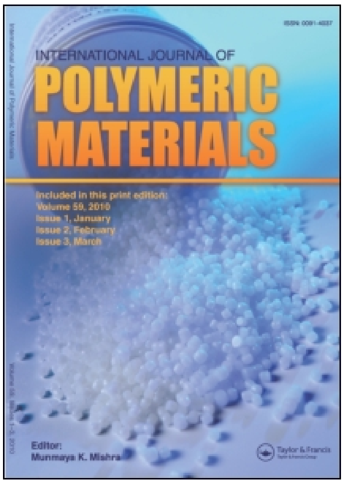

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Metal Macrocyclic Complexes as Novel High Temperature Stabilizing Agents and Flame Retardants for Polymers

R. M. Aseeva[a]; G. E. Zaikov[a]
[a] Institute of Chemical Physics, USSR Academy of Sciences, Moscow

To cite this Article Aseeva, R. M. and Zaikov, G. E.(1994) 'Metal Macrocyclic Complexes as Novel High Temperature Stabilizing Agents and Flame Retardants for Polymers', International Journal of Polymeric Materials, 25: 1, 13 — 28

To link to this Article: DOI: 10.1080/00914039408028573

URL: http://dx.doi.org/10.1080/00914039408028573

Intern. J. Polymeric Mater., 1994, Vol. 25, pp. 13–28
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Metal Macrocyclic Complexes as Novel High Temperature Stabilizing Agents and Flame Retardants for Polymers

R. M. ASEEVA AND G. E. ZAIKOV

Institute of Chemical Physics USSR Academy of Sciences, 4, Kosygin str., 117334 Moscow

Metal macrocyclic complexes are considered as noval high temperature stabilizing agents and flame retardants for polymers.

KEY WORDS Metal macrocyclic complexes, stabilizers, flame retardants

1. INTRODUCTION

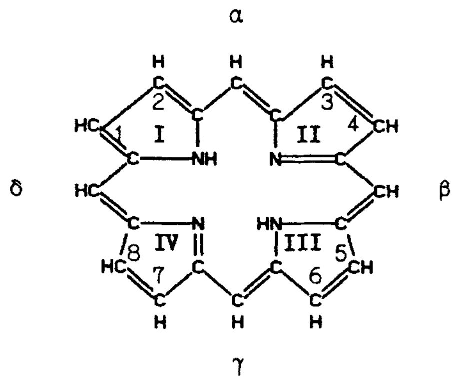
A macrocyclic compound is usually defined as a compound with nine or more members (including hetero atoms) in the cycle and with three or more donor atoms.

It is known that these compounds have the ability to function as macrocyclic ligands for coordination of various metal ions. The coordination chemistry of macrocyclic compounds has undergone intensive growth in the 1960's. In that time a considerable number of compounds containing ligating atoms of nitrogen, oxygen, sulphur, phosphorus and others have been synthesized. The most important classes of macrocyclic compounds are porphyrins (I), azaporphyrins (II), their valent-saturated azamacrocyclic analogs (III), crown-ethers (IV), bi- or polycyclic cryptands (V) and compounds with a mixed structure (Figure 1). The interest in macrocyclic compounds and their metal complexes is due first of all to the realization that some may serve as models for important natural products (chlorophyll, hemoglobin) and also as objects for modeling important life processes (photosynthesis, inversive oxygen-fixation etc.).

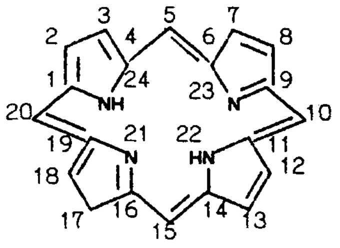
Owing to intensive investigation in the field of synthesis of macrocyclic compounds and the development of a raw material base many of the compounds have become accessible for use in practice.[1–4] From an analysis of published data it may conclude that metal macrocyclic compounds are in the main used as catalysts in different chemical, electrochemical and photochemical reactions. The high catalytic activity was found for complexes of macrocyclic compounds with a continuous system of π-conjugated bonds.[3–5]

Metal complexes of phthalocyanine and its substituted derivatives are used as commercial dyes. Phthalocyanine dyes are characterized by tonal purity, high light resistance and migrational stability. The problem in the use of metal macrocyclic complexes as high temperature stabilizing agents or flame retardants for polymers

PORPHIN

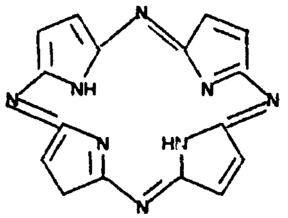


I



Ia

Atoms numbering by H.Fischer **Atoms numbering by JUPAC**



II

tetraazaporphyn

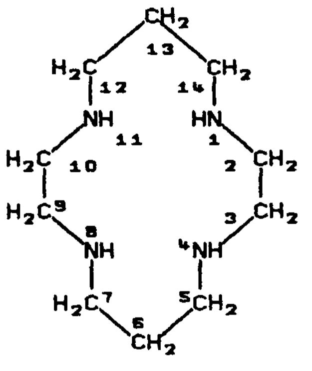
FIGURE 1a Some types of macrocyclic compounds.

is of special interest to us. The work in this direction was begun in the 70's and temporarily was interrupted because of technical reasons.

In this report we want to give an account of ideology in the use of metal complexes of azaporphyrin macrocyclic compounds and their analogs. It was necessary to find the interrelation between the chemical structure and the inhibition effectiveness of the macrocyclic compounds and their metal complexes.

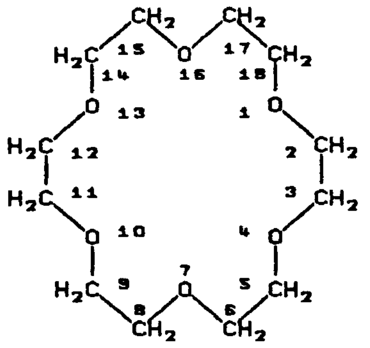
Azaporphyrin ligands and their metal complexes have a specific geometrical and electronic structure. Due to the presence of a continuous system of π-conjugated bonds in the macrocycle, the compounds show both donor and acceptor properties. They may be able to join or give back electrons with the formation of ion-radical particles. Thus, these compounds may participate in redox reactions and in reactions of the radical type.

The considerable variation in the properties of metal macrocyclic complexes may be attained by changes in the nature of the metal and/or the structure of the



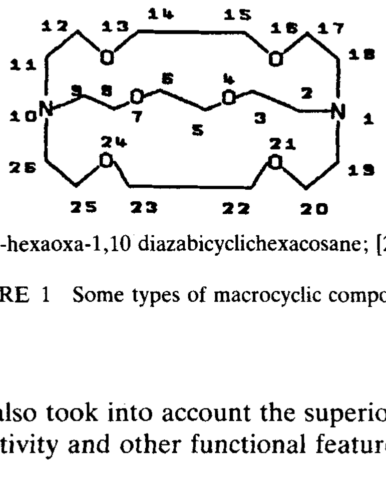
III

1,4,8,11—tetraazacyclotetradecane;
—[14]-ane-N_4
by D. Busch—A. Melson



IV

1,4,10,13,16-hexaoxa-cyclooctadecane; [18]-ane-crown-6



4,7,13,21,24-hexaoxa-1,10 diazabicyclichexacosane; [2]-cryptand

FIGURE 1 Some types of macrocyclic compounds.

macrocyclic ligand. We also took into account the superior thermal stability, non-toxicity, corrosive nonactivity and other functional features of these products.

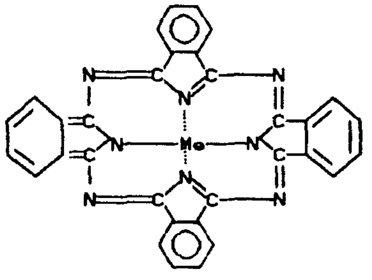
2. EXPERIMENTAL

Figure 2 shows the types of macrocyclic compounds and their metal complexes used in the present work. The first direction is concern with the metal complexes of monomeric phthalo- and naphthalocyanines. The products were obtained by the reaction between the corresponding dinitriles and metal salts at a ratio of 4:1 in the presence of 18–20 mol% urea in a melt at 250–300°C during 5 hours. The compounds obtained were purified by toluene extraction and long heating at 200°C *in vacuo* of 10^{-4} mm Hg.

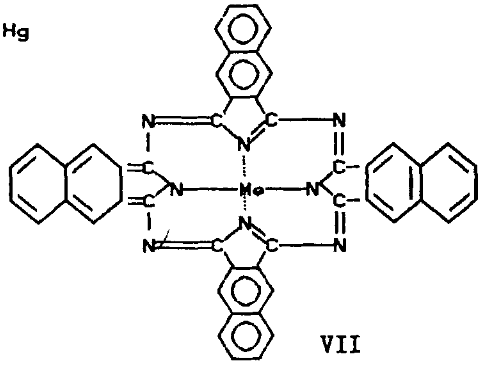
The second direction is concern with the polymeric macrocyclic compounds based of tetracyaneethylene and tetracyanebenzene. Macrocyclic polymers were prepared

1. Phthalo- and Naphthalocyanine complexes with

Cu, CO, Ni, Fe, Zn, Ag, Hg

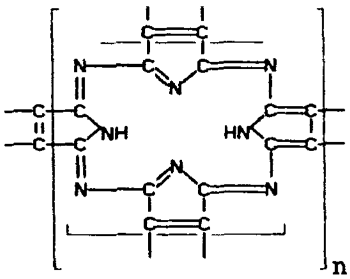


VI

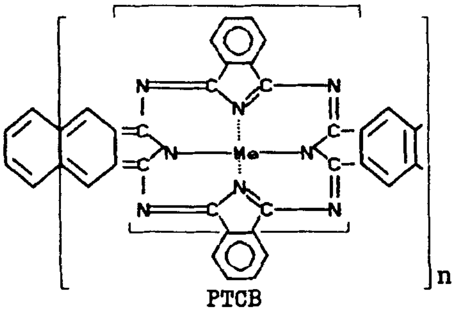


VII

2. Polymeric Macrocyclic Compounds with the Azaporphyrine Structure obtained on a Silica Surface.

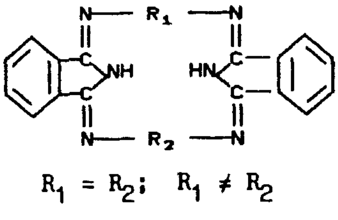


PTCE



PTCB

3. Metal Complexes with Macroazacyclic Compounds of Symmetrical and Nonsymmetrical Structure.



$R_1 = R_2$; $R_1 \neq R_2$

FIGURE 2 Metal complexes of macrocyclic compounds with azaporphyrine and analogous structures.

by the polymerization of monomeric tetranitriles in the gaseous state on the surface of a silica filler. The silica filler of fumed Aerosil type is usually used for polyorganosiloxane elastomeric materials. The template synthesis of polymeric azaporphyrins was carried out in a two sectioned horizontal rotating reactor in vacuum at 270–300°C over 5–10 hours. Vapours of monomer from the first section move towards the second section of the reactor with the silica filler. The weight ratio of monomer to filler was varied from 2.5 to 7.5 per 100 weight part of filler. After modification the specific surface area of the silica filler was practically invarible (*S*

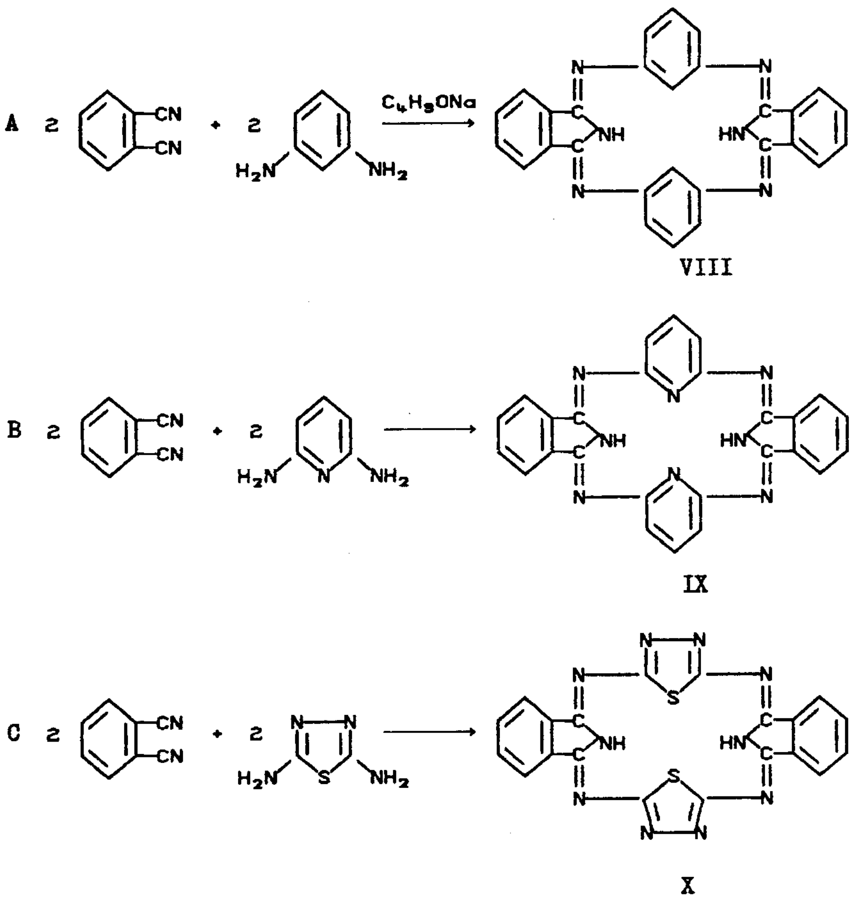
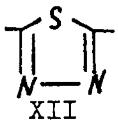


FIGURE 3a Synthesis of symmetrical macrocyclic compounds.

= 155–160 m^2/g). Free monomer on the surface was absent. The colour reaction with benzene was used for the determination of free monomer. The fillers modified by macrocyclic polymers had a greyish or dark brown colour depending on the polymer content. The concentration of paramagnetic centers was equal to 1.10^{17}–$8.5.10^{19}$ spin/g.

The third direction of the study is concerned with the metal complexes of analogs of azaporphyrin macrocyclic compounds with symmetrical or non-symmetrical structure.

The symmetrical macroazacyclic compounds were obtained by a procedure described for compounds with $R_1 = R_2$ in the following papers for

 (6),  (7) and  (8)

X XI XII

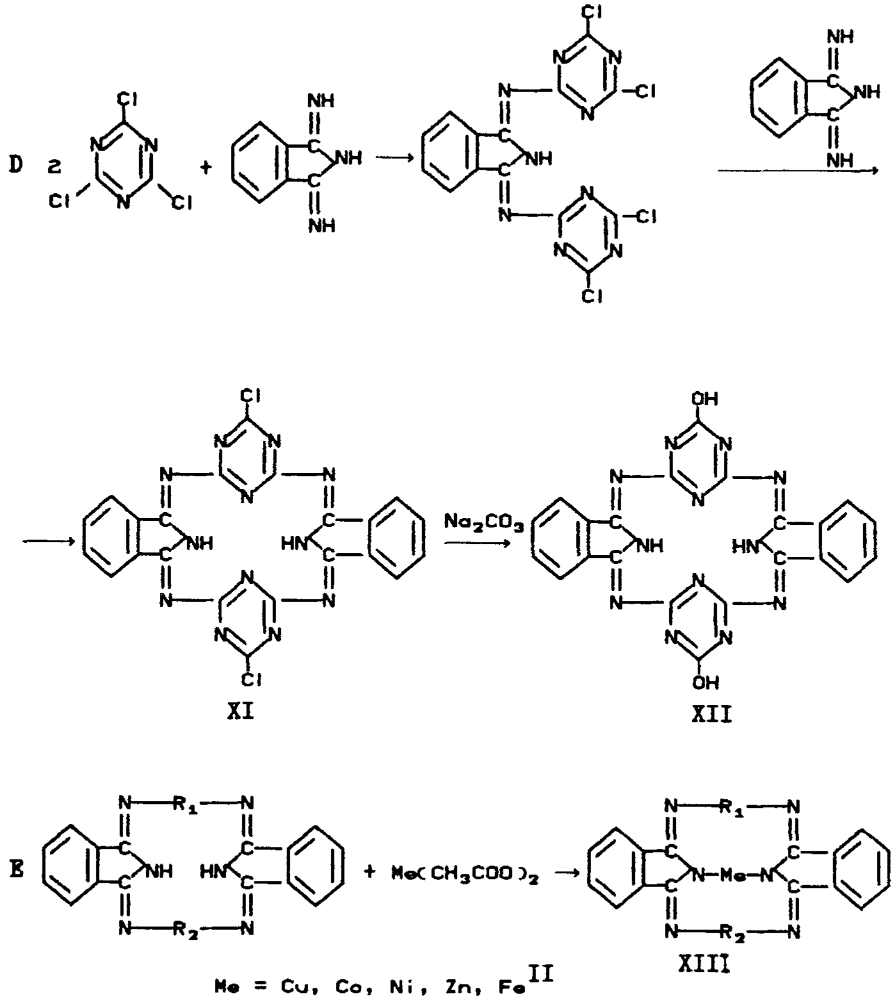


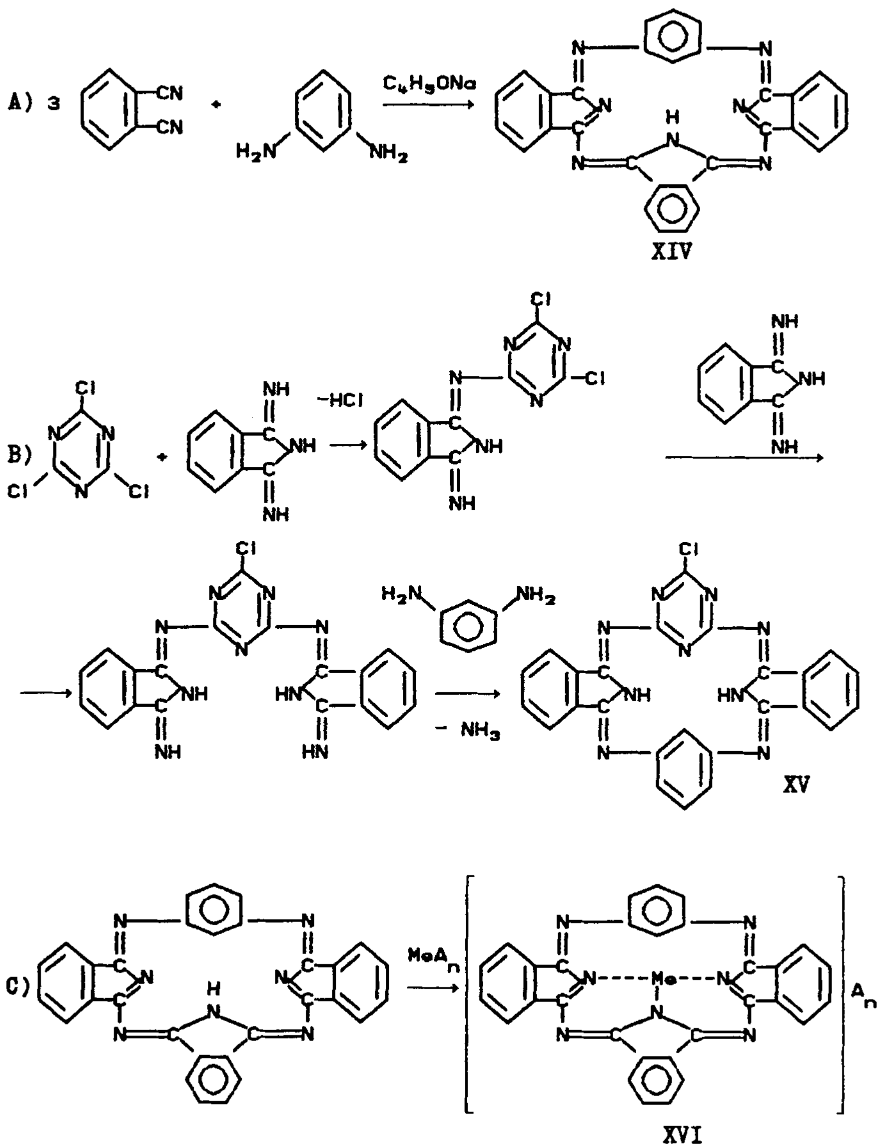
FIGURE 3b Synthesis of symmetrical macrocyclic compounds and their metal complexes.

The synthesis of these compounds was based on the reaction of phthalonitrile with m-phenylenediamine or 2,6-diaminopyridine and 2,5 thiadiazol correspondingly (Figure 3a). The reaction carried out in an organic solvent in the presence of sodium alcoholate.

For the case of symmetrical macrocycles with triazene rings, the stepwise condensation of diiminoisoindolenine with cyanuric chloride was realized (Figure 3d). Analogous reactions were used for the synthesis of non-symmetrical macrocyclic compounds (Figure 4).

Triisoindolbenzenemacrocycle, XIV, (it's trivial name) was obtained by the reaction of phthalonitrile and m-phenylenediamine into a butanol solution in the presence of sodium butylate first at room temperature and then in the refluxing solvent.

Other macrocyclic compounds of XV type were synthesized by stepwise con-



$Me = Cu, Co, Ni, Zr, Y, Pr, Al$

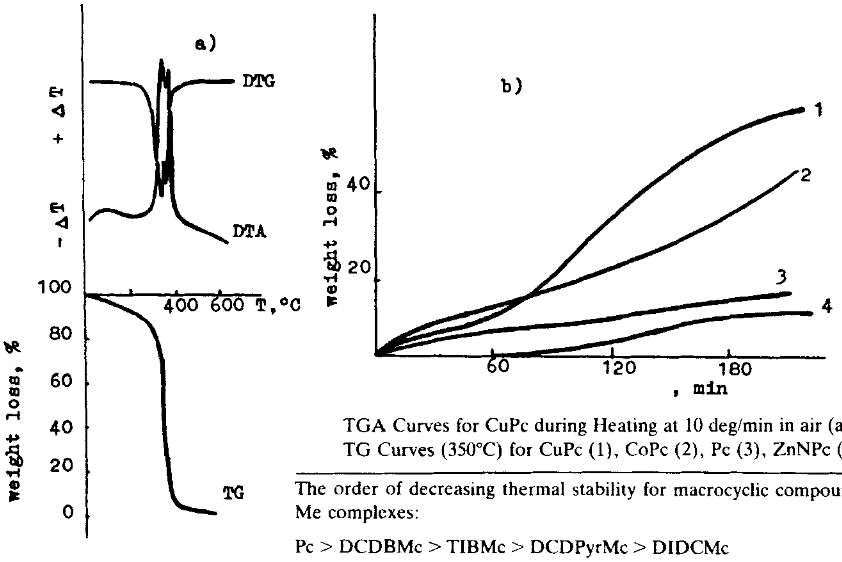
$A_n = Cl^-, CH_3COO^- ; n = 1\text{-}3.$

FIGURE 4 Synthesis of non-symmetrical macrocyclic compounds and their metal complexes.

densation of diiminoisoindolenine with cyanuric chloride and the diaminoderivative (Figure 4b).

Metal complexes were obtained by the interaction of equimolecular quantities of the macrocyclic ligand and the corresponding metal chloride or acetate in boiling solvent.

After purification the macrocyclic compounds and their metal complexes were



TGA Curves for CuPc during Heating at 10 deg/min in air (a); Isothermal TG Curves (350°C) for CuPc (1), CoPc (2), Pc (3), ZnNPc (4) in air (b)

The order of decreasing thermal stability for macrocyclic compounds and their Me complexes:

Pc > DCDBMc > TIBMc > DCDPyrMc > DIDCMc
VI VIII XIV IX XI
CuPc > CuDICBMc > CuDIDTMc > CuDIDCMc > CuTIBMc > CuDCDBMc
XV X XI XIV VIII

Me X: NiDIDTMc > ZnDIDTMc > CoDIDTMc > FeDIDTMc > CuDIDTMc
Me XIV: Ni > Co > Cu

FIGURE 5

characterized by different methods. Elementary composition, IR and electronic spectra, thermal stability during heating in isothermal and dynamic conditions with or without air were determined.

The model reactions of cumene oxidation and methylphenyltrizene (MPT) decomposition were studied in order to ascertain the ability of the metal complexes of the macrocyclic compounds to take part in radical reactions. [Cumene oxidation was carried out with molecular oxygen at 97–98°C in a reactor shaking with a frequency of 500 times/min. The content of the metal complex was 8.3 g/l.] Absorbed oxygen was measured with a gas burette. Hydroperoxide content was determined by the iodometric method. Selectivity of oxidation was evaluated by the ratio of oxygen absorbed and oxygen reacted to form cumene hydroperoxide (Figure 5).

It is known that methylphenyltriazene decomposition is a radical reaction accompanied by formation of methane and nitrogen. The relative decrease in the CH_4/N_2 ratio in the presence of a macrocyclic compound was a measure of its ability to react with methyl radicals. MPT decomposition was carried out in cumene at 110°C over 80 min in an inert atmosphere. The molar ratio of MPT:MeMc:cumene is equal to 1:2:70. The reaction at 200°C was carried out in tetradecamethylhexasiloxane with a molar ratio of MPT:MeMc:siloxane as 1:2:50 over 15 min. Macrocyclic compounds and their metal complexes were studied in detail as high temperature stabilizing agents for polyorganosiloxane (POS) systems. Various elastomers were used: polydimethylsiloxane with SKT and SKTN trade marks; polydimethylvinylsiloxane (SKTV); polydimethylmethylphenylsiloxane (SKTPV-803). POS compositions included 10–40 phr silica filler (Aerosil); vulcanizing agent (1–3 phr) and stabilizer (0.25–5 phr). The components were mixed at room temperature. The POS composition was vulcanized in a press at 150°C and 70 kg/cm^2 for 20 min and then in thermostatted at 200°C for 6 hours. A composite based on low molecular weight SKTN rubber was cured in a special mold at room temperature during 1 day.

Parameters were then used to evaluate the stabilizing action of metal macrocyclic complexes:

1. The change in the mechanical appearance of vulcanizates after ageing in air at high temperature.
2. The influence of MeMc on the thermal characteristics (weight loss, initial temperature of decomposition, and the displacement of exothermal peaks). An ATV thermobalance (USSR) and MOM derivatograph (Hungary) were used for the purpose.
3. The change in the solubility and the equilibrium swelling of a POS composition in toluene after ageing.

The flammability of the POS samples with metal complexes of macrocyclic compounds was evaluated by the USSR standard method (GOST 190094). The self-extinguishing time for samples after removal of the ignition source was determined. In this work the method of limiting oxygen index was also used.

3. RESULTS AND DISCUSSION

Macrocycles with azaporphyrin or analogous structures and their metal complexes studied in this work are highly thermally stable organic compounds. *In vacuo* ($>10^{-4}$ mm/Hg) they volatilize without decomposition when heated to over 300–500°C. The compounds are hardly soluble in polar solvents. Metal macrocyclic

TABLE I

The properties of metal triisoindolbenzene macrocyclic complexes

N Compound	T_d, °C	λ_{max}, nm
1. TIBMc	328–339	500.8 668.2 699.8
2. TIBMc Cu	>340	—
Co	345	—
Ni	360	—
Zr	375	602.4 669.9 700.3
Pd	257	635; 665.5 700.9
Y	350	665.9; 701.4
Al	280	626.5; 696.4

complexes are intensively coloured. Electronic spectra show a number of strong absorption bands in the visible and ultraviolet region. Phthalo- and naphthalocyanines are the most stable due to their polar structures and T_1-electron delocalisation in the macrocyclic plane which leads to an increase in the compounds aromatic character. The distortion of the macrocycle structure from planar is accompanied by a short-wave shift of the bonds in the electronic spectra. This situation is found for nonsymmetrical macrocycles, for example TIBMC. Coordination with metals also has an effect on the intensity and location of absorption bands in the 200–800 nm region of the spectrum. Table I shows the influence of the metal's nature on the properties of complexes with TIBMC. In comparison with the original macrocycle a long-wave shift is observed as result of the strength of the

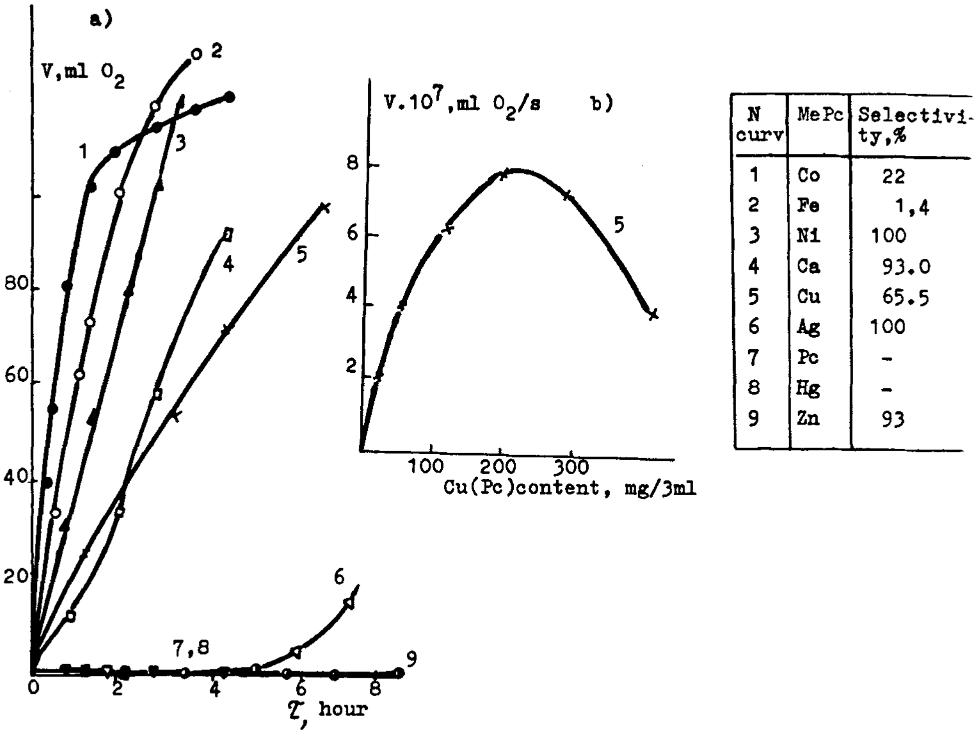
$$\mathrm{Me} \overset{/1}{—} \mathrm{N}$$

bond or extracoordination effect. Thermooxidative stability of macrocyclic complexes also depends on the metal's nature.

It is interesting to note that nonmetal phthalocyanine is more stable than its copper and cobalt complexes. As shown in Figure 5, the autocatalysis of degradation is observed for these compounds. The order of decrease in thermooxidative stability of macrocycles and their copper (II) complexes is quite different (Figure 5). However, in the case of triisoindolbenzene and diisoindolthiadiazol macrocyclic complexes the order of change in the thermal stability was similar for the metal sequenced: Ni > Co > Cu. Thus the stability of the compounds depends on the character of T_1-conjugated bonds system in macrocyclic and steric factors.

It was interesting to study the activity of the macrocyclic compounds in the radical reactions of cumene oxidation. Figure 6 shows the influence of phthalocyanine complexes on oxygen uptake by cumene. Complexes of Zn, Hg, Ag are inactive as catalysts. The rate of oxygen uptake by cumene in the presence of phthalocyanine complexes with transition metals decreases in the sequence: Co > Fe > Ni > Cu. High selectivity is observed for phthalocyanine complexes with Ni and Cu. The catalytic activity of CuPc in cumene oxidation depends on compound content. As shown in Figure 6b with an increase in CuPc content, the oxidation rate decreases. It is possible, owing to the dual function of the compound, i.e., its ability to both initiate and inhibit radical reactions. It is interesting to note that the inhibition function correlates with the low thermo-oxidative stability of CuPc. Nonsymmetrical CuTIBMc is inactive as a catalyst of cumene oxidation. The compound reacts with methyl radical formed in the decomposition of methylphenyltriazene. As shown in Table II, TIBMc can also react with methyl radicals. However the Cu complex is more active than the original macrocycle. The reaction of methyl radicals with CuTIBMc is observed at high temperature.

Hydrocarbon autooxidation at ambient pressure to yield hydroperoxide is promoted by solid MeMc at 80–110°C. The Kinetic scheme of hydrocarbon oxidation would involve the steps of initiation, propagation, branching of kinetic chains, and destruction of active radicals. Metal complexes of macrocycles are involved in at least three steps of the chain radical oxidation process. Figure 7 shows the kinetic scheme for hydrocarbon oxidation in the presence of a metal macrocyclic complex.



N curv	MePc	Selectivity,%
1	Co	22
2	Fe	1,4
3	Ni	100
4	Ca	93.0
5	Cu	65.5
6	Ag	100
7	Pc	-
8	Hg	-
9	Zn	93

FIGURE 6 The influence of the nature of phthalocyanine metal complexes on their catalytic activity (a, b) and selectivity in the cumene oxidation reaction.

TABLE II

The reaction of Cu macrocyclic complexes with methyl radical

	110°C, 80 min		200°C, 15 min	
Compound	CH_4/N_2	R_{accept}, %	CH_4/N_2	R_{accept}, %
No additive	0.55	—	0.43	—
Triisoindolbenzene-macrocycle, XIX(TIBMc)	0.52	5.4	0.43	—
Cu complex of TIBMc	0.36	34.5	0.35	18.6

In reaction (2) the oxygen molecule is bound and activated presumably by electron transfer to it from MeMc. MeMc acts as an electron donor. The activated intermediate reacts with the hydrocarbon molecule and forms free radicals which initiate the oxidation. It is believed that at high temperature the metal complexes decompose hydroperoxide by reaction.[6] The Pc complexes with copper (II), Zn(II), Ag do not catalyze the decomposition of the peroxide. They are characterized by high selectivity of action. Metal macrocyclic compounds can react with free radicals as in reaction.[8] It is a reaction of inversional inhibition. The cycle of catalytic inhibition is described by reactions 9 and 10 of the scheme. According to the scheme the

KINETIC SCHEME OF HYDROCARBON OXIDATION IN THE PRESENCE OF METAL MACROCYCLIC COMPLEXES

The Initiation

1. $RH+O_2 \longrightarrow [R^\bullet+HO_2^\bullet] \longrightarrow \delta R$

2a. $MeMc+O_2 \rightleftharpoons MeMc^+\ldots O_2^-$

2b. $MeMc^+\ldots O_2^- + RH \longrightarrow MeMc+R^\bullet+HO_2^\bullet$

The Propagation

3. $R^\bullet+O_2 \longrightarrow RO_2^\bullet$

4a. $RO_2^\bullet + RH \longrightarrow ROOH + R^\bullet$ 4b. $RO^\bullet+RH \longrightarrow ROH + R^\bullet$

The Branching

5. $ROOH + RH \longrightarrow \delta RO_2^\bullet$

6a. $MeMc+ROOH \longrightarrow MeMc^+ + RO^\bullet + HO^-$

6b. $MeMc^+ + ROOH \longrightarrow MeMc + RO_2^\bullet+H^+$

The Chain Breaking

$$\left.\begin{array}{l} \text{7a. } R^\bullet+R^\bullet \longrightarrow \\ \text{7b. } RO_2^\bullet + R \longrightarrow \\ \text{7c. } RO_2^\bullet + RO_2^\bullet \longrightarrow \end{array}\right\}\ \text{nonactive products}$$

8. $R+MeMc \rightleftharpoons RMeMc$

9. $RMeMc \longrightarrow HMeMc+R(=)$

10. $HMeMc+R \longrightarrow RH+MeMc$

FIGURE 7

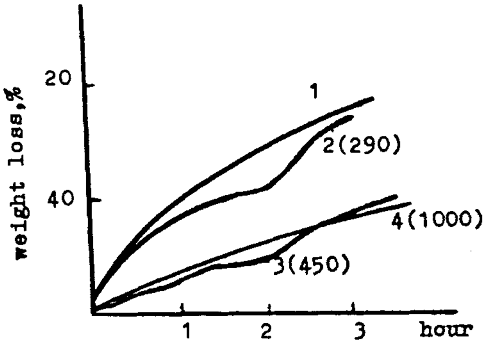


FIGURE 8 The influence of aerosil modified on siloxane rubber decomposition at 350°C in air: (1) with filler nonmodified; (2) silica + Fe_2O_3(3 phr) (3) filler modified PTCE; (4) filler modified PTCB; in brackets—% equilibrium swelling of rubber in toluene after 3.5 hours ageing at 350°C in air. Filler content is 35 phr.

transfer of a hydrogen atom from a radical acceptor to MeMc takes place. Hydrides of macrocyclic complexe react with free radicals and are reduced. In the hydride transfer the macrocyclic ligand is an acceptor. The effect of catalytic inhibition by the hydride transfer mechanism was seen in the polymerization reaction of (meth)acrylates.[3]

The metal macrocyclic compounds were used by us as stabilizing agents for POS systems. Cu complexes of phthalo- and naphthalocyanine retard polyorganosiloxane decomposition during ageing in air at 250–350°C. However, the stabilizing activity is low. Polymeric azaporphyrines produced on a silica filler surface are more effective. Figure 8 illustrates the influence of Aerosil modified by PTCE or PTCB on the weight losses of a polydimethylsiloxane composition on ageing in air at 350°C for 3.5 hours. A composition with standard Fe_2O_3 stabilizer for comparison is shown. It is seen that the polymeric macrocyclic compounds obtained on the filler surface are more effective than the standard stabilizing agent. The compositions maintain a high % equilibrium swelling of the elastomer in a solvent. For analogs of azaporphyrin macrocyclic complexes the stabilizing activity depends on both the macrocycle structure and the metal's nature. The breaking of the azaporphyrin structure and the distortion of symmetry of the macrocyclic molecules is accompanied by an increase in their stabilizing activity. High activity is observed for copper macrocyclic complexes. The influence of ligand structure can be considered for Cu complexes. The following sequence is found:

$$\text{CuDICBMc} \geq \text{CuTIBMc} > \text{CuDIDTMc} > \text{CuDIDBMc} > \text{CuDIDCMc}$$

Thus complexes of nonsymmetrical macrocycles show higher stabilizing activity than symmetrical ones. The effectivity of complexes of triisoindolbenzenemacrocycle decreases in the order: Cu > Ni > Co. The same order as for the change of effectiveness is observed for metal complexes of diisoindoldithiazolmacrocycle during SKTV ageing: Cu > Ni > Zn > Co > Fe. The regularities observed are apparently not accidental. It is interesting to note that the concentration of the macrocyclic compounds in the POS composition has an influence on the stabilizing effect. Table III shows how the content of CuMc affects the physicomechanical properties of SKTV vulcanizates after ageing in air at 330°C for 2 days. Here the numerator is CuTIBMc, and the denominator is CuDICBMc. Vulcanizates without a stabilizing agent or with 5 phr of Fe_2O_3 were completely destroyed in this time.

TABLE III

The influence of CuMc content on the change in polydimethylvinylsiloxane vulcanizate properties after ageing in air (330°C, 2 days)

	Content additive, phr				
Properties	0.1	0.25	0.5	1.0	5.0
Tensile strength kg/cm^2	33/–	38/42	44/42	38/42	43/–
Elongation %	110/–	195/60	215/180	130/110	110/–

numerator—CuTIBMc.
denominator—CuDICBMc.

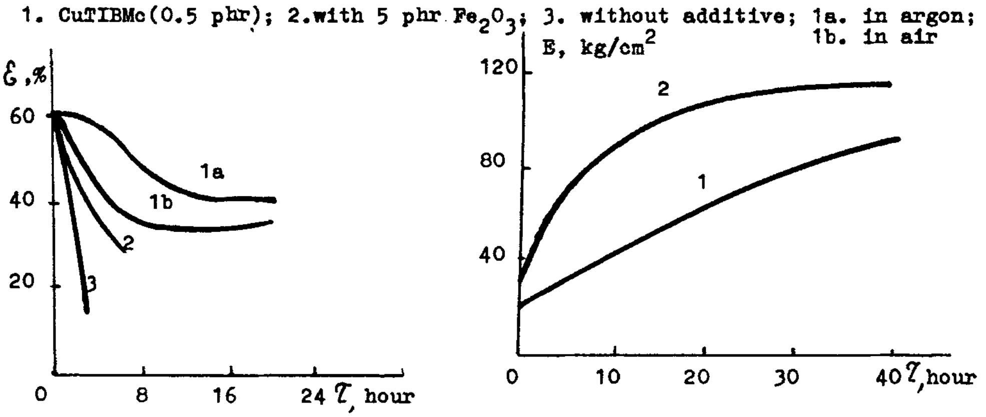


FIGURE 9 The change of elasticity (a) and elastic modulus (b) of siloxane resins during ageing in air (300°C).

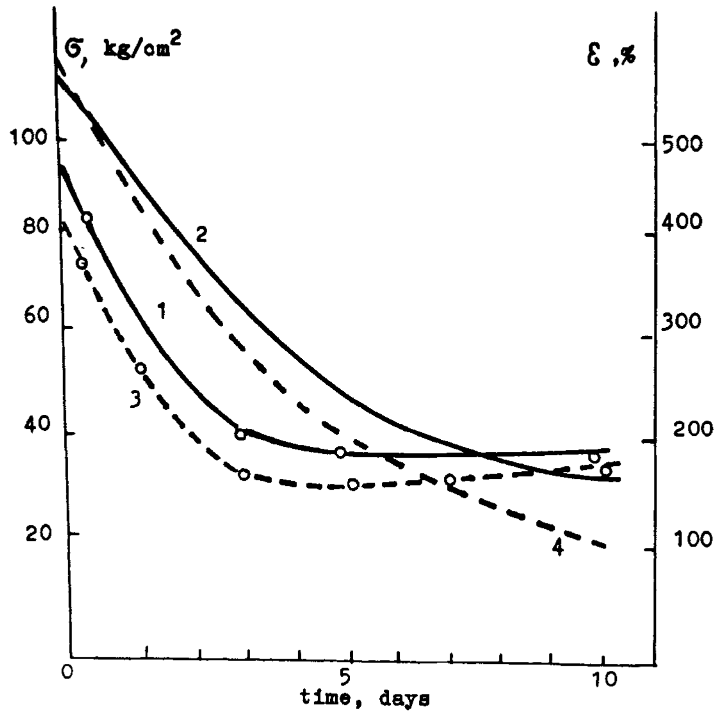


FIGURE 10 The change of tensile strength (1, 2) and elongation (3, 4) of polydimethylvinylsiloxane vulcanizates during ageing in air at 300°C: 1, 2 with 0.5 phr CuTIBMc; 3, 4 with 5 phr Fe_2O_3.

There is a certain optimum concentration of CuMc complex over which stabilizing effect decline. This optimum lies within the limits of from 0.25 to 0.5 phr. Figures 9 and 10 illustrate the influence of CuTIBMc taken in optimum amount for the change in the physical mechanical properties of polydimethylvinylsiloxane vulcanizates in the course of their ageing in air at 300°C. The corresponding curves concern

TABLE IV

The influence of the nature of the metal in complexes with triisoindolbenzene macrocycle on the self-extinguishing time of nonfilled polydimethylsiloxane films (s = 0.4 mm)

Additive content, phr	Self-extinguish Time, s[a] without Me	Cu	Pd	Al	Y	Zr
1	50	10	46	40	38	30

[a]By standard: OST-190094.

vulcanizates without additives or with 5 phr Fe_2O_3 for comparison. It is seen from Figure 9 that the elasticity of SKTV compositions fall more slowly during ageing in an inert atmosphere than in air. We observed a dramatical decline in the value of elasticity for the compositions without a stabilizing agent. Red oxide, as standard stabilizer, is less effective than the copper macrocyclic complex. Elastic modules, tensile strength and elongation values for polydimethylvinylsiloxane vulcanizates with CuMc are changed more slowly than for those with Fe_2O_3 (Figures 9 and 10).

The stabilizing effect of metal macrocyclic complexes is observed for all types of polyorganosiloxanes used. The high temperature stabilizers proposed are able to double the lifetime of polyorganosiloxane vulcanizates during ageing in air and to increase it under limited access to air by 20–30 fold. It was determined that the copper complex of triisoindolbenzenemacrocycle is an effective stabilizer for phenoloformaldehyde foams and also polyamides. A study of metal complexes of macrocycles as flame retardants for POS and PF foam was carried out.

Table IV shows the influence of the nature of the metal in the coordination sphere of the triisoindolbenzene macrocycle on the self-extinguishing time of nonfilled SKT films. It is interesting to note that the original macrocycle also decreases the self-extinguishing time of a POS sample. Additives in an amount of 1 phr permit an increase in the limited oxygen index of SKT films of 5 units in comparison with the original composition. At the present time the influence of CuTiBMc on thermostability and flammability of polyethylene is being studied. The possibility of an increase of the LOI of PE composites was established.

CONCLUSION

Some properties of the metal complexes of macrocyclic compounds with azaporphyrin and analogous structure were studied. The thermal stability of these compounds decreases when they are distorted from planarity in the macrocycle or when there is a breach of the continuous system of J_1-conjugation in the ligand. Metal complexes of macrocycles are able to react with free radicals. The compounds can catalyze or inhibit the oxidation reaction. It was shown that the copper complex of the triisoindolbenzene macrocycle is a very effective high temperature stabilizer for the polyorganosiloxane system. The compounds may be used as flame retardants.

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