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QUARTERLY REPORT NO. 4

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DEVELOPMENT AND FORMULATION OF LOW TEMPERATURE POLYISOBUTYLENE (BUTYL) RUBBER COMPOUNDS

REPORT FOR QUARTER ENDING DECEMBER 31, 1948

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INTRODUCTION

Our previous work with mixtures of p-quinone dioxime, benzothiazyl disulfide and sulfur, as a vulcanizing combination for Butyl rubber compounds, revealed that such a combination produced compositions having (1) rapid rate of cure without scorch at processing temperatures, (2) a flat curing curve as regards tensile strength vs. curing time, and (3) marked superiority to conventionally sulfur-cured compositions with regard to heat resistance. A fundamental study of the overlapping vulcanization mechanisms by means of which such a combination functions, would undeniably be justified and would offer an almost unlimited amount of theoretical work to those disposed and equipped to undertake it. We have felt however, since this is, in the strict sense, a program of development and application research, that its objectives might more quickly be attained by an empirical study of the critical quantities of each ingredient in the aforementioned combination. Such a study was undertaken and completed in the period covered by this report.

A masterbatch base stock consisting of Butyl rubber, zinc oxide, carbon black, and plasticizer, was first prepared and used throughout the investigation of vulcanizing combinations. Use of the stock minimized processing time and increased the uniformity of results. The amount of each ingredient of the vulcanizing combination was varied between practicable limits while keeping the quantities of remaining components constant.

In no instance was the amount of any ingredient found to be exceptionally critical. Both p-quinone dioxime and benzothiazyl disulfide were found to be essential to vulcanization, since omission of either component resulted in severely undercured compositions, but from 2 to 4 parts by weight per hundred of rubber could be used without significant variation in physical properties. From 2 to 3 parts of p-quinone dioxime were optimum, while 4 parts of benzothiazyl disulfide gave best results. The amount of sulfur used in the combination was found to be even less critical, but 1.5 parts was of definite value in speeding up the rate of cure, boosting ultimate tensile strength, and increasing heat resistance.

Substitution of other organic accelerators for benzothiazyl disulfide in the combination was quick to reveal the importance of such accelerators in the quinoid-sulfur cure. Thiazole, thiuram, and dithiocarbamate accelerators were all investigated in this regard. Accelerators such as diphenyl guanidine when substituted in comparable quantity for the benzothiazyl disulfide produced no cure at all. very Mercaptobenzothiazole was only slightly more effective. The cupric salt of mercaptobenzothiazole was moderately activating, while zinc diethyl dithiocarbamate was comparable to the original benzothiazyl disulfide. Tetramethyl thiuram disulfide produces compositions with good physical properties, and the selenium and tellurium diethyl dithiocarbamates were especially effective in producing a fast curing rate and high ultimate tensile strength. Experimentation indicates that tellurium diethyl dithiocarbamate is slightly inferior to the original benzothiazyl disulfide in regard to heat resistance of the vulcanized composition, but the curing rate and ultimate tensile are much superior.] to here

The heat resistance of quinoid-sulfur cured compositions was found to be vitally affected by the type of filler used. Carbon blacks were by far the most effective in this connection, and considerable work was done with combinations of clay and carbon black to obtain compositions with both low temperature flexibility and some measure of heat resistance. The function of carbon black in the quinoid-sulfur cure is not fully understood, but it undoubtedly plays a dual role of filler and activator. Increasing the carbon black content materially increased both the rate and ultimate degree of cure. Moduli of over 2000 pounds per sq. inch at 500 percent elongation were obtained with carbon black filled compositions.

The addition of small percentages of polyisobutylene (Vistanex) was also found to be of value in improving the heat resistance of Butyl rubber compounds. A critical factor in this effect is the molecular weight of the polyisobutylene used, since only the material of about 100,000 molecular weight was effective. Material of lower or higher molecular weight gave a negative result.

Low temperature evaluation of quinoid-sulfur cured compositions indicated they were all capable of passing the "Thiokol bend" test, ASTM designation D736-46T, at -55°C, and some could survive this test at -65 C. None could pass at -70°C. At a discussion between the Squier Signal Laboratory and representatives of this company, it was agreed that we should continue our evaluation at low temperatures by means of this simple flex test. The opinion was mutually held that while many complex testing devices were known to be capable of supplying information on a variety of theoretical properties of rubber compounds at low temperatures, and while such information would be of fundamental value, the benefit to this program was not sufficient to justify the required expenditure of time and money.

It was decided therefore, that we would submit to the Squier Laboratory those compositions which we believe to be of merit after such initial testing as mentioned above, and that they in turn will mold and cure the compositions into such practical items as grommets and push button covers, and evaluate these from an application standpoint in their low temperature rooms. We believe it is essential that we witness molding, curing, and testing of these compounds at the Squier Laboratory, in order that we may observe their behavior at first hand. In this way we can correlate our own test results with those obtained in the low temperature rooms.

Such a practical evaluation of the low temperature performance of Butyl rubber compounds will be, we believe, more valuable to this program than any number of theoretical tests.

EXPERIMENTATION

Polyisobutylene (Vistanex B100) in Butyl Rubber Compounds

Various proportions of polyisobutylene having a molecular weight of 100,000 were incorporated into crude Butyl Rubber GR-I-Y15, and the resulting blends conventionally compounded and cured. The polyisobutylene was added to the GR-I-Y15 after the latter had formed a thin band on a warm two roll mill. Mixing was easy and rapid. The mill was then cooled and the remaining compounding ingredients added. No abnormalities in compounding or milling behavior could be observed. The compounds were subsequently cured for 15 and 30 minutes at 287°F, and their physical properties recorded.

Increasing amounts of polyisobutylene were observed to effect a reduction in curing rate and an increase in compression set commensurate with the reduction in unsaturation. Tensile strength was not appreciably affected providdd an adequate cure was obtained, but the ability of Butyl rubber compounds to retain their tensile strength after exposure to air at high temperatures, was considerably improved. This latter effect is shown in Table I. Samples were aged in a ventilated air oven at 150°C for 48 hours. They were then allowed to remain at room temperatures for 24 hours and their tensile strength compared with that of samples of the same compound which had been aged at room temperature for the same period of time. Percent tensile retained was then expressed as:

$$\% \text{ tensile} = 100 \times \frac{\text{tensile of sample aged at 150 C}}{\text{tensile of sample aged at room temp.}}$$

TABLE I

EFFECT OF VISTANEX B-100 ON HEAT RESISTANCE*

Parts Vistanex	% Tensile Retained
0	60
1	63
2	69
5	73
10	64
15	60
20	58

*Samples aged 48 hours in air at 150°C.

Base Formula (by weight)

GR-I-Y15	100
Zinc oxide	5
Dioctyl sebacate	15
p-Quinone dioxime	2
Benzothiazyl disulfide	4
Sulfur	1.5
Vistanex	(as shown)

All subsequent heat resistance data in this section of the report was so obtained and is so expressed.

Zinc Oxide Content of Butyl Rubber Compounds

From 2 to 50 parts of zinc oxide (Protox 166) were incorporated into Butyl rubber compounds. At least 2 parts were essential to cure and at least 5 parts were required to obtain a maximum rate of cure. Some slight improvement in heat resistance was noted with higher amounts of zinc oxide, and this effect is shown in Table II

Component Ingredients in the Quinoid Type Cure

The p-quinone dioxime-benzothiazyl disulfide-sulfur curing combination for Butyl rubber was thoroughly investigated to determine the part played by each of the ingredients in the vulcanization mechanism. In order to facilitate the investigation, and to insure uniformity of results, 15 pounds of a masterbatch were prepared containing the following base stock:

GR-I-Y15	100 parts
Zinc oxide	5
Fine thermal black (P-33)	50
Dioctyl sebacate	15

Portions of this masterbatch were then used to prepare the desired compounds by adding the curing ingredients on a cold two roll mill until they were completely dispersed. The masterbatch was kept at room temperature in the laboratory over a three month period with no detectable change in properties.

TABLE II

EFFECT OF ZINC OXIDE ON HEAT RESISTANCE*

Parts Zinc Oxide	% Tensile Retained
2	49
5	60
10	62
20	63
50	63

*Samples aged 48 hours in air at 150°C.

Base Formula (by weight)

GR-I-Y15	100
Dioctyl sebacate	15
p-Quinone dioxime	2
Benzothiazyl disulfide	4
Sulfur	1.5
Zinc oxide	(as shown)

The amount of p-quinone dioxime in the compound was varied from zero to 4 parts per hundred of rubber hydrocarbon (RHC). The effect of this variation is shown in Table III. At least one part of the dioxime appears to be essential to cure but above that the amount is not critical. 2 or 3 parts seem to give optimum physical properties and maximum rate of cure.

The amount of benzothiazyl disulfide in the compound was varied from zero to 8 parts. The effect of this variation is shown in Table IV. 4 parts produce optimum physical properties and maximum rate of cure.

The amount of elemental sulfur in the compound was varied from zero to 3 parts. The effect of this variation is shown in Table V. This substance is not essential to cure but its inclusion improves ultimate tensile strength and speeds up the rate of cure. The amount used does not appear to be critical but 1.5 parts were selected as optimum. 2 parts or more produced an appreciable bloom.

A further study of the part played by component ingredients in the quinoid type cure was made by substituting various other accelerators for benzothiazyl disulfide in the curing combination. Accelerators so substituted were (1) diphenyl guanidine, (2) tetramethyl thiuram disulfide, (3) mercaptobenzothiazole, (4) cupric salt of mercaptobenzothiazole, (5) zinc diethyl dithiocarbamate, (6) tellurium diethyl dithiocarbamate, and (7) selenium diethyl dithiocarbamate. 4 parts per hundred of rubber hydrocarbon were used in every case. The compound containing diphenyl

TABLE III

EFFECT OF p-QUINONE DIOXIME ON PHYSICAL PROPERTIES

Parts Dioxime	Cure* Minutes	Tensile lb./sq.in.	Elong %	Modulus 500%	Hardness Shore
0	15	430	1000	negligible	28
	30	450	1000	negligible	28
1	15	1090	990	250	33
	30	1810	850	510	34
2	15	1290	710	360	36
	30	1440	780	580	38
3	15	1470	890	420	40
	30	1420	710	600	41
4	15	1260	870	425	42
	30	1300	750	590	42

*287°F

Base Formula (by weight)

GR-I-Y15	100
Zinc oxide	5
Dioctyl Sebacate	15
P33 Carbon	50
Benzothiazyl disulfide	4
Sulfur	1.5
p-Quinone dioxime	(as shown)

TABLE IV

EFFECT OF BENZOTHIAZYL DISULFIDE ON PHYSICAL PROPERTIES

Parts Disulfide	Cure* Minutes	Tensile lb./sq.in.	Elong %	Modulus 500%	Hardness Shore
0	15	450	1000	negligible	35
	30	710	980	130	37
1	15	830	910	250	37
	30	1300	870	400	38
2	15	1260	860	310	37
	30	1420	850	480	39
4	15	1300	800	580	41
	30	1530	760	640	42
8	15	1310	750	600	43
	30	1300	770	520	42

*287°F

Base Formula (by weight)

GR-I-Y15	100
Zinc oxide	5
Dioctyl sebacate	15
P33 Carbon	50
p-Quinone dioxime	2
Sulfur	1.5
Benzothiazyl disulfide	(as shown)

TABLE V

EFFECT OF SULFUR ON PHYSICAL PROPERTIES

Parts Sulfur	Cure* Minutes	Tensile lb./sq.in.	Elong %	Modulus 500%	Hardness Shore
0	15	960	960	280	36
	30	1500	880	390	41
0.5	15	1500	890	380	41
	30	1590	870	400	42
1.0	15	1610	850	400	43
	30	1610	850	480	45
1.5	15	1700	750	380	46
	30	1730	760	640	46
3.0	15	1550	740	590	45
	30	1500	770	520	46

*287°F

Base Formula (by weight)

GR-I-Y15	100
Zinc oxide	5
Dioctyl sebacate	15
P33 Carbon	50
p-Quinone dioxime	2
Benzothiazyl disulfide	4
Sulfur	(as shown)

guanidine would not cure at 287°F. The compound containing mercaptobenzothiazole showed only partial cure. The physical properties of compounds incorporating the accelerators listed above are shown in Table VI.

Carbon Black-Clay Filler Combinations in Butyl Rubber Compounds

Carbon black, represented by Philblack A, and Clay, represented by Whititex, were combined in various proportions and added to Butyl rubber stocks so that their total weight equalled 60 parts per 100 of rubber hydrocarbon. The filler combinations were added to the crude rubber on a two roll mill. Zinc oxide was then added, followed by dioctyl sebacate, and finally by the curing agents. The base formula was as follows:

GR-I-Y15	100
Filler Combination*	60
Zinc oxide	10
Dioctyl sebacate	15
p-Quinone dioxime	2
Tellurium diethyl dithiocarbamate	4
Sulfur	1.5

*	A	B	C	D	E	F
Clay (Whititex)	60	48	36	24	12	0
Carbon (Philblack A)	0	12	24	36	48	60

Physical properties of compounds containing these filler combinations are shown in Table VII. The effect of these filler combinations on the physical properties of the same compounds

TABLE VI

ORGANIC ACCELERATORS IN DIOXIME CURE*

Accelerator 40 parts	Tensile lb./sq.in.	Elong. %	Modulus 500%
Mercaptobenzothiazole	400	1100	
Cupric salt mercaptobenzothiazole	1440	1050	270
Benzothiazyl disulfide	1680	830	510
Tetramethyl thiuram disulfide	2280	780	520
Zinc diethyl dithiocarbamate	1670	880	470
Tellurium diethyl dithiocarbamate	2300	740	585
Selenium diethyl dithiocarbamate	2160	790	500
Diphenyl guanidine	no appreciable cure		

* 15 minutes at 287°F

Base Formula (by weight)

GR-I-Y15	100
Zinc oxide	5
Dioctyl sebacate	15
P33 Carbon	50
p-Quinone dioxime	2
Sulfur	1.5
Accelerator	4.0

TABLE VII

EFFECT OF CLAY AND CARBON FILLER ON PHYSICAL PROPERTIES

Filler per 100 g. RHC		Cure*	Tensile	Elong.	Modulus	Hard.
Whititex	Philblack A	Min.	lb./sq.in.	%	500%	Shore
60g.	--	15	2070	870	330	35
		30	910	560	690	38
48g.	12g.	15	1950	860	480	38
		30	1710	660	940	41
36g.	24g.	15	1990	770	840	44
		30	2030	630	1380	44
24g.	36g.	15	2030	730	1120	46
		30	2150	630	1580	48
12g.	48g.	15	1990	700	1320	50
		30	2130	570	1900	52
--	60g.	15	1690	640	1390	51
		30	2120	500	2060	56

* 287°F

when heat aged is shown in Table VIII, and their effect on tensile strength retention is graphically illustrated in Fig. 1.

All of the compounds in this series passed the Thickol bend test, ASTM designation D736-46T, at -65°C. All failed at -70°C. Manual examination of the samples indicated however, that flexibility decreased with increasing carbon black content.

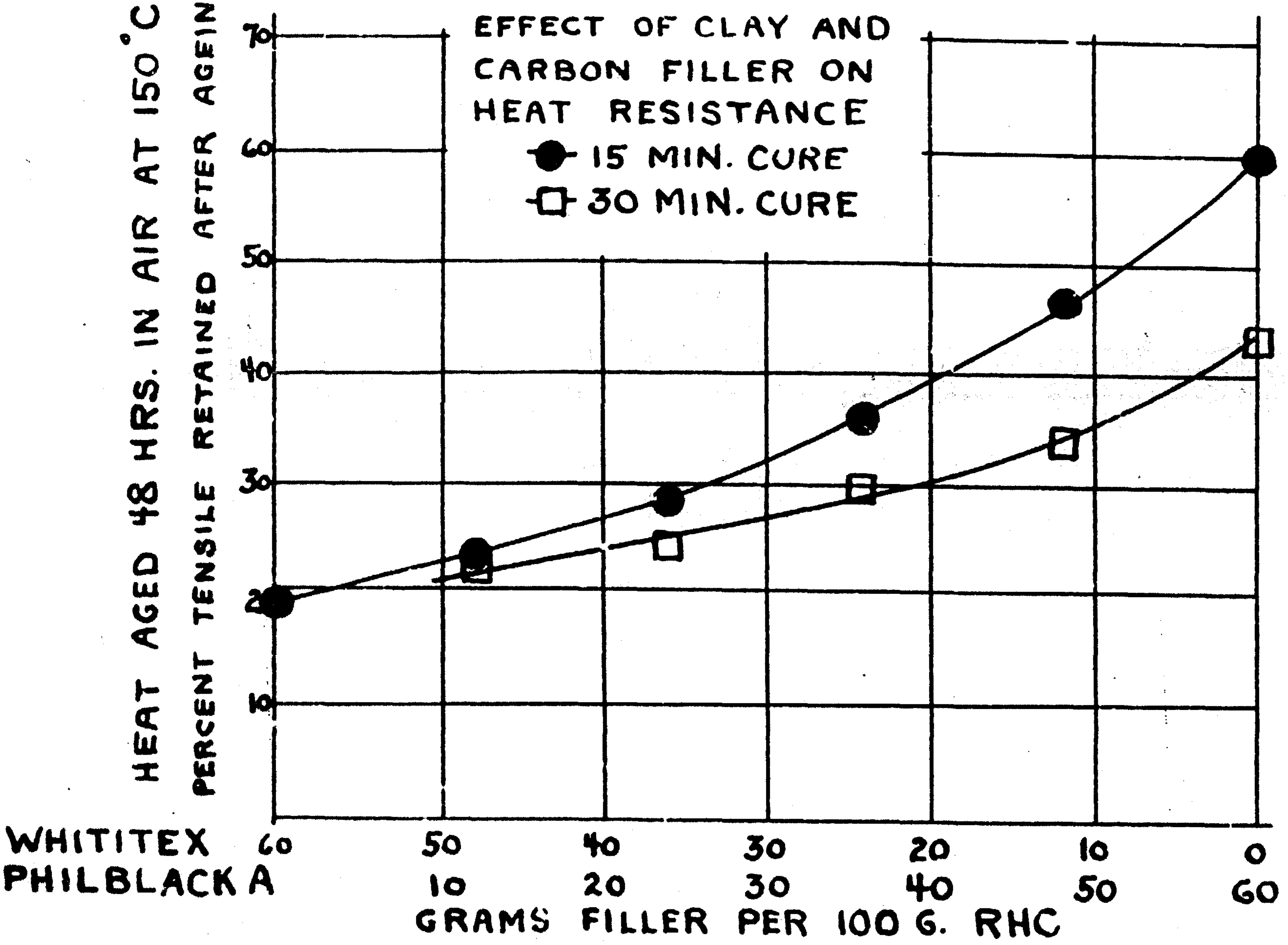
TABLE VIII

EFFECT OF CLAY AND CARBON FILLER ON HEAT RESISTANCE

Filler per 100 g. RHC			Aged 48 hours in Air at 150°C		
Whititex	Philblack A	Cure* Min.	Tensile	Elong.	Hardness
60g.	--	15	395	500	35
		30	310	490	34
48g.	12g.	15	450	470	44
		30	370	480	41
36g.	24g.	15	560	450	49
		30	490	460	47
24g.	36g.	15	730	390	53
		30	610	390	54
12g.	48g.	15	940	350	62
		30	710	370	63
--	60g.	15	1010	320	65
		30	910	320	72

* 287°F

Fig. 1


EFFECT OF CLAY AND
CARBON FILLER ON
HEAT RESISTANCE
● 15 MIN. CURE
□ 30 MIN. CURE
HEAT AGED 48 HRS. IN AIR AT 150°C
PERCENT TENSILE RETAINED AFTER AGEING
70
60
50
40
30
20
10
WHITITEX
PHILBLACK A
60
50
40
30
20
10
0
10
20
30
40
50
60
GRAMS FILLER PER 100 G. RHC

PROGRAM PROSPECTUS

Work carried out previous to this writing has resulted in the formulation of Butyl rubber compounds possessing properties which, in a majority of instances, equal or surpass specifications set forth by the Signal Corps in the original contract. Compounds have been prepared which (1) are flexible below -55°C, (2) have less than 30 percent compression set at constant deflection, and (3) have adequate tensile strength and elongation. These same compounds retain 70% of their original tensile strength after ageing in air at 150°C for 48 hours. This latter figure is, of course, not sufficient to meet the specification of stability at 200°C. Moreover, the Shore hardness of these compounds exceeds 80 at -55°C, as compared to the specification figure of 50.

We believe, however, that further improvement in both low and high temperature performance is entirely possible. Work is now under way to reduce the extreme hardness of these compounds below -55°C by the introduction of non volatile "plasticizers" such as thermally reverted crude Butyl rubber.

Low temperature performance especially, is vitally affected by degree or "tightness" of cure, and heat resistance has proved subject to drastic variation when the mechanism of vulcanization is altered. Consequently further refinement of the quinoid-sulfur cure will be undertaken, and efforts will be made to obtain a higher degree of cure in the shortest possible curing time.

In connection with cure studies, a method for the evaluation of scorch by means of solvent swell will be set up.

Heat resistance may conceivably be increased by the use of certain antioxidants and inhibitors. It is our intention to investigate this possibility fully.

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