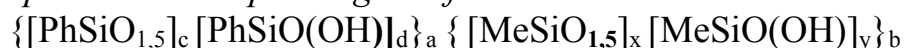


New Methylphenylsiloxane Resins and High Temperature Resisting Enamels on Their Basis.

New competitive heat resistant methylphenylsiloxane resins (MPhSR) with fragment composition corresponding to a formula:



$$a=0.35\div 0.69; b=0.31\div 0.65;$$

$$c=0.92-0.95; d=0.05-0.08$$

$$x=0.69-0.78; y=0.22-0.31$$

$$a+b=1$$

were studied.

Alkoxysilanes and oligophenylsiloxanes were used as reactants. Phenyl and methyl fragments ratio in the new MPhSR varied from 0.47 to 5.77. Studies have shown that MPhSR are characterized by narrow molecular-mass distribution, higher thermal and thermal oxidative stability. Based on new MPhSR high temperature enamels with improved capabilities: coating impact strength, heat and proportional liquid (water, gasoline, industrial oil) action resistance were developed.

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].

Therefore the development of new MPhSR with improved capabilities and competitive price is an urgent task [2, 3].

Organochlorosilanes are the main 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 [4], are unstable in solvent absence at storage (when stored for a long time in the presence of chlorine ions viscosity increases resulting in operational performance change), the process of their preparation is accompanied with a lot of waste [2,5,6].

This paper deals with the study of competitive heat resistant green MPhSR with improved capabilities, stable as grains or powders in solvent absence, based on environmentally friendly raw material free from chlorine ions, namely: alkoxysilanes and oligophenylsiloxanes.

Experimental

MPhSR were synthesized according to the techniques described in [4-7] and taken as a basis.

All MPhSR were characterized by Fourier-transform IR spectroscopy on «Specord» M-80 infrared spectrometer, by thermogravimetric analysis on

DERIVATOGRAPH-C. Thermogravimetric analysis was performed in argon environment and in air at the heating rate of 10 °C/min.

Molecular-mass distribution was determined by means of GPC. 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 polystyrene samples.

Kinematic viscosity determination of 50 wt % MPhSR solutions in toluene was performed on VPG-2 flowmeter at 20 °C.

^1H and ^{29}Si NMR spectra were recorded on Bruker AM-360 spectrometer with operating frequency of 360.13 MHz. The spectra were recorded at ambient temperature in deuteroacetone. The obtained MPhSR were characterized by ^1H and ^{29}Si NMR spectroscopy.

In PMR spectra in deuteroacetone proton signals of all structural MPhSR fragments are recorded in regions (fig.1a): $\text{CH}_3\text{SiO}_{1.5}$ (ch.sh. 0.10 – 0.19 ppm) and $\text{C}_6\text{H}_5\text{SiO}_{1.5}$ - (ch.sh. 6 – 7 ppm), as well as residual toluene proton signals. $\text{C}_6\text{H}_5\text{CH}_3$ fragments proton signals coincide with the signal of $(\text{C}_6\text{H}_5\text{Si})$ fragment of MPhSR therewith due to chemical shifts proximity.

In contrast with PMR spectra (fig. 1a) in ^{29}Si spectra silicon signals of all structural fragments: $\text{CH}_3\text{SiO}_{1.5}$ (ch.sh - 65 ppm); $\text{CH}_3(\text{OH})\text{SiO}$ (ch.sh - 58 ppm); $\text{C}_6\text{H}_5\text{SiO}_{1.5}$ (ch.sh -78 ppm), $\text{C}_6\text{H}_5\text{SiO}(\text{OH})$ (ch.sh. -70 ppm), are not only recorded but their signals overlapping is absent.

Therefore according to ^{29}Si spectra by silicon signals integrated intensities in ^{29}Si spectra of MPhSR (fig. 1b) obtained MPhSR fragment composition was quantitatively determined. Phenyl and methyl fragments ratio in MPhSR that was found by ^{29}Si spectra of MPhSR are shown in Table 1.

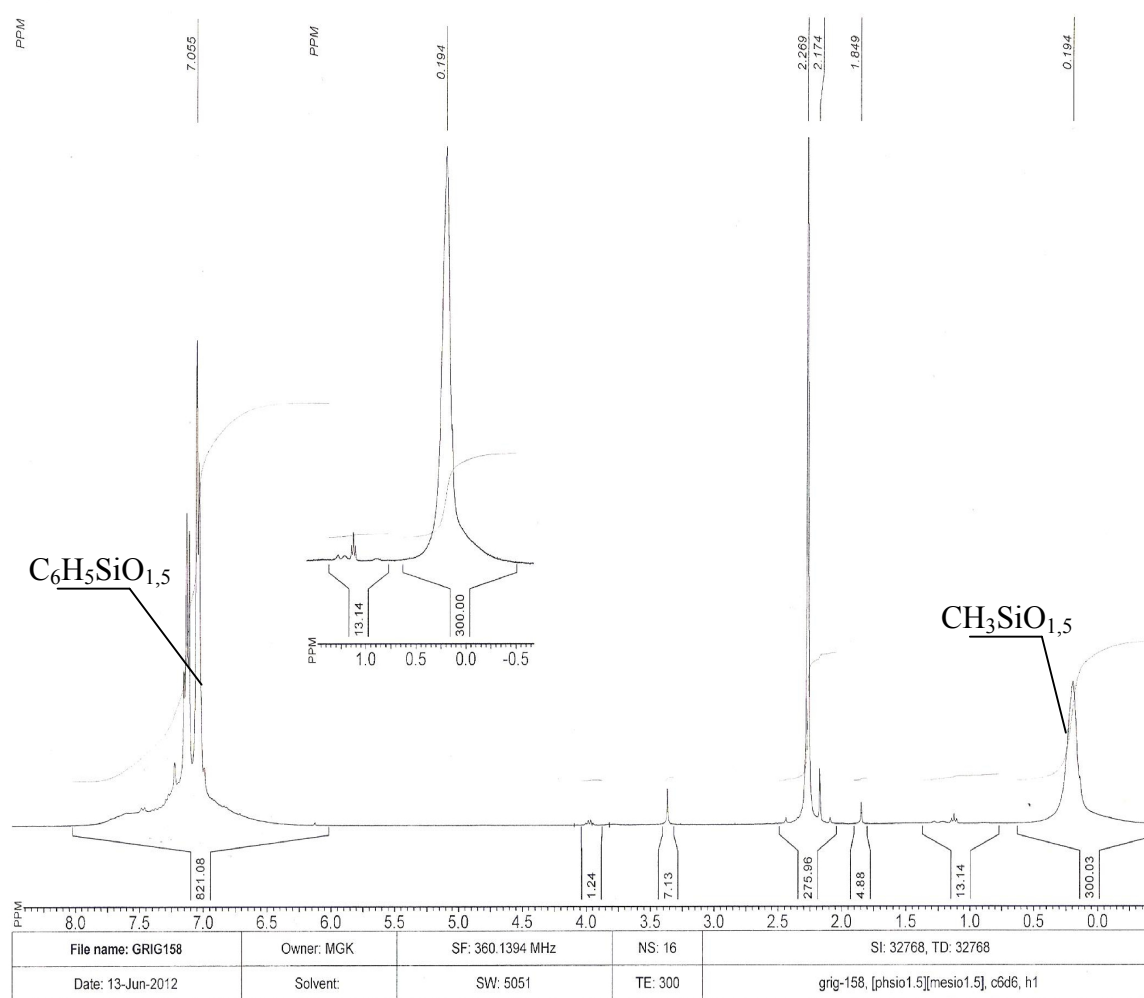


Figure 1a. PMR spectrum of MPhSR (sample 2) in deuterioacetone.

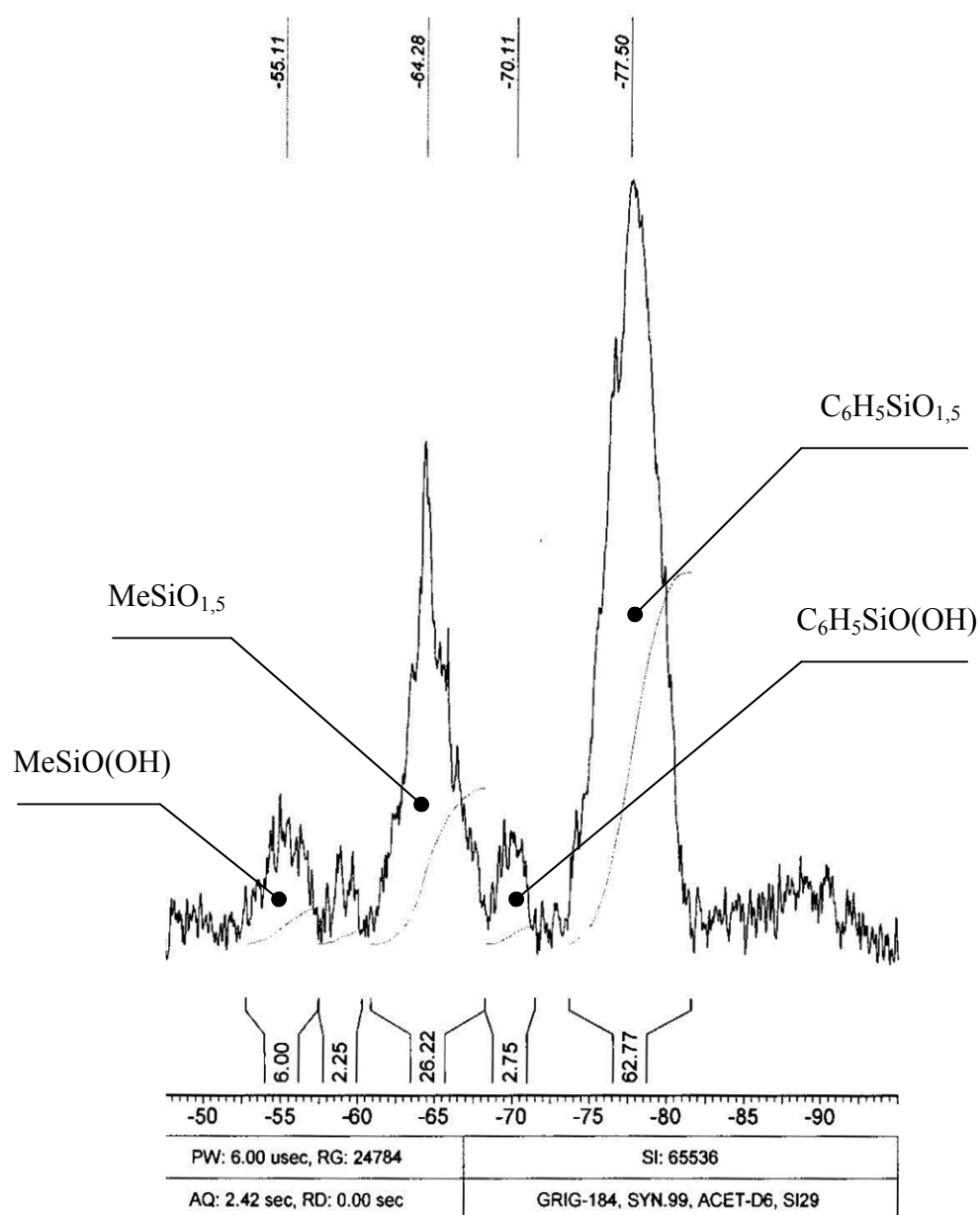
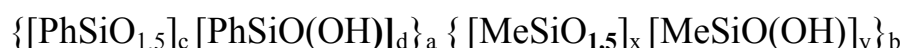


Figure 1b. ^{29}Si NMR spectrum of MPhSR (sample 2) in deuterioacetone
 ^1H , ^{29}Si NMR spectra type of samples is similar to those of the samples shown in fig. 1a and 1b .

Results and Discussions

The study of new MPhSR by NMR spectroscopy demonstrated that ^{29}Si spectra are more informative when fragment composition is quantitatively determined. By silicon signals integrated intensity in ^{29}Si NMR spectra MPhSR fragment composition that is described by a formula:



where $a=0.35\div0.69$; $b=0.,31\div0.65$; $c=0.92-0.95$; $d=0.05-0.08$;

$x=0.69-0.78$; $y=0.22-0.31$, $a+b=1$;

$a=c+d$, – mole fraction of phenyl containing fragments;

$b=x+y$ - mole fraction of methyl containing fragments was determined.

Investigation results of new MPhSR by TGA and functional analysis are presented in Table 1.

Table 1. Properties of new MPhSR.

Test	*[PhSi] _a / [MeSi] _b ratio	Functional group contents, mole%			Destruction point °C (air/argon)	Residue weight, weight% (air/argon)
		OH	OC ₂ H ₅	Si		
1	0.47	3.9	0.51	23.9	599/607	77/86
2	1.17	1.3	0.26	19.8	597/605	80/85
3	1.34	2.3	0.42	22.7	495/497	62/86
4	1.87	1.3	0.28	20.2	486/507	55/82
5	2.03	2.1	0.27	27.6	480/491	68/86
6	5.77	1.3	0.3	18.7	501/487	47/84

* - $\text{PhSi}]_a / [\text{MeSi}]_b = [(\text{PhSiO}_{1,5})_{0,7}(\text{PhSiO}(\text{OH}))_{0,3}]_a / [\text{MeSi}(\text{OEt})_3]_b$, determined by ²⁹Si NMR spectra.

Table 1 shows that in the process of MPhSR synthesis high degree of ethoxy group substitutions is observed. The residual ethoxy groups are within the range of 0.26-0.51 mole %. The residual hydroxyl groups are within the range of 1.3-3.9 mole %.

All the analyzed MPhSR are characterized by gelation time within the range of 45-50 minutes.

Thermal and thermal oxidative stabilities of MPhSR were studied by TGA. Typical thermograms are presented in fig. 2a and 2b, but thermal and thermal oxidative destruction parameters are shown in Table 1. Destruction of the analyzed MPhSR proceeds in a few stages both in air and argon environment. The first stage with the temperature range of 20-350⁰C evidently corresponds to MPhSR curing. The observed weight loss (3-8 wt %) is related to condensed water removal. The following decomposition stages correspond to destruction processes themselves occurring in MPhSR samples. Thermal and thermal oxidative stability of the analyzed MPhSR as follows from Table 1 increases when phenyl containing fragments content decreases in MPhSR and drops in case of its increase. The identified behavior of thermal and thermal oxidative stability of MPhSR is evidently due to MPhSR molecular weight modifying (Table 1).

Thus, temperature range of thermal transformation occurring in the samples and inorganic residue amount on various destruction stages depend on fragmental composition of the analyzed MPhSR. It should be noted that thermal oxidative destruction in air proceeds to deeper degrees of transformation than in argon. This is evidenced by higher values of inorganic residue at pyrolysis in argon environment (Table 1).

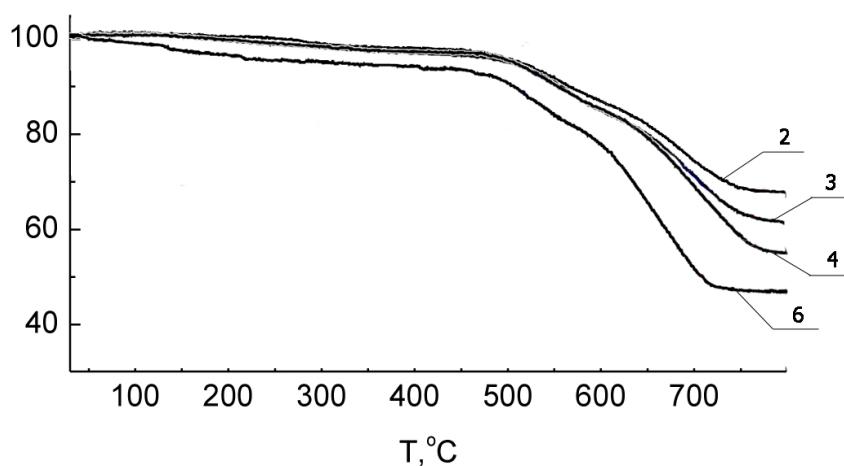


Figure 2a. TGA curves at heating rate of 10°C/min for MPhSR (samples 2,3,4,6) in air

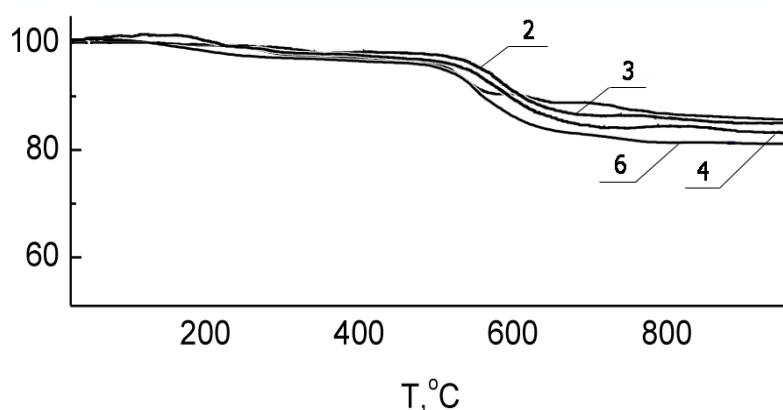


Figure 2b. TGA curves at heating rate of 10°C/min for MPhSR (samples 2,3,4, 6) in argon

The synthesized MPhSR were studied by gel-penetrating chromatography. As can be seen in Table 2, MPhSR are characterized by insignificant molecular weight below 6337.2 (M_w). Depending on reactant ratio M_w variations are within the range of $1.023 \cdot 10^3$ - $6.337 \cdot 10^3$, moreover M_w increase is observed at initial methyltriethoxysilane concentration increase. Kinematic viscosity therewith also increases (Table 2).

Table 2 **Molecular-mass characteristics of MPhSR.**

No.	M_n	M_w	M_p	$D = \frac{M_w}{M_n}$	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

* -the numbering of the samples corresponds to their values specified in Table 1,.

Behavior of MPhSR molecular-mass characteristics is similar to M_w modifying, namely: when phenyl containing fragments number in the oligomer increases number-average molecular weight (M_n) and average molecular weight decreases which is accompanied with MPhSR uniformity raise (D value decreases, Table 2).

Based on the obtained MPhSR with various methyl and phenyl fragments ratio high temperature resisting enamels were developed with the employment of standard fillers and pigments.

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. Based on MPhSR with phenyl fragment contents twice as large as methyl ones the enamels with temperature resistance up to 650 °C were produced.

Quality indexes of the produced high temperature resisting enamels are presented in Table 3.

Table 3. Quality indexes of the produced high temperature resisting enamels based on MPhSR.

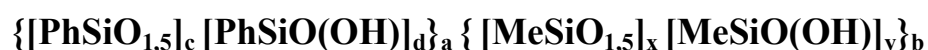
No	Index	Properties		
		Sample 1	Sample 2	Sample 3
		Ph/Me=1/2	Ph/Me=1/1	Ph/Me=2/1
1	Enamel coating appearance	After drying uniform surface free from pinholes, pores and wrinkles		
2	Nonvolatile matters mass fraction, %	42.8	42.4	43
3	Relative viscosity by B3-246 flow meter of 4mm nose piece diameter at a temperature of (20.0±0.5) °C	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 by 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, minimum	-	-	3
8	Coating temperature resistance up to (600±5) °C, minimum	3	5	5
9.	Coating resistance to alternate heating effect at a temperature of (600±5) °C, and distilled water, cycles, minimum	5	5	5
10	Coating resistance to proportional liquid action at a temperature of (20±2) °C, minimum			
	-water	100	100	100
	gasoline (Nefras C2 80/120 brand)	48	48	48
	-industrial oil	48	48	48

MPhSR use in high temperature enamels, as can be seen in Table 3, allows to raise coating heat resistance to 650 °C, 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.

Conclusions

1. New competitive heat resistant methylphenylsiloxane resins were synthesized; their fragment composition was confirmed by ^1H , ^{29}Si NMR and correspond to a formula:



where $a=0.35\div0.69$; $b=0.31\div0.65$; $c=0.92-0.95$; $d=0.05-0.08$;

$x=0.69-0.78$; $y=0.22-0.31$. $a+b=1$;

$a=c+d$, – mole fraction of phenyl containing fragments;

$b=x+y$ - mole fraction of methyl containing fragments;

2. New methylphenylsiloxane resins with different ratios of phenyl and methyl fragments were studied by TGA and MMD methods, their kinematic viscosity was analyzed. It was demonstrated that the produced resins are distinguished by narrow molecular-mass distribution, high thermal and thermal oxidative stability.

3 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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