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MODIFYING THE ADHESION OF A POLYURETHANE COMPOSITE USABLE AS INSULATION ANTICORROSIVE AND ANTIFOULING ON A METAL SURFACE DEPENDING ON THE NATURE OF THE METAL SURFACE TREATMENT

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ABSTRACT: Considering that high-tonnage industrial landmarks - such as pipelines for transporting hydrocarbons from offshore to the shore - cannot be made from expensive types of steel such as stainless steel based on chromium alloys which could provide a satisfactory anti-corrosion protection but not an anti-fouling one, is the use of adequate insulation. The insulation is a non-metallic, polymeric material, that is deposited on the metal surface. It can be initially in the form of a liquid that is deposited through a painting process or in the form of strips of an elastic material that wrap around the metal pipe. The technological process of isolation after the manufacture of the metal landmark it has both an economic advantage - it is cheaper to insulate a metal landmark made of a cheaper variety of steel as well as technologically, since through adequate modification of the insulation material both anti-corrosion protection and anti-fouling protection are achieved. The only problem that needs to be solved is the realization of a proper adhesion of the insulation on the metal surface it protects. In the current paper, the doctoral student proposed to highlight the effect of various surface treatments on the adhesion of the protective composite on the metal surface.

KEYWORDS: steel pipes, anticorrosive protection, polyurethane, adhesion

1. INTRODUCTION

In most cases, the metal products made for industrial purposes are made of steel of various types and qualities of steel. Some of these products must work in corrosive environments such as sea water. Sea water is an environment that exerts its destructive influence in two ways: Sea water is a solution of salts - predominantly NaCl, which has a strong corrosive effect as a result of electrochemical action on the one hand. On the other hand, sea water is a living ecosystem in which micro and macroorganisms live and develop. These life forms have the quality to adhere to the surfaces of immersed objects and to develop further once they have adhered to those surfaces. The enzymes secreted by these micro- and macro-organisms that adhere to metal surfaces immersed in seawater also exert a strong corrosive effect. Considering that high-tonnage industrial landmarks - such as pipelines for transporting hydrocarbons from offshore to the shore - cannot be made from expensive types of steel such as stainless steel based on chromium alloys which could provide a satisfactory anti-corrosion protection but not an anti-fouling one, is the use of adequate insulation. The insulation is a non-metallic, polymeric material, that is deposited on the metal surface. It can be initially in the form of a liquid that is deposited through a painting process or in the form of strips of an elastic material that wrap around the metal pipe. The technological process of isolation after the manufacture of the metal landmark has both economic advantages - it is cheaper to insulate a metal landmark made of a cheaper variety of steel as well as technologically, since through adequate modification of the insulation material both anti-corrosion protection and anti-fouling protection are achieved. The only problem that needs to be solved is the realization of proper adhesion of the insulation on the metal surface it protects. In the current paper, the doctoral student proposed to highlight the effect of various surface treatments on the adhesion of the protective composite on the metal surface. The the doctoral student researcher opted for the polyurethane matrix to achieve the anti-corrosion and anti-fouling protection because polyurethane is a versatile material, which can be easily modified with various components so as to acquire appropriate technological properties, at the same time, the polyurethane matrix has a very good adhesion to metal surfaces, which makes it suitable for these uses. For the purpose of checking adherence of the polyurethane matrix on metal area, a series of test pieces were obtained during the research work, on which a series of shear tests were performed. Three groups of samples were made for a comparative study. The first group of samples were those whose surface was subjected to a mechanical treatment to increase the surface by abrasion without any other type of treatment. A second group of samples consisted of samples with chemical surface treatment. The chemical treatment consisted in the initial immersion of the metal samples in an acidic solution of aqua regia - 3HCl /1HNO_3. A third group of samples was obtained through physical surface treatment. The physical treatment consisted in the application of a thin layer of graphite by means of electrical impulse discharges. Following an electrical discharge process carried out with the help of a 600microfarad capacitor battery, small portions of material are released from a pyrolytic graphite cathode in the form of vapors [1]. As a result of the fact that they are in an electric field, they are transported from the cathode to the metal anode where they condense and are deposited on its surface. as a result of the very high kinetic energy, the graphite molecules thus transported in the electric field are projected onto the metal surface of the metal anode and acquire a high adhesion relative to it. A series of samples were made without any surface treatment to be considered as control samples to which the results obtained in the other cases are compared.

2. EXPERIMENTAL RESEARCH METHODOLOGY

The research works that made up the subject of this article are part of the works related to the doctoral thesis with the title *Procedure for application of composite materials based on elastomers on metal surfaces, in view of increasing anti-corrosion and anti-vegetation resistance,* of PhD student Mrs. Marin Catalina Daniela under the supervision of Mr. Professor PhD Pavel Topala.

2.1 Materials and equipment used

For the research works related to this article, a series of raw materials, materials and devices from the ICECHIM endowment were used. These consisted of the raw materials for the realization of the polyurethane matrix, metal plates made of laminated steel type OL 37, hydrochloric acid, nitric acid, apparatus for tensile tests.

2.1.1 Obtaining the polyurethane matrix

Polyurethanes [2, 3] are polymers that are mostly manufactured "in situ". Practically, in a majority component that contains all the elements of the composition (hydroxyl component, antioxidants, dyes, catalysts), called the polyol component, due to the fact that in its molecular structure it contains groups with active hydrogen (-OH or -NH2), it is introduced into time of use, a cross-linking agent, which is a di or polyisocyanate. Following the chemical reaction between the groups with active hydrogen (-OH or -NH2) and the isocyanate group – N=C=O, strong chemical bonds result which give rise to a macromolecular chain with a molecular weight between 100,000 and 300,000 UAM. A polymer matrix is synthesized the reactants specified below:

- **A polyol or a mixture of polyols** - carriers of OH groups [4]. Polyols are compounds with a strong acidic character which contain OH chemical groups in their molecule. Polyether polyols that are used in the synthesis of polyurethanes have molecular masses between 350 and 5500 UAM [5]. The synthesis of these chemical compounds containing OH groups occur as a result of successive additions of ethylene oxide or propylene oxide to a molecule containing OH groups. Polyols that have the R-O-R group in their molecule are called polyether polyols, and polyols that contain the R-CO-R group in their molecule are called polyester polyols. [6]. Depending on the molar ratio of –OH groups /epoxy groups, a polyol with a higher or lower molar mass is obtained. The chemical process is known as a "step-growth polymerization" synthesis.
- **A reaction catalyst** for the polyaddition reaction. The catalysts of the polyaddition reaction leading to the formation of a polyurethane macromolecule can be classified into two categories:
  - **Organic amines** [6, 7] especially tertiary amines – DABCO or 1,4-diazobicyclo [2.2.2] octanes [8], Dimethylaminoethanol, also known as DMAE or dimethylethanolamine [9], triethylamine N(CH2CH3)3 [10],
  - **organic salts** of heavy metals Sn, Pb, Hg [11] Bi, of fatty acids (octoates, carboxylated naphthenates [12 ,13]
- **A crosslinker** -N=C=O group carrier

To obtain the polyurethane matrix in the laboratory, the following raw materials were used: Polyether polyol type PETOL 36 3 BR hygroscopic substance, having a linear chain with three branches, obtained from the polycondensation reaction between glycerine and propene oxide. It has a molecular weight of 4800-5000 UAM, isocyanuric component [84] 12, TDI and MDI were used in the laboratory, TDI - 2.4 and 2.6, 80/20 – 80% isomer 2.4 and 20% isomer 2.6), MDI - diphenylmethane – 4, 4` diisocyanate monomer, The reaction catalyst: Sn^{2+} octoate and Pb^{2+} octoate were used as the reaction catalyst. Regarding the antifouling protection agent, a mixture of monovalent copper oxide Cu_2O and copper pyrithionate was used in a ratio of 10/1. The raw materials mentioned above were mixed into the polyol in a well-established recipe that together with a quantity of crosslinker, that would only achieve a pre-crosslinking UAM max 20,000. The raw materials mentioned above were mixed in the polyol in a recipe whose final crosslinking will be achieved when the polyurethane is used as a protective film by adding the rest of the crosslinker in excess of the reaction stoichiometry. The crosslinker surplus will be 20-25% compared to the required reaction stoichiometry.

2.1.2 Obtaining experimental samples

To carry out scientific research on this topic, a series of markers were made from stamped steel sheet type OL 37 and a polyurethane adhesive – scientific conception of the PhD student, with a very good compatibility, which determines a good adhesion to metal supports.

Figure 1. Metal samples [14]

The metallic surface is non-oxidized silver-white with a roughness resulting from the technological lamination process. There was no intervention on the area of the samples in order to change the roughness (polishing) or to remove the superficial layer of oxide. The samples thus obtained were subjected to the acid surface treatment, graphitization procedure. Some of them were kept without any treatment to be witness evidence.

2.1.3 Graphite film application device

This can be found in the endowment of the Alecu Russo State University in the city of Balti, Republic of Moldova. Performing superficial treatment with the help of this device was achieved.

The experimental research on graphite deposits was carried out under normal conditions in an air environment, in the under-excitation regime of electrical impulse discharges. The electrotechnical device with which the tests were carried out has the following technological characteristics: the energy released in the gap WS = (0 – 5.8) J; the energy accumulated on the capacitor bank Wc= (0 – 14) J; charging electromotive force of the capacitor bank Uc = (0 – 250) V, capacity C = (100 – 600) μF in steps of 100 μF, gap S = (0.05 – 2.5) mm; frequency of electrical discharges f = (0 – 50) Hz, pulse duration (0 – 250) μs [14]. With the help of these constructive characteristics of the electrotechnical device, DEI operations can be performed both in the "hot" mode, which also produces the melting of the electrode, and in the "cold" mode, which induces changes at the nanometric level of the surface subjected to superficial treatment. [1]. The electrotechnical device that generates electrical impulses is made up of functional blocks, developed before the research works related to the doctoral thesis, The electrotechnical device that generates electrical impulses is made up of functional blocks these functional blocks are presented as follows : the power and priming pulses, the power impulse generator, the priming block (intended for the initiation of electrical discharges), the control block, whose role is to synchronize it was concluded that, for the application of graphite films on the surfaces of conductive parts, RC generators with parallel priming can be successfully used the control block, whose role is to synchronize it was concluded that, for the application of graphite films on the surfaces of conductive parts, the control block, whose role is to synchronize it was concluded that, for the application of graphite films on the surfaces of conductive parts, RC generators with parallel priming can be successfully used RC generators with parallel priming can be successfully used [16].

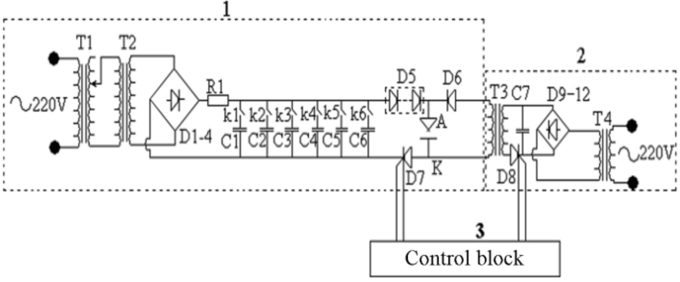

Figure.2 Functional diagram of the electrotechnical device [14]

1 – electrical pulse generator; 2 – the priming block; 3 – the command and execution block

The control block allows to carry out not only the synchronization of the pulses, but also the modification of the working frequency of the generator. The principle of operation of the electrotechnical device, the electrical diagram of which is presented in fig. 2, is as follows: The capacitor bank is charged with static electricity by means of a charging electromotive force of 250V then followed by a voluntary command given, by the discharge of the capacitor bank in the form of an electric pulse DEI (t = 50-220 μs). From a source of continuous current, which is an autotransformer T1, the power transformer T2 and the rectifier D1-4, the capacities C1-C6 are fed through the load impedance R1. Autotransformer T1 allows fine adjustment of the working voltage and supplies electrotechnical device. The electrotechnical device by construction has the electronic block containing the diode D5 which has the role of protecting the device from high voltages intrusion into it. Resistor R1 has the function of limiting the charging current, which prevents the transformation of the electrical impulse discharge into the electric arc discharge. During operation of installation, the set of capacitors C 1-C 6 and the capacitor C 7 are loaded simultaneously. At this moment the control block emits an electrical signal which causes the thyristor D8 to open. As the result of this phenomenon, capacitor C 7 discharges through the primary coil of the high voltage transformer T3 and the electric current begins to flow through it. This electric current produces an electrical discharge on the terminals of the secondary coil, which are connected to the electrotechnical device at the anode and cathode poles. As a result of the high value of the electromotive force at the gap, a conductivity channel is produced. At the same time, the thyristor D 7 opens as a result of a signal given by the control block. The opening of the thyristor D 7 causes the discharge of the capacitors C1-C6. with the formation of the basic pulse. This process is repetitive. The time interval between the opening of thyristor D7 and thyristor D8 is very short. It can be adjusted using the control block. As a control block, the standard pulse generator Г5-60 can be used, which allows both the modification of the working frequency and the synchronization of the power and priming pulses [14,15,16,17].

2.1.4 Electrodes

Graphite electrodes are rods with a length of 50 mm and a diameter of 4 mm. (fig. 2.5). The graphite electrode is caught in the electrical scheme of the device for applying impulses to the cathode [14]

Figure 3. Pyrolytic graphite electrode

2.1.5 Other devices and equipment elements used

For the research works the following were used: desiccator, analytical balance, laboratory glassware, containers, hydrochloric acid HCl, nitric acid HNO_3

2.2 Performing experimental research

The PRINCIPLE of the experimental research was the following: a series of samples were kept without any kind of superficial treatment. A series of samples were treated superficially by the action of the acid mixture and some of the samples were treated superficially by applying a graphite film through the impulse electric discharge process. cross-linked polyurethane with 20% cross-linking agent was applied to the surface of these samples. Overlapping assemblies of two metal plates glued with the applied polyurethane were made. the assemblies thus obtained were left for crosslinking in a desiccator for 24 hours after their creation. After 24 hours, the assemblies were subjected to a shear test on a dynamometer.

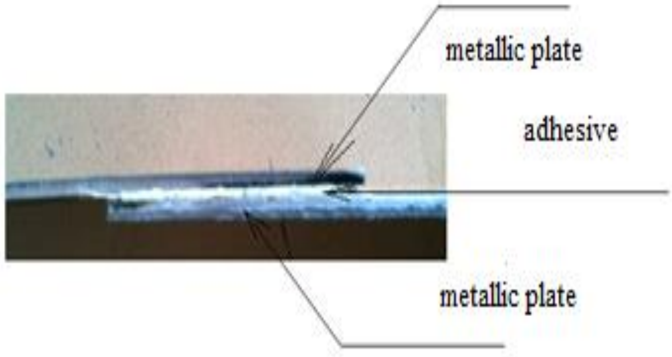

Figure 4. Assembly made in order to carry out the shear test [14,15,16,17]

The differences in values of the shear forces were studied depending on the surface treatment applied to the experimental samples. At the end, conclusions were drawn regarding the influence of the surface treatment on adhesion.

2.2.1 Making samples for the shear test by treating the metal surfaces in an acid environment

The metal plates shown in figure 1 were subjected to the action of a mixture of acids. the acid mixture was obtained in turn by bringing hydrochloric HCl acid and nitric acid HNO_3 into contact in a proportion of 3/1 gravimetric percentages. this mixture of acids is called aqua regia and has strong oxidative properties especially through the nitric component. After the superficial treatment which consisted in immersing the metal plates for 2 minutes in the acid mixture. on the metal surface to obtain chemical species such as oxides, nitrates, nitrites, chlorides, which increase the degree of polarity of the metal surface making it much more compatible with the strongly polar pelliculogen that is polyurethane.

The immersion time should not exceed 2 minutes because the reaction between the acid and metal mixture is particularly violent and would lead to the total degradation of the metal plates. The time of 2 minutes is enough to achieve the above-mentioned polarity poles on the metal surface. After immersion in the acid bath, the metal plates were rinsed with water, then they were completely dried by rinsing with acetone and placing them in a desiccator.

After 24 hours of keeping in the desiccator, the metal plates are removed and glued at one end on a 2.5 cm x 2.5 cm surface.

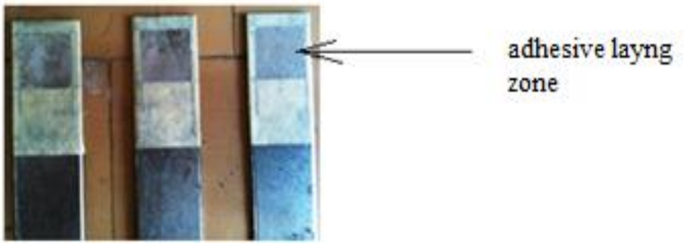

Figure 5. Test pieces to be glued with polyurethane

After overlapping, the assemblies made in this way are placed in a desiccator for 24 hours so that the crosslinking/adhesion process is complete. After 24 hours, the assemblies thus made from plates initially subjected to surface treatment with acids are subjected to shear loading.

They overlap so that the adhesive on the plate above reaches the adhesive on the plate below as shown in fig.4, 5

Figure 6. Assembly made in order to carry out the shear test [14] (normal view).

Shear tests were carried out on a HECKERT FPZ 100 machine, Germany.

Figure 7. Shear tests HECKERT FPZ 100 machine

Clamping the sample assembly in the type traction device HECKERT FPZ 100 was performed cf. fig. 6.

Figure 8. Clamping the sample assembly in the type traction device HECKERT FPZ 100

2.2.2 The realization of the test-piece assemblies by gluing the plates subjected to the application treatment of graphite films through the impulse electric discharge procedure

On a set of plates of the same type of steel and the same dimensions as those from point 2.2.1, graphite films were applied through the process of electrical discharges in pulses [14]. Before the application of this procedure, the metal plates were degreased with acetone, they were left to dry in the desiccator and then caught in the graphite film application device shown in fig.2. The fastening of the metal plates in the device was done at the anode, cf.fig.10

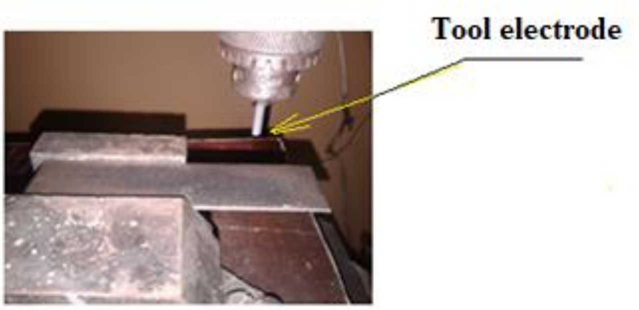

Figure 9. The fastening of the metal plates in the device at the anode pole

The pulsed electric discharge treatment is applied and metal plates are obtained which have deposited a fine graphite film at one end as seen deposited by impulse electric discharge process in fig.10 [14]

Figure.10 The test piece with the graphite film

These metal plates are also treated with polyurethane as the end where the treatment was carried out with electrical impulse discharges. Then overlap so that the treated and glued ends overlap cf. fig. 4. the subsequent procedure of reticulation and shear test is identical to the one carried out in point 2.2.1.

2.2.3 Making the control samples

The construction of the control sample assemblies was carried out identically with the method of obtaining presented at point 2.2.1 and 2.2.2. Opposed to the previous cases, the metal plates with which the control test assemblies were made no treatment was performed on their metallic surface. The metal plates were only degreased with acetone. The shear test of the control test-piece assemblies was done identically to the other test-piece assemblies.

3. RESULTS OBTAINED AND THEIR INTERPRETATION

The results obtained in the three cases were found after performing the shear test on the type apparatus HECKERT FPZ 100 using the scale of 0-100 daN and with a pulling speed of 10 mm/min. 10 sample assemblies were used in each case. The results were presented in fig. 11-14, and table 1-4, and interpreted later. The difference between them was given only by the method of surface treatment in the system, there being no other unknowns.

3.1 Results obtained with blank samples

Table 1. The variation of the values for the shear stress for the samples without surface treatment – control samples.

Sample number	Shear stress values, N/cm^2
1	44
2	44
3	42
4	45
5	46
6	46
7	47
8	45
9	44
10	42

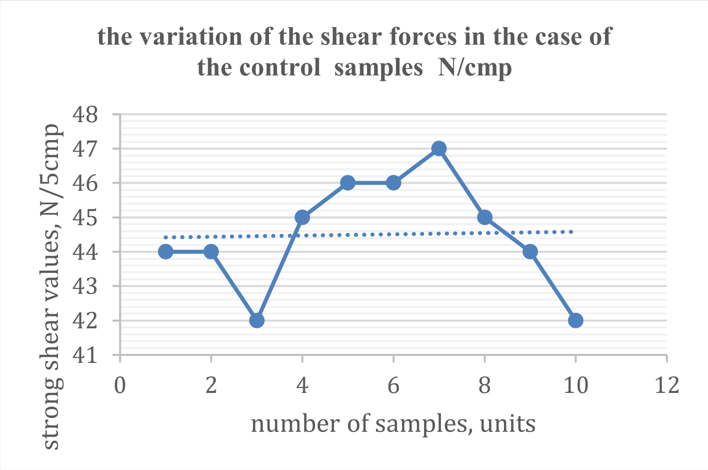

Figure 11. The variation of the values for the shear stress for the samples without surface treatment – control samples.

Table 2. The variation of the values for the shear stress for the samples with acid surface treatment

Sample number	Shear stress values, N/cm^2
1	67
2	65
3	65
4	68
5	64
6	67
7	67
8	66
9	64
10	65

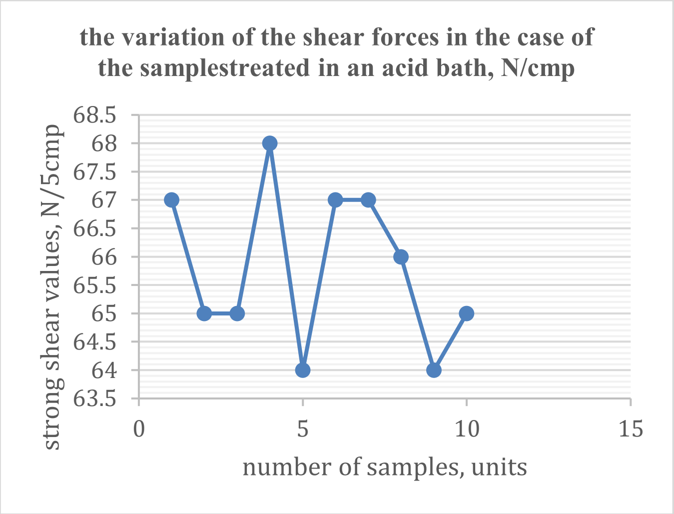

Figure 12. The variation of the values for the shear stress for the samples with acid surface treatment .

Table 3. The variation of the values for the shear stress for the samples with graphite surface treatment.

Sample number	Shear stress values, N/cm^2
1	27
2	27
3	25
4	24
5	24
6	23
7	25
8	26
9	26
10	26

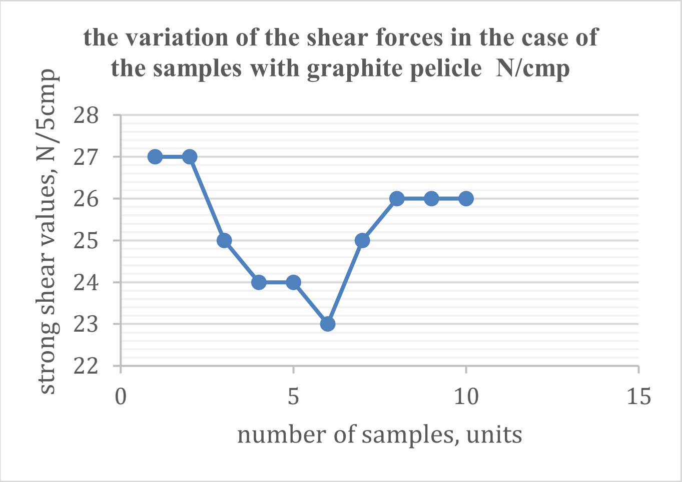

Figure 13. The variation of the values for the shear stress for the samples with graphite surface treatment surface treatment[14].

4. CONCLUSIONS TO THE CONDUCTED STUDY

Following the determinations made in three different technological situations, the following conclusions were reached:

4.1 Control samples

The shear forces expressed in N/cm^2 have values between 42 and 47 N/cm^2. These values are relatively high values for a metal/non-metal adhesion system due to the fact that the polyurethane matrix has a high compatibility and a good adhesion to polar surfaces. The main forces that ensure the adhesion of the polyurethane film to the support are in this case the Wan Der Waals physical forces These values were comparison values for the other two cases presented in this paper.

4.2 Acid surface treatment samples

Shear forces expressed in N/cm^2 have values between 64 and 67 N/5cmp. these values are relatively high values for a metal/non-metal adhesion system due to the fact that the polyurethane matrix has a high compatibility and a good adhesion to polar surfaces. These values are higher than in the case of the control samples as a result of the fact that the acids react with the metal creating polar centers (-NO_2, Cl^- - NO_3, -OCl^-) on its surface. These centers increase the polarity of the surface and at the same time ensure anchors of chemical bonds made between the macro molecules polyurethane and metal surface. to these additional adhesion forces, in this case, add the Wan Der Waals physics forces that occur between the polyurethane matrix and the remaining metal surface.

4.3 Graphite surface treatment samples

The shear forces expressed in N/cm^2 have values between 27 and 23 N/5cmp. these forces are substantially reduced both compared to the adhesion forces identified in the case of control samples and especially in the case of samples with superficial acid treatment. this is due to the fact that the deposited graphite film blocks the metal surface and Wan Der Waals physical forces no longer occur.

Table 4. The variation of the values for the shear stress for all the samples comparable

Sample no	Control samples	Acid treatment samples	Graphite treatment samples
1	44	67	27
2	44	65	27
3	42	65	25
4	45	68	24
5	46	64	24
6	46	67	23
7	47	67	25
8	45	66	26
9	44	64	26
10	42	65	26

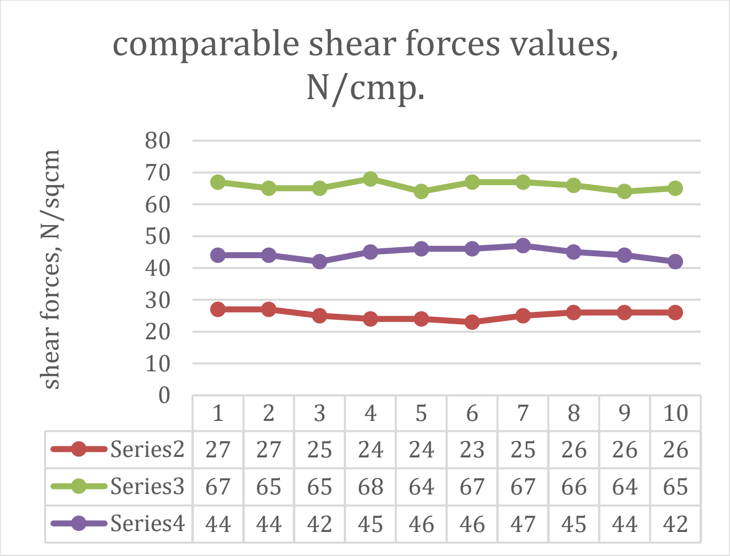

Figure 14. The variation of the values for the shear stress for all the samples comparable

5. ACKNOWLEDGEMENTS

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