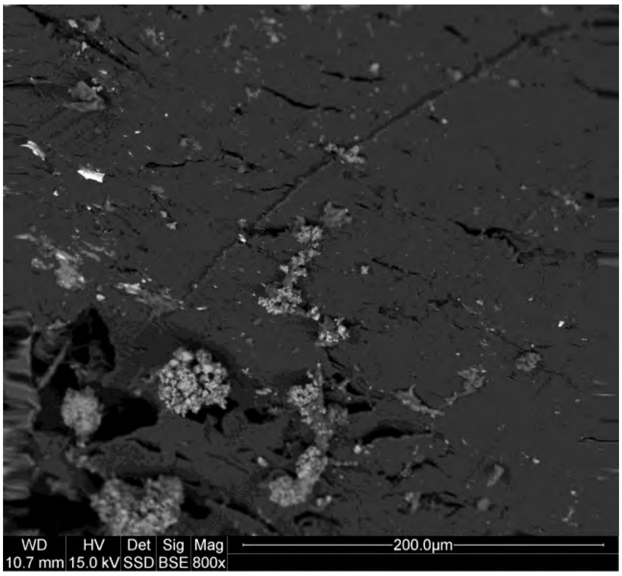


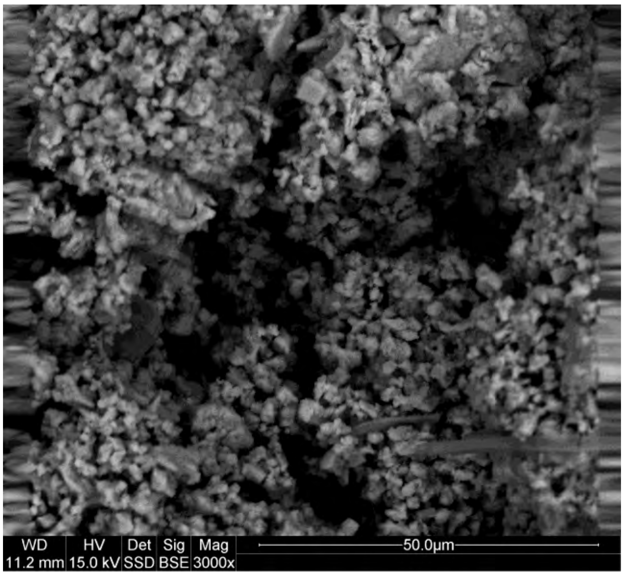
Figure 8. EDS spectrum of celluloid near the hinge of eye glasses (Sample 5).

Sample 6. Razor . Black ebonite.

The scanning microscope observations of ebonite, from which the razor was made, show that the surface of the material is well preserved (Picture 25). Only in some parts has the analyzed ebonite small hollows, in which a corroded ebonite structure is visible (Picture 26). The chemical analyses carried out in the EDS system show that the ebonite could be covered with the secondary coating of calcium carbonate (Fig. 9). It also contains sulfur, which is a natural component of the examined material and copper, which is secondary component (Fig. 10).



Picture 25. Microscopic picture of the ebonite surface, where are observed small cavities. Magnification by the scale (Sample 6).



Picture 26. The corroded structure of ebonite.
Magnification by the scale (Sample 6).

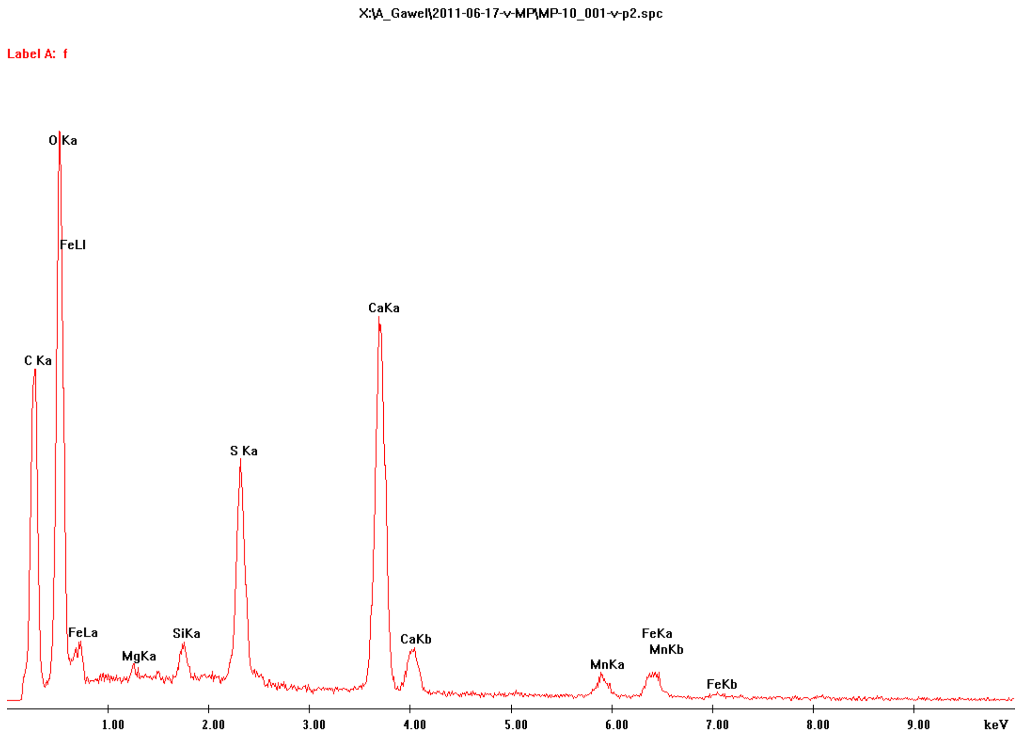


Figure 9. EDS spectrum of ebonite covered with the secondary coating of calcium carbonate (Sample 6).

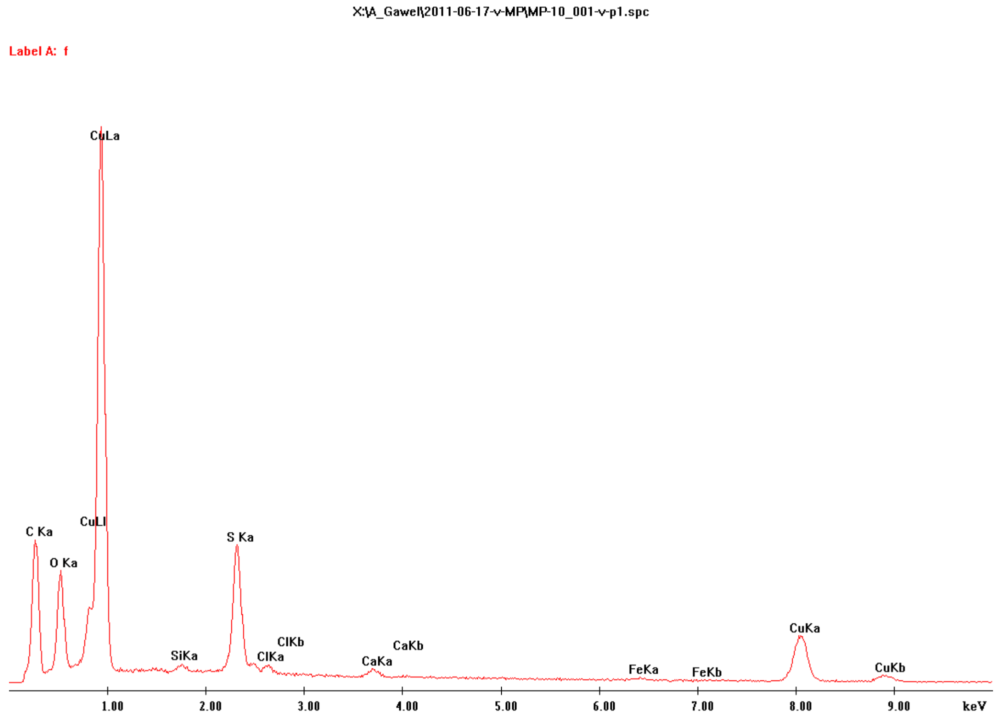


Figure 10. EDS spectrum of ebonite of the razor holder. Sulphur is a natural component of ebonite while the copper is the secondary component (Sample 6).

Sample 7. Pocket knife. Dyed celluloid.

The analyses carried opt with the use of the scanning microscope enabled to observe structure and morphology of celluloid. The microscopic image shows almost parallel system of cellulose fibres and in some places the surface is covered with numerous secondary aggregates of silt minerals (Picture 27). The EDS chemical analyses show that the pocket knife's frame near a copper bolt is enriched in the calcium, sulphur and copper coming from the copper bolt destruction (the pocket knife's hinge of the blade) (Fig. 11). The examined fragment of the pocket knife's celluloid frame is strongly enriched in phosphorus deriving from decomposition of the bones of human corpses (Fig. 12).

Picture 27. Morphology of the celluloid from the case knife. There is visible nearly parallel arrangement of cellulose fibers. The surface covered with numerous secondary aggregates of clay minerals. Magnification by the scale (Sample 7).

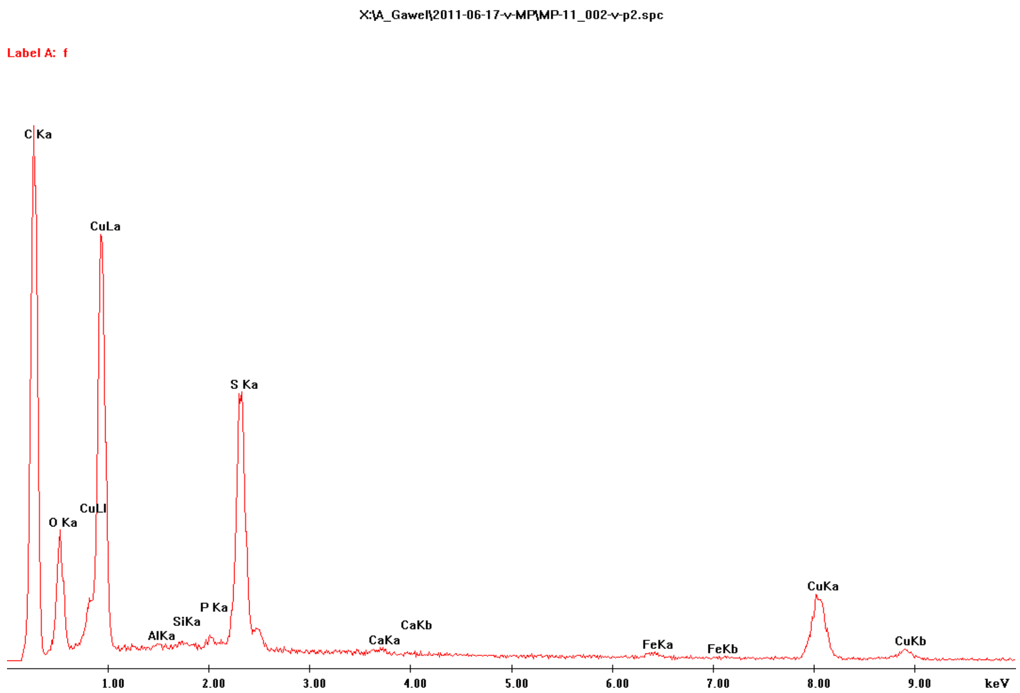


Figure 11. EDS spectrum shows that the pocket knife's frame near a copper bolt is enriched in the calcium, sulphur and copper coming from the copper bolt destruction (the pocket knife's hinge of the blade) (Sample 7).

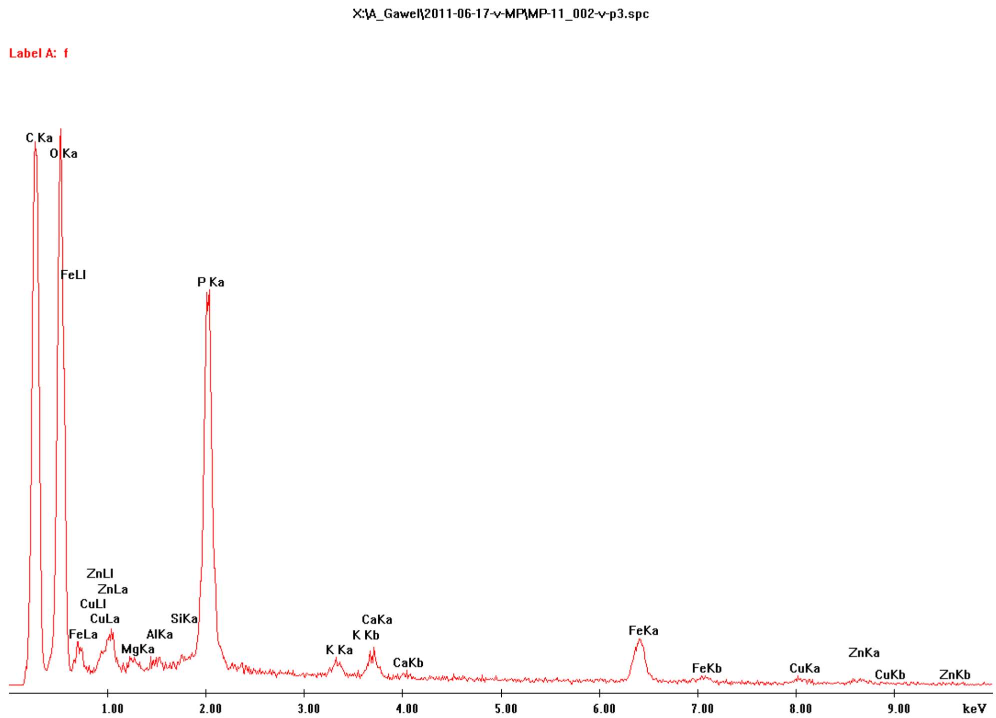


Figure 12. EDS spectrum of the pocket knife's celluloid frame knife enriched in phosphorus migrating from decomposed bones of human corpses (Sample 7).

Summary and conclusions

Remembering the origin and characteristics of the examined materials we should consider their physical and chemical properties. The knowledge of the properties is a basis of restoration, including "plastic" objects. Celluloid, the oldest thermoplastic polymer, is obtained by plasticization of the cellulose nitrate in camphor. It is composed of nitrocellulose (70-74%), camphor (20-30%) as well as dyes and fillers (1.5-3%). This material is inflammable and not very resistant to the influence of chemical compounds and light. It dissolves in esters, ketones and alcohol and ether mixture (Kiełbasiński 1954, Pabst 1955).

Ebonite is a plastic obtained by vulcanization of natural or synthetic rubber, containing 20-33% of sulfur. It is insoluble, infusible and can easily undergo mechanical processing. It also has good insulation properties

(Kiełbasiński 1954). In the past ebonite was appreciated as material for accessories. Nowadays it is substituted with other plastics.

The examined objects undergo several processes varying in intensity. It depends on the plastic itself as well as on the conditions occurring in the Katyn graves.

The main process observed in the examined objects (their plastic parts) is a kind of recrystallization i.e. ordering of the polymer structure. This process is a concentration of atoms around centres, which can be compared to crystallization centres. The condensation process leads to the volumetric changes in a polymer, particularly to shrinking of fragments of a polymer. The outcome of such phenomena is formation of systems of fractures leading to the material destruction.

A vital factor which influences the described phenomenon is the polymer type as well as conditions in which it occurs (environment). Polymers, being organic compounds, undergo oxidation. Speed of oxidation depends on a polymer and other substances found in the environment including e.g. acids. of the burial grounds In the Katyn graves there was decomposition of corpses which resulted in forming different complex organic acids. Their activity, together with oxidation and polymer concentration processes (a kind of recrystallization) led to destruction, the effects of which were observed during the examinations.

There are methods which prevent the destruction of polymers. They are discussed below.

- Polymer condensation – the process of polymer ageing.

The speed of the process depends on the polymer itself and the external conditions (chemistry of the environment). The only element which can be eliminated in order to slow down this process, is reduction of the influence of the environment.

The examined historic objects, with the elements made of plastic, were taken out of the Katyn graves and thus separated from the negative influence of the decomposition products of dead bodies. In this way the process of polymer condensation (ageing) was slowed down. It is still in progress, but the speed is lower because even after excluding all factors causing destruction of polymers it will still occur naturally.

- Oxidation of the examined “plastics”.

It is a process which causes reaction of carbon, coming from polymers, with air, specifically with the oxygen coming from air resulting in CO_2 formation. In this way a solid substance (plastic) changes into gas. This slow process leads to polymer destruction. It also develops in the fractures formed in the polymer, due to condensation of its atoms (its ageing). So the fractures in the polymer expand, which sometimes leads to its total destruction. This phenomenon was observed, for example, in toothbrushes.

- Migration of substances into the structure of the examined objects.

It has been found out that different substances penetrate the examined “plastics”. It is connected with their original porous structure (celluloid) as well as with the cases of destruction leading to formation of systems of fractures and other kinds of destruction.

The penetrating substances (in the past – while lying in graves) into the structure of “plastics” can be divided into natural and anthropogenic.

Natural substances are:

- Minerals, which got into the fractures of “plastics” from the environment (including quartz and silt minerals),
- Minerals, which secondarily crystallized in the fractures of plastics (including carbonates and oxides as well as iron hydroxides),

- Microorganisms (recognized diatoms).

Anthropogenic substances are:

- Substances connected with corrosion of the objects (including products of iron, bronze and copper corrosion from which elements of the objects were made),
- Substances connected with corrosion of other metal objects found on the dead bodies (including metal buttons, whistles, emblems, fragments of wire, spoons etc.),
- Substances connected with decomposition of corpses (including organic acids and derivatives of destruction of bones (phosphates and others)).

All the substances contribute to the destruction of "plastics" by crystallizing in their fractures. Some of them are hygroscopic and absorb water, increasing their volume (e.g. silt minerals).

An extremely interesting element of the results is occurrence of the diatoms' remains in the fractures of plastics. These organisms live in small and only open water reservoirs. Their presence in the fractures of the analysed objects proves unanimously that the graves with bodies were not filled in right after the soldiers had been murdered. But they were left and filled in with water ,which remained there for some time. Only then were the graves filled in or they filled in by themselves.

Summing up the research and the gained knowledge about the examined "plastics", it should be stated that there are no effective methods to stop completely the process of ageing of polymers.

As the mentioned phenomenon is influenced by the environment with polymers and one of the factors is moisture, an effective method is to eliminate the influence of free air and moisture.

There are several methods of isolating the objects from the influence of the air. One of them is coating of plastics with an additional layer of polymers. However, the polymers covering the objects will also undergo ageing, cracking and destruction. Over time it will lead to complete destruction of the objects.

The research results and data about celluloid, ebonite and resins (toothbrush) indicate that the best solution to protect the objects suggested by researchers would be vacuum packaging in transparent plastic bags. It will stop the influence of moisture and air on the plastics. It will also allow to keep them in an unchanged shape and colour and strengthen them by shrinking plastic packaging of the object. This method is efficient, permanent and, depending on the vacuum bag, it will protect the historic object for many years. The mentioned method enables to observe the objects and does not lead to the colour changes. Over the years, when the vacuum in the bags decreases, the historic objects can be put into new containers without any damage.

The suggested technology of protecting the "plastic" historic objects is cheap, efficient and does not cause any "substantial" changes. It keeps them in the same shape and form as after taking them from the graves. What is more, they can be taken out and examined in any moment.

References:

1. Pabst F. (1955). Tworzywa sztuczne – poradnik. Państwowe Wydawnictwo Techniczne. Warszawa
2. Hyla I. (1984). Tworzywa sztuczne – własności, przetwórstwo, zastosowanie. Państwowe Wydawnictwo Naukowe. Warszawa
3. Pielichowski J., Puszyński A. (1998). Technologia tworzyw sztucznych. Wydawnictwo Naukowo – Techniczne, Warszawa
4. Kiełbasiński S. (1954). Kauczuki i tworzywa sztuczne. Państwowe Wydawnictwo Naukowe, Łódź