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STUDY OF NEW NITROSOAMINE-FREE VULCANIZATION SYSTEMS OF RUBBER COMPOUND

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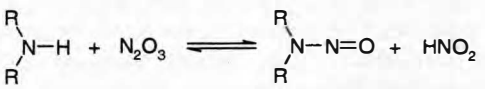
ABSTRACT: Creation of Nitrosamine-free vulcanization systems is one of the important environmental problems in the car tyres production. Present work deals with the creation of Nitrosamine-free vulcanization system of a rubber compound for passenger car tyres. Its formation was provided by the substitution of commercially used benzothiazolic accelerator with some new accelerators on the base of Dithiophosphates which do not form dangerous Nitrosoamines. In the newly prepared ecologically modified vulcanization systems, the commercial accelerator was substituted with new dithiophosphate accelerators in the according amount. In all of the prepared systems, low-aromatic oil (RAE) was used in the function of plasticizer. Vulcanization characteristics and physical-mechanical properties of newly prepared systems were compared to properties of commercial rubber compound for passenger car tyres.

KEY WORDS: nitrosamine-free vulcanization system, dithiophosphate accelerator, vulcanization characteristics, physical-mechanical properties, passenger car tyres

1. INTRODUCTION

At the present time one of the main priorities in rubber industry is ecologization of rubber compounds according to the high quality of products. The environmental requirements are narrowly connected to the environmental protection and mainly to the human health protection. So in the first position comes the replacement of dangerous substances with their ecological substituents. Many accelerators which are important components in all sulfur curing systems must be considered as critical from toxicological aspects. Accelerators, containing secondary amine fragments may form dangerous carcinogenic Nitrosamines according to the reaction [1]



Commercially used accelerators on the base of Dithiocarbamates and Benzothiazoles are classified among the problematic group accelerators containing secondary amine fragments (Fig. 1).

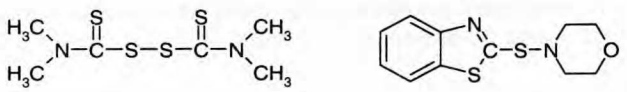


Fig. 1: Accelerators containing secondary amine fragments:
A - Dithiocarbamate, B - Benzothiazole

The creation of Nitrosamine-free vulcanization systems is one of important environmental problems in the car tyres production. The formation of Nitrosamine-free vulcanization system may be provided by the way of substitution of commercially used benzothiazolic accelerator with some new accelerators on the base of Dithiophosphates which do not form dangerous Nitrosoamines.

General advantages of dithiophosphate accelerators are well-known:

- Highly stable sulfur networks, heat resistant vulcanizates
- N-Nitrosamine free, non toxic, non hazardous
- Highly soluble in all rubbers
- Easy and homogeneously dispersing
- High curing speed
- Not blooming in non polar rubber (i.e. EPDM)
- Easy handled as "Dry liquid" or Polymer Bound [2]

Dithiophosphates tend to form monosulfidic or disulfidic crosslinks which, because of their higher bond energies, are much more resistant to reversion, so they add to enhanced heat stability [3].

2. EXPERIMENT

The creation of Nitrosamine-free vulcanization systems of rubber compounds for passenger car tyres was provided by the way of substitution of commercially used benzothiazolic accelerator (S-DZ) with new accelerators on the base of Dithiophosphates. Six new vulcanization systems were prepared with the addition of three new dithiophosphate accelerators (P-SDT, P-ZDT and P-TP) [4]. In all of the prepared systems we used low-aromatic oil (RAE) in the function of plasticizer. Contents of accelerators in the reference rubber compound 1-R and modified compounds 2 - 7 are given in Tab. 1.

Tab. 1: Content of accelerators in the reference rubber compound 1-R and modified compounds 2 - 7

Accelerator	Content (phr)						
	1-R	2	3	4	5	6	7
S-DZ	1.29	0	0	0	0	1.20	1.04
P-TP	0	1.29	0	1.29	0	0	0
P-ZDT	0	0	1.29	0	0	0.70	0
P-SDT	0	0	0	0	1.29	0	0.70
Σ Accelerators	1.29	1.29	1.29	1.29	1.29	1.90	1.74

Rheology and vulcanization characteristics (ML, MH, tS, t90, RV) of newly prepared systems were tested and physical-mechanical properties of vulcanized rubber were studied. Determination of vulcanization characteristics was made by vulcameter Monsanto 100 by STN 62 1416 at the temperature of 150 °C during 60 min. Determination of physical-mechanical properties of vulcanized rubber - stress-strain properties (Tensile strength, Modulus 200, Elongation) was made by instrument INSTRON at the temperature of 23 ± 2 °C by STN 62 1436 (ISO 37). Hardness was measured by hardness tester IRHD by STN 62 1433 at the temperature of 23 ± 2 °C [1].

Obtained values of ecologically modified rubber compounds were compared with the properties of commercial rubber compound for passenger car tyres.

3. RESULTS AND DISCUSSION

Results of rheology and vulcanization characteristics measurements are given in Tab. 2. Graphical dependences of optimum of cure t_{90} and density of modified rubber compounds are in Figs. 2 and 3. Obtained values of physical-mechanical properties study are given in Tab. 3 and graphs of Tensile strength and Elongation of vulcanized modified rubber are in Figs. 4 and 5.

Tab. 2: Rheology and vulcanization characteristics of reference rubber compound 1-R and ecologically modified compounds 2 - 7

Characteristics	**1-R**	**2**	**3**	**4**	**5**	**6**	**7**
M_{MIN} [N.m]	12.0	12.0	13.0	13.0	13.0	13.0	13.0
M_{MAX} [N.m]	98.0	87.0	85.0	84.0	84.5	88.0	89.0
t_{02} [min]	1.5	2.0	2.0	2.0	2.0	2.5	2.0
t_{90} [min]	19.0	15.0	16.0	17.5	16.5	19.5	20.0
R_V [min^{-1}]	5.714	7.692	7.143	6.452	6.897	6.874	6.501
Mooney viscosity 100 °C, 1+4, ML	35.4	36.8	36.9	37.4	38.3	34.5	33.5
Density II.°[g/cm^3]	1.17	1.16	1.17	1.17	1.18	1.17	1.17

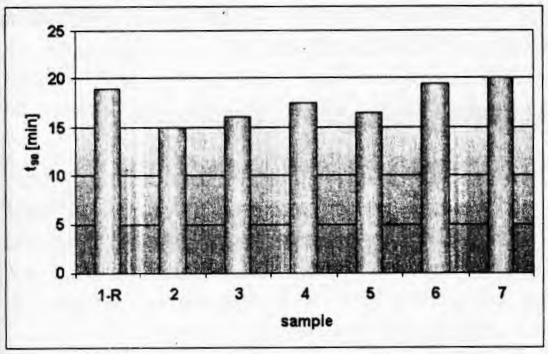


Fig. 2: Optimum of cure t_{90} [min]

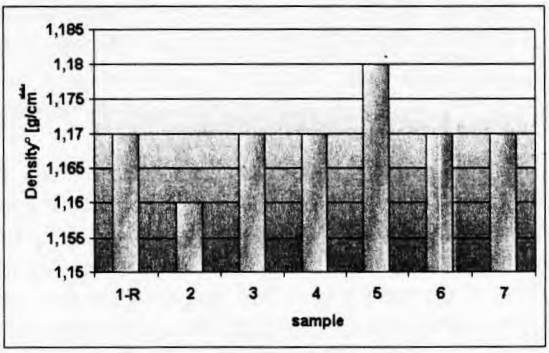


Fig. 3: Density [$g.cm^{-3}$]

Tab. 3: Physical-mechanical properties of reference rubber compound 1-R and ecologically modified compounds 2 - 7

Property	**1**	**2**	**3**	**4**	**5**	**6**	**7**
M_{200} [MPa]	10.98	10.87	11.05	11.16	11.18	11.08	11.32
Hardness [Sh A]	69.8	70.4	69.6	71.0	69.5	70.5	69.8
Tensile strength [MPa]	12.44	13.41	13.52	13.71	13.92	13.54	13.05
Elongation [%]	372	475	442	429	488	444	450
Elasticity [%]	45.7	46.5	44.3	43.5	44.8	46.5	45.2

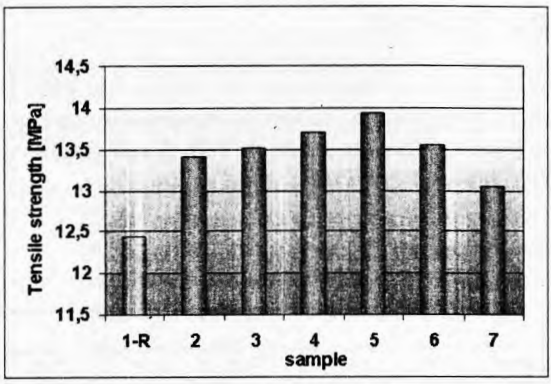


Fig. 4: Tensile strength [MPa]

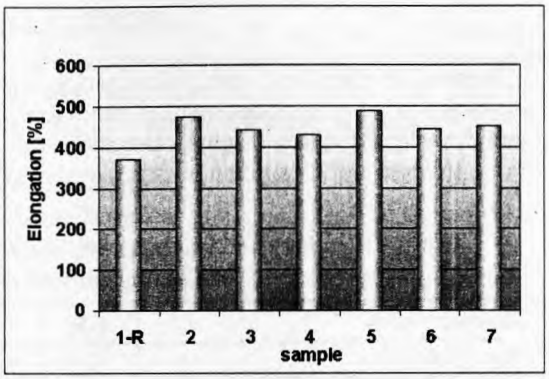


Fig. 5: Elongation [%]

Obtained values of vulcanization characteristics and physical-mechanical properties of newly prepared modified rubber compounds generally show a positive influence of dithiophosphate accelerators on main properties of studied rubber systems of passenger car tyres in comparison with the properties of commercial rubber compound.

In majority of studied properties values the results of measurements show the synergistic effect of combination of dithiophosphate accelerator (P-ZDT, P-SDT) with S-DZ (modified rubber compounds 6 and 7). Above stated modified rubber compounds achieved qualitative properties comparable with commercial rubber compound containing problematic benzothiazole accelerator.

4. CONCLUSION

In six newly prepared vulcanization systems, commercial benzothiazolic accelerator (S-DZ) was substituted by new dithiophosphate accelerator in according amount. In two of new systems we used the combination of Dithiophosphate (P-SDT or P-ZDT) and Benzothiazole (S-DZ). In all prepared systems was low-aromatic oil (RAE) used in the role of plasticizer. Vulcanization characteristics and physical properties of newly prepared systems were compared with the properties of commercial rubber compound for passenger car tyres containing benzothiazolic accelerator.

On the basis of evaluated results two optimal synergistic vulcanization systems 6 and 7 were selected [5].

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