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Influence of Fillers and Curing Systems on the Physico-Mechanical Properties and Stability of EPDM Vulcanizates

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The thermal stability was investigated for ethylene propylene diene terpolymer (EPDM) rubber loaded with different white and black fillers, namely, kaolin, quartz, polyvinylchloride PVC, talc, graphite, medium thermal carbon black MT, semi reinforcing furnace black SRF, and high abrasion carbon black HAF. The fillers were added at a fixed level of 20 phr. Two curing systems were used, tetramethyl thiuram disulfide (TMTD) and sulfur/N-cyclohexyl-2-benzothiazyl sulfenamide (S/CBS). The effects of the curing system and type of filler on the physico-mechanical properties, before and after thermal aging were investigated. It was found that the vulcanizates cured with S/CBS system gave better physico-mechanical properties than the TMTD cured samples. However, TMTD cured EPDM has thermal stability performance superior to the other vulcanizing system.

Keywords: EPDM vulcanizates, physico-mechanical properties, thermal stability, black fillers, white fillers, curing systems

INTRODUCTION

Most polymeric materials are subjected to oxidation. The rate of oxidation depends on the polymer type, processing method, and end use conditions.

Rubber is one of the most versatile construction materials used throughout the world. Raw rubber has poor physico-mechanical properties. To improve these properties ingredients such as accelerators, activators, antioxidants, and softeners must be added in small

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quantities. Oxidation of rubber can result in loss of physical properties such as tensile strength, elongation, and flexibility. Thus, the service life is determined by oxidation stability.

The properties and performance of a rubber product depend on many factors including the chemical nature of the rubber, the amount and kinds of ingredients incorporated into the rubber compound, processing and vulcanizing conditions, design of the product, and service conditions. Optimization of rubber properties by different methods of vulcanization and tests are required for the various rubber vulcanizates so that one can select the product, which will perform satisfactorily in service.

Normally, rubbers are vulcanized by systems based on sulfur or peroxide. The common feature of these systems is that they all require activation energy in the form of heat [1–2]. The properties of elastomers depend on their chemical structure and the number of their intermolecular bonds (crosslinking density).

Fillers have an important direct action on the physico-mechanical properties of the mixes. Some particulate fillers generally are uniformly distributed throughout the rubber during mixing. They influence the crosslinking reaction and, consequently, the physical and mechanical properties [3].

EPDM polymers are the fastest growing general-purpose elastomers on the market today. They have several advantages, including high resistance to ozone and oxidation, low temperature flexibility, color stability, and the ability to accommodate large quantities of filler and oil without creating unnecessary instability. This is due to both their hydrocarbon nature and their almost saturated backbone [4]. EPDM vulcanizates have been used extensively in electrical power cable, automotive radiator hose, and white sidewalls of tires. Moreover, the insulator compound used in solid propellant rocket motors is based on ethylene-propylene diene rubber because of their unusual ability to accept high loading of fillers and because of their excellent ozone, heat, and weathering resistance [5].

Considerable research efforts have been directed towards the aging of natural rubber and some synthetic rubbers vulcanizates. The effect of aging on physicomechanical properties of natural rubber and some synthetic rubbers loaded with white and/or black fillers has been studied [6–18], but few investigations have been devoted to the aging of EPDM rubber [3–5, 19–25].

The present investigation focuses on the effects of fillers, curing systems, and aging on the physico-mechanical properties of EPDM vulcanizates.

MATERIALS AND EXPERIMENTAL

Materials

The EPDM rubber (Vistalon 7000), with Mooney viscosity at 127°C = 55 cP, specific gravity = 0.86, and an ethylene content = 70% was supplied by Exxon Chemical. Eight fillers, namely, kaolin, quartz, PVC, talc, graphite, MT, SRF, and HAF and the rubber additions (stearic acid, zinc oxide [ZnO], sulfur [S], tetramethyl thiuram disulfide [TMTD], N-cyclohexyl-2-benzothiazyl sulfenamide [CBS], and processing oil) were of industrial grade and were supplied by USP, Jeddah, Saudi Arabia.

Sample Preparation

All rubber ingredients were accurately weighed and mixing was carried out in a laboratory mill with a roll diameter of 460 mm, working distance 300 mm, speed of the slow roll 24 rpm, and gear ratio 1:1.4. The roll temperature was kept at about 50°C during mixing.

The fillers (white and black) were added at a fixed level of 20 phr (part per hundred parts of rubber). TMTD was used as accelerator as well as a vulcanizing agent for samples W_1–W_8 because it is a sulfur-bearing compound as given in Table 1. Another vulcanizing system composed of CBS as the accelerator and sulfur as the crosslinking

TABLE 1 Rubber Formulations Containing Different White and Black Fillers Cured with TMTD

	Formula No.							
Ingredient, phr	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
EPDM	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
Processing oil	3	3	3	3	3	3	3	3
TMTD	3	3	3	3	3	3	3	3
Kaolin	20	—	—	—	—	—	—	—
Quartz	—	20	—	—	—	—	—	—
PVC	—	—	20	—	—	—	—	—
Talc	—	—	—	20	—	—	—	—
Graphite	—	—	—	—	20	—	—	—
MT	—	—	—	—	—	20	—	—
SRF	—	—	—	—	—	—	20	—
HAF	—	—	—	—	—	—	—	20

Phr: part per hundred parts of rubber.

TABLE 2 Rubber Formulations Containing Different White and Black Fillers Cured with S/CBS System

Ingredient, phr	Formula No.							
	W_9	W_{10}	W_{11}	W_{12}	W_{13}	W_{14}	W_{15}	W_{16}
EPDM	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
Processing oil	3	3	3	3	3	3	3	3
S	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Kaolin	20	—	—	—	—	—	—	—
Quartz	—	20	—	—	—	—	—	—
PVC	—	—	20	—	—	—	—	—
Talc	—	—	—	20	—	—	—	—
Graphite	—	—	—	—	20	—	—	—
MT	—	—	—	—	—	20	—	—
SRF	—	—	—	—	—	—	20	—
HAF	—	—	—	—	—	—	—	20

agent was used for samples W_9–W_{16} as given in Table 2. The compounded rubber was left overnight before vulcanization. The vulcanization press was operated at $162^\circ C \pm 1^\circ C$ for EPDM mixes under a pressure of about 4 MPa.

Torque Measurements

The rheometric characteristics of EPDM mixes were measured using a Monsanto Oscillating disk rheometer R- 100. The vulcanization process was operated at $162^\circ C \pm 1^\circ C$.

Physico-Mechanical Properties

From the vulcanized sheets, five individual dumbbell-shaped specimens were cut by a steel die of constant width (0.4 cm). The minimum thickness of the specimens was determined using a dial gauge. Benchmarks 15-mm apart were placed on the working part of the specimen being tested. The tensile strength and elongation at break were determined using a fully computerized Instron tensile testing machine-5586. The tensile strength is defined as the applied force per unit area of the original cross-sectional area at the time of rupture of the specimen, calculated in MPa. Ultimate elongation is the elongation at the moment of rupture. It is defined as the extension between two benchmarks.

Equilibrium swelling was carried out using toluene. It has been demonstrated by Kraus [26] that the swelling of vulcanizates in good solvents for the rubber gives an accurate measure of the degree of crosslinking.

Thermal Aging

The rubber samples were subjected to thermal oxidative aging at 90 $\pm$ 1°C for different time periods using air-circulating heating oven.

Tests of Rubber Mixes and Vulcanizates

The following standard methods were used:

- ASTM D 2084-95, (1994) for determination of t_{S2}, t_{C90}, ML, MH, and CRI using a Monsanto Rheometer-100.
- ASTM D412-98a (1998) for determination of physico-mechanical properties using Instron tensile testing machine (model-5568).
- ASTM D471-97 (1998) for swelling of rubber vulcanizates in toluene.
- ASTM D573-88 (1994) for thermal aging.

RESULTS AND DISCUSSION

Effect of the Type of Fillers and Curing System on the Rheological and Physico-Mechanical Properties of EPDM Vulcanizates

The rheometric characteristics and the physico-mechanical properties of EPDM vulcanizates containing white and black fillers cured by either TMTD (W_1–W_8) or S/CBS system (W_9–W_{16}) are presented in Tables 3 and 4, respectively.

From Table 3, it can be seen that for the vulcanizates containing white fillers and cured with TMTD system (W_1–W_4), the sample containing kaolin (W_1) had the lowest cure time (tc_{90}) and highest cure rate index (CRI). Also it had the highest tensile strength, elongation at break, and the lowest equilibrium swelling. Whereas the sample containing PVC (W_3) had the lowest tensile strength, elongation at break, and the highest equilibrium swelling. At the same time, the white fillers vulcanizates (W_9–W_{12}) cured with S/CBS system, which are presented in Table 4, possessed a shorter cure time and higher rate index compared with those cured with TMTD. Furthermore, S/CBS vulcanizates (W_9–W_{12}) possessed approximately similar tensile strength results.

TABLE 3 Rheometric Characteristics and Physico-Mechanical Properties of the Investigated Vulcanizates Cured with TMTD

	Formula No.							
Ingredient, phr	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
Rheometric characteristics at 162°C								
ML (dN m)	10	8	8	11	7.5	9	9	9
MH (dN m)	58	58	58	49	49	55	51	48
tc_{90} (min)	20	24	24	24	20	20	19	17
ts_2 (min)	2	2.5	2.5	3.7	2.5	2	2	2
CRI $(min)^{-1}$	5.56	4.65	4.65	4.76	5.71	5.56	5.88	6.67
Physico-mechanical properties								
TS, MPa	4.15	1.20	1.10	3.70	4.50	7.30	9.40	9.50
E, %	455	372	278	390	460	520	550	570
Q, %	195	205	232	199	172	161	149	142

Where: ML: minimum torque, MH: maximum torque, tc_{90}: Optimum cure time, ts_2: Scorch time, CRI: Cure rate index, TS: tensile strength, E: elongation at break, Q: equilibrium swelling.

On the other hand, for the vulcanizates containing black fillers cured with TMTD (W_5–W_8), the sample containing HAF (W_8) had the lowest cure time (tc_{90}) and highest cure rate index (CRI). The obtained data also show that the vulcanizates containing HAF had the highest tensile strength, elongation at break, and the lowest equilibrium swelling. While the vulcanizates containing graphite (W_5) had the lowest tensile strength, elongation at break and the highest equilibrium swelling for the same curing system. The vulcanizates (W_{13}–W_{16})

TABLE 4 Rheometric Characteristics and Physico-Mechanical Properties of the Investigated Vulcanizates Cured with S/CBS System

	Formula No.							
Ingredient, phr	W_9	W_{10}	W_{11}	W_{12}	W_{13}	W_{14}	W_{15}	W_{16}
Rheometric characteristics at 162°C								
ML (dN m)	8	8	10.5	8	7	8	8	8
MH (dN m)	85	85	85	85	85	89	82	84
tc_{90} (min)	21	16	19	21	18	18	17	18
ts_2 (min)	7.5	6.5	7.5	7.5	5.0	7.0	7.0	3.5
CRI $(min)^{-1}$	7.41	10.53	8.7	7.41	7.69	9.1	10.0	6.9
Physico-mechanical properties								
TS, MPa	4.15	1.25	1.12	3.80	4.80	7.70	10.1	10.9
E, %	310	293	210	300	450	470	505	510
Q, %	137	142	160	136	125	118	116	110

cured with S/CBS (Table 4) exhibit a shorter cure time and higher rate index in contrast with those cured with TMTD.

Therefore, it can be concluded from the obtained data presented in Tables 3 and 4 that vulcanizates cured with S/CBS system possessed slightly higher tensile strength values compared to vulcanizates cured with TMTD for both black and white fillers, whereas the equilibrium swelling shows reverse order. In addition, the mechanical properties of the EPDM vulcanizates containing black fillers exhibit higher values than those containing white fillers. Thus, the mechanical properties for the samples under investigation can be arranged in a descending order according to the type of fillers as follows:

$$\text{HAF} > \text{SRF} > \text{MT} > \text{graphite} > \text{kaolin} > \text{talc} > \text{quartz} > \text{PVC}$$

This can be attributed to the reinforcing effect of carbon black, which results in the increase of crosslinking density [5].

Effect of Thermal Stability on the Physico-Mechanical Properties of EPDM Vulcanizates

The EPDM mixes W_1–W_{16} containing the compounds shown in Tables 1 and 2 were vulcanized at $162 \pm 1^{\circ}C$ for the optimum cure time. The

TABLE 5 The Physico-Mechanical Properties of EPDM Rubber Vulcanizates Cured with TMTD after Aging for Different Time Periods

Formula No.		W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
Tensile strength, MPa.									
Time (days)	0	4.15	1.20	1.10	3.70	4.50	7.30	9.40	9.50
	2	3.94	1.10	1.06	3.48	4.50	7.30	9.40	9.50
	4	3.49	0.96	0.95	3.03	4.19	6.86	8.93	9.12
	6	2.86	0.76	0.80	2.48	3.83	6.35	8.37	8.65
	7	2.49	0.62	0.72	2.11	3.56	5.91	7.80	8.08
Elongation at break, %.									
Time (days)	0	455	372	278	390	460	520	550	570
	2	410	316	259	343	428	484	517	547
	4	378	279	236	312	405	463	495	524
	6	332	246	214	273	377	437	468	502
	7	309	223	203	254	359	421	451	496
Equilibrium swelling, %.									
Time (days)	0	195	205	232	199	172	161	149	142
	2	176	180	213	177	163	153	142	135
	4	156	154	190	155	153	145	136	131
	6	127	119	162	125	139	134	127	124
	7	107	96	139	103	129	126	119	116

TABLE 6 The Physico-Mechanical Properties of EPDM Rubber Vulcanizates Cured with S/CBS after Aging for Different Time Periods

Formula No.		W_9	W_{10}	W_{11}	W_{12}	W_{13}	W_{14}	W_{15}	W_{16}
Tensile strength, MPa.									
Time (days)	0	4.15	1.25	1.12	3.80	4.80	7.7	10.1	10.9
	2	3.49	1.01	0.96	3.15	4.22	6.93	9.29	10.25
	4	3.03	0.86	0.85	2.66	3.89	6.47	8.79	9.70
	6	2.57	0.73	0.73	2.28	3.41	5.78	7.78	8.72
	7	2.37	0.64	0.67	2.05	3.12	5.39	7.27	8.18
Elongation at break, %.									
Time (days)	0	310	293	210	300	450	470	505	510
	2	264	243	183	255	405	428	475	485
	4	233	199	162	213	374	400	434	459
	6	211	170	147	189	347	376	414	434
	7	195	161	141	180	329	357	394	418
Equilibrium swelling, %.									
Time (days)	0	137	142	160	136	125	118	116	110
	2	108	107	130	105	106	101	101	99
	4	90	88	109	87	94	92	94	92
	6	75	74	93	72	84	83	84	83
	7	71	65	88	67	75	77	79	77

rubber samples were subjected to thermal oxidative aging in an oven at $90 \pm 1^{\circ}C$ for various periods up to 7 days. The physico-mechanical properties of the aged samples were determined and are given in Tables 5 and 6. The retained values of tensile strength, the elongation

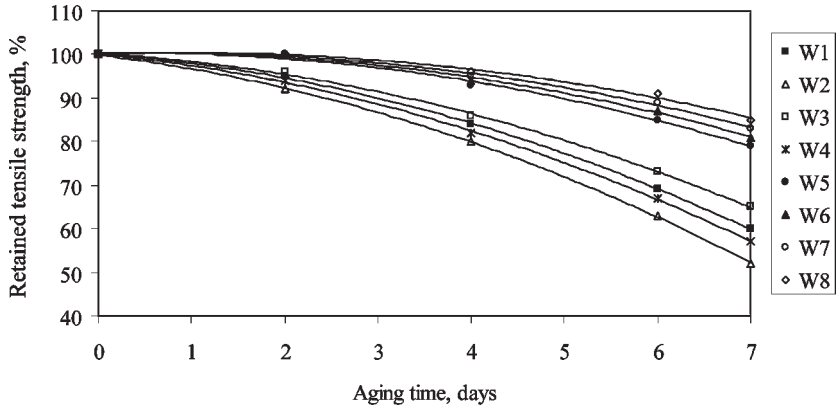

FIGURE 1 Retained tensile strength, % of EPDM vulcanizates cured with TMTD after aging for different time periods.

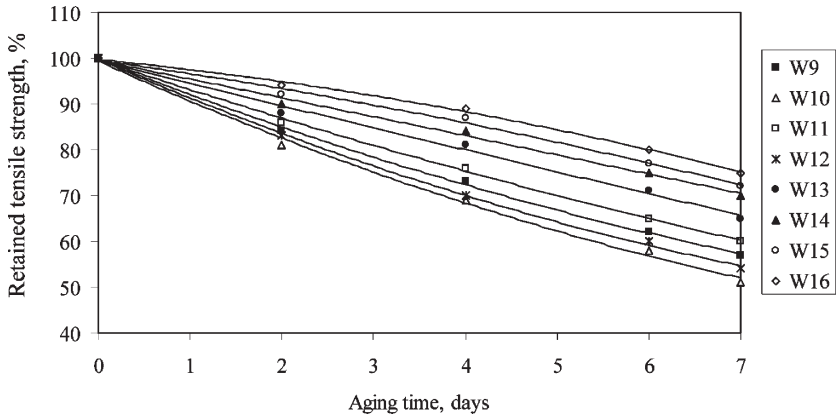

FIGURE 2 Retained tensile strength, % of EPDM vulcanizates cured with S/CBS after aging for different time periods.

at break, and the equilibrium swelling were calculated and plotted versus the aging time in Figures 1–6. Those values are taken as a measure of the heat resistance of EPDM vulcanizates. From these figures, it is clearly seen that the retained values of physico-mechanical properties decrease with increasing aging time.

Generally, it is clear from the obtained data, that the investigated white and black fillers can protect EPDM against thermal oxidative aging for up to 7 days. The enhancement and protection of EPDM properties found as a result of using the investigated fillers may

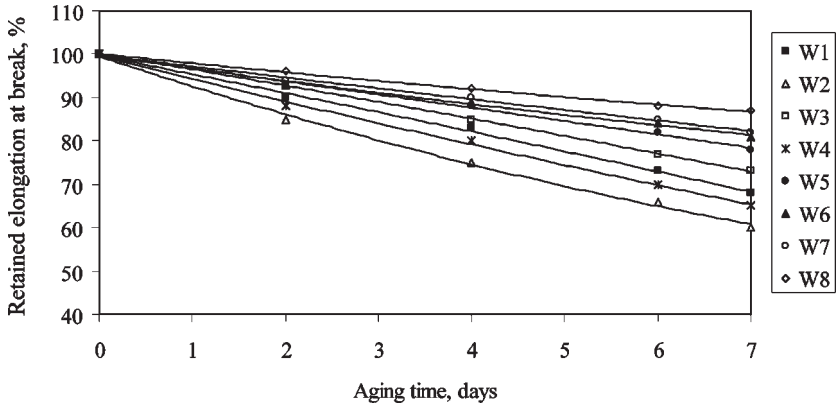

FIGURE 3 Retained elongation at break, % of EPDM vulcanizates cured with TMTD after aging for different time periods.

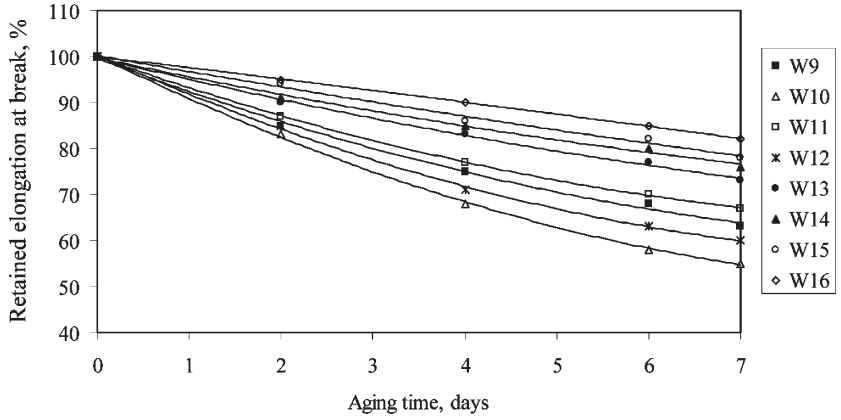

FIGURE 4 Retained elongation at break, % of EPDM vulcanizates cured with S/CBS after aging for different time periods.

be due to the specific activity of the solid surface or to a reduced diffusivity of air-oxygen caused by the filler particles. The activity was determined by the physical and chemical nature of the filler surface in relation to that of EPDM.

Also it is clear from Figures 1–4 that TMTD cured EPDM retains the tensile strength and elongation at break to a higher extent than sulfur cured EPDM. This may be attributed to the high bond strength cross-link (C-S-C, i.e., TMTD) that are superior in thermal stability than

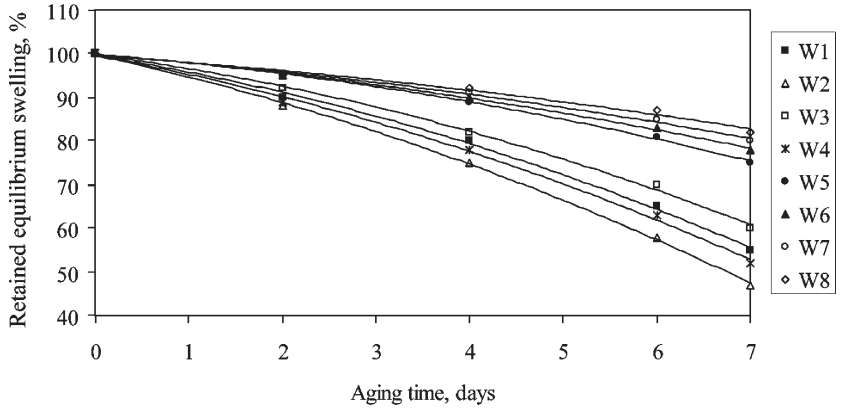

FIGURE 5 Retained equilibrium swelling, % of EPDM vulcanizates cured with TMTD after aging for different time periods.

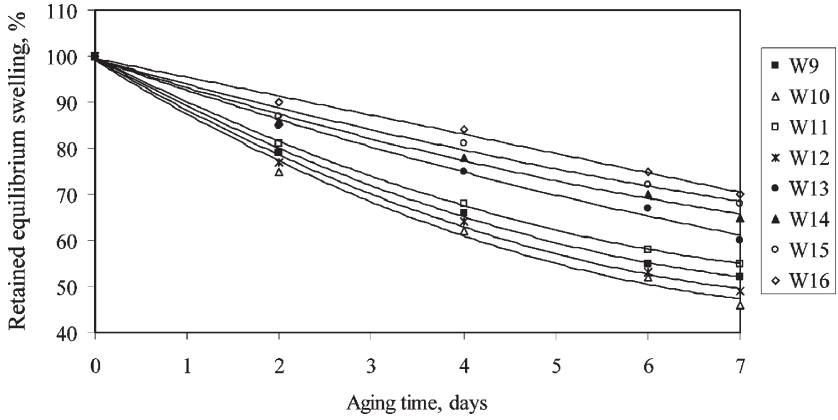

FIGURE 6 Retained equilibrium swelling, % of EPDM vulcanizates cured with S/CBS after aging for different time periods.

those of sulfur-cured compounds, with lower bond strength (C-Sx-C bonds). It can be concluded that TMTD cured EPDM has performance superior to the other vulcanizing system used against thermal aging. The heat resistance of vulcanizates can be arranged according to the vulcanizing systems used, in a descending order as follows:

$$\text{TMTD} > \text{S/CBS}$$

CONCLUSION

1. The vulcanizates containing S/CBS gave better physico-mechanical properties than TMTD.
2. EPDM vulcanizates containing black fillers had better physico-mechanical properties than those containing white fillers.
3. TMTD cured EPDM has thermal stability performance superior to the other vulcanizing system.

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