

**Vith ALL-UNION CONFERENCE ON THE AGEING AND
STABILIZATION OF POLYMERS**

Ufa, U. S. S. R., June 1983

The following papers were presented:

Plenary lectures

Results in the physical chemistry of polymer ageing and stabilization

N. M. Emanuel (Moscow)

Some stabilization problems of polymerization plastics

Z. N. Polyakov (Moscow)

Role of sulfur-containing fragments in ageing and stabilization processes of polymers

S. R. Rafikov and G. V. Leplyanin (Chemical Institute of the Bashkirian Branch
of the Academy of Sciences of the U. S. S. R., Ufa)

State and prospects of supplying the plastics industry with domestic stabilizers

V. H. Gorbunov and V. I. Paramonov (Tambov)

Section 1. Thermooxidative decomposition and stabilization of polymers

Some problems of ageing and stabilization processes in polyolefin and polystyrene
plastics

S. S. Ivanchev and L. I. Lugova (Leningrad)

Study of the catalytic decomposition of polyisobutylene in the presence of aromatic
hydrocarbons

Yu. A. Sangalov, Z. I. Khudayberdina and Yu. V. Asman (Ufa)

Stabilization of polyolefins with intermolecular synergism

Yu. P. Losev, Z. N. Nesterovich and K. M. Paushkin (Minsk)

Structural stabilization of polyhaloalkylacrylates

A. D. Tillyaev and A. T. Dzhailov (Tashkent)

Relationship between the stability and structure of polyethylene

E. A. Sviridova, A. P. Marin, M. S. Akutin and E. D. Lebadeva (Moscow)

Characteristics of the stabilization of oligoesteracrylates with polyarylenemethylenes

V. V. Rozhkov and A. E. Chuchin (Moscow)

Study of the kinetics and mechanism of the retarding effect of transition metal diaryl-
thiophosphates on polypropylene oxidation

Z. G. Chebotareva, T. I. Kondrateva and D. G. Pobelimsky (Kazan)

Polyarylenemethylene stabilizers

A. E. Chuchin (Moscow)

Oxidation of polyolefins containing benzimidazolpyrazoline dyes

V. V. Filippov, N. V. Skuratova and V. G. Nikolsky (Moscow)

Characteristics of oxidation of polymeric materials

Yu. A. Shlyapnikov (Moscow)

On the differences in reactivity of peroxide macroradicals in solid polyperfluoroolefins

I. S. Gaponova, G. B. Parycky and D. Ya. Toptygin (Moscow)

Polyfunctional organophosphorus stabilizers for polymers

N. A. Mukmeneva and P. A. Kirpichnikov (Kazan)

On the interrelation between solubility, diffusion and reactivity of low-molecular substances dissolved in the polymer

N. N. Kolesnikova and S. G. Kiryushkin (Moscow)

Simultaneous dissolution of two different antioxidants in the polymer

G. V. Gedraytite and S. S. Yushkevichute (Vilnius)

A study of the chemical behaviour of the polymer matrix by means of the probing reaction of benzoyl peroxide decomposition

Yu. A. Mikheev, L. N. Guseva, V. P. Pustoshny, G. G. Makarov,
L. E. Mikheeva and D. Ya. Toptygin (Moscow)

Introduction of antioxidants in solution. The role of the solvent

Ya. I. Shatayte and S. S. Yuskevichyute (Vilnius)

Separation of oxygen isotopes at the oxidation of polymers

L. L. Yasina, A. V. Fedorov and A. L. Buchachenko (Moscow)

Effect of thermal ageing on the supermolecular structure of aliphatic polyamides

G. A. Kudravtseva, N. N. Pavlov, I. M. Abramova, V. A. Vatagina,
L. A. Vezina and L. G. Kazaryan (Moscow)

Oligomeric methylphenols as thermal stabilizers for polyethylene

V. M. Tryupina (Ufa)

Theoretical selection of the optimum oxidation inhibitor for hydrocarbons and polymers

E. T. Denisov (Chernogolovka)

Characteristics of the thermocatalytic degradation of polyethylene in the presence of electrophilic catalysts

S. R. Ivanova, Z. F. Gumerova and N. V. Tolmacheva (Ufa)

A study on the stability of epoxy compounds using methods of non-isothermal kinetics

K. I. Vesnebolotsky, I. A. Krasovskaya, A. A. Varunin and
D. S. Masloboev (Leningrad)

A method for calculating the dissociation energy of chemical bonds in simple and complex macromolecules

Yu D. Orlov and L. I. Pavlinov (Kalinin)

Fundamental relationships in structural stabilization of oriented polymers

K. E. Perepelkin (Leningrad)

The role of circular and translational diffusion of radicals in the cell effect at the thermal decomposition of dialauryl peroxide in polypropylene

A. P. Griva and L. N. Denisova

- Mechanism and kinetics of the thermocatalytic decomposition of isobutylene polymers
Yu. A. Sanganov, T. V. Romanko, S. R. Ivanova, I. Yu. Ponedelkina,
A. A. Berlin and K. S. Minsker (Ufa)
- Multiple chain rupture on bisphenols and quinones in oxidizing polypropylene containing hydroperoxide groups
Yu. E. Shilov and E. T. Denisov
- Oxidation inhibitors for mon- and polyacetals
E. M. Kuramshin, V. A. Dyachenko, V. K. Gumerova, M. S. Klyavlin,
S. S. Zlotsky and D. L. Rakhmankulov (Ufa)
- Structural ageing of oriented polymers
K. E. Perepelkin (Leningrad)
- Phenolic stabilizers – present and future
G. A. Gurvich, I. G. Avzamanova, S. T. Kumok and M. M. Yarovikova (Moscow)
- Thermal stability of cross-linked ethylene-acrylic acid copolymers
I. F. Osipenko, A. P. Polikarpov, H. R. Prokopchuk and L. D. Krul (Minsk)
- Degradation of active polymethylmethacrylate obtained on polyfunctional organo-silicon peroxides
L. N. Nistratova, N. A. Kopylova and Yu. D. Semchakov (Gorky)
- Cause of ageing and potential for stabilization of methyl methacrylate, β -oxyethyl-methacrylamide and β -oxyethylaminomethacrylate copolymers
L. F. Antonova, L. N. Golodkova, M. V. Purtova and B. A. Andreson (Ufa)
- A study of the reactivity and stabilization efficiency of bisphenols and trisphenols
I. I. Hayman, Ya. A. Gurvich, I. G. Arzamanova, S. T. Kumok,
R. M. Popova and M. M. Yarovikova (Moscow)
- A study on thermal oxidation of ABS copolymers
Z. I. Kirillova, A. T. Emelyanova and G. P. Malakova (Leningrad)
- On the kinetics of the thermal degradation of stabilized polystyrene
M. G. Babakhanova and O. M. Yariev (Tashkent)
- Kinetics of non-steady-state oxidation of isotactic polypropylene at ambient temperature
A. L. Margolin, Yu. V. Makedonov, L. S. Shibryaeva, N. Ya. Rapoport
and V. Ya. Shlyapintokh (Moscow)
- Thermooxidative degradation of polymerization-filled polyethylene
M. D. Sizova, L. V. Karmilova and S. A. Volfson (Moscow)
- Initiated thermooxidative degradation of polyvinyl alcohol in solution
T. G. Khanlarov (Baku)

Section 2. Photo- and irradiation ageing and stabilization of polymers

- Photosensitized reactions of peroxyde macromolecules
A. S. Smolyansky, G. S. Edanov and D. K. Milinchuk (Moscow)
- Synergism of antioxidants in the oxidation of γ -irradiated polyethylene
V. P. Pleshakov and S. M. Berlyant (Obninsk)

A study on the thermooxidative stability of radiation-modified polyethylene in the presence of carbon black and various-type stabilizers

G. A. Burukhina, V. O. Pleshanov and S. M. Berlyant (Obninsk)

Effect of irradiation-setting conditions on the accelerated ageing of oligomeric compounds

V. V. Bydanova, N. Kh. Fayzi, G. V. Shiryaeva, E. R. Klinshpont and I. V. Isakov (Obninsk)

Thermal stabilization of electroconductive compounds for subsequent modification by irradiation

L. K. Dolgina, G. J. Ovechkina and Yu. H. Firsov (Moscow)

Mechanism and kinetics of photoradical ageing of some carbon- and heterochain polymers

E. N. Seropegina, M. Ya. Melnikov and N. V. Fok (Moscow)

Photooxidation and light stabilization of aliphatic polyamides for long-wave irradiation

L. M. Postnikov, I. N. Smolensky and E. V. Vichutinskaya (Moscow)

A study of the phosphorescence of thermooxidized polyethylene

R. A. Baltenas (Vilnius)

Photodissociation reactions of peroxide radicals. Photodissociation of radicals leading to the rupture of C—C bonds in polyisobutylene at 77 K

M. Ya. Melnikov (Moscow)

Mechanochemical degradation of polyalkylmethacrylates under the effect of ultrasound

S. V. Golubev, A. A. Tikhonova and Yu. D. Semchikov (Gorky)

A study of polycarbonate ageing effected by UV light

N. N. Pavlov, V. A. Sade and G. O. Naydenova (Moscow)

Structural changes and some properties of polydodecanoamide in the photoageing process

A. L. Ivankina, I. I. Dubovnik, A. N. Neberov and V. S. Papkov (Moscow)

Deactivation of the electron excitation energy by light stabilizers — UV absorbers

A. A. Efimov (Tambov)

Change of molecular mass distribution in photosensitized low-density polyethylene at atmospheric ageing conditions

E. L. Ponomareva, N. I. Kondrachkina, V. P. Budtov and

T. N. Zelenkova (Leningrad)

The role of the crystalline phase in radiation-oxidative degradation of polyolefins

V. A. Gorelik, A. G. Grigorev, E. G. Khruleva and

E. I. Semenenko (Moscow)

Effect of stabilizers on the thermo- and photodegradation processes of self-extinguishing polyethylene

Z. K. Kulikova, L. L. Kholkhova and V. G. Shepetkova (Moscow)

Structural stabilization of photosensitive polymers used to record informations in corona discharges

N. A. Barov, L. Ts. Panasyuk, I. D. Balan, G. A. Dratalina,
G. N. Manushevich and S. V. Robu (Kishinev)

Photostabilizing effect of antioxidants in butadiene–styrene block copolymers

Z. N. Tarasova, A. F. Efremkin, V. B. Ivanov and
V. Ya. Shlyapintokh (Moscow)

Aggregation and disaggregation of vat dyes in cellophane film and photoageing of the dyed cellulose

G. T. Khachaturova, R. N. Nirmukhametov, G. E. Krichevsky,
V. V. Bulgaru and L. A. Polyakova (Moscow)

Light stabilization of the colour of polymeric textile materials by compounds of transition metals

V. M. Anisimov, L. A. Lovanova and O. M. Anisimova (Moscow)

Mechanism of the light stabilizing activity of azo compounds in polydienes and copolymers of dienes

V. E. Ivanov, A. F. Efremkin and B. Ya. Shlyapintokh (Moscow)

Mechanism of the light-stabilizing activity of disperse dyes on the photodegradation of polyamide

N. V. Lysin, O. M. Anisimova and G. E. Krachevsky (Moscow)

Light-protective properties of piperidine derivatives

A. A. Efimov, V. L. Kolomytsin, Z. G. Popova, T. A. Pankova (Tambov)
and P. F. Ivanenko (Grozny)

Diffusion stabilization of irradiation-modified polyolefins

L. P. Krul, V. D. Ryasnoy, L. Yu. Brazhnikova, Yu. I. Matusevich
and E. P. Petryaev (Minsk)

Problems of thermal stabilization for irradiation-modified electroinsulating materials based on polyethylene

S. I. Naumkina, Z. N. Nevedomskaya, N. S. Soboleva and Z. Z. Shnikel (Moscow)

A study on the thermostabilizing efficiency of mono- and diamides of maleic acid in irradiation-crosslinked polyolefins

Z. Z. Shnikel, G. N. Ovechkina, S. N. Naumkina (Moscow),
N. V. Korkin and G. V. Lyachkova (Tambov)

Effect of humidity on the ageing of photothermoplastic carriers

L. A. Mitrofanov, V. Ya. Pochinok, A. M. Chukarev and S. A. Shevchenko (Kiev)

Section 3. Ageing and stabilization of PVC

Degradation of some halogen-containing polymers and elastomers

K. S. Minsker (Ufa)

Study on the degradation and stabilization of polyvinyl chloride modified with benzazoles

N. A. Abduvaliev, O. P. Tumanova and V. P. Krapchatkin (Tashkent)

Chemical stabilization of vinyl chloride polymers

S. V. Kolesov (Ufa)

Effect of impurities in vinyl chloride on the structure of defects in the PVC chain and on its thermal stability

V. I. Zegelman, V. A. Titova, S. I. Mitoshnichenko and

V. A. Popov (Dzerzhinsk)

Liquid-phase degradation and stabilization of vinyl chloride polymers

M. I. Abdullin (Ufa)

Mechanism and stabilization of vinyl chloride copolymers

R. B. Panchesnikova and R. M. Akhmetkhanov (Ufa)

Modelling of the thermal degradation process of PVC

V. M. Yanborisov, S. V. Kolesov and K. S. Minsker (Ufa)

Raising the stability of compounds based on PVC and non-polar elastomers to thermal and ozone ageing

O. Yu. Soloveva, N. D. Zakharov, L. V. Makarova and

T. A. Rogova (Yaroslavl)

Effect of the nature of the co-monomer in the degradation of copolymers based on vinyl chloride

N. V. Lavinenko, R. B. Panchesnikova and L. S. Brodsko (Ufa)

Recent results in the theory and practice of PVC stabilization

B. B. Troitsin (Gorky)

Mixtures of oligosilanes with salts of coordinatively unsaturated metals – stabilizers of PVC in thermal decomposition

L. S. Troitskaya, B. B. Troitsky, A. S. Yakhnov and M. A. Novikova (Gorky)

Effect of salts of acylated amino acids on the properties of PVC and its compounds

I. K. Pakhomova, G. G. Bochkareva, A. F. Lepaev, V. L. Belyaev,

I. K. Dembinsky and V. I. Markov (Dzerzhinsk)

Kinetic characteristics in photoageing of PVC due to spatial effects

V. N. Genkin (Gorky)

Action mechanism of mixtures of carboxylates of metals of groups I–IV with polyols in the thermal decomposition of PVC

B. B. Troitsky, L. S. Troitskaya, V. H. Denisova and G. A. Razuvaev (Gorky)

Ageing of plasticized PVC at service conditions of cables

R. Yu. Lazauskene, V. K. Aleksa, V. A. Kuznetsov, D. H. Dikerman

and A. N. Elagina (Vilnius)

Kinetics, decomposition products and their spatial distribution in the photoageing of thermostabilized PVC with light close to the solar spectrum

A. P. Aleksandrov, V. N. Genkin, V. V. Sokolov and

D. D. Strelkova (Gorky)

Thermal decomposition of PVC in phosphate plasticizers

A. F. Valeev, G. M. Trosman and V. P. Biryukov (Moscow)

Effect of hydrogen chloride on the oxidation process of PVC

R. A. Varbanskaya (Moscow)

- Ageing mechanism of plasticized PVC in realistic application conditions
R. P. Braginsky (Moscow)
- Thermal decomposition of vinyl chloride homo- and copolymers in solution
R. R. Gistullin, M. I. Abdullin and D. M. Bikbulatova (Ufa)
- A study of γ -irradiated plasticized PVC
R. Yu. Lazauskene, Ya. I. Shatayte, D. N. Dikerman and
V. A. Kuznetsov (Vilnius)
- Inhibition of HCl formation in the thermooxidative decomposition process of PVC by various types of antioxidants
R. A. Barbanskaya, I. S. Belostotskaya, N. L. Komisarova and
V. S. Pudov (Moscow)
- The role of ester plasticizers in decomposition and stabilization processes of PVC
N. P. Zueva, N. A. Grekhanova and R. I. Ableev (Ufa)
- Thermooxidative decomposition of PVC in the presence of glycidyl phosphites
L. N. Yamalieva, N. A. Mukmeneva, V. Kh. Katsyrova, V. M. Zharkova
and D. A. Kirpichnikov (Kazan)
- The role of the thermal action of light in effecting spatial inhomogeneities at the photoageing of PVC
A. P. Aleksandrov and N. M. Bityurin (Gorky)

Section 4. Chemical resistance of polymers

- Ageing of elastomers in ozone and protection against it
S. D. Razumovsky and G. E. Zaikov (Moscow)
- Ageing of polymeric materials in their interaction with water
T. P. Komarova, E. I. Semenenko and A. E. Chalykh (Moscow)
- Biodegradation of polymers
K. Z. Gumargalieva, Yu. B. Moiseev, A. A. Ryzhkov and
S. A. Semenov (Moscow)
- Effect of composition and supermolecular structure on the kinetics of ozone oxidation of polyethylene and polypropylene mixtures
A. V. Russak and A. A. Popov (Moscow)
- Mechanism of hydrolytic degradation of polyacetalurethanes
A. Yu. Sokolov, V. V. Pchelintsev, V. D. Semenov, Yu. G. Kamene
and A. D. Klevansky (Leningrad)
- Effect of mechanical stresses on the reactivity of the C—H bonds in the polymer, presented on the example of the model reaction of ozone with polypropylene
B. E. Krisyuk and A. A. Popov (Chernogolovka)
- Atmospheric stability of polymers filled with complex metal compounds
S. I. Kuznetsov, E. M. Battalov, G. V. Laplyanin and S. R. Rafikov
(Chemical Institute of the Bashkirian Branch of the Academy of
Sciences of the U. S. S. R., Ufa)

Effect of thermal stabilization of cellulose acetate fibres on their resistance to alkaline solutions

Yu. Yu. Libonas, V. V. Pashkevichyus and
Ya. P. Arlauskene (Vilnius)

Chemical ageing of polymeric materials in organosilicon monomers and polymers

N. A. Bokshitskaya, Yu. V. Razorenov and O. O. Perekhodtseva (Moscow)

Stress relaxation in elastomers at ozone ageing

V. V. Podmasterev and S. D. Razumovsky (Moscow)

Characteristics of degradation of aromatic polyamides in concentrated sulfuric acid solutions

O. A. Mukhina, S. S. Kuleva and P. P. Nechaev (Moscow)

Section 5. Ageing and stabilization of thermally stable polymers

Thermochemical transformations in polyheteroarylenes

S. A. Pavlova (Moscow)

Effect of metal atoms contained in the polymer chain on the thermooxidation kinetics of polyarylene metal sulfides

N. P. Sheblakova, I. A. Serenkova, S. A. Pavlova, V. I. Nedelkin and
V. A. Sergeev (Moscow)

Decomposition of cross-linked polymers based on diepoxides and amines

T. S. Sarkhina, L. S. Zarkhin, A. N. Zelenetsky, L. V. Karmilova
and E. V. Prut (Moscow)

Determination of the kinetic parameters of the decomposition of polymers by dynamic TGA data

L. N. Sakharova, V. N. Klyuchnikov, V. M. Arshava and
L. I. Golubenkova (Moscow)

A study on the molecular mass characteristics of polysulfone in the thermooxidation by gel permeation chromatography

V. V. Guryanova, A. L. Narkon, I. I. Levantovskaya, L. I. Reytsburd
and A. V. Pavlov (Moscow)

Effect of the chemical nature of modifying additives on the thermal stability of polyphenylquinoxaline

P. N. Gribkova, I. V. Zarubina, I. A. Gribova, A. P. Krasnov and
G. V. Mamatsashveli (Moscow)

Thermal transformations of carborane-containing polyorganosiloxanes

L. N. Sakharova, I. I. Miroshnikova, N. L. Fedorova, V. T. Minakov
and M. G. Zaytseva (Moscow)

Structural features of compounds stabilized with polyamidocarborane

P. N. Gribkova, T. V. Polina and V. V. Korshak (Moscow)

Impurities and thermal stability of thermoplastics based on diphenylolpropane

I. I. Levantovskaya, A. B. Blyumenfeld, G. V. Dralyuk,
A. L. Norkon, V. V. Amerik and M. I. Siling (Moscow)

Thermal ageing and stabilization of polyimides

N. G. Annenkova, A. L. Vdovina, L. N. Emelyanova, M. L. Dobrokhotova,
P. M. Tanunina and V. V. Rodionov (Moscow)

Structural-chemical model of thermostable polymers (on the example of polyhetero-
arylenecarboranes)

P. M. Valetsky (Moscow)

Thermal stabilization of polybenzoxazoles

T. N. Novotortseva, V. V. Guryanova, V. A. Isaeva, S. N. Nikonova
and A. N. Chernikhov (Moscow)

Thermochemical transformations of carborane-containing polymers

V. I. Sidorenko, Yu. A. Kabachy, P. M. Valetsky and
S. V. Vinogradova (Moscow)

Effect of the synthesis method on the thermooxidative stability of aromatic poly-
esters

Kh. M. Batyrova, V. N. Shelgaev, G. B. Shustov, I. Kh. Emisheva,
E. R. Kekharsaeva and A. M. Kharaev

A study on thermal ageing and stabilization of polyimides with cycloalcanes in the
chain

B. A. Khubanov, N. P. Lyubchenko and I. A. Arkhipova (Alma-Ata)

A study on the mechanism of the thermooxidative decomposition of polyphenyl-
quinoxalines

K. A. Voloshuk, G. M. Tseytlin and N. S. Zabelnikov (Moscow)

A comparative study on the thermooxidative stability of arylate-arylenesulfonoxide
block copolymers

A. S. Shabaev, V. N. Shelgaev and A. K. Mikitaev (Nalchik)

On oxidation kinetics of cellulose triacetate

E. P. Gorelov, V. O. Myatezh and G. I. Burdygina (Moscow)

A study on the mechanism of the thermal decomposition of polyphenylquinoxalines

K. A. Boloshuk, A. B. Blyumenfeld, G. M. Tseytlin and
N. S. Zabelnikov (Moscow)

Thermooxidative ageing of polyphenylquinoxaline

A. L. Vdovina, V. M. Ryaboy and N. G. Annenkova (Moscow)

Characteristics of the production of semiquinone and phenoxy type polyradicals
based on polyconjugated inhibitor systems and semiconductors with controlled con-
ductivity

B. I. Liogonky (Moscow)

Thermal ageing of polysulfones and stabilization paths

A. I. Vorobeva, A. M. Polivin and I. I. Furley
(Chemical Institute of the Bashkirian Branch of the Academy of Sciences
of the U. S. S. R., Ufa)

A study on the thermal stability of modified polypyromellitoimide

A. I. Volozhin, E. T. Krutko, N. R. Prokopchuk and
L. B. Yakimova (Minsk)

Stabilization of polyarylatesulfone block copolymers

M. A. Gazaev, A. K. Mikitaev, G. V. Shustov and A. S. Shabaev (Nalchik)

Thermooxidative decomposition of carbonized polymers

Yu. N. Sazanov and G. N. Fedorova (Leningrad)

Thermal stability of rigid-chain polyimides

L. A. Layus and E. N. Dergacheva (Leningrad)

Development of thermal decomposition processes in polyimides modified with triphenyl phosphate

E. N. Dergacheva, I. L. Ushakova, L. A. Layus, A. G. Boldyrek
and E. V. Kuvshinsky (Leningrad)

On some aspects of thermal decomposition and stabilization of polymethylsilsesquioxanes

N. I. Fomina, V. I. Pakhomov, V. S. Papkov, M. I. Levitsky,
B. G. Zavin and O. Yu. Shilkloper (Moscow)

Kinetics of high-temperature ageing of polyimides

N. G. Stepanov, T. M. Bulina, L. A. Shibaev and Yu. N. Sazanov (Leningrad)

Thermal stability of polybismaleimidoamines

A. V. Khablenko, L. I. Marikyuk, S. A. Dolmatov and
Z. L. Titkova (Obninsk)

Section 6. Forecast of the service life of polymeric materials

Forecast of the service life of polymeric materials in processed products. Modern methodological approach, problems and prospects

O. N. Karpukhin (Moscow)

Acceleration of tests and possibilities to forecast the light-fastness of dyes on polymeric textile materials

V. M. Anisimov (Moscow)

A method to determine the period of reliable service for stabilized polyethylene from accelerated testing data

A. P. Maryn, N. K. Tyuleneva and E. S. Torsueva (Moscow)

Checking of the statistic hypothesis on the reliability of materials

V. F. Brin, O. N. Karpukhin and A. L. Pomerantsev (Moscow)

A study on the ageing kinetics of compounds based on polyolefins utilizing secondary (waste) material to forecast their service life

E. G. Lyubeshkina, L. S. Gavrikova and V. E. Gul (Moscow)

Extension of the service life of plasticized PVC at their processing with cold plasma

A. I. Solovev, Yu. V. Moiseev, V. V. Malunov and R. P. Braginsky (Moscow)

Equivalent thermal-humid conditions of storage for polymeric processed products

V. A. Buryachenko and B. D. Goykhman (Moscow)

Calculation of the kinetics of chemical reactions of ageing in a climatic temperature field

V. A. Buryachenko, B. D. Goykhman and T. P. Smekhunova (Moscow)

A study of the ageing processes of polyethylene terephthalate and forecast of storage life

A. N. Neberov and T. M. Savchuk (Moscow)

Description of the effect of stabilizers of thermooxidative decomposition on the kinetic mass loss curves of fibre-forming polymers

A. P. Molotkov (Moscow)

Testing of the stability of organosilicon sealing compounds using accelerated methods

R. I. Vafin, Yu. P. Tarasov, I. V. Zakonov, E. I. Minsker and

V. A. Petukhov (Moscow)

Section 7. Ageing and stabilization of elastomers

A study on structural and property changes in hetero-chain cured rubbers during ageing

A. A. Dontsov, T. V. Khokhlova and A. A. Kanauzova (Moscow)

Role of microheterophase rubber in the stabilization of the properties of polyurethane compounds

G. A. Enikezva, V. V. Markov, I. A. Tutorsky and V. S. Kulikov (Ufa)

Modification of polytrichlorobutadiene-1,3 with peroxide monomers

A. I. Rakhimov, O. S. Bogdanova, A. S. Suprun and

N. V. Klimentova (Volgograd—Moscow)

Stabilization of ethylene—propylene rubber compounds modified with commercial inhibitors

V. N. Isakovich, A. V. Smolyakov, N. N. Bukanova, V. I. Grachek

and S. F. Naumova (Moscow—Minsk)

Thermal stability of cured butadiene—nitrile rubbers containing chemically bonded antioxidants

A. I. Andreeva, L. I. Sergunova, L. G. Angert, A. A. Lontsov

and V. V. Moiseev (Moscow)

Cross-linking of ethylene—propylene copolymers with sulfonyl-containing peroxides

A. I. Rakhimov, A. V. Baklanov, Yu. V. Shatalin, L. N. Alekseeva

and A. M. Ogrel (Volgograd)

A study on the behaviour of inhibitors chemically bonded to the surface of the active filler in rubbers

A. S. Kuzminsky, I. E. Lepeshenkova and L. A. Lyapina (Moscow)

Effect of the composition and structure of cast polyurethane elastomers on their ageing in the stressed state

L. I. Lyubchanskaya, B. V. Nikoshkov, A. S. Kusminsky and

D. L. Fedyukin (Moscow)

Structural—mechanical study of the ageing process of cis-1,4-isoprene rubber

A. N. Neverov and A. I. Ershova (Moscow)

A study of the thermal stability of polydienes modified with sulfenil chlorides

Z. G. Shamaeva, V. V. Popova, A. A. Berg, Yu. V. Monakov,

G. A. Tolstikov and S. R. Rafikov (Ufa)

Inhibition of the thermal decomposition process of polydimethylsiloxanes by π -complexes of tricarbonyl chromium

V. E. Ditsent, I. I. Skorokhodov, E. I. Vovshin, L. P. Silaeva,
O. V. Afanosova and Yu. E. Zubarev (Moscow)

Effect of secondary aromatic amines on the oxidation of the rubber SKS-30ARK

N. M. Rodionova, T. S. Kavina, L. V. Koshkin, V. P. Burgov
and P. O. Yablonsky (Yaroslavl)

A study on the inhibitive activity of the binary system N-phenyl-N'-isopropyl-n-phenylenediamine-2-mercaptobenzothiazole in the thermal oxidation of cis-1,4-polyisoprene and its cured products

A. Ya. Borzenkova and S. P. Gerasimovich (Minsk)

Ageing of cured rubbers in detergent solutions

Z. N. Tarasova, E. G. Sekretareva, I. D. Khodzhaeva and
T. N. Pyatakova (Moscow)

A study on the inhibitive activity of the system phenyl- β -naphthylamine-N-phenyl-N'-isopropyl-n-phenylenediamine in the thermooxidative process of the rubber SKI-3 and its unfilled cured products

S. P. Gerasimovich and A. Ya. Borzenkova (Minsk)

A study on the efficiency of the antioxidant in the presence of commercial carbon in the thermal oxidation of the rubber SKI-3

G. D. Kudinova (Minsk)

On the thermal stability of polyisobutylene with functional end groups

Z. G. Shamaeva, V. V. Popova, Yu. B. Monakov and
G. A. Tolotikov (Ufa)

Mechanism of inhibited thermooxidative decomposition of cis-1,4-polyisoprene in bulk

V. V. Pchelintsev and E. T. Denisov (Leningrad)

Polymeric stabilizers based on liquid epoxy-cis-polybutadiene and aniline

N. A. Koshen, B. S. Turov and V. V. Popova (Yaroslavl)

A study on the action mechanism of 3,3',5,5'-tetra-*tert*-butyldiphenohydroquinone as inhibitor of the oxidative decomposition of cis-1,4-polyisoprene

Yu. A. Lvov, E. E. Senderskaya and N. F. Balasheva (Leningrad)

On the stability of isoprene rubbers and their cured products

N. A. Mikulenko, L. V. Masagutova, L. E. Poluektova,
V. F. Evstratov and V. A. Sapronov (Moscow)

Stabilization of butadiene rubbers with 4,4'-bis(2,6-di-*tert*-butylphenol)

V. F. Smirnova, Yu. A. Lvov, V. A. Krol and V. L. Zolotarev (Leningrad)

On the decomposition and cross-linking mechanism of the macromolecules at the thermal oxidation of cured cis-1,4-polyisoprene

N. L. Panteleeva, E. A. Ilina and S. M. Katun (Moscow)

Thermal stabilization of polydimethylsiloxane with carbamates and phosphates of transition metals

I. A. Metkin, T. V. Dykina, N. A. Silina and G. N. Nikiforova (Leningrad)

Chemical and physical paths of stabilizer consumption in tyre rubber at laboratory and service conditions

M. Yu. Tokareva, S. M. Kavun, A. S. Lykin and L. V. Andreev (Moscow)

Non-chain type inhibition of the thermooxidative decomposition of polyorgano-siloxane

O. A. Vasnetsova and E. N. Ovcharenko (Moscow)

A study on the permanent stability of liquid oligodimethylsiloxanes at high temperatures and ultrahigh frequency fields

K. B. Ryazanov, R. I. Vafin, A. A. Kushnarev, T. S. Kupriyanovich and V. I. Tarasova (Moscow)

Kinetics of the thermal decomposition of chlorobutyl rubber

R. F. Gataullin, V. M. Yanborisov and S. B. Sainikov (Ufa)

Ageing of elastomers based on liquid rubbers with functional end groups

G. K. Klimenko, K. Yu. Salkis, L. M. Mirosidi, V. F. Antipova and M. G. Sharabrina (Moscow–Leningrad)

Section 8. Ageing and stabilization of polymeric materials and products

A study of the light and thermal ageing of new low-density polyethylene utilized in the cable industry

L. I. Lugova, G. P. Makarova, L. K. Sotnikova, A. I. Tsvetkova and L. L. Khokhlova (Leningrad)

Effect of mechanical loads on the decomposition process and accumulation of hydroperoxide during processing polypropylene in melt

V. M. Goldberg and N. N. Komova (Moscow)

Stabilization of the properties of alloyed thermoplastics

Z. A. Romanova, M. S. Akutin and A. A. Romanov (Kharkov)

Ageing of epoxy resins and composites

V. F. Stroganov (Donetsk)

A study on the ageing of cable insulations made of poly-4-methylpentene-1 and its copolymers

V. M. Demidova, L. V. Shiraeva, M. P. Eydelnant and M. Ya. Sherman (Leningrad)

A kinetic study of the ageing of polymeric composites

A. N. Rassokha, V. L. Avramenko, L. I. Kirkach and A. S. Zhilak (Kharkov)

Effect of various additives on the electric properties of low-density polyethylene film

M. A. Bagirov, T. F. Abbasov and F. Sh. Kerimov (Baku)

Atmosphere-stable polyethylene pipes with protective paint coatings

V. L. Avramenko, A. N. Rassokha, V. P. Lebedev and I. G. Kashavtsev (Kharkov)

Ageing of plastic foams

O. G. Tarakanov and A. G. Dementev (Vladimir)

Effect of the method for curing the varnish UR-231 on the thermal stability of the film

G. A. Enikeeva and E. P. Borisova (Ufa)

Effect of thermostabilizers on the stability of pentaplast and on the adhesive power of pentaplast coatings to metals

Yu. A. Mulin, L. D. Bakirova, A. L. Goldenberg and
A. D. Yakovlev (Leningrad)

Some characteristics of the thermal decomposition of pentaplast

V. P. Malinskaya, F. N. Varmanova and A. I. Ilyasova (Ufa)

Thermal stability of polyoxazolidones

N. S. Gromakov and V. G. Khozin (Kazan)

Stabilization of oligomeric films at the conditions of corona discharge

Yu. P. Getmanchuk, V. N. Staretskaya and S. V. Robu (Kiev)

Stabilization of polymethylmethacrylate with thioacetals and thioketals

Yu. I. Puzin and G. V. Leplyanin (Ufa)

Quantum chemical investigation of the effect of the structure of the starting isocyanates on the primary thermal decomposition reactions of polyurethanes

I. B. Dorofeeva and O. G. Tarakanov (Vladimir)

Effect of the stabilizing additive on the supermolecular structure and mechanical properties of polyethyleneterephthalate

P. A. Matusevich (Minsk)

New catalysts for the selective depolymerization of polyolefins

D. V. Kazachenko, I. Yu. Ponedelkina and Z. M. Tayupova (Ufa)

On specific molecular mass changes of vinylidene fluoride-tetrafluoroethylene copolymers at the prolonged action of high temperature

G. A. Otradina, V. P. Budtov, G. A. Ryvkin and E. A. Fedorovich (Leningrad)

Property changes in tetrafluoroethylene-hexafluoropropylene copolymer at thermal ageing

G. A. Ryvkin, E. A. Fedorovich, L. A. Lazutkina, N. N. Loginova
and N. A. Panteleeva (Mytishchi)

Ageing and stabilization of electron-sensitive thermoplastics

V. G. Syromyatnikov, E. V. Blazhko and L. P. Paskal (Kiev)

Stabilization of asphaltic resins from crude petroleum

V. M. Bogolyubov and A. A. Sidorenko (Tomsk)

Thermal decomposition of diallyl phthalate copolymers

I. G. Litvinenko, V. V. Zaytseva, A. P. Andreev and
Yu. S. Zaytsev (Donetsk)

A study on the thermal ageing processes of modified epoxy resins

V. M. Kuznetsova, Ya. D. Kolesnikova, R. A. Yakovleva
and Yu. V. Popov (Kharkov)

Investigation of the processes taking place in polytetrafluoroethylene at the prolonged action of high temperatures

G. A. Ryvkin, E. A. Fedorovich, Yu. A. Zubov and N. G. Shirina (Mytishchi)

Stabilization of polyethyleneterephthalate with *o*-benzoquinone derivatives

Yu. I. Matusevich (Minsk)

Effect of thermal ageing in some partially crystalline polymers on their relaxation properties

V. P. Perfilov and Yu. V. Zelenev (Moscow)

Stabilization of protective–decorative properties in paint coatings with free nitroxyl radicals

V. I. Paramonov, V. V. Pavlikov, Z. G. Popova, V. I. Rubinsteyn (Tambov),

E. A. Andryushenko, R. M. Marinina, A. B. Shapiro and

P. I. Dmitriev (Moscow)

Effect of cellulose acetate fibre ageing on the light-fastness of the colour

D. P. Shablinskene, R. T. Baerunayte and V. V. Brazauskas (Kaunas)

A study on the thermal decomposition of oligoorganosiloxane–styrene copolymers

N. M. Khvoynova, S. S. Ziolina and L. M. Terman (Gorky)

Problems of the complex study of microcracks in plastic products

A. P. Molotkov, N. A. Yurkov and V. G. Manisadzhyan (Moscow)

Effect of substituents on the silicon atom on the mechanism of thermal decomposition of silicon-containing polyacrylates and polymethacrylates

L. M. Terman and V. A. Khudakova (Gorky)

Application of complex quality characteristics in composition optimization of PVC compounds

S. Yu. Rushalkin, V. P. Biryukov (Moscow) and

E. I. Nagumanova (Kazan)

Thermal transformations of polyphenylsiloxanes

N. I. Fomina, V. I. Pakhomov, V. M. Gelperina and

D. N. Mukhina (Moscow)

Modification of cured fluororubbers with fluorine-containing benzoyl peroxides

E. R. Androsyuk and L. M. Yagopolsky (Volgograd)

Effect of halogen- and phosphorus-containing antipyrene on the thermal stability of cellulose acetate

R. M. Aseeva, T. N. Kolosova, G. E. Zaikov and V. V. Korshak (Moscow)

A study on permanent and fatigue strength of metal to plastic pipe joints

V. I. Agapchev, N. G. Karimova and V. D. Kalyagin (Ufa)

EXTENDED ABSTRACTS OF PAPERS DEALING WITH THERMAL ANALYSIS AT THE VIth ALL UNION CONFERENCE ON THE AGEING AND STABILIZATION OF POLYMERS

RESULTS IN THE PHYSICAL CHEMISTRY OF POLYMER AGEING AND STABILIZATION

N. M. Emanuel (Moscow)

A kinetic classification of ageing characteristics for polymers at various conditions is presented. A general two-parameter equation is proposed which allows to describe the ageing kinetics for all widespread polymers, and is suited to estimate the efficiency of stabilizers and to forecast service life for polymers and processed products. A combined method for forecasting is discussed. On the example of inhibited oxidation of hydrocarbons as model process, quantitative approaches to determine stability of polymers and to select optimum antioxidant concentrations are presented. The existence of limit concentrations of inhibitor (stabilizer) is demonstrated; additions exceeding the limit concentration do not result in a further increase of the stability of the material being oxidized.

The kinetic analysis of the inhibited self-oxidation of polyolefins allows to calculate the basic kinetic characteristics of self-oxidation and to compare the antioxidative activity of phenolic antioxidants with different structures. A modified chemiluminescence technique to determine the nature, efficiency and quantity of antioxidants in the polymeric sample is presented. The technique allows quality control and estimation of service suitability of products during their ageing as well as the screening of antioxidants.

An automated system to evaluate the efficiency of antioxidants by computerized processing of kinetic data is described.

New methods were developed to increase the efficiency of stabilizers, based on the existence of a diffusion mechanism of synergism and on the phenomena of increasing the solubility of light stabilizers in the polymer.

New features of the mechanism and kinetics of mechano- and mechanothermooxidative decomposition, photooxidation of polymers, interaction of polymers with ozone are discussed. Data on the photochemistry of macroradicals are presented.

SOME STABILIZATION PROBLEMS OF POLYMERIZATION PLASTICS

Z. N. Polyakov (Moscow)

Fundamental approaches and principles of choosing stabilizing systems and stabilizer mixtures for industrial processing of polyolefin plastics are analyzed. Attention is called to the actual situation of supplying plastics-producing enterprises with modern, efficient stabilizers and stabilizer systems.

Properties and efficiency of the most important types and classes of thermal and light stabilizers commercialized in the Soviet Union and abroad are discussed and compared, in view of their action mechanism, technology of utilization and economy.

Stabilizer systems with best prospects for polystyrenes, ABS, polyethylene, polypropylene and higher polyolefins are discussed. Problems of shortage in stabilizers for large-volume plastics are considered. The problems of introducing the stabilizers into the compound are mentioned, taking into account equipment at disposal and safety of equipment.

The most timely tasks of developing stabilizing systems, improving the technology of introducing them into the polymer and developing the scientific principles for the application of various-type stabilized compounds are discussed.

ROLE OF SULFUR-CONTAINING FRAGMENTS IN AGEING AND STABILIZATION PROCESSES OF POLYMERS

S. R. Rafikov and G. V. Lepyanin

(Chemical Institute of the Bashkirian Branch of the Academy of Science of the U. S. S. R., Ufa)

On the example of organosulfur compounds belonging to various classes (sulfides, sulfoxides, sulfones) the ageing and stabilization mechanism of carbon chain and heterochain polymers containing organosulfur fragments as end groups, side groups or in the main chain, or else in the form of additives not bound chemically to the polymer are discussed. It is demonstrated that the processes of thermal, thermooxidative, photochemical and radiochemical ageing are limited by the break-off of the chain reaction of decomposition and by the formation of low-activity sulfur-centred radicals created in the polymer matrix at extreme conditions, this being one of the examples for earlier established principles of self-stabilization of polymers and plastic compounds.

The relationship between the stabilizing activity of the sulfur-containing fragments and their behaviour in radical chain polymerization processes is discussed.

The problems of creating "defectless" macromolecules into them sulfur-containing fragments under the conditions of copolymerization, and the activation methods of the sulfur-containing monomers in the stabilization and polymerization processes by irradiating the reaction system with light, γ -quanta or by complex-formation is discussed.

The stabilizing and inhibiting mechanism of the sulfur-containing compounds is discussed.

Some examples are presented demonstrating the utilization of sulfur-containing compounds in the technology of macromolecular compounds for the synthesis of polymeric materials stable to heat, light and high-energy irradiation.

SOME PROBLEMS IN THE AGEING AND STABILIZATION PROCESSES OF POLYOLEFIN AND POLYSTYRENE PLASTICS

S. S. Ivanchev and L. I. Lugova (Leningrad)

With the objective to choose optimum stabilizing systems regarding service, technological and economic characteristics, ensuring the conservation of the properties of the polymeric material under processing conditions and those of the product under service conditions, the major scientific research results achieved at "Plastpolimer" on the processes of thermal and light oxidation of polyolefins and polystyrenes are discussed.

Various multi-component stabilizing systems are compared, taking into account the interaction of the components under the conditions of thermooxidation and photooxidation of polyolefins.

The characteristics of utilizing stabilizing systems, using primary and secondary antioxidants combined with light stabilizers and metal deactivators at actual service conditions of the plastic products are discussed.

The possibilities to utilize polyfunctional stabilizing systems for polyolefin and polystyrene plastics are evaluated.

The technological level and state of supply with domestic stabilizers for large-volume production of polyolefin and polystyrene plastics is analyzed.

The assortment with good prospects of stabilizers capable of mutually replacing one another for polyolefins and polystyrenes, in view of the application areas of the processed products in the national economy of the Soviet Union is considered.

To supply industry and to enlarge the mentioned assortment of stabilizers, the necessity is pointed out to establish a large plant for phenolic derivatives, based on uniform and available raw material and intermediates, and integrated technological processes.

POLYARYLENEMETHYLENE STABILIZERS

A. E. Chuchin (Moscow)

We detected the inhibitive effect of polyarylenemethylene additives on the thermooxidative decomposition of polymers 15 years ago. This novel class of inhibitors, having already found industrial application, has a number of specific characteristics and advantages not present in other known stabilizers. Polyarylenemethylenes do not inhibit free-radical polymerization of vinyl monomers at normal conditions and can therefore be introduced into monomeric-oligomeric polymerizable systems, this being of major importance to obtain stabilized cross-linked polymers obtained by radical polymerization *in situ*. Polyarylenemethylene additives are most efficient in stabilizing polyalkylmethacrylates and compounds on this basis. Commercial polymeric materials manufactured at present stabilized with polyarylenemethylenes belong to this class of polymers.

Extensive studies on the free-radical transformations of polyarylenemethylenes and their hydroperoxides obtained by liquid-phase oxidation in solution were performed. The role of oxygen in the inhibition process was established, the effect of structure, of the presence of alkyl and aralkyl substituents, of the degree of branching and of molecular mass of polyarylenemethylenes on their inhibiting activity was determined. Chemical bonding of the polyarylenemethylene stabilizers to the matrix protected against thermooxidative decomposition by means of the homolytic decomposition of the hydroperoxide groups in polyarylenemethylene hydroperoxides or opening of the double bonds in the vinylated polyarylenemethylenes results in increased protective effect.

Polyarylenemethylene stabilizers are the first representatives of efficient non-polyconjugated hydrocarbon inhibitors of free-radical reactions; this activity is based on their polymeric nature.

These powder-like or resin-like oligomeric products are obtained by the well-known Friedel-Craft or Nastyukov reactions; depending on their designation, they are applied in concentrations between 0.1 and 10 mass-%.

CHARACTERISTICS OF OXIDATION OF POLYMERIC MATERIALS

Yu. A. Shlyapnikov (Moscow)

Polymeric materials consist of long chain molecules having very low translational mobility, and hence their structure is characterized by inhomogeneity stable in time. Zones of crystalline order coexist with zones where close order in the arrangement of segments of the macromolecule is permanently deranged. The different zones largely differ regarding the mobility of the material contained in them.

Low-molecular substances dissolved in the polymer are contained mainly in the zones where order is deranged. Molecules of the dissolved substance and also its transformation products, including free radicals, must overcome a potential barrier in order to leave the zone of disarrangement. Hence the role of intracellular reactions is increased in polymeric materials.

The sorption isothermal of the low-molecular substance by the polymer — if this substance does not change the structure of the polymer — is analogous to the Langmuir adsorption isothermal, and the limit value towards which the concentration of the sorbed substance tends is independent of temperature. Different low-molecular substances may displace one another from their solution in the polymer.

Before a reaction in the polymer can take place, the reagent must diffuse to the site of the reaction, and diffusion coefficients depend on the concentrations of the diffusing substances. The role of diffusion in the oxidation of thick polymer samples is discussed.

Owing to the low mobility of the polymeric materials, low-molecular substances formed in the course of the reaction, namely free radicals and peroxides will play an important role. Effects are observed connected with part of the free radicals being emitted from thin samples into the gas phase.

In crystalline polymers the elements of the crystalline phase do not contain oxygen. The capture of free radicals by these elements has a role in linear rupture of the chain in the period of the self-accelerating development of the reaction and has practically no effect on the course of the reaction after the induction period is ended.

FUNDAMENTAL RELATIONSHIPS IN THE STRUCTURAL STABILIZATION OF ORIENTED POLYMERS

K. E. Perepelkin (Leningrad)

Structural stabilization of oriented polymers is an imperative operation in their manufacture and processing. This operation is carried out at temperatures exceeding the glass transition temperature, at conditions of maximum rates of the crystallization and relaxation processes T_{cr}^* , corresponding to the relative temperature $\Theta_{1,cr} = 0.8 \dots 0.9$ ($\Theta_{1,cr} = T_{cr}^*/T_m$, where T_m is the melting temperature). To lower the stabilization temperature, the operation is performed in the presence of plasticizers (solvents), lowering the glass transition and melting temperatures.

The rates of crystallization and relaxation processes in the absence of external stresses, accompanied usually by shrinkage (in the case of flexible-chain polymers) depend exponentially on time. In certain ranges of low orientation spontaneous orientation and elongation may occur, also exponentially dependent on time.

The temperature dependence of the rate of structural stabilization processes within a defined temperature interval follows the Arrhenius equation, where the value of the potential barrier is defined both by the nature of the polymer and the effect of external stress. The presence of external stress increases the potential barrier and hence requires longer periods for the operation.

In practice, the criterium for the completeness of the structural stabilization processes is the value of the residual shrinkage of the polymeric material at repeated heating to T_{cr}^* not exceeding 1–3%.

Attention should be paid to the circumstance that in structural thermostabilization processes of oriented flexible-chain polymers accompanied by shrinkage, their mechanical properties will change: strength will decrease and deformability will increase. At structural thermostabilization under stretching, with fixed dimensions of the sample, these properties change slightly only.

In the case of rigid-chain oriented polymers, structural thermostabilization proceeds with spontaneous orientation and elongation. This is accompanied by strength increase and deformability decrease.

The discussed relationships are illustrated by a number of examples for various flexible-chain and rigid-chain polymers: vinyls, aliphatic and aromatic polyamides, polyesters etc.

PHENOLIC STABILIZERS -- PRESENT AND FUTURE

G. A. Gurvich, I. G. Avzamanova, S. T. Kumok and M. M. Yarovikova (Moscow)

The first patent on the application of phenolic stabilizers was issued in 1870, long before the development of modern polymeric materials. In latter years, thousands of compounds belonging to various classes have been tested for their stabilizing capacity, but phenolic compounds have retained and confirmed their technological importance.

The role of phenolic derivatives in solving problems of replacing natural rubber by light-coloured synthetic rubbers, in the synthesis of white and coloured rubbers and rubbers utilized in contact with foods, pharmaceutical products and biological media are discussed.

Some problems of applying phenolic derivatives as photostabilizers are considered.

The prospects of novel stabilizing system, including phenolic derivatives of various structures for protecting rubber, latex and other polymer products are discussed.

Growth dynamics of application of new stabilizers belonging to various classes are demonstrated. The reasons owing to which phenolic stabilizers possess particular importance: technological, economic, ecological, aesthetic reasons are analyzed.

It may be expected that the demand for phenolic stabilizers will increase in the future. The reasons are as follows:

- wide spectrum of protective action by phenolic stabilizers,
- low toxicity as compared to other classes of stabilizers, particularly to aromatic amines,
- a trend to increased manufacture of white and coloured polymers,
- availability of the raw material and simplicity of technology for manufacturing phenolic stabilizers.

DEGRADATION OF SOME HALOGEN-CONTAINING POLYMERS AND ELASTOMERS

K. S. Minsker (Ufa)

Thermal stability and decomposition characteristics of halogen-containing polymers are defined by the following: chemical structure of the macromolecules; physical properties of the polymeric products; action of various catalytic agents. A study of a number of chlorine-containing polymers and elastomers: polyvinyl chloride, polyvinylidene chloride, vinyl chloride copolymers, pentaplast, chlorinated butyl rubber, polychloroprene demonstrates that in some cases the decomposition rate of the polymer is controlled by the thermal stability of the units forming the main chain (polyvinylidene chloride, pentaplast) which is sometimes very low (polyvinylidene chloride). In the majority of cases, reduced stability of halogen-containing units in the polymer chain is caused by the effect of neighbouring groups of close or farther order. The effect of neighbouring groups of close order is related to the destabilizing effect of isolated $>C=C<$ groups (defective units, structural units) or to comonomer units in copolymers; it is prevalent in the thermal dehydrochlorination of chlorinated butyl rubber (groups $-CH=C(CH_3)-CHCl-$, $-C(=CH_2)-CHCl-$), of polychloroprene (β -chloroallyl $-CH_2-CCl(CH=CH_2)-$ groups), of vinyl chloride copolymers containing more than 10...15% of the second monomer (heterotriades of monomer units $\chi VC\chi$, where χ is vinyl ester, acrylate, olefin, vinylidene chloride etc.)

The effect of the farther-order neighbour manifests itself in polymeric molecules with conjugated polyene groups $-(C=C)_n-$, where $n > 1$, or oxovinylene groups $O=C-CH=CH-$; it is of primary importance for PVC and for vinyl chloride copolymers containing less than 3 mol-% of the second monomer. For chlorine-containing elastomers, thermal dehydrochlorination is controlled not only by the chemical structure of the polymer chain, but also by their physical properties, particularly by their low permeability to gases. Diffusion difficulties for the evolved HCl explain

The thermal properties of some polyheteroarylenes in vacuum were studied and their decomposition processes were quantitatively described. It was stated that the overall thermal stability of polyheteroarylenes, at "ideal" structures of the macromolecule, will be defined by the nature of the chemical bond of the heterocycle.

The study of the kinetic characteristics of the reactions proceeding at the decomposition of polyheteroarylenes allows to state that the character of their decomposition is described by radical reactions and is caused – at otherwise equal conditions – by the statistical splitting of the covalent bonds in the heterocyclic fragments. Compounds containing naphthylene-benzimidazole cycles have highest thermal stability.

In the investigated series of polyheteroarylenes, heterocyclic systems were pointed out, in which thermochemical transformations are defined by heterolytic reactions resulting in opening of the cycle.

A comparative study of the character of the thermooxidative decomposition of polyheteroarylenes allowed to state that in almost all classes of the polymers, in the early stages of oxidation – simultaneously with oxygen absorption – oxidation products are evolved. Polybenzimidazoloquinazolines are exceptional, insofar as their first stage of oxidation is characterized by oxygen absorption only, owing to the formation of *N*-oxides.

While the thermal stability of polyheteroarylenes in vacuum is defined by the stability of the heterocyclic systems, for those in contact with the oxidizing medium stability is practically independent of the chemical nature of the heterocycle. It follows from this statement that the aromatic fragments of the macromolecule belonging to one and the same type are responsible for thermooxidative decomposition.

A STRUCTURAL-CHEMICAL MODEL OF THERMOSTABLE POLYMERS (ON THE EXAMPLE OF POLYHETEROARYLENECARBORANES)

D. M. Valetsky (Moscow)

In our age the necessity has ripened to develop thermostable polymers of a new generation, destined for service at temperatures in the range of rather intense homolytic splitting of the main chemical bonds and active oxidative processes. Two basic paths may be conceived to transform the polymer matrix: one is intense decomposition in which large amounts of volatiles are evolved; the other is the formation of new bonds, maintaining or rather densifying the three-dimensional cross-linked system. In the second case, the final stage is carbonization or graphitization of the polymer in the product before its utilization. However, many application problems exist which cannot be solved in this manner, and a polymer matrix must be created in which the thermally more stable secondary structure will be formed at lower temperatures, in the application process of the product itself, without substantial loss of its initial strength properties. Frequently it is necessary to simultaneously ensure thermooxidative stability; this is performed by diffusional retarding of the process.

The above problems are discussed on the example of polyheteroarylenecarboranes and future prospects of developing thermostable polymers are presented.

A STUDY ON THERMAL AGEING AND STABILIZATION OF POLYIMIDES WITH ALICYCLES IN THE CHAIN

B. A. Khubanov, N. P. Lyubchenko and I. A. Arkhipova (Alma-Ata)

Changes in some properties of glass-reinforced plastics based on polyimides with alicycles in the chain were studied at prolonged thermal ageing in air at 200–300 °C. The polymers were prepared with solutions in dimethylformamide of polyamidoacids from tricyclodecane-tetra-

carboxylic dianhydride and 4,4-diaminodiphenyloxide, of polyamidoacids modified by adding small amounts of tetrahydrophthalic anhydride and maleic anhydride and oligobismaleimid, including fragments of tricyclodecenetetracarboxylic dianhydride. It is demonstrated that the modified products are characterized by high initial mechanical strength before and after ageing. The cause of the stabilizing effect is cross-linking of the polyimides as a result of the thermal polymerization of the double bond located at the end of the polymer chain. The best strength properties were observed with the oligomers cross-linked by the maleic groups: after thermal ageing for 100 hrs at 250 °C, static flexural strength was 80% of the initial value.

Some other properties of the glass-reinforced plastics: stability to moisture, electrical properties, mass loss at heating were found to vary little between unmodified and modified samples.

A STUDY ON THE MECHANISM OF THE THERMAL DECOMPOSITION OF POLYPHENYLQUINOXALINES

*K. A. Boloshuk, A. B. Blyumenfeld, G. M. Tseytlin and
N. S. Zabelnikov (Moscow)*

The fundamental relationships of thermal degradation of polyphenylquinoxalines (PPQ) in the temperature range between 532 and 873 K were studied. The effective rate constants of mass loss, and of accumulation of volatile decomposition products were determined. Changes in the chemical structure of PPQ-s, in their elemental composition and solubility were studied. Kinetic data were obtained on accumulation and consumption of intermediate structures.

It could be experimentally confirmed that thermal decomposition of PPQ proceeds by a radical chain mechanism. The initiation process is defined by the mobility of the hydrogen atoms in the α -position of the benzene ring in the quinoxaline group.

It was demonstrated that the decomposition of PPQ proceeds in two stages. The first stage is condensation by the double bonds $>C=N$. In this reaction, intermolecular secondary cyclization takes place. The process is accompanied by a change in the conjugation of the phenylquinoxaline structure, reflected in the decrease of the thermal stability of the quinoxaline ring system's heterocyclic part. For PPQ, this stage appears clearly at 473–673 K, with rapid decrease of solubility in conc. H_2SO_4 . No volatile decomposition products are formed. In the case of low-molecular model compounds, at 773–873 K soluble heavy fractions of the oligomeric type were separated by liquid chromatography and fractional sedimentation in organic solvents. Their structure was determined from IR, UV and mass-spectroscopic data and also by liquid screen analysis, thin-layer chromatography and elemental composition.

The second stage is pyrolysis of the condensed systems at the expense of further decomposition of the pyrazoline ring in quinoxaline, accompanied by the formation of the main volatile decomposition products of PPQ: toluene, benzene, benzonitrile, hydrogen and methane, and by the accumulation of the cross-linked, nitrogen-containing carbonized residue (60 mass-%).

Besides the main process, a decomposition of the side groups of the polymer and of the heterocycle of the quinoxaline group is also feasible, by-passing the condensation stage. From the quantitative ratio of toluene to benzonitrile, one may find out, which of the processes takes place at a given pyrolysis temperature, toluene being the product of decomposition of the condensed phenylquinoxaline system, and benzonitrile that of the direct decomposition of the quinoxaline ring.

THERMOOXIDATIVE DECOMPOSITION OF CARBONIZED POLYMERS

Yu. N. Sazanov and G. N. Fedorova (Leningrad)

Carbonization processes in high vacuum in the temperature range of 400–1000 °C were studied for a number of nitrogen-containing polymers: polyacrylonitrile, aliphatic and aromatic polyamids, polyoxydiazoles and polyimides. Based on thermovolumetric analysis, gas chromatography and elemental analysis, the correlation between the chemical structure of the polymer, the amount of the carbonized residue and its nitrogen content was established. It was demonstrated that nitrogen participates in the formation of the carbonized residue in heterocyclic polymers, nitrogen in the benzimide ring being of highest importance in this process, a significant part of which is maintained in polyimide at 1000 °C. In the thermooxidation of carbonized polymers a rather close agreement in the decomposition kinetics (from TG data) between carbonized and non-carbonized polyheterocyclic compounds was found, in contrast to the decomposition of linear polymers. Analogous experiments with model compounds (various types of commercial coals, graphite, gasified coal and other carbonized and coal-like materials) demonstrated that thermal oxidation of carbonized polymers takes place in the temperature interval between 500 and 700 °C. It could be concluded from the rate of carbon oxides formation and from the thermal effects accompanying this process that heterocyclic polymers and their carbonized residues are similar to the parameters of the thermooxidative decomposition of graphite.

THERMAL STABILITY OF RIGID-CHAIN POLYIMIDES

L. A. Layus and G. N. Fedorova (Leningrad)

The changes in mechanical properties of polyimides of different chemical structure at isothermal ageing in air in the temperature range of 275–500 °C were studied. The polymers investigated were aromatic polyimides differing in the presence and distribution of hinge-like bridging (ether) groups in the diamine or dianhydride part of the polymer chain.

It was found that rigid-chain polyimides (not containing bridging ether groups) keep their high-level mechanical properties longer under the conditions of high-temperature than flexible-chain polyimides. The differences are particularly significant in the high-temperature range; in the lower-temperature range investigated the differences are less. They reflect the fact that the activation energy of rigid-chain polyimides is lower than that of flexible-chain polyimides. It was also found that for one and the same polymer the activation energy of strength loss determined at temperatures above the softening point is higher than the value determined below the softening point.

The concept existing in the scientific literature that the conjugation system in polymers affects thermal stability proved useful in the interpretation of the high thermal stability of polyimides in general, and rigid-chain polyimides in particular; it does not, however, explain the differences between the activation energies of rigid-chain and flexible-chain polyimides.

The data obtained in this work regarding the kinetics of the strength changes in polyimides differing in their chemical structure and their analysis demonstrated that in addition to conjugation, the physical state of the polymer (softened or glassy) is of high importance, defining the stability of the polymer to the effect of high temperatures. Considering degradation as a series of elementary processes, one may demonstrate that an increase in molecular mobility must lead to an increased temperature coefficient of the reaction rate (activation energy) both in thermal and thermooxidative decomposition.

The rigid-chain polyimides investigated by us do not soften at temperatures up to 500 °C. Their decomposition in the whole studied range takes place in the solid state, this being apparently a further factor increasing their thermal stability.

FORECAST OF THE SERVICE LIFE OF POLYMERIC MATERIALS IN PROCESSED PRODUCTS – MODERN METHODOLOGICAL APPROACH, PROBLEMS AND PROSPECTS

O. N. Karpukhin (Moscow)

The forecast of service life of the material in the product is a complex problem; specialists with various profiles and levels of responsibility participate in its solution.

The forecast is made on the basis of initial data on the material Y_0 , service conditions of the material in the product X , characteristics of service suitability of the material Y_{st} , requirements of reliability in service of the product, results of ageing studies of the material $Y_j = f(X_j, t)$ and the selected ageing model $Y = F(X, k, t)$. The quality of the forecast will also depend on the strictness of mathematical processing of the obtained results.

The paper deals with the extent to which each of the above seven factors affects the quality of the forecast of service life in various situations and how far modern standards and methods correspond to modern demands of forecasts.

The stability of the material at various conditions is defined as the function of its ageing

$$Y = f(X, t)$$

Obviously, the ageing function of the material will never be known absolutely accurately. Therefore forecasting the kinetics of property changes in the material will always remain, to a certain extent, an incorrect mathematical task.

The result of the forecast will always be affected by three different types of accidents:

1. Accidents connected with the non-identity of two samples of one and the same material or two products from the same material.

2. Accidents connected with experimental error and insufficient volume of measurements.

3. Accidents connected with the ambiguity of selecting an ageing function for the material.

Modern methods allow an objective characterization of the effect of the first two types of accident on the quality of the forecast (characteristics of the reliability of the forecast and the safety of these characteristics).

The paper discusses the error caused by the third type of accident, its dependence on the length of the extrapolated section, and research of methods for a quantitative characterization of this accident.

NON-CHAIN TYPE INHIBITION OF THE THERMOOXIDATIVE DECOMPOSITION OF POLYORGANOSILOXANES

O. A. Vasnetsova and E. N. Ovcharenko (Moscow)

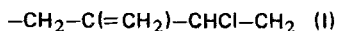
The stabilizing activity of finely dispersed metals and their lowest oxides formed from the corresponding formates in the decomposition process of a number of polyorganosiloxanes was studied by thermal analysis. Earlier established results were confirmed that the decomposition e.g. of polyorganosiloxane in the presence of air oxygen proceeds at a higher rate as compared to the decomposition of this polymer in an inert atmosphere. The nature and composition of the gaseous products essentially depend on oxygen present in the system. The presence of "non-chain type" inhibitors in the compound, e.g. finely dispersed Fe or FeO originating from the formate of trivalent iron directly in the sample has little effect on the rate and character of the decomposition of the polymer in an inert atmosphere, but substantially decelerates the decomposition process in air. These facts demonstrate that in the case of thermooxidative degradation, this process, as it were, is combined with the thermal process regarding the absorption of oxygen by

the acceptor-stabilizer. Analogous data were obtained with a number of compounds based on linear and cross-linked polymethyl-, polymethylphenylsiloxanes, on ladder-type polymers like polyphenylsilsesquioxane and polychlorophenylsilsesquioxane. The relationship between the life time of stabilized compounds and the rate of decomposition in air was established. The results obtained allow to confirm that thermal analysis may be used for screening potential non-chain inhibitors. An analysis of new data allowed to state that in stabilization of organosilicon liquids and finishes on the basis of polymethylsiloxanes and other polymers in the presence of oxygen acceptors like Fe and FeO, corresponding cerium, manganese, cobalt, vanadium and other compounds, regeneration of the oxygen acceptor is feasible. It was established that formaldehyde evolved in oxidative decomposition (and also, if oxygen is insufficient, other reducing substances like H₂, CO, CH₄ etc.) will reduce (regenerate) the initial acceptor-stabilizer used up in the reaction with oxygen.

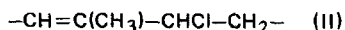
KINETICS OF THE THERMAL DECOMPOSITION OF CHLORINATED BUTYL RUBBER

R. F. Gataulin, Y. M. Yanborisov and S. V. Salnikov (Ufa)

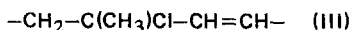
The relationship between the chemical structure of chlorinated butyl rubber (CBR) and its thermal stability is studied in the paper. When butyl rubber is being chlorinated, a number of chlorine-containing structural units are formed in the macromolecules; to determine their shares is important from both the theoretical and the practical point in view. Using ozonolysis, the content and distribution of unsaturated bonds was determined in CBR samples with differing degrees of chlorination. It could be demonstrated that a redistribution of the $>C=C<$ bonds in the macromolecules takes place in the chlorination process. While in the initial butyl rubber practically all $>C=C<$ bonds ($\bar{\gamma}$) are internal, $\bar{\gamma}$ decreases regularly with increasing chlorination, and the concentration of unsaturated side groups with the structure



increases up to 90%. The internal double bonds in the chlorinated product have the structures



and



The kinetics of the thermal decomposition of thin CBR films have exponential character and are described by the expression $\alpha_t = \alpha_1[1 - \exp(-K_1t)] + \alpha_2[1 - \exp(-K_2t)]$, where α_t is the amount of hydrogen chloride evolved in the moment t , α_1 and α_2 are the contents of structures I and II, resp., K_1 and K_2 are the dehydrochlorination rate constants for the structures I and II, resp. To render the value α_2 more accurate and to determine K_1 and K_2 , the least squares approach was applied. The stability of structure I exceeds that of structure II by more than one order of magnitude ($K_1 = 10^{10} \exp(-140) \text{ kJ mol}^{-1} (\text{RT})^{-1}$, $K_2 = 10^7 \exp(-94) \text{ kJ mol}^{-1} (\text{RT})^{-1}$).

The quantum mechanical calculation by the method PPD-2 of the relative stabilities of the models with structures I and II, approached by the isolated molecule's reactivity index (order of the C-Cl bond) is in satisfactory agreement with the dehydrochlorination constants found.

The thermal stability of CBR depends on total chlorine content only in the case when the ratio between the amount of chlorine introduced and the content of $>C=C<$ bonds in the initial butyl rubber is < 1 , and is controlled by the structures I and II whose ratio in the macromolecules varies from 7:1 to 9:1.

SOME CHARACTERISTICS OF THE THERMAL DECOMPOSITION OF PENTAPLAST

V. P. Malinskaya, F. N. Varmanova and A. I. Ilyasova (Ufa)

The paper deals with the thermal decomposition of 3,3-bis(chloromethyl) oxacyclobutane (pentaplast) in the range of 423–573 K. In vacuum the polymer is practically stable up to 473 K. At higher temperatures, thermal decomposition begins, by splitting of the main macromolecular chain, manifesting itself in the decrease of intrinsic viscosity of the degraded samples as compared to the initial value.

No changes indicating the appearance of new functional groups were observed in the IR spectra of the degraded pentaplast samples. However, a decrease in the ratio of optical density in the absorption bands at 705 cm^{-1} (D_{705}) and 1120 cm^{-1} (D_{1120}) was found in the course of decomposition. The absorption band at 705 cm^{-1} characterizes the valence vibration of the C–Cl bond, the band at 1120 cm^{-1} the asymmetric valence vibration of the ether bond C–O. The change in the ratio D_{705}/D_{1120} demonstrates that either the C–Cl bonds are splitted or the chloromethyl groups are split off. Reduced chlorine content in the polymer is confirmed by the data of elemental microanalysis. Consequently, in the thermal degradation of pentaplast not only splitting of the macromolecular chain takes place, but also volatile substances are evolved.

It was found that the thermal decomposition of pentaplast is accompanied by the evolution of hydrogen chloride. The kinetic parameters of dehydrochlorination of the polymer were determined.

The chemical structure of the pentaplast molecules excludes the possibility of HCl elimination combined with double bond formation. The following paths of HCl elimination may be conceived:

1. intermolecular dehydrochlorination, resulting in cross-linked structures,
2. intramolecular dehydrochlorination with the formation of three-membered rings in the molecule,
3. dehydrochlorination as the result of radical reaction, formed at the splitting of the main macromolecular chain.

The obtained experimental results (steady decrease of the molecular mass of the polymer during decomposition, absence of an insoluble fraction, deceleration of the dehydrochlorination reaction by radical-type inhibitors, low value of activation energy) confirm the third path as the mechanism of HCl elimination in thermal decomposition of pentaplast.

INVESTIGATION OF THE PROCESSES TAKING PLACE IN POLYTETRAFLUOROETHYLENE AT THE PROLONGED ACTION OF HIGH TEMPERATURE

G. A. Ryvkin, E. A. Fedorovich, Yu. A. Zubov and N. G. Shirina (Mytishchi)

The processes taking place in PTFE at prolonged (up to 15 thousand hours) heating at 290°C were studied. Three isotropic block samples from dispersion PTFE differing in initial crystallinity and two film samples from suspension PTFE, one of them isotropic, the other oriented by calendaring at a stretch ratio of 2:1 were studied.

No changes in molecular mass were observed at prolonged heating. The overall share of crystalline formations increased during heating, and after 12–15 thousand hours the degree of crystallinity was practically identical in the three samples made of dispersion PTFE. The general characteristics of changes in mechanical properties were as follows: the yield point decreases by 15–20%, strength by 30–35% as compared to maximum strength, and elongation to break increases by a factor of 2–3. Simultaneously the differences in the mechanical properties obtained in preparing samples with differing crystallinities are retained.

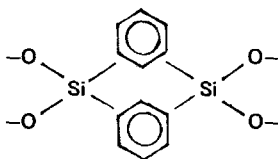
Prolonged heating of the oriented film exposed to heat in isometric conditions results in reorganization of its supermolecular structure. The diagram of isometric heating demonstrates that the internal stresses in the amorphous regions decrease with heating time, practically retaining the overall level at temperatures exceeding the melting temperature T_m . Shrinkage above T_m is identical for the initial and heat-treated film, shrinkage below T_m decreases in the film exposed to heat, and is practically absent after 10 thousand hours. Electron microscopic studies of samples with analogous characteristics obtained by short-time exposal of the oriented film to a temperature above T_m , and also DSC data of the studied specimens allow to explain the stabilization of geometric dimensions of the samples with simultaneous full retaining of mechanical strength properties in oriented PFTE by the existence of large crystals with straightened chains and some relaxation of the chains in the amorphous regions.

The results allow to conclude that exposure to heat of cable insulation made of isotropic or oriented PTFE will not affect the parameters of the cable products adversely during their service.

THERMAL TRANSFORMATIONS OF POLYPHENYLSILOXANES

*N. I. Fomina, V. I. Pakhonov, V. M. Gelperina and
D. N. Mukhina (Moscow)*

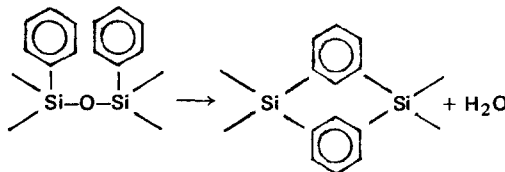
Thermal decomposition of cross-linked polyphenylsiloxanes (PPS) is connected with the split-off of organic groups and formation of benzene up to 53 mass-% of the volatile products of decomposition. By dynamic thermochromatogravimetric analysis we established that benzene formation in air corresponds to the low-temperature range of decomposition (within the same temperature range as in an inert atmospheres). The differential curve of CO_2 evolution corresponds to the DTG curve of the polymer in the low-temperature oxidation range of PPS. Analogous kinetic relationships regarding the formation of benzene and CO_2 were observed in the thermo-oxidative decomposition of hydrolysis products of tetrachlorodisilaanthracene containing no phenyl groups in its structure, but only phenylene groups



The course of the decomposition transformations of the hydrolysis products of hexachloro-

silylbenzene $\text{Cl}_3\text{Si}-\text{C}_6\text{H}_4-\text{SiCl}_3$ has a decomposition section in the high-temperature range of

oxidation common with PPS. It may be assumed that elimination of benzene from PPS is preceded by a rearrangement reaction of the polymer



and benzene is formed by the hydrolysis of the thermal rearrangement products of PPS. Mass-spectroscopic analysis of the thermal and thermooxidative decomposition products of PPS confirmed thermochromatogravimetric results, demonstrating the acceleration of benzene formation in the presence of air oxygen. Using marked oxygen ^{18}O it could be stated that about half of the oxygen in the oxidation products of PPS derives from the polymer chain. A study on the effect of transition metals demonstrated that transition metals reduce thermal stability of PPS, but in the presence of oxygen their action is essentially different. Thus, copper compounds substantially accelerate processes of PPS oxidation, while iron compounds have a stabilizing effect.

THERMAL DECOMPOSITION OF VINYL CHLORIDE HOMO- AND COPOLYMERS IN SOLUTION

R. R. Gistullin, M. I. Abdullin and D. M. Bikbulatova (Ufa)

Liquid-phase decomposition of PVC and vinyl chloride copolymers with methylacrylate dissolved in *o*-dichlorobenzene, *p*-dichlorobenzene, cyclohexanone, benzyl alcohol, acetophenone and in mixed solvents varying in composition according to good and poor solvents was studied.

Thermal decomposition of the studied polymers dissolved in solvents chemically inert to vinyl chloride homo- and copolymers is characterized by substantially slower kinetics of decomposition reactions as compared to the process at analogous conditions, but in the solid state. This experimentally found effect is common for PVC and VC copolymers. It is important that slowing-down of the thermal decomposition of VC homo- and copolymers when passing from the solid phase to the liquid phase is accompanied in all cases by retardation of the formation of polyconjugated double bond systems >C=C< in the macromolecules.

A particular feature of liquid-phase decomposition of VC copolymers as compared to thermal decomposition of PVC is the deceleration of the statistical evolution of HCl. The reduced rate of liquid-phase dehydrochlorination of copolymer macromolecules is connected with the decrease of the destabilizing effect of the comonomer on the intermediate VC members, resulting from the interaction of the macromolecules of the copolymer with the solvent. The specific characteristics of liquid-phase decomposition of VC copolymers rely on the fact that in the decomposition of copolymers the close order effect is of greatest significance, whereas this effect is not characteristics for PVC.

The nature of the solvent has a significant effect on the kinetics of liquid-phase thermal decomposition of VC homo- and copolymers and is defined mainly by the dipole moment, dielectric constant and basicity of the solvent. In the paper each of the parameters is discussed regarding its share on the kinetics of thermal decomposition processes of polymers in solvents.

The thermal decomposition process of VC homo- and copolymers in the liquid-phase are characterized by a number of particularities as compared to decomposition in the solid phase, caused by solvation and confirmation effects.

THERMAL AGEING AND STABILIZATION OF POLYIMIDES

*N. G. Annenkova, A. L. Vdovina, L. N. Emelyanova, N. L. Dobrokhotova,
P. M. Tanunina and V. V. Rodionov (Moscow)*

The gradual decrease of the high initial characteristics of polyimides during their prolonged thermal ageing is caused by thermooxidative processes taking place. During 1000 hours of ageing at 200 °C a polyimide film absorbs about 0.8 mol oxygen per mol, and evolves 0.003 mol CO_2 per mol. Mass-spectrometric and IR data indicate that the oxidation reaction consumes aromatic rings in the macromolecules to a greater extent than heterocyclic fragments.

The decomposition processes in polyimides are substantially retarded by stabilizing additives, namely organophosphorus compounds. The stabilizing effect is observed both when the additive is introduced into the non-cyclized prepolymer, the polyamidoacid and when it is introduced into the final polyimide. A comparison of the stabilizing efficiency of various classes of organophosphorus compounds allowed to follow the relationship between the structure of the additives and the value of the stabilizing effect.

The effect of the most efficient stabilizers on the kinetics of evolution of the major thermo-oxidation products of polyimides, on the accumulation of paramagnetic centres in them, on the cyclization processes of polyamido acids and on intermolecular cross-linking was studied. By using oxygen containing ^{18}O isotope for the thermal oxidation of polyimide film and subsequent analysis of the carbon dioxide evolved for the marked isotope content allowed to demonstrate that the major aspect of the stabilizing activity of the additives consists in decelerating the oxidative transformation of the aromatic rings. The multistage mechanism of the effect of organophosphorus compounds on polyimides is discussed.

Thermal ageing of polyimide films, glass-reinforced products and moulding compounds demonstrates the feasibility of raising the service capacities of these materials by means of using stabilizers.