ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

Quarterly Report No. 2

INVESTIGATION OF ORGANIC CURING AGENTS FOR GR-S RUBBER

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Project 2376

DEPARTMENT OF THE ARMY
ORDNANCE CORPS, DETROIT ORDNANCE DISTRICT
CONTRACT NO. DA-20-018-508-ORD-(P)-42
PROJECT NO. 1180, RAD ORDER NO. 57180100-99-00604

September 1955

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ABSTRACT

Apparatus and methods used in the preparation of vulcanized GR-S rubber samples are described; aging and physical testing of these rubber vulcanizates are also discussed.

Repeatability tests showed that our apparatus and methods were satisfactory for preparing experimental samples of cured GR-S rubber.

GR-S cured with Methyl Tuads—El Sixty or Methyl Tuads—Captax had excellent aging properties. Optimum physical properties were obtained when 1.75 PHR of Methyl Tuads was used with either 1 PHR of El Sixty or Captax. The changes in the 300% modulus and the percent elongation on aging showed that the Methyl Tuads with El Sixty or Captax were superior to either the Santocure-Sulfur or the Tetrone A—Captax cures.

GR-S cured with Di Cup 40 C had aging properties superior to any curing system investigated with little, if any, change in physical properties on aging at 212°F for 72 hours. However, the original percent elongation was not as high as with the other curing systems. The addition of one extra PHR of PBNA over that in the GR-S improved the physical properties of the vulcanizate substantially.

The scorch tendencies of the nonfree sulfur systems were compared with Santocure-Sulfur using the "crumbling scorch test" and the Mooney viscometer. The latter method was shown to be preferable. The scorch of the Di Cup 40 C was nearly comparable to Santocure-Sulfur while Tetrone A—Captax was very poor and Methyl Tuads with Captax or El Sixty were intermediate. Addition of retarders to the Tetrone A—Captax or the Methyl Tuads—Captax systems did not show any marked improvement in scorch.

OBJECT

The object of this study was to investigate nonfree sulfur curing systems for GR-S rubber with the purpose of improving the aging properties of rubber without sacrificing any other important physical properties.

INTRODUCTION

Reproducibility of results and reasonable agreement with results from other laboratories were essential; therefore, check samples were prepared, tested, and compared with data from Rock Island Arsenal.

Experimental rubber vulcanizates were prepared and subjected to various physical tests in order to evaluate their processing and aging properties.

EXPERIMENTAL EQUIPMENT AND METHODS

MILLING

All batches were milled on a 3- x 8-in. Thropp mill using the following mixing procedure: (1) the GR-S 1500 was passed three times through a cold-tight mill (1 min); (2) the mill was opened to 0.055 in. and the rubber masticated, a 3/4 cut being made each half minute (10 min); (3) the ZnO was added (2 min); (4) one half of the carbon black was added, one 3/4 cut being made from each side and then the remainder of the black added (10 min); (5) the stearic acid and antioxidant were added (2 min); (6) the accelerator and vulcanizer were added (2 min); (7) three 3/4 cuts were made from each side (2 min); (8) the batch was cut from the mill and passed endwise through the mill six times at a mill setting of 0.030 in. (2 min); and finally (9) the mill was opened and the batch run out to give two uncured pads of approximately 6- x 6- x 0.1-in.

CURING

An electric-heated Preco hydraulic press and a 6- x 6- x 0.080-in. chromium-plated steel mold were used to cure the samples. The uncured pads were placed in the hot mold at 307°F, the pressure was raised to 2200 psi, the sample cured for 30 minutes at 307°F, and the cured pads were quenched in cold water.

AGING

A Precision-Freas mechanical convection oven was used for aging all specimens. The temperature control at 212°F was ± 0.7°F and the air flow used was 100 linear feet per minute through the aging chamber.

SPECIMEN TESTING

An Instron tensile testing instrument was used to obtain tensile, modulus, and percent elongation measurements. Eight specimens were cut from two 6- x 6-in. cured pads using an ASTM Die C; four were used as originals and four for aging.

A Shore durometer, Type "A", was used to determine specimen hardness.

A Mooney viscometer with a 1-3/16-in. rotor was used for determining scorch of the uncured rubber.

EXPERIMENTAL RESULTS

The use of the 3- x 8-in. mill required that single batches be limited to approximately 160 g, from which two 6- x 6-in. cured pads could be obtained. Thus, it was of primary importance to be able to repeat batches and obtain satisfactory check values on physical properties. Separate batches 1 and 7 (see Table I for compositions of all samples), using Santocure-Sulfur, and 2 and 8, using Tetrone A—Captax cures (Table II), showed that batches could be repeated and good check values obtained for the physical properties of the rubber vulcanizates. In addition, the values obtained for the physical properties were in satisfactory agreement with results on vulcanizates containing identical compositions reported by the Rock Island Arsenal staff. Therefore, we are satisfied that our methods are satisfactory for evaluating other vulcanizing systems.

It has been reported that thiuram disulfides (e.g., Methyl Tuads), used either alone or as accelerators, empart better aging properties to rubber vulcanizates than thiuram tetrasulfides (e.g., Tetrone A). The curing systems Methyl Tuads—El Sixty and Methyl Tuads—Captax were, therefore, investigated to determine their aging properties. Table III lists the physical properties of the rubber vulcanizates prepared using various PHR of Methyl Tuads with one PHR of either El Sixty or Captax.

When the PHR of Methyl Tuads were increased in the Methyl Tuads—El Sixty curing system, both the original and aged tensiles were increased. How-

TABLE I

COMPOUND FORMULATIONS*

Compounding Ingredient	Batch No.																				
	1,7, 23	2,8, 24	9	10	11	12	13	14	15	16,26	17	18,29	19	20	21	22	25	27	28	30	31	32
GR-S 1500	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc Oxide	3	3	3	3	3	3	3	3	3			3	3	3			3	3	3	3	3	3
Stearic Acid	1	1	1	1	2	2	2	2	1			1	1	1			1	1	1	1	1	1
PBNA					2	2	2	2		1	1		1	1								
Philblack A	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Sulfur	1.75				1.75	1.75												1.75				
Santocure	1				1	1												1				
Tetrone A		1					1.5	1.5											1			
Captax		1					1	1	1								1		1	1	1	1
Methyl Tuads			2	3					2			1.75					1.75			1.75	1.75	1.75
El Sixty			1	1								1										
Di Cup 40 C										2.5	5		2.5	5.0	2.5	5.0						
Vultrol						1		1										1	1	1		
Santoflex AW																					1	
Tenamene-2																						1

*All samples were cured at 307°F for 30 minutes.

TABLE II

REPEATABILITY OF COMPOUNDING, CURING, AND AGING METHODS*

Batch No.	Curing System	Tensile, psi		200% Modulus, psi		300% Modulus, psi		% Elongation		Shore A	
		Orig.	Aged	Orig.	Aged	Orig.	Aged	Orig.	Aged	Orig.	Aged
1	1.75 Sulfur + 1 Santocure	2680	2920	--	2330	2140	--	400	250	68	74
7	1.75 Sulfur + 1 Santocure	2870	2980	1180	2260	2170	--	410	250	68	73
2	1 Tetrone A + 1 Captax	2210	2380	--	1090	1330	1830	470	380	66	67
8	1 Tetrone A + 1 Captax	2230	2460	700	1030	1340	1850	460	390	65	67

*Aged specimens were air oven aged at 212°F for 72 hours.

TABLE III

PHYSICAL PROPERTIES OF VARIOUS NONFREE SULFUR CURES*

Batch No.	Curing System	Tensile, psi		200% Modulus, psi		300% Modulus, psi		% Elongation		Shore A	
		Orig.	Aged	Orig.	Aged	Orig.	Aged	Orig.	Aged	Orig.	Aged
101	1.5 Methyl Tuads 1 El Sixty	1970	2680			800	1270	650	610	63	65
18	1.75 Methyl Tuads 1 El Sixty	2310	2650			950	1290	650	580	65	65
9	2 Methyl Tuads 1 El Sixty	2620	2830			1200	1620	610	320	64	69
10	3 Methyl Tuads 1 El Sixty	2970	2890			1750	2070	500	270	67	72
100	1 Methyl Tuads 1 Captax	970	2080			440	950	640	600	61	64
25	1.75 Methyl Tuads 1 Captax	2350	2725			1020	1440	610	550	66	66
15	2 Methyl Tuads 1 Captax	2580	2850			1200	1610	580	490	66	66
21	2.5 Di Cup 40 C	2220	2270	1370	1420	--	--	280	290	67	67
22	5.0 Di Cup 40 C	1830	1940	--	--	--	--	130	130	75	76
16	2.5 Di Cup 40 C 1 PBNA	2420	2300	930	900	1730	1680	390	390	65	65
17	5.0 Di Cup 40 C 1 PBNA	2000	2060	--	--	--	--	190	190	72	71
19	2.5 Di Cup 40 C 3 Zinc Oxide 1 Stearic Acid 1 PBNA	2370	2290	800	820	1600	1550	430	430	65	66
20	5.0 Di Cup 40 C 3 Zinc Oxide 1 Stearic Acid 1 PBNA	2170	2350	1930	1970	--	--	210	220	72	72

*All cures were at 307°F for 30 minutes; all aged specimens were air oven aged at 212°F for 72 hours.

ever, the original tensile increased faster than the aged tensile and thus the two values approached each other at 3 PHR. The original percent elongation (%E) decreased gradually with increasing PHR of Methyl Tuads; however, the aged %E decreased very rapidly between 1.75 and 2 PHR of Methyl Tuads.

The Methyl Tuads—Captax curing system was similar to the Methyl Tuads—El Sixty system when the original and aged tensiles were compared. The aged %E, however, did not decrease as fast between 1.75 and 2 PHR of Methyl Tuads in the Captax as in the El Sixty system.

The optimum concentration of Methyl Tuads was 1.75 PHR in combination with 1 PHR of either El Sixty or Captax. Original and aged tensile values were about 2350 and 2700 psi, respectively, and original and aged %E values were about 630 and 570%, respectively. The optimum Methyl Tuads—El Sixty cure had slightly better physical properties than the optimum Methyl Tuads—Captax cure but the former had a noticeable bloom while this property was not serious with the latter. When the physical properties of these two systems were compared with Tetrone A—Captax (Table II) they both showed superior aging properties.

One of the most promising nonfree sulfur cures was the Di Cup 40 C cure (40% dicumyl peroxide on $CaCO_3$). Table II lists results obtained using 2.5 and 5.0 PHR of Di Cup 40 C alone, plus 1 PHR PBNA (GR-S 1500 contains 1.25 PHR PBNA) and with 3 ZnO + 1 stearic acid + 1 PBNA PHR. Although the original %E values were not as high as the thiuram cures no decrease in the %E occurred on aging for 72 hours at 212°F. The remaining physical properties were satisfactory and showed no change on aging. The results showed that 2.5 PHR of Di Cup 40 C was much better than 5.0 PHR in all cases. It is somewhat surprising that 1 extra PHR of PBNA using 2.5 Di Cup 40 C increased the tensile by 200 psi and the %E by 100 percent. Although Hercules Power Company advised against the use of ZnO and stearic acid, formulations containing these materials showed a slight improvement in the %E. However, considerably more variation was observed in the testing results with these materials present.

One objection to the nonfree sulfur cures has been that they are "scorchy." Efforts to use the "crumbling scorch test" described in Rock Island Arsenal TR-54-4255 were not completely successful. Table IV lists the physical properties for increasing aging times before curing for Santocure-Sulfur and Tetrone A—Captax with and without Vultrol. The data, with the exception of the low tensile and 300% modulus values for 1 and 2 days' aging with Santocure-Sulfur-Vultrol, are in fair agreement with those listed in the above-mentioned report. However, the "crumbling scorch tests" were inconclusive since in the Santocure-Sulfur combinations smearing on the mill rolls occurred. Even with the Tetrone A—Captax system without Vultrol, cracking, not crumbling, of the aged uncured pad occurred. The difficulty with the "crumbling scorch test" may have been with the size of the mill rolls.

Satisfactory scorch evaluations were made using a Mooney viscometer. Table V lists results obtained on a number of nonfree sulfur systems compared

TABLE IV

PHYSICAL PROPERTIES OF SAMPLES USED IN CHECKING THE "CRUMBLING SCORCH TEST"

Batch No.	Curing System	Time Aged at 212°F Before Curing	Tensile, psi	200% Modulus, psi	300% Modulus, psi	% Elongation	Shore A
11	1.75 Sulfur + 1 Santocure	0 days	3000	--	2020	420	68
11		1 ↑	2350	--	1560	440	65
11		2	2170	--	1310	500	59
11		3	2200	--	980	600	58
12	1.75 Sulfur + 1 Santocure + 1 Vultrol	0	2560	--	1480	430	66
12		1	640	--	310	640	61
12		2	670	--	400	580	56
12		3	1270	--	600	610	56
13	1.5 Tetrone A + 1 Captax	0 min	2300	1200	2040	320	69
13		15 ↑	2170	1330	--	300	70
13		30	2040	--	--	220	67
13		60	1860	970	--	250	65
14	1.5 Tetrone A + 1 Captax + 1 Vultrol	0	2210	1130	1980	320	68
14		30	2250	1130	1930	330	67
14		90	2000	1120	--	310	66
14		120	1900	1050	--	300	65

TABLE V

SCORCH EVALUATION BY MOONEY VISCOMETER (1)

Batch No.	Curing System	Mooney Scorch, min		1 PHR Vultrol Added Mooney Scorch, min		1 PHR Santoflex AW Mooney Scorch, min		1 PHR Tenamene-2 Mooney Scorch, min	
		t_i (2)	t_{20} (3)	t_i	t_{20}	t_i	t_{20}	t_i	t_{20}
23,27	1 Santocure 1.75 Sulfur	47	74	50	120				
24,28	1.5 Tetrone A 1 Captax	5	9	10	19				
25,30,31,32	1.75 Methyl Tuads 1 Captax	15	32	15	32	15	27	10	18
29	1.75 Methyl Tuads 1 El Sixty	12	26						
26	2.5 Di Cup 40 C 1 PBNA	25	94						

(1) All scorch runs were made at 250°F.
(2) Time in minutes for initial rise.
(3) Time in minutes for a 20-unit rise.

to Santocure-Sulfur. The time in minutes for an initial rise above the minimum, t_i, and the time in minutes for a rise of 20 units above the minimum, t_{20}, were recorded. A good criterion is usually t_i if the rate of increase in viscosity of the two systems compared is nearly equal. However, if the rate of increase in viscosity of the two systems is very different it is also important to determine t_{20}. The Santocure-Sulfur system had very good scorch properties and was used as a standard for comparison. The systems listed in the order of increasing scorch tendency were: Santocure-Sulfur, Di Cup 40 C—PBNA, Methyl Tuads—Captax, Methyl Tuads—El Sixty, and Tetrone A—Captax. Although t_i for Di Cup 40 C—PBNA was 25 minutes compared to 47 minutes for Santocure-Sulfur, the viscosity increase with time was very slow for the former and t_{20} was 94 minutes compared to 74 minutes. Therefore, the scorch properties of Di Cup 40 C were almost as good as for Santocure-Sulfur. The addition of Vultrol to the Tetrone—Captax cure improved the scorch properties; however, the addition of retarders to the Methyl Tuads—Captax cure at best did no good and with Tenamene-2 the scorch tendency was increased.

FUTURE WORK

Investigation of nonfree sulfur cures will continue with emphasis on the Di Cup 40 C system. It is planned to determine optimum compositions for this system and to study the action of various antioxidants since the concentration and type appear to be very important. Other physical tests than those listed in this report, such as flex life, will be investigated to determine whether other physical properties of nonfree sulfur vulcanizates are important.