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Modification of chemical additives to elastomeric compositions

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Abstract. The physicochemical principles of the modification of crystalline chemical additives to elastomeric compositions are examined. A classification of various types of modifications based on scientific principles is given. The modifications are subdivided into physical and physicochemical depending on the configuration of the molecules in the crystals, the defectiveness and dispersity of the crystalline particles, the melting points of the crystals, and the presence of nucleophilic and electrophilic centres in the molecules of the components of binary and complex eutectic mixtures. The effectiveness of the modification of the chemical additives is determined by the manifestation in binary systems of these components in elastomeric compositions of physical and chemical synergism due to the occurrence of the relevant processes in such systems. A relation has been discovered between the physical and chemical phenomena accompanying the modification of the chemical additives in binary and complex eutectic mixtures, their influence on the properties of the elastomeric composition is examined, the ecological problems associated with the processing of such materials are discussed, and the relation between the structure and properties of the molecules of the additives is analysed using quantum-chemical calculations. The bibliography includes 92 references.

I. Introduction

Chemical additives to elastomeric compositions, i. e. the components of sulfur-based vulcanising systems and antiageing agents, constitute molecular crystals (zinc oxide and liquid accelerators are an exception) whose structures are formed via intermolecular forces in accordance with the close packing principle.[1] In the processing of elastomeric compositions, it is essential that the crystalline chemical additives should be well dispersed and dissolved in the elastomer and that they should manifest at a certain instant a high chemical reactivity as moderators of prevulcanisation and as accelerators of the vulcanisation of elastomeric compositions and as antiageing and antifatigue agents in rubbers.

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In the existing methods for the preparation of elastomeric compositions, the main criterion of the uniform distribution of crystalline chemical additives in the elastomer is their solubility. According to Gardiner[2] and Ikeda et al.,[3] the limiting solubilities of crystalline accelerators and sulfur in elastomers depend greatly on temperature. However, not the limiting but current solubilities of the components in the elastomers are more important. It has been established[4] that the times required for the dissolution of sulfur, di(2-benzothiazolyl) disulfide (DBTD), and *N*,*N*′-diphenylguanidine (DPG) with a 0.2 mm particle size in butadiene rubber at 130 °C are respectively 2.8, 11.4, and 4.6 min. Similar times are characteristic also of other chemical additives.

Crystalline accelerators and sulfur are introduced into elastomeric compositions at a temperature below 112 °C and the mixing time is 2.5 min. Under such conditions, a proportion of the additives introduced into the elastomer remains in the form of small crystalline particles, which behave as centres for the formation of defects in rubbers.[5]

Another important index of the effectiveness of chemical additives in elastomeric compositions is the extent to which they manifest their functional properties. In order to attain the maximum effectiveness of the chemical additives, compounds of different classes have been synthesised.[6] It was found that the effective manifestation of the properties of chemical additives cannot be achieved by using traditional methods for their introduction into elastomeric compositions. The use of chemical additives in the form of dustlike powders and readily fragmented grains leads to the impairment of the environment in the processing of elastomeric compositions[7–13] and polymers.

Various methods for the modification of chemical additives are used to improve their effectiveness. Some of them are listed below.

1. The preparation of dispersions of powdered components in mineral oils in the form of pastes of different consistencies.[14,15] The use of such pastes facilitates the dispersion of the components in elastomeric compositions as a result of their preliminary wetting by the oil and prevents the formation of a dust during mixing.[16] However, the preparation and application of viscous pastes is associated with technological difficulties.

2. The mixing of the powdered components with polymeric binders, including encapsulation in microcapsules made from high-molecular-mass amino-compounds,[17–19] which melt during the vulcanisation of the elastomeric compositions, and also in capsules made from a polymer based on cellulose acetate.[20] However, the preparation of such microcapsules is difficult.

3. The use of binary and complex synergistic chemical additive systems (for example accelerators of the sulfur-based vulcanisation of elastomers[21] and antioxidants[22]). The synergistic effect, manifested by such systems in elastomeric compositions and rubber, has a both physical and chemical nature.[23] The chemical interaction of the components of synergistic systems takes place in the highly viscous elastomer under diffusional conditions, which lowers the probability of encounters of the molecules and prevents the complete manifestation of the synergistic effect.

4. The preparation on the basis of binary and complex chemical additive systems of simple eutectic mixtures, substitutional solid solutions, molecular complexes, and new chemical compounds,[21,24-26] which can form strong and readily diffusable granules at the temperature corresponding to eutectic fusion. The molecules retain their individuality in the eutectic mixtures and substitutional solid solutions, whilst in the molecular complexes there is a redistribution of electron density.[27]

In contrast to synergistic systems of chemical additives, introduced into the polymer compositions in the form of individual powders, in the eutectic mixtures and molecular complexes the components interact in the kinetic region in both the crystalline and fused states, which promotes the most complete manifestation of the synergistic effect.

Depending on the extent of the processes in the binary and complex chemical additive systems promoting an increase in their effectiveness in elastomeric compositions, physical and physicochemical modification procedures are distinguished.[28]

II. Physical modification of chemical additives

The physical modification of chemical additives is based on the increase in the defectiveness and dispersity of the crystals and the increase in the melting points of the components in the binary and complex eutectic systems and substitutional solid solutions.[28] All these factors tend to increase their effectiveness in elastomeric compositions.

The aim of the physical modification of chemical additives is the most complete manifestation of the synergism of their functional properties, which promotes a more complete and rapid (compared with the use of individual solvents) vulcanisation reaction of elastomeric compositions, an increase in the duration of the induction period for the process, and a decrease of reversion in the vulcanisation process. This ensures the formation of rubbers with effective physicomechanical parameters.

Physical synergism is manifested when the accelerators in the binary systems form only simple eutectic mixtures or substitutional solid solutions. These binary systems include CBS (*N*-cyclohexylbenzothiazole-2-sulfenamide)–OBS (morpholinobenzothiazole-2-sulfenamide), TMTD (tetramethylthiuram disulfide)–TMTM (tetramethylthiuram monosulfide), CBS–DBTD, TMTD–TETD (tetraethylthiuram disulfide), TMTD–DPG, TBTD–MBT (2-mercaptobenzothiazole), etc. The synergism of the properties of these systems of accelerators in elastomeric composition is due to the following causes.

The increase in the defectiveness and dispersity of the crystalline particles in the eutectic mixtures, which leads to an increase in the surface free energy and hence in the chemical reactivity of the accelerator, and the latter increases the rate of vulcanisation of elastomeric compositions.

The increase in the solubility of one accelerator in the elastomeric composition in the presence of another accelerator.

The sharp decrease in the melting points of the accelerators in the eutectic mixtures, which promotes their dispersion and improves their distribution in the elastomeric compositions and hence ensures a more complete vulcanisation with formation of a uniformly distributed and less defective three-dimensional network in rubbers.

The possibility and the effectiveness of the physical modification of chemical additives is determined primarily by the following characteristics of the components of binary and complex mixtures: the structure of the molecules in the crystals, the defectiveness of the crystals in eutectic mixtures, the dispersity of the crystalline particles, and the melting points of the components.

1. The conformation of the molecules in crystals of chemical additives

Analysis of the results of X-ray diffraction studies on the components of sulfur-based vulcanising systems[21] indicates different configurations of their molecules (with the exception of MBT and DBTD).

Even activated molecules are known[29] to react with one another only when they are oriented relative to one another in a specific manner. The configuration of the molecules in organic crystals is determined in its turn by the spatial disposition of the bonded atoms making up the molecule.[30] Thus the thiocarbamic acid residue in dithiocarbamate and thiuram accelerators has a planar structure.[31-33] The same configuration is characteristic also of stearic acid[34] and the benzothiazolyl group in MBT and DBTD.[35] On the other hand, the benzothiazolyl group in CBS–OBS has the chair configuration.[36,37]

Simple eutectic mixtures in binary systems of accelerators are formed when the molecules have significantly different configurations and are characterised by approximately the same nucleophilicity or electrophilicity (for example, the TMTD–TETD and CBS–DBTD systems). If the molecules of the components have similar configurations, as in the DBTD–MBT system, a substitutional solid solution is formed. When the energy of the interaction of unlike molecules is appreciable, i. e. when they contain nucleophilic and electrophilic centres and have a favourable orientation, molecular complexes (π- and *n*-complexes) may be formed in the eutectic mixtures. Then the composition of one of the phases will correspond fairly closely to an integral molar ratio of the components within certain temperature limits.[38]

The addition of zinc oxide to binary mixtures of accelerators may promote a change in the conformation of the molecules as a result of their adsorption.[39,40] This alters the ratio of the components in the eutectic mixtures or the substitutional solid solution and hence increases or lowers the eutectic melting point (T_{eu}) and the enthalpy of fusion (ΔH_m), which has been confirmed by studies on binary and ternary mixtures of the components of sulfur-based vulcanising systems by differential scanning calorimetry (Table 1).[28]

Table 1. Variation of the properties of the eutectic mixtures as a function of composition.

Binary or ternary mixture	Mass ratio of components	T_{eu}/ °C	ΔH_m/kJ mol^{-1}
MBT–TMTD	0.5:0.5	103	18.40
MBT–ZnO–TMTD	0.5:2.0:0.5	102	24.07
DBTD–TMTB	0.5:0.5	106	29.47
DBTD–ZnO–TMTD	0.5:2.0:0.5	112	27.08
CBS–TMTD	0.7:0.3	76	24.47
CBS–ZnO–TMTD	0.7:2.0:0.3	84	26.75

2. Defectiveness of crystals of chemical additives in eutectic mixtures

Crystal defects include dislocations and point, volume, and surface defects.[41] In organic crystals, dislocations are crystal lattice defects which disturb the regular disposition of molecular planes. Point defects comprise vacancies and interstitial impurity molecules introduced by substitution and volume effects comprise pores, cracks, and inclusions of other phases. Surface defects are defects in the packing of the crystals and in their surface relief.

The state corresponding to an ideally regular crystal is the most stable.[42] Such a crystal has the minimum entropy and free energy. Structural defects diminish the stability of the crystal because they lead to an increase in entropy and free energy.

Substances with more defective crystals exhibit a higher chemical reactivity. A mixture of defective crystals is characterised by a higher reactivity than a mixture of crystals with an ideal structure.

Surface, volume, and point defects, the number of which may be increased by the physical modification of the components leading to the formation of simple eutectic mixtures and substitutional solid solutions, promote an increase in the effectiveness of crystalline chemical additives in elastomeric compositions.

Table 2 presents the principal characteristics of binary mixtures of crystalline components of sulfur-based vulcanising systems obtained by the method of thermal analysis.[25,28] Evidently the formation of equilibrium eutectic systems is accompanied by a significant decrease in the enthalpy of fusion and an increase in the activity coefficients of the components, which is due to the increase in the defectiveness and dispersity of the crystals.

The increase in the defectiveness of the crystals (up to 42%) during the formation of simple eutectic systems, substitutional solid solutions, and molecular complexes (Table 3) has been confirmed quantitatively by the results of investigations by NMR (analysis of broad lines) and differential scanning calorimetric methods.[25]

According to Zalkin,[43,44] the increase in the defectiveness of the crystals in eutectic mixtures of the components of sulfur-based vulcanising systems is caused by the following factors. In the solid eutectic mixtures, the surfaces of two crystals 'trap one another' via intermolecular forces, which leads to the elastic deformation of the crystal lattices in the boundary regions. The surface of the crystal with a higher melting point is then the 'active substrate' and tends to distort the surface of the low-melting crystals in conformity with its surface relief. As a result, the excess free energy is concentrated in the contact zone together with the increased number of surface and volume defects, such free energy being the cause of the increased chemical reactivity of the components of the eutectic mixture.

In the solid solutions, the substitution of one molecule in the crystal lattice of the first component by a larger molecule of the second component leads to loosening of the packing and to the appearance of strains and distortions in neighbouring molecules, the number of which may reach 400 and more.[1] When a larger molecule is substituted by a smaller one, contraction takes place, whereupon the number of molecules subjected to strain and distortions does not exceed 350. Accordingly, the increase in the activity coefficient of DBTD in the DBTD–MBT substitutional solid solution (Table 3) is due to the fact that, when one DBTD molecule in the DBTD unit cell is substituted by two MBT molecules (the volume of two MBT molecules is greater than the volume of the DBTD molecule by the volume of two hydrogen atoms), the structure is loosened, which is accompanied by an increase in the free energy of DBTD and hence also in its activity coefficient. On the other hand, the replacement of two MBT molecules by one smaller DBTD molecule leads to contraction of the unit cell of MBT and to some decrease in the free energy and in the activity coefficient of MBT.[28] The introduction of such eutectic mixtures and substitutional solid solutions into elastomeric compositions makes it possible to increase the rate of vulcanisation whilst retaining the duration of the prevulcanisation period at the level of control specimens. The rubbers thus obtained have a higher tensile strength, a greater wear resistance on repeated deformations, and a greater resistance to thermal ageing.

Table 3. Defectiveness of the crystals of binary mixtures of accelerators.

Binary mixture	Degree of defectiveness of crystals			Increase in degree of defectiveness of crystals in eutectic mixture compared with additive value (%)
	A	M	E	
MBT–TMTD	0.365	0.44	0.51	39.72
DBTD–TMTD	0.305	0.36	0.42	37.70
CBS–TMTD	0.370	0.42	0.46	24.32
OBS–TMTD	0.360	0.38	0.38	5.55
MBT–DBTD	0.365	0.48	0.52	42.46
DBTD–ZDMDTC	–	0.46	0.48	–

Remarks. The following notation has been adopted: A—additive mixture, M—mechanical mixture, E—eutectic mixture..

3. The dispersity of crystalline particles of chemical additives

An increase in the dispersity of a crystal is known to diminish its stability owing to the increase in the surface free energy. As a result of this, more highly dispersed crystals exhibit a higher chemical reactivity. For this reason, the properties of elastomeric compositions depend to a large extent on the dispersity of the particles of the powdered chemical additives; the smaller the particle size the more effectively are they dispersed in the elastomeric compositions and the greater their functional effectiveness.[16,45,46]

The distribution of the powdered accelerators, sulfur, and antiageing agents in elastomeric compositions occurs most effectively at the level of crystalline particles, which cannot ensure

Table 2. Certain thermodynamic characteristics of the components of the binary systems for the sulfur-based vulcanisation of elastomers.

Binary mixture	Molar ratio of components	T_{eu}/ °C	T_{per}/ °C	Enthalpy of fusion/kJ mol^{-1}			Activity coefficients of components[a]		Type of mixture formed
				ΔH_{ad}	ΔH_{mix}	ΔH_{eq}	1	2	
Sulfur–MBT	0.49:0.51	104	–	18.70	17.00	15.20	1.816	1.686	Simple eutectic
Sulfur–OBS	0.30:0.70	77	–	20.00	18.00	12.60	2.070	1.750	" "
Sulfur–CBS	0.50:0.50	80	–	22.47	18.35	15.05	1.250	1.180	" "
DBTD–MBT	0.33:0.67	137[b]	–	26.63	13.10	8.36	1.296	0.891	Solid solution
OBS–TMTD	0.80:0.20	76	90	23.34	17.20	16.69	1.320	2.200	Molecular complex
DBTD–TMTD	0.42:0.58	106	111	35.65	29.47	18.33	1.522	2.100	" "
CBS–DTDM	0.57:0.43	79	83	25.50	18.00	11.80	1.220	2.150	" "
DBTD–ZDMDTC	0.56:0.42	144	151	–	22.60	4.50	1.360	1.950	" "
TMTD–ZDMDTC	0.84:0.16	136	142	–	30.00	16.72	1.266	1.900	" "

Remarks. ΔH_{ad} is the additive enthalpy of fusion; ΔH_{mix} and ΔH_{eq} are the enthalpies of fusion of mechanical and equilibrium eutectic mixtures; T_{eu} and T_{per} are the eutectic and peritectic melting points. [a] The activity coefficients of the components were calculated from Wilson's equation for the known eutectic conditions.[49] [b] The lowest temperature of a liquidus with a minimum is quoted.

Table 4. The structure of the particles of certain crystalline powdered components of sulfur-based vulcanising systems.

Component	Average particle size $10^2 d$/mm	Volume of spherical particle $10^8 V$/mm^3	Volume of unit cell $10^{18} V$/mm^3	Number of unit cells in particle $10^{-12} n$	Number of molecules	
					in unit cell	in spherical particle $10^{-11} N$
TMTD	2.33	662	1.138	5.81	4	232
MBT	2.27	612	0.768	7.97	4	318
DTDM	2.40	723	1.171	6.178	4	247
Orthorhombic sulfur	2.07	464	3.296	1.40	16	225
Monoclinic sulfur	2.07	464	1.298	3.57	6	214
Stearic acid	–	–	2.349	–	–	–
Zinc oxide	1.89	353	–	–	–	–

the same concentration gradients of these components throughout the bulk of the elastomer because in the vicinity of the particles themselves an increase in the concentration of dissolved molecules is maintained.[4,28] This is indicated also by the structure of the particles of certain powdered components established on the basis of crystal-chemical data (Table 4).

If it is assumed that the particles of crystalline components are approximately spherical,[47] it is possible to calculate the number of unit cells in them and, knowing the number of molecules in each cell,[21] it is possible to determine the total number of molecules in each spherical particle. It is seen from the data presented in Table 4 that the particles of the powdered components contain an enormous number of molecules and their uniform distribution in the particles solely as a result of dissolution is hardly possible despite the fairly high solubility of sulfur and of the accelerators in elastomers at the mixing temperatures.[3,4] Under these conditions, a uniform distribution of the chemical additives in the bulk of the elastomeric composition can be attained by increasing their dispersibility in the fused state.

By analogy with the diffusion of gases in liquids,[48] the following equation is used for the mathematical description of the distribution and diffusion of chemical additives in an elastomer:[28]

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2},$$

where dc/dt is the rate of accumulation of the molecules of the component in a unit elementary volume, D the diffusion coefficient of the molecules of the component in the elastomer, and d^2c/dx^2 the derivative of the concentration gradient characterising the distribution of the component in the elastomer.

Evidently the rate of increase in the concentration of the component is dissolved in the elastomer depends on the rate of distribution of its molecules, and the more effectively the component is dispersed in the bulk of the elastomer in the form of small fused particles, the faster the equalisation of the concentration gradient of its molecules throughout the bulk of the elastomer.

The dispersion of powdered and fused components during the mixing of chemical additives and the diffusion of the dissolved molecules of the component accompanied by the equalisation of the concentration throughout the entire bulk of the substance are illustrated schematically in Fig. 1.

It follows from the foregoing that, in order to improve the distribution of chemical additives in elastomeric compositions, it is necessary to fuse them at the very beginning of the mixing process. The fusion of the particles after their dispersion in the crystalline state does not promote an improvement in the dissolution of the components because, in conformity with thermodynamic ideas, under identical conditions a solid and its melt dissolve in the same way.[49] On the other hand, the component fused initially is dispersed in the elastomeric composition much more effectively than the same component in the powdered state and it executes its functional task more effectively, for example as an accelerator,[50] a vulcanising agent, an antiageing agent, etc. Nevertheless, the melting points of the majority of the widely used chemical additives, except for CBS, OBS, and stearic acid (StA), are higher than the temperatures corresponding to their introduction into elastomeric compositions. The dispersion of such chemical additives in elastomeric compositions is improved in the presence of zinc stearate, which is capable of forming reversed micelles in the nonpolar elastomer; these solubilise the accelerators and sulfur in the polar core.[51] The low critical concentration for micelle formation (2×10^{-3} M) confirms the possibility of accumulating sufficient zinc stearate for the formation of micelles in elastomeric compositions as a result of the reaction of stearic acid with ZnO at the very beginning of the mixing process.[53]

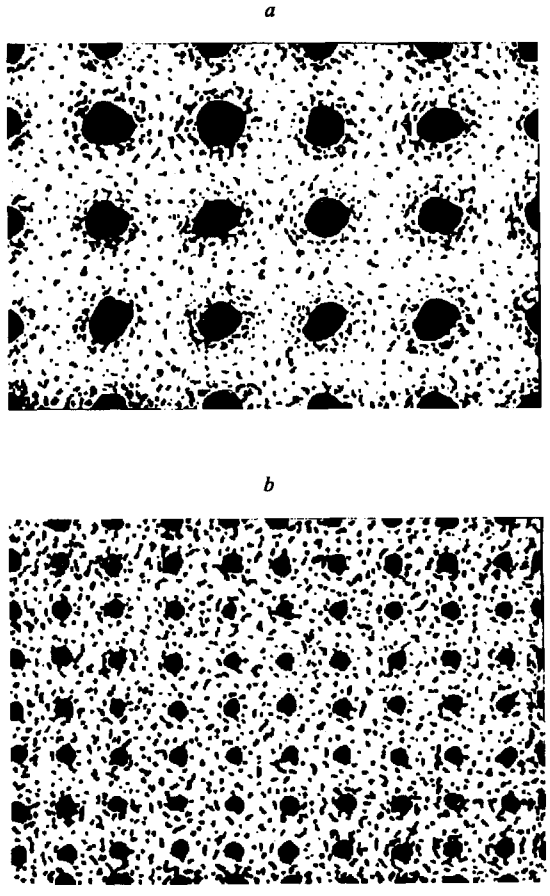


Figure 1. Schematic illustration of the dispersion and dissolution of powdered (*a*) and fused (*b*) components in the elastomer during the mixing process.

When the components of sulfur-based vulcanising systems are used in the form of readily fusible eutectic mixtures, the dispersity of the particles can influence the properties of the elastomeric compositions and rubbers if the mixing temperature is lower than the temperature of eutectic fusion or the equilibrium temperature on the liquidus of the phase diagram, determined by the ratio of the concentrations of the initial accelerators in the binary eutectic system. If the temperature of the preparation of the elastomeric composition is above the liquidus line, the eutectic mixture is dispersed in the elastomeric composition in the fused state and the dispersity of the particles of the components constituting the eutectic mixtures does not affect the properties of the elastomeric compositions and rubbers.

The formation of eutectic mixtures is known[49] to be accompanied by an increase in the dispersity of the crystalline particles of the constituent components, which increases their chemical reactivity as a consequence of the increase in the surface free energy. Hence it follows that, when the eutectic mixtures are introduced into elastomeric compositions at temperatures below the temperature of eutectic diffusion, the accelerators are more highly dispersed and are more chemically reactive than in the initial state. This applies also to the case where the temperature of the preparation of the elastomeric composition is below the liquidus line of one of the components. The crystalline particles of the accelerator in equilibrium with the melt are more highly dispersed than the particles of the initial accelerator.

In those cases where the accelerators and sulfur are adsorbed in the form of eutectic mixtures on zinc oxide, the dispersity of the particles of these components undergoes an additional increase as a consequence of the retardation of the crystallisation of the adsorbed components and the formation of a large number of nuclei.[54]

4. The melting points of crystals of chemical additives

In simple eutectic systems, the eutectic temperature (T_{eu}) is lower and closer to the centre of the phase diagram the smaller the difference between the melting points (T_m) of the components. The greater the difference between the melting points T_m of the components of eutectic mixtures the greater the displacement of T_{eu} towards the low-melting component. This type of variation of T_{eu} as a function of the T_m of the constituent components makes it possible to attain the maximum synergistic effect by varying the proportions of the accelerators with different T_m within wide limits (by virtue of the better dispersion and distribution of the accelerators in the elastomeric compositions in the fused form and the increase in the defectiveness and dispersity of the crsytalline particles). This promotes an increase in the free surface energy and hence in the chemical reactivity of the components.

Furthermore, the properties of the binary eutectics are influenced by the polymorphic transformations of the crystals of the chemical additives[34,56,57] occurring following an increase in temperature and promoting a change in the miscibility of the components in the solid state.

* * *

Thus the effectiveness of the physical modification of chemical additives in binary and complex eutectic mixtures and substitutional solid solutions is determined by the differences between the configurations of the molecules and the melting points of the components as a result of the increase in the defectiveness and dispersity of the crystalline particles. The physical modification not only improves the distribution of the components in elastomeric compositions and increases their chemical reactivity but also facilitates the formation of strong (0.35–0.4 MPa) and readily fusible granules of the eutectic melts of the chemical additives without the introduction of binders.[28] This is one promising way of solving the environmental problems in the processing of elastomeric compositions and polymers.

III. Physicochemical modification of chemical additives

An increase in the chemical reactivity of the components of binary eutectic mixtures, exhibiting nucleophilic and electrophilic properties relative to one another, leads to the formation of molecular π- and n-complexes or new more active accelerators exhibiting a high thiophilicity in relation to free sulfur and hence increasing the rate of vulcanisation of the elastomeric compositions and reducing the activation energy for the process. The physical and chemical transformations occurring under these conditions can be regarded as the physicochemical modification of the chemical additives.[28]

The synergistic effect in the binary systems on formation of molecular complexes and new accelerators may intensify also as a result of the retardation of the migration of the molecules of the complexes to the surfaces of the elastomeric compositions as a consequence of the increase in molar volume and the more complete functional utilisation of the system of accelerators.

The combination of physical and chemical synergism is characteristic of binary systems such as OBS–TMTD, DBTD–TMTD, CBS–TMTD, OBS–DTDM (*N,N'*-dithiodimorpholine), CBS–ZDMDTC (zinc dimethyldithiocarbamate), CBS–MBT, etc., whose components form molecular complexes and new compounds—more active accelerators of the sulfur-based vulcanisation of the elastomers than the initial compounds.[28,58,59]

Thus the presence in the crystals of the components of active centres capable of interacting with one another is very important in the physicochemical modification of chemical additives.

1. The active centres in the molecules of chemical additives

The molecular diagrams of components of sulfur-based vulcanising systems have been obtained[60–63] by quantum-chemical methods. Analysis of the results of the quantum-chemical calculations and of the molecular diagrams presented in a number of studies[59–62,64–66] makes it possible to arrange the components of the sulfur-based vulcanising systems in the following series in terms of the increase in their nucleophilicity:

$$ZnO < ZnX_2 < S_8 < DTDM < OBS < CBS \leqslant DBTD \leqslant MBT < DPG < TMTD.$$

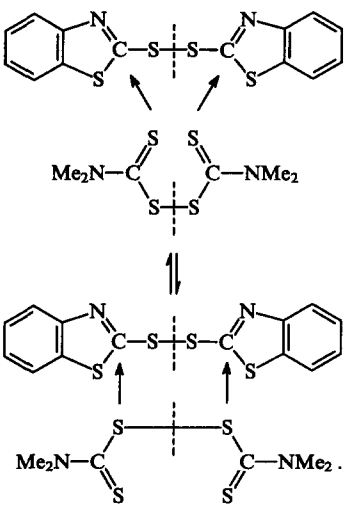
Zinc oxide, zinc mercaptide, zinc dialkyldithiocarbamates, sulfur, and DTDM exhibit electrophilic properties in relation to CBS, DBTD, MBT, DPG, and TMTD. In binary systems containing the zinc salts of mercaptobenzothiazole or dialkyldithiocarbamic acid, on the one hand, and thiazole, sulfenamide, or thiuram accelerators, on the other, the latter behave as ligands coordinated to the zinc atom and bound to it both as a result of the partial shift of the n electrons of the nitrogen or sulfur atoms to the unoccupied p orbitals of the zinc atom[67] and also as a result of the formation of a π-bond when the occupied d orbitals of zinc overlap with the antibonding π^* orbital of the ligand.[68] The involvement of the zinc atom in the formation of a π-bond has been confirmed by the fact that the transfer of one of its d electrons to a higher energy level requires an energy of only 15.5×10^{-19} J cm^{-1}.[69]

2. The formation of molecular complexes

Together with the eutectic point, a peritectic point appears on the phase diagrams of binary systems of accelerators exhibiting donor–acceptor properties relative to one another, which confirms the formation of a molecular complex in the mixture.[55] This shows that the charge transfer from the donor to the acceptor molecule in a mixture of crystalline substances is facilitated on eutectic fusion. Consequently the formation of π- and n-complexes is preceded by an increase in the chemical reactivity of the components in the eutectic mixtures. The light hypsochromic shift characteristic of the UV spectra of dilute solutions of such binary systems indicates the preferential formation of n-complexes in the latter.[63]

The nature of the molecular complexes formed and the factors promoting the mutual activation of their components can be discovered by comparing the crystal-chemical properties of the initial components and the binary systems.

In the TMTD–DBTD binary system, the nucleophilic centres are the sulfur atoms of TMTD, while the electrophilic centres are the carbon atoms of the benzothiazolyl fragments of DBTD.[62] The TMTD molecule can be represented by several structures,[70] which form the following *n*-complexes:



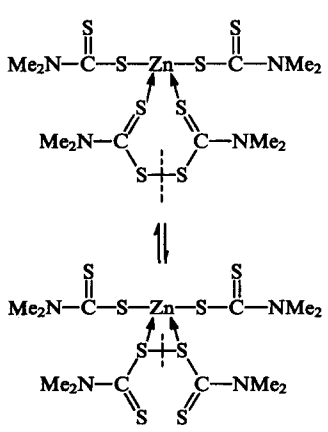
The enhancement of the accelerating function of such complexes can be explained by the weakening of the disulfide linkage in the latter and by the more ready addition of free sulfur to the complex.

The interaction of the accelerators in the TMTD–CBS and TMTD–OBS binary systems is accompanied by the formation of similar complexes with the sole difference that the electrophilic centres in the CBS and OBS molecules are the carbon atoms involved in the double bond of the benzothiazolyl fragment, the carbon atoms in the cyclohexyl group,[65] and the nitrogen atom in the morpholine fragment.[71]

The synergistic effect of the accelerators in the *n*-complexes is caused by, firstly, their more effective functional employment as a consequence of the better dispersion of the eutectic mixture in the fused form and, secondly, by the facilitation of the interaction of the complexes with S_8. Such interaction leads to the formation of tetramethylthiuram polysulfide, polythiobissulfenamide, and dibenzothiazolyl polysulfide,[72] as well as the hydroammonium polysulfides $[H_3NR]^+S_x^-$ and $[H_2NR']^+S_x^-$ (R = cyclohexyl, R′ = morpholinyl), which ensure a high rate of vulcanisation of elastomeric compositions.[71]

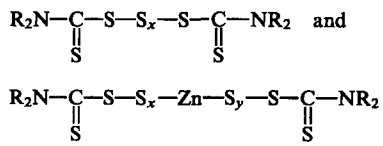
In binary systems where one of the accelerators is zinc dialkyldithiocarbamate or zinc mercaptide, the electrophilic zinc atom plays a significant role in the formation of molecular complexes.

Scheme 1

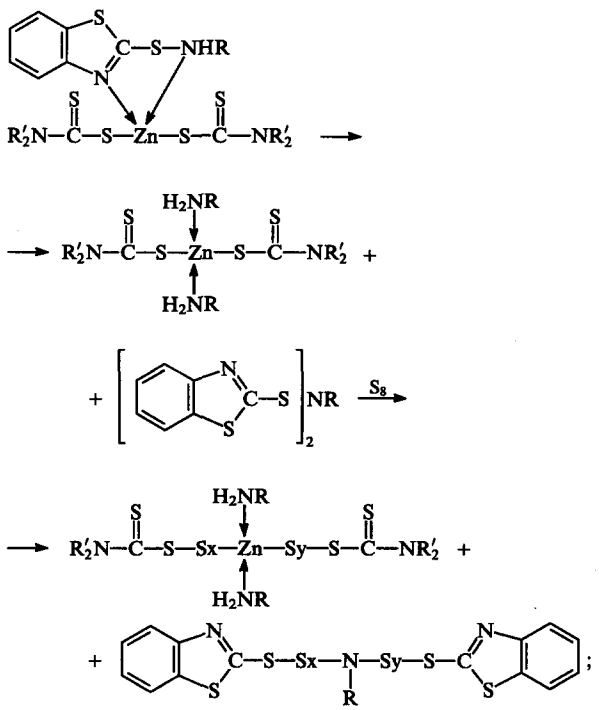


The structure of the ZDMDTC–TMTD complex is presented in Scheme 1.[73]

Complexes of this type prevent premature vulcanisation[70] and also ensure a higher rate of vulcanisation compared with the accelerators taken separately, owing to the weakening in the latter of the Zn–S and S–S bonds and facilitation of the interaction with S_8 leading to the formation of polysulfide compounds.[74]



The formation of a *n*-complex, an amine complex, and a number of other compounds in the ZDMDTC–CBS system can be represented as follows:[73]



R = cyclo-C_6H_{11}; R′ = Me.

The properties of the molecular complexes described above are determined by the nature of the orbitals provided by the components of the complexes for the formation of intermolecular bonds.[75] The nucleophilic centres are the sulfur atoms in the TMTD molecules, the nitrogen atoms in the MBT and DBTD molecules, the nitrogen atoms in the benzothiazolyl and exocyclic HN groups in CBS, and the nitrogen atoms of the secondary amino- and imino-groups in DPG. As regards the excess negative charge, the accelerators containing the benzothiazolyl group hardly differ from one another.[62] On the other hand, the carbon atoms involved in the double bond of the benzothiazolyl fragment of BD and BTD, the carbon atoms of the cyclohexyl group in CBS, and the nitrogen atom in the morpholine fragment of OBS relative to TMTD and DPG, as well as the zinc atoms in ZDMDTC and zinc mercaptide relative to CBS, DBTD, MBT, DPG, and TMTD differ significantly in their electrophilicity.[62,67,71] Therefore the greatest overlap of the molecular orbitals of the donor and the acceptor and hence the formation of the most stable π- and *n*-complexes is to be expected in the ZDMDTC–X and ZnS–X binary systems, where X = TMTD, DPG, CBS, DBTD, or MBT. This is confirmed by the presence of an appreciable convexity in the phase diagrams for these systems between the peritectic and

eutectic points,[28] which indicates the formation of stable complexes[55] and also that some of them exist in an individual state.[76] The absence of a convexity between the peritectic and eutectic melting points on the phase diagrams for the OBS–TMTD, DBTD–TMTD, CBS–TMTD, etc. binary systems[28] is evidence for the low stability of such complexes and for the possibility of their existence only in the presence of the initial components.[55]

The comparative stability of the molecular complexes formed in the physicochemical modification of binary systems of accelerators promotes synergism in their action in elastomeric compositions because, according to the theory of molecular complexes, the more intense the interaction of the molecules of the complexes the more marked their activation on dissociation.[77]

When complex mixtures of the components of sulfur-based vulcanising systems are used, it is essential to take into account the presence in them of zinc oxide, which adsorbs the molecules of the accelerators, sulfur, and aliphatic acids.[53,78] Zinc oxide is not a molecular crystal and cannot therefore form simple eutectic mixtures or substitutional solid solutions with accelerators and sulfur. On the other hand, the electrophilicity of the zinc atoms ensures the physical and chemical adsorption of the accelerators, stearic acid, and sulfur on zinc oxide as a result of the formation of the corresponding zinc salts of the accelerators and of zinc stearate and through them of dialkyldithiocarbamate, amine, and carboxylate complexes.[78–81]

The adsorption of the accelerators and stearic acid on zinc oxide can be selective and dissociative. In those cases where the components exhibit approximately the same nucleophilic or electrophilic properties, the selective adsorption depends on the configuration of the molecules, which determines the accessibility of the active centres of the interaction with the surface of zinc oxide.

Dissociative adsorption on zinc oxide is characteristic of TMTD, DBTD, and DTDM, which contain disulfide bonds.[53] It is known[75] that aliphatic disulfides react with acceptors (metal oxides) to form 1:1 complexes, which increases the length of the disulfide bond and weakens it. The interaction of aromatic disulfides, having relatively weak S–S bonds, with strong acceptors leads to the homolytic dissociation of these bonds. One can therefore postulate that zinc mercaptide is formed initially in the DBTD–TMTD–ZnO mixture and then the dimethyldithiocarbamate complex is produced. This was subsequently confirmed by other data.[28,79]

The conventional heats of adsorption of chemical additives on zinc oxide, presented in Table 5 and obtained by differential scanning calorimetry,[28] indicate the dependence of the selectivity of the adsorption on the nucleophilicity and configuration of the molecules and also on their ability to be dissociatively adsorbed with formation of the corresponding zinc salts.

Table 5. Conventional heats of adsorption of the crystalline components of elastomeric compositions on zinc oxide.

Component	Heat of fusion/kJ mol^{-1}		Conventional heat of adsorption[a]/kJ mol^{-1}
	of individual component	in mixture with zinc oxide	
TMTD	33.2	4.8	28.4
MBT	20.4	4.3	16.1
Stearic acid	43.4	29.9	14.5
Phthalic anhydride	19.7	14.0	5.7
Diafen FP	27.9	23.7	4.8
CBS	27.4	23.8	3.6
DBTD	35.3	32.6	2.7
Sulfur	16.2	15.2	1.0
Santogard PVI	21.4	20.6	0.8
OBS	21.2	21.2	0.0

[a] The measurements were performed at the melting points of the adsorbed components.

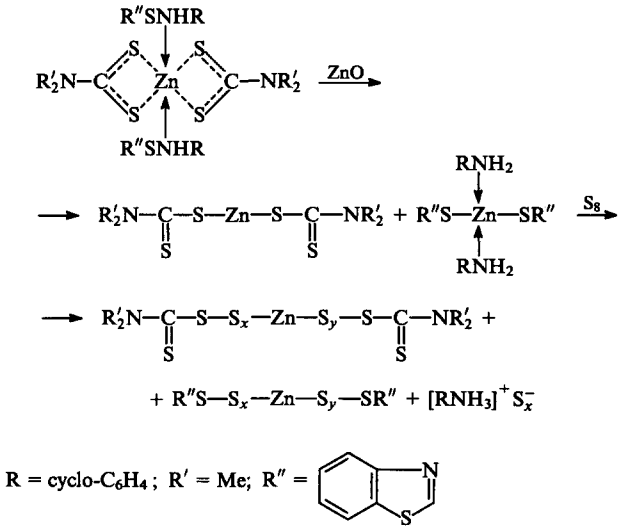
The foregoing suggests the following consecutive mechanism of the physicochemical modification of chemical additives in binary and complex eutectic systems.

In the first stage, the crystalline components interact, which is accompanied by an increase in the free energy of the system in the region of contact between the surfaces of unlike crystals. This results in the eutectic fusion of the mixture.

In the second stage, the components pass to the activated state on eutectic fusion, which results in the formation of π- and n-complexes between the nucleophilic and electrophilic molecules. This leads to an increase of their reactivity relative to free sulfur.[75]

In the third stage, the molecules to the π- and n-complexes interact chemically on raising the temperature with formation of amine, dialkyldithiocarbamate, and carboxylate complexes, whereas in the presence of free sulfur polysulfide compounds with hydroammonium polysulfides are produced.

The interaction of the components of sulfur-based vulcanising systems in complex mixtures can be described schematically in relation to the CBS–ZDMDTC–ZnO–S_x system.

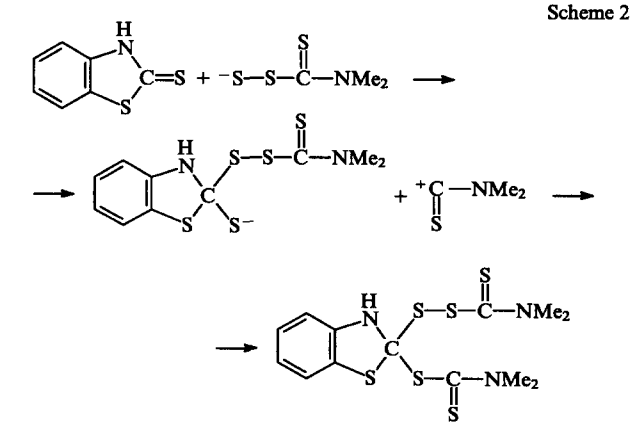


The hydrogen adsorbed in the atomic or ionic form on zinc oxide may participate in the formation of amine ligands and hydroammonium polysulfides.[39]

$$H_2 \longrightarrow 2H \longrightarrow 2H^+ + 2e^-$$

The above mechanism of the physicochemical modification of chemical additives may be applied also to the highly effective synergistic systems of antioxidants obtained in the form of granules from eutectic melts of binary and complex mixtures of components and used in the synthesis of polymers.

Scheme 2

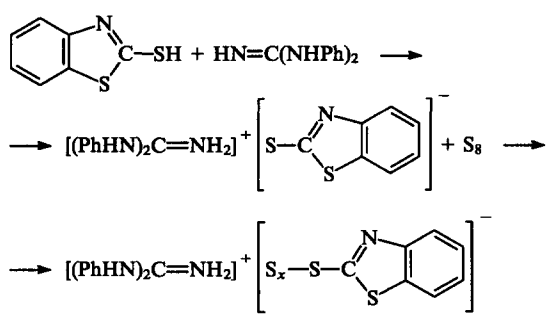


3. The formation of new accelerators

On chemical interaction of the accelerators and binary eutectic systems, two eutectic melting points and a singular point, corresponding to the melting point of the new compound formed, appear on the phase diagram.

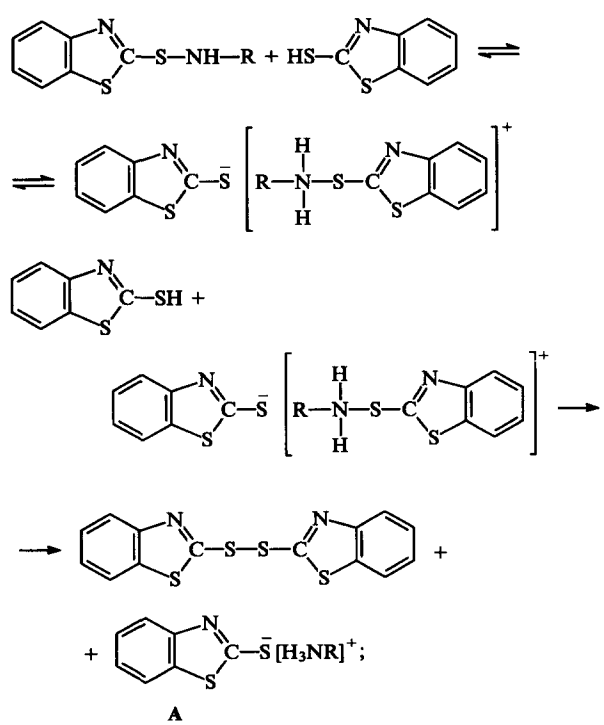
In the TMTD–MBT eutectic mixture, the products of the heterolytic decomposition of TMTD which occurs at 100–110 °C interact with the thiono-form of MBT (Scheme 2).[58] This increases the duration of the induction period for the vulcanisation of elastomeric compositions. The higher rate of vulcanisation can be explained by the decomposition of the compound obtained on raising the temperature into the highly reactive benzothiazolyl and dimethyldithiocarbamate fragments. Quantum-chemical cal-culations of the electronic characteristics of the accelerators[62] confirm the possibility of the nucleophilic addition reaction between the products of the heterolytic decomposition of TMTD and MBT.

The reaction between the accelerators in the MBT–DPG binary eutectic mixture leads to the formation of the diphenylguanidinium salt of mercaptobenzothiazole (DSMB), which, as a consequence of the increased nucleophilicity of the benzothiazolyl ion, is more thiophilic relative to free sulfur and is capable of forming an ionic polysulfide compound.[26]



Like hydroammonium polysulfides,[71] this compound exhibits a high vulcanising activity.

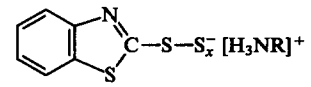
According to Ignatov's data,[59] the accelerators CBS and MBT in the CBS–MBT binary eutectic mixture interact in accordance with the following schemes:



A

R = cyclo-C_6H_{11}.

The chemical synergism manifested by this system in elastomeric compositions is due to the formation of more active accelerators than the initial MBT and CBS. Like DSBM, the ionic complex A can interact readily with S_8 to form hydro-ammonium polysulfides



which ensure a high rate of vulcanisation of elastomeric compositions.

The mutual activation of chemical additives, caused by the formation of eutectic mixtures, molecular complexes, and new chemical compounds, also occurs when they are introduced separately into elastomeric compositions. The eutectic mixtures are then obtained only as a result of the collision of the crystalline particles of the components on shear deformations arising during the preparation of the elastomeric compositions, while the main bulk of the components interact with one another in the diffusion regime, i. e. after the dissolution of the accelerators and sulfur and by diffusion of their molecules to the surface of zinc oxide with formation of molecular complexes and polysulfide compounds. Part of the sulfur and of the accelerators fail to interact with one another under these conditions and migrate to the surface on cooling of the elastomeric compositions.

Thus the physical and physicochemical modifications of the crystalline components of sulfur-based vulcanising systems in binary and complex mixtures do not alter the principal characteristics of the sulfur-based vulcanisation of unsaturated elastomers. They merely induce a decrease in the activation energy and a change in the kinetics of the process because its rate-limiting stage—the chemical activation of sulfur by molecular, amine, dialkyldithiocarbamate, and carboxylate complexes—takes place in the kinetic region under favourable conditions and is more effective than in the separate introduction of the chemical additives into the elastomeric compositions.

Furthermore, the modification of chemical additives ensures the most complete fulfillment by the latter of their functions, which makes it possible to diminish the concentrations of the components in the elastomeric compositions (the concentration of zinc oxide in the modified sulfur-based vulcanising systems can be decreased by a factor of 2–2.5 and that of the accelerators by a factor of 1.1–1.3).[28]

4. The influence of the crystal-chemical characteristics of chemical additives on the structure–property relation in the specific formation of their molecules

The attempts to employ quantum-chemical calculations to achieve the deliberate formation of the molecular structure of the chemical additives, starting with the specified properties of polymer compositions, which have been undertaken in recent years,[62,82–85] have not led to the desired results because in these calculations no account was taken of the change in the physical and chemical properties of the components as a result of their interaction with one another in the crystalline state.

Therefore, in the quantum-chemical calculations it is essential to take into account the presence of other crystalline components and the possibility of their interaction with the initial compounds to form eutectic compositions and molecular complexes.

Theoretical studies of the mechanism of the antioxidant activity of sterically hindered phenols in polyalkenes established[83] that their antioxidant activity is determined by the donor–acceptor properties of the *para*- and *ortho*-substituents. It is known[86–87] that the effectivenss of the accelerator increases with increase in its nucleophilicity. On the other hand, studies on the inhibiting effect of aromatic amines for different types of ageing of rubbers have shown[85] that the experimental molecular reactivity indices, characterising the ability of amines to enter into heterolytic and homolytic reactions, differ from the calculated values.

This is due to the physicochemical interaction of aromatic amines in elastomeric compositions with the components of sulfur-based vulcanising systems. Such interaction results in the formation of eutectic mixtures and molecular complexes in which the configuration and orbital state of the molecules [75] and hence the π-electron density and the free valence index have been altered relative to those in the initial components. This hypothesis has been confirmed by the satisfactory correlation between the calculated and experimental data obtained in the study of the influence of sterically hindered phenols in polyalkenes (in the absence of other crystalline components) and in elastomeric compositions — thiophthalimide derivatives — on the vulcanisation processes. [88] They exhibit a low reactivity relative to the nucleophilic and electrophilic components of the vulcanising systems as a consequence of their tendency to enter into homolytic reactions. [89]

The effectiveness of antioxidants and antiozonants in polymer ageing processes is determined by the formation of hydrogen bonds in these systems. It has been established [90] that the presence of hydrogen bonds in crystalline antioxidants and antiozonants is one of the causes of their relatively low solubility in elastomers. An increase in the polarity of the elastomer increases the solubility of the antiageing agent by intensifying the intermolecular interaction up to the formation of hydrogen bonds between the elastomer macromolecules and the molecules of the antioxidants and antiozonants. On the other hand, the formation of hydrogen bonds in the polymer–antioxidant system reduces the effectiveness of the antioxidant. [91]

The functional effectiveness of chemical additives diminishes on formation of hydrogen bonds between the molecules of different components. Thus hydrogen bonds decrease the activity of the amine accelerator in the sulfur-based vulcanisation and the inhibiting activity of resorcinol in the oxidation of rubber. [92]

The molecules of chemical additives incapable of forming hydrogen bonds but exhibiting nucleophilic and electrophilic properties relative to one another can form π- and *n*-complexes, which induces an increase in the effectiveness of the components. The increase in the reactivity of molecules in such complexes compared with their ground state [63] occurs as a result of the interaction of the π* antibonding orbitals of one component with the nonbonding orbitals of the nitrogen, sulfur, or oxygen atoms of the other component or with the occupied 3*d* orbitals of the zinc atom. [68]

Thus, in order to increase the functional effectiveness of chemical additives to elastomeric compositions, it is useful to achieve a decrease in the probability of the formation of hydrogen bonds between the components and an increase in the probability of the formation of molecular complexes. This can be done by selecting chemical additives on the basis of a comparison of their molecular structures and crystal-chemical characteristics and the phase diagrams for binary systems of the components. [28]

IV. Conclusion

The above analysis shows that comparison of the melting points of the chemical additives, the configurations of their molecules, and the π-electron densities and free valence indices of the atoms in the molecules makes it possible to regulate the formation in the binary and complex mixtures of these components of simple eutectic systems, substitutional solid solutions, molecular complexes, and polysulfide compounds and also to determine the optimum conditions for the formation of systems with prespecified properties. Such systems and compounds are more effective than the initial components, since they ensure a greater defectiveness and dispersity of the crystalline particles and this increases the chemical reactivity of the components. The formation of molecular complexes and new compounds in the eutectic mixtures increases still further the effectivenss of the crystalline accelerators in vulcanisation processes, because this leads to their thiophilicity and facilitates their interaction with sulfur molecules in the formation of polysulfide compounds and hydroammonium polysulfides, which exhibit a high vulcanising activity.

The formation of polysulfide compounds in such mixtures makes it possible to reduce the concentrations of the accelerators and of zinc oxide in sulfur-based vulcanising systems without a decrease or even with an increase in their effectivenss compared with control vulcanising systems. [28] Furthermore, the sharp fall in the melting points of the chemical additives in eutectic mixtures makes it possible to granulate the melts without introducing binders, obtaining thereby strong, friable, and readily fusible granules. The use of such granules eliminates the formation of dust from the powdered components and improves the environmental situation in the processing of elastomeric compositions and polymers.

An important advantage of the physical and physicochemical modification of chemical additives is the possibility of predicting on the basis of the crystal-chemical characteristics and molecular structures of the components the formation in binary and complex systems of simple eutectic mixtures, substitutional solid solutions, and molecular complexes and of estimating their influence on the properties of the elastomeric compositions and rubbers. This advantage may be used for the development of a fundamentally new scientifically based approach to the creation of recipes for elastomeric compositions.

References

1. A I Kitaigorodskii *Molekulyarnye Kristally* (Molecular Crystals) (Moscow: Nauka, 1971)
2. I B Gardiner *Rubber Chem. Technol.* **41** 13129 (1968)
3. M Ikeda, T Yamamoto, Y Shinozaki, N Wada, Y Kaneko *Radioisotopes* **22** 556 (1973)
4. B S Grishin, I A Tutorskii, E E Potapov *Vysokomol. Soedin., Ser. A* **16** 130 (1974)
5. I A Landa, A S Kuz'minskii, S A Reitlinger, N G Kolyadina *Kauch. Rezina* (9) 12 (1973)
6. *Khimicheskie Dobavki k Polimeram. Spravochnik* (Chemical Additions to Polymers. Handbook) (Moscow: Khimiya, 1973)
7. B Spiegelhalder, R Preussman *Carcinogenesis* **4** 1147 (1983)
8. J M Fajen, G A Carson, D P Rounbehler, T Y Fan, R Vita, V E Goff, G S Edwards, D H Fine, V Reinhold, K Biemann *Science* **205** 1262 (1979)
9. W Hoffman *GAK: Gummi, Fasern, Kunstst.* **43** 562 (1990)
10. D W Chasar, P D Matheny *Kautsch. Gummi Kunstst.* **44** 435 (1991)
11. I Zieltow *Kunststoffberater* **81** 427 (1991)
12. G Catania *Umwelt* **20** 631 (1990)
13. A V Acaraglu *Proc. Eng. News* **15** 52 (1987)
14. Yu N Neienkirkhen, A A Dontsov, B S Grishin, G V Insarova *Kauch. Rezina* (2) 35 (1983)
15. BRD P. 1 570 125; *Ref. Zh. Khim.* 5 T 570P (1978)
16. D L Fedyukin, T I Vinogradova, L A Danchenko, N V Ermilova *Kauch. Rezina* (1) 11 (1973)
17. A A Dontsov, B S Grishin *Kauch. Rezina* (2) 40 (1984)
18. Jpn. Appl. 59-80438; *Ref. Zh. Khim.* 8 U 27P (1985)
19. Jpn. Appl. 62-537; *Ref. Zh. Khim.* 24 U 52P (1987)
20. US P. 4 895 884; *Ref. Zh. Khim.* 6 U 30P (1991)
21. A A Mukhutdinov *Modifikatsiya Sernykh Vulkaniziruyushchikh Sistem i Ikh Komponentov* (Modification of Sulfur Vulcanising Systems and Their Components) (Moscow: TsNIITEII, 1989)
22. N M Emanuel' *Usp. Khim.* **50** 1721 (1981) [*Russ. Chem. Rev.* **50** (901) (1981)]
23. G V Karpukhina, N M Emanuel' *Dokl. Akad. Nauk SSSR* **276** 1163 (1984)
24. A A Mukhutdinov, V N Zelenova *Kauch. Rezina* (7) 28 (1988)
25. A A Mukhutdinov, S L Smol'yaninov, V S Minkin, I G Shaikhiev *Kauch. Rezina* (4) 22 (1989)
26. A A Mukhutdinov, I G Shaikhiev, R Z Musin *Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov* (Chemistry and Technology of Organoelement Compounds and Polymers) (Kazan: KKhTI, 1991)

27. V M Bilobrov *Vodorodnaya Svyaz'. Vnutrimolekulyarnye Vzaimodeistviya* (Hydrogen Bond. Intramolecular Interactions) (Kiev: Nauk Dumka, 1991)
28. A A Mukhutdinov, Doctoral Thesis in Chemical Sciences, KGTU, Kazan, 1993
29. P Saike *Mekhanizm Reaktsii v Organicheskoi Khimii* (The Mechanisms of Reactions in Organic Chemistry) (Moscow: Khimiya, 1971)
30. J Mathieu, R Panico *Mécanismes Réactionnels en Chimie Organique* (Translated into Russian; Moscow: Mir, 1975)
31. A Walberg *Acta Crystallogr.* **34** 392 (1978)
32. T Adzami, X Sudzuka, F Ono *J. Soc. Rubber Ind. Jpn.* **39** 62 (1966)
33. K Marry *Acta Chem. Scand.* **19** 1509 (1965)
34. V Malta, R Celotti, R Zannetti, A F Martelli *J. Chem. Soc., B* **3** 548 (1971)
35. J P Chesik, J Donohue *Acta Crystallogr., Sect. B* **27** 1441 (1971)
36. T Adzami, I Imazu *J. Soc. Rubber Ind. Jpn.* **37** 413 (1964)
37. A Radha *Z. Kristallogr.* **171** 225 (1985)
38. S P Popkov *Fiziko-Khimicheskie Osnovy Pererabotki Rastvorov Polimerov* (Physicochemical Principles of the Processing of Polymer Solutions) (Moscow: Khimiya, 1976)
39. L H Little *Infrared Spectra of Adsorbed Species* (Translated into Russian; Moscow: Mir, 1969)
40. A F Wells *Structural Inorganic Chemistry* (Translated into Russian; Moscow: Mir, 1987)
41. *Fizicheskaya Entsiklopediya* (Physical Encyclopedia) (Moscow: Sov. Entsiklopediya, 1990)
42. A I Kitaigorodskii *Smeshannye Kristally* (Mixed Crystals) (Moscow: Nauka, 1983)
43. V M Zalkin *Zh. Fiz. Khim.* **43** 299 (1969)
44. V M Zalkin *Zh. Fiz. Khim.* **57** 499 (1983)
45. A Ya Erchenkova, M Z Rakhman, M A Shtern, L N Gogina *Kauch. Rezina* (11) 12 (1973)
46. T Yanon, M Macno, S Maeda *J. Soc. Rubber Ind. Jpn.* **64** 605 (1991)
47. P A Kouzov, A D Mal'gin, G M Skryabin *Ochistka ot Pyli, Gazov i Vozdukha v Khimicheskoi Promyshlennosti* (Purification from Dust, Gases and Air in Chemical Industry) (Moscow: Khimiya, 1982)
48. P V Danckwerts *Gas–Liquid Reactions* (Translated into Russian; Moscow: Khimiya, 1973)
49. S M Walas *Phase Equilibriums in Chemical Technology* (Translated into Russian; Moscow: Mir, 1989)
50. E V Zimin, A B Kusov *Kauch. Rezina* (6) 23 (1968)
51. I D Khodzhaeva, V V Markov, G V Insarova, L D Filippovich, Z N Tarasova, G M Plavnik *Kolloidn. Zh.* **41** 315 (1979)
52. B S Grishin, V I Borisov, I D Khodzhaeva, V A Shershnev, Z N Tarasova *Kolloidn. Zh.* **40** 972 (1978)
53. A A Dontsov, V A Shershnev *Zh. Vses. Khim. O-va im. D I Mendeleeva* **31** 88 (1986)
54. P A Rebinder *Poverkhnostnye Yavleniya v Dispersnykh Sistemakh* (Surface Phenomena in Dispersed Systems) (Moscow: Nauka, 1978)
55. I Hauben-Weyl *Methoden der Organischen Chemie* (Translated into Russian; Moscow: Khimiya, 1967)
56. L P Bondar', V A Borokhovskii, G I Brolinskii *Fiziko-Khimicheskie Svoistva Sery* (Physicochemical Properties of Sulfur) (Moscow: TsNIITEII, 1985)
57. M A Menkovskii, V T Yavorskii *Tekhnologiya Sery* (Technology of Sulfur) (Moscow: Khimiya, 1985)
58. L B Simanenkova, K V Markushevskaya, M N Voloktrub, G V Tarkhov *Kauch. Rezina* (7) 18 (1982)
59. V A Ignatov *Zh. Obshch. Khim.* **49** 1122 (1979)
60. A I Zubenko, A G Pilipenko, L I Savranskii *Koord. Khim.* **10** 1219 (1984)
61. N V Mel'nikova, A I Zubenko, A G Pilipenko *Ukr. Khim. Zh. (Russ. Ed.)* **53** 472 (1987)
62. A A Shurkus, P P Pipiraite, A B Bolotin, L B Simanenkova *Teor. Eksp. Khim.* **20** 627 (1984)
63. K Higasi, H Baba, A Rembaum *Quantum Organic Chemistry* (Translated into Russian; Moscow: Mir, 1967)
64. V A Ignatov, L S Degtyarev, L F Protopopova, M S Fel'dshtein *Kauch. Rezina* (9) 18 (1975)
65. S I Satava *J. Soc. Rubber Ind. Jpn.* **44** 356 (1971)
66. A B Bolotin, P P Pipiraite, A Yu Ruzhene, B N Gorbunov, G V Tarkhov, L B Simanenkova *Zh. Strukt. Khim.* **29** 19 (1988)
67. A S Kuz'minskii, S M Kavun, V P Kirpichev *Fiziko-Khimicheskie Osnovy Polucheniya, Pererabotki i Primeneniya Elastomerov* (Physicochemical Principles of the Preparation, Processing, and Application of Elastomers) (Moscow: Khimiya, 1976)
68. L J Andrews, R M Keefer *Molecular Complexes in Organic Chemistry* (Translated into Russian; Moscow: Mir, 1967)
69. G Zundel *Hydration and Intermolecular Interaction* (Translated into Russian; Moscow: Mir, 1972)
70. V I Ovcharov, B L Pikalov, M V Bykov *Kauch. Rezina* (5) 20 (1985)
71. T V Shestakova, A M Evdokimov, E V Korotyshev, V O Reikhsfel'd, A B Kusov *Zh. Org. Khim.* **6** 1929 (1970)
72. T V Tarasov, I I Vishnyakov, B S Grishin *Kauch. Rezina* (5) 39 (1991)
73. A A Mukhutdinov *Kauch. Rezina* (6) 38 (1993)
74. A A Dontsov *Protsessy Strukturirovaniya Elastomerov* (Structure Formation Processes in Elastomers) (Moscow: Khimiya, 1978)
75. E N Gur'yanova, I P Romm *Zh. Fiz. Khim.* **62** 2687 (1988)
76. T D Skinner, A A Watson *Rubber Age* **99** 76 (1967)
77. A V Mashkina *Geterogennyi Kataliz v Khimii Organicheskikh Soedinenii Sery* (Heterogeneous Catalysis in the Chemistry of Organic Compounds of Sulfur) (Novosibirsk: Nauka, 1977)
78. V A Shershnev *Rubber Chem. Technol.* **55** 537 (1982)
79. V Dukhachek, R Sh Frenkel' *Tr. Mezhdunar. Konf. po Kauchuku i Rezine* (Proceedings of International Conference on Raw and Cured Rubber) (Kiev, 1978)
80. B Milligan *Rubber Chem. Technol.* **39** 1115 (1966)
81. R N Campbell, R M Wise *Rubber Chem. Technol.* **37** 650 (1964)
82. A B Bolotin, B N Gorbunov, A A Efimov, P P Pipiraite, A Yu Ruzhene *Teor. Eksp. Khim.* **25** 594 (1989)
83. A B Bolotin, P P Pipiraite, A Yu Ruzhene, L B Simanenkova *Teor. Eksp. Khim.* **26** 73 (1990)
84. A B Bolotin, P P Pipiraite, B N Gorbunov *Teor. Eksp. Khim.* **27** 165 (1991)
85. P K Liplyanin, in *Tez. Dokl. Pervoi Rossiiskoi Nauch.-Prakt. Konf. Rezinshchikov "Syr'e i Materialy dlya Rezinovoi Promyshlennosti: Nastoyashchee i Budushchee"* (Abstracts of Reports of the First Russian Scientific Practical Conference of Rubber Specialists "Resources and Materials for the Rubber Industry: The Present and The Future") (Moscow, 1993) p. 68
86. L B Simanenkova, K V Makushevskaya, G V Tarkhov, A A Shurkus *Kauch. Rezina* (5) 23 (1983)
87. G Mathew, B Kuriakose, A C Kuriakose *Kautsch. Gummi Kunstst.* **45** 490 (1992)
88. S M Kavun, V A Palyulin, M M Donskaya, Yu M Genkina, in *Tez. Dokl. Pervoi Rossiiskoi Nauch.-Prakt. Konf. Rezinshchikov "Syr'e i Materialy dlya Rezinovoi Promyshlennosti: Nastoyashchee i Budushchee"* (Abstracts of Reports of the First Russian Scientific Practical Conference of Rubber Specialists "Resources and Materials for the Rubber Industry: The Present and The Future" (Moscow, 1993) p. 65
89. G A Blokh *Organicheskie Uskoriteli Vulkanizatsii i Vulkanizuyushchie Sistemy dlya Elastomerov* (Organic Vulcanisation Accelerators and Vulcanising Systems for Elastomers) (Leningrad: Khimiya, 1978)
90. L S Fel'dshtein, A S Kuz'minskii *Kauch. Rezina* (10) 16 (1970)
91. M L Andropov, G E Zaikov, Z K Maizus, N M Emanuel' *Zh. Fiz. Khim.* **41** 2002 (1967)
92. E E Potapov, I A Tutorskii, L E Chernukha, E T Golovin, B A Dogadkin *Kauch. Rezina* (11) 18 (1970)