The study of polyurethane adhesive composition in aggressive environments

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Abstract. As a result of the research, the effectiveness of the use of the proposed fast-curing adhesive composition based on cold-curing polyurethanes during car repairs was confirmed. Prerequisites have been created for creating a new generation of universal polyurethane adhesive compositions for restoring vehicles with improved adhesion, physical engineering and performance properties that are highly resistant to aggressive environments and are made from materials of domestic production. The feasibility of the work is due to the presence in the market of expensive analogs of foreign production for the restoration of car parts, and therefore the task is to develop import-substituting compositions.

1. Introduction
In today's market economy conditions, operations for the restoration of transport and technological machines and complexes, as well as their maintenance, should be involved in a single, unified system of material and technical equipment. As a result, there was a need for new technologies that do not require large investments of material, monetary and labor resources, and could be applied not only by specialized technical repair services, repair companies but also by private owners of equipment.

The technical operation of modern mobile equipment and equipment requires targeted search and modern methods of their repair and restoration. One of these methods can be called bonding. A long experience in the use of adhesive polymeric materials in the restoration of specialized equipment, including in the field, has shown: bonding is the most universal of its restoration methods. Compared to such traditional methods as welding, brazing, mechanical hardening, etc., it is much simpler from a technological point of view.

The method of repairing and restoring elements of agricultural and special equipment due to adhesive bonding is a rather economical, high-performance and energy-intensive process because it allows for repairs without disassembling remanufactured components and assemblies. The advantage of bonding is that this method of restoring vehicle elements is applicable to materials of different nature.

2. Object and research methods
At the Penza State University of Architecture and Construction, a fast-curing adhesive composition based on cold curing polyurethanes was developed to restore the cost of parts of various transport and technological machines [8]. It can be used for the restoration and repair of plastic elements of the car, as well as in mechanical engineering.
Quite an important role in the selection and further use of adhesive polymer composite, subject to the impact of negative, aggressive environments is chemical resistance [4].

The performance of adhesive compositions in contact with aggressive environments of various kinds is determined by the activity of the fluids of these environments; chemical structure of adhesive polymer; the ratio and compatibility of the interacting components of adhesive compositions; their physical and phase state, as well as the type of mechanical load and exposure temperature [7].

The process of establishing the mechanism of action of aggressive environments on adhesive composition is very difficult. In general, it includes a number of points:

- adsorption of environmental molecules on the surface layer of polymeric adhesive materials;
- diffusion of the environment into the volume of materials;
- physicochemical interaction of the aggressive environment with a filler and polymer matrix;
- removal of reaction products from the surface;
- formation of a layer from the reaction products, which prevents diffusion and convective penetration of the environment aggressively into the adhesive material [1, 3].

The occurrence of the above factors, as a rule, contributes to the change (most often the deterioration) of the main operational properties, for example, mechanical, diffusion, sorption, as well as a change in the mass of the adhesive polymer, its appearance. Under the influence of chemically active environments, a process of destruction occurs, which helps to reduce the strength of the polymer material.

The chemical resistance of adhesive compositions depends on their structural features, as well as chemical ones. Various factors affect the chemical resistance when exposed to aggressive environments:

- the nature of the basis of the adhesive composition, since the modified polyurethane polymers are hetero-chain (in their main chain there are, besides carbon, other atoms), they are subject to destruction under the action of high temperatures and aggressive substances;
- the presence of functional reactive groups that are part of the adhesive composition;
- the speed of the process of diffusion and swelling is influenced by the structure of the base of the adhesive composition, as well as the degree of crystallinity;
- the nature and amount of filler. For example, when introducing into the composition of inert fillers, combined with the polymer, resistance to aggressive environments increases [2, 6].

The degree of mass absorption after exposure of the prototype of aggressive environments, namely chemical reagents was according to the method of ISO and GOST 12020-72 [5].

The method of determination was that the adhesive compositions in the form of cubes with a size of $1 \times 1 \times 1$ cm were initially located for two weeks under normal conditions. Subsequently, all obtained samples were weighed on electronic scales with an accuracy of 0.001g. Then the samples of adhesive compositions completely immersed in the environment:

- Water.
- Alkali NaOH, 10%.
- Alkali NaOH, 20%.
- Alkali NaOH, 30%.

Studies of the action of aggressive environments were carried out on adhesive compositions of the obtained samples. Measurements were made within 2 months because the swelling by this time significantly stops. To determine the quantitative diffusion of alkaline environments in an adhesive
polymer material, experimental studies of the degree of mass absorption were performed. Before the control weighing, the samples were removed, rubbed to dryness, weighed to the nearest 0.001 g.

3. Results of research and discussion

![Graph showing the degree of mass absorption in water.](image1)

\[ y = 0.76(1 - e^{-0.065x}); R = 0.99; S = 0.04 \]

**Figure 1.** Change in the degree of mass absorption in water.

![Graph showing the degree of mass absorption in 10% NaOH solution.](image2)

\[ y = 0.93 \cdot (1 - e^{-0.0688x}); R = 0.98; S = 0.07 \]

**Figure 2.** Change in the degree of mass absorption in a 10% NaOH solution.
In the considered aggressive environments swelling is observed, but this process is limited. Changes in the mass of samples of adhesive compositions differ in the range of temporal stabilization and a certain depth of diffusion of the environment.

From the conducted studies of kinetic dependencies, it should be noted that among the environments considered, the most aggressive is water. It is the most polar of all the considered aggressive environments, has a number of features, for example, the small size of molecules. In 10 percent solution of NaOH, there is no sharp decrease in the degree of mass absorption.

![Graph](image)

**Figure 3.** Change in the degree of mass absorption in a 20% solution of NaOH.

Experimental studies of the degree of mass absorption of the developed samples of adhesive compositions in acid environments were carried out by a similar method. As a result, it was found that the degree of mass absorption in a 10 percent solution of sulfuric acid was higher than in 20-30 percent solutions. This phenomenon can be attempted to be explained by the fact that the decrease in the amount of solvent decreases the degree of electrolyte dissociation, which helps reduce the rate of penetration of acid ions into the internal structure of samples.

![Graph](image)

**Figure 4.** Change in the degree of mass absorption in a 30% NaOH solution.
As a result of the experiment, it was found that in most cases the effects of aggressive environments on samples of adhesive materials, there was a sharp increase in the degree of mass absorption for 15 days, and then the process is balanced. This is due to the fact that in the process of diffusion, molecules of aggressive environments penetrate into the pores of the surface layer, as well as its defects until the samples are completely filled.

\[ y = 0.8(1-e^{-0.069x}); \quad R=0.97; \quad S=0.06 \]

**Figure 5.** Change in the degree of mass absorption in a 10% solution of H2SO4.

\[ y = 0.588(1-e^{-0.066x}); \quad R=0.98; \quad S=0.045 \]

**Figure 6.** Change in the degree of mass absorption in a 20% H2SO4 solution.
The next stage is a slight dissolution, due to the softening of weak chemical bonds. This stage goes into a smooth swelling at a constant speed, until the moment when the process of mass increase, that is, swelling, stabilizes.

Thus, an experimental test showed that the developed polyurethane modified adhesive compositions of a new generation with improved adhesive properties, reduced curing time, have high chemical resistance in almost all aggressive environments.

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