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TEZĂ DE DOCTORAT

Innovation management with applications in the development of products for the protection of noble metals

(ABSTRACT)

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DOCTORAL THESIS

Innovation management with applications in the development of products for the protection of noble metals

(ABSTRACT)

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Introduction

The protection of noble metals against corrosion represents a field of research of great current interest, having a significant impact on the durability and performance of components used in industry and technology. In the current global context, where durability and sustainability become major priorities, the development of efficient and ecological solutions for corrosion prevention is essential.

The protection and conservation of noble metals, such as gold, silver and platinum, represent an essential concern both in the scientific field and in industry, due to their economic, aesthetic and functional value, and even cultural heritage. These metals are widely used in jewelry, heritage objects, electronic devices, catalysts and other high applications, where their durability and long-term performance are crucial.

However, corrosion and degradation of these metals can lead to significant losses, both from an economic and technological point of view. In this context, the development of efficient, durable and ecological solutions for protecting noble metals becomes a major research priority.

In recent decades, research in the field of metal protection has increased in complexity and diversity, being directed towards innovative and sustainable methods, which replace techniques based on synthetic chemical substances, often toxic and polluting. In this paradigm, innovation management plays a fundamental role, as it allows the exploration, development and implementation of original solutions, compatible with the principles of sustainable development, where trans and interdisciplinary studies have a complex role in the development of original solutions.

In this context, in the doctoral thesis, entitled "Innovation management with applications in the development of products intended for the protection of noble metals", the scientific approach had two major components:

exploration and implementation of innovative strategies, respectively the use of plant extracts as natural protection agents for noble metals (corrosion inhibitors) and demonstrating their effectiveness.

analysis of the dynamics of the precious metals market on the national and international economy, in order to understand the factors that influence their price and their economic role.

Through the integrated approach of innovation management, this thesis aims to highlight the potential of plant extracts to develop efficient, eco-compatible solutions adapted to the current requirements of industry and environment, offering a new perspective on the protection of noble metals and opening paths towards future research and practical applications, as well as monitoring the evolution of prices on international (spot) markets and the macroeconomic factors that generate volatility, such as geopolitical tensions, inflation and the policy of the US dollar.

Through the experiments carried out and the complexity of the study, a contribution was made to the evolution of the field of noble metal protection, promoting innovative and sustainable solutions that combine technological efficiency with respect for the environment. Thus, this work takes an important step towards renewing and optimizing the methods of protection of precious metals, offering promising perspectives for research and development of alternative and environmentally friendly technologies, as well as forecasting future trends, such as the impact of the green transition on silver demand or the impact of technology on platinum demand.

Precious metals (gold, silver, platinum and palladium) are a specific type of financial asset and are among the most popular investment instruments. The development of this segment of the financial market directly affects the financial and investment opportunities of the country, which it is able to achieve, using the mediation of both its own financial institutions and the most relevant structures with foreign capital. A sufficiently valuable reserve asset makes it possible to increase the economic and social advantages of a country at the international level.

Obviously, the individual reserves of precious metals of each country are formed primarily depending on the financial and economic situation, as well as exchange rate fluctuations. Therefore, we can speak about the mutual influence of the precious metals market and other subjects on the national economy.

These elements of originality position the work as an important and innovative contribution in the field of innovation management and technologies for the protection of precious metals, having the potential to influence both research and practical application.

This summary selectively reproduces the original results (part II – Original contributions), preserving the original numbering of the bibliography from the doctoral thesis (selection), as well as the original numbering of the figures, tables and equations.

Part II – Original Contributions

Chapter 4. Materials, analysis methods, characterization and testing

4.1. Objectives of the doctoral thesis

The scientific approach had two major components:

- exploration and implementation of innovative strategies, respectively the use of plant extracts as natural protection agents for noble metals (corrosion inhibitors) and demonstrating their effectiveness. The use of coatings with corrosion inhibitors on old silver artifacts, from an economic point of view, aims to minimize long-term costs related to restoration, maintenance and conservation, by preventing irreversible degradation of heritage assets, considering the evolution of prices of precious metals necessary for restorations, in conditions of replacing missing or heavily corroded parts.
- an analysis of the dynamics of the precious metals market on the national and international economy was carried out, in order to understand the factors that influence their price and their economic role.

The experiments carried out in order to fulfill the first major component of the research clearly demonstrated the benefits of using plant extracts in the development of materials for protection against corrosion of noble metals. A key aspect of the research was the investigation of the potential of plant extracts as active substances for forming protective layers against corrosion.The use of natural resources in this regard represents a promising and sustainable alternative to traditional formulations rich in synthetic chemical substances. Plant extracts, due to their complex chemical composition, which includes compounds with corrosion inhibiting properties, can provide an efficient and ecological barrier. In addition, these extracts are accessible, biodegradable and non-toxic, which makes them ideal for applications in the field of metal protection, in accordance with sustainable development objectives and ecological responsibility. They can prevent corrosion formation and can extend the lifetime of components, while reducing the negative impact on the environment.

Moreover, the natural approach to protection has the potential to be adapted and integrated into modern industrial processes, being compatible with existing technologies and allowing customization of formulations depending on the specific requirements of users. These coatings are relatively inexpensive compared to the complex restoration processes required after advanced corrosion, ensuring a longer “life” of objects in museum or private collections, eliminating major costs for extensive repairs.

The practical aim of the work was:

- experimenting the possibilities of using phytoconstituents from two plants (mint and lavender) in protective formulations against silver corrosion, in various environments. In this regard, several extractive techniques were used to obtain natural extracts, which were characterized by various analytical methods. The protective layers were based on acrylic resins (Paraloid 44 and Paraloid 72).
- preserving the artistic and market value, essentially, the objective being the economic sustainability of the conservation and restoration process of old silver artifacts, which are very fragile after exposure to environmental factors.

- analyzing the dynamics of the precious metals market on the national and international economy, respectively, in order to understand the factors that influence their price and their economic role.

Through an integrated approach to innovation management, this thesis aims to highlight the potential of plant extracts to develop efficient, eco-compatible solutions adapted to the current requirements of industry and the environment, offering a new perspective on the protection of noble metals and opening paths for future research and practical applications, as well as tracking the evolution of prices on international markets (spot) and macroeconomic factors that generate volatility, such as geopolitical tensions, inflation and US dollar policy. Through the experiments carried out and the complexity of the study, it contributed to the evolution of the field of noble metal protection, promoting innovative and sustainable solutions that combine technological efficiency with respect for the environment. Thus, this work takes an important step towards renewing and optimizing precious metal protection methods, offering promising perspectives for the research and development of alternative and environmentally friendly technologies, such as forecasting future trends, such as the impact of the green transition on silver demand or the impact of technology on platinum demand.

4.2. Characterization and analysis methods

4.2.1. Chromatographic techniques

From a technical perspective, chromatographic analyses focus on the separation, identification and purification of mixtures in order to study their components. This process involves two phases: the mobile phase and the stationary phase. The mixture, dissolved in a solvent during the mobile phase, passes through the stationary phase. In this context, the interactions between the components of the mixture and the stationary phase generate variations in movement rates, thus facilitating the separation of components. These discrepancies can be caused by adsorption, partition, ionic exchange and molecular weight. There are various techniques used depending on the analyzed substances, including gas chromatography, liquid chromatography, thin layer chromatography and column chromatography. This technique is very suitable for identifying bioactive compounds from plants, which may subsequently have various applications [189, 190].

4.2.2. Spectrometic methods

Fourier transform infrared spectroscopy is a measurement technique for acquiring infrared spectra. Instead of recording the amount of energy absorbed when the frequency of infrared light is varied (monochromator), IR radiation is guided through an interferometer. After passing through the sample, the measured signal represents the interferogram. By applying the Fourier transform to this signal, we obtain a spectrum identical to the conventional (dispersive) IR spectroscopy form. The method is based on the detection of molecular vibrations and is a suitable technique especially for samples that may contain numerous pigments, allowing the detection of both organic and inorganic functional groups.

UV-Vis spectrometry (UV-VIS): Ultraviolet and visible absorption spectroscopy (UV-ViS) is one of the oldest molecular spectroscopy methods. Light represents a flux of photons, each photon carrying an energy equal to the energy of a quantum. When the wavelength increases, the frequency and energy per photon decrease. The energy at photon level determines the way it interacts with the surrounding environment. Photons with high electromagnetic energy (such as X and gamma radiation) can induce direct ionization of the environment they interact with, while IR radiation and microwaves can only have thermal effects. Color is an important property of a substance. The visible domain of the electromagnetic spectrum is

between 400 and 700 nm and corresponds to the domain of human visual perception. Materials have their own specific color due to the absorption of wavelengths in the visible domain (400 nm $<\lambda <$ 800 nm) and their brightness due to the emission of visible light wavelengths. These principles are very important in photosynthesis, where natural organic dyes (chlorophylls and carotenoids) absorb visible light from the sun and convert it into energy [191, 192].

4.2.3. Electron microscopy

In Scanning Electron Microscopy (SEM) the produced image is based on surface processes and not on transmission, the microscope being capable of visualizing larger samples and having a much greater penetration depth, thus obtaining images that are a good three-dimensional representation of the sample.

Electron microscopy images are obtained by scanning the surface with an electron beam whose energy can be from 50 keV up to hundreds of keV, thus obtaining information about the morphology of the investigated material surface [193].

4.2.4 X-ray fluorescence spectrometry (XRF)

X-ray fluorescence spectrometry (XRF) is a non-destructive, rapid method and allows simultaneous multielement analytical measurements, both in solid and liquid samples. X-ray fluorescence represents the emission of characteristic "secondary" X radiation (or fluorescence) from a material excited by bombardment with high-energy X-rays or gamma radiation.

Its applications are multiple, and XRF spectra cover most elements over a concentration range of 100% ÷ μg/g. X-ray fluorescence spectrometry is a basic analytical method, but it is also one of the few atomic spectrometric techniques that can be used in portable instruments. Having advantages such as simple sample preparation, rapid multielement and non-destructive analysis, and the ability to provide an overview of unknown samples in a wide range of matrices (liquids, solids, slurries, powder, paste, thin films, air filters and many others), XRF represents a perfect complementary analysis to other types of analytical equipment in laboratories. Due to these advantages, the technique has numerous applications in research, industry and quality assurance [194].

4.3. Establishing and optimizing modern methods for the extraction of phytoconstituents from plants. Characterization studies of the obtained materials

4.3.1 Vegetal material

Plants of **Lavandula L.** (lavender) and **Mentha piperita** (peppermint) are recognized not only for their aromatic and therapeutic properties, but also for their potential in the field of material protection technologies, especially as corrosion inhibitors.

Lavender, with its dark violet flowers and distinct aroma, is often used in perfumery and aromatherapy. In addition, its extracts contain various bioactive compounds, such as linalool and linalyl acetate, which have demonstrated antioxidant and antimicrobial effects. These properties can help protect metallic surfaces from deterioration caused by corrosion agents.

On the other hand, peppermint, recognized for its fresh aroma and cooling effect, contains menthol, a compound with significant antioxidant activity. Studies have shown that peppermint extracts can reduce rust formation on metallic surfaces, by inhibiting electrochemical processes that lead to corrosion.

In the context of obtaining plant extracts, both lavender and peppermint are excellent choices due to the ease with which they can be cultivated and processed.

4.3.2. Obtaining extracts

A. Preparation of plant material

Drying of the plant raw material was carried out under controlled temperature conditions (T < 35°C). Subsequently, the plant material is brought to the appropriate degree of grinding for processing, by grinding/mortar crushing.

B. Extracting methods

B1. Microwave extraction (Mw) of vegetal material

Reagents and materials

Hydroalcoholic mixture distilled water : ethanol 96% (Roth) (ratio 1:1); graduated cylinders; digestion system in closed vessel (Milestone Ethos Easy MA182-001); teflon digestion tubes.

Working method

The samples taken into work were treated similarly, for all plant materials, but also with the blank sample. As extraction solvent, a hydroalcoholic mixture water:ethanol, ethanol and water was used, applying a ratio of 1:10 g/v, respectively 3 g plant material : 30 mL solvent. The samples and solvent were individually added into teflon tubes.

The plant materials were subjected to extraction at 55°C (with T1 = 20 min heating up to 55°C, T2 = 30 min maintained at 55°C and T3 = 10 min cooling down to T° = 25°C), with a microwave power of 1000W. After completion of the extraction, all samples were filtered on filter paper and stored in the refrigerator (Figure 4.4.). The same procedure was used for all three solvents used.

B2. Classical extraction of vegetal material at temperature

Reagents and materials

Hydroalcoholic mixture distilled water : ethanol 96% (Roth) (ratio 1:1); graduated cylinders; Berzelius beakers (100 mL); watch glass; Biobase Bov-T70C oven.

Working method

As in the case of microwave extraction, a plant material : solvent ratio of 1:10 g/v was used. In Berzelius beakers, the ground plant material was mixed with the extraction solvent, after which they were covered with a watch glass and introduced into the oven. Extraction took place for 2 hours at a temperature of 50°C. After completion of the extraction, the obtained samples were filtered on filter paper and stored in the refrigerator for future determinations (Figure 4.5.).

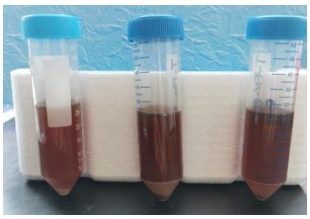

Figure 4.1. Samples obtained by MW

Figure 4.2. Samples obtained at temperature

The same procedure was used for all three solvents used. In Table 4.1 the coding of the samples used within this doctoral thesis is presented.

Table 0.1. Sample codification

Plant	***Clasical temperature extraction***			***Microwave extraction***		
Solvent	***Water***	***Hydroalcoolic***	***Ethanol***	***Water***	***Hydroalcoolic***	***Ethanol***
lavander	*lavander* Et H_20	*lavander* Et H_20 EtOH	*lavander* Et EtOH	*lavander* Mw H_20	*lavander* Mw H20 EtOH	*lavander* Mw EtOH
mint	*mint* Et H_20	*mint* Et H_20 EtOH	*mint* Et EtOH	*mint* Mw H_20	*mint* Mw H_20 EtOH	*mint* Mw EtOH

4.4. Characterization studies of the obtained materials (extracts in different solvents and oils)

4.4.1. Characterization by liquid chromatography (HPLC) – extracts

The quantification of selected components was performed using high-performance liquid chromatography with diode array detector (HPLC-DAD, Rigol Technologies Inc., Beijing, China) using a Kinetex EVO C18 column (150 × 4.6 mm, particle size = 5 μm) at a temperature of 30°C. The solvent mixtures applied were as follows: solvent A consisted of H_2O with 0.1% trifluoroacetic acid (TFA), and solvent B consisted of acetonitrile (ACN) with 0.1% TFA. The flow rate was 1 mL/min, with a gradient elution between 2% and 100% B. The duration of the process was set at 60 minutes, and detection was performed at a wavelength of 280 nm. Reference compounds were of reagent grade (Merck KGaA, Darmstadt, Germany) and were used without further purification. These stock solutions were prepared at a concentration of 1000 μg/mL. To create calibration curves, different concentrations were used depending on the measured compound, exemplified by those for caffeic acid, syringic acid and epicatechin.
HPLC characterizations were carried out for the extracts obtained in solvent mixtures of ethanol, water and hydroalcoholic. Following the analysis of chromatogram peaks, depending on the quantities of plant material taken into work, it can be observed that significant quantities of phenolic compounds were extracted (concentrations are expressed in mg/L) – Table 4.2 and 4.3.

Table 4.2. *Calculated concentrations for lavender extracts*

concentration - mg/L	*lavander* oven H_20	*lavander* oven EtOH	*lavander* oven EtOH-H_20	*lavander* Mw H_20	*lavander* Mw EtOH	*lavander* Mw EtOH H_20
Acid protocatehic	0.462	0.628	0.627	0.655	0.645	0.780
Acid cafeic	0.059	1.711	1.711	1.225	2.056	2.519
Acid siringic	0.535	1.049	1.761	0.387	1.855	1.497
Epicatechina	25.441	181.673	385.651	623.333	294.443	630.037
Acid ferulic	5.520	33.376	73.493	119.071	64.365	125.854
Acid sinapic	5.919	8.204	12.023	12.756	14.080	16.799
Isoquercetina	5.824	12.288	30.504	13.265	20.172	70.650
Naringina	0.908	7.067		7.630	9.577	9.415
Acid rozmarinic	0.160	0.753	0.500	6.693	3.190	7.300
Resveratrol	0.484	0.291	1.462	1.688	2.1	1.571

Tabel 4.3. *Calculated concentrations for mint extracts (mg/L)*

	mint etuva H_20	*mint* etuva EtOH	*mint* etuva EtOH H_20	*mint* Mw H_20	*mint* Mw EtOH	*mint* Mw EtOH H_20
Acid protocatehic	0.380	0.550	0.396	0.272	1.084	1.651
Acid cafeic	1.149	2.682	9.123	2.858	7.123	14.326
Acid sinapic	32.248	132.702	473.166	369.063	374.548	863.263
Isoquercetina	56.583	39.498	7.846	104.662	129.348	356.225
Naringina	2.275	2.201	3.029	2.631	4.367	6.099
Acid rozmarinic	0.170	2.17	33.547	0.607	2.432	4.878
Resveratrol	4.113	3.180	4.259	0.536	5.577	18.990

From the performed analyses, differences between the sets of samples can be observed regarding their chemical composition: in the lavender extract epicatechin has a high content, while in the peppermint extract it is absent, isoquercetin and rosmarinic acid are found in both plant extracts, while naringin is found only in the peppermint extract (Figures 4.13–4.14)

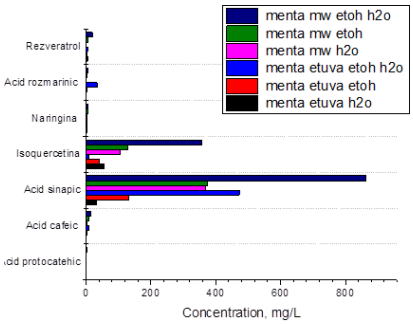

Figure 4.3. *Graphical representation of compound concentrations in mint extracts*

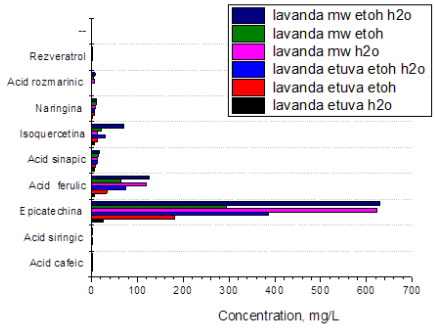

Figure 4.4*. Graphical representation of compound concentrations in lavender extracts*

4.4.2 Characterization by gas chromatography (GC-MS) of essential oils

The most suitable method for testing the chemical composition of oils is gas chromatography (GC-MS). Essential oil analyses were performed using a GC system (HP GC System 6890 Series) coupled with a mass spectrometer (HP Mass Selective Detector 5973) (Agilent Technologies, Diegem, Belgium).

Separation was performed using an Agilent J&W capillary column (FactorFour VF-5 ms, 30 m × 0.25 mm ID, 0.25 µm film thickness). Helium was used as carrier gas at a flow rate of 1 ml/min. The injector temperature was set at 250 °C, and the temperature program was as follows: 8 minutes at 40 °C, followed by a linear increase of 5 °C/min up to 250 °C and then 2 °C/min up to 300 °C, where it was maintained for 20 minutes.

From the obtained spectra, it can be observed that they present a composition rich in phytochemical compounds and can be considered potential candidates as corrosion inhibitors for further testing in polymer matrices, considering that their presence in the analyzed samples has a probability greater than 90% (Table 4.4 – Table 4.6).

Table 4.4. *Phytochemical compounds from GC-MS chromatogram – lavender oil*

Compound	Retention time	Width peack	Height peack	Area peack	Scor	Base peack
Bicyclo[3.1.1]hept-2-ene, 3,6,6-trimethyl-; C10 H16; 8.682	8.682	0.176	867501	8E+06	73.41	93
beta.-Myrcene; C10 H16; 11.154	11.15	0.204	126856	1E+06	76.1	93
Cyclohexene, 1-methyl-5-(1-methylethenyl)-, (R)-; C10 H16; 12.768	12.77	0.143	221446	5E+06	76.4	68
Eucalyptol; C10 H18 O; 12.857	12.86	0.176	93753	3E+06	76.49	43
Bicyclo[3.1.1]hept-2-ene, 3,6,6-trimethyl-; C10 H16; 13.282	13.28	0.16	123423	1E+06	73.69	93
Camphor; C10 H16 O; 18.110	18.11	0.22	336604	7E+06	74.91	95
3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-, (R)-; C10 H18 O; 19.690	19.69	0.204	147730	3E+06	88.77	71
alpha.-Terpineol; C10 H18 O; 20.323	20.32	0.248	197479	5E+06	76.23	59
Geranyl angelate; C15 H24 O2; 28.222	28.22	0.253	785848	2E+07	79.83	69

4-Hexen-1-ol, 5-methyl-2-(1-methylethenyl)-, acetate; C12 H20 O2; 29.038	29.04	0.242	410317	7E+06	74.64	69
Cyclohexene, 4-[(1E)-1,5-dimethyl-1,4-hexadien-1-yl]-1-methyl-; C15 H24; 35.487	35.49	0.149	282835	5E+06	71.29	93

Tabel 4.5. *Phytochemical compounds from GC-MS chromatogram – mint oil*

Compound	Retention time	Width peack	Height peack	Area peack	Scor	Base peack
Bicyclo[3.1.1]hept-2-ene, 3,6,6-trimethyl-; C10 H16; 8.692	8.692	0.165	410560	4E+06	93.49	93
Bicyclo[3.1.0]hex-2-ene, 4-methyl-1-(1-methylethyl)-; C10 H16; 10.347	10.35	0.11	164132	1E+06	95.81	93
Cyclohexene, 4-methylene-1-(1-methylethyl)-; C10 H16; 10.446	10.45	0.22	391864	4E+06	92.39	93
Cyclohexene, 1-methyl-5-(1-methylethenyl)-, (R)-; C10 H16; 12.783	12.78	0.143	469305	1E+07	97.02	68
Eucalyptol; C10 H18 O; 12.873	12.87	0.231	738091	3E+07	97.77	43
l-Menthone; C10 H18 O; 18.678	18.68	0.292	3E+06	9E+07	93.67	112
Benzofuran, 4,5,6,7-tetrahydro-3,6-dimethyl-; C10 H14 O; 19.073	19.07	0.226	1E+06	8E+06	81.08	108
Cyclohexanone,5-methyl-2-(1-methylethyl)-, trans-; C10 H18 O; 19.107	19.11	0.248	890808	2E+07	89.92	112
Cyclohexanemethanol, .alpha.,.alpha.,4-trimethyl-, acetate; C12 H22 O2; 19.143	19.14	0.292	643847	1E+07	72.34	71
Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1.alpha.,2.beta.,5.alpha.)-(.+/-.)-; C10 H20 O; 19.652	19.65	0.017	2E+06	1E+08	97.9	81
alpha.-Terpineol; C10 H18 O; 20.349	20.35	0.198	69017	2E+06	93.1	59
Pulegone; C10 H16 O; 22.564	22.56	0.275	296807	7E+06	97.14	81
2-Cyclohexen-1-one, 3-methyl-6-(1-methylethyl)-; C10 H16 O; 23.234	23.23	0.242	99565	2E+06	90.77	82
Cyclohexanol, 5-methyl-2-(1-methylethyl)-, acetate, (1.alpha.,2.alpha.,5.beta.)-; C12 H22 O2; 25.122	25.12	0.017	2E+06	3E+07	96.9	95
Caryophyllene; C15 H24; 30.442	30.44	0.215	291090	1E+07	97.37	133

Chapter 5. Evaluation of the electrochemical behavior of some resins on Ag substrate for the protection/cleaning of artifacts

5.1. Obtaining coating material

5.1.1. Materials

The solvent used were analytical grade reagents (max. 0.005% H_2O), supplied by Merck KGaA (Darmstadt, Germany), Paraloid B44® and Paraloid B72® from CTS (Italy, Original Rohm and Haas), NaCl (Chimreactiv, Romania), and respectively peppermint and lavender essential oils (Fares, Romania).

Solutions of Paraloid B72 and Paraloid B44 were obtained in the form of strong adhesive by dissolving 5 g of each resin in 25 ml toluene. In each solution, 2 ml peppermint essential oil and respectively 3 ml lavender essential oil were added, under continuous stirring on a magnetic stirrer (600 rpm).

Silver discs (diameter 22 mm, height 2 mm) were washed with distilled water and ethanol, in order to remove residual contamination from handling. After air drying, they were coated with 150 µL of each solution and dried at room temperature until a glossy surface was obtained and any trace of solvent was completely evaporated. In Table 5.1 the obtained samples are presented.

Table 0.1. *Coding of samples used in the evaluation of electrochemical behavior*

Nr.crt.	Sample	Observations
1	Ag	Uncoated silver disc
2	R1	Silver disc coated with Paraloid B72 polymer
3	R1-M	Silver disc coated with Paraloid B72 polymer to which 2 mL of peppermint essential oil was added
4	R1-M-L	Silver disc coated with Paraloid B72 polymer to which 2 mL of peppermint essential oil and 3 mL of lavender essential oil were added
5	R2	Silver disc coated with Paraloid B44 polymer
6	R2-M	Silver disc coated with Paraloid B44 polymer to which 2 mL of peppermint essential oil was added
7	R2-M-L	Silver disc coated with Paraloid B44 polymer to which 2 mL of peppermint essential oil and 3 mL of lavender essential oil were added

5.1.2. Characterization and testing methods

The characterization of the silver substrates was carried out by X-ray fluorescence (XRF) and scanning electron microscopy with EDX accessory (SEM-EDX) in order to confirm the purity of the silver discs used in the tests. Gloss studies were also performed (using a glossmeter PCE-GM80-ICA), while Fourier transform infrared spectroscopy (FTIR) analyses were carried out to evaluate the composition of the developed coatings.

To evaluate the metal content of the tested silver substrates and to identify potential impurities in their structure, X-ray fluorescence analysis was used, namely a Vanta C Series Handheld XRF equipment equipped with a 40 kV X-ray tube, rhodium anode and silicon detector. Each beam had an acquisition time of 60 seconds during the analysis process.

For scanning electron microscopy (SEM), a Hitachi TM4000plus II (Hitachi HiTech) instrument was used, coupled with an energy-dispersive X-ray spectrometry accessory (EDX - Oxford Instruments). To obtain a broad characterization, the following technical characteristics were considered: BSE detector, acceleration voltages of 5 kV, 10 kV or 15 kV and magnification range between x100÷x100000.

The aesthetic effects of the treatment on the silver discs were carried out by gloss tests in several points. For the tests, a glossmeter (PCE-GM80-ICA, equipped with an external gloss sensor) was used, and measurements were made on a surface of 4.5 mm at an angle of 60°.
FTIR spectra were obtained using a Jasco FTIR 6300 spectrometer (Jasco Corporation, Tokyo, Japan) coupled with an attenuated total reflectance accessory with diamond crystal (KRS5 lens). Measurements were performed in the range 400–4000 cm^{-1}, involving 30 scans, with a resolution of 4 cm^{-1}.

The electrochemical behavior of some resins on Ag substrate was determined within the Electrochemistry and Surface Functionalization Laboratory from rooms JK209-JK214, within the Faculty of Materials Science and Engineering (SIM), National University of Science and Technology POLITEHNICA Bucharest (UNSTPB).

Corrosion resistance was determined by the polarization resistance technique (Tafel technique). This technique consists in plotting linear polarization curves involving the following steps:

- measurement of the open circuit potential (EOC), for a duration of 1 hour;
- plotting potentiodynamic polarization curves from -0.2 V (vs EOC) to +0.2 V (vs EOC) – Tafel curves, with a scan rate of 0.167 mV/s.

The corrosion resistance evaluation tests were carried out using a Potentiostat/Galvanostat (model PARSTAT 4000, manufacturer Princeton Applied Research, USA) to which a low current module (LCI, manufacturer Princeton Applied Research, USA) was coupled, and the potentiodynamic curves were acquired using VersaStudio software v.2.62. For performing the tests, a corrosion cell was used consisting of a saturated calomel electrode (SCE) – reference electrode, a platinum electrode – auxiliary electrode and the working electrode consisting of the investigated samples (Ag and Ag coated with different resins).

The tests were performed at room temperature (25±1°C) using a saline solution (NaCl 3.5%) as electrolyte.

5.2. Physico-chemical characterization of coated and uncoated Ag discs

From the characterization performed by XRF analysis (average of five determinations), it was observed that silver is the major element (approx. 94.5±2.3%) with impurities due to the manufacturing process (Cu – approx. 5.3%, Ni – 0.05%, Zn – 0.01%, Sb – 0.01%, Pb – 0.05%) (Figure 5.7). SEM analysis revealed that the surface support does not present major scratches or other types of imperfections (Figure 5.8).

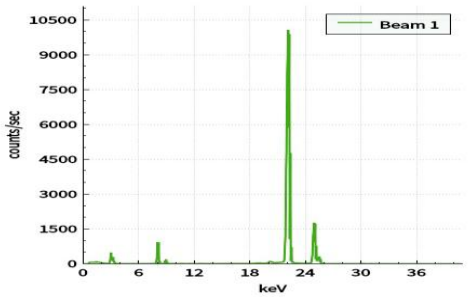

Figure 0.1. *XRF Spectrum of untreated samples*

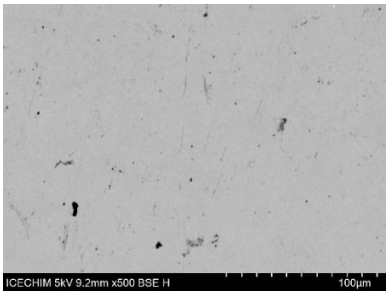

Figure 0.2. *SEM Microscopy of untreated samples*

Figure 5.9 presents the distribution map of Ag (Figure 5.9 left) and Cu (Figure 5.9 middle), while the recorded EDX spectra are presented in Figure 5.9 right.

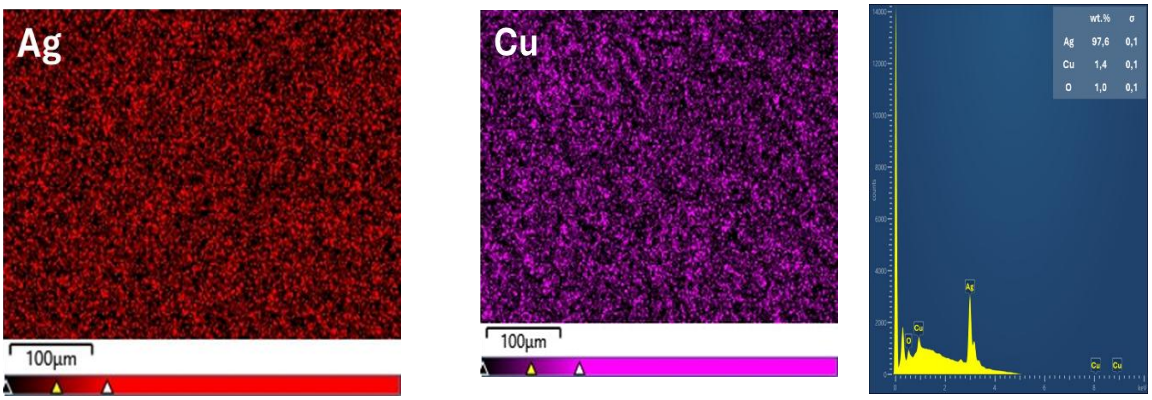

Figura 0.3. Elemental distribution map of silver (left), copper (middle) and EDX spectra (right).

The results presented in Figure 5.9 confirm the findings of XRF analyses. Thus, the differences recorded between the two methods can be explained by the characteristics of each method as follows. While the XRF method characterizes the entire sample, EDX analysis is performed only on a specific area of the sample.

The FTIR spectra presented in Figures 5.11 and 5.12 reveal a minor influence of essential oils on the final composition of the coating, without specific absorption maxima being recorded.

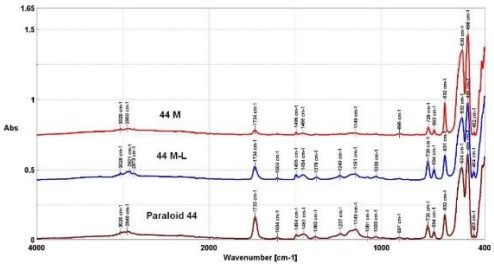

Figure 0.4. *FTIR spectra of Paraloid B44 with Mint and Lavandula essential oil compared to the control solution*

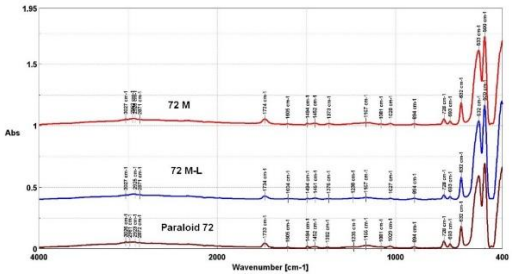

Figure 0.5. *FTIR spectra of Paraloid B72 with Mint and Lavandula essential oil compared to the control solution*

To evaluate the FTIR results, the composition of the two base materials must be considered: both Paraloid samples are copolymers, B44 representing an ethyl acrylate/methyl methacrylate copolymer, while B72 represents a polyethyl methacrylate/methyl acrylate.

The maxima recorded in all six samples can be attributed to polymer mixtures: for both samples, the peaks appearing at 1733 cm^{-1} can be attributed to the characteristic stretching vibration of the ester carbonyl group, those at approx. 2981 and 2950 cm^{-1} can be attributed to C–H groups, 1494 and 1452 to CH_3 groups, those around 1380 cm^{-1} to symmetric CH_3 bonds, peaks at 1150 and 1030 cm^{-1} to C–C(=O)–O bonds, while peaks around 894 and 728 cm^{-1} can be attributed to C–H vibrations [198].

A major conclusion that can be drawn from FTIR analysis is that the addition of essential oils does not negatively influence (degrade) the polymer base, thus maintaining the Paraloid samples.

Gloss test measurements were performed in triplicate and the result was the average of the measurements. The tests were performed before and after treatment at 24 and 48 hours, using an uncoated disc as control sample. Colorimetric studies and gloss tests did not reveal any major modification after adding essential oils to the coating treatment in the aesthetics of the silver discs (Table 5.2 and Figure 5.12).

Table 0.2. Results obtained from colorimetric and gloss tests

Material	Time [hours]	
	24h	48h
M (untreated disc)	375.7	375.7
R1-M	345.1	344.9
R1-M-L	336.7	332.4
R2-M	329.9	328.3
R2-M-L	348.5	337.1
R1	367.3	366.2
R2	354.1	352.3

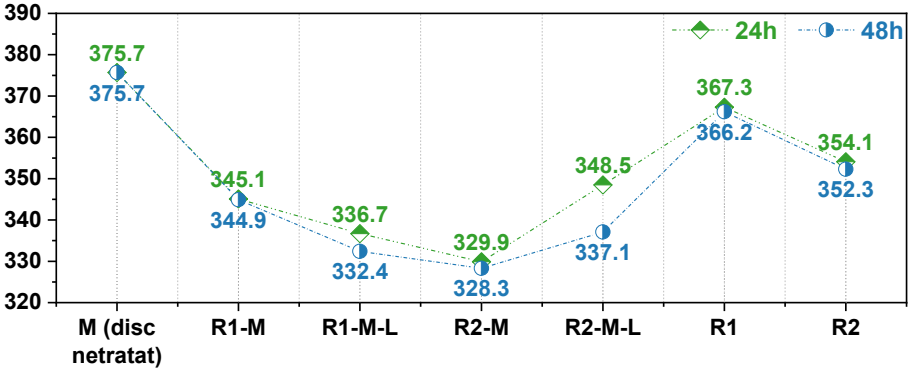

Figure 0.6. Evolution at 24 and 48 hours of the results obtained from the colorimetric and gloss tests

The influence of the coating material is expressed by a minor reduction of the gloss parameter, further reduced by the addition of essential oils.

5.3. Evaluation of electrochemical behavior

The tested materials consisted of discs (uncoated and coated) with a diameter of 22 mm that were introduced into a special Teflon holder so that only one of the surfaces was in contact with the electrolyte and subjected to electrochemical tests.

The Tafel curves corresponding to the tested samples are presented in Figure 5.20.

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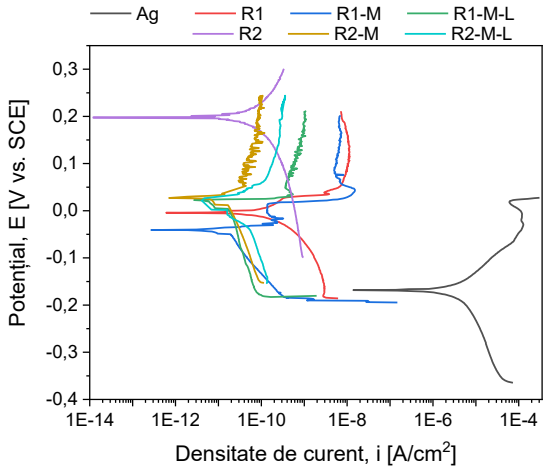

Figure 0.7. Tafel curve corresponding to the samples investigated in 3.5% NaCl saline solution

By extrapolating the Tafel curves, the main electrochemical parameters were obtained that provide important information about the electrochemical behavior of the materials studied in

this doctoral thesis [199]. Table 5.3 contains the obtained values for corrosion potential and corrosion current density.

Table 0.3 Main electorchemicals parameters

Nr.crt.	Sample	E_{cor} (mV)	i_{cor} (A/cm^2)
1	Ag	-167	4,98 x 10^{-6}
2	R1	-42	3,36 x 10^{-10}
3	R1-M	-40	3,83 x 10^{-11}
4	R1-M-L	20	5,03 x 10^{-11}
5	R2	198	5,88 x 10^{-11}
6	R2-M	27	2,20 x 10^{-11}
7	R2-M-L	22	4,83 x 10^{-11}

Corrosion resistance/electrochemical behavior can be examined based on several evaluation criteria. Among the most important electrochemical parameters are corrosion potential (E_corr) and corrosion current density (i_corr). For a better visualization of the obtained results, the values of parameters E_corr and i_corr are graphically represented in Figure 5.21.

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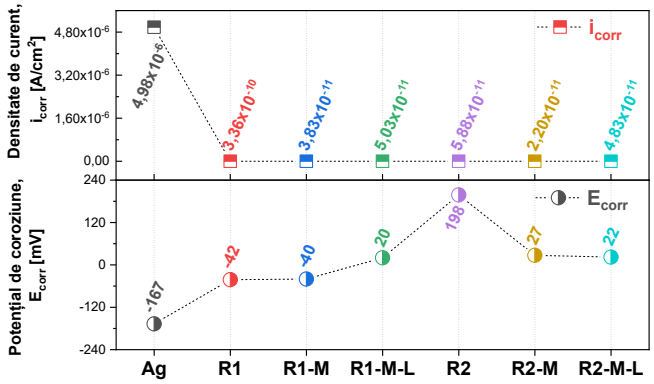

Figure 0.8. Evolution of the main corrosion parameters for the investigated materials

If we consider the value of the corrosion potential (Ecor), it is considered that the more electropositive Ecor corrosion potential values show a better electrochemical behavior.

Comparing the values in table 5.3, it is observed that all coatings have a more electropositive potential than silver, highlighting the fact that regardless of the nature of the coatings, they improve the corrosion resistance of the substrate. The most electropositive values were recorded for the type 2 resin-based coatings, Paraloid B44 – samples coded with R2.

The electrochemical measurements showed that the most electropositive potential and consequently a better electrochemical behavior is that of the R2 sample (198 mV), followed by the R2-M (27 mV) and R2-M-L (22 mV) samples. It is also noted that the coatings for which Paraloid B44 was used have lower Ecor parameter values than those based on Paraloid B72. Thus, among the coatings based on Paraloid B44, the R1-M-L sample stands out, which recorded the most electropositive Ecor (20 mV), followed by the R1-M sample (−40 mV) and the R1 sample (−42 mV) [199].

Thus, from the analysis of the evolution of the Ecor parameter, it is observed that the use of Paraloid B72 leads to a better electrochemical behavior, compared to Paraloid B44. It is also noted that the addition of mint and lavender essential oils have different effects depending on each type of acrylic resin used. Therefore, when essential oils are added to Paraloid B72, the potential values are more electronegative, highlighting a weaker corrosion behavior compared to the resin without oils (sample R2), while the Paraloid B44-based coatings present more

electropositive values after the addition of oils, compared to the coating without oils (sample R1).

It is known that Paraloid B72 is the most widely used polymer material in Europe for the preservation of historical and art objects, often used for objects based on iron, copper alloys and silver [202,201] that are kept inside museums or other specialized buildings. Paraloid B44 is also used, the difference between the two resins being given by the chemical composition and the fact that in terms of glass transition temperature (Tg), Paraloid B44 has a higher Tg value, which is also higher than ambient temperature [202].

It is known that a low corrosion current density (icor) indicates good corrosion resistance. Thus, if we consider this criterion, the lowest value is that of the R2-M sample (2.20 x 10^{-11} A/cm2) followed by the value recorded for the R1-M sample (3.83 x 10-11 A/cm2). It is observed that all coatings, regardless of their nature, lead to a considerable improvement in the electrochemical behavior, the icor values decreasing by several orders of magnitude. It is also observed that the introduction of mint extract leads to a decrease in icor regardless of the type of resin and the introduction of lavender extract causes the icor values to increase slightly but do not exceed the value recorded in the case of coatings based only on resin [199]. Analyzing the electrochemical parameters in the table above, it can be observed that all coatings, regardless of their nature, lead to an improvement in the electrochemical behavior of silver.

5.4. Conclusions

Rezistența la coroziune / comportamentul electrochimic poate fi examinat pe baza mai multor criterii de evaluare. Dintre cei mai importanți parametrii electrochimici sunt potențialul de coroziune (E_{cor}) și densitatea de curent de coroziune (i_{cor}).

Dacă luăm în considerare valoarea potențialului de coroziune (E_{cor}), se consideră că valorile potențialului de coroziune E_{cor} mai electropozitive prezintă un mai bun comportament electrochimic. Din studiile efectuate, se observa că toate acoperirile au un potențial mai electropozitiv decât al argintului evidențiind faptul că indiferent de natura acoperirilor acestea îmbunătățesc rezistența la coroziune a substratului.

Din analizele fizico chimice se poate observa că adăugarea uleiurilor esențiale nu influențează negativ (degradează) baza polimerică, menținând astfel probele de Paraloid.

Materialele sintetizate nu afectează efectul estetic al suportului de argint.

Din analiza parametrilor electrochimici se poate observa că toate acoperirile, indiferent de natura lor, au o rezistență sporită la coroziune a argintului, si conduc la îmbunătățirea comportamentului electrochimic al argintului.

Chapter 6. Precious metals - global demand, supply, quotes

Precious metals (gold, silver, platinum and palladium) are a specific type of financial asset and are one of the most popular investment instruments. The development of this segment of the financial market directly affects the financial and investment opportunities of the country, which it is able to realize, using the mediation of both its own financial institutions and the most relevant structures with foreign capital. A sufficiently large reserve asset of precious metals makes it possible to increase the economic and social advantages of a country at the international level.

Obviously, the individual reserves of precious metals of each country are formed, first of all, depending on the financial and economic state, as well as changes in exchange rates. Therefore, we can talk about the mutual influence of the precious metals market and other subjects on the national economy.

6.1. Information on precious metals supply

Current precious metal supplies come mainly from the following sources: mining production (primary), scrap gold (secondary), official sales, private sector sales, loans, forward sales and CIS sales. However, mining production can be considered to be the only primary source that physically produces these metals and thus underpins the other activities. In fact, for the last four activities listed above, the metal comes from stocks and the operations themselves are speculative in nature.

* The first supply, namely the one from mining, will be presented below.

A precise statistic of the total production of gold and silver since the beginning of their extraction is difficult to make, more precise data dating back to 1493. The figures presented above are collected and processed from the works "Aurul si Argintul", authors Ion Lăzărescu and Vasile Brana, "Les Poincons de Garantie Internationaux pour L'or et L'argent", "Aurul Romanesc" by Ion Rusu Abrudeanu, "Aurul mit și realitatea" by Nicolae Murgu and Mugur Isărescu, the publications "Gold și World Silver Survey".

It can be estimated that the gold extracted until the year 2000 is at the level of approximately 138,442 tons, and for silver, starting from 1493, an extraction of approximately 651,698.2 tons was achieved.

The world extractive production of gold and silver, in certain periods of time is presented in table no. 6.1.

Table 0.1. World extractive production of gold and silver, in certain periods of time

Gold			Silver		
Period	Year	Quantity,t	Period	Year	Quantity,t
5000-500 i.e.n.	-	4500			
501-146 i.e.n.	-	1062			
147-395 i.e.n.	-	3652			
396-1095	-	70			
1096-1493	-	1466			
1493-1602	-	772	1493-1600	-	1167
1603-1815	-	3030	1601-1830	-	6518
1816-1938	-	36535	1831-1938	-	346843
1939-1968	-	29116	1939-1970	-	221472
Total partial period		80204	Total partial period		576000
1970-1977	1970	1676	1971-1978	1971	9310
	1971	1639.6		1972	9330
	1972	1580.5		1973	9530
	1973	1516		1974	9230
	1974	1428		1975	9614
	1975	1368		1976	10850
	1976	1404		1977	10556
	1977	1411.1		1978	10977
Total partial period		12023.2	Total partial period		79397
1986-1997	1986	1637	1979-1986	-	96447

	1987	1733.6	1987-1996	1987	13485
	1988	1909.9		1988	14123
	1989	2064.5		1989	14357
	1990	2135		1990	14314
	1991	2159.5		1991	12901
	1992	2233		1992	15016
	1993	2289.8		1993	14289
	1994	2280		1994	13801
	1995	2272		1995	14894
	1996	2357.1		1996	15320
	1997	2464.4			
Total partial period		25535.8	Total partial period		238947
1998-2023	1998	2481	1998-2023	1998	2060
	1999	2543		1999	1950
	2000	2528		2000	
	2001	2557		2001	
	2002	2503		2002	
	2003	2516		2003	
	2004	2411		2004	
	2005	2446		2005	
	2006	2396		2006	
	2007	2331		2007	
	2008	2285		2008	
	2009	2481		2009	
	2010	2586		2010	
	2011	2573		2011	
	2012	2558		2012	
	2013	2920		2013	
	2014	3020		2014	
	2015	3100		2015	
	2016	3236		2016	
	2017	3247		2017	
	2018	3310		2018	27000
	2019	3463		2019	27000
	2020	3241		2020	25000
	2021	3090		2021	25000
	2022	3100		2022	26000
	2023	3000		2023	26000
Total partial period		71922	Total partial period		160010

Note: No information was found for the period 2000-2017, related to the amount of Ag extracted worldwide.

The comparative evolution of the quantities of metals offered from mining extractions and those offered from scrap and old metals, during the period 1988-1996 was:

The total world quantity of metals coming from offers of industrial scrap and old metal, during the period 1988-1996, compared to that from production, was between 17.9% - 25.4%, on average 20.45% for silver and 19%-27.4%, on average 24.14% for gold.

It is interesting to show that in some countries with more limited natural resources, therefore with a lower extractive production, the offers of gold coming from industrial scrap and old objects are much higher than the average percentage mentioned above (annex). Thus: 362% in Japan, 107.4% in Argentina, 80.5% in France, 51.0% in Yugoslavia, 42.8% in the Dominican Republic, 36.0% in Spain, etc.

The quantities of metals recovered in the form of old objects are influenced by a series of factors, as follows:

• the increase in the selling price of scrap and old gold objects makes those who have invested interested in reselling them at higher prices than they were purchased;

• conversely, the decrease in prices determines a decrease in the quantities offered for sale as well as the use of money for the purchase of new objects instead of the practice of paying for new products with old jewelry; this situation determines the decrease in the supply of old metals, increasing the demand for new metal;

• the lack of adequate technologies for recycling old metals that meet the requirements imposed by demand in terms of the quality of newly manufactured objects limits the demand for old metals;

• monetary crises determine the increase in the activity of waste markets due to the increased supply of old objects.

• massive supplies of old objects (in the case of liquidation of some stocks) have as an immediate consequence the decrease in their capitalization prices;

• an interesting practice is the one used in some areas of Asia, where traditionally jewelry is sold by the manufacturer in advance, which means that the gold purchased can be sold back to the manufacturer at any time in the future at a higher price; usually the objects in this area have a title of 965%;

• due to the fluctuation of the dollar, the producers have oriented themselves towards the purchase of old objects in order to sell them on the international market; at the same time, bars (ingots) with the title mentioned above have been exported for refining and subsequent return in the form of bars.

As for Romania, before 1989, industrial activities, jewelry manufacturing, dentistry, etc., resulted in annual waste and scrap metals in quantities of about 20-30 tons of silver, about 140-160 kg of gold, about 800-1000 kg of platinum and 60-80 kg of rhodium. Silver came (approximate values) from the following activities: 29% electrical engineering, 31% from special activities, 7% from chemistry, 6% from metallurgy, 5% from machine construction and 22% from other activities. Gold resulted from the following activities: about 80% from electrical engineering, about 6% from chemistry, about 3% from jewelry manufacturing and about 11% from other activities. Platinum and rhodium were recovered from: chemistry approximately 76%, light industry approximately 10% and from other activities approximately 14%. After 1989, recovery activity decreased significantly in the first period, after which, in the absence of clear regulations in the field, it dispersed, being carried out by private companies, without any statistical evidence on the quantities of metals resulting from processing.

* The third source of precious metal supply is sales from the official sector, represented by institutions such as the International Monetary Fund, the Central Banks of the world's countries and other government authorities. These institutions hold large quantities of gold in their treasuries for monetary purposes, which exceed by several dozen times the annual world production.

During the period 1970-1979, significant sales of gold from the stocks of the aforementioned institutions took place, with the IMF in first place with approximately 200 t/year and the U.S. Treasury with approximately 500 t/year. The motivations behind these sales were different, namely: the 1976 agreement on the gradual liquidation of the IMF's gold monetary stock and the 1978 program of the American authorities to support the dollar, due to its weakness on the exchange markets.

In 1971, some sales were made in the amount of 85 tons, with the intention of stopping the increase in the price of gold due to the undesirable evolution of the dollar.

According to the IMF, the world gold reserves of the official sector in 1990 totaled 29,206.5 tons of gold, and at the end of 1997 they stood at 27,742.1 tons of gold.

From the comparative analysis of the two graphs, a downward trend in the monetary gold reserves of banks results. Thus, in a period of 25 years, it decreased by approximately 11%, as a result of a voluntary action to reduce these stocks.

The evolution of the monetary gold stock, by continents and industrialized countries, during the period 1990-1997, highlights the fact that in 1997 it presents variations compared to 1990, as follows: Europe with 835 tons compared to 376 tons, Asia with 1755 tons compared to 1628 tons, Africa with 392 tons compared to 375 tons and decreases in: South America with 799 tons compared to 973 tons, the Middle East with 1087 tons compared to 1102 tons, industrialized countries with 22873 tons compared to 24753 tons. Sales in the private sector usually represent speculative actions and they consist of buying large quantities of gold in the event of currency depreciation, followed at a certain time interval by selling part of the quantity purchased in order to benefit from the price increase. The quantities sold by individuals at any one time can be significant, representing 20-30% of the total supply of gold. Gold loans and forward sales (investment liquidations) represent the repayment of contracted debts in metal. Gold sales by the CIS, the world's fourth largest producer, represent the payment of international currency debts contracted by Russia. According to data presented by "Metals and Minerals" 1989-1993, these sales had a minimum level of 90 tons in 1980 and a maximum of 425 tons in 1990.

6.2. Precious metals demand data

The demand for precious metals represents the consumption requirement which is divided into the following areas of activity: industrial consumption, purchases in the official sector (authorities), loans, investments in gold and purchases of bullion for hoarding.

During the period 1987-1996 the total world demand for precious metals was: 32,024 tons of gold and 222,018 tons of silver.

Of these quantities, jewelry manufacturing activities used about 21,696 tons of gold, respectively 67.7%, those in the electronic field about 1,562 tons of gold, respectively 4.9% and various other activities about 2,786 tons, respectively 8.7%. The silver used in the various manufacturing processes was distributed as follows: in industry about 88,077.7 tons, respectively 40%, in the photographic field about 64,385.6 tons, respectively 29%, in the jewelry field about 57,601 tons, respectively 26% and in the official coin sales activity about 8,911.3 tons, respectively 4.1%. Official gold purchases were 357 tons, which represents approximately 1.1% of total demand. Gold loans, at the level of 275 tons, represented about 0.8% of total demand. Ingot purchases for hoarding were 2,733 tons of gold, respectively 8.5% of total demand.

From the above, it follows that currently for manufacturing operations, silver has been used in a proportion of 99.1%, and gold in a proportion of 81% compared to the beginning of the century, when they were used for this purpose in a proportion of 25%.

During the period 1989-1998, there was a tendency for investments to decrease by approximately 140 tons compared to disinvestment, a quantity by which the supply on the market actually increased. Also, a decrease in hoardings was observed from 530 tons in 1989 to 155 tons in 1998.

The quantity used for investments and hoarding represents, in the analyzed period, 11% of the total demand for manufacturing.

Regarding platinum, the total demand in 1992 was 114.9 tons, of which 107.7 tons for industrial consumption, distributed as follows: 43.9 tons for the automotive industry; 42.8 tons for jewelry and 21.0 tons for other activities. Investments for hoarding were 7.2 tons.

The demand for palladium in 1993 was approximately 76 tons, of which: about 19 tons for car catalysts; about 51 tons for dental and electronic activities and about 6 tons for jewelry.

Regarding the demand and supply of precious metals on a national level, two periods can be distinguished:

a) Before 1989, when the annual supply fluctuated around 2000 kg of gold and 100 tons of silver. These quantities were provided for gold entirely from extractive production, and for silver about 50-60% from extractive production and 40-50% from B.N.R. stocks. Platinum metals were provided from imports (primary ones), from old platinum metals usually recovered in the country (about 1000 kg of platinum, about 200 kg of rhodium and palladium) and from B.N.R. stocks.

The demands for precious metals came from the industrial and banking sectors. Thus, about 300-400 kg of gold, 80-100 tons of silver, 1300-1500 kg of platinum, 180-200 kg of rhodium/palladium were used annually in industrial activities.

The main consuming activities were:

- gold: electrotechnical (90%), other activities (10%);
- silver: electrotechnical (55%), chemistry (25%), photosensitive materials (15%), other activities (5%);
- platinum: chemistry (80%), electrotechnical (11%), other uses (8%);
- rhodium and palladium: electrotechnical and electronics (60%), chemistry (30%), other activities (8%).

The gold and silver waste that could no longer be processed by the economic agents that owned them through reuse was taken over by the B.N.R., after their processing in the extractive industry, in the form of standard bars.

The other types of offers or requests (demands) that appear on the Western market were prohibited and were not practiced, except for a period before 1973, when individuals could buy dental gold from the B.N.R., based on a medical prescription.

b) After 1989, the industrial supply and demand for precious metals gradually decreased, each year, simultaneously and proportionally with the decrease in industrial activities. In contrast, due to an unsupervised liberalization process, without creating specific institutions for the field, similar to those existing in Western countries, some activities characteristic of a market economy, not always licit, began to develop.

6.3. European markets for precious metal objects and ingots

6.3.1. General information

Regarding the situation of objects made of precious metals, it must be pointed out that in order to ensure the free circulation and trade of products under the conditions of the existence of unitary regulations, the European common market was established. The countries that founded this organization as well as those that are about to join have different regulations regarding the guarantee of objects made of precious metals, which creates significant difficulties in carrying out this activity. Thus, as has been shown, some countries such as England, the Netherlands, France have exercised control over several centuries through official guarantee offices, others such as Portugal, Switzerland, Finland, etc. have the same point of view, while countries such as Germany oblige the manufacturer to apply the national mark, Greece gives the right, but not the obligation, to certify the jeweler, and in Italy and Belgium state control is optional.

In 1972, the E.F.A. (E.F.T.A) countries signed a convention, which imposed on the national regime existing in each country a hallmarking system applicable only to objects intended for import-export within the area. In this situation, some countries such as England, Finland, Portugal and Switzerland kept the previous national system, while applying at the same time the one established by the convention. Other countries, such as Sweden and Norway, gave up the national system in favor of the one established by E.F.A. This convention, which had a small number of member countries, while the number of officially recognized titles was three for gold and one for platinum, aimed to regulate international trade between the member countries of a free trade area. The convention could in no way solve the problems that arose within the European Common Market, which assumed an area without internal borders, where the free movement of goods would be ensured.

In view of the above, the need for harmonisation was considered in order to eliminate obstacles and ensure the free movement of articles made of precious metals in the Community. Thus, the Commission of the European Community drew up in 1993 a proposal for a Council Directive on articles made of precious metals. This regulation, which was still in draft form in 1995, abolished the mandatory nature of marking by an official office and proposed that the manufacturer, the authorized representative or the person responsible for placing on the market should be the ones to ensure the guarantee rules. The proposal made in the Directive provides that in order to ensure the conformity of the articles, the manufacturer or his authorized representative must choose between:

- the manufacturer, under the supervision of the notified body, undertakes and justifies, based on documentation, that he applies the quality systems of the E.C. he is the one who applies the title stamp and the notoriety stamp

- the manufacturer, in addition to applying the two stamps, issues a C.E. certificate of conformity containing the name and address of the manufacturer, the authorized representative or the person in charge, the letter “e” the description of the work the title and the specification of the notified body

- Subjecting the works to a third-party verification, which means a notified body that verifies and certifies that the objects meet the required requirements, it carries out a statistical control of the titles operating by sampling, taking into account the fact that the standard quality level corresponds to a probability of acceptance of 95% with a percentage of non-conformity lower than 1%.

In conclusion, the provisions established in 1972 by the E.A.L., although not satisfactory from the point of view of the free movement of products, constitute the only official regulation in force. In contrast to the confusing situation of the regulations regarding the market for metal objects in the form of bars, ingots, plaques and coins, they are carried out in a well-organized framework and according to well-established regulations. Thus, the European trading centers are located in London, Zurich, Frank furt and Paris. As for the USA, until 1974 American citizens did not have the right to carry out trading and hoarding operations with gold, which is why, only after the repeal of this provision, the New York market returned to a central place in this trade, the barometer of activity remaining the center in London.

6.3.2. Detailed situation on the Swiss market

The Zurich Gold Pool, headquartered in Zurich, Switzerland, is made up of three members: Union Bank of Switzerland (U.B.S.), Swiss Bank Corporation (S.B.C.) and Credit Suisse and the specialists of the precious metals trading offices in Zurich, Basel, Geneva, Lausanne, Chiasso and Lugano. The three banks, with their share of capital and published reserves of over 20 billion USD, are among the most renowned financial organizations, recognized by international rating agencies. The members of the refineries associated with the banks are Argor-Heraeus S.A., Mendrisio (U.B.S.), Métaux Précieux S.A. Metalor, Neuchâtel (S.B.C.) and Valcambi S.A., Balerna (C.S.). They produce a diversified assortment of precious metal bars of all qualities, so that it corresponds to the widest possible range of investor requirements. These bars are recognized as good delivery throughout the world. In addition, precious metal processing services are offered, including metal refining, scrap recycling and the production of products with broad industrial applications. Specialized companies also offer competent sales services for professional operators.

The Swiss precious metal market is a free interbank market, where prices are established after negotiation, based on supply and demand. The specific legislation governing the trade in precious metals is the "Swiss Federal Act" of 1933, concerning the control of transactions in precious metals and is primarily intended to protect the consumer. Several other regulations were established by the "Swiss Federal Banking Act" with reference to the justification of transactions in precious metals and the ratio of capital requirements for interested companies. According to these regulations, any person may engage in such transactions, provided that he limits his activity to the minting of official coins and the appropriate hallmarking of bars with a fineness of 995% for gold, 999% for silver and 999.5% for platinum and palladium. The manufacture of refined products may be carried out only if the legal entity holds a refining license issued by the Central Bureau for the Control of Precious Metals. Professional trade requires a trade license issued by the same authority to the producing refinery. Through the measures taken, Switzerland has ensured a favorable framework for activities on the precious metals market, as follows: the absence of official restrictions on the inflow or outflow of capital or precious metals; movements of precious metals are declared only for statistical purposes; gold in the form of official coins and stamped bars intended for banking transactions are exempt from any taxes, silver, platinum and palladium are subject to the usual duties and sales taxes (6.2-9.3% depending on the nature of the transaction) and the creation of a developed financial system.

Prices

The members of the Zurich Gold Cartel operate as principals, buying and selling on their own account. Prices are quoted continuously between 08:00 and 17:00 at local banks, every business day. Quotes are expressed in USD/fine ounce or in Sfr/fine kg. On request, quotes can be made

in any currency convertible on the day, according to the exchange rate of the foreign exchange market in the respective region. Transactions with customers are made at a price agreed upon by all members of the Cartel and which is usually around 3S/fine ounce or 250 Sfr/kg. This price may vary, depending on market conditions. The Cartel price is considered the official price on the Zurich gold market. The quoted prices apply to standard bars, and for smaller or higher quality bars, prices are formed by adding an additional value to the price of the standard bar.

Orders

The members of the Zurich Gold Cartel accept the execution of buy and sell orders at the market price at the time of receipt of the order or at a later date. Orders, unless otherwise agreed, are only accepted during trading hours.

Payment

I n the case of gold bars, the price is based on the weight of pure gold contained in the bar, approximated with 3 decimals for ounces and 5 decimals for kilograms, and gold in the form of a wafer or "biscuit" which usually have a fineness of 999.9% is paid per piece.

Storage of gold or silver bars and coins

Storage of ingots and coins can be done in collective or individual deposits. In the absence of special provisions, all gold bars will be stored in collective deposits, provided that they are of the usual quality, size and shape. The coins must be standardized and of large production series. The bars or coins of each depositor can also be stored in individual deposits, in the form of their own stocks. When depositing standard bars, the depositor receives a list with the series and weight of each bar.

Metal Accounts

Metal accounts are understood to mean that gold bars or coins are entrusted to the deposit, by weight in the case of bars or by number of pieces in the case of coins. During the period when the metals are left in the account, the depositor holding the deposit is not the legal owner thereof. The detonator title of the account refers to standard bars or coins that meet commercial quality standards. If the detonator title of the account is requested for a quantity less than the weight of a standard bar, the account applicant must pay an appropriate surcharge for the surrender of smaller quantities.

Delivery

Delivery and payment must be made within two business days from the date of the transaction. The place of delivery is the office of the Cartel members where the transaction was made or another preferred place on the date of the operation.

Delivery is made to the office of the Cartel members where the account is opened. In the event that, for reasons beyond the control of the cartel members, delivery in the form provided for in the contract or at this place is not possible, delivery may be made to any place and in any form, in the interest of the client, at his risk and expense.

Physical delivery of the metal existing in an account or part thereof is made without the involvement of the Cartel members with whom the account is opened. The costs related to delivery to another place are paid by the persons receiving the goods. Physical delivery to a safe deposit account or to a credit account in metals is made without conditions, with the obligation that the recipient bears all expenses related to the transport of the metal to the place where the account is opened.

The transfer of metals from an account opened by a Cartel member to an account opened by another Cartel member is generally exempt from obligations. Cartel members reserve the right, however, to charge a fee for the individual transfer, if a metal account is used partly or exclusively for transfers between third parties and not directly between Cartel members.

Safe Deposit Boxes

Buyers or depositors can store gold in personal safes of any size, rented from Cartel members.

Forward transaction (in anticipation)

he members of the Zurich Gold Cartel carry out operations of buying and selling precious metals for delivery to the applicants at any date, within a period of 12 calendar months from the date of the transaction. The price requested for advance delivery (compared to the payment date) represents the price of standard bars on the date of the transaction, to which a discount is added. Contracts can be concluded for quantities of at least 100 ounces. Customers who do not guarantee with an open credit line for gold transactions, must deposit an advance on the transaction date. This may be in the form of a "cash" deposit or, by mutual agreement with the bank, in other forms. It may also be deposited as collateral in safety accounts. The liquidation of a previously concluded forward contract can be carried out at any time before the term, by making another transaction with the same term as the original transaction.

At maturity, the two contracts are settled, with the client being debited or credited with the price difference. If the client decides to make or withdraw a significant delivery of metals from the contract, this is debited or credited to the metal account, and the contract value is credited or debited to the current account with effect from the contract maturity date. In the event that the client wishes to renew a forward contract at maturity, the old contract is liquidated, and the price difference is debited or returned to the client with effect from the term date. The new contract, concluded on the same date, is made at the market price at that time.

In Switzerland, physical deliveries (on the country's territory) of silver, platinum and palladium, unlike gold, are subject to sales taxes, as follows:

- for the sale by a wholesaler (bank) to another wholesaler who buys for personal interest or for investment, a tax of 6.2% of the sales price is charged;
- for the sale by a wholesaler to another wholesaler who buys for resale, a tax of 9.3% is charged.

In the case where the buyer asks the bank to deposit the metal in an individual or collective account, in his own name, the buyer is considered the owner of the metal. When the purchase and delivery of the metal to a security account are not carried out simultaneously, taxes are charged for the deposited metal. If the deposited metal comes from abroad, the depositor must present a copy of the import declaration, stamped by the authorities, from which it can be seen that the duties and taxes have been paid at the border. Physical sales of metal to a wholesaler are exempt from taxes if it is to be exported from Switzerland. The buyer must prove to the bank, by means of a copy of the export declaration stamped by the authorities, that the metal has been exported.

Transactions whereby metal enters a metal account without physical delivery are also exempt from tax. If the account holder exercises his right to withdraw the metal delivery in physical form from the account on Swiss territory, the metal becomes taxable at the market value on the date of delivery.

The minimum value for concluding a contract is 5,000 silver ounces.

Of the six metals in the platinum group, only platinum and palladium are important as investment instruments. These two metals enter the interbank market. The price quotation is used mainly for loco Zurich deliveries. Cooperation between the Zurich and London markets began in 1979 with the standard for "good delivery" bars and the list of accepted smelters and assayers. In 1989, the members of the London Platinum and Palladium Market (LPPM), in collaboration with the members of the Zurich Gold Pool, began to fix twice daily for the two metals.

The platinum and palladium market being, compared to that of gold and silver, quite small, the global demand for these two metals does not exceed 100 tons/year and the volume of negotiations on the free market represents only a fraction of this quantity, their price being very easily influenced by the two producers: South Africa and the CIS. The narrowness of the market favors speculation, which is why the two metals can only be recommended to brave investors.

6.3.3. Financial transaction in gold

Regarding gold, it is specified that worldwide it is presented in a multitude of typical forms, which can be grouped as follows: standardized, for industrial purposes or for investments and non-standardized or innovative, with the most diverse forms, many of which have decorative elements applied. These have small dimensions and weight, usually in the order of grams or tens of grams and are presented in the forms of: decorated plated, pendant bars, commemorative bars, card plated, animals, hologram bars etc.

he main financial transactions with gold carried out on the stock exchange are:

- forward operations: take place directly between the producer and the metal trader, using as collateral an open credit line for gold transactions. The operation takes place on the basis of a contract concluded between the parties for the physical delivery of the metal, in advance of the moment of payment. The price of standard bars on the date of the transaction is used. This operation is usually practiced as protection against fluctuations in the price of gold.
- gold loan operations: the producer makes a physical loan of gold, which, at the established term, is subsequently returned to the one who granted the loan and thus reintroduced on the market. The purpose of this action consists in the immediate sale of the borrowed quantity, the capital obtained being used to expand the extractive capacity. Part of the extracted gold is used to repay the loan;
- hedging operations: the producer sells part or all of the production estimated to be obtained over a period of several years. This operation is carried out through a bank to which the producer is contractually obligated to deliver quantities of gold on established terms. The bank, based on the agreement concluded, borrows quantities of gold from a central bank and sells immediately. The resulting money is placed in deposits until the moment when it is to pay for the gold delivered by the producer. The difference between the interest rate (higher) charged for dollar deposits and that for gold deposits (lower), allows the bank to grant a premium at the daily price. The gold received by the intermediary bank from the producer is returned to the central bank. The procedure has proven to be profitable in the long term, bringing greater benefits to the producer than selling it when he would have physically owned it. This advantage is justified by the fact that in the last decades the price of an ounce of gold has had a more downward trend, to which is added the premium granted by the bank at the daily price;
- OTC market operations: transactions on a secondary market with securities not listed on the stock exchange, of the "OTC counter transactions" type. The secondary market is understood to be a component of the capital market on which financial securities are sold/bought, after they have been issued to the original investors. Unlike standard options practiced on the stock

exchange, OTC options do not have a fixed expiration date, and thus cannot be identified by those who analyze the gold market, thus protecting producers who use hedging operations from the risk of an increase in the price of gold occurring before the maturity of the physical contract. Another type of operation that can be carried out on the market is the conversion of silver into gold, which means selling it at a given amount and buying a quantity of gold, equivalent in value. The choice of the right moment to carry out this operation is dictated by the ratio between the price of gold and that of silver. Depending on the value of this ratio, the amount of gold equivalent in value is greater or less. Thus, the lower the value of the ratio, the greater the amount of gold equivalent.

Value investments

These operations are carried out in order to preserve the purchasing power of money, or speculative actions. Unlike other types of investments (bank deposits, government bonds, shares), those in gold represent real value and a major advantage compared to paper banknotes. Thus, gold cannot be depreciated, through inflation, by governments that for economic reasons, order the devaluation of banknotes by printing large quantities of money without coverage. History has proven that the value of gold is preserved over time, surviving calamities caused by nature and man.

Validation or investment placements can be made by individuals, legal entities or governments, through gold purchases, for which gold bars and coins are used. As shown, bars have various weights, with 10 types of standard sizes with a 995% fineness. 12.5 kg good delivery bars are used for hoarding in central banks, and small-sized bars (the smallest is 8 grams) are used by individuals as small investors. Gold bars and bars are sold at the value of the gold they contain.

Gold coins, representing the second form of investment, come in various sizes and weights, bearing insignia and inscriptions on both sides. They can be made of 24K gold or gold in alloy form. Coins intended for hoarding, called "trillion coins" on the precious metals market, represent coins minted in the 20th century, especially for those who want to make small investments. The advantages of this investment instrument are related to the fact that they are easy to keep, easy to recognize and can be sold faster. A certain disadvantage is determined by their valuation at a price 5-20% higher than the value of the gold they contain. The most famous coins for hoarding are: Krugerrand (South Africa) of 24 K and weighing 31.1035 g, 4 ducats (Austrian Empire), 50 pesos (Mexico) weighing 37.5 g and other coins minted today and which were in circulation in the past.

The history of gold coins dates back more than 2500 years, so to date more than 1200 states have minted over 20,000 different gold coins.

6.4. Conclusions

The precious metals market is one of the main factors in the efficient functioning of the national economy. In our country, its main function is the accumulation of precious metals in the state register, which makes it possible to carry out operations on the world precious metals market, which is truly necessary in the era of globalization and European integration.

he banking metals market in Romania is more of a cash nature. The use of direct and indirect methods in Romania influences the regulation of the precious metals market.

In recent years, many Romanian banks have already gained some experience in conducting operations in the banking metals market. But its level of development compared to the world metals market is still insufficient. The development of the domestic banking metals market is

constrained not only by objective (insignificant socio-economic level of well-being of potential market participants), but also by subjective factors. These include the insufficient practice of using banking metals, in particular: guarantees, obtaining loans, placing deposits, the insignificant level of development of the infrastructure of the Ukrainian banking metals market.

Chapter 7. Functions of precious metals in the economy. Monetary standards

7.1. Functions of precious metals in the economy

7.1.1. Functions of precious metals

Depending on their purpose and use, precious metals can perform several functions:

– Industrial function, when precious metals are used as raw materials (commodities) in industrial activities for the manufacture of certain goods. All four metals analyzed (gold, silver, platinum and palladium) are also found in this situation. They are presented in the form of bars, ingots, other forms derived from them and do not necessarily have the dimensions and the "good delivery" stamp, certificates that raise its selling price

– Investment instrument, in which metals are used by individuals or legal entities, or by international organizations, for the purpose of making valuable investments. Precious metals for investment are presented in the form of bars, ingots, plaques and coins, quoted on one of the markets of the European Union. Their precious metal content was shown in a previous chapter. Investment operations with precious metals are carried out both through physical delivery and through operations in precious metal accounts or securities expressed in these metals, held by banks. The order of preference of investors for these metals is: gold, silver, platinum and palladium.

In terms of gold, investments cover a very wide spectrum, starting with the purchase of a gold coin, to portfolio investments of government bodies that can amount to hundreds of tons of gold, by "portfolio* being understood shares or bonds held by a bank or a company with the aim of obtaining an income from dividends, interest or exchange rate differences.

The attitude towards investments in gold varies from one geographical region to another. Thus, if in Europe these are presented in the form of simple deposits in metal accounts or as a component part of the portfolio held by a private bank, in Asia they can take the form of physical holdings.

With the year 1972, when the link between the dollar and gold was broken, the demand for investments in gold became a determining factor for the increase in the price of gold in the period after 1990 there were changes in the concept related to the investment in gold, in the sense that due to a relative political and economic stability, gold funds in Europe and the USA opt for holding shares in gold rather than the metal itself. In Asia, due to the uncertainty that dominates the Arab world, there is no other alternative than investing in physical gold. Thus, investors in Hong Kong, Indonesia, Taiwan, Thailand and even Japan bought over 1000 tons of gold for investment purposes, to which are added other undeclared deposits (deposited in London).

The financial function represents the gold purchased and used as an investment instrument in order to constitute a reserve of purchasing power. According to the European System of Integrated Economic Accounts, it is presented in the form of bars, ingots or coins with a fineness of 995%, accompanied by a guarantee certificate and the smelter's mark. All institutionalized (public) sectors can hold financial gold.

Monetary gold is that part of financial gold used as assets and held as official reserves by monetary authorities or other entities under their control. Monetary gold is usually presented in the form of coins with a fineness of 900% ingots, as well as standard bars with a fineness of at least 995%. Monetary gold transactions consist of purchases and sales made only between monetary authorities (e.g. central banks, international financial institutions).

To be considered among the values that are traded financially, it must be the subject of a market, official or not, but authorized and organized, so that potential buyers or sellers have the daily opportunity to purchase or sell financial gold at prices established at regular intervals.

Monetary gold is a financial asset (international reserve) only for central banks or central administrations that carry out operations specific to central banks, such as: monetary issuance, maintenance and management of exchange reserves and management of exchange stabilization funds. Other French companies may still hold gold considered monetary but only under government control.

According to the System of National Accounts, monetary gold represents an official reserve of countries and can be used by the authorities to engage in international financial operations, as well as to pay off debts. The valuation of the gold stock is made based on the market price, in accordance with the agreements between most countries, abandoning the use of officially fixed prices.

Non-monetary gold represents the result of operations with gold, which is not held as an official reserve by the monetary authorities. Transactions with non-monetary gold are treated as purchases if the gold is used as an accumulation of wealth, or as any other commodity if it is used for commercial or industrial purposes.

It is considered that when gold is sold from reserves to private holders or users, gold is demonetized, and when new quantities of gold from mining or purchases are added to official reserves, gold is monetized.

7.1.2. On monetary standards as a measure of the material values of society

Over time, there have been several types of standards: commodity, metallic, sterling, dollar, etc. The first monetary systems that gave the expected results were established on the basis of precious metals that were used to make coins. The history of banks has known several types of standards made of precious metals, as follows: the silver standard a the gold standard representing the monometallist period and the gold-silver standard, representing the bimetallist period

The silver standard was used in the 16th-18th centuries. In the period before the 1914 gold standard, most European countries already used the gold + silver bimetallism as a standard, after which the first country to adopt the gold monometallist system was England, in 1816. Due to the difficulties related to the use of two monetary systems, in the period 1865-1867 several states decided to adopt the gold monometallist system, the other countries that remained with the bimetallist system having the right to maintain it only as a title.

Thus, gold no longer effectively circulates, being a reserve in the form of bars (ingots) of the issuer of banknotes. Under these conditions, gold coins no longer circulate as a means of payment, but are used as a means of hoarding. According to this system, the definition of the monetary unit is maintained by a quantity of gold, the conversion of banknotes is made into gold ingots, the need for the existence of an official gold reserve in the form of ingots is justified, there are no restrictions on the transfer of funds. The convertibility of banknotes or money into gold was limited by the fact that gold was sold only in the form of ingots, much

heavier than currency, so being much more expensive it could not be purchased by the mass of the population.

In 1922, a mixed form of the gold-bullion standard was adopted, called gold-currency, by which the monetary unit could be defined by a quantity of gold or by a certain stronger currency, convertible into gold (dollar, pound sterling, etc.). In this situation, monetary reserves were held in gold and in foreign currency convertible into gold, also called reserve currencies.

During the 16th-18th centuries, a Dutch silver coin, called the leu-thaler, circulated on the current territory of Romania. After its disappearance from circulation, it was kept as the reference currency for calculations, establishing the name leu which was printed on the reverse of the Dutch thaler.

In Romania, the bimetallic monetary system was adopted in 1867. The leu, being considered as the standard of prices, had: the gold one a content of 0.3226 g of gold with a title of 900% (0.290322 g of fine gold), and the silver one a content of 5 g of silver with a title of 835% (4.175 g of fine silver). The legal value ratio between gold and silver was 1/14.38. Later, in 1380, the National Bank of Romania was established, and in 1889 the bimetallic system was switched to the monometallic gold system. The BR was authorized by law to issue bank notes covered in a proportion of at least 40% in gold. In 1929, Romania adopted the gold-barrel and gold-currency standard, only to abandon it in 1947. Starting with 1947, the gold content of the leu evolved as follows: 0.00594 g gold fim in the period following 1989, respectively towards the end of the last decade of this century, Romania pursued a policy of gradual liberalization, but uncorrelated with the rules of the market economy, of gold operations, trying to overcome the state monopoly phase. After more than 10 years of liberalization policy, from a legal point of view, the law that established the state monopoly regime over these operations in 1978 is still in force, a regulation that operators in this field do not take into account.

The functioning of the bimetallistic system necessarily required the establishment of a value ratio between gold and silver so that when measuring the value of a product, an equivalent could be established between the number of gold coins or the number of silver coins corresponding to its value. Since maintaining a fixed ratio was quite difficult to achieve, and economic evolution required a functional and rapid monetary system, silver as a standard began to lose ground to gold, being replaced in the last instance by banknotes in the sense of "credit note", paper money and checks.

The different values of the gold-silver ratio established by the countries that still used the bimetallic system caused over time the migration of gold or silver coins from one country to another, causing disruptions in the monetary systems. Thus, the fact that in France the ratio was 1/15.5, and in the USA it was 1/15 meant that gold was better valued in France and as a result gold coins from the USA flowed into Europe, practically transforming the American monetary system into a silver monometallic one. After several fluctuations like those shown above as well as the unsuccessful attempt to switch to an inconvertible standard in precious metals, resulting in the depreciation of the dollar, in 1879, the gold standard was switched.

After the period 1900-1914, considered the golden age of gold monometallism, the First World War followed, when the belligerent countries abandoned the gold standard for economic reasons. The attempt to return to the gold standard after the war was not crowned with success due to changing social and economic conditions. The limited production of gold offered by the extractive industry led to a chronic shortage of gold that affected the economic growth of the countries and international trade. The economic crisis of 1929-1933, caused by overproduction, falling prices, unemployment and state interventions in economic activity, in order to avoid the

crisis, no longer agreed with the mechanisms of the gold standard, which was characterized by a deflationary effect (decrease in prices). The concentration of gold reserves in economically developed countries (two-thirds of the world's total amount of monetary gold was in the treasuries of five countries), favored their economic and political expansion. The aspects presented, as well as others such as the circulation of gold associated with unlimited convertibility, could lead to situations in which holders (individuals) would request large quantities of gold for exchange, causing a gold outflow capable of considerably restricting the money supply or limiting the ability to make external payments. These led to the introduction of restrictive measures.

In fact, the introduction of the gold-bullion standard represented the first form of restriction of convertibility into gold. Its concentration in the treasuries of central banks and the limitation of convertibility reduced the functions of monetary gold domestically, which was increasingly used in international relations. The second restriction was the introduction of the "limited form gold-bullion" standard, which, in certain situations, prohibited the export of gold, and the convertibility of money into bullion was carried out only in certain cases regulated by the legislation in force.

The year 1936 is considered representative because it practically means the disappearance of the gold standard. It is interesting to emphasize that in the USA, considered today as the most democratic country, very harsh measures were taken. Thus, in 1934, the internal monetary functions were abandoned by prohibiting the circulation of gold as money and its possession in the form of bullion for monetary purposes or as a means of investment by private individuals and legal entities, maintaining only the function of the dollar standard. Operations with gold, with the exception of the one that fulfilled the function of a commodity, became an exclusive right of the state, therefore a monopoly. Gradually, in all countries, the money supply in circulation was no longer quoted according to this metal. In 1970, the USA also repealed the obligation to cover money in gold, as well as the restrictive regulations established in 1934 regarding the marketing and keeping of gold as a means of investment for private individuals and legal entities..

In 1944, the foundations of a new international monetary system were laid, which led to the formation of the International Monetary Fund (IMF). According to its statute, its main objectives were:

- to promote international monetary cooperation;
- to facilitate the expansion and balanced growth of international trade;
- to promote and maintain high levels of employment and real incomes;
- to develop the productive resources of member states as a primary objective of economic policy;
- to promote exchange stability and avoid competitive depreciation of exchange rates
- to organize a multilateral system of payments for current transactions between parties and to eliminate exchange restrictions that hinder the growth of world trade;
- to temporarily make available to members the general resources of the IMF, on a guarantee basis, in order to enable them to correct imbalances in their balance of payments without resorting to measures that would affect national or international prosperity.

In the new vision, gold has an important role as an international reserve for financial transactions between countries, and can be considered as an international currency, alongside the US dollar. This new vision actually represents the generalization of the gold-currency standard principle and was based on the fact that the dollar had become the strongest currency,

and the official US gold reserves had increased considerably, being about 22 times larger than those of the main European countries.

The gold status mainly included the following references: the national currency of the member states must have a legal definition (parity), calculated in gold or dollars, taking as a basis the gold content of a dollar in July 1944 (0.888618 fine gold); trade in gold and coins between IMF member countries must be carried out on the basis of rules established by the statute: for bars priced at 35 S/ounce, coins at prices that vary by no more than +1% compared to parity; the volume of the international monetary reserves of the member countries had to correspond to the needs of balancing the balance of payments, being made up of: monetary gold, convertible currencies (usually the dollar) and later a new reserve asset called SDR; the American authorities ensured the convertibility into gold of dollars held by the central banks of the member countries at the fixed price of 35 S/ounce.

In the following period 1950-1970, as a result of the provision in the agreement that ensured the convertibility of dollars into gold by the USA, European countries were given the opportunity, after their main currencies became convertible, to massively purchase dollars which they later converted into gold. Thus, 58% of the US gold reserve returned to European countries. At the same time, the dollar also decreased, as a result of the deficit of the American balance of payments and the reduction of the level of gold reserves, followed later by the devaluation of the pound sterling. Under these conditions, those who held funds preferred to invest in gold.

The following period was characterized by a high demand for gold, which determined the increase in the price of this metal on the free market, forcing the central banks of the main Western countries to remove significant quantities of gold from the reserve in order to temper the increase in the price and maintain it at the official level of 35 S/ounce. In 1969, the IMF introduced a monetary instrument, called SDR-special drawing right, with the aim of creating a unit of account and reserve intended to supplement international gold and foreign exchange reserves. The ownership and circulation of SDRs are limited to official institutions, with private individuals not having access to them. The valuation of this new monetary instrument was initially based on a content of 0.888671 g of fine gold, equal to that of the dollar in 1944, after which, in 1974, the definition by gold was abandoned and a daily valuation was carried out, based on a so-called weighted currency basket. This is the basis for creating an artificial standard of value instead of the "gold standard", which was demonetized, and the "dollar standard", which is unstable and consists of choosing representative currencies followed by establishing their weight within the currency basket.

Member countries, central banks and other official bodies can use the SDR to carry out the following operations: buying convertible currency from other member countries; redeeming their own currency from abroad; obtaining an equivalent amount in foreign currency from another country; paying taxes, interest and commissions to the IMF. Thus, it can be concluded that the SDR was created so that at least part of the international liquidity would no longer be influenced by the national policy of the currency-detonating state, such as the USA, as well as by gold reserves under the conditions of the existence of the gold standard.

Starting with 1971, the central rates of Western currencies were no longer quoted in gold, which lost its role as an international monetary standard. However, only two years later the dollar devalued again. This decision practically led to the blocking of official transactions with gold. Central banks could not carry out transactions on the free market and under conditions in which the free market price was double the official one.

In 1974, the EEC member countries agreed on the possibility of using gold in the regulations between the community central banks, so that the IMF then decided that the official monetary gold reserves of the states could be used as a guarantee for obtaining international loans, by evaluating at the market price.

Finally, in 1978, the IMF decided to give up the function of the gold standard for the international monetary system and to cancel the mandatory payments in gold of the member countries to the IMF, which allowed the central banks of the member countries to trade gold at the market price, the gradual liquidation of the monetary gold stocks of the IMF and the central banks.

Of course, all this history, related to the evolution of the monetary standard and especially the gold standard, was not exempt from controversies and long disputes for and against the gold monetary standard. These different positions were reflected in the changes made over time to the IMF statute. Beyond the needs to correct functional imperfections of the gold standard, the position of some parties was often dictated by economic or political interests. Thus, the USA, which fervently supported the elimination of monetary gold, had the interest of continuing to maintain the supremacy of the dollar, eliminating the instrument that allowed the official measurement of its declining purchasing power. On the other hand, France claims, on the contrary, that gold is the basis of the international monetary system, the denial of its usefulness being refuted by market reality. In the same context, some economists believe that the elimination of gold from monetary systems is the cause of the imbalances that caused large-scale inflations, such as those of the 1960s and 1970s, while others believe that maintaining gold can lead to deflation and consequently to overproduction crises such as the one of 1929-1933. In fact, the struggle of interests for the seizure of the international payment system means gaining supremacy for world domination.

Despite the decisions taken by the IMF, there is a lack of interest in putting them into practice. Thus, no central bank has rushed to significantly reduce its gold reserves, with the exception of the USA and Portugal, which have capitalized on a certain amount of metal, but in order to overcome some financial difficulties. On the contrary, there is an intention to use the international gold reserves of some central banks as collateral for contracted loans. It should also be highlighted the remark of some analysts who emphasized that the banks that most resolutely maintain their gold reserves are those with the highest degree of independence, namely the central banks of the USA, Germany, Switzerland.

7.1.3.Conclusions

Precious metals are important components of portfolio investments for both individual and institutional investors due to their physical and chemical properties, which allow them to play the role of a reliable hedging instrument for long-term prospects. As for the effectiveness of precious metals as investment instruments, they should be invested not only for hedging, but also in periods when there are high risks to profit. At the same time, the impact of economic and political situations, financial instability should be taken into account in relation to the profitability of precious metals. Analysis of price trends in the precious metals market has shown that price fluctuations are different for each metal, as it is formed under the influence of supply and demand and market conditions in general. It is important that supply and demand react differently to price fluctuations. Central banks and stock exchanges are active participants in the precious metals market.

The process of trading metals on the stock exchange is a complex and multifactorial process, each participant has its own functions and traders must have certain knowledge to make predictions about their price.

7.2. Silver - demand, deficits and surpluses, waste recycling

7.2.1. Demand

Ag demand is defined in this report as the sum of its industrial components, photography, jewelry, and silverware, and therefore excludes all coins, medals, and bullion and bar demand. The reason is that coins, medals, and bullion demand are investment categories more suited to analyzing their relationship with the silver price.

Between 1990 and 2022, manufacturing demand accounted for an average of 86% of total silver demand. Taken in isolation, this might suggest a close relationship between the level and changes in manufacturing and silver prices. However, the data tell a more nuanced story. While manufacturing and price are negatively correlated, as expected, the correlation values over the period 1990-2022 for both levels and series changes are not significant at just -0.09 and -0.12, respectively. (The correlation for changes at -0.18 is little changed for 1990-2003, when manufacturing's share of total demand averaged 95%).

The fact that there is only a weak negative correlation is not surprising given that the majority of silver production was industrial and photographic demand (an average of 69% for 1990-2022). These demand categories were driven much more by technological developments than by silver prices. Hence, manufacturing demand was constant from 2003 to 2008, despite a tripling of the price and its remarkable resilience in 2010-12 to the rise in the price of silver. Furthermore, industrial demand and, to a lesser extent, demand for jewellery and silverware are strongly influenced by changes in industrial production and GDP growth. This does not mean that manufacturing demand is price insensitive. Its jewelry and silverware component certainly does so even more these days, as much of that demand has shifted to India and China, where consumers are more price-sensitive and items are typically sold at lower margins. And even when it comes to industrial demand, higher prices over time can lead to savings and, in a few cases, total substitution. Photovoltaic demand was the first to experience the rise in silver prices, and the amount of silver used in solder alloys has long since declined due to substitution by cheaper alternatives.

Looking ahead, manufacturing demand can also potentially have a significant impact on the final price if it exceeds the supply from mining and scrap. The precedent for this was in the 1990s, when increased manufacturing demand and a reduced supply from silver mines and scrap led to large market shortages that depleted bullion stocks on the market, setting the stage for a larger price increase. With investment demand still reasonably high (implying a general market surplus), such a scenario may seem unlikely, but a derivative of it is plausible. This would be based on continued high levels of manufacturing demand and net demand for silver bullion and coins (i.e., the Net Physical Investment category in the World Silver Survey) plus stable ETF holdings, which together would require a reduction in other bullion stocks overall, but silver demand and supply to be in balance. This would, over time, lead to upward pressure on the price if the other conditions mentioned above remained in place.

7.2.2. Deficits and surpluses

The silver market tends to move through cycles of shortages and surpluses. These are caused by changes in the main components of supply and demand that can result in extended

periods when there is a requirement to withdraw bullion stocks to fill a shortage or when a surplus results in a build-up of bullion stocks.

In the 1950s and early 1960s, the supply from mining and scrap was insufficient to meet industry's demand for silver. The deficit in those years was covered by government sales, particularly from the United States. From the late 1960s to the early 1970s, the silver market was in surplus, with excess silver being purchased by investors. Some of these inventories were later liquidated in the 1970s, as the market was in deficit and needed additional supplies of the metal. Higher silver prices were needed to remove silver from inventories. From the late 1970s to the mid-1980s, the silver market had a substantial surplus. Higher prices reduced manufacturing demand and stimulated additional supply from mines and recycling. Investors were eager buyers of silver in an (initially) environment characterized by rising silver prices, high inflation, and negative real interest rates. The subsequent decline in silver prices for a period simply encouraged more investment as investors bet on a price rebound. In contrast, in the 1990s, the market went into deficit, and this was complemented by a substantial decline in investors' bullion holdings. The depletion of much of the bullion stock near the market in that decade facilitated a price recovery in the following decade. In the period since, the market has returned to a substantial surplus that has been absorbed by very high levels of investment demand.

Taking the 1990-2022 data on deficits and surpluses—defined in this report as the difference between supply from mine production plus scrap and manufacturing demand, excluding coins and bars—shows a strong positive correlation between bar surpluses and the price of silver. A correlation coefficient of 0.86 for price levels and surplus/deficit is not surprising, given the prominent role of investors in determining prices. (Regression analysis also shows a strong relationship with an adjusted r-square of 0.72.) As will be noted, the most important component in the 1970s of these swings back and forth from surplus to deficit was investment or divestment. It is also worth noting that while higher prices were needed in the 1970s to stimulate supply from investors' bullion stocks, the same was not true in the 1990s, when selling from stocks was driven more by low price expectations and a desire to raise cash for more promising investments.

7.2.3. Waste recycling

Aboveground silver reserves can be divided into two main categories: manufactured products and bullion (ingots and coins). The aboveground stock of silver in manufactured products is enormous. In the period 1990-2023 alone, 25,600 Moz (725,747 tonnes) of raw silver were converted into manufactured products (excluding bullion, coins and medals). The World Silver Survey database for the last 40 years, from 1950-1989, shows that another 13.448 billion ounces (381 tonnes) were used for industrial purposes in (excluding communist bloc countries). To this figure of 39 billion ounces (1,143 tonnes) could be added the manufacturing demand in communist bloc countries before 1990 and the inherited stocks worldwide accumulated over the centuries, before 1950, which in this latter case would consist mainly of silverware.

However, while in theory a good deal of this seemingly huge pool of metal could be available on the market, in practice the reality is very different. First, a not insignificant portion of the silver produced since the 1950s will already have been recycled. Based on an analysis of historical data, the cumulative recycling over these 70+ years has been the equivalent of just under a fifth of the total production, excluding coins, over the same period. Second, most of the legacy silver is found in religious objects which will not usually be recycled, regardless of the

price of the silver. Third, when it comes to a large proportion of industrial products, the silver content is generally too low to warrant economic recycling, and where it is not, recycling is driven more by end-of-life and environmental considerations than by any price factor.

The recycling and price data confirm the above observations that the level of recycling is only to a limited extent related to the level or change in the price of silver. (At 0.29, the correlation coefficient for the levels is positive but quite low, while the figure for the changes in the two series between 1990 and 2022 is 0.52.) Experience during the last major silver market also demonstrates that even the very rapid growth and high prices of silver have had a relatively small impact on the supply of silver scrap. For example, at its peak in 2011, at 223 Moz and an average price of $35/ounce that year, silver scrap was only 10% higher than it had been in 2008, when silver averaged $15/ounce. Indeed, independent of price, other factors have intervened in stimulating recycling volumes, such as the transformation of silver halide photography to digital technology (leading to a halving of the amount of silver waste from this source since 2012) or the substantial increase in ethylene oxide capacity (80% between 2010 and 2022) and the associated jump in the recycling of these silver-rich catalysts.

7.3. Conclusions

Silver is less correlated than gold to the economic and financial factors that drive financial asset prices. It is more closely correlated than gold to those factors that typically drive commodity prices. And while silver is the most volatile of the Au-Ag pair, due to its larger trading range, gold and silver typically move in the same direction.

In the 1970s, a general increase in the price of silver led to a depletion of the bullion stocks that had been accumulated in the 1960s. In 1979, the increase in the price prompted both profit-taking by existing holders and fresh buying by new investors, but with a net increase in bullion stocks. 1980 and the rest of that decade were characterized by a considerable increase in stocks held by investors, despite the downward trend in the price of silver. The 1990s, by contrast, saw a depletion of these bullion stocks as investors eventually gave up hope of a return to a major silver market, or those who inherited these positions liquidated them to invest in other assets or to finance consumption. It is certainly the case that the rise in bullion stocks cushioned the decline in silver in the 1980s and exacerbated the bear market in the 1990s. Since 2008, bullion stocks have risen substantially as investors have been net buyers of silver year after year. (Government sales, which were substantial from 1999 to 2006, have been small for the past 15 years.) The steady increase in stocks has occurred during a period when silver prices have, for the most part, been highly volatile. Investment demand has largely eliminated all of the excess silver available on the market. Occasionally, such as in 2015, bargain hunting, particularly in India, has dominated investment and the associated build-up of implicit bullion inventories. This has helped to establish a price ceiling when silver has been under pressure. At other times, the build-up of inventories has been more closely tied to investment driven by rising silver prices, particularly in 2020.

Conclusions, own contributions and future research directions

General conclusions

In the doctoral thesis, entitled "Innovation Management with Applications in the Development of Products for the Protection of Noble Metals", the scientific approach had two major components:

- exploration and implementation of innovative strategies, namely the use of plant extracts as natural protective agents for noble metals (corrosion inhibitors) and demonstration of their effectiveness.

- analysis of the dynamics of the precious metals market on the national and international economy, respectively, in order to understand the factors that influence their price and their economic role.

In the context of carrying out a complex study to demonstrate the effectiveness of the use of plant phytoconstituents as natural corrosion inhibitors (objective 1 of the thesis), various constituent parts of the ***Lavandula* L.** (lavender) and ***Mentha piperita*** (peppermint) plants were used as plant materials. For obtaining plant extracts, both lavender and mint are excellent choices due to the ease with which they can be cultivated and processed.

- The conclusions obtained from the experiments can be summarized as follows (for objective 1 of the thesis):
- Both the extracts obtained (by two extraction methods – classical at temperature and microwave-assisted extraction) and the essential oils were analyzed by various chromatographic techniques. The results obtained supported the hypothesis of using essential oils in the acrylic resin layers with a protective role (Paraloid B44 and Paraloid B72) for silver discs, since they present a much broader spectrum of phytoconstituents.
- The characterization of the silver substrates was performed by X-ray fluorescence (XRF) and scanning electron microscopy with EDX accessory (SEM-EDX) to confirm the purity of the silver discs used in the tests.
- Gloss studies were also performed (using a PCE-GM80-ICA glossmeter), while Fourier transform infrared spectroscopy (FTIR) analyses were performed to evaluate the composition of the developed coatings.
- Corrosion resistance was determined by the polarization resistance technique (Tafel technique), using a saline solution (NaCl 3.5%) as electrolyte.
- All coatings have a more electropositive potential than silver, highlighting that regardless of the nature of the coatings, they improve the corrosion resistance of the substrate. The most electropositive values were recorded for the type 2 resin-based coatings, Paraloid B44 – samples coded R2.

Electrochemical measurements showed that the most electropositive potential and consequently a better electrochemical behavior is that of the R2 sample (198 mV), followed by the R2-M (27 mV) and R2-M-L (22 mV) samples. It is also noted that the coatings for which Paraloid B44 was used have lower values of the Ecor parameter than those based on Paraloid B72. Thus, among the coatings based on Paraloid B44, the R1-M-L sample stands out, which recorded the most electropositive Ecor (20 mV), followed by the R1-M sample (−40 mV) and the R1 sample (−42 mV).

Thus, from the analysis of the evolution of the Ecor parameter, it is observed that the use of Paraloid B72 leads to a better electrochemical behavior, compared to Paraloid B44. It is also noted that the addition of essential oils of mint and lavender have different effects

depending on each type of acrylic resin used. Thus, when essential oils are added to Paraloid B72, the potential values are more electronegative, highlighting a weaker corrosion behavior compared to the resin without oils (sample R2), while the coatings based on Paraloid B44 show more electropositive values after the addition of oils, compared to the coating without oils (sample R1).

It is observed that all coatings, regardless of their nature, lead to a considerable improvement in electrochemical behavior, with icor values decreasing by several orders of magnitude. It is also observed that the introduction of mint extract leads to a decrease in icor regardless of the type of resin and the introduction of lavender extract causes the icor values to increase slightly but do not exceed the value recorded in the case of coatings based on resin alone.

If we take into account the value of the corrosion potential (Ecor), it is considered that more electropositive Ecor corrosion potential values present a better electrochemical behavior. From the studies carried out, it is observed that all coatings have a more electropositive potential than silver, highlighting the fact that regardless of the nature of the coatings, they improve the corrosion resistance of the substrate. From the physicochemical analyses it can be observed that the addition of essential oils does not negatively influence (degrade) the polymer base, thus maintaining the Paraloid samples. The synthesized materials do not affect the aesthetic effect of the silver support. From the analysis of electrochemical parameters it can be seen that all coatings, regardless of their nature, have an increased resistance to silver corrosion, and lead to an improvement in the electrochemical behavior of silver.

Precious metals trading on the stock exchange, in the near future. is defined by processes of digitization, tokenization, as well as the integration of Environmental, Social, and Governance (ESG) criteria, thus transforming the way precious metals are owned, bought, and sold. This evolution aims to increase accessibility, transparency, and operational efficiency.

Own contributions

The original elements of this thesis can be defined as follows:

1. Innovative approach to innovation management for precious metal protection

The thesis introduces and explores an integrated innovation management strategy applied to the field of precious metal protection. Adapting and implementing a model for the development of eco-innovative technologies represents an original contribution, facilitating the large-scale development process.

2. Use of plant extracts as protective agents on noble metals

One of the most significant innovations consists in demonstrating the potential of plant extracts (lavender and mint) as active substances for the formation of protective films against corrosion of noble metals (silver case study). Although the use of plant extracts in the protection of metallic bodies has been explored previously, their specific application on precious metals, with the clear demonstration of efficiency, represents an original contribution.

3. Development of natural and sustainable formulations for the protection of noble metals

The thesis proposes and tests new compositions based on plant extracts (lavender and mint), optimized to provide an effective barrier against corrosion, being among the first to combine this approach with the principles of sustainability and ecological protection, for this type of formulation (acrylic resins type Paraloid 44 and Paraloid 72). The contribution consists

in creating environmentally compatible solutions, with potential for integration into existing industrial processes.

4. **Practicability and applicability in industry**

The thesis advances a "proof of concept" approach with potential for practical applicability, the technologies being feasible for industrial implementation.

5. **Contribution to the development of new technologies in the field of ecological protection**

Finally, the original contribution consists in positioning the research as an important advance in the field of bioinspired protection, promoting a protection model based on natural resources, with reduced impact on the environment, and opening perspectives for future research in the field of sustainable materials and environmental protection.

6. **Contribution to the way in which annual reports are made as well as the analysis of transaction costs specific to alternative markets dedicated to trading metals on the stock exchange.**

The process of trading metals on the stock exchange is a complex and multifactorial process, each participant has its own functions and traders must have certain knowledge to make predictions on their price, which implies a series of commissions, financial contributions, as well as tax obligations.

Future research directions

- Regarding the development of future research directions, these will be achieved through:
- Evaluation of the possibilities of transposing the experiments to a pilot scale;
- Evaluation of the possibilities of developing protective materials for other types of metals;
- Use of IA to analyze trends and automatically execute precious metal trading orders based on data provided in real time.
- Recycling precious metals and trading them through the stock exchange, which thus becomes a hub for recycled precious metals, thus supporting the circular economy.

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