

## Metalloporphyrazines – Catalysts of Vulcanization of Liquid Siloxane Rubbers

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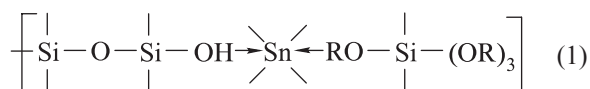
*Vulcanization of liquid low-molecular siloxane rubber SKTN with use of such catalysts as phthalocyanines of Sn<sup>II</sup>, Co<sup>II</sup>, Fe<sup>II</sup>, Cu<sup>II</sup>; octaphenyltetraazaporphyrinatocobalt(II) and octa(p-bromophenyl)tetraazaporphyrinatocobalt(II) is studied.*

**Keywords:** Porphyrazine, catalysts, siloxane rubber, vulcanization, kinetics.

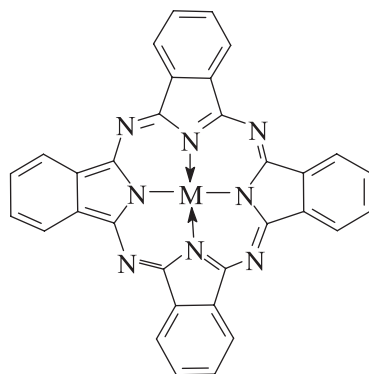
The vulcanization of liquid siloxane rubbers is widely used in various branches of industry. Organic compounds of tin (tin octanoate, tin diethyldicaprylate and others) are applied as catalysts. The defect of the compositions, containing these compounds, is a small time of their stabilization at room temperature (5-15 min).

Here, the phthalocyanines as catalysts of vulcanization were investigated for the first time.

It is known, that when mixing the polysiloxanediols with structuring agents and the organic catalyst with tin at room temperature the complex **1** is formed:<sup>[1]</sup>



Similar complexes are formed when mixing the polysiloxanediols with structuring agents and the metalloporphyrazines.<sup>[2]</sup> So, research of IR spectrum of compositions showed that the characteristic absorption band of silanol group is displaced from 3690 cm<sup>-1</sup> to 3300 cm<sup>-1</sup> in this case. These complexes exist in a form of lyophobic sol,



M = Sn<sup>II</sup>, Fe<sup>II</sup>, Cu<sup>II</sup>, Co<sup>II</sup>

representing a colloidal solution (sol-fraction). At temperature increase lyophobic sol undergoes regrouping with formation of the vulcanized polysiloxane (gel-fraction). The kinetics of vulcanization of siloxane rubber SKTN, containing different metalloporphyrazines as catalysts was studied according to the content of gel-fraction.

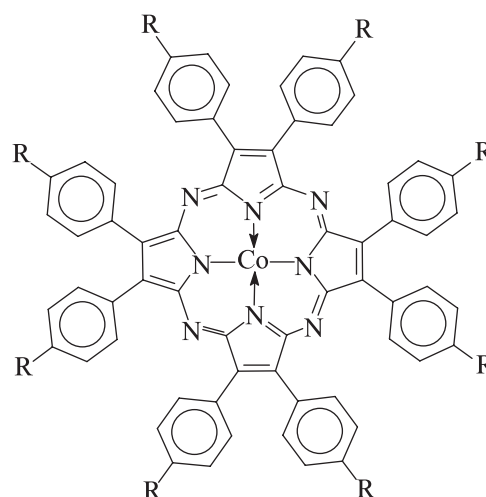
Metallophthalocyanines were obtained by fusing phthalodinitrile with chlorides of tin(II), iron(II), copper(II) as described earlier.<sup>[3,4]</sup>

The compositions were prepared by mixing a low molecular liquid siloxane rubber SKTN, hardener and a catalyst to form a homogeneous mass.

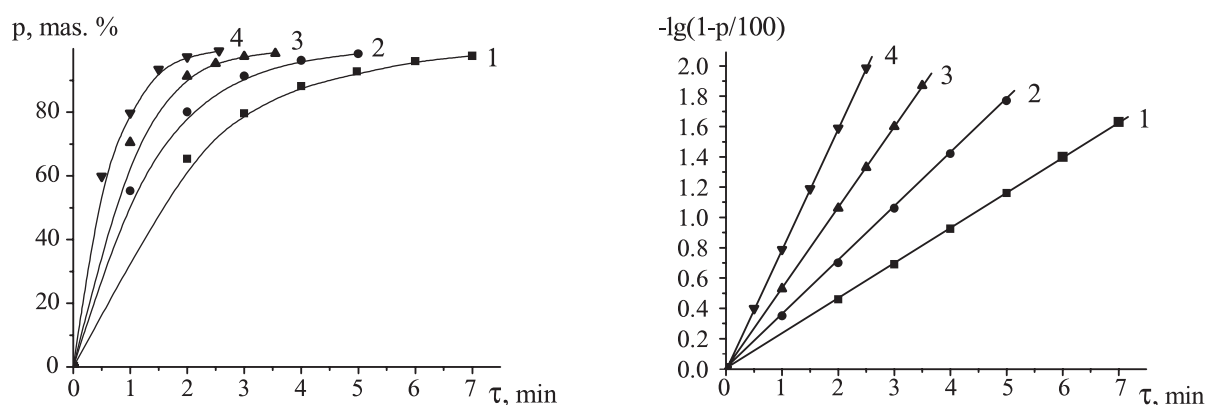
The stability of the compositions was visually installed by a loss of liquidity of the paste due to the beginning of gelation (start of gel formation).

Determination of the gel-fraction content in the hardened siloxane compositions was carried out as follows.

<sup>[2]</sup> The compositions were deposited by the squeegee blade on a glass, treated with thermofixed at 160 °C fluorine-containing water and oil repellent drugs Kratal (Russian specification 2484-120-05800142) or Flurotex FO-53 (Italy). Then the compositions were heated at various temperatures



R = H, Br



**Figure 1.** The dependence of the gel-fraction content on time of vulcanization of the siloxane rubber, which contains 12 mass % of ethylsilicate-40 and 1 mass part of cobalt phthalocyanine (left), and also logarithmic anamorphosis of kinetic curves of vulcanization (right) at temperatures (°C): 1 – 130, 2 – 140, 3 – 150 and 4 – 160.

and different times. The obtained films were weighted; then an unhardened sol-fraction was extracted by benzene during 24 hours. The remaining gel-fraction was dried to constant weight at 100-120 °C, weighted and the content of gel-fraction relatively the initial sample was determined.

The dependence of the gel-fraction content on vulcanization time of the siloxane rubber, which contains 12 mass % of ethylsilicate-40 and 1 mass % of cobalt phthalocyanine at 130, 140, 150 and 160 °C, and also logarithmic anamorphosis of kinetic curves of vulcanization are presented in Figure 1.

Figure 1b shows, that the vulcanization reaction is described by the kinetic equation of the first order for nonreversible reactions. In a logarithmic form this equation looks like:

$$-\lg\left(1 - \frac{p}{100}\right) = \frac{k_{\text{eff}}}{2.303} \cdot \tau, \quad (2)$$

where  $p$  – content of gel-fraction inside of harden samples, mass %;  $k_{\text{eff}}$  – the effective rate constant of vulcanization the rubbers,  $\text{s}^{-1}$ ;  $\tau$  – time of vulcanization, s.

Similar dependences are observed for vulcanization reactions of rubbers of others marks, as well as of that containing  $\text{Sn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  phthalocyanines, octaphenyl-tetraazaporphyrintocobalt(II)<sup>[5]</sup> and octa(*p*-bromophenyl)tetraazaporphyrintocobalt(II).

Values of effective rate constants of vulcanization, calculated on the Equation (2), and values of reaction activation energy are presented in Table 1.

It was established, that  $\text{Sn}^{\text{II}}$  phthalocyanine exhibit the highest catalytic activity. For the siloxane compositions, containing  $\text{Sn}^{\text{II}}$  phthalocyanine, vulcanization activation energy has the lowest value. It is caused by higher reaction ability of  $\text{Sn}^{\text{II}}$  phthalocyanine in interaction with ethylsilicate-40 with formation of the corresponding metallosiloxane and higher coordination ability of tin.<sup>[6,7]</sup>

Compositions on the basis of liquid siloxane rubbers are stable at room temperature within 15-18 days, whereas at temperatures 150 and 160 °C – within 2-3 minutes. It is possible to explain by high chemical and thermal stability of metalloporphyrazines.<sup>[8]</sup> Interaction of metalloporphyrazines with structuring monomers (ethylsilicat-40 or tetraethoxysilane) proceeds only at the increased temperatures. During this process metallosiloxanes are formed, which possess the great reaction ability in comparison with ethylsilicate-40 or tetraethoxysilane.<sup>[9]</sup> High reaction ability of metallosiloxanes is due to the great polarity of metal-oxygen bonds and higher ability of metals to coordination.<sup>[6,7]</sup> The vulcanization of rubbers proceeds at interaction of liquid siloxane rubbers with metallosiloxane.

Our research allows to make the conclusion, that the central metal ion nature influences greatly on the catalytic

**Table 1.** The effective rate constants\* and values of activation energy of vulcanization of liquid siloxane rubbers, containing 12 mass % of ethylsilicate-40 and 1 mass % of metalloporphyrazine.

Metalloporphyrazine**	$k_{\text{eff}} \cdot 10^{-3}, \text{sec}^{-1}$ at temperature, °C				E, kcal/mol
	130	140	150	160	
$\text{Sn}^{\text{II}}\text{Pc}$	8.95	13.6	20.5	30.5	14.34
$\text{Co}^{\text{II}}\text{Pc}$	5.40	9.14	15.1	24.3	17.45
$\text{Fe}^{\text{II}}\text{Pc}$	5.52	8.96	14.2	22.0	16.01
$\text{Cu}^{\text{II}}\text{Pc}$	4.60	7.67	12.5	19.9	16.97
$\text{Co}^{\text{II}}(\text{C}_6\text{H}_4\text{Br})_8\text{TAP}$	4.87	8.18	13.7	22.4	17.93
$\text{Co}^{\text{II}}(\text{C}_6\text{H}_5)_8\text{TAP}^{[5]}$	5.79	9.52	15.3	24.0	16.49

\* – error for the rate constant is about 5-7 %.

\*\* – Pc – phthalocyanine

$\text{Co}^{\text{II}}(\text{C}_6\text{H}_5)_8\text{TAP}$  – octaphenyltetraazaporphyrintocobalt(II)

$\text{Co}^{\text{II}}(\text{C}_6\text{H}_4\text{Br})_8\text{TAP}$  – octa(*p*-bromophenyl)tetraazaporphyrintocobalt(II)

activity of metalloporphyrazine, whereas the ligand structure have less influence.

Thus, compositions on the basis of liquid siloxane rubbers, containing metalloporphyrazine as high-temperature catalyst, are stable at room temperature, but at 150-160 °C undergo rapid hardening (within 2-3 minutes) that allows to use such compositions in technological processes.

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