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Influence of chemical cleaning of adhesive bonded surface on working environment and adhesive bond quality

A. Krofova[1,*], M. Müller[1] and P. Kic[2]

[1]Czech University of Life Sciences Prague, Faculty of Engineering, Department Material Science and Manufacturing Technology, Kamýcká 129, CZ165 21, Czech Republic
[2]Czech University of Life Sciences Prague, Faculty of Engineering, Department of Technological Equipment of Buildings, Kamýcká 129, CZ165 21, Czech Republic
[*]Correspondence: krofovaa@tf.czu.cz

Abstract. Undesirable chemical substances are released into the environment at single manufacturing operations, namely at a chemical treatment /cleaning of an adhesive bonded surface. The chemical treatment /cleaning of namely metal adhesive bonded surface before an application of the adhesive represents a significant factor having an influence on a resultant adhesive bond strength, i.e. adhesive and cohesive strength.
Producers do not provide information about releasing harmful substances into the atmosphere, i.e. mass values of a flow of polluting substances used at the chemical cleaning of the adhesive bonded surface. These cleaning agents were experimentally investigated.
The aim was to evaluate an adhesive bond quality depending on the chemical treatment of the adhesive bonded surface and the intensity of the chemical agent release into the atmosphere. The adhesive bond quality was evaluated by means of mechanical tests and SEM analysis.
The increase of the adhesive bond strength does not conclusively occur when using the chemical treatment of the adhesive bonded surface compared to the adhesive bonds with only mechanical treatment of the adhesive bonded surface, except for the chemical cleaning in the acetone bath. This treatment proved always in a positive way.

Key words: adhesive bond, chemical treatment, chemicals contamination, evaporation.

INTRODUCTION

Undesirable chemical substances are released into the environment at single manufacturing operations. Chemical substances or aerosols should be caught and ventilated according to technical possibilities directly at their source, i.e. e.g. in a production hall. Namely the production of adhesive bonds at using the chemical cleaning of the adhesive bonded surfaces is a problem (Bjørgum et al., 2003; Lunder et al., 2004; Müller et al., 2011; Müller & Valášek, 2013; Müller, 2015).

The proper preparation of the surface by different mechanical, physical or chemical processes or by their combination removes impurities, i.e. 'weak boundary layer'. If the impurity is not removed from the surface or if there are layers on the surface which are not firmly connected to the adhesive material, the adhesive is either not able to wet the adhesive bonding surface or a thin adhesive layer is made, thus it is reducing the strength of the adhesive bond (Messler, 2004; Prolongo et al., 2006).

Treatments of the adhesive bonded surface usually involve mechanical, chemical and combined methods of the preparation (Müller & Valášek, 2014; Cidlina & Müller, 2015; Krofová & Müller, 2016. It is not always technologically desirable to use all combinations of the adhesive bonded surface treatments (Krofová & Müller, 2016).

The chemical cleaning of the adhesive bonded surface represents a significant factor having an influence on the resultant adhesive bond strength (Lunder et al., 2004; (Rudawska, 2014). Producers of chemical cleaning agents usually do not provide technical data about releasing these undesirable substances. Most of manufacturing facilities are equipped with ventilation equipment which do not sometimes fully remove polluting substances. Subsequently, namely the working environment is significantly deteriorated.

Owing to the fact that producers do not provide information about releasing harmful substances into the atmosphere, i.e. mass values of a flow of polluting substances used at the chemical cleaning of the adhesive bonded surface, these cleaning agents were experimentally investigated. The research based on determining the mass flow of polluting substances which leak into the production hall was performed at different chemical agents used for the adhesive bonded surface cleaning. An intensity of the ventilation equipment was calculated in a model space determined for the production of adhesive bonds for different chemical cleaning agents used for the adhesive bond preparation.

The chemical cleaning is a process in which we remove coarse impurities and an antiadhesive layer. Its task is to create an original clean surface by removing the fats, oils, grease etc. on the surface of the adherent. It is also used to increase the adhesion of the adhesive to the adherent surface which results in a creation of surface chemical bonds allowing the reaction molecules of the adherent and the adhesive to form strong bonds (Comyn, 1990; Habenicht, 2002; Krofová & Müller, 2016).

The secondary aim was to evaluate an adhesive bond quality depending on the chemical treatment of the adhesive bonded surface and the intensity of this chemical agent release into the atmosphere. The adhesive bond quality was evaluated by means of mechanical tests and SEM analysis.

A benefit of this research is a comparison of reached values of the adhesive bond strength and a wettability of the adhesive bonded surface depending on values of an evaporation of chemical cleaning agents.

MATERIALS AND METHODS

The amount of substances released into the air during handling with them is not defined by a producer anywhere, due to the many different factors that affect the speed and the amount of evaporated substances. For example depending on the area of evaporation (Fig. 1). The requirements of health and safety at work are summarized in Decree no. 361/2007 Coll., (Act No. 262/2006 Coll.). Referred Exposure Limits OEL and MEL valid for the Czech Republic may be in some cases slightly different (usually higher) from exposure limits valid in the EU or in other countries, however, the principles and solution of this research these small differences do not affect. The evaporation was determined in the following way. The experiment was performed in a ventilated laboratory at 22 ± 2 °C, humidity of 60 ± 3% and an atmospheric pressure of 986 hPa. For the determination of the evaporation laboratory bowls of three different areas (diameter: 190 mm, 95 mm and 60 mm) were used and using analytical weights mass losses were recorded in real time to the laptop for each substances used for the chemical preparation of the surface of bonded specimens at intervals of 45 minutes.

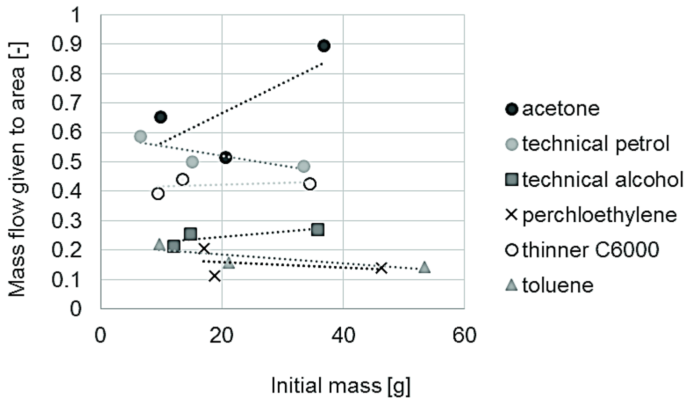

Figure 1. Influence of area on mass flowing.

The evaluation of the adhesive bond quality depending on the chemical treatment of the adhesive bonded surface was performed in accordance with the standard CSN EN 1465. Experiments were performed on standardized test specimens of structural carbon steel S235J0 and manufactured according to the standard EN 1465 by cutting the steel workpiece (100 x 25 x 1.5 mm). The overlapping length of the adhesive bond was 12.5 ± 0.25 mm. Test specimens with the mechanical treatment of the adhesive bonded surface were used for the bonding. The grit blasting by a garnet MESH 80 was the mechanical treatment. The adhesive bonded surface was chemically treated prior to the bonding process. The chemical cleaning of the adhesive bonded surface was performed in the following substances: a bath of acetone, a bath of technical petrol, a bath of technical alcohol, a bath of perchlorethylene, a bath of thinner C6000 and a bath of toluene.

The comparing standard was the surface only mechanically treated by grit blasting without the chemical cleaning. Ethanol was mechanically treated surface the grid blasting without chemical cleaning adhesive bonding surface.

For bonding three structural two-component epoxy adhesives were applied. Structural epoxy adhesives are particularly applied in an industrial manufacturing. The epoxy based adhesive-bonded steel is known to have a good stiffness and the strength, providing a potentially wide range of applications, especially in vehicle structures (Lin et al., 2011; Lu et al., 2011; Krofová & Müller, 2016).

Following adhesives were used: two-component epoxy adhesives Bison metal (further marked as BM), GlueEpox Rapid (further marked as GER) and GlueEpox Rapid F (further marked as GEF).

The roughness parameters Ra and Rz were measured on the adherent's surface designated for the adhesive bonding. Roughness parameters were measured with the portable profilometer Mitutoyo Surftest 301. The boundary wave length of cut-off was placed to 0.8 mm. The roughness parameter Ra was 1.82 ± 0.19 µm and Rz was 11.16 ± 0.97 µm.

Adhesive bonds were chemically cleaned in a chemical bath (except for the comparing standard). The adhesive was applied to the first adhesive part (adherent). Subsequently, the second bonded part (adherent) was attached and the adhesive bond was fixed with a weight of 750 g.

The testing sample was kept with the laboratory temperature 22 ± 2 °C for 48 hours after the fixation of the adhesive bond. After that the destructive testing followed.

Fig. 2 shows the cut through the adhesive bond. The cohesive layer of the adhesive, the adhesive layer of the adhesive and the adhesive bonded material at the same time are essential for the adhesive bond strength.

The tensile strength test (according to CSN EN 1465) was performed using the universal tensile strength testing machine LABTest 5.50ST (a sensing unit AST type KAF 50 kN, an evaluating software Test&Motion). The loading speed of the deformation corresponded to 5 mm min^{-1}. The failure type was determined at the adhesive bonds according to ISO 10365.

Fracture surfaces and an adhesive bond cut were examined with SEM (scanning electron microscopy) using the microscope MIRA 3 TESCAN (the fracture surfaces were dusted with gold) at the accelerating voltage of the pack (HV) 5.0 kV and the stereoscopic microscope Arsenal. The surface of specimens was coated with the gold dust using the device Quorum Q150R ES – Sputtering Deposition Rate using Gold.

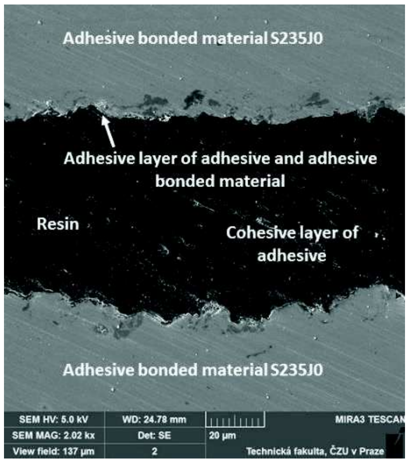

Figure 2. SEM images of cut through adhesive bond (MAG 2.02 kx).

The results of measuring were statistically analysed. Statistical hypotheses were also tested at measured sets of data by means of the program STATISTICA. A validity of the zero hypothesis (H_0) shows that there is no statistically significant difference ($p > 0.05$) among tested sets of data.

RESULTS AND DISCUSSION

Results of the effect of the surface treatment of the structural carbon steel S235J0 to an adhesive bonding strength (Fig. 3) did not prove the essentiality of this factor at all chemical treatments of the adhesive bonded surface compared to the comparing standard. The adhesive bond strength was not conclusively increased when using the chemical treatment of the adhesive bonded surface.

When using the chemical treatment (acetone, technical petrol, technical alcohol, thinner C6000 and toluene) of the bonded surface the adhesive bond strength was increased in the interval from 7.5 to 51.5% at the adhesive BM. When using the chemical treatment (perchlorethylene) of the bonded surface the adhesive bond strength was decreased of 1.3% at the adhesive BM.

When using the chemical treatment (acetone, technical petrol, technical alcohol, thinner C6000 and toluene) of the bonded surface the adhesive bond strength was increased in the interval from 1.2 to 7.7% at the adhesive GEF. When using the chemical treatment (perchlorethylene) of the bonded surface the adhesive bond strength was decreased of 3.8% at the adhesive GEF.

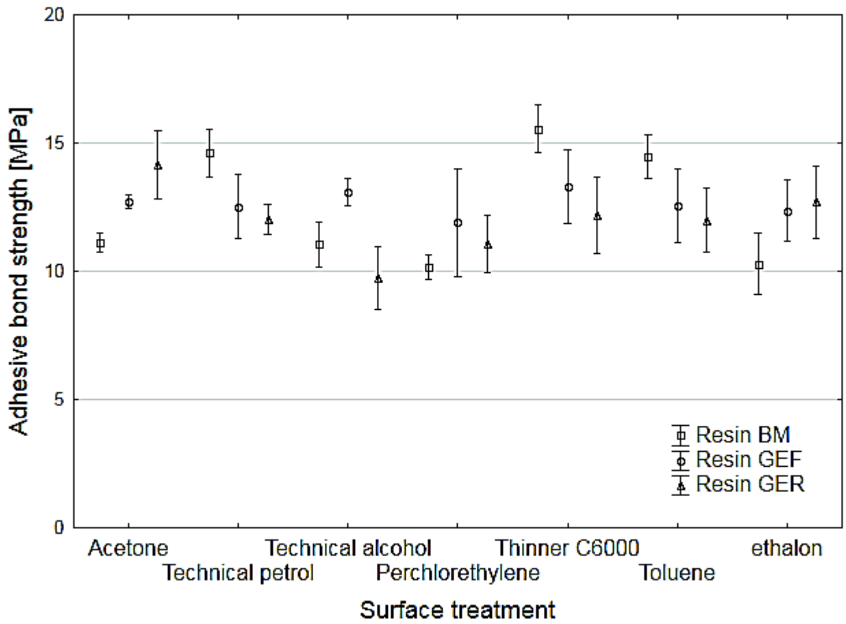

Figure 3. Influence of different treatments on adhesive bond strength.

For the adhesive GEF it was not been demonstrated so significant effect of the bonding surface treatment as for other tested adhesives.

When using the chemical treatment (technical petrol, technical alcohol, thinner C6000, toluene and perchlorethylene) of the bonded surface the adhesive bond strength was decreased in the interval from 4.1 to 23.5% at the adhesive GER.

When using the chemical treatment (acetone) of the bonded surface the adhesive bond strength was increased of 11.4% at the adhesive GER.

It follows from the results that most of chemical treatment affect the adhesive bond strength (the adhesive GER) in a negative way.

The influence of different chemical treatments of the adhesive bonded surface on the adhesive bond strength was proved. These conclusions are also agreed by other researches (Krofová & Müller, 2016).

In terms of the statistical testing of the effect of the surface treatments it is possible to state that different chemical treatments are statistically non-homogeneous groups at the application of adhesives BM and GER. The hypothesis H_0 of these adhesives was not confirmed, i.e. there is a difference in the strength of the adhesive bond at a significance level of *0.05* among different treatments of the adhesive bonded surface. From the statistical analysis it is obvious that the treatment of the adhesive bond significantly influences the adhesive bond strength, i.e. adhesive BM ($p = 0.000$) and adhesive GER ($p = 0.001$).

In terms of the statistical testing of the effect of the surface treatments it is possible to state that various chemical treatments are statistically homogeneous groups at the application of the adhesive GEF. The hypothesis H_0 was certified, i.e. there is not difference in the adhesive bond strength in the significance level *0.05* among single adhesive bonded surface treatments when using the adhesive GEF. It is visible from the statistical testing that the adhesive bond treatment does not significantly influence the adhesive bond strength at the adhesive GEF ($p = 0.446$).

Fig. 4 presents results of the elongation of the adhesive bonds. A significant change of the elongation occurred only at the adhesive bonds bonded with BM (technical petrol, thinner C6000 and toluene). The hypothesis H_0 was certified, i.e. there is no difference in the elongation of the adhesive bond in the significance level 0.05 among single adhesive bonded surface treatments when using the adhesives GEF and GER. It is visible from the statistical testing that the adhesive bond treatments does not significantly influence the elongation of the adhesive bond when using the adhesive GEF ($p = 0.140$) and GER ($p = 0.163$).

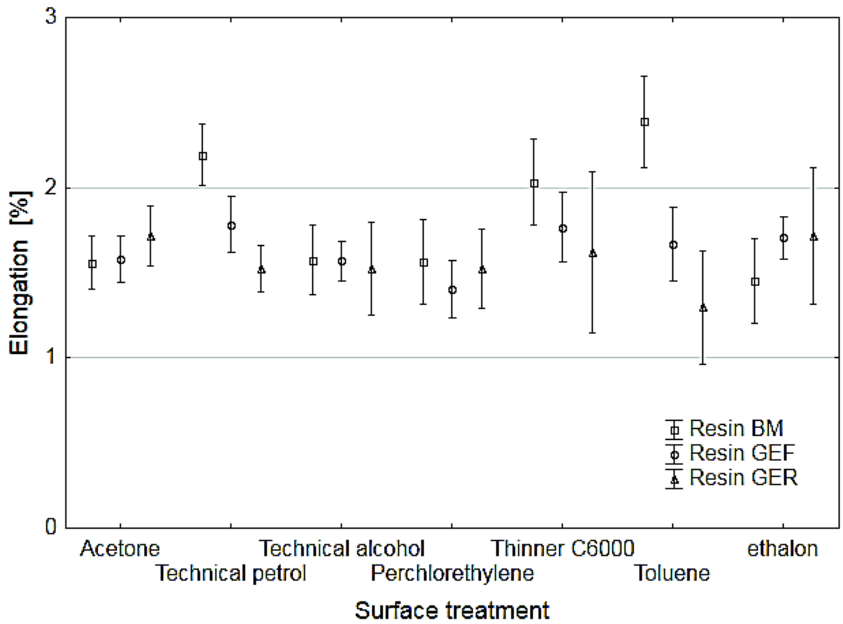

Figure 4. Influence of different treatments on adhesive bond elongation.

In terms of statistical analysis of the velocity (Fig. 5) of the evaporation of chemical substances intended for the chemical treatment of the bonded surface, it is possible to state that this is a statistically inhomogeneous group, i.e. the difference between the individual chemicals.

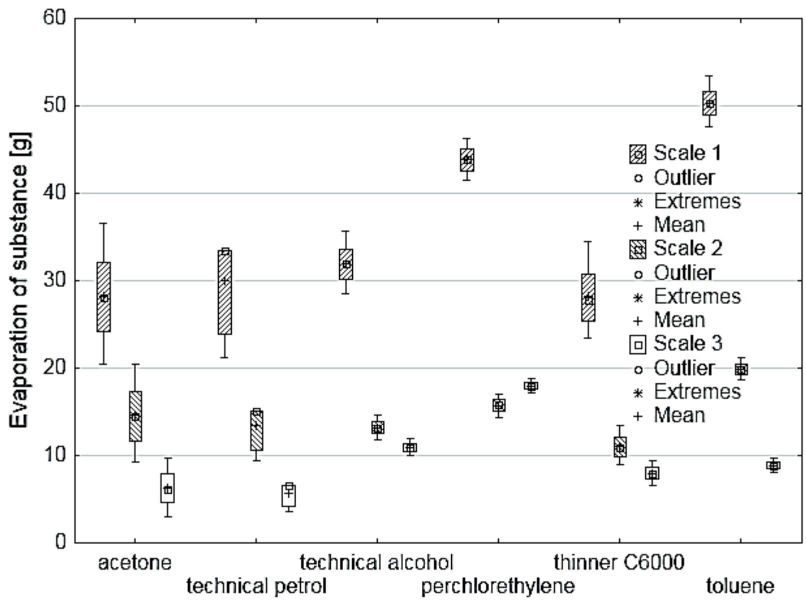

Figure 5. Velocity of the evaporation of chemical substances.

H_0 hypothesis was not confirmed, ie. there is a difference in significance level of *0.05* between the test chemical degreasers, ie. $p < 0.05$ even at the level of different sizes, from which there were evaporation (scale1: $p = 0.000$, scale2: $p = 0.000$ and scale3: $p = 0.000$). Statistically difference was detected in the tested products intended to modify the chemical bonding surface. Toluene and trichloroethylene are agents which vaporized the most significantly. Other tested agents for the chemical treatment showed similar values evaporation.

The mass flow values of produced pollutant according to the different surfaces M_{sm} were measured experimentally in the laboratory. Determined productions M_{sm} of harmful substances presented at the Table 1.

Table 1. Evaporation of chemical substances

Agent	Equation
acetone	$y = 0.0101M_p + 0.4630$
technical petrol	$y = -0.0033M_p + 0.5873$
technical alcohol	$y = 0.0017M_p + 0.2117$
perchlorethylene	$y = -0.0009M_p + 0.1783$
thinner C6000	$y = 0.0006M_p + 0.4089$
toluene	$y = -0.0015M_p + 0.2160$

* y = mass flow given to area, Mp = initial mass.

The cohesive failure was ascertained at all treatments of the adhesive bonded surface at the adhesive BM. The adhesive failure was ascertained at all treatments of the adhesive bonded surface at the adhesive GER. The adhesive/cohesive failure was ascertained at the chemical treatments with acetone, toluene and perchlorethylene at the adhesive GEF.

A presence of cracks in the interface of the adhesive boned material and the adhesive was proved by use of the electron microscopy (SEM) within the experimental research (Fig. 6, A, B). So, there was a poor wettability. The poor wettability was namely at the grit blasting without the chemical cleaning of the adhesive bonded surface (Fig. 6, A). The abrasivum from the mechanical treatment of the adhesive bonded surface was left between the adhesive bonded material and the adhesive layer (Fig. 6, A). Nor the chemical cleaning of the adhesive bonded surface did not secure a sufficient wettability of the adhesive bonded surface, i.e. the presence of cracks in the interface of the adhesive bonded material and the adhesive was proved (Fig. 6, B). Good wetting of the adhesive bonded surface is obvious from Fig. 6, C.

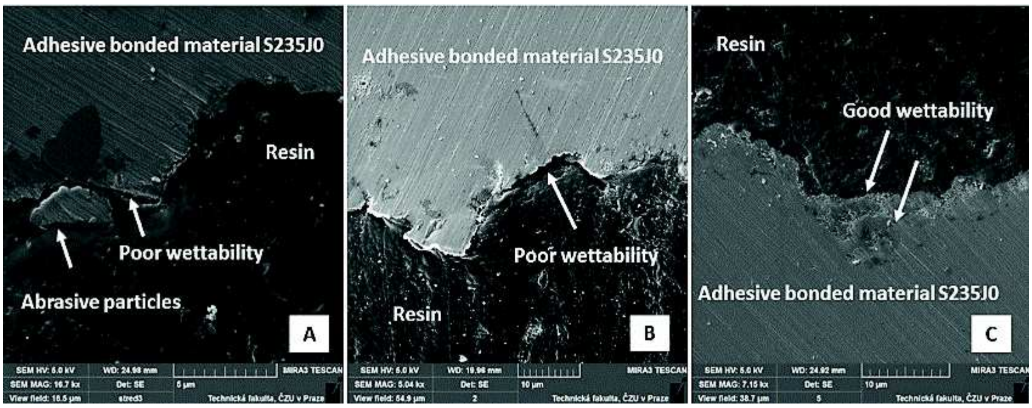

Figure 6. SEM images of interaction of adhesive layer and adhesive bonded material, adhesive GER (secondary electron): A: mechanical treatment (grit blasting) without chemical cleaning of adhesive bonded surface (MAG 16.7 kx), B: mechanical treatment (grit blasting) with chemical treatment, technical alcohol (MAG 5.04 kx), C: mechanical treatment (grit blasting) with chemical treatment, acetone (MAG 7.175 kx).

The research results showed that the adhesion of the adhesive layer was strongly dependent on the type of the treatment of the adhesive bonded surface (Bajat et al., 2007; Müller, 2015; Krofová & Müller, 2016). The efficiency of chemical methods was not as crucial to the adhesive bonding strength (Bockenheimer et al., 2002). That conclusion was confirmed for the adhesive GEF. It was not confirmed for the adhesives BM and GER.

The surface preparation was done in order to achieve the maximum surface wettability of selected adhesives. This creates ideal conditions for contacting the adhesive with the adherent surface and the formation of adhesive bonds (Gent & Lai, 1994; Harris & Beevers, 1999; Elbing et al., 2003; Packham, 2003).

Experimental results clearly demonstrated that different values of the adhesive bond strength depending on the type of the chemical cleaning of the bonded surface had been achieved even with the same roughness of the adhesive bonded surface. Analogical conclusions were reached also at the electrolytic galvanized steel (Krofová & Müller, 2016).

CONCLUSIONS

The paper describes the influence of the adhesive bonded surface treatment and the intensity of releasing the chemical cleaning agents into the air on the strength and the quality of the adhesive bond. The comparison of reached values of the adhesive bond strength and the wettability of the adhesive bonded surface depending on the values of the evaporation of the chemical cleaning agents was done within the research.

Following conclusions can be deduced from the research results:

- When using the chemical treatment of the adhesive bonded surface (the structural carbon steel S235J0) the adhesive bond strength increase did not conclusively occur compared to the adhesive bonds with only the mechanical treatment of the adhesive bonded surface. The difference in the adhesive bond strength values ranged in the horizon: a fall of ca. 25% and an increase up of ca. 51%. The strength increase was always only at the chemical treatment with acetone, at all three tested structural adhesives.
- The presence of cracks in the interface of the adhesive bonded material and the adhesive was proved by the use of the electron microscopy (SEM) within the experimental research at the mechanical treatment by the grit blasting (without the chemical cleaning of the adhesive bonded surface) and at the mechanical treatment by the grit blasting and with the chemical treatment with the technical alcohol. The residues of the abrasivum from the grit blasting process remains on the surface at the comparing standard, i.e. only at the mechanical treatment.
- There is a difference between the test chemical degreasers. Statistically difference was detected in the tested products intended to modify the chemical bonding surface. Toluene and trichloroethylene are agents which vaporized the most significantly.

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