Fluorine-containing rubbers: practical aspects of ionic vulcanisation

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NOTATION

VF vinylidene fluoride
HFP hexafluoropropylene
TFE tetrafluoroethylene
PFMVE perfluoro(methylvinyl ether)
QAS quaternary ammonium salt
QAB quaternary ammonium base
QPS quaternary phosphonium salt
ITC interphase transfer catalyst
DBU 1,8-diazabicyclo[5.4.0]7-undecene
BTPPC benzyltriphenylphosphonium chloride
BDIC bis(benzyldiphenylphosphino)iminimum chloride

strength nominal tensile strength
elongation breaking elongation
CS compression set
100% modulus nominal stress under 100% elongation

The present paper contains a review of publications on the vulcanisation of fluorine-containing rubbers by heterolytic vulcanising agents (amines, diols) and on the properties of rubbers in the period from 1986 to 1998. Earlier data are given in ref. 1.

TYPES OF FLUORINE-CONTAINING RUBBER

The main industrial fluorine-containing rubbers are of two types:

1. Copolymers of VF with HFP, a ternary copolymer (terpolymer) of VF, HFP, and TFE, and also cold-resistant copolymers of PFMVE with VF and other copolymers, including those containing chlorine, bromine, or iodine instead of fluorine and capable of being vulcanised by peroxides.

2. Copolymers of propylene and TFE, and also ternary copolymers (ref. 1, p. 13).

Rubbers of the second type possess a higher resistance to amines, which are, in particular, corrosion inhibitors (ref. 2); they are resistant to the action of technical oils, transmission fluids, and coolants (ref. 3). Therefore, rubbers based on propylene and TFE may be preferable for many purposes to rubber compounds based on fluorine-containing rubbers of the first type. A separate group comprises entirely fluorinated (perfluorinated) copolymers of TFE and PFMVE, the most chemical and heat resistant of the industrial elastomers; well-known rubbers of this type are Calres (of the Du Pont company) and SKF-460 (Russia). The use of such elastomers, resistant to the action of different chemical agents and to temperatures of up to 316°C (ref. 4), has broadened considerably in recent years (ref. 5).

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Perfluororubbers should contain chemically active groups in their structure, giving the rubbers the capacity to be vulcanised, for example cyano groups or chlorine, bromine, or iodine atoms. Thus, rubber containing cyano groups is vulcanised by ammonium salts (ref. 6) and by bis(amidrazones) (ref. 7) of the type
\[
\left(\text{H}_2\text{NNH}\right)\left(\text{HN=}\right)\text{C}-\text{Fl}-\text{C(=NH)}\left(\text{NHNH}_2\right)
\]
where Fl is a fluoroalkyl aromatic group.

Fluoroelastomers of the first type are most widely used (ref. 8). The structure of such fluorine-containing rubbers and mixes based on them and its relationship with the properties of the vulcanised rubbers were investigated.\(^{19}\) NMR spectroscopy established the distribution of monomer units in the rubbers and its influence on the physical and dynamic properties of vulcanised rubbers containing different amounts of filler and vulcanising agent (ref. 9), and the influence of the composition of the composites on their high-temperature elasticity, crossbreaking strength, and flow resistance (ref. 10). New diol vulcanising systems resulting in rapid and safe vulcanisation are being developed (ref. 11).

MECHANISM OF VULCANISATION AND COMPONENTS OF VULCANISING SYSTEMS

So-called diol (bisphenol) vulcanising systems are mainly used for the vulcanisation of VF–HFP and VF–HFP–TFE copolymers. However, amine vulcanising agents are still used for some purposes.

A study was made of the mechanism of diol vulcanisation of VF and HFP copolymers (refs. 12–15), including with the use of the model compound (ref. 13)
\[
\left(\text{CF}_3\right)_2\text{CF}\left(\text{CH}_2\text{CF}_2\right)_n\text{CF}\left(\text{CF}_3\right)_2
\]
Indispensable components of the vulcanising system are aromatic or aliphatic diol, QAS, or QPS, calcium hydroxide, and magnesium oxide.

Crosslinking is cyclic and proceeds in several stages:

1. The formation of a QAB when the corresponding salt reacts with calcium hydroxide.
2. The formation of a phenoxy ion when arenediol reacts with a base.
3. Replacement of the fluorine atom in the polymer by a hydroxyphenoxo group with regeneration of the quaternary salt.
4. The formation of a phenoxy ion in a group combined with a rubber molecule.
5. Reaction of this anion with the next rubber molecule with crosslink formation:

\[
\text{R}_4\text{X}^+\text{Cl} + \text{Ca(OH)}_2 \rightarrow \text{R}_4\text{X}^+\text{OH} + \text{Ca(OH)}\text{Cl} \quad (1)
\]
\[
\text{Ar(OH)}_2 + \text{R}_4\text{X}^+\text{OH} \rightarrow \text{HO}–\text{Ar–O}^– \text{R}_4\text{X}^+ + \text{H}_2\text{O} \quad (2)
\]
\[
\begin{align*}
-\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{HO}–\text{Ar–O}^– \text{R}_4\text{X}^+ & \rightarrow -\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{R}_4\text{X}^+ \text{F}^- \\
\text{CF}_3 & \text{O–Ar–OH} \\
\text{CF}_3 & \text{O–Ar–O}^– \text{R}_4\text{X}^+ \quad (3)
\end{align*}
\]
\[
\begin{align*}
-\text{CF}_2\text{CFCH}_2\text{CF}_2^- & \rightarrow -\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{H}_2\text{O} \\
\text{CF}_3 & \text{O–Ar–OH} \\
\text{CF}_3 & \text{O–Ar–O}^– \text{R}_4\text{X}^+ \quad (4)
\end{align*}
\]
\[
\begin{align*}
-\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{CF}_3 & \rightarrow -\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{CF}_3 \\
\text{O–Ar–O}^– \text{R}_4\text{X}^+ & \quad (5)
\end{align*}
\]

where X = N or P, and Ar is the residue of fluorine-containing arenediol.

The cycle is then repeated until the bisphenol has entered entirely into the reaction. Thus, the quaternary salt is a vulcanisation accelerator, and, more accurately, a catalyst for the interphase transfer of the crosslinking agent (diol anion) from the hydrophilic phase of the diol to the hydrophobic phase of the rubber. Under the action of a QAB, dehydrofluorination of the polymer molecule also occurs, with the formation of double bonds:
\[
\begin{align*}
-\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{R}_4\text{X}^+\text{OH} & \rightarrow \\
\text{CF}_3 & \\
-\text{CF}_2\text{CFCH}_2\text{CF}_2^- + \text{R}_4\text{X}^+\text{F}^- + \text{H}_2\text{O} & \rightarrow
\end{align*}
\]

the fluorine atom of which again can be replaced by a crosslinking group.
The occurrence of dehydrofluorination was shown by means of IR spectroscopy (ref. 14). This reaction was used to produce a fluorine-containing rubber containing double bonds (ref. 15). For this, a solution of VF–HFP copolymer in pinacolin was treated with benzyltriphenylphosphonium chloride and calcium hydroxide at 85°C for 44 h. Similarly, the treatment of a mixture of 100 parts VF–HFP copolymer and 4 parts DBU (1) in acetone for 8 h produced a rubber containing 0.44 mol double bonds per 1 kg of rubber. After vulcanisation of a mix of 100 parts of this rubber, 10 parts carbon black, 3 parts magnesium oxide, and 2 parts Na salt of bisphenol AF for 15 min at 170°C, a rubber with a strength of about 15 MPa, a hardness of 63 units (here and below, standard JIS A unless indicated otherwise), and a CS of 15% (200°C, 70 h) was obtained (ref. 16).

The diol used is mainly bisphenol AF – 1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxyphenyl)propane (n-HOC₆H₄)₂C(CF₃)₂), and the ITC is mainly BTPPC (C₆H₅CH₂P+(C₆H₅)₃Cl⁻) (ref. 1, p. 88). To eliminate dust formation, the components of the vulcanising system are used in the form of mixes with rubber (curative 20 contains 33% BTPPC, while curative 30 contains 40% bisphenol AF (balance fluorine-containing rubber)). A standard mix contains 2 parts bisphenol AF, 6 parts calcium hydroxide, 3 parts highly active (150 mg/g) magnesium oxide, and 30 parts low-activity carbon black and ITC. The standard vulcanisation schedule is as follows: 10–15 min in a press at 170–177°C and 24 h in an oven at 230–232°C. Below in this review, the standard proportioning and vulcanisation schedules are not given, and only altered parameters are given.

The use of amines and their derivatives and QASs of the most varied structure as ITCs has been described. Alkylamines of the RₙNHₙ⁻ type have been proposed as ITCs for the production of rubbers possessing high strength (ref. 17). An industrial surfactant – alkamine OS-2 – was used for the vulcanisation of fluorine-containing rubber SKF-26 by bisphenol AF (ref. 18). The following QASs were proposed as ITCs in diol vulcanisation: 1-benzyl-4-(1-pyrrolidinyl)pyridinium chloride (ref. 19), 5-azoni-aspiro[4.4]nonane bromide (II), tetrabutylammonium hydrosulphate [(C₄H₉)₄N⁺HSO₄⁻] (ref. 21), and tetrabutylammonium bromide (ref. 22). The latter, in a quantity of 0.1 parts in the presence of 0.5 parts wax of Brazilian wax palm (carnauba wax), improves the adhesion of rubber to metal (ref. 23).

For the case of phosphonium salts with different alkyl substituents at the phosphorus atom (ref. 27) it was shown that the nature of the substituents hardly affects the activity of the salt. The use of crown ethers as ITCs has also been described. The rubbers obtained in this case have high elongation with a low compression set (ref. 28).

RUBBERS WITH IMPROVED PROCESSING PROPERTIES

A large number of studies have been devoted to creating rubber mixes with a long storage life, improving the moulding properties of mixes, controlling the vulcanisation rate, and improving the capacity of MRGs to be removed from compression moulds.

Mixes that are stable during storage are produced using 1-phthalimido-4-butylenetriphenylphosphonium bromide (IV) as the ITC.
A mix containing 1 part salt IV, 100 parts 78:22 VF–HFP copolymer with a Mooney viscosity of 53 units (at 121°C), 2 parts bisphenol AF, 3 parts magnesium oxide, 5 parts calcium hydroxide, and 25 parts carbon black has a Mooney viscosity of 73 units (at 121°C) and a scorch time of 28.1 min. The rubber has a hardness of 76 units, a modulus (here and below, 100% modulus unless stated otherwise) of 5 MPa, a strength of 14 MPa, an elongation of 241%, and a CS of 11% (200°C, 22 h) (ref. 29).

(1,3-Dioxanyl-2)ethyltriphenylphosphonium chloride (V) produced from triphenylphosphine and 2-(2′-ethyl bromide)-1,3-dioxane is used to prepare mixes that are not prone to scorching, has good storage stability, and yields a rubber with high physico-mechanical properties.

A blend containing 100 parts 78:22 VF–HFP copolymer, 25 parts MT carbon black, 5 parts calcium hydroxide, 3 parts magnesium oxide, 0.8 parts salt V, and 2 parts bisphenol AF has a Mooney viscosity of 72 units (at 121°C) and a scorch time of 17.6 min. After vulcanisation of the mix at 180°C for 5 min in a press and at 230°C for 22 h in an oven, the strength of the rubber produced is 1.4 MPa, the modulus 6 MPa, and the elongation 236%, whereas when DIC is used instead of salt V these indices amount to 11.5 MPa, 5 MPa, and 182% respectively (ref. 30).

Salt VI has also been suggested as an ITC. Its introduction in a quantity of 0.58 parts per 100 parts VF–HFP copolymer in a standard mix gives a rubber with a hardness of 71 units, a modulus of 4.5 MPa, a strength of 17 MPa, an elongation of 275%, and a CS of 19%, as against 76 units, 62 MPa, 165 MPa, 205%, and 22% respectively for a rubber with BTPPC instead of salt VI (ref. 31).

For rubber mixes with a long storage life and a high vulcanisation rate, an alkylamine salt of diethylenetriamine-pentaacetic acid has been proposed (ref. 32):

\[
\text{HOOCCH}_2\text{N(CH}_2\text{H}_2\text{N(CH}_2\text{COOH})_2\text{nRNH}_2 \quad \text{CH}_2\text{COOH}
\]

where \( n = 1-4 \).

One way of improving the processing characteristics of rubber mixes is to prepare them from a blend of high molecular weight and low molecular weight polymers. A mix with good moulding properties is obtained, containing fluorine-containing rubber with a Mooney viscosity at 100°C of over 60 units (90 parts), a fluorine-containing rubber with a viscosity of 2–25 units at 100°C (10 parts), a wax or low molecular weight polyethylene (0.5–1.0 parts), a filler, and a standard vulcanising group (ref. 33). A vulcanisate obtained from a 95:5 blend of solid and liquid fluorine-containing rubbers, with good moulding properties, 15 parts barium sulphate, and 3.32 parts Daiak No. 1 has a strength of 14 MPa and an elongation of 430% and loses 19% strength and 5% elongation after holding in benzene for 72 h, whereas for nitrile rubber the losses of strength and elongation amount to 85 and 79% respectively (ref. 34). A composite with good moulding properties was obtained by mixing 8 parts Valtom LN (liquid fluorine-containing rubber), 15 parts carbon black, and 3.5 parts magnesium oxide until the production of a free-flowing mix, with the subsequent addition of 72 parts Technoflon NML and 1.5 parts N, N′-dicinnamylidene-1,6-hexamethylenediamine (Daiak No. 3) (ref. 35). Mixes based on SKF-26 rubber with N, N′-difurfurylidene-hexamethylenediamine (bifurgin) as the vulcanising agent, possessing high scorch resistance and improved processing characteristics, are obtained by adding 1–10 parts iron sulphide. The proportion of bifurgin in such a mix can be lowered from the normal 4–5 parts to 2 parts (ref. 36).

To produce technologically highly effective rubber mixes with good moulding properties, of great importance is the monomeric composition of the rubber and its molecular characteristics (refs. 37–44) (Table 1).

To improve the mouldability of mixes and their extractability from the moulds after vulcanisation, use is made of special plasticising additives and bisphenol with blocked hydroxyl groups (hydrophobised bisphenol). To improve the processing properties, 0.5–5% amorphous copolymer of ethylene with propylene or some other alkene is added, containing 0.5–10 wt.% COOR groups in the polymer chain. Thus, a standard mix of 100 parts Technoflon NML (VF–HFP copolymer) and 1.9 parts bisphenol AF, additionally containing 5 parts ethylene–propylene copolymer with diethylmaleate groups, has a Mooney viscosity (ML 1+ 10) of 70 units, a flow rate of 39 g/min (without an additive — 86 units and 34 g/min respectively). The mix is vulcanised for 10 min at 170°C in a press and for 24 h at 250°C in an oven, and a rubber is produced (values of the characteristics without an additive are given in brackets) with a modulus of 8.2 (8.7) MPa, a strength of 14.4 (16.3) MPa, an elongation of 143% (159%), and a Shore A hardness of 77 (75) units (ref. 45).

A mix based on rubber Technoflon NM containing (per 100 parts rubber) 0.5 parts salt VII, 2 parts process additive polyfluoropolyether alcohol (M = 600) (VIII), 1.6 parts bisphenol AF, 3 parts magnesium oxide, 6 parts calcium hydroxide, and 25 parts carbon black is vulcanised for 10 min at 175°C in a press and for 16 h at 250°C.
The properties of the vulcanisates produced with the addition of alcohol VIII and without it (ref. 46) are given in Table 2.

\[
\text{C}_6\text{H}_5\text{CH}_2\text{P(C}_6\text{H}_5)\text{2N(C}_2\text{H}_5)\text{2Cl}^{\text{VIII}}
\]

\[
\text{CF}_3\text{O(C}_3\text{F}_6\text{O})_m\text{(CF}_2\text{O})_n\text{CF}_2\text{CH}_2\text{OH}^{\text{VIII}}
\]

A composite with good processing properties and a high vulcanisation rate, based on Technoflon NM, is produced using 0.45 parts compound VII, 0.5 parts bis(n-chlorophenyl)sulphone (n-ClC\text{6}H\text{4})\text{2SO}_2, and 2.2 parts bisphenol AF. The vulcanisation rate in the press amounted to 34 min\(^{-1}\) (in the absence of sulphone 32 min\(^{-1}\)); the rubber has a CS of 19\% (200\°C, 70 h) and an extrudability of 8 (to ASTM 2230), and in the absence of sulphone a CS of 18\% and an extrudability of 7 (ref. 47).

Rubber with good scorch resistance and mouldability was produced from a mix containing 100 parts FC 2260 (VF–HFP–TFE) copolymer, 50 parts liquid fluorine-containing rubber G101, 2.8 parts silylated crosslinking agent (produced by treating 33.6 g of bisphenol AF with 16.1 g of hexamethyldisilazane), 1 part carbon black, 6 parts calcium hydroxide, and 3 parts magnesium oxide. The mix was vulcanised for 40 min at 150\°C in a press and for 24 h at 230\°C in an oven, producing a rubber with a hardness of 41 units, an elongation of 381\%, a strength of 4.2 MPa, and a CS of 12\% (ref. 48).

The blocking of end groups of rubber with the formation of non-ionogenic end groups leads to an appreciable reduction in the viscosity of a mix based on such a rubber. Such, for example, is a ternary copolymer VF–HFP–TFE (40:30:30) with a Mooney viscosity (at 121\°C) of 68 units, produced in the presence of hexamethyldisilane, which is a polymerisation regulator (ref. 50).

Composites with good vulcanisation characteristics are produced using equimolar mixtures of BTPP with bisphenol AF and 1,5-diazabicyclo[4.3.0]-5-one or 4-dialkylaminopyridine, N-alkylamide or polyalkylene glycol, or their mono- and dialkyl ether. These substances have lower melting points than BTPPC and are therefore dispersed better in the mix (ref. 51).

The properties of the vulcanisates produced with the addition of alcohol VIII and without it (ref. 46) are given in Table 2.

<p>| Table 1 Influence of molecular characteristics of rubber on properties of rubber mixes and rubber compounds |
|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>VF-HFP-TFE*</th>
<th>HFP-VF (molar ratio 25:75)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Intrinsic viscosity, cm(^3)/g</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>9.1</td>
</tr>
<tr>
<td>Mooney viscosity (at 121\°C), units</td>
<td>40(\uparrow)</td>
</tr>
<tr>
<td>Hardness, units</td>
<td>76</td>
</tr>
<tr>
<td>Modulus, MPa</td>
<td>5.5</td>
</tr>
<tr>
<td>Strength, MPa</td>
<td>17.0</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>235</td>
</tr>
<tr>
<td>CS, %</td>
<td>23</td>
</tr>
</tbody>
</table>

\*VF/HFP/TFE mass ratio: (1) 54.1:29.0:16.9; (2) 43.5:30.3:26.2; (3) 24.9:53.7:21.4; (4) 52.8:25.2:22.0; (5) 64.7:26.0:9.3; (6) 64:14:18 (mol)

\(\uparrow\) At 120\°C

The addition of a diol with blocked hydroxyl groups – a bis(trimethylsiloxy) derivative of bisphenol AF – to a mix based on Dai-el G801 gives it excellent flow, while a 25\% solution of this mix in acetone has a lifetime of 20 h and can be used for coatings (ref. 49).

Rubber with good scorch resistance and mouldability was produced from a mix containing 100 parts FC 2260 (VF–HFP copolymer), 50 parts liquid fluorine-containing rubber G101, 2.8 parts silylated crosslinking agent (produced by treating 33.6 g of bisphenol AF with 16.1 g of hexamethyldisilazane), 1 part carbon black, 6 parts calcium hydroxide, and 3 parts magnesium oxide. The mix was vulcanised for 40 min at 150\°C in a press and for 24 h at 230\°C in an oven, producing a rubber with a hardness of 41 units, an elongation of 381\%, a strength of 4.2 MPa, and a CS of 12\% (ref. 48).

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Composites with good vulcanisation characteristics are produced using equimolar mixtures of BTPP with bisphenol AF and 1,5-diazabicyclo[4.3.0]-5-one or 4-dialkylaminopyridine, N-alkylamide or polyalkylene glycol, or their mono- and dialkyl ether. These substances have lower melting points than BTPPC and are therefore dispersed better in the mix (ref. 51).

The properties of the vulcanisates produced with the addition of alcohol VIII and without it (ref. 46) are given in Table 2.

<table>
<thead>
<tr>
<th>Table 2 Properties of vulcanisates based on Technoflon NM rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>With addition of alcohol VIII</td>
</tr>
<tr>
<td>Shore A hardness, units</td>
</tr>
<tr>
<td>Brittle point, °C</td>
</tr>
<tr>
<td>Swelling, vol. %: in methanol (20\°C, 3 days)</td>
</tr>
<tr>
<td>in fuel (70\°C, 7 days)</td>
</tr>
</tbody>
</table>
The use of methyltriphenylphosphonium salt of methyl ester of methanephosphonic acid (IX) makes it possible to produce a rubber mix that does not corrode the steel compression mould and does not form a deposit on it during repeated compression moulding of articles.

\[
\text{IX} \quad \text{(C}_6\text{H}_3)_3\text{P}^+\text{CH}_3\text{O}(\text{CH}_3\text{O})\text{P(O)}\text{CH}_3
\]

A mixture of 1.05 parts of this salt, 100 parts VF–HFP–TFE copolymer, 1.94 parts bisphenol AF, 6.3 parts calcium hydroxide, 3.15 parts magnesium oxide, and 26.2 parts carbon black MT is vulcanised for 1.5 min at 177°C. The properties of rubber produced using salt IX or with the latter replaced with BTPPC are given in Table 3. After 67 vulcanisation cycles of a mix with the trial salt, the surface of the steel remained clean, whereas when the control mix was vulcanised the mould was coated with a black deposit (ref. 52).

Elastomeric material with low hardness that is extracted well from compression moulds after vulcanisation is produced from a mix of 70 parts fluorine-containing rubber with \( M = 2 \times 10^5 \) and 30 parts fluorine-containing rubber with \( M = 6 \times 10^3 \), 5 parts carbon black, 15 parts lead dioxide, 2 parts 4,4′-4-ammonio-1,1′-methylenebis(cyclohexyl)carbamate (X), 0.5 parts \( N,N \)-dimethyloctadecylamine, and 2 parts polyether \( \text{F}[\text{CF(CF}_3)]\text{CF}_2\text{O}]_n\text{CF}_2\text{CF}_3 \). After vulcanisation for 8 min at 180°C in a press and for 22 h at 230°C in an oven, the hardness of the vulcanisate is 47–48 units (ref. 53).

\[
\text{X} \quad +\text{CH}_2\quad \text{NHCOO}
\]

Moulding mixes are produced from fluorine-containing rubber containing iodine with the use of tetrabutylphosphonium benzotriazolate as the ITC in a standard mix (ref. 54).

### Table 3 Properties of rubbers based on VF-HFP-TFE copolymer with additions of salt IX and BTPPC

<table>
<thead>
<tr>
<th></th>
<th>With salt IX</th>
<th>With BTPPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS, %</td>
<td>21.7</td>
<td>24.4</td>
</tr>
<tr>
<td>Modulus, MPa</td>
<td>6.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Strength, MPa</td>
<td>15.5</td>
<td>15.4</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

Rubber with a strength of 24 MPa, a modulus of 9 MPa, a hardness of 79 units, an elongation of 220%, a CS of 20% (200°C, 72 h), and a high heat and chemical resistance was produced from a mix of standard composition based on a 66:15:19 VF–HFP–TFE ternary copolymer with 0.1 parts DBU and 2 parts dimethylsulphone (ref. 59). Similarly, a rubber from a mix of 100 parts 80:20 VF–HFP copolymer with the DBU replaced with 0.4 parts N-butyldiDBU chloride has a strength of 18 MPa, a modulus of 8 MPa, an elongation of 190%, a hardness of 81 units, and a CS of 20% (200°C, 72 h) and 27% (200°C, 166 h) (ref. 60). When DBU is replaced with its complex compound with diphenylphosphine, the CS is even lower (14%) (ref. 61). With the introduction of N-butyldiDBU salt and benzthiazolothiazole (XI) in a quantity of 0.8 parts per 100 parts terpolymer, 20 parts carbon black MT, 4 parts calcium hydroxide, and 1 part hydroquinone after vulcanisation in a mould for 10 min at 170°C and a pressure of 5.4 MPa and prevulcanisation in an oven for 24 h at 230°C, a rubber with a CS of 16% (200°C, 72 h) is produced (ref. 62). Salt XI is insoluble in water and is not moistened during storage in air for 24 h, in contrast to normal hygroscopic quaternary salts.

**RUBBERS WITH IMPROVED SERVICE PROPERTIES**

For the preparation of rubber products with improved mechanical properties and resistant to aggressive media, use is made both of specially synthesised rubbers and of mixes of different composition.

Solid articles are produced using 0.5 parts tetrabutylammonium hydroxysulphate with 1.5 parts bisphenol AF as the ITC (ref. 55). Rubber with a hardness of 67 units, a modulus of 4.9 MPa, a strength of 185 MPa, and an elongation of 370% is produced from a blend of 100 parts 25:40:35 propylene–TFE–VF copolymer, 10 parts 40:49:11 copolymer of propylene with TFE and 4-trifluorovinylxylo-2,2,3,3,4,4-hexafluorobutanol, and 0.8 parts tetrabutylammonium hydroxysulphate in a standard formulation (ref. 56). A blend of 100 parts 6:4 VF–HFP copolymer of standard composition with 0.5 parts trimethylphosphomonium chloride as the ITC yields a rubber with a hardness of 72 units, a modulus of 4 MPa, a strength of 15 MPa, an elongation of 310%, and a CS of 10% (70 h, 200°C) (ref. 57). A mix with good moulding properties that yields a vulcanisate with high physicomchanical properties contains 100 parts 60:40 VF–HFP copolymer, 2 parts bisphenol AF, 0.2 parts BTPPC, and 0.02 parts DBU in a standard formulation. The mix was premoulded into sheets at 70°C and then vulcanised to produce rubber with a hardness of 74 units, a modulus of 7.5 MPa, a strength of 17 MPa, and an elongation of 200% (ref. 58).

Rubber with a strength of 24 MPa, a modulus of 9 MPa, a hardness of 79 units, an elongation of 220%, a CS of 20% (200°C, 72 h), and a high heat and chemical resistance was produced from a mix of standard composition based on a 66:15:19 VF–HFP–TFE ternary copolymer with 0.1 parts DBU and 2 parts dimethylsulphone (ref. 59). Similarly, a rubber from a mix of 100 parts 80:20 VF–HFP copolymer with the DBU replaced with 0.4 parts N-butyldiDBU chloride has a strength of 18 MPa, a modulus of 8 MPa, an elongation of 190%, a hardness of 81 units, and a CS of 20% (200°C, 72 h) and 27% (200°C, 166 h) (ref. 60). When DBU is replaced with its complex compound with diphenylphosphine, the CS is even lower (14%) (ref. 61). With the introduction of N-butyldiDBU salt and benzthiazolothiazole (XI) in a quantity of 0.8 parts per 100 parts terpolymer, 20 parts carbon black MT, 4 parts calcium hydroxide, and 1 part hydroquinone after vulcanisation in a mould for 10 min at 170°C and a pressure of 5.4 MPa and prevulcanisation in an oven for 24 h at 230°C, a rubber with a CS of 16% (200°C, 72 h) is produced (ref. 62). Salt XI is insoluble in water and is not moistened during storage in air for 24 h, in contrast to normal hygroscopic quaternary salts.
The use of salts of bicyclic amidines of type (XII) as catalysts has been described. Thus, from a mix of standard composition with 1.8 parts bisphenol AF, 20 parts carbon black MT, and 0.27 parts salt XII, a rubber with a strength of 16 MPa and an elongation of 230% was produced (ref. 63). Slightly higher strengths are obtained when salt XIII is used (ref. 64).

High-modulus rubber (modulus 16.3 MPa, strength 19.2 MPa, elongation 117%) is produced from a ternary copolymer using bicyclic guanidine (XIV) or its quaternary salt as the catalyst (ref. 65).

![Diagram](XIV)

Quaternary salts of the DBU derivatives mentioned above are more active catalysts and possess a better capacity for distribution in the mix than a QAS of simple structure, which results in higher thermal stability of rubbers in the stress state. A Vaiton E60 mix of standard composition, 0.4 parts DBU phenoxide, and 1 part phthalic anhydride possesses good flow and, after vulcanisation, yields a rubber with a modulus of 7.3 MPa, a strength of 18 MPa, an elongation of 180%, a hardness of 77 units, and a CS of 15% (230°C, 24 h) (ref. 66). The use of a complex compound of DBU with magnesium chloride (2DBU.MgCl₂) as the ITC gives mixes that retain plasticity for a long time, in contrast to a quaternary salt of DBU with butyl chloride (ref. 67). A mix of 100 parts fluorine-containing rubber, 25 parts carbon black, 5 parts calcium hydroxide, 3 parts magnesium oxide, 2 parts bisphenol AF, and 0.5 parts complex 2DBU.MgCl₂ after vulcanisation for 5 min at 230°C in a press and for 22 h at 180°C in an oven yields a vulcanisate with the following properties (in brackets, data for a vulcanisate of a similar mix but with N-butyldiDBU chloride): scorch time $t_s$ (121°C) 29.5 (18.5) min, hardness 74 (75) units, modulus $E$ (5.1) MPa, strength 14 (13) MPa, elongation 225% (190%), and CS 15% (31%) (70 h, 200°C). The use as an ITC in this system of a salt of DBU with perfluorooctanesulphonic acid C₈F₁₇SO₂N(CH₃)Na to a mixture of 100 parts fluorine-containing rubber, 25 parts carbon black, 6 parts calcium hydroxide, 0.77 parts BTPPC, and 0.625 parts bisphenol AF yields a rubber with a strength of 20 MPa, an elongation of 550%, and a modulus (under 300% elongation) of 9.51 MPa, whereas for a rubber without the additive these properties are 7.51 MPa, 718%, and 4.79 MPa respectively (ref. 73).

A slight improvement in the properties of the rubber was noted when salt $\text{CH}_3(\text{C}_6\text{H}_5)_2\text{PN}^+\text{Cl}^-$ was used instead of BDIC (ref. 74). Lower oil permeability is possessed by vulcanised rubbers produced from rubbers with an increased fluorine content, for example based on a blend of binary and ternary copolymers (ref. 75). An organosilicon Schiff base (XV) has been proposed for the vulcanisation of Vaiton C. Rubber produced in this case has a strength of 30 MPa, an elongation of 654% at 150°C, and a 23% reduction in elongation after 15 min at 150°C, as against 25 MPa, 250%, and 30% respectively for a vulcanisate with Daicel No. 3 (ref. 76).

\[
\begin{align*}
\text{CH}=\text{CHPh} & \quad \text{PhCH}=\text{CH} \\
\text{CH}=\text{N}(\text{CH}_2)_3(\text{SiMe}_2\text{O})_5\text{SiMe}_2(\text{CH}_2)_3\text{N}=\text{CH} & \quad \text{XV}
\end{align*}
\]

To produce rubber compounds, use is made of rubbers of the second type. A rubber compound with a high breaking elongation is produced by mixing 67 parts thermoplastic rubber Aflon LM720 (a copolymer of ethylene and propylene with a melting point of 230°C) with 100 parts Aflas 170 rubber (a copolymer of propylene and TFE) and 0.7 parts benzenophenonetetracarboxylic acid dihydride. The mix is heated for 3 min at 250°C and is then placed in a press and vulcanised for 10 min. The rubber compound produced has a strength of 19 MPa and an elongation of 403%, whereas for a rubber from a mix of Aflon 170 with 30 parts carbon black, produced at 170°C, these properties amount to 15 MPa and 230% respectively (ref. 77).

**RUBBERS WITH IMPROVED COLD RESISTANCE AND THERMAL STABILITY**

Without the use of a special formulation and technology, the rubbers examined in the review do not form cold-resistant rubbers. To produce the latter, use is made of different additives and special methods, including covulcanisation with other rubbers.
During the vulcanisation with Daiak No. 3 (2 parts) of a mix containing 100 parts Vaiton C, 10 parts magnesium oxide, and 20 parts carbon black, and also 10 parts ethylene–propylene–ethylene–propylene rubber crosslinked in emulsion with divinylbenzene and peroxide, a rubber with a brittle point of –42°C is produced (ref. 78).

The addition to a rubber mix based on fluorinated rubber of fluorinated polyester with a molecular weight of 250–3000 that contains one or two OH end groups leads to the production of a rubber with improved cold resistance and good extractability from the compression mould (ref. 79). Rubber with a brittle point of –26°C (–20°C for rubber compounds based on normal rubbers) and a CS of 20% are obtained from a 30.6:63:6.4 HFP–VF–TFE copolymer (ref. 80).

To increase the resistance to thermal degradation, 0.5 parts phenothiazine is added to a rubber mix containing 100 parts HFP–TFE–VF copolymer, 16 parts carbon black MT, 10 parts calcium hydroxide, 3 parts bisphenol AF, and 0.5 parts BDIC, held overnight, and vulcanised. The rubber obtained has the following properties (the changes in the properties after ageing at 275°C for 70 h of trial and control (without phenothiazine) rubbers respectively are given in brackets; the initial values of the properties for both rubbers were practically identical): a hardness of 77 units (1 and 2%), a strength of 16 MPa (–35 and –41%, and an elongation of 225% (2 and 21%) (ref. 81).

The outer thermally stable layer of floating rollers for copiers is manufactured from a mix based on an VF–HFP copolymer containing no metal oxides with an amine vulcanising agent. The working life of such rolls is several times higher than that of rolls coated with a rubber containing magnesium oxide or calcium hydroxide (ref. 82). For similar coating, a mix based on a VF–HFP–TFE ternary copolymer with aluminium oxide as the filler has also been recommended (ref. 83).

Rubber with an improved resistance to impact failure at low temperatures was obtained by using epoxy-containing silicone rubber with a particle size of no more than 100 mm as an additive. A mix of 100 parts 20:80 HFP–VF copolymer, 2 parts bisphenol AF, 0.25 parts BDIC, 20 parts Trefil E601 (a powder silicone rubber), 10 parts silica filler Niposil ES10, and 3 parts highly active magnesium oxide were vulcanised in a press and heated. The rubber obtained had a strength of 15 MPa, an elongation of 205%, a CS of 27% (200°C, 70 h), and a swelling in kerosine (70 h, room temperature) of 5.9 vol.%; the rubber did not fail at –26°C, at –34°C it became brittle, and it failed entirely at –45°C (ref. 84).

**LAYERED ARTICLES**

To produce durable articles with alternating layers of rubber compounds based on fluorine-containing rubber and another rubber or plastic, it is necessary to ensure sufficient bond strength between the layers. Different methods are used for this. Amine vulcanisation has been suggested for the production of multiply articles, in particular in the case of the covulcanisation of sheets of rubber mixes based on fluorine-containing rubber and rubbers not containing fluorine. Thus, a sheet produced from a mix of 100 parts Vaiton A (100), 15 parts magnesium oxide, 20 parts carbon black, and 1.2 parts Daiak No. 1 is covered with a sheet of a mix of 100 parts butadiene rubber (BROIU), 60 parts carbon black, 2 parts stearic acid, 1.5 parts sulphur, 0.9 parts N-cyclohexyl-2-benzthiazyl sulphenamide, 10 parts silicon dioxide, and 10 parts salt of DBU and p-toluenesulphonic acid and vulcanised in a press for 20 min at 170°C to produce a material with a bond strength between the plies of 6.9 N/cm (without DBU and SiO₂; this is 0.1 N/cm) (ref. 85). To bond a rubber compound based on fluorine-containing rubber to a polysulphone plastic, use was made of Daiak No. 3 (ref. 86). After cleaning with methyl ethyl ketone, the plastic sheet was coated with adhesive containing 5 parts methyl ethyl ketone and 1 part rubber mix (containing 100 parts Vaiton C, 15 parts magnesium oxide, 10 parts carbon black MN, and 3 parts Daiak No. 3), and dried at room temperature for 1 h. Then it is covered with a sheet of untreated mix based on Vaiton C of the indicated composition and vulcanised for 25 min at 160°C and a pressure of 9.8 MPa. The resistance to direct pull amounted to 0.43 MPa, whereas for the control specimen with a polysiloxane adhesive instead of the composite with Vaiton C it was 0.08 MPa.

Quaternary ammonium salts have been proposed as ITCs for the production of two-ply fuel hoses of rubbers based on a fluorine-containing rubber and butadiene-acrylonitrile rubber containing diethylaminomethyl acrylate units (ref. 87). Sheets produced from a mix of 100 parts Technoflon NM, 3 parts magnesium oxide, 6 parts calcium hydroxide, 20 parts carbon black MT, and 2 parts catalyst (tetrabutylammonium-sym-triazinedithiolate (XVI)) are covulcanised with sheets of a mix of 100 parts epichlorohydrin–ethylene oxide copolymer (Dzhekhron 3120), 1 part stearic acid, 40 parts carbon black FIF, 5 parts Pb₃O₄, and 2 parts mercaptobenzthiazole for 10 min at 160°C and a pressure of 3.9 MPa; the bond strength between the sheets is 39 N/cm with failure of the rubber layer (ref. 88).

![Chemical Structure](image)  

Bisphenol and phosphonium salts are used to manufacture multiply articles, for example fuel hoses for motor vehicles, membranes, etc. Sheets of 2 mm thickness
from a mix of 100 parts Dai-el G603 rubber (with a diol vulcanising system), 3 parts magnesium oxide, 5 parts calcium hydroxide, and 15 parts carbon black are coated with sheets of a mix of 100 parts 10:25:25:40 copolymer of ethylene, vinyl acetate, butyl acrylate, and methoxyethyl acrylate, 1 part stearic acid, 60 parts carbon black, 5 parts dioctyl sebacinate, 5 parts Adekasizer P, and 4 parts guanidine compound and are vulcanised at 160°C for 30 min at a pressure of 0.44 MPa to produce a material with high bond strength between the sheets and high thermal stability and oil resistance (ref. 89). High bond strength of rubber layers based on fluorine-containing rubber and butadiene–acrylonitrile rubber (42.5 N/cm) was obtained by the covulcanisation of sheets of 4 mm thickness of a standard mix of Vaiton E45, 20 parts carbon black, 1.2 parts bisphenol, and 0.2 parts phosphonium salt with sheets of 4 mm thickness of 100 parts butadiene–acrylonitrile rubber JSR N230 S, 1 part stearic acid, 5 parts zinc oxide, 20 parts calcium hydroxide, 3 parts peroxide, and 3 parts vulcanisation coagent (triallylisocyanurate) in a press at 170°C and a pressure of 15 MPa for 15 min; the key role here is played by calcium hydroxide, since, without it, the bond strength is zero (ref. 90).

Hose for petrol pumps with a high interply adhesion is manufactured from layers of thermally stable, oil-resistant fluorine-containing rubber (inner layer) and an ethylene–vinyl acetate copolymer (outer layer). For the inner layer, use is made of a rubber mix containing 100 parts rubber Dai-el G703 (which contains a diol vulcanising system), 5 parts calcium hydroxide, and 15 parts carbon black, and for the outer layer a 15:10:50:25 copolymer of butyl acrylate, ethylene, 2-methoxyethyl acrylate, and vinyl acrylate with 4 parts guanidine vulcanising agent. Layered tubes of these mixes are produced by combined extrusion with subsequent braiding with polyester fibre (ref. 91). Technology has been described for the manufacture of two-ply petrol-resistant hose. Various types of butadiene–acrylonitrile rubber and an outer layer of chloroprene rubber (ref. 92). Multiply fluorine-containing rubber and an outer layer of petrol-resistant hosing with an inner layer of fluorine-containing rubber with a diol vulcanising system, based on butadiene and based on butadiene–acrylonitrile rubber JSR N230 S, 1 part stearic acid, 5 parts zinc oxide, 20 parts calcium hydroxide, 3 parts peroxide, and 3 parts vulcanisation coagent (triallylisocyanurate) in a press at 170°C and a pressure of 15 MPa for 15 min; the key role here is played by calcium hydroxide, since, without it, the bond strength is zero (ref. 90). High bond strength of rubber layers based on fluorine-containing rubber and butadiene–acrylonitrile rubber (42.5 N/cm) was obtained by the covulcanisation of sheets of 4 mm thickness of a standard mix of Vaiton E45, 20 parts carbon black, 1.2 parts bisphenol, and 0.2 parts phosphonium salt with sheets of 4 mm thickness of 100 parts butadiene–acrylonitrile rubber JSR N230 S, 1 part stearic acid, 5 parts zinc oxide, 20 parts calcium hydroxide, 3 parts peroxide, and 3 parts vulcanisation coagent (triallylisocyanurate) in a press at 170°C and a pressure of 15 MPa for 15 min; the key role here is played by calcium hydroxide, since, without it, the bond strength is zero (ref. 90).

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Triethylbenzylammonium chloride (TEBAC) in a quantity of 0.3 parts was used to prepare rubber mixes with the addition of n-aminobenzenesulphonamide in order to improve the adhesion characteristics (ref. 100). N-ButylDBU chloride was used in the production of a composite of fluorine-containing rubber with polyphenylene sulphide fibre. A mix containing 90 parts fibre Fortron 1140A (polyphenylene sulphide containing glass fibre), 10 parts ternary copolymer (Vaiton B), 0.2 parts bisphenol AF, 0.035 parts N-butylIDBU chloride, 0.3 parts magnesium oxide, and 0.6 parts calcium hydroxide was injection moulded at melting temperature (310°C) and vulcanised at 170°C, producing a composite with an increased impact strength compared with a composite without fluorine-containing rubber and additives (ref. 101). A vulcanisate of a ternary copolymer, produced using bisphenol AF and a salt of the latter with BTPPC and tetrabutylammonium bromide, showed good adhesion to treated metal; in the absence of the given bromide, adhesion was zero (ref. 102).

The activity of magnesium oxide has a strong influence on adhesion of the rubber to metal coated with adhesive. Thus, a mix containing 100 parts VF-HFP-TFE copolymer, 20 parts carbon black, 6 parts calcium hydroxide, 15 parts magnesium oxide of grade Kyowamag 150 with an activity of 148 mg/g, 2 parts bisphenol AF, and 0.3 parts BDIC was vulcanised on metal with adhesive of grade SUS 304. The bond strength of the rubber to metal is higher than that of the same composite but with magnesium oxide with an activity of 32 mg/g (ref. 103).

Compound VII was used as an ITC for the vulcanisation of a 21:79 VF-HFP copolymer containing 0.15% bromine (ref. 104). The bond strength of rubber (standard formulation) with the given salt to a steel plate treated with adhesive Chemosil S11 at 170°C and a pressure of 6 MPa amounted to 8 MPa (for a rubber compound based on rubber not containing bromine, 2.9 MPa). To increase the adhesion of a rubber compound based on fluorine-containing rubber, the substrate was pretreated with aminosilane and a fluoroaliphatic compound, containing sulphonamide or sulpho groups (ref. 105), or with an oil-soluble chelate-forming substance (ref. 106).

For the production on textile material of a microporous composite of 100 parts Vaiton E60C, 4 parts magnesium oxide, 3 parts calcium hydroxide, and 400 parts methyl ethyl ketone and dried; impregnation and drying is repeated three more times, producing composite sheets. Vulcanisates of these sheets have a modulus (under 20% elongation) of 5 MPa and a permeability for hydrogen of 4.1×10⁻¹⁰ and 6×10⁻¹⁰ ml/(cm² s MPa) after 0 and 10 elongations, whereas for material produced by mixing in solution of a rubber mix and PTFE this characteristic amounts to 4.5×10⁻⁸ ml/(cm² s MPa) (ref. 109). Prolonged heating of a vulcanised rubber mix of standard composition at 250°C or at a higher temperature leads to a reduction in gas permeability (ref. 110).

Microporous articles are produced using azodicarbonamide as the blowing agent. Mix A containing 100 parts Technoflon NM (20:80 HFP-VF copolymer), 2 parts curing agent Technoflon FOM1 (1:1 mixture of bisphenol AF and Technoflon NM), 3 parts catalyst Technoflon FOM2 (a 3:7 mixture of aminophosphonium salt and Technoflon NM), 0.3 parts polyethylene glycol (Gligogum 4000), 2 parts zinc stearate, and 2 parts bis(butoxyethoxyethyl)-adipinate (TR 95) is mixed with mix B containing 1 part magnesium oxide, 2 parts calcium hydroxide, 10 parts calcium silicate treated with aminosilane, 5 parts carbon black, 3 parts azodicarbonamide (Porofor ADC/K), and 2 parts TR 95 in terms of 100 parts mix A. The mix is extruded, vulcanised at 140°C for 90 min under pressure and for 24 h at 235°C in an oven to produce a foam with a density of 600 kg/m³ with a uniform distribution of pores and a CS of 23% (200°C, 24 h, 50% compression) (ref. 111).

Similarly, a standard mix based on fluorine-containing rubber Technoflon FOR 65BI with 5 parts fine colloidal silica and 15 parts barium sulphate (without carbon black) can be mixed with 4 parts azodicarbonamide to produce a foam with a strength of 6.1 MPa, a modulus of 2.3 MPa, an elongation of 190%, and a hardness of 10 units (ref. 112). Foam is also produced from a standard mix with the use of a silylated vulcanising agent (ref. 113).

The additional structure formation of the surface of the rubber for improvement of abrasion resistance is carried out by applying vulcanising agents on to the surface from
solution. In particular, 6-dibutylamino-1,3,5-triazine-2,4-dithiol (XIX) has been used as a vulcanising agent (ref. 114).

\[
\text{XIX}
\]

In the first variant of the method, the vulcanised article was held in an aqueous solution of XIX, sodium hydroxide, and tetrabutylammonium bromide at 50–95°C for 15–60 min and then heated for 20 h at 200°C. In the second variant, use was made of an acetone solution of ammonium salt of compound XIX, again with subsequent heating. In both cases, there is a considerable reduction in the friction coefficient of the surface, and in the second case the antifriction properties of the rubber article are better.

For additional structure formation of the surface, use is also made of normal vulcanising agents. A mix of 100 parts standard composition Vaiton B and 0.3 parts BDIC is vulcanised for 15 min at 177°C. The vulcanise sheet is held in a solution of bisphenol AF (10%) and BDIC (2%) in a 1:1 mixture of acetone and methanol, left overnight in air, and then dried for 60 min at 120°C and held in the oven for 24 h at 232°C. On an instrument where friction is measured by the shear force of a steel disc against the surface, for this rubber the shear force is zero, the hardness 80 units, and the elongation 205% (for rubber with an untreated surface the shear force amounts to 21 kg, the hardness to 77 units, and the elongation to 240%) (ref. 115). Similarly, a plate of the same mix but containing 2 parts dimethylsulphone and 2 parts carnauba wax is held for 30 min at 20°C in an acetone-methanol solution of bisphenol AF (10%) and DBU (2%), dried, and held for 24 h at 232°C to produce a material with a hardness of 80 units and coefficients of friction of 0.47 (static) and 0.46 (kinetic), whereas for material with an untreated surface these coefficients amount to 1.76 and 1.36 respectively (ref. 116). Rubber with maximum crosslink density in the surface layer is given by impregnation of the same vulcanisate by a 33% solution of bisphenol AF in acetone for 4 h with subsequent drying in air and heating (ref. 117).

Salt XX is used as an ITC in the standard rubber mix which is vulcanised for 15 min at 177°C, held for 15 min at 30°C in a methanol solution of DBU, dried, and vulcanised in an oven for 24 h at 232°C to produce a rubber with a non-tacky surface that does not crack during bending (ref. 118).

\[
\left[\left(C_6H_5CH_2\right)_2NH\right]_+\left[\left(C_6H_5\right)_2P\right]_2^- \quad 2Cl^- \quad XX
\]

Rubber with a non-tacky surface is also produced by vulcanisation with Daiak No. 1 of a mix based on Vaiton A with subsequent surface treatment with DBU and heating at 230°C (ref. 119).

Rubber composites with low friction contain fluorine-containing rubber and thermoplastic fluorine-containing resin and can also include powder of cured thermosetting resin or a thermally stable resin with a glass transition temperature no lower than 300°C. Thus, from a mix containing 70 parts Technoflon FOR 420 (VF–HFP copolymer), 30 parts Aflon COP-30, 30 parts low molecular weight polytetrafluoroethylene Lubricant L 169, 5 parts carbon black MT, 1 part sodium stearate, 3 parts magnesium oxide, and 6 parts calcium hydroxide after vulcanisation in a press for 10 min at 170°C, and then for 16 h at 230°C, plates were produced with a non-tacky surface, a kinetic friction coefficient of 0.25, a strength of 24.5 MPa, an elongation of 200%, and a hardness of 85 units (refs. 120–122). These materials have been used for the manufacture of components operating under intense friction conditions.

Of great interest are thermally stable thermoplastic elastomers produced by dynamic vulcanisation. Thus, from a mix containing 25 parts polyphenylene sulphide, 75 parts Technoflon TN (terpolymer), 1.5 parts bisphenol AF, 0.5 parts BTPC, 2 parts magnesium oxide, 5 parts calcium hydroxide, and 5 parts carnauba wax, after dynamic vulcanisation, a material is produced with a strength of 5.2 MPa and an elongation of 250% (after holding at 200°C for 3 days, the strength is 4.2 MPa and the elongation 200%) and with swelling in methyl ethyl ketone of 89% and in toluene of 3.3% (ref. 123). Similarly, thermoplastic material that is combustion resistant was obtained by extrusion at 300°C of a mix of 80 parts polyphenylene sulphide and 20 parts VF–HFP copolymer with subsequent pelletising and drying at 120°C; the material is capable of being injection moulded at 290°C; its strength was 5 MPa, and its elongation 20% (ref. 124).

The production of a thermoplastic elastomer by the dynamic vulcanisation of a mix of fluorine-containing rubber with polyamide and a block copolymer of polyamide with polyester with a particle size of the dispersed phase of less than 5 μm has also been described (ref. 125). A quantity of 14 parts nylon 612 is mixed with 8 parts thermoplastic resin Pexab 4011 at 230°C by adding 147 parts slightly scorched fluorine-containing rubber; after 3 min, 1 part N,N-diphenylethylenediamine and 1 part Structural TR065 are added and mixed for 10 min. The cured composite obtained has a strength of 9.5 MPa, an elongation of 111%, a CS of 71% (150°C, 70 h), a Shore A hardness of 40 units, and a weight loss at 260°C of 1.9 and 11.7% after 1 and 22 h respectively (ref. 126). To improve the working properties of the heads in solid discs, optical discs, etc., a thermoplastic is used as the microshock absorber, produced by mixing 100 parts Elastolan 1154D (a thermoplastic urethane elastomer) and 5 parts Dai-el
thermoplastic T-550 (a thermoplastic elastomer containing ethylene–TFE and VF–HFP–TFE copolymers); the material has a hardness of 97 units and tan δ of 0.20 at room temperature (ref. 127). Smooth membranes are produced by polymerisation of polysiloxane with end unsaturated groups with dehydrofluorinated fluorine-containing rubber and mixing of the copolymer obtained with a reactive metal oxide, for example CuO (ref. 128).

CONCLUSIONS

Comparing the given data on the influence of different factors on the properties of rubbers, it is possible to draw the following conclusions:

1. The standard formulation, containing bisphenol A as the crosslinking agent and benzyltriphenyl-phosphonium chloride as the interphase transfer catalyst, in most cases ensures the production of technologically effective rubber mixes and rubbers of high thermal stability. Similar results are given by the use, instead of phosphonium salt, of more readily available ammonium salts – tetrabutylammonium or triethylbenzylammonium chloride. The use of catalysts of more complex structure in a number of cases leads to an improvement in the properties of rubber mixes and rubbers, although the mechanism of this effect has not been studied.

2. Improvement in the processing properties of mixes, necessary, for example, for the moulding of articles by injection moulding, is achieved most simply by using blends of high molecular weight and low molecular weight rubbers and certain additives.

3. To produce rubbers with special properties, there are many methods that can be combined to achieve the desired results.

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