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## **New Heat-Proof Methylphenylsiloxane Resins and High Temperature Resisting Enamels on Their Basis**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors read and  
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### **ABSTRACT**

New heat resistant methylphenylsiloxane resins produced by methyltriethoxysilane and oligophenylsilsesquioxane acidolysis were investigated. The synthesized resins are characterized by narrow molecular-mass distribution, higher thermal and thermal oxidative stability, reduced gelation period as compared to starting oligophenylsiloxane characteristics. Based on the produced resins high temperature resisting enamels with the improved properties: coating impact strength, heat resistance, proportional liquid (water, gasoline, industrial oil) action resistance were developed.

**Keywords:** *Methylphenylsiloxane resins; oligosilsesquioxanes; thermal and thermal oxidative stability; <sup>29</sup>Si; <sup>1</sup>H NMR spectroscopy; high temperature resisting enamels.*

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## **1. INTRODUCTION**

Methylphenylsiloxane resins (MPhSR) are widely used in the heat-resistant materials manufacturing: as binders in fiber-glass plastics production, protective coatings, organic resins and varnishes modifiers [1,3,4]. Also functionalized silsesquioxanes are used as a nanoscale building block for the preparation of hybrid nanocomposites. [5,6] Therefore the development of new MPhSR with improved capabilities and competitive price is an urgent task [2,3].

Organochlorosilanes are most frequently used as raw material for MPhSR production. However despite their cheapness, MPhSR produced on their base have a few drawbacks: they are characterized by relatively low heat resistance [7], are unstable in solvent absence (when stored for a long time in the presence of chlorine ions impurities viscosity increases resulting in operational performance change), the process of their preparation is accompanied with a lot of waste [2,8,9].

Oligophenylsilsesquioxanes (OPhS) are widely used in the production of heat resistant glass-fiber plastics, varnishes, enamels. However in spite of low price OPhS characteristics are not sometimes able to provide the production of the enamels with tailor-made properties. Therefore in the present research it was of interest to undertake comparative study of new MPhSR and OPhS properties, their homogeneity, heat resistance, rheological behavior.

This paper deals with the study of the properties of price competitive MPhSR with improved capabilities produced by a new process – acidolysis of methyltriethoxysilane (MTEOS) and hydroxy group terminated OPhS [3] that are environmentally friendly raw material as compared to chlorosilanes MPhSR produced on their basis contain much less chlorine ions in the form of impurities.

## **2. EXPERIMENTALS**

MPhSR were synthesized according to the techniques described in [7-10] similar to the following example (synthesis No 5 Table 1).

Table 1 presents starting reagent concentration, their ratios, as well as structural fragments ratios in the starting reaction mixture and in the synthesized MPhSR. While producing MPhSR (Table 1) OPhS, MTEOS and AA content was varied within the range of 0.21÷0.42 mole, 0.05÷0.42 mole, 1.58÷3.3 mole, respectively.

Description of synthesis No. 5. Place 200 g of toluene, 68.6 g of OPhS, 37.3 g of MTEOS, catalytic amounts of sulphuric acid to the reactor equipped with temperature controlled heating, a stirrer and a backflow condenser. Heat the reaction mixture to 60-70°C under continuous stirring, hold for an hour and then add acetic acid (AA) dropwise. Hold the reaction mixture for 1-4 hours at a temperature of 75-85°C depending on required resin properties. Further distill ethyl acetate reaction by-product and bring the reaction mass to neutral environment by means of conventional procedures. Then distill the solvent till volatiles content is not above 3 wt %.

Elemental analysis data: %C=47.20, %H=4.63 %Si=23.18.

Table 1. Starting reagents concentrations, structural fragments ratios in the starting reaction mixture and MPhSR

No.	* Reaction mixture composition	Starting reagents concentrations and ratios					
		Starting reagents concentrations, (mole)				Ratios	
		**OPhS (a)	MTEOSC (b)	AA	AA/ MTEOS	*** [PhSi] <sub>a</sub> / [MeSi] <sub>b</sub>	**** [PhSi] <sub>a</sub> / [MeSi] <sub>b</sub>
1	2	3	4	5	6	7	8
1	$[(\text{PhSiO}_{1,5})_{(1-x)} (\text{PhSiO}(\text{OH}))_x]_{0,33n} [\text{MeSiO}_{1,5}]_{0,67}$	0,21	0,42	2,00	4,76	0,50	0,5
2	$[(\text{PhSiO}_{1,5})_{(1-x)} (\text{PhSiO}(\text{OH}))_x]_{0,50n} [\text{MeSiO}_{1,5}]_{0,50}$	0,22	0,22	2,00	9,09	1,00	1,2
3	$[(\text{PhSiO}_{1,5})_{(1-x)} (\text{PhSiO}(\text{OH}))_x]_{0,56n} [\text{MeSiO}_{1,5}]_{0,44}$	0,20	0,16	1,58	10,00	1,26	1,3
4	$[(\text{PhSiO}_{1,5})_{(1-x)} (\text{PhSiO}(\text{OH}))_x]_{0,61n} [\text{MeSiO}_{1,5}]_{0,39}$	0,25	0,16	1,88	11,80	1,58	1,9
5	$[(\text{PhSiO}_{1,5})_{(1-x)} (\text{PhSiO}(\text{OH}))_x]_{0,67n} [\text{MeSiO}_{1,5}]_{0,33}$	0,42	0,21	2,00	9,52	2,00	2,2
6	$[(\text{PhSiO}_{1,5})_{(1-x)} (\text{PhSiO}(\text{OH}))_x]_{0,85n} [\text{MeSiO}_{1,5}]_{0,15}$	0,26	0,045	3,30	73,30	5,77	5,1

\*- structural fragments molar fractions of the reaction mixture (Table 1, line 2) were calculated on the basis of starting reagents concentrations (Table 1, line 7). Their variation intervals amount to:  $a=0.33\div 0.85$ ;  $b=0.15\div 0.67$ ;  $a+b=1$ ;

\*\* - according to integral intensities of silicon signals in  $^{29}\text{Si}$  spectra the following data were determined:  
fragmentary composition of main chain unit  $\text{OPhS} = [\text{PhSiO}_{1,5}]_{(1-x)} [\text{PhSiO}(\text{OH})]_x$ ,  $\forall x=0.3, 1-x=0.7$ ,  
 $\text{OPhS}$  is 45 wt % solution of phenyl containing resin in toluene;

\*\*\*-  $[\text{PhSi}]_a / [\text{MeSi}]_b$ , ratio in the synthesized MPhSR was determined by integral intensities of silicon signals in  $^{29}\text{Si}$  spectra (Table 1, line 8)

The  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra were recorded at ambient temperature in deuteroacetone on Fourier spectrometer Bruker AM-360 with operating frequency of 360.13 MHz.

$^{29}\text{Si}$  NMR spectra were measured with the employment of "Inverse Gated Heteronuclear Decoupling" pulsed program. To reduce the relaxation period chromium tris (acetylacetonate) was added to the solution. The delay between pulses was 10 seconds.

Residual functional (Si-OH, Si-OEt) groups content in MPhSR was determined by functional analysis. Ethoxy- and hydroxyl-groups were determined by iodimetric and alumohydride methods respectively.

Molecular-mass distribution (MMD) characteristics was determined by means of gel permeation chromatography (GPC) on the Aglient 1200 chromatograph with refractometric detector. MPhSR samples of 5 wt % concentration in THF were filtered through a Millipore filterglass fluoropor filter of 0.5 micrometer. Chromatographic experiment conditions: Aglient 1200 chromatograph, refractometric detector, PlmixC column, temperature 25°C, eluent – THF, velocity 1 ml/min, sample volume 50 mcl. Calibration test was performed by Waters polystyrene standards.

Thermo-gravimetric analysis (TGA) was conducted on DERIVATOGRAPH-H (Mom). Thermogravimetric analysis was performed in argon environment and in air at the heating rate of 10°C/min up to 1100°C.

Kinematic viscosity determination of 50 wt % MPhSR solutions in toluene and starting OPhS was performed on VPG-2 flow meter at 20°C.

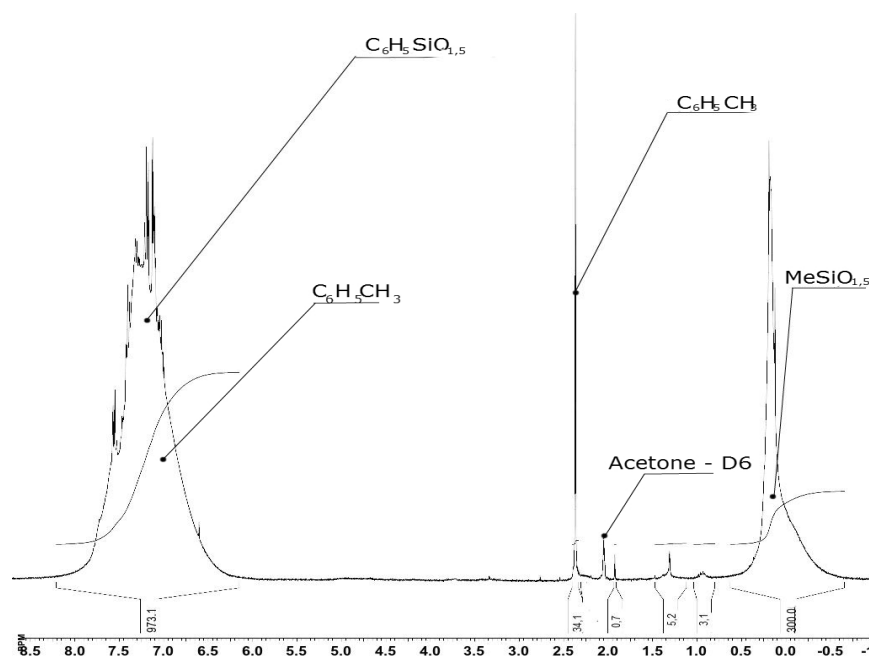
Physical and mechanical properties of the produced enamels were studied in conformity with the Russian State standard GOST-9.401-91.

### **3. RESULTS AND DISCUSSION**

In contrast to conventional techniques of MPhSR production by alkoxy silanes acidolysis [5,6] a mixture consisting of MTEOS and OPhS in various ratios was used as a starting raw material in the proposed paper. OPhS is hydroxy groups terminated oligophenylsesquioxane solution in toluene. OPhS introduction in the reaction mixture instead of expensive phenyltriethoxysilane [8,9] significantly decreases new MPhSR cost.

The produced MPhSR were analyzed and defined by  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectroscopy. In PMR spectra in deuteroacetone (a typical example is presented in Fig 1a) proton signals of all structural MPhSR fragments: methyl protons at silicon in the region of  $\delta$  0.10 – 0.19 ppm and phenyl protons in the region of  $\delta$  6 – 7 ppm., as well as residual toluene proton signals are observed. Phenyl proton signals of toluene and MPhSR are overlapped.

$^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra for sample 5 are shown below.  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra type of samples (1, 2, 3, 4, 6) (Table 1) is similar to the spectra of sample (5) presented in Fig. 1a and 1b. The attribution of structural MPhSR fragments signals in PMR and  $^{29}\text{Si}$  spectra coincides with the attribution of similar structural fragments presented in [11,12].



**Fig. 1a. PMR spectrum of MPhSR, sample 5, (Table 1) in deuterioacetone**

Fig. 1b demonstrates that  $^{29}\text{Si}$  nuclei signals of various structural fragments are well separated and are manifested in the following spectrum regions:  $\text{CH}_3\text{SiO}_{1.5}$  at  $-65$  ppm;  $\text{CH}_3(\text{OH})\text{SiO}$  at  $-58$  ppm.;  $\text{C}_6\text{H}_5\text{SiO}_{1.5}$  at  $-78$  ppm and  $\text{C}_6\text{H}_5\text{SiO}(\text{OH})$  at  $-70$  ppm respectively.

Therefore according to  $^{29}\text{Si}$  spectra qualitative composition of MPhSR samples can be successfully determined. However, quantitative determination of MPhSR fragment composition by silicon signals integrated intensities, particularly fragments with low  $(\text{C}_6\text{H}_5(\text{OH})\text{SiO}$ ;  $\text{CH}_3(\text{OH})\text{SiO}$ ) content is possible only approximately. So for determination of  $[\text{PhSi}]_a/[\text{MeSi}]$  ratio in MPhSR total integral intensities of silicon signals of  $\{[\text{PhSiO}_{1.5}]_{(1-x)}[\text{PhSiO}(\text{OH})]_x\}_{an}$  and  $\{[\text{MeSiO}_{1.5}]_{(1-y)}[\text{MeSiO}(\text{OH})]_y\}_{bn}$  fragments were used. In view of the foregoing phenyl and methyl fragments ratios of MPhSR main chain determined by  $^{29}\text{Si}$  NMR spectra and calculated on the basis of starting reagent concentrations differ only slightly as shown in Tables 1 and 2.

Due to low content of  $=\text{Si}-\text{O}-\text{H}$  and  $=\text{Si}-\text{O}-\text{CH}_2-\text{CH}_3$  fragments in the produced MPhSR their signals are observed neither in  $^{29}\text{Si}$  NMR spectra (Fig. 1b) nor in PMR spectra (Fig. 1a). Therefore residual functional content in MPhSR was determined by means of functional analysis. The obtained data and their measurement intervals are presented in Table 2.

As one may see from Table 2, high degree of ethoxy groups substitution is observed in the MPhSR synthesis. The content of residual ethoxy and hydroxyl groups that did not enter polycondensation reactions is within the range of 0.1-0.5 mole % and 1.2-3.9 mole %, respectively.

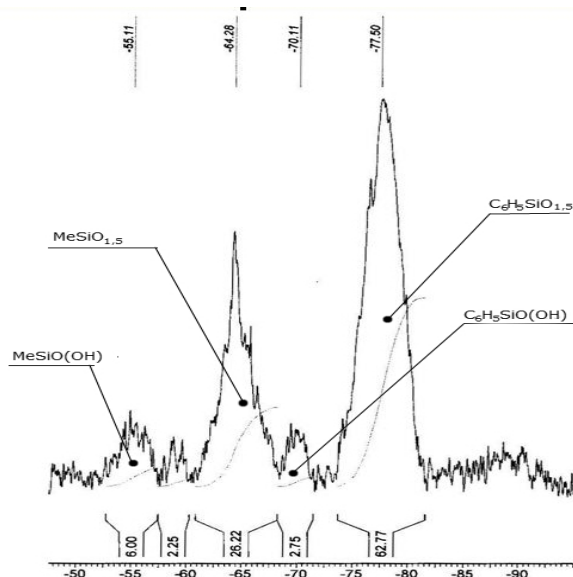

 Fig. 1b.  $^{29}\text{Si}$  NMR spectrum of MPhSR, sample 5, (Table 1) in deuteroacetone

Table 2. Produced oligomers characteristics

Test No	*[PhSi] <sub>a</sub> / [MeSi] <sub>b</sub> ratio (calculated)	**Functional group contents, mole%/molar fr.		Thermal decomposition point °C (air/argon)	***- IRY weight% (air/argon)
		OH (c)	OC <sub>2</sub> H <sub>5</sub> (d)		
OPhS	---	---	---	<b>549/512</b>	<b>45/77</b>
1	0.5	3,9/0.039	0,5/0.005	595/589	77/86
2	1.0	2,3/0.023	0,4/0.004	597/605	80/85
3	1.3	1,3/0.013	0,3/0,003	495/497	62/86
4	1.6	1,3/0.013	0,3/0.003	486/507	55/82
5	2.0	2,1/0.021	0,3/0,003	480/491	68/86

- \* [PhSi]<sub>a</sub>/ [MeSi]<sub>b</sub> = {[PhSiO<sub>1,5</sub>]<sub>(1-x)</sub> [PhSiO(OH)]<sub>x</sub>]<sub>na</sub> / [MeSi(OEt)<sub>3</sub>]<sub>bn</sub> - mole ratio (estimated) of OPhS and MTEOS corresponds to their values, specified in Table 1., where x=0.3, 1-x=0.7, n=24.7-66.3

- \*\* Functional group contents is shown in mole% and molar fractions

- \*\*\*- IRY- Insoluble residue yield

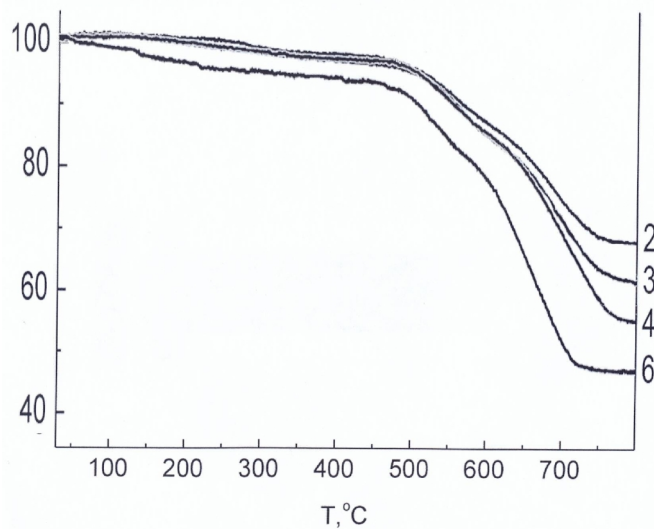
So, based on NMR spectroscopy and functional analysis data MPhSR fragment composition may be presented by a general formula:



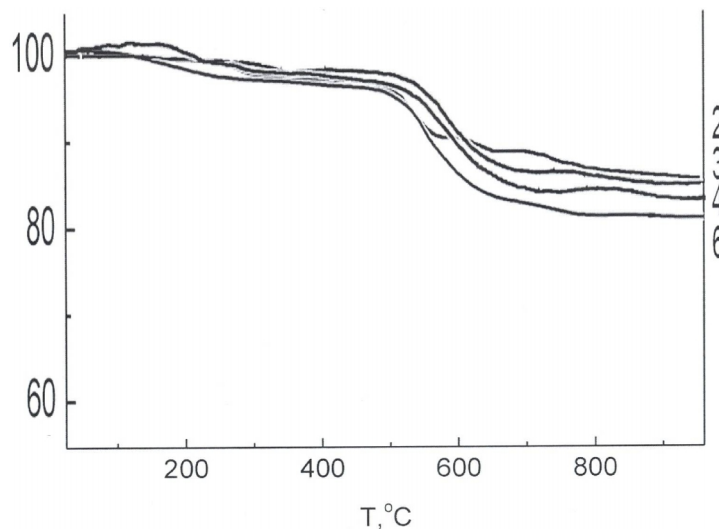
$R = \text{Ph, Me}$ ;  $a=0, 33 \div 0, 85$ ;  $b=0, 15 \div 0, 85$ ;  $c=1, 3-3, 9$ ;  $d=0, 3-0, 5$ ,  $n=24, 7-66, 3$   $a+b+c+d=1$ ;

The analysis of the above indexes (a, b, c, d) shows that terminal groups with c and d indexes make negligible contribution to the molecular weight of MPhSR.

Thermal and thermal oxidative decomposition parameters and typical thermograms are shown in Table 2 and Figs. 2a and 2b.



**Fig. 2a. TGA curves of MPhSR at heating rate of 10°C/min in air:  
-\*samples 2, 3, 4, 6**



**Fig. 2b. TGA curves of MPhSR at heating rate of 10°C/min in argon:  
-\*samples 2, 3, 4, 6**

*-\* Numbering of samples in figures 2a and 2b corresponds to numbering in Tables 1, 2, 3*

Comparative study of thermal and thermal oxidative stability of MPhSR and OPhS by TGA testify to higher thermal resistance of MPhSR as compared to OPhS. Decomposition of the analyzed compounds proceeds in a few stages both in air and argon environment. The first stage with the final temperature about 350°C evidently corresponds to MPhSR curing. The observed weight loss (3-8 wt %) is related to highly volatile reaction products removal (condensed water, ethanol). The following decomposition stages correspond to

decomposition processes occurring in MPhSR samples. In the range of 350-500°C silicon bond rupture with methyl and phenyl fragments takes place. The main weight loss is observed on the third stage at a temperature above 500°C and is caused by the processes related to basic chain breakdown. Temperature range of thermal transformation occurring in the samples and inorganic residue yields (IRY) on various decomposition stages depend on fragment composition of the analyzed MPhSR. It should be noted that thermal oxidative decomposition in air proceeds to deeper degrees of transformation than in argon resulting in IRY increase at decomposition under inert environment (Table 2).

Table 2 shows that MPhSR heat resistance raises when phenyl containing fragment contents is decreased and MTEOS content is increased. Found behavior of MPhSR thermal and thermal oxidative stability may be caused by molecular weight ( $M_w$ ) growth at MTEOS content increase (Table 2).

To clarify this assumption the synthesized MPhSR were studied by gel-penetrating chromatography. As can be seen in Table 3, all the analyzed MPhSR are characterized by insignificant molecular weight below 6337.2 ( $M_w$ ). Initial MTEOS concentration increase results in the increase of  $M_w$  and kinematic viscosity of 50 wt % of toluene MPhSR solution (Table 3). Table 3 presents molecular-mass characteristics of MPhSR and kinematic viscosity of their 50 wt % toluene solutions.

**Table 3. Molecular-mass distribution (MMD) characteristics of MPhSR**

No.	$M_n$	$M_w$	$M_p$	$D = M_w / M_n$	Kinematic viscosity, $m^2/s$
2	2372.2	6337.2	5563.4	2.6715	32.8
3	2011.36	4718.4	1052.1	2.3433	30.8
4	1951.9	4007.5	1052.1	2.0531	27.5
6	1740.3	3050.8	1023.2	1.7530	15.0

- kinematic viscosity of 45 wt % OPhS solution in toluene amounts to 12.6  $m^2/s$

As you can see in Table 3 all the analyzed MPhSR have low molecular mass, below 6337.2 ( $M_w$ ). An increase of starting MTEOS concentration results in molecular mass gain and kinematical viscosity growth of 50 wt % toluene solution of MPhSR (Table 3).

Data presented in Tables 2 and 3 testify that better heat resistance is achieved as compared to OPhS when fragment ratios:  $[PhSi]_a / [MeSi]_b$  - are within the range of 0.5-1.2 ; AA/ MTEOS - within the range 3-9; ( Tests 1, 2 Table 1).

When MPhSR is produced within the selected  $[PhSi]_a / [MeSi]_b$  ratios ranges, thermal stability increases due to two parameters combination, namely: phenyl radicals content and  $M_w$  increase. Within the specified ranges high homogeneity (low value of D, Table 3) of the synthesized MPhSR is achieved which testifies to starting reagents copolymerization with the formation of new MPhSR copolymers. As follows from Table 3 (test 6) further increase of phenyl fragments content at  $[PhSi]_a / [MeSi]_b$  ratios above 1.5 results in the decrease of molecular weight ( $M_w$ ), kinematic viscosity that is close to similar value of the starting OPhS and as a consequence to thermal stability drop.

As you can see in Table 3 all MPhSR feature shorter gelation time (45-50 min) as compared to OPhS gelation time (7 hours) [3] which raises their efficiency in heat resistant material compositions.



Methyltriethoxysilane and oligophenylsilsesquioxane acidolysis reaction is a convenient method of new heat resistant MPhSR synthesis. The reaction proceeds in toluene medium with the addition of sulphuric acid catalytical quantities and formation of ethyl acetate as a reaction by-product. By means of this reaction methyl containing fragments were introduced in oligosilsesquioxanes. Thus, by the example of the reaction studied a possibility of oligophenylsilsesquioxane modifying by structure fragment of specified architecture. The conducted research expands the range of previously obtained heat resistant MPhSR [5,6], giving new MPhSR high competitive ability in terms of the price.

Unique character of the studied MPhSR lies in the fact that it may be produced with various methyl and phenyl radicals ratio that allows to make enamels with heat resistance up to 650°C with the employment of standard fillers and pigments (when phenyl fragment content is twice as large as methyl ones).

High temperature resisting enamels based on MPhSR after drying form smooth solid surface resistant to significant temperature differential and have efficient protective properties against water, gasoline and industrial oil effects. For high temperature resisting enamels synthesis three MPhSR samples with various methyl and phenyl radicals ratios (1:2, 1:1, 2:1) were taken as a film-forming element. Quality indexes of the produced high temperature resisting enamels are presented in Table 4.

**Table 4. Quality indexes of the produced high temperature resisting enamels based on MPhSR**

No	Index	Value		
		Sample 1 Ph/Me=1/2	Sample 2 Ph/Me=1/1	Sample 3 Ph/Me=2/1
1	Enamel coating appearance	After drying uniform surface free from pinholes, pores and wrinkles is formed		
2	Nonvolatile matters mass fraction, %	42.8	42.4	43
3	Relative viscosity by B3-246 flow meter of 4 mm nose-piece diameter at a temperature of (20.0±0.5) °C, sec.	32	35	34
4	Drying time to degree 3 at a temperature of (20.0±0.5) °C, h., not above	1	1	1
5	Coating impact strength according to Y-1A device, cm, minimum	50	50	50
6	Adherence of coating, scores, not above	1	1	1
7	Coating temperature resistance up to 650 °C, h minimum	-	-	3
8	Coating temperature resistance up to (600±5) °C, h, minimum	3	5	5
9.	Coating resistance to heating effect at a temperature of (600±5) °C, and distilled water, cycles, minimum	5	5	5

**Table 4 Continued.....**

10	Coating resistance to proportional liquid action at a temperature of (20±2) °C, minimum	100	100	100
	-water	48	48	48
	gasoline (Nefras C2 80/120 brand)	48	48	48
	-industrial oil			

Test results showed that MPhSR use in high temperature enamels allows to raise coating heat resistance to 650°C, increase service life and environmental friendliness, as well as to extend application areas and bring down production cost of the formulation in terms of raw material due to MPhSR amount decrease in the formulation. High temperature enamels based on the synthesized MPhSR may be employed for painting external surface of tanks, engine components, exhaust system in vehicles, as well as for the protection of metal surfaces exposed to temperature up to 650°C during operational process.

#### 4. CONCLUSION

Methylphenylsiloxane resins produced by methyltriethoxysilane and oligo phenyl silsesquioxane acidolysis were described by <sup>1</sup>H, <sup>29</sup>Si, NMR spectroscopy and molecular-mass distribution, TGA, DTA. The produced resins were found to be thermally stable under the inert atmosphere and in air up to 650°C, they exhibited narrow molecular mass distribution, shorter gelation time as compared to starting oligo phenyl silsesquioxane properties. Based on the produced MPhSR high temperature enamel compositions with improved capabilities: coating impact strength, heat and proportional liquid (water, gasoline, industrial oil) action resistance were developed.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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