

Study of new rubber to steel adhesive systems based on Co(II) and Cu(II) sulphides coats

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Abstract. The presented paper deals with the preparation of new rubber to steel adhesive systems using the steel surface treatment with deposition of adhesive coats based on Co(II) and Cu(II) sulphides. Efficiency of new prepared adhesive systems containing Co(II) and Cu(II) sulphides has been compared with the efficiency of double layer adhesive system commonly used in industry. The chemical composition of prepared adhesive systems was determined using the EDX analysis. Scanning Electron Microscopy (SEM) was used for study of topography and microstructure of prepared rubber to steel adhesive systems (Co(II), Cu(II) sulphide, double layer adhesive system). For determination of adhesion strength between rubber blends and metal pieces with various adhesive systems deposited on these pieces, the test according to ASTM D429 standard relating to Rubber to metal adhesion, method A was used. For all test samples, the same type of rubber blend and the same curing conditions have been used.

Keywords: Rubber blend, adhesive systems, cobalt sulphide, copper sulphide, double adhesive system

1 Introduction

In many applications of rubber blends, the reinforcing materials is used for achievement of the required properties. Adhesive systems have important function in the interface between two main materials, such as rubber blend and steel reinforcement material. There are many types of adhesive systems (e.g. adhesive systems mixed into rubber blends, spray application adhesive systems and two components adhesive systems), the effectivity of which is influenced by many factors. Effectivity of adhesive systems can be defined by strength of joint, which is expressed as force (N) on the surface of the joint (mm²). The other factors, that affect effectivity of adhesive systems are: composition of rubber blend, type of reinforcing material and surface treatment of reinforcing material. The gradual development of reinforcing materials leads to development and innovation of the adhesive systems. Adhesive systems have application in many sectors of industry, where there is a requirement to ensure bonding of rubber blends and reinforcing materials, such as steel, fibers or textile. The automobile industry represent one of the largest consumers of

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adhesive systems, because these systems are used for tyres, silenblocks and sealings. The life time as well as safety of final product can be ensured the hight strength of joint.

2 Experimental

2.1 Materials and methods

2.1.1 Preparation of Co(II) and Cu(II) sulphides coats

Co(II) and Cu(II) sulphides coats have been prepared using the adsorption procedure involving treatment of the working electrode representing the tested metal piece in a solution containing heptahydrate of cobalt sulphate (high purity, purchased from Kemcore), hydroxylamine sulphate, and ammonia (pH 12) for Co(II) sulphide coat and pentahydrate of copper sulphate, hydroxylamine and ammonia(pH 12) for Cu(II) sulphide coat, respectively. After preparation of coats, the reduction to sulphides in the solution of sodium sulphide was carried out and then the samples were washed with distilled water [1, 2].

2.1.2 Preparation of samples for adhesion test

Steel test samples have been prepared according to ASTM D 429 method A (ASTM D429 - Rubber to Metal Adhesion Test Equipment). For preparation of metal parts of test samples, the common type of steel was used. The test samples preparation procedure is in Table 1.

Table 1. Sample number and following preparation procedure

Sample number	Test samples preparation procedure
Sample 1	sample without surface treatment, only degreasing in KOH
Sample 2	surfaces of sample treated only with sandblasting
Sample 3	surfaces of sample treated only with phosphating
Sample 4	sandblasting with following application of commonly used double adhesive system (this process is commonly used in industry)
Sample 5	phosphating with following application of commonly used double adhesive system (this process is commonly used in industry)
Sample 6	sandblasting with following preparation of Co(II) sulphide coat
Sample 7	sandblasting with following preparation of Cu(II) sulphide coat
Sample 8	phosphating with following preparation of Co(II) sulphide coat
Sample 9	phosphating with following preparation of Cu(II) sulphide coat
Sample 10	degreasing in KOH solution, etching in HCl, with following preparation of Co(II) sulphide coat
Sample 11	degreasing in KOH solution, etching in HCl, with following preparation of Cu(II) sulphide coat

All of the mentioned steel test samples (Fig. 1) were used for the preparation of samples for adhesion test, where these steel samples were combined with the industrially used rubber blend of the same composition. Samples for adhesion test were cured in the curing press at the temperature of 160 °C during 6 minutes. After the curing procedure, the

samples were conditioned for 16 hours. After the condition, all samples were tested with HOUNSFIELD H20K-W tensile testing machine.

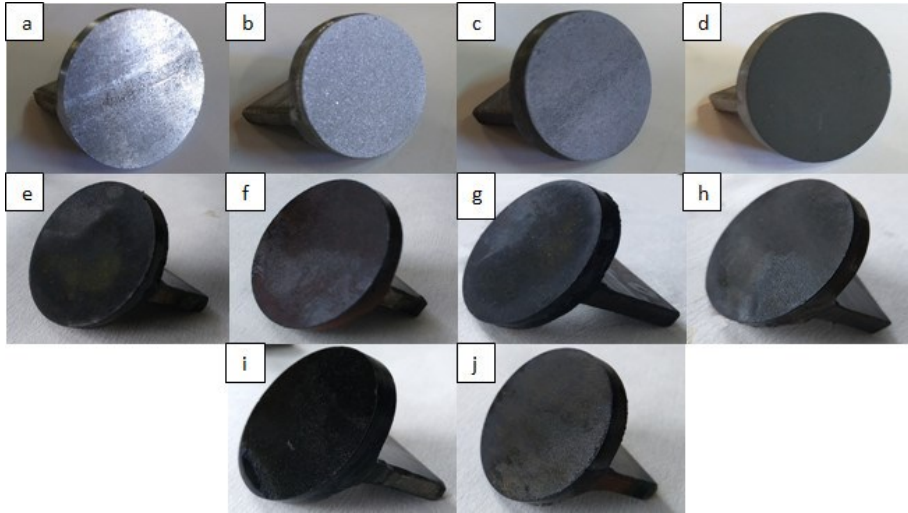


Fig. 1. Steel test sample after preparation procedure : a) Sample 1, b) Sample 2, c) Sample 3, d) Sample 4 and sample 5 – the same image of surface after preparation procedure, e) Sample 6, f) Sample 7, g) Sample 8, h) Sample 9, i) Sample 10, j) Sample 11

2.2 Testing and analysis

EDX analysis

The chemical composition of prepared Co(II) and Cu(II) sulphides coats and chemical composition of basic steel material was evaluated using Shimadzu EDX-7000 Energy Dispersive X-ray Fluorescence Spectrometer.

Microstructural SEM analysis

Microstructure and thickness of Co(II) and Cu(II) coats were studied using TESCAN VEGA 3 scanning electron microscope. The microanalysis was focused on the evaluation of topography and microrelief of the sulphide layers using detector operating in the secondary electrons mode in a high vacuum.

Adhesion test

Adhesion test of prepared test samples was performed using the HOUNSFIELD H20K-W tensile testing machine. Adhesive strength was calculated using the equation [3]:

$$R_A = \frac{F_A}{A_A} \quad (1)$$

R_A = adhesion strength (N.mm⁻²)

F_A = maximum force (N)

A_A = surface of sample (mm²)

3 Results and discussion

In results and discussion, there are summarized the results of : EDX analysis, tensile test of samples with adhesive strength, study of topography and microrelief of prepared sulphides coats and double adhesive system.

3.1 Energy Dispersive X-Ray Analysis (EDX)

Prepared Co(II) and Cu(II) sulphides coats and basic material were subjected to the EDX analysis for demonstration of chemical composition. In Table 2., there are the chemical composition of basic material (steel) and the chemical compositions of the prepared sulphides coats. The common type of steel was used for preparation of metal parts of test samples (basic material).

Table 2. Chemical composition of Co(II) and Cu(II) sulphide coat and basic material

Sample	Fe	Mn	Cr	Cu	Co	S
Basic material	98.301	0.914	0.182	0.245	-	-
Basic material + Cu(II) sulphide coat	50.192	0.462	0.201	33.254	-	15.686
Basic material + Co(II) sulphide coat	79.541	0.696	0.304	0.723	3.253	15.332

In both cases, sulphide coats were too thin, and therefore EDX analysis machine measured also the basic material together with coats. Thickness of sulphides coats was measured with scanning electron microscope.

3.2 Microstructural SEM analysis

In the Figs. 2-7. there are SEM images of topography and microrelief of double adhesive system, Co(II) and Cu(II) sulphides coats.

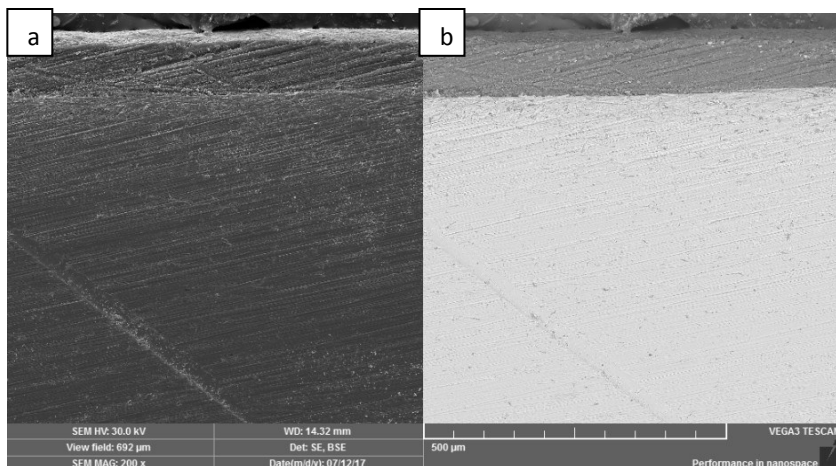


Fig. 2. SEM images of double adhesive system a) SE detection, b) BSE detection

In figure 2, it can be seen the structure of double adhesive system. In the figure 2b, it can be seen the interface between double adhesive system and basic material. It is interesting that in the figure 2b (BSE detection of double adhesive system, which is compound of two layers), the interface between two layers in double adhesive system is not visible. From this finding it possible to assume that the layers in double adhesive systems have similar composition. Lighter area in the figure 2a (SE detection) represents only the surface of sample, because the sample was not placed perpendicularly in the holder.

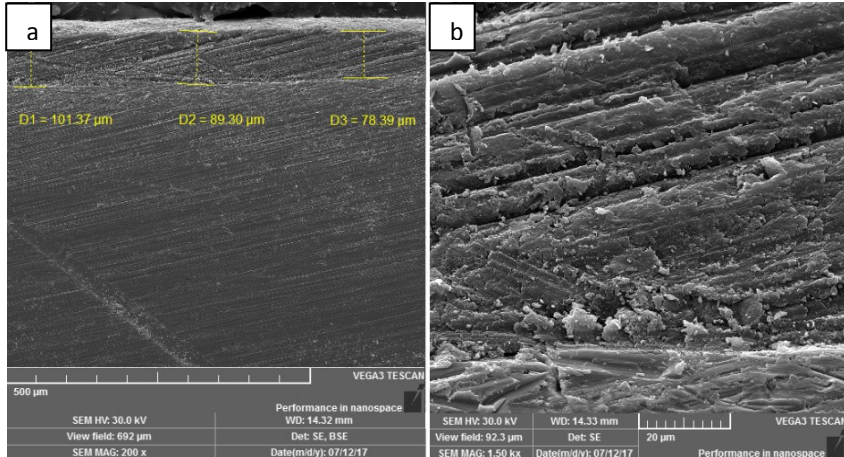


Fig. 3. SEM images of double adhesive system a) thickness measurement, b) detail of structure of double adhesive system

From the figure 3, it is visible that thickness of double adhesive system was uniform in the interval from 78 to 102 μm. Even the detailed view of double adhesive system did not reveal the interface between two individual layers of double adhesive system.

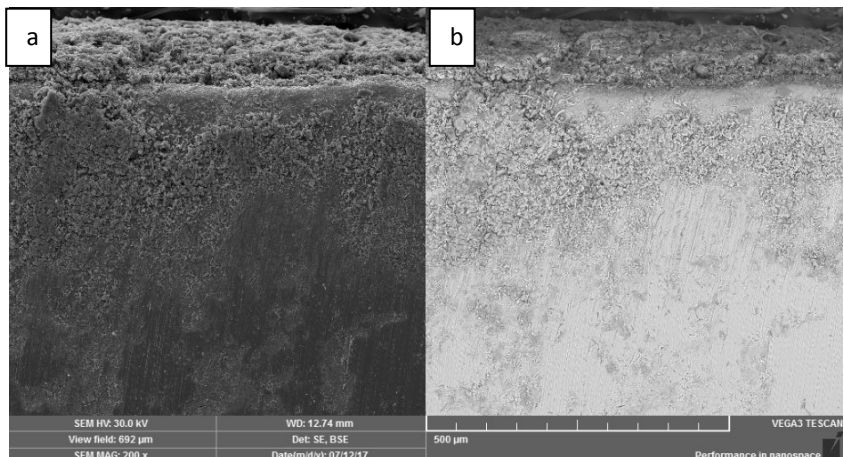


Fig. 4. SEM images of Co(II) sulphide coat a) SE detection, b) BSE detection

In figure 4, the structure of Co(II) sulphide coat can be seen. In figure 4b, the interface between Co(II) sulphide coat and basic material can be seen. In figure 4a, the pores, which are in coat of Co(II) sulphide, are visible.

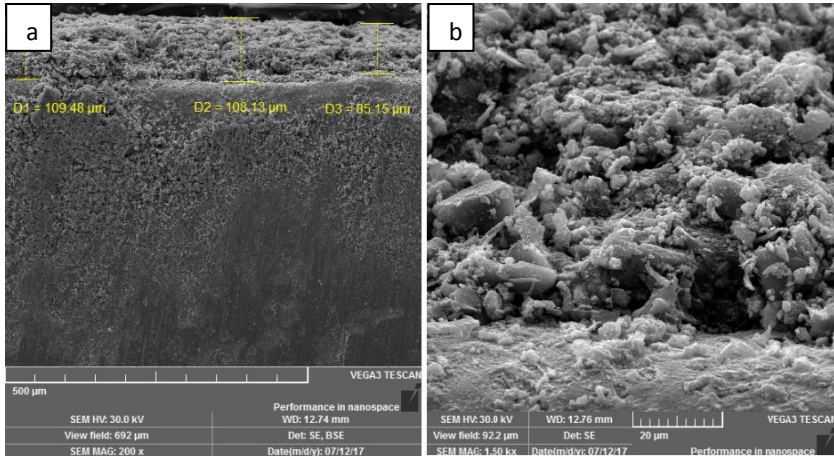


Fig. 5. SEM images of Co(II) sulphide coat a) thickness measurement, b) detail of structure of Co(II) sulphide coat

Prepared Co(II) sulphide coat is uniform and thickness of coat was in interval from 85 to 110 μm . In figure 5b, crystals in the coat can be seen. Detailed view (Fig. 5b) was compared with the images of cobalt sulphides from scientific paper [4]. From comparison of images, it is possible to consider that crystals in figure 5b are Co(II) sulphide crystals. In detailed view of Co(II) sulphide coat (Fig. 5b), there are the pores visible in coat (dark areas), and these pores can be considered as beneficial feature for adhesion strength of this coat.

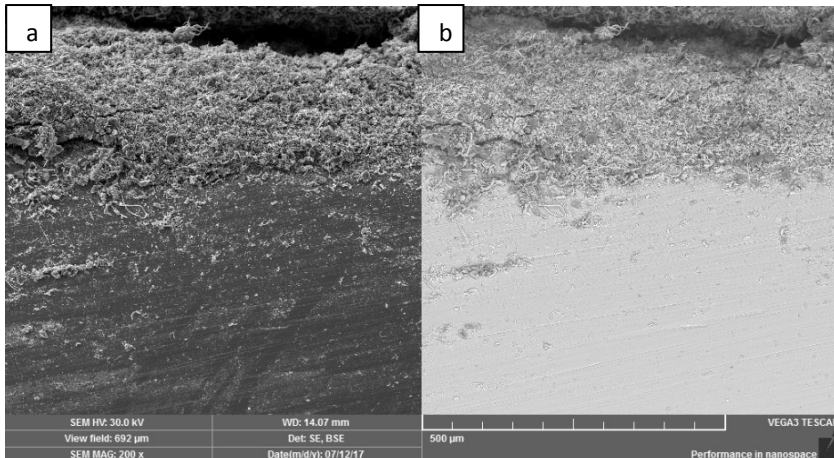


Fig. 6. SEM images of Cu(II) sulphide coat a) SE detection, b) BSE detection

In figure 6, the structure of prepared Cu(II) sulphide coat can be seen. In figure 6b, there are the visible cracks in the coat, which can lead to brittleness of prepared coat. In figure 6a, there is also the visible crack in interface area between Cu(II) sulphide coat and basic material.

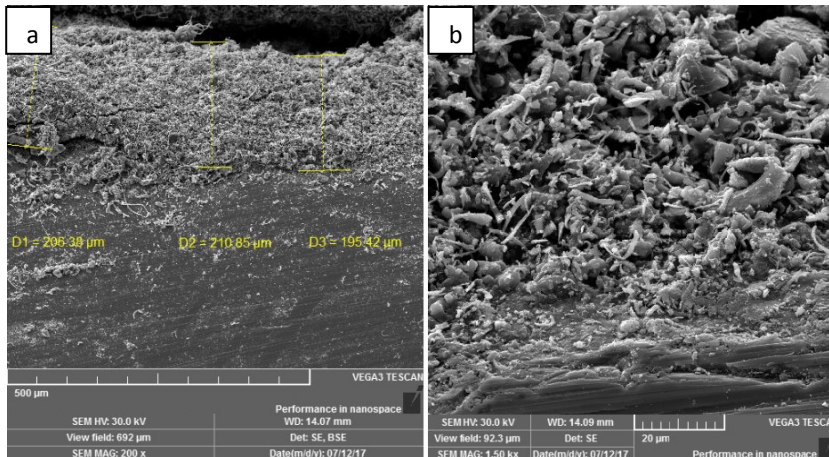


Fig. 7. SEM images of Cu(II) sulphide coat a) thickness measurement, b) detail of structure of Cu(II) sulphide coat

Prepared Cu(II) sulphide coat had greater thickness in comparison with double adhesive system and Co(II) sulphide coat. The figure 7a represents measurement of Cu(II) sulphide coat. Thickness of prepared coat was in interval from 195 to 207 μm . The detailed view (Fig. 7b) revealed the more visible pores in Cu(II) sulphide coat in comparison with Co(II) sulphide coat. This phenomenon can be beneficial feature for adhesion strength of this coat.

3.3 Adhesion test

In Table 3, there are records of the results (maximum force, adhesion strength) of adhesion test of prepared samples. These results are also graphically depicted in Fig. 8 and Fig. 9. During the test of adhesive strength, two cases of breakage may occur. There can be either breakage in interface between rubber blend and basic metal part or breakage in rubber blend (it was seen in the case of sample 4 and 5) and it means that adhesive strength is higher than strength of rubber blend.

Table 3. Values of maximum force and adhesive strength of samples

Sample number	Maximum force [N]	Adhesion strength [$\text{N}\cdot\text{mm}^2$]
Sample 1	268.67	0.214
Sample 2	915.33	0.728
Sample 3	1590.00	1.265
Sample 4	9286.00	7.390
Sample 5	6553.33	5.215
Sample 6	2023.33	0.178
Sample 7	2107.33	1.677
Sample 8	1648.67	1.312
Sample 9	1580.67	1.258
Sample 10	776.00	0.618
Sample 11	2091.33	1.664

According to the obtained results of adhesion test, it can be concluded that maximum force and thus maximum adhesive strength were seen for the sample 4, the preparation of which was based on sandblasting with following application of commonly used double adhesive system.

The second highest value of maximum force and adhesive strength was represented by the sample 5, which was prepared by phosphating with following application of commonly

used double adhesive system. These two samples present the commonly used process in industry. In contrast, the minimal values of measured characteristics were seen for Sample 1, which was only degreased in KOH. Adhesive strength of Sample 1 had only mechanical character. Mechanical character of adhesive strength is based on mechanical interlocking. From results of adhesion test, it can be concluded, that surface treatment can influence the value of adhesive strength and it was confirmed by the results of adhesive strength for sample 2 and 3. Sample 2 and 3 had higher values of adhesive strength than Sample 1. Increasing of adhesive strength may be caused by greater amount of pores and cavities after surface treatment, because there is the increase in amount of mechanical interlocking. Influence of surface treatment (sandblasting, phosphating) was reflected in Samples with new adhesive systems based on Co(II) and Cu(II) sulphides. In comparison with the other samples with Cu(II) sulphide coat, the highest value of adhesive strength was reached by sample 7. The sample 6 had the highest value of adhesive strength in comparison with the other samples with Co(II) sulphide coat. Before preparation of new adhesive system, surfaces of samples 6 and 7 were treated with sandblasting. The mutual comparison of the samples with new adhesive systems revealed the lowest values of adhesive strength in relation to sample 9 (phosphating with following preparation of Cu(II) sulphide coat) as well as sample 10, which is based on Co(II) sulphide coat (degreasing in KOH solution, etching in HCl, with following preparation of Co(II) sulphide coat).

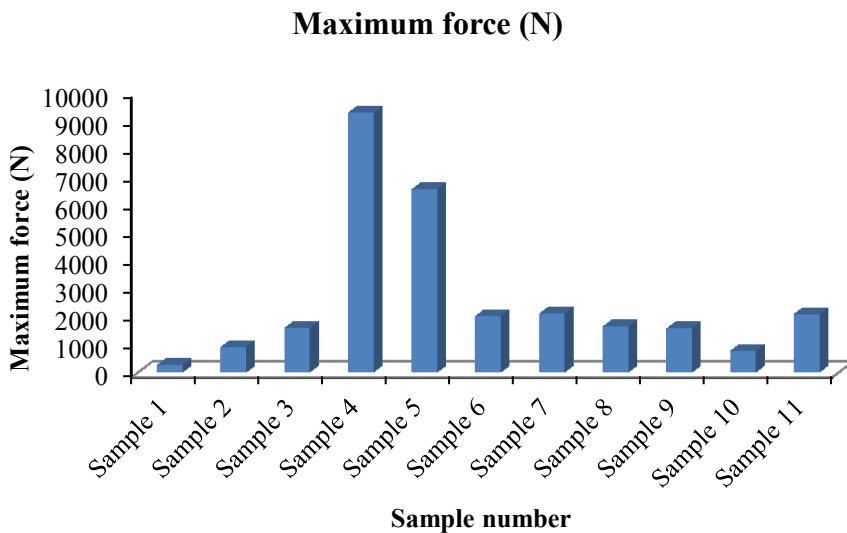


Fig. 8. Graphical representation of values of maximum force [N]

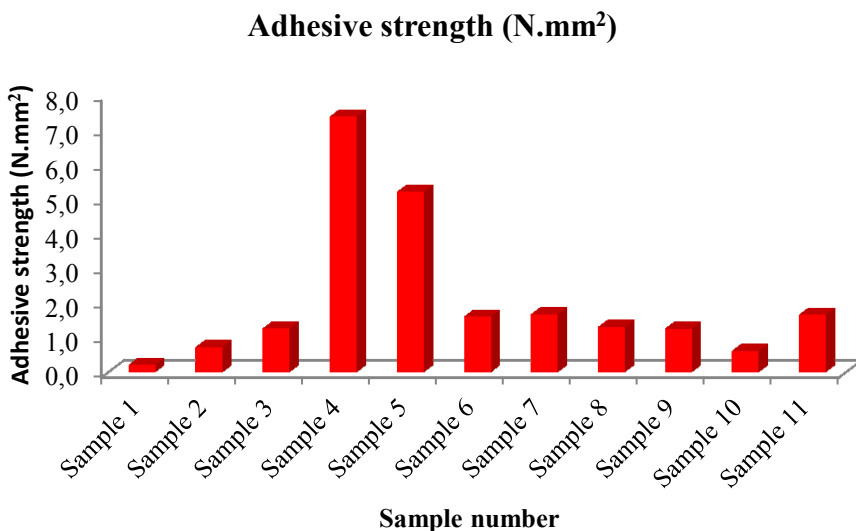


Fig. 9. Graphical representation of adhesion strength (N.mm²)

Conclusion

Results of EXD analysis have confirmed the presence of Co, Cu and S elements contained in Co(II) sulphide coat and Cu(II) sulphide coat. SEM microstructural analysis was used for measurement of thickness of all adhesive systems and structure of adhesive systems. According to the obtained results of adhesion test, it can be concluded that maximum force and thus maximum adhesive strength were revealed in the case of the Sample 4, which was prepared by sandblasting with following application of commonly used double adhesive system. The second highest value of maximum force and adhesive strength was seen for sample 5, which was prepared by phosphating with following application of commonly used double adhesive system. From the Samples with new adhesive systems, Sample 7 with adhesive system based on Cu(II) sulphide coat exhibited the highest value of adhesive strength. New adhesive systems based on Co(II) and Cu(II) sulphide coats reached lower values than double adhesive system, which is commonly used in industry. Based on the obtained results and following analysis, it can be summarised that the surface treatment had influence on adhesive strength. Surface treatment had also influence on adhesive strength of all adhesive systems.

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