

Article

Stainless Steel Deposits on an Aluminum Support Used in the Construction of Packaging and Food Transport Containers

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Abstract: A series of chemical elements from the chemical composition of the packs of liquid food products migrate inside them or they combine with other chemical elements existing in the food, resulting in chemical compounds that worsen the quality of the food. In the present paper, layers of food stainless steel were deposited using thermal arc spraying on an aluminum alloy substrate to stop the migration of aluminum ions inside liquid food products. The physical-chemical and mechanical properties of the protection system: stainless steel layer used in the food industry (suggestively called: food-grade stainless steel)—aluminum substrate were investigated, and then the organoleptic properties of the food liquids that came into contact with the deposit were evaluated. It was found that food-grade stainless steel deposits have low porosity (3.8%) and relatively high adhesion and hardness, which allows complete isolation of the substrate material. The investigations carried out on the properties of food liquids that come into contact with the stainless steel deposit revealed the fact that it perfectly seals the aluminum start. The food-grade stainless steel coating (80T) was much better and safer for preserving dairy products maintaining a constant acidity up to 17 degrees Thorner, wines (with an average acidity of 3.5–4 degrees), juices (with natural pigments), and oils (with a good absorbance level correlated with clarity). This aspect suggests that the created system can be successfully used to manufacture containers for the transport of liquid products.

Keywords: coating; food-grade stainless steel; packaging; food transport containers



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1. Introduction

In recent years, there has been an increasing demand for fresh food products, packaged and transported in containers that are biologically, chemically, and physically safety [1].

In the food industry, there are two types of packaging on the market: (a) packaging that comes into direct contact with food products, made of some aluminum alloys, food-grade stainless steel, or even plastic materials [2]; (b) coated packaging, (which doesn't come into direct contact with food products), made of materials such as cardboard or polymers covered with a thin foil made of food-grade stainless steel, steel plate covered with a thin layer of chemically inert varnish or steel sheet covered by physical processes of vacuum deposition [3].

The use, in the construction of transport containers, of traditional materials (aluminum, paper, biodegradable composite materials, etc.) covered with different layers that are chemically inert and resistant to the physical, mechanical, and thermal demands of the operating environment represents both a sustainable alternative solution necessary to reduce environmental pollution and a solution to avoid the use of non-degradable plastic packaging, generated by the petrochemical industry [4]. The latter, as it is known, by their non-biodegradable and non-recyclable nature, generate huge amounts of waste that eventually end up in landfills or in the oceans, representing a serious threat to the soil,

aquatic life, and biodiversity [5–7]. It is known that the choice of material for making the necessary containers for the transport of food products is made depending on the nature of the transported food product, its physical and chemical properties, as well as the nature of the mechanical demands that occur during transport [8,9]. The function of mechanical protection of food products can be exercised by using packaging made of metal materials, glass, wood, cardboard, plastic materials, or complex composite materials. The attractiveness of aluminum packaging in its pure form or alloyed with manganese [10], with thicknesses over 6 μm , is due to both the high barrier properties—for food products—and its high mechanical properties (resistance to traction, compression, shear, shock, vibrations, etc.) compared to other packaging made from traditional materials. Aluminum is used to obtain food packaging in various forms, such as collapsible tubes, bottles, caps, closures, retort pouches, and laminated and metallized films, which are discussed in the following sections.

The negative impact of aluminum on some food products or on the environment causes it to be used in reduced proportions or to be used covered with different reproducible layers made of metallic materials, oxides, or thin films (which contain chemically inert nanomaterials) [11]. These protective systems, allow both the use of aluminum alloys in the manufacture of receptacles for transporting food and their recycling [12]. Thus, Santos JS et al. [13] deposited aluminum oxide films containing small amounts of silver by electrolytic plasma oxidation of aluminum (97%) in different electrolytes (sodium citrate, citric acid, and sodium silicate containing Ag nanoparticles (Ag- NPs) or Ag^+ ions (AgNO_3)), having as purpose the synthesis of some bactericidal coatings over aluminum for food packaging applications. Zhijian Y. et al. [14] comparatively studied Al_2O_3 and Al_2O_3 -Al composite coatings obtained by atmospheric plasma jet spraying. The results indicated that the addition of Al powders to Al_2O_3 was beneficial for reducing the flattened particle sizes and increasing the deposition efficiency. The Al_2O_3 -Al composite coating presented homogeneously dispersed pores, and the sputtered Al particles were considered to be distributed within the flattened particle boundary. Compared with the Al_2O_3 coating, the composite coating showed slightly lower hardness, while the coexistence of the Al metal phase and the Al_2O_3 ceramic phase effectively improved the hardness, strength, and wear resistance of the coatings [15]. However, Marogu N. et al. [16] showed that the quality and safety of wine are affected by the materials that come into contact with it by performing tests on different materials, such as polyethylene terephthalate (PET) bottles, aluminum glasses, cardboard boxes, food-grade stainless steel vats, and oak barrels. Their paper demonstrated that although the materials from which the storage receptacles are made should protect the wine from any chemical, physical, or biological danger and keep its composition stable throughout its shelf life, there are still cases when certain migratory chemical compounds of industrial origin—such as phthalate plasticizers, monomers (bisphenol A), antioxidants (Irganox 1010), low amounts of Al_2O_3 , degradation products, oxidation products (nonylphenol), polyurethane adhesive by-products, oligomers, and inorganic elements—contaminate the wine, thus affecting safety or altering its organoleptic properties [17]. Burrell SA et al. [18] showed the variable presence of aluminum in milk transported in aluminum containers (176–700 $\mu\text{g/L}$) as well as their negative effect on children. Redgrove J et al. [19] reported that, in processed milk transported to consumers in aluminum containers, there is a variable aluminum concentration between 49.9 and 1956.3 $\mu\text{g/L}$, responsible for some allergic effects or diseases related to renal failure in infants. An overview of some chemical contaminants—including metals, polymeric contaminants, and biogenic amine contaminants originating from packaging or metal processing equipment—present in some liquid food products is provided by Zheng J. et al. [20]. In general, the materials used to make packaging and containers for storage and transport, as well as the processing equipment in the food sector, must fulfill the following conditions [21]:

- To have a high degree of physicochemical stability, which does not allow the release of foreign substances into the extraction media, which reproduce the exploitation conditions;

- Not to confer toxicity to the food product it comes into contact with;
- To ensure efficient protection for the food product against other accidental contamination during the entire period of processing, storage, and transport of the respective product.

In this work, layers of food -grade stainless steel were deposited by thermal spraying in an electric arc on an aluminum alloy substrate in order to stop the migration of aluminum ions into liquid food products.

Such a protection system consisting of a thin chemically inert layer and aluminum substrate, which would work at temperatures up to 150 °C, could prevent the occurrence of corrosion, the dissolution of aluminum in liquid food products, and would present chemical inactivity. The physicochemical and mechanical properties of the deposition of food-grade stainless steel on aluminum substrate—obtained by thermal spraying in an electric arc—were investigated. This research was extended by carrying out comparative studies on the organoleptic characteristics—for milk, respectively wine and on the color (pigment oxidation)—for juices and oils.

These characteristics were determined after the liquids were stored in aluminum containers and in in containers made of aluminum covered with a layer of food-grade stainless steel obtained by thermal spraying in an electric arc.

2. Materials and Methods

2.1. Materials Used

In order to carry out our own research, aluminum alloy samples—EN AW 2007 with dimensions 120 mm × 180 mm × 15 mm—were covered by thermal spraying in an electric arc with layers of food-grade stainless steel wire, type 80T made by Tafa-Praxair Co., Miami, FL., USA, according to Toma SL et al. [22]. A total of 64 samples were coated. In Table 1, the commercial chemical composition of the substrate and wire material used is presented.

Table 1. Chemical composition of the materials.

Materials	Chemical Compositions (wt.%)										
	C	Cr	Mn	Ni	Si	Ti	Cu	Mg	Al	Zn	Fe
80T	0.12	18	1.5	8	0.5	-	-	-	-	-	Balance
EN AW-2007	-	0.1	0.8	0.1	0.8	0.2	3.7	0.8	Balance	0.8	0.8

2.2. Obtaining Coating

Before being coated, the aluminum samples were previously cleaned by sandblasting with corundum of a grain size of EKF 14 at pressure $p = 3.2$ bar, and then they were chemically cleaned by washing with ethanol in order to eliminate traces of fats. The operation was necessary to ensure the minimum roughness of $R_a = 11.5$ µm necessary to obtain a high adhesion [23–25]. In Table 2, the process parameters used to cover the aluminum samples with a layer of food-grade stainless steel are presented. It can be observed that all the parameters have been kept constant with the exception of the current voltage, which varied across three levels.

Table 2. Technological parameters.

Parameters	Value
Current intensity (A)	220
Voltage (U)	30/32/34
Primary air pressure (bar)	6
Movement speed of the gun (m/s)	0.14
Stand-off distance—SOD (mm)	100
Number of passes	3

2.3. Coating Characterization

It is known that the existence of a layer with reduced porosity and high adhesion determines a perfect sealing of the substrate [24–26]. For this reason, the obtained deposits were characterized microstructurally, their adhesion was evaluated, the microhardness and the degree of porosity were determined.

The microstructural and chemical characterization of the deposits was carried out with the help of an electronic SEM scanning microscope, type Vega II LSH (Tescan s.r.o., Libušina, Czech Republic), equipped with an EDAX spectroscope in order to determine the chemical composition. Thus, after being cut in the transverse plane, mounted in conductive resin, ground, and then polished on the cross-section—in compliance with standard metallographic procedures—the samples were investigated on the cross-section using SEM, [27].

The IQ materials image analysis software, version 1 (manufactured by Media Cybernetics, Rockville, MD, USA) was used to evaluate the porosity of the deposits. Thus, by analyzing the micrographs with an area of approx. 0.1 mm^2 , taken in the bright field at $300\times$ magnification, using the optical microscope Optika SZM2 (made by Optika s.r.l., Ponteranica (BG), Italy)—the porosity of the deposited layer was evaluated, [28].

After porosity determination, on the same samples, Vickers microhardness determinations were performed using a CV-400DAT digital microdurometer (produced by CV Instruments, Zervex, Singapore). A number of 15 determinations were made, using a load of 300 gf, and a penetration time of 15 s—according to Zare MA et al. [29].

The adhesion tests of the deposited layer to the substrate were carried out by tensile testing, in accordance with the European norm EN 582, on a total of 5 samples with dimensions of $40 \times 40 \times 15 \text{ mm}$ [30].

2.4. Organoleptic Analysis of Food Liquids

In order to study if the 80T coating, with different degrees of porosity, tightly isolates the aluminum alloy, we carried out investigations on the chemical composition of the wine and the food oil that comes into contact with the deposition. To determine the chemical composition of the wine and milk, we used the method of inductively coupled plasma-mass spectroscopy (ICP-MS) [31], and the determinations were made as previously described by Pasvanka, K et al. [32]. The method is considered to be a very powerful discriminating technique for the metal content of wine samples [33] and allows the simultaneous determination of several chemical elements with low concentrations present in the samples. In this sense, we used an inductively coupled plasma mass spectrometer ELAN DRC(e) (made by Perkin Elmer Inc. Massachusetts, USA) for fast multielement analysis, with the following characteristics: detection limit $0.001\text{--}0.01 \text{ }\mu\text{g/L}$ and accuracy $<2\%$ for 20 min. In order to determine the degree of protection of each deposition, we analyzed the chemical composition of the wine with the highest acidity (Merlot) and milk—which came into contact for 1 year with the deposited layers, using ICP-MS method.

We preferred to determine first the chemical composition of the food products that came into contact with the protective system of the food-grade stainless steel layer–aluminum alloy substrate in order to identify the deposition that best seals the aluminum from the liquid food product. Then, we carried out comparative studies on the organoleptic properties of liquid food products that came into contact with aluminum packaging, as well as with the deposition characterized by minimal porosity and a high degree of sealing.

The organoleptic analysis of the food liquids that came into contact with the layer of food—grade stainless steel deposited on the aluminum support consisted in carrying out acidity tests as well as tests to determine absorbency. The acidity tests were performed using milk and red wine; the test for determining the level of absorbency used fruit juice; and the test for determining the level of absorbance used oil—according to the rules of good practice in the field. The absorbance level at oils provided better results because the color of the oils has close shades and is transparent. The acidity of the dairy milk products was tested. In a titration glass, 10 mL of yogurt was homogenized with 20 mL of distilled

water (using the same pipette), and a few drops of phenolphthalein were introduced. The contents of the glass were homogenized and titrated with NaOH 0.1 n, until the appearance of a pale pink coloration, persistent for 30 s. Acidity is expressed in Thorner degrees ($^{\circ}\text{T}$) and was calculated according to the formula $^{\circ}\text{T} = V \times 100/v$, where V = mL NaOH 0.1 n used in titration and v = mL yogurt used in the analysis [34]. The principle of the method and reagents is based on the titration of the wine sample with a sodium hydroxide solution (NaOH 0.1 n) in the presence of phenolphthalein—a red indicator (0.02% sol.), after the prior removal of carbon dioxide. The preparation of the sample for analysis consists in removing CO_2 by stirring 50 mL of wine sample in a 100 mL vessel, in which a vacuum is created with a vacuum pump. Agitation should continue for 1 or 2 min, until the release of dissolved gas stops. Procedure: In a 100 mL Erlenmeyer beaker, introduce 10 mL of the prepared wine sample and titrate with 0.1 n NaOH solution under continuous stirring, observing the color change of the sample. When the white wine sample darkens to gray-brown or the sample becomes gray-green, or gray-blue in the case of red wine, remove a drop of sample with a glass rod and mix with 2 drops of phenol red on a porcelain titration plate or on a paraffin glass slide. Continue the titration, drop by drop, trying as above after each addition, until the indicator stops. This means that the neutralization point has been reached. From this moment, more sodium hydroxide is added until the indicator turns pink-orange in the case of white wine samples or pink for colored wines. Calculation and expression of results: total acidity $\times 1000$ (milliequivalents/l), where V_1 is the volume of the 0.1 n NaOH solution used for the titration, in mL; and V is the sample volume taken for analysis, in mL. As a result, the arithmetic mean of the 2 determinations performed in parallel is taken if the repeatability conditions are met [35].

The absorbance measurement of the fruit juice samples was carried out with a UV spectrophotometer. The equipment used for molecular absorption spectroscopy was the Cecil CE 3021 3000 Series UV spectrophotometer (manufactured by Buck Scientific Instruments, Norwalk, CT, USA). The light and color sensations perceived were between 400 and 750 nm in the visible range. The research methodology used reference standards for determining the absorbance and transmittance of fruit juices by comparison with a series of standard solutions. Distilled water does not absorb any radiation in the visible range, and the absorbance read was $A\% = 0\%$. The standard solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, prepared with concentrations from 2% to 40%, were then introduced. The absorbances of the standard solutions were recorded, as well as those of the solutions that came into contact with orange juice or apple juice, [36].

The oil samples were analyzed for absorbance and transmittance values at a wavelength in the range of 570–650 nm using a Vertex UV–VIS spectrophotometer (manufactured by Bruker Company, Massachusetts USA). This analysis was performed following the study conducted by Kumar and Viswanathan [37] and Orozco et al. [38] on UV transmission of edible oils, chicken oil, and biodiesel. Distilled water was used as a reference or control for the absorbance and transmittance measurements. The data were subjected to statistical analyses using STATISTICA 13 software [39] by applying basic statistics (correlation analysis), general linear models (repeated measures ANOVA and multiple regression), and Duncan post hoc tests at a 5% significance level. The statistical analysis was applied to all types of food liquids studied.

The transmittance measurement of the oil samples was carried out with a UV spectrophotometer. The device was calibrated by inserting the cuvette with the reference solution (distilled water) into the compartment. Distilled water did not absorb any radiation in the visible range, and the absorbance read was $A\% = 0\%$. The transmittance of standard solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, with concentrations from 2% to 40%, were prepared and then determined—analogueous to the absorbance determination, [40].

3. Results and Discussion

In Figure 1, the SEM micrograph of the cross-section of food-grade stainless steel layers deposited by thermal spraying in an electric arc on an aluminum support is presented. The

lamellar structure of the layer, which presents flattened particles, pores, communication channels between pores, and non-melted particles, is a typical structure of coatings obtained by thermal spraying in an electric arc. The different brightness values, as well as the predominantly light-gray shades, also indicate an almost complete mixing of the various alloying components.

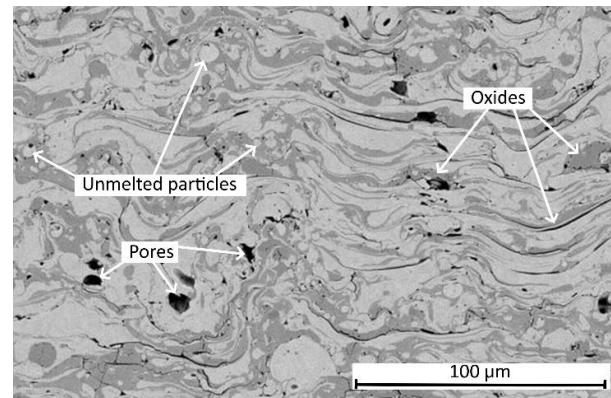


Figure 1. Scanning electron micrograph (secondary electrons) of the cross-section of the 80T coating.

In Table 3, the average values of adhesion, porosity, thickness, and microhardness HV_{300} obtained after performing the specific tests are presented. The thickness of the deposits was obtained after a total of three consecutive passes.

Table 3. Average values of adhesion, porosity, microhardness, and hardness of 80T deposits.

Coating	Sample	Voltage, [V]	Adhesion, [MPa]	Porosity, [%]	HV_{300}	Thickness, [mm]
80T	01CS30	30	28.3 ± 7.3	6.7 ± 2.1	308 ± 25	1.2 ± 0.3
	02CS32	32	32.7 ± 3.6	3.8 ± 0.7		1.3 ± 0.2
	03CS34	34	33.1 ± 2.8	3.1 ± 1.2		1.2 ± 0.4

The obtained values are in accordance with the results obtained by other researchers in the field [40].

The layers obtained present close microhardness values. The high value of the microhardness of the deposit is due to the presence of chromium in the wire used (18% Cr—see Table 1), a fact that determines the formation of complex carbides of chromium, known as constituents with high relative microhardness. Increasing the voltage of the electric current causes the temperature to increase: the electric arc, the molten droplets and the sprayed particles. This aspect allows for better anchoring of the particles in the asperities of the substrate—a fact that determines the increase in deposition adherence—see Table 3. Relatively high variations in adherence are obtained at low values of spring tension. For tensions over 32 V, the adherence of the layer presents close values. The increase in the electric arc voltage also influences the porosity of the layer. It can be affirmed that by increasing the temperature of the electric arc, the sprayed particles have higher temperatures, and upon impact with the surface of the layer, they flatten more, which causes the reduction in porosity—see Table 3. These results obtained on food-grade stainless steel are similar to the results reported by Toma et al. [40] on 60T steel layers. The high value of the average adhesion—obtained at voltages above 32 V—as well as the low value of the porosity of layers 02CS32 and 03CS34, allow their use for the purpose of protecting aluminum surfaces.

In order to check if food grade stainless steel deposits insulate the aluminum alloy, we analyzed the chemical composition of the wine and milk that come into contact with the deposited layers. A number of 16 tests were performed for each type of deposition, and for control we analyzed the chemical composition of a control sample that does not come

into contact with the deposited layer or the aluminum alloy. Synthetically, the average values obtained after the analyses are presented in Tables 4 and 5. The t-test analysis was applied to the obtained results, resulting in a significance level of up to $p = 0.086$. The lowest values were obtained by rare-earth elements, which had a significance level of $p < 0.001$, and whose presence in the wine is attributed to the soil. It can be observed that although all layers of food-grade stainless steel have the same thickness, the presence of open pores and microchannels of communication between pores existing in the porous deposit (P1) allows the wine to come into direct contact with the aluminum alloy and certain chemical elements in the alloy (Al, Mn, Cu, Zn, etc.) to migrate into the wine. The decrease in the porosity of food-grade stainless steel deposits below 3.7% stops the phenomenon of migration and reduces the possibility of contaminating the wine with some chemical elements from the aluminum alloy. It can be observed that there are insignificant differences in the concentration of the chemical elements in the wine that comes into contact with layers 02CS32 and 03CS34, an aspect explained by the fact that the two layers have close degrees of porosity. Although the food-grade stainless steel layer has some chemical elements (Cr, Ni) that could migrate into the wine, it can still be seen from Tables 4 and 5 that this phenomenon does not occur. It can be suggested that the chemical elements existing in the food-grade stainless steel layer are strongly bound in the form of stable chemical compounds and do not migrate into the liquid food substance.

Table 4. Chemical elements present in Merlot wine after it comes into contact with 80T layer (after 1 year).

Chemical Element	Control Sample	01CS30	02CS32	03CS34
Cr, [wt.%]	0.0006	0.00061	0.000606	0.000604
Mn, [wt.%]	0.00014	0.00021	0.000145	0.000146
Ni, [wt.%]	0.00037	0.00038	0.000371	0.00037
Si, [wt.%]	0.000012	0.00003	0.000012	0.000012
Ti, [wt.%]	0.0001	0.0052	0.0001	0.0001
Cu, [wt.%]	0.04	0.0586	0.04	0.04
Mg, [wt.%]	56.124	56.237	56.125	56.124
Al, [wt.%]	0.0006	0.42263	0.0006	0.0006
Zn, [wt.%]	0.0016	0.0036	0.0016	0.0016
Fe, [wt.%]	0.0032	0.0033	0.0032	0.0032
Na, [wt.%]	14.14505	14.1451	14.14505	14.14505
Se, [wt.%]	0.003	0.0031	0.0031	0.0032
Be, [wt.%]	0.0005	0.0005	0.0005	0.0005
Ca, [wt.%]	0.0012	0.0012	0.0012	0.0012
Nb, [wt.%]	0.00002	0.00002	0.00002	0.00002
Te, [wt.%]	0.00003	0.00003	0.00003	0.00003
Pd, [wt.%]	0.0005	0.0005	0.0005	0.0005
Other elements, [wt.%]	Balance	Balance	Balance	Balance

The acidity of the fermented dairy products was tested for a period of 7 days. In the case of using aluminum containers with food-grade stainless steel, there is constant maintenance of the acidity from 90 Thorner degrees for yogurt with 2% fat content and up to 125 Thorner degrees for kefir with 2% fat content. The increase in acidity by 30 units in the case of aluminum containers shows an accelerated increase in the acidity of the milk.

In the case of aluminum containers covered with food-grade stainless steel, the increase in acidity occurred from 89.9 Thorner degrees on the first day for yogurt with 2% fat content up to 95.7 Thorner degrees on the seventh day, which means a slow increase in the acidity of acidophilic milk (only by 5.8 Thorner degrees). Statistically, the evolution of the obtained results shows a confidence limit of $R^2 = 0.871$, slightly higher for the material made of aluminum with food-grade stainless steel than the confidence limit of $R^2 = 0.8547$ obtained for the containers made of aluminum, the classic material—see Figure 2a,b.

Table 5. Chemical elements present in milk after it comes into contact with 80T layer (after 1 year).

Chemical Element	Control Sample	01CS30	02CS32	03CS34
Cr, [wt.%]	0.0000239	0.0000241	0.0000239	0.0000238
Mn, [wt.%]	0.0000107	0.0000183	0.0000116	0.000109
Ni, [wt.%]	0.000074	0.000081	0.000079	0.000076
Si, [wt.%]	-	0.000001	0.00000082	0.0000086
Ti, [wt.%]	-	-	-	-
Cu, [wt.%]	0.00000015	0.00000018	0.00000016	0.00000015
Mg, [wt.%]	-	0.000025	-	-
Al, [wt.%]	0.000395	0.008655	0.000002	0.0000001
Zn, [wt.%]	0.0032	0.0038	0.00321	0.00319
Fe, [wt.%]	-	-	0.00000012	0.00000012
Na, [wt.%]	0.248	0.24803	0.24793	0.24801
K, [wt.%]	1.1468	1.1445	1.1472	1.1462
Se, [wt.%]	0.000048	0.00004802	0.00004812	0.0000481
Ca, [wt.%]	0.8882	0.882205	0.88241	0.88224
Rb, [wt.%]	0.00195	0.00191	0.0019508	0.00192
Se, [wt.%]	0.000082	0.0000821	0.00008187	0.0000821
Br, [wt.%]	0.00084	0.0008402	0.0008411	0.0008398
Other elements, [wt.%]	Balance	Balance	Balance	Balance

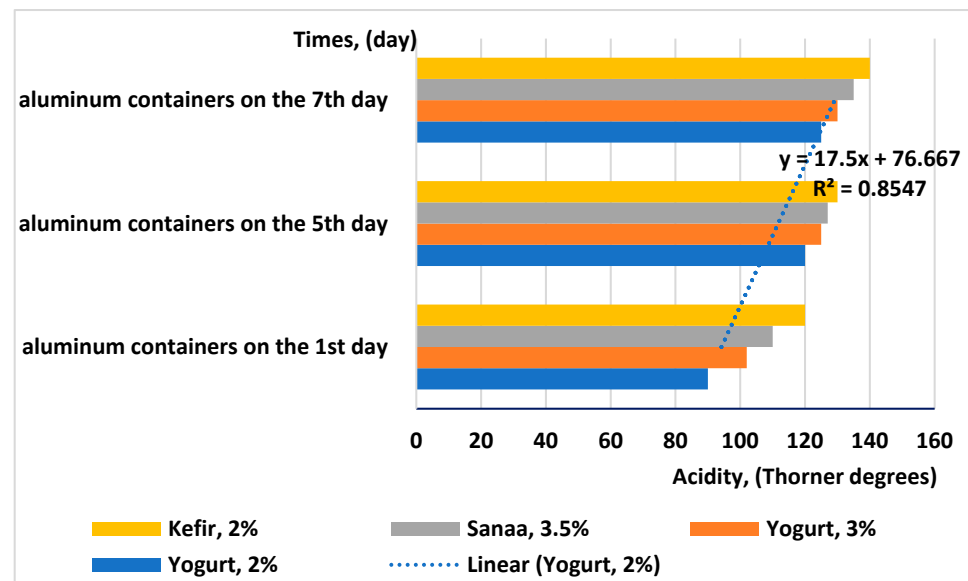
In the case of drinking milk, the acidity varies depending on the fat content from 15 to 17 Thorner degrees, but also depending on the packaging used. Thus, in the case of aluminum containers, the acidity of the milk increased by 3.5% to 19.5 Thorner degrees—see Figure 3a, while the acidity of the milk stored in aluminum containers with food-grade stainless steel increased from 15 up to 19 Thorner degrees—see Figure 3b. The multiplication of lactic bacteria, is influenced by the nature of the packaging—see Figure 3a,b. The values on the OX axis represent the content of milk fats (0.1%, 1.2%, 3%, and 3.5%), and the values on the OY axis represent the acidity of milk (at 1st day, 5th day, and 7th day) in correlation with the content of fats.

The statistical confidence level was $R^2 = 0.8909$ for the values of milk acidity during storage in the aluminum containers—from the 1st day to the 7th day. The level of confidence was $R^2 = 0.9076$ for the values of acidity of milk stored in the aluminum containers covered with stainless steel on the 1st day, 5th day, and 7th day (Figure 3b).

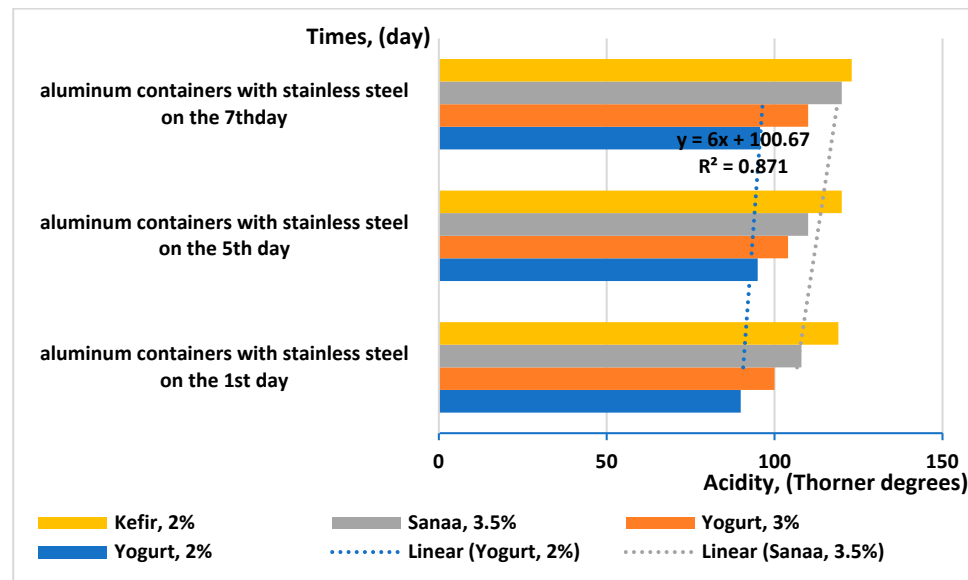
In the linear approximation functions, represented by dotted lines, y represents the absorbance and x represents the content of drinking milk fats—see Figure 3a,b. The reduction in the acidity of the drinking milk was also influenced by the porosity of the aluminum alloy covered with food-grade stainless steel, which recorded values of 3.8%.

The level of acidity in wines also determines their oxidation level. Thus, young wines have higher acidity. As they age, wines acquire a bouquet through the esterification of the aroma compounds, a process also being accompanied by a decrease in acidity. Thus, storing wines in aluminum containers in conditions of increased acidity is not recommended because this material is sensitive to high acidities. That is why it is recommended to store and mature wines in food-grade stainless steel tanks, which are expensive. The coating solution for the aluminum containers with food-grade stainless steel on the inside is intended to prevent the oxidation and spoilage of the wines, the reduction in alcohol and aroma losses through evaporation, and, implicitly, the reduction in costs.

From the testing of the four varieties of wine, it can be seen that the Chardonnay white wine changed its acidity from 4 degrees to 3.5 degrees, which is an optimal situation after a year of aging. The same is observed in the case of Pinot Gris wines, from 4.2 to 3.75, and for Ottonel, from 3.7, too. The decrease in the acidity of the aromatic wine to 3 degrees of acidity changes its taste properties; it becomes oxidized and flat, i.e., without aroma and a pleasant acid taste.



(a)



(b)

Figure 2. (a) Evolution of the acidity of acidophilic dairy products in aluminum containers (7 days); (b) evolution of the acidity of acidophilic dairy products in an aluminum container covered with food-grade stainless steel.

The decrease below 3% may also favor the appearance of wine flowers and other spoilage defects, or the appearance of the wine souring or fermentation. In Merlot wine, the acidity of the young wine decreased from 6 degrees to 4.9, which is a normal index of technological maturation—see Figure 4. The 6.7% porosity of covered containers can represent a major risk of wine damage because advanced oxidation takes place, accelerating spoilage. The use of a new packaging material with an approximately three times lower porosity represents a significant technological advantage, keeping white wines young and protecting the bouquet of red wines—see Figure 4.

In Figure 5 the calibration curve for the absorption level of the standard solutions is shown.

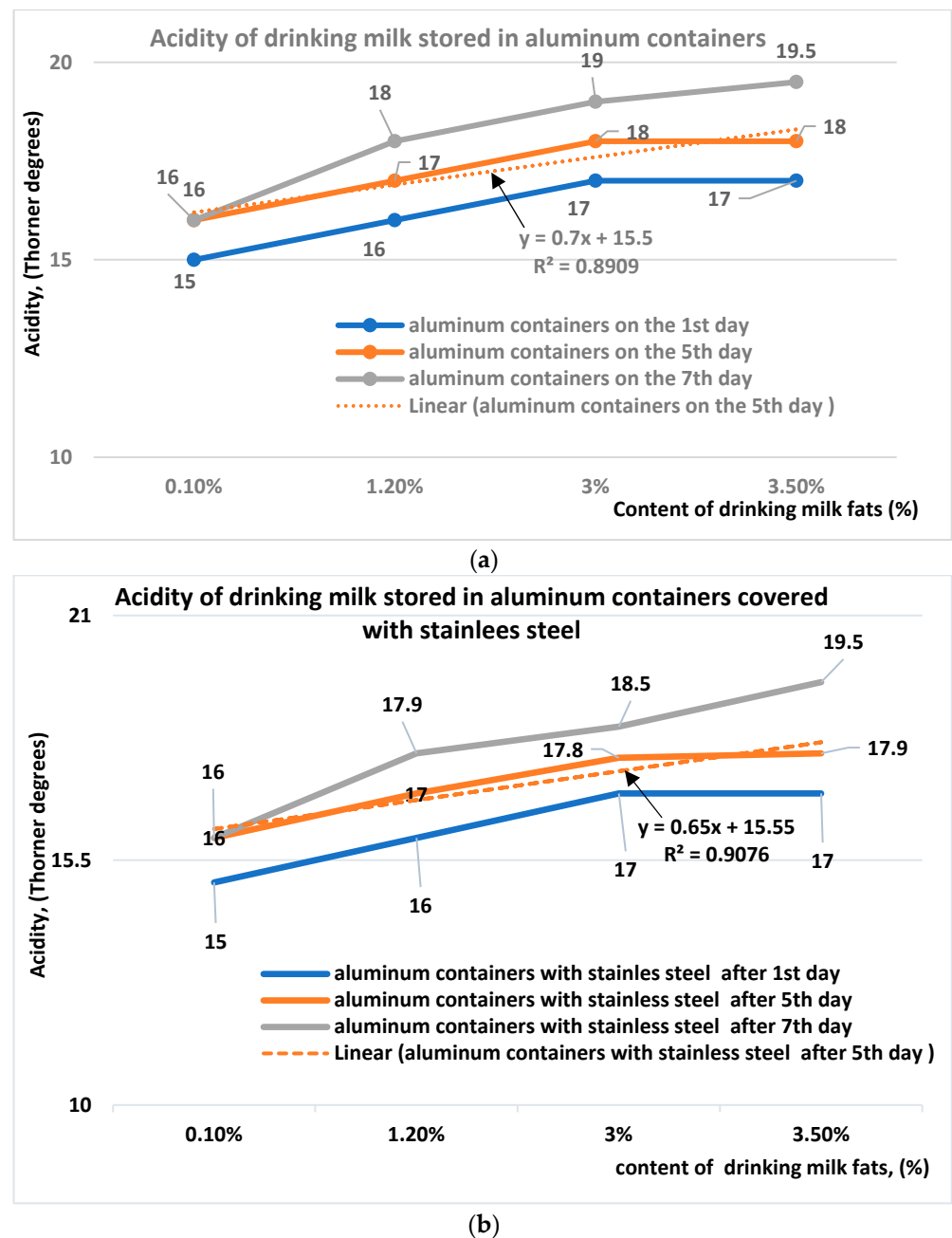


Figure 3. Dynamics of the acidity of drinking milk in the aluminum containers/the aluminum containers with food-grade stainless steel (1, 5, 7 days): (a) in the aluminum containers after stored; (b) in the aluminum containers covered with food-grade stainless steel.

The dynamics of the absorbance measured at a wavelength of 570 nm with a UV spectrophotometer show us higher absorbance values in the case of juice storage in aluminum and food-grade stainless steel containers compared to orange juices stored in aluminum containers (see Figure 6, var. I aluminum alloy vs. var. II aluminum with food-grade stainless steel). The absorbance of the juices was lower because aluminum migrates into liquid solutions and the introduction of oxygen causes a decrease in absorbance through the oxidation of the natural coloring substances in juice sample 1 (Fresh orange juice) or even the identical natural substances in sample 2 (Prigat orange juice), sample 3 (Cappy orange juice), and sample 4 (Fanta orange juice) (commercial names of some fruit juices)—see Figure 6. The solution of the new alloy obtained by coating aluminum with food-grade stainless steel also favors the preservation of the color characteristics of the fruit juices. As

experimentally demonstrated, the porosity of the innovative material was only 3.8%, which also positively influenced the absorbance dynamics of the orange and apple juices—see Figure 6.

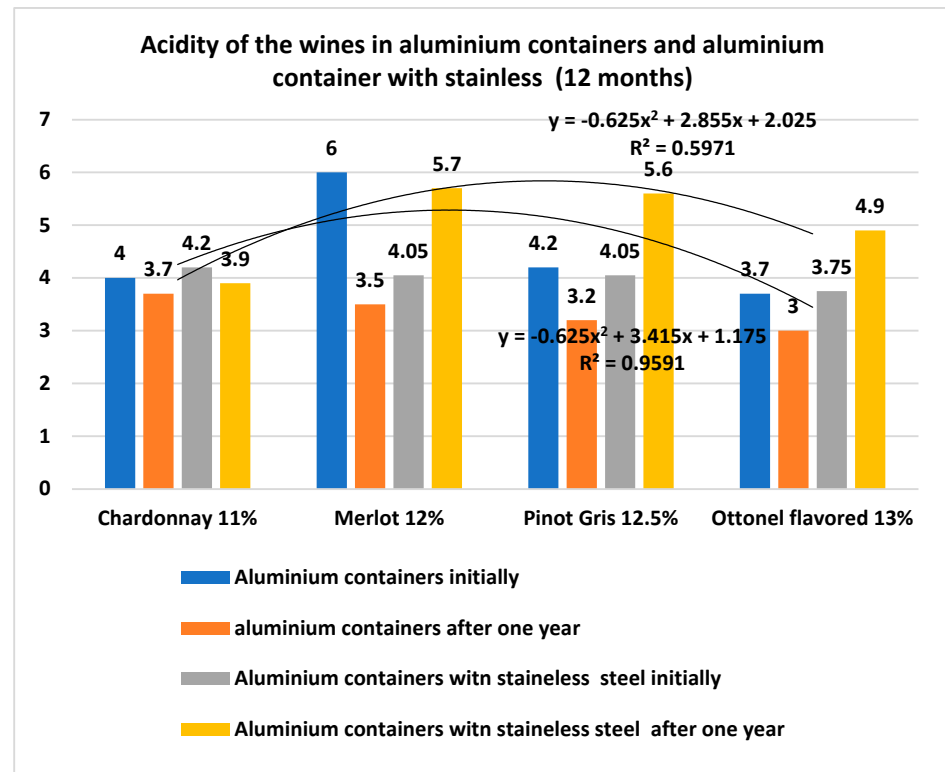


Figure 4. Acidity of the wines in aluminum containers/aluminum with food-grade stainless steel (after 12 months).

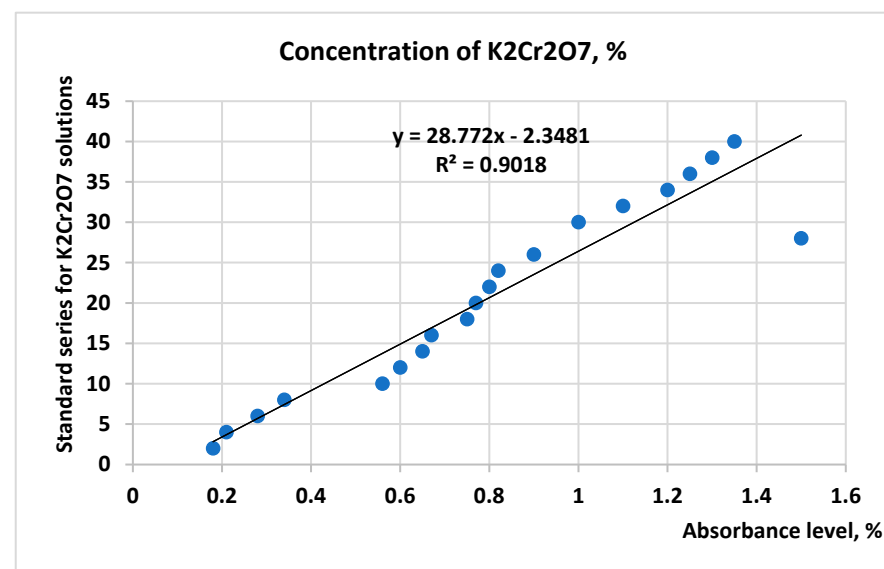


Figure 5. The absorbance level for the standard series of K₂Cr₂O₇ solutions.

The evolution of the absorbency in the fresh apple juices, as well as in the Prigat and Cappy apple juice recipes, induces a higher absorbency in the case of the aluminum containers coated with food-grade stainless steel on the inside compared to the aluminum containers.

Thus, the var. I chromatogram dynamically indicates that, in the case of fresh Golden and Wagner apple juices, the absorbance levels at a wavelength of 570 nm were 3.08 and 2.589, compared to 2.5 and 2.215 in the apple juices stored in aluminum containers—see Figure 6.

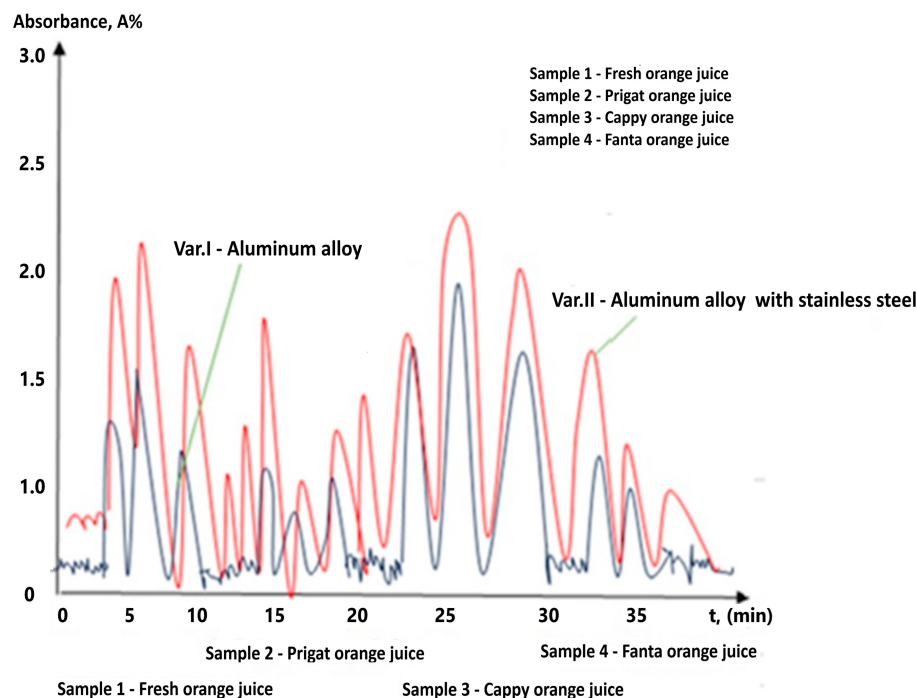


Figure 6. The dynamics of absorbance in the orange juices stored in aluminum alloy/aluminum alloy with food-grade stainless steel containers (sample 02CS32), determined after 7 days, using a wavelength of $\lambda = 570$ nm.

In the case of the Cappy and Prigat juices, the absorbance levels were higher in the juices stored in aluminum and food-grade stainless steel containers, with absorbance levels of 0.507–0.898, compared to the absorbance levels of the juices stored in aluminum containers (0.247–0.346)—see Figure 7.

Thus, it has been experimentally demonstrated that the properties of the packaging material made of aluminum and coated on the inside with food-grade stainless steel bring benefits to the fruit juices, which retain their natural pigments, as reflected by the higher levels of absorbency—see Figures 6 and 7. Table 6 presents the statistical analysis of the juice absorbance.

Table 6. Absorbance parameter estimates and statistical evaluation.

Factors Effect	Parameter	Sum of Squares	Factor Effect	Parameter	p-Value
Intercept	2.514	25.64	25.64	467.88	<0.05
WL	−0.00129	10.301	10.291	470	<0.05
TP	0.0058	2.578	2.578	89.0089	<0.05

WL: wavelength (nm); TP: temperature (°C); A: absorbance; $R^2 = 0.237$; p-value < 0.05 implies significance.

The oxidation levels of the olive, sunflower, and soybean oils were measured using the absorbance values determined with a UV spectrophotometer calibrated with reference solutions at 570 nm wavelength.

The absorbance of sample solutions 1–20 with $K_2Cr_2O_7$ concentrations ranging from 2% to 40% was measured. Thus, it was experimentally demonstrated that the properties

of the packaging material made of aluminum and coated on the inside with food-grade stainless steel bring benefits too, which retain their natural pigments, as reflected by the higher level of absorbance—see Figure 8.

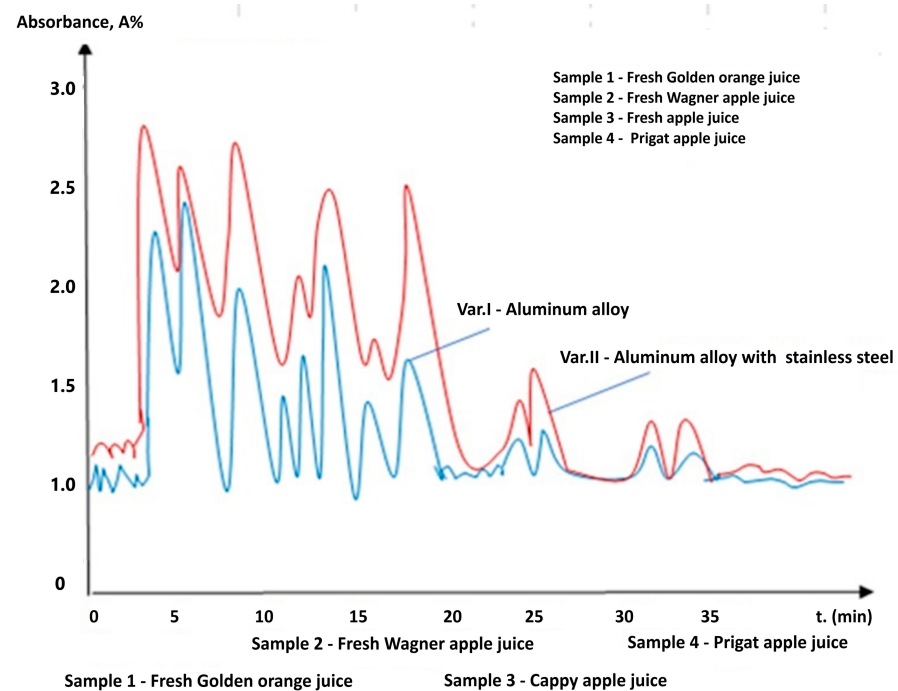


Figure 7. The evolution of the absorbance level for apple juices stored in aluminum containers/aluminum containers covered with food-grade stainless steel (sample 02CS32), determined after 7 days, using a wavelength of $\lambda = 570$ nm.

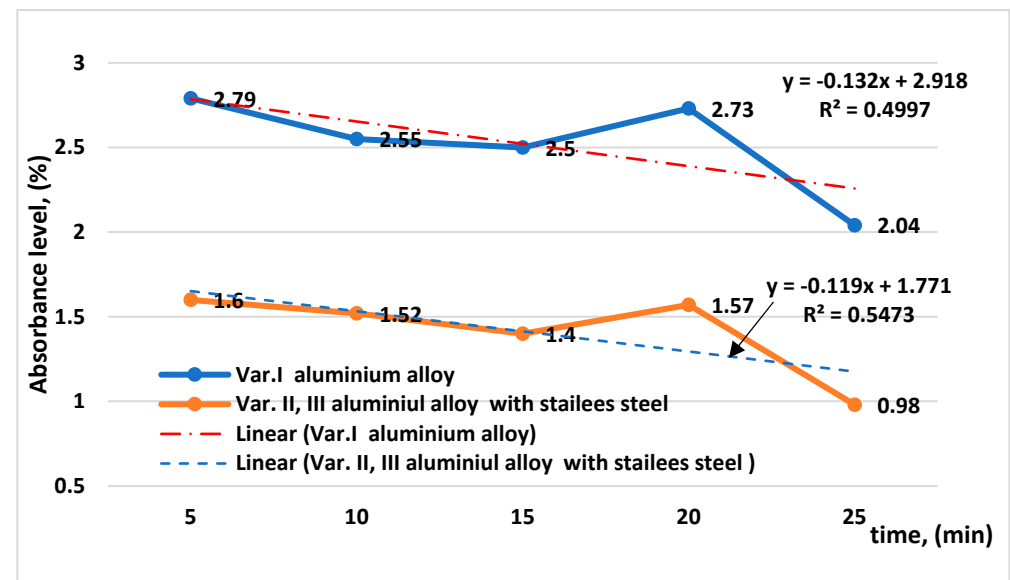


Figure 8. The average values of the absorbance level variation with extinction time, obtained on five different types of oils, stored in containers made of aluminum alloys/aluminum alloy containers covered with food-grade stainless steel, obtained at a wavelength of $\lambda = 570$ nm after one year.

Figure 8 shows the average absorbance values according to the extinction times obtained on five different types of oils (olive, sunflower, soybean, corn, and sesame). The values are close to those of the standard series in Figure 5.

The evolution of the absorbance levels for edible oils shows lower values for sesame oil and higher values for olive oil when stored in aluminum containers with food-grade stainless steel, exhibiting 3.8% porosity. This means that the clarity qualities of olive oil are superior—Figure 8. The level of absorbance is significantly higher, ranging from 2.04% for extinction times of 25 min up to 2.79% for extinction times of 5 min, which means a semi-positive increase in sensory characteristics, including appearance, color, and clarity, see Figure 8,—The oxidation levels of olive, sunflower, and soybean oils were measured by the values determined with a UV spectrophotometer calibrated with reference solutions at a wavelength of 650 nm, at which part of the monochromatic radiation at 570 nm was absorbed in proportion to the concentration of the solution.

The data on the absorbance spectra within the wavelength range of 570 nm are described in the Section 2.

In the regression functions, represented by a black line, the value of y is the absorbance and x is the extinction time used in the experiment. The confidence level for var. I was $R^2 = 0.4997$, and for var. II it was better at $R^2 = 0.5473$ —see Figure 8.

4. Conclusions

The investigations carried out on the physical, chemical, and mechanical properties of the food food-grade stainless steel layer–aluminum substrate protection system, obtained by thermal spraying in an electric arc, in contact with food liquids, have shown the following:

- The deposits of 80T of food-grade food-grade stainless steel, which have low porosity (below 3.8%), can be used for the purpose of isolating the aluminum alloy and stopping the phenomenon of migration of aluminum ions inside food liquids;
- The adhesion and high microhardness of the deposits make them resistant to shock and variable tests that occur during the transport of liquid food products;
- Increasing the acidity of the milk causes the multiplication of lactic bacteria. The aluminum alloy has a higher specific density than the alloy of aluminum alloy combined with food-grade stainless steel. That is why the new material in contact with the milk will not influence the development of lactic bacteria;
- The innovative solution of the new material composed of aluminum alloy combined with food-grade stainless steel offers advantages for the advanced preservation of acidophilic milk, drinking milk, wines, juices, and oils because the low porosity of food-grade stainless steel deposits prevents the migration of chemical elements from the packaging material into the liquid food;
- The coating solution for aluminum alloy containers with food-grade stainless steel on the inside prevents the oxidation and alteration of the wines, reducing the loss of alcohol and bouquet through evaporation and implicitly reducing the costs as well;
- Also, the innovative material significantly improves the sensory characteristics of the juices and the oils, like the appearance, color, and clarity of the oils that have been stored in aluminum alloy containers covered with food-grade stainless steel through the arc spraying process.

The relatively low weight of the food-grade stainless steel layer–aluminum substrate protection system, obtained by thermal spraying in an electric arc, along with the fact that the food-grade stainless steel coating does not interact with food liquids, allows for its successful use in the realization of the receptacles required for the transport of food liquids.

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