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Organosilicon varnishes, such as polymethylphenylsiloxane and polyaluminomethylphenylsiloxane, filled with modified clay minerals are the object of research. The most vulnerable place of the organosilicon coating is insufficient mechanical properties (hardness, impact strength, etc.) and low adhesive strength of the film to the surface, especially when operating at elevated temperatures. Various oxides, ceramic compounds, natural and synthetic silicate materials are introduced into organosilicon compositions to improve the specified properties. But only individual units can comprehensively improve both the mechanical and heat-resistant properties of organosilicon compounds although the range of such materials is quite wide.

The clay minerals palygorskite, which is classified as an intermediate type between strip and layered silicates, and montmorillonite from the subclass of layered silicates, which have a natural high dispersion, were used as fillers during the study.

The choice of palygorskite and montmorillonite is explained by the sufficient study of their behavior in organic environments by a number of scientists, availability and economic advantages for introduction into production. Existing clay minerals, which are traditionally used to solve the problem of improving the physical and mechanical properties of organosilicon coatings, are not sufficiently active due to the hydrophilic properties of the particles surface. Based on this, a modifier that has proven itself well in this field was used for the study.

A number of compositions of heat-resistant organosilicon varnishes with modified fillers based on the abovementioned clay minerals were obtained. It was established that the introduction of modified forms of natural aluminosilicates contributes to the increase of temperature resistance in filled coatings, compared to coatings made of pure polymer. At the same time, the best effect is achieved when using montmorillonite. This is related with the fact that the proposed compositions of polymethylphenylsiloxane varnish and montmorillonite have a number of features, in particular, the highest comprehensive result of simultaneous improvement of the physical, mechanical and thermal properties of the specified coatings.

It is possible to obtain compositions with stable physico-mechanical properties, as they withstood heat treatment at 400 °C for 100 hours without visible changes in integrity, due to the introduction of the optimal amount of modified montmorillonite into organosilicon varnishes KO-08K and KO-921. Compared to similar heat-resistant polymethylphenylsiloxane varnishes, longer service life at elevated temperatures is ensured.

**Keywords:** polyorganosiloxanes, dispersed fillers, palygorskite, montmorillonite, polymethylphenylsiloxane varnish, thermogravimetric analysis, thermooxidative destruction.

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# **1.** Introduction

Organosilicon varnishes and enamels confidently occupy their place, finding more and more widespread use with a large range of paint and varnish materials presented in the industry. Organosilicon polymers, as heat-resistant materials, have become widely used in the field of electrical insulating materials, which are used in the form of thin films at high temperatures.

As a component of composite materials organosilicon polymers main advantages is their high thermo-oxidative resistance. If the most of organic polymers burn out by more than 90 % as a result of exposure at a temperature of 250 °C for one day, then the mass loss of organosilicon polymers under the same conditions is less than 10 %. That's why polyorganosiloxanes have found a predominant application in the technology of heat-resistant composites.

The study of the interaction of organosilicon compounds with fillers is of great interest, since there is no consensus among researchers about the mechanism of this process, as well as about its chemical or physical nature. It is known that organosilicon varnishes are well combined



with fillers, while it is necessary to choose such types of them, that would be stable at different temperatures and do not lose color. Organic fillers are unsuitable for this reason.

To solve the problem of increasing the resistance to elevated temperatures of organosilicon coatings while maintaining the stability of physical and mechanical characteristics, it is actual to research available and effective fillers that have natural high dispersion, such as palygorskite and montmorillonite.

# 2. The object of research and its technological audit

The object of research is organosilicon varnishes, such as polymethylphenylsiloxane and polyaluminomethylphenylsiloxane, filled with modified clay minerals. However, polyorganosiloxanes are relatively high-priced and coatings based on them do not meet the full range of practical requirements, especially regarding insufficient mechanical properties [1]. One of the most active ways of creating materials with required technological and operational properties is the introduction into polymers the dispersed fillers.

Modified clay minerals of the Cherkasy deposit (Ukraine) – palygorskite and montmorillonite were studied as mineral fillers. Adsorption modification of minerals was carried out by dispersing powders in the presence of optimal additions of cationic surfactant – octadecylamine in toluene. Technical stearic octadecylamine is widely used as a hydrophobizer for pigments and fillers, a flotation agent in the enrichment of potash ores [2].

Polymethylphenylsiloxane KO-08K, polymethylphenylsiloxane KO-921, polyaluminomethylphenylsiloxane KO-978 and polymethylphenylsiloxane modified KO-916K, which are widely used in various industries, have been studied as binders.

#### 3. The aim and objectives of research

The changing the thermal stability processes of and mechanical parameters study of binary compositions, consisting of organosilicon varnishes and clay minerals as fillers are *the purpose of this work*. To achieve the aim, the following objectives must be completed:

1. To determine the influence of the degree of filling with palygorskite and montmorillonite on the thermal stability of the compositions and to determine the optimal measure of filling.

2. To conduct a derivatographic analysis to determine the quantitative mass losses of filled organosilicon varnishes.

3. To find out the effect of the most effective filler on the physical and mechanical characteristics of the compositions in the process of thermo-oxidative destruction.

# 4. Research of existing solutions of the problem

The most important properties of polymethylphenylsiloxane polymers are thermostability, thermoelasticity, and good dielectric properties that are little dependent on temperature changes. The authors of the work [3] found out that thermal-oxidative destruction of polyorganosiloxane varnish films occurs, when working at elevated temperatures. This process is accompanied by the polymer weight loss and the formation of a cross-linked structure, ultimately, the loss of elasticity of the system. But as a result of thermo-oxidative destruction of organosilicon polymers, conductive bridges are not formed, thanks to which the dielectric properties are preserved.

Scientific schools are quite steadily dealing with the problem of increasing the thermal resistance and thermal stability of organosilicon coatings. This is the subject of works [4-6] that analyze the effect of mineral fillers of various phase and chemical composition on the thermal properties of polyorganosiloxanes and give recommendations for their use.

Scientists in the paper [7] studied organosilicon varnish KO-921 as an electrical insulating material, which makes it possible to increase heat resistance by means of its chemical modification. Although this is an effective method compared to this study, but it is economically unavailable.

An important point that is taken into account when choosing the type of organosilicon varnish for research is taking into account its composition and properties, which are of key importance in creating working protective coatings. The authors concluded that the properties of organosilicon varnish depend on the type and number of radicals present in the atom [8]. Therefore, in this case, polymers with the necessary parameters, such as heat resistance, hardness, elasticity, which correspond to the operating conditions of the finished product and the needs of the technological process, are being studied.

The heat resistance of organosilicon polymers largely depends on the main chain of the molecule structure, the nature of organic radicals near the silicon atom, as well as various additives (pigments, fillers, modifiers). Research scientists [9, 10] considered ways to increase the heat resistance of organosilicon compositions when they are filled with mineral substances. Among the main methods of solving the problem of thermal stability found in scientific and technical sources, work [11] can be singled out, but it deals with elastomers, so the recommendations can hardly be applied to thermosetting polymers.

The works [12, 13] are the most informative, as they are as close as possible to the topic of interest and reveal the possibility of using fillers for a comprehensive solution to the problem.

By varying the filling interval, it is possible to get information about the amount and benefits of each supplement. This, in turn, is the basis for choosing optimal compositions of filled organosilicon polymers.

Thus, the conducted analysis shows the perspective of this kind of research, since these clay minerals have not been studied in this aspect.

# 5. Methods of research

When studying the effect of prolonged exposure at elevated temperature on the physical and mechanical properties of filled polyorganosiloxanes, the formation of coatings on substrates made of duralumin D16 alloy, 1.5 mm thick and 90x120 mm in size, was carried out by the pouring method.

The thickness of single-layer coatings, hardened for 2 hours at a temperature of 200 °C, was  $30-35 \mu m$ .

The hardness of the coatings was determined on the ME-3 pendulum device (Russia), the impact strength of the films on the U1-A device (Russia), the bending strength of the coatings was determined on aluminum plates with a thickness of 0.25 mm using the flexibility scale on the Constanta-ShG1 device (Ukraine).

Heat resistance was determined by visual observation of surface changes during thermostating at a certain temperature in a muffle furnace; the appearance of cracks was taken as a sign of coating destruction.

Resistance to thermocycling was determined by alternately holding coated substrates in a muffle at 400  $^{\circ}$ C (300  $^{\circ}$ C) for 15 min. and in running water for 2 min.

For derivatographic studies, coating films with a thickness of  $80-100 \mu m$  were formed from a solution by pouring on fluoroplastic substrates. The properties of films and coatings were studied after drying at 200 °C for 2 hours and after 100 hours warm-up at different operating temperatures:

- for compositions based on KO-08K and KO-921 varnishes at 400 °C;

- for compositions based on KO-916K and KO-978 varnishes at 250  $^\circ\mathrm{C}.$ 

The determination of structural changes in the process of thermo-oxidative destruction is of great importance, when studying the influence of mineral fillers on the heat resistance of polyorganosiloxanes and the development of highly heat-resistant composite materials.

On the basis of thermogravimetric analysis, it is possible to determine, at least in the first approximation, the heat resistance and working temperatures of the compositions, which will eventually allow offering an express method for determining the heat resistance of polymeric materials.

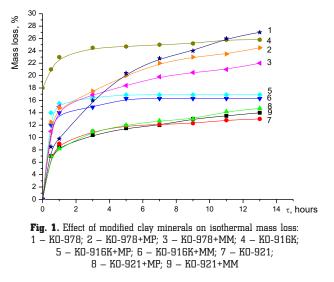
Therefore, a dynamic thermogravimetric analysis was performed on a derivatograph with simultaneous recording of differential-thermal and thermogravimetric curves in an air atmosphere at a speed of 10 degrees/min and an isothermal gravimetric analysis at 400 °C. Determination of isothermal mass loss for all compositions was carried out at a temperature of 400 °C, despite the different maximum operating temperatures of the investigated polyorganosiloxane varnishes. The temperature of 250 °C reveals the processes of destruction of the filled films to an insignificant extent, which does not allow stating a noticeable difference in the thermal stability of the samples. In harsher conditions, at 400 °C, destruction processes proceed more intensively.

It is recommended to hold the samples to a constant mass at 300 °C for maximum removal of solvent residues and low molecular weight volatile products Before carrying out thermogravimetric analyzes of polyorganosiloxanes Heat treatment was carried out in muffle furnaces with a thermostat accuracy of  $\pm 20$  °C.

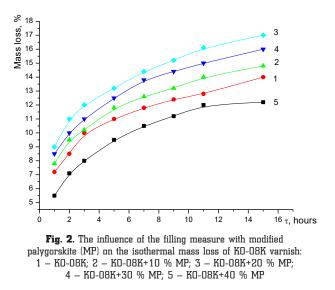
#### **6**. Research results

The pyrolysis by mass loss at a temperature of 400 °C research (for compositions with 30 % content of modified clay minerals) was studied by weighing the samples on analytical balances every 2 hours. The same pattern of mass change is observed for all curves. Significant mass losses correspond to the initial period of heat treatment. In the future, the rate of destruction drops significantly, which is associated with the siloxane structuring of polymers and the difficulty of detaching organic radicals.

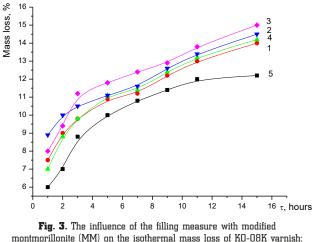
The relative thermal stability of unfilled varnishes KO-08K and KO-921 (Fig. 1, 2) is approximately the same. Filling KO-921 varnish with modified palygorskite (MP) and montmorillonite (MM) leads to a slight increase in mass loss (Fig. 1). It is characteristic that mass loss of the filled films is less during the initial time of heat treatment (up to 3 hours). Filled compositions based on KO-916 are characterized by significantly lower mass loss compared to unfilled varnish, and high thermal stability is ensured by the introduction of MM into the composition, as in the case of KO-921. The unfilled film is characterized by significant thermo-oxidative destruction. Mass loss occurs first due to oxidation and destruction of organic substances, and then organic radicals associated with the silicon atom. Films based on KO-978 filled with MM and MP in the initial period of thermostating (up to 3 hours) are characterized by reduced heat resistance compared to pure varnish. This is due to the weakening of the intermolecular interaction in films, characteristic of this varnish, when modified minerals are introduced. With subsequent heat treatment, the relative thermal stability of the filled films increases, especially with MM.



In Fig. 2, 3 show the results of the influence of the measure of films filling, based on KO-08K varnish on their thermal stability. Filling the varnish with 30 % modified palygorskite and montmorillonite leads to a slight increase in mass loss, especially for films with MM, which provides significant thermal stability in the initial period.



The structure of the hardened coating is partially loosened due to interglobular plasticization with the introduction the small amounts of fillers into polymers. A further increase in the content of MM and MP leads to the denser structure formation and deterioration of the diffusion conditions of oxygen penetration into the thickness of the films, since the rate of oxidative destruction of siloxane resins is proportional to the rate of diffusion of oxygen into the sample.

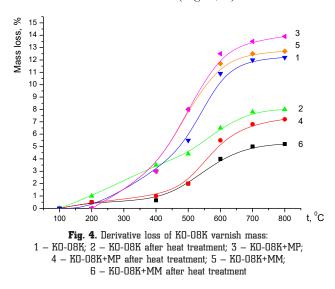


montmorillonite (MM) on the isothermal mass loss of K0-08K varnish: 1 – K0-08K; 2 – K0-08K+10 % MM; 3 – K0-08K+20 % MM; 4 – K0-08K+30 % MM; 5 – K0-08K+40 % MM

The probable cause of inhibition of the process with a significant content of fillers may be mechanical difficulty in removing organic radicals (especially phenyl radicals) after breaking the Si–C bond from the polymer mass and their interaction with oxygen. At the same time, the probability of the reverse recombination of organic radicals with the formation of the Si–C bond increases significantly, which leads to an increase in heat resistance.

In Fig. 4 shows the mass loss curves of compositions based on KO-08K varnish, calculated according to the data of derivatographic analysis.

Weight loss of varnish and filled films before heat treatment begins, approximately, at 300 °C and occurs mainly in the range of 400–600 °C. At the same time, the mass loss of filled films exceeds the mass loss of varnish, especially for MP compositions, which is consistent with data on isothermal mass loss (Fig. 2, 3).

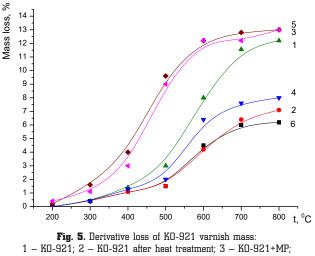


Weight loss of varnish and filled films before heat treatment begins, approximately, at 300 °C and occurs mainly in the range of 400–600 °C. The mass loss of filled films exceeds the mass loss of pure varnish, especially for compositions with MP, which is consistent with data on isothermal mass loss (Fig. 2, 3).

Change in samples mass loss after preliminary heat treatment at 400 °C for 100 hours occurs most intensively in the temperature range of 500–700 °C, but begins already at 100 °C. This is due to the removal of air moisture absorbed by heat-treated films, which is especially significant for unfilled varnish. The smallest mass losses are characteristic of films with MM, which ensures maximum thermo-oxidative stability of coatings.

A similar pattern of changes in mass loss is observed for compositions based on KO-921 varnish (Fig. 5), with the difference that significant mass losses of filled compositions begin at 300 °C, and varnish at 400 °C. This allows to conclude that the KO-921 varnish is more heat resistant under the given test conditions compared to the KO-08K varnish.

After heat treatment, the mass loss of compositions with MP and MM is greater than the mass loss of pure varnish, and only in the area of slow mass loss it is lower for compositions with modified montmorillonite.



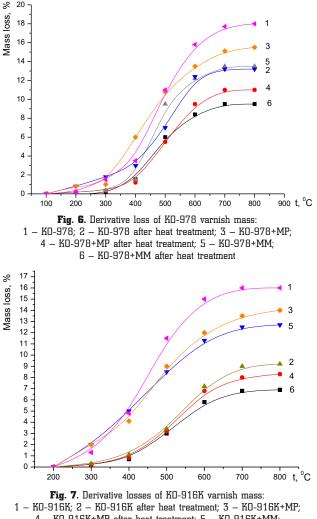
KO-921; 2 – KO-921 after heat treatment; 3 – KO-921+MP;
KO-921+MP after heat treatment; 5 – KO-921+MM;
KO-921+MM after heat treatment

When the temperature increases at a rate of 20 degrees/min, intense destruction of KO-978 varnish occurs in the range of 300-600 °C, and the introduction of fillers leads to a decrease in mass losses, and they are significantly smaller for filled films (Fig. 6).

After heat treatment of the films, the mass loss decreases significantly, but the nature of the change remains similar.

It is necessary to note the low sorption activity of filled heat-treated films in relation to air moisture, which is important for increasing the arc resistance of compositions based on KO-978 varnish. Low sorption of air moisture is also characteristic of films based on KO-916K (Fig. 7). This is explained by the milder mode of long-term heat treatment adopted for these compositions and the peculiarities of their chemical structure.

Maximum heat resistance is characteristic of MM compositions, especially after long-term heat treatment. It is characteristic that both for all studied varnishes and for filled compositions, the rates of thermo-oxidative destruction processes in the area of sharp mass loss, which are approximately determined by the angle of inclination to the temperature axis, are respectively equal to each other. It is noteworthy that the mass loss of the samples before and after thermostating differ quantitatively, this is due to partial thermo-oxidative destruction in the process of the corresponding heat treatment.



4 – KO-916K+MP after heat treatment; 5 – KO-916K+MM; 6 – KO-916K+MM after heat treatment

All compositions are also characterized by an increase in temperatures, corresponding to the transition from the region of relative stability to the zone of energetic action of thermo-oxidative destruction, after preliminary thermostating. Isothermal mass data, as well as mass loss data from derivatographic curves, make it possible to differentiate the influence of different fillers on the destruction processes of filled polyorganosiloxanes, which is confirmed by studies of the nature of their surface on the thermooxidative stability of polyorganosiloxanes. This assumption needs experimental verification regarding other types of binders.

Since one of the disadvantages of unfilled polyorganosiloxanes is their insufficient mechanical strength, the next step was to find out the effect of fillers on the compositions physical and mechanical characteristics in the process of thermo-oxidative destruction. Studies of physical and mechanical properties were carried out for compositions based on KO-08K and KO-921 varnishes filled with modified montmorillonite, as they withstood heat treatment at 400 °C for 100 hours without visible changes in integrity. In the process of thermo-oxidative destruction, a significant decrease in hardness occurs for unfilled films (Table 1), which is probably related to loosening of the coating structure.

#### Table 1

Composition	Hardness		Bending strength, MPa		Impact strength, MPa	
	before heat treat- ment	after heat treat- ment	before heat treat- ment	after heat treat- ment	before heat treat- ment	after heat treat- ment
KO-921	0.590	0.440	0.3	0.3	5	5
KO-921+30 % MM	0.545	0.471	0.3	0.3	5	5
KO-08K	0.609	0.561	0.33	0.1	5	5
KO-08K+10 % MM	0.590	0.546	0.11	0.1	5	5
KO-08K+30 % MM	0.570	0.560	0.11	0.1	5	5

Physical and mechanical characteristics of coatings

During the destruction of polyorganosiloxanes, the decrease in the molecular volume of polymers due to the release of volatile products cannot be compensated by the viscous flow. This leads to an increase in internal stresses and, ultimately, to cracking of the coating.

## 7. SWOT analysis of research results

*Strengths.* The introduction of modified montmorillonite into organosilicon varnishes KO-08K and KO-921 reduces the destruction of films under the influence of high temperatures and prevents the reduction of their physical and mechanical properties.

*Weaknesses.* Since montmorillonite has the highest swelling capacity among clay materials, it is necessary to additionally check weatherproof coatings based on used filled varnishes. It is possible to increase resistance to external factors with the same filler by changing the modifier.

*Opportunities.* Since clays have shown their strength in this study, the next step may be to use other clay minerals of Ukrainian production, but taking into account their cost and availability, for example, kaolins.

*Threats.* It should be noted that the costs of implementing such coatings will be minimal, since the industry itself is interested in increasing the heat-resistant characteristics of the coatings. In addition, the application of this type of coating does not require special equipment.

#### 8. Conclusions

1. When determining the influence of the degree of filling with modified palygorskite and montmorillonite on the thermal stability of compositions based on organosilicon varnishes KO-08K, KO-921, KO-978 and KO-916K, it was concluded that the optimal filling interval is 10–20 %.

2. After carrying out the derivatographic analysis, it can be stated that the composition of varnishes KO-08K and KO-921 with filled modified montmorillonite had the smallest mass loss after heat treatment. This gave reason to conduct further research specifically for such compounds.

3. Modified montmorillonite is an optimal filler for varnishes KO-08K and KO-921, and its effective amount is 30 %.

### **Conflict of interest**

The authors declare that they have no conflict of interest in relation to this research, including financial, personal, authorship, or any other nature that could affect the research and its results presented in this article.

#### References

- Andrianov, K. A., Manucharova, I. F. (1962). Differential thermal analysis study of the thermal stability of polyorganosiloxanes and polyheteroorganosiloxanes. *Bulletin of the Academy of Sciences* of the USSR Division of Chemical Science, 11 (3), 389–392. doi: https://doi.org/10.1007/bf00909526
- Terlikovskii, E. V., Kruglitckii, N. N. (1982). Opredelenie optimalnoi stepeni modifitcirovaniia napolnitelei kompozitcionnykh polimernykh materialov. *Kompozitc. polimer. materialy*, 15, 14–18.
- Hyvliud, M. M., Yemchenko, I. V. (2005). Pokryttia dlia vysokotemperaturnoho zakhystu konstruktsiinykh materialiv. *Mekhanika i fizyka ruinuvannia budivelnykh materialiv ta konstruktsii*. Lviv: Kameniar, 472–476.
- Kruglitckii, N. N., Kruglitckaia, V. Ia. (1981). Dispersnye struktury v organicheskikh i kremniiorganicheskikh sredakh. Kyiv: Naukova dumka, 316.
- Sviderskii, V. A., Tkach, V. V. (1980). Vzaimodeistvie poliorganosiloksanov s silikatami i oksidami metallov. *Fiziko-khimicheskaia mekhanika dispersnykh sistem i materialov*. Kyiv: Naukova dumka, 202–207.
- Krupa, A. A., Melnichuk, T. V., Sviderskii, V. A. (1984). Prevrashcheniia v napolnennykh kremniiorganicheskikh sistemakh pri nagrevanii. Ukrainskii khimichnii zhurnal, 50 (6), 599–603.
- Gulai, LO. I., Serednitskii, Ya. A. (2002). Properties of Composite Materials Based on Organosilicon Lacquer KO-921 Cross-

linked with ED-20 Epoxy Resin. International Polymer Science and Technology, 29 (11), 35–37. doi: https://doi.org/10.1177/ 0307174x0202901107

- Burger, C., Kreuzer, F.-H.; Kricheldorf, H. R. (Ed.) (1996). Polysiloxanes and Polymers Containing Siloxane Groups. *Silicon in Polymer Synthesis*, 113–222. doi: https://doi.org/10.1007/ 978-3-642-79175-8\_3
- Shul'pekov, A. M., Lyamina, G. V., Radishevskaya, N. I., Kal'yanova, T. V. (2007). Structure and properties of nickel-organosilicon polymer composites. *Russian Journal of Applied Chemistry*, 80 (10), 1732–1736. doi: http://doi.org/10.1134/s1070427207100278
- Chuppina, S. V. (2008). Investigation of the functional role of sepiolite in organosilicate composites. *Glass Physics and Chemistry*, 34 (2), 166–172. doi: http://doi.org/10.1134/s1087659608020090
  Knight, G. J., Wright, W. W. (1989). Thermal stability of some
- Knight, G. J., Wright, W. W. (1989). Thermal stability of some heat-resistant elastomers. *British Polymer Journal*, 21 (3), 199–204. doi: https://doi.org/10.1002/pi.4980210304
- Zin, I. M., Chervins'ka, N. R., Kotsyuk, D. A., Gulai, O. I. (1996). Effect of hardeners on the thermal stability of organosilicon lacquer coatings. *Materials Science*, 31 (1), 134–136. doi: https://doi.org/10.1007/bf00565988
- Hulai, O. I., Tselyukh, O. I., Nironovych, I. O., Serednyts'kyi, Ya. A. (1996). Effect of mineral fillers on the properties of silicone coatings. *Materials Science*, 32 (5), 588–591. doi: https://doi.org/ 10.1007/bf02539071

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