THE UNIVERSITY OF MICHIGAN
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NON-FREE SULFUR CURING SYSTEMS FOR AGE RESISTANT BUTADIENE-STYRENE RUBBER

L. M. Hobbs
R. G. Craig
C. W. Burkhart

Engineering Research Institute
and
Michigan Memorial-Phoenix Project
University of Michigan
Ann Arbor

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ABSTRACT

The resistance to air-oven aging of styrene-butadiene synthetic rubber vulcanizates cured, (a) with accelerators, (b) with dicumyl peroxide and with phenyl β-naphthyl amine, and (c) with combinations of (a) and (b), has been studied. Attention was given to the processing stability of the uncured compositions, and limited work was devoted to the supression of the blooming tendencies of certain vulcanizates from (a).

It was found that vulcanizates from all of these non-free sulfur curing systems possessed substantially greater resistance to aging than did the vulcanizate from the conventional free sulfur-accelerator combination, with vulcanizates from (c) showing the greatest resistance.

The tensile properties of the unaged vulcanizates from (c) were essentially equivalent to those from the free sulfur-accelerator system, while the tensile and tear strengths of vulcanizates from (a) and (b) were somewhat less than those of vulcanizates from the free sulfur-accelerator combination. It is noteworthy that the presence of phenyl β-naphthyl amine and certain accelerators make the dicumyl peroxide vulcanizate both stronger and more age resistant.

The time of resistance to scorch and thermal decomposition of the raw unvulcanized compositions at 250°F was found to be: 20-30, 30, and 30-40 minutes for compositions (a), (b), and (c), respectively, as compared with 60 minutes for the free sulfur-accelerator composition.

The raw materials cost of the dicumyl peroxide-phenyl β-naphthyl system (b) is 1.8% greater, and of the other systems, (a) and (c), 5.2 - 5.8% greater than that of the free sulfur-accelerator system, as calculated for a composition containing 50 PHR carbon black.

It is concluded that the age resistance and physical properties of vulcanizates formed by the action of dicumyl peroxide in combination with certain accelerators and phenyl β-naphthylamine (c), can justify some limitation in processing stability and the small increase in materials cost for the production of rubber articles for applications in which good age resistance is necessary.

INTRODUCTION

There is a general need to improve the age resistance of rubber vulcanizates. Non-free sulfur curing systems (1-6) have been shown to yield vulcanizates of improved age resistance. However, the uncured compositions (1, 5, 6) have been reported to be sensitive to scorching or precuring during processing, and to yield vulcanizates with poor tensile properties. Furthermore, the non-free sulfur systems comprising complex synthetic organic chemicals are more expensive than those based on elemental sulfur.

The purposes of this study were to examine several non-free sulfur curing systems with the hope of identifying combinations which could be processed at reasonable cost and which would yield vulcanizates of satisfactory physical properties and age resistance.

Three types of curing systems for styrene-butadiene-41°F. synthetic rubber (SBR-1500) were studied:

(a) Combinations of vulcanization accelerators

(b) Dicumyl peroxide with phenyl-β-naphthyl amine

(c) Combinations of (a) and (b)

The results presented below show that each of the three systems yield vulcanizates with substantially greater age resistance than the vulcanizates produced by the action of free sulfur-accelerator systems with vulcanizates from (c) being the most age resistant. Rubber compositions containing dicumyl peroxide and accelerators (b) could be held in air at 250°F. for 30-40 minutes without damage, and on curing for 30-40

minutes at 307°F they yielded vulcanizates with physical properties essentially equivalent to those of the free-sulfur cured products. The raw materials cost of the compound containing peroxide (b) is 1.8% greater, and of the other compounds 5.2-5.8% greater than the cost of the conventional free sulfur-accelerator composition.

The details of the study are presented in the following sections.

EXPERIMENTAL PART

Materials

SBR-1500, styrene (30) - butadiene (70) copolymer prepared at 41°F., was used as the base rubber throughout this study. The SBR-1500 was compounded with 50 PHR of medium abrasion furnace black (MAF) and with various vulcanizing agents. In the subsequent sections the particular rubber composition will be specified simply by identifying the nature and proportions of the vulcanizing agents. In the production of SBR-1500, approximately 1.25 PHR of phenyl-β-naphthylamine (PBNA) are added by the manufacturere, however, in identifying the experimental formulations PBNA will be specified only when an additional quantity of the material was used in compositions containing dicumyl peroxide.

In Table I, the compositions of the important formulations are listed. Other compositions of the same basic types were used and will be referred to by reference to the composition type and the amount of the curing agents. Compositions I and II were chosen as reference compositions for the preparation of the corresponding vulcanizates I and II; these reference vulcanizates were used as standards for comparing the physical properties and the age resistance of experimental vulcanizates. Composition I contained a commonly used vulcanizing system consisting of free sulfur plus N-cyclohexyl-2-benzothiazyl sulfenamide (NCHBTSA) and composition II contained the sulfur-bearing accelerators dipentamethylene-thiuram-tetrasulfide (DPMTTS) and 2-mercaptobenzothiazole (MBT). This latter curing system has received considerable attention by Ossefort, Shaw and Bergstrom (6) as a non-free sulfur curing system which yields a vulcanizate with excellent age resistance.

Preparation of Vulcanizates

All compositions were prepared on a 3" x 8" two roll mill using the ASTM mixing procedure for SBR rubber (D 15-55T). Since 200 grams of material represented the maximum amount that could be easily handled on this equipment, special care during compounding was required in order that separate batches of the same composition yielded vulcanizates having the same physical properties.

The rubber compounds were placed in a single cavity (ASTM specification D 15-55) 6" x 6" x 0.075" chromium plated steel compression mold, cured for 30 minutes at 2200 psi and 307°F, and the cured sheets were quenched in cold water.

The same lot of SBR-1500 was used throughout this research with the exception of a few aging experiments which were carried out on a second lot. The curing systems consisting of free sulfur and accelerator and combinations of sulfur-bearing accelerators yielded vulcanizates having comparable physical properties with each lot of SBR-1500. However, in curing systems containing DCP-40, it was necessary to increase the amount of DCP-40 by 0.25 PHR for the second lot in order to obtain comparable physical properties with the first. In order to avoid confusion, the amount of DCP-40 recorded has been on the basis of the first lot.

Physical Measurements

Tensile and tear specimens were cut from the test sheets by ASTM tensile die C (ASTM D 412-51T) and ASTM tear die C (ASTM D 624-54), respectively. The tensile and tear measurements were made on an automatic, recording tensile testing machine at 77°F and 50% relative humidity. The physical properties of the vulcanizates reported in succeeding tables are average values of four or more determinations.

Hardness values were determined according to ASTM Method D 676-55T.

The scorch characteristics of the uncured compositions were determined by use of a shearing disk viscometer at 250°F according to ASTM Method D 1077-55T. Duplicate experiments were made on all compounds evaluated.

The scorch test, ASTM D 1077-55T, was not entirely satisfactory for the compositions containing dicumyl peroxide since the peroxide tends to decompose without forming cross-links at temperatures approaching 250°F. Another procedure was devised to indicate the processing behavior of uncured compositions containing dicumyl peroxide in the temperature range of 230-250°F. The uncured compound was sheeted on the mill at about 0.080" thickness and 4" x 4" pads were cut out of the sheets. The pads were placed in a circulating air oven at a temperature in the range of 230-250°F for periods up to three hours. After this heating period, the pads were cured by the procedure described above for thirty minutes at 307°F and 2200 psi. The tensile properties of the cured sheets could then be used as the basis for estimating the extent of the decomposition of the peroxide due to heating of the uncured compositions.

A mechanical convection oven was used for the aging experiments. The temperature variation of the oven at 212°F was within ±1°F. The conditions for most of the aging experiments were 72 hours at 212°F. However, the aging properties of selected compositions were determined for periods of 32 days at 212°F, 7 days at 250°F and for 12 hours at 300°F.

Since it had been shown by Fackler and Rugg (7) that migration of compounds such as antioxidants can take place between specimens during air-oven aging experiments, only similar types of vulcanizates were aged at a given time.

PRESENTATION OF RESULTS

Accelerator Vulcanizing Systems

As mentioned in the Introduction, combinations of the accelerators (which are frequently used with free sulfur) were employed as the total vulcanizing system in the absence of added free sulfur. Three systems were studied:

(a)	1 PHR	Dipentamethylene-thiuram-tetrasulfide	(DPMTTS)
	1 PHR	2-Mercaptobenzothiazole,	(MBT)
(b)	1 PHR	Dibenzothiazole-dimethylthiol urea	(DBTDMTU)
	1-3 PHR	Tetramethyl-thiuram-disulfide, and	(TMTD)
(c)	1 PHR	2-Mercaptobenzothiazole	
	1-2 PHR	Tetramethyl-thiuram-disulfide.	

Also, as previously mentioned, the first composition (a) was selected as a reference standard (reference composition II).

The ultimate tensile and elongation values of the vulcanizates prepared from the second and third compositions, (b) and (c), are plotted in Figures 1a and 1b. The values of the physical properties after air-oven aging are also shown on the graph. It may be seen from these curves that the optimum compositions are approximately:

(III)	1.75 PHR	TMTD
	1 PHR	DBTDMTU, and
(IV)	1.75 PHR	TMTD
	1 PHR	MBT.

The physical properties of vulcanizates prepared from the two optimum compositions, III and IV, as well as those of the reference vulcanizates I and II are listed in Table II. Vulcanizates from compositions III and IV possessed lower values of tensile strength, stress at 300% elongation (300% modulus), and hardness, about the same tear resistance and considerably higher elongation values than reference vulcanizate I which was cured with

sulfur plus NCHBTSA. Vulcanizates III and IV had physical properties which were generally comparable to the non-free sulfur cured reference standard II, although the elongation values of vulcanizates III and IV were somewhat higher.

When the physical properties of the aged samples in Table II are compared, however, it is apparent that vulcanizates from compositions III and IV were somewhat more resistant to aging than the reference vulcanizate II and they were substantially more resistant than reference vulcanizate I.

The scorch resistance of compositions III and IV and reference compositions I and II, as measured by a shearing disk viscometer, are also reported in Table II. Compositions III and IV were considerably more scorch resistant than reference compositions II but less than reference composition I.

Vulcanizates III and IV exhibited a tendency to bloom, the blooming properties of the former being the more pronounced. It was learned (8) that the addition of low molecular weight polyethylene waxes to rubber compositions might hinder or completely prevent blooming. A few vulcanizates of the composition III (TMTD with DBTDMTU) were prepared with 2 PHR of the polyethylene wax. These products had slightly lower tensile strengths and slightly higher per cent elongations and no bloom. While this study was limited to a few mixes of only one type of composition, the results do offer encouragement for the possibility of better control of bloom.

Dicumyl Peroxide Vulcanizing System

The improved aging qualities of vulcanizates produced in the absence of added free sulfur, such as presented in the preceding section, have increased interest in curing systems containing no sulfur at all.

Much of the early work on various types of peroxides (1,4,9) did not indicate much promise for commercial applications. During the early stages of the present investigation, however, the commercial availability of dicumyl peroxide (10) was announced and the first information indicated that it possessed promising qualities for rubber vulcanization. Thus, it was of considerable interest to examine this material. Also, during the course of this work successful vulcanizations of Hevea and nitrile rubbers with dicumyl peroxide were reported (5,11).

The ultimate tensile and elongation values of vulcanizates cured with various amounts of dicumyl peroxide are shown in Figures 2a and 2b.

The vulcanizates used to obtain the curve in Figure 2a were prepared from rubber compounds which contained only the PBNA originally present in the SBR-1500 (approximately 1.25 PHR) while those in Figure 2b contained one additional PHR of PBNA. It should be noted that the concentration of DCP-40 corresponding the maximum tensile value shifted from approximately 1.5 to 2.25 PHR of DCP-40 by the addition of 1 PHR of PBNA. Thus, it was apparent that portions of the amine antioxidant and the dicumyl peroxide reacted.

The physical properties of the optimum vulcanizates V and VI cured with DCP-40 are recorded in Table II. These vulcanizates had somewhat low values of tensile strength, per cent elongation, stress at 300% elongation and tear resistance in comparison with those of the standard NCHBTSA-sulfur cured vulcanizates while the hardness values were comparable. These peroxide cured vulcanizates also had lower per cent elongation and tear resistance values than the DPMTTS-MBT reference vulcanizate II but otherwise the original physical properties were similar. After air-oven aging, however, the values of the tensile properties of the DCP-40 cured vulcanizates were higher than those of the reference vulcanizates I and II.

The Mooney scorch resistance of composition VI containing 2.25 PHR of DCP-40 appeared to be comparable to that of the reference composition I which contained free sulfur and NCHBTSA. This conventional scorch test, however, was not entirely meaningful for the peroxide compositions since some peroxide decomposed without causing vulcanization during the test (12). Therefore, the supplementary test described in the Experimental Part was used which involved heating sheets of the compounded rubber, as obtained directly from the mill, in a circulating air-oven for periods up to three hours at temperatures from 230 to 250°F, followed by curing at 307°F for 30 minutes, and finally determination of the physical properties. The physical properties of vulcanizates from compositions heated at 230°, 240°, and 250°F and containing originally 2.25 PHR of DCP-40 and one additional PHR of PBNA are summarized in Table III. It may be seen that the compositions withstood heating in air for about 30 - 40 minutes at 250°F and somewhat longer periods at the lower temperatures before changes in the physical properties of the corresponding vulcanizates were substantial. Thus, the safe processing time is judged to be approximately 30 - 40 minutes rather than 54 minutes as measured by the Mooney scorch test.

Since the supplementary test seemed more realistic than the Mooney scorch test for evaluating the processing safety of rubber compounds containing dicumyl peroxide, it was of interest to determine the safe processing times of compositions III and IV by this heating procedure. Table III contains the results of these experiments on compounds containing accelerator combinations. These data indicate that periods in which the raw compositions can be held at 250°F without causing substantial changes in the tensile properties of the final vulcanizates are in the range of 20 - 30 minutes. The heating of the compositions for periods of 30 - 60

minutes resulted in products which, after curing, possessed higher tensile strength than those which had not been pre-heated. It is interesting that after heating the raw composition III for 2 hours at 250°F, the formulation could still be compression molded at 307°F to yield a sound sheet. These results emphasize the arbitrariness associated with the rating of general processing stability from specific laboratory tests.

Dicumyl Peroxide - Sulfur-Bearing Accelerator Vulcanizing Systems

The third type of vulcanizing system comprised the use of accelerators in combination with dicumyl peroxide and PBNA. They included the compounds in the following groups:

1) Zinc dibutyl-dithiocarbamate (ZDBDTC)
   Tetramethyl-thiuram-disulfide (TMTD)
   Tetrabutyl-thiuram-monosulfide (TBTM),

2) 2-Mercaptobenzothiazole (MBT)
   Diphenylquanidine (DPG), and

3) 2,4-Dinitrophenyl-dimethyl-dithiocarbamate (DMPDMDTC).

Vulcanizates cured with combinations of DCP-40 and members of the first group generally possessed the highest values of physical properties, those formed from the use of the second group of accelerators appeared to have some less desirable properties, and those prepared by use of DCP-40 and the compound of the third group had the least desirable physical properties.

The ultimate tensile and elongation values for vulcanizates cured with various amounts of DCP-40 with TMTD, and with ZDBDTC are shown in Figures 3a and 3b. Typical sets of physical properties for the vulcanizates cured with combinations of DCP-40 and members of the three groups mentioned above are listed in Table II (composition numbers VII - XII).

It was found necessary to add 1 PHR of stearic acid and 3 PHR of

zinc oxide to the compositions containing DCP-40 plus TMTD or ZDBDTC as curing agents in order to obtain vulcanizates with good physical properties. The optimum composition VII contained 3.75 PHR of DCP-40, 0.75 PHR of TMTD, 1 PHR of PBNA, 1 PHR of stearic acid and 3 PHR of zinc oxide. When the properties of the vulcanizate from this compound are compared with those of the optimum vulcanizate VI, containing DCP-40 as the only curing agent (Table II), it is apparent that the use of TMTD with DCP-40 has caused some increase in tensile strength and a large increase in elongation, with little effect on the other physical properties and the age resistance.

Similar and somewhat more pronounced changes resulted from the use of DCP-40 with ZDBDTC and PBNA. The optimum composition VIII as determined from Figure 3b was 3.75 PHR of DCP-40, 1 PHR of ZDBDTC, 1 PHR of stearic acid and 3 PHR of zinc oxide, and it can be seen in Table II that the resulting vulcanizate had considerably higher tensile and elongation values than the DCP-40 cured vulcanizate with equally good resistance to aging.

The values of the physical properties of the unaged vulcanizates of composition VIII are therefore similar but not identical with those of the vulcanizates from the free sulfur-accelerator combination. It should be noted, however, that the concentration of DCP-40 required to yield a product possessing maximum tensile strength is greater than the concentration necessary to give the product with maximum tear strength.

The tensile values for the aged vulcanizates in Figures 3a and 3b were higher than those of the comparable unaged samples, the effect being the more pronounced for the products formed in the presence of DCP-40 and TMTD. The reasons for this effect are not completely clear but must be due at least in part to additional curing during the aging process. This effect

will be discussed further in the following section.

Mooney scorch values for compositions VII and VIII were 26 and 40 minutes, respectively; and the time of heating of composition VII, at 250°F, which did not produce changes in the physical properties of the vulcanizate was 30 minutes.

Effect of Curing Time on Dicumyl Peroxide Systems

As anticipated above, it was of interest to examine the effect of curing time at 307°F on the unaged physical properties of vulcanizates cured with dicumyl peroxide alone and in combination with accelerators.

In Figures 4a, 4b and 4c, variations of tensile properties with curing time are shown for vulcanizates cured with DCP-40 and with combinations of DCP-40 and TMTD or ZDBDTC. Figures 4a and 4c show that the tensile properties of the vulcanizates have reached or are rapidly approaching limiting values at curing times of 30 to 35 minutes at 307°F. The tensile properties of the DCP-40 - TMTD cured samples (Figure 4b), however, appear to be rising at the 40 minute point. It seems likely, therefore, that postcuring during aging may account, at least in part, for the large increase in tensile strength after air-oven aging shown in Figure 3a.

Aging of Selected Vulcanizates at Various Temperatures

The vulcanizates III to VIII were resistant to air-oven aging at 212°F during 72 hours. To gain further information about their age resistance under morestringent conditions, vulcanized test specimens were subjected to air-oven aging at 212°F for periods up to 32 days, at 250°F for periods up to 15 days, and at 300°F for periods up to 12 hours. The effects of extended aging at 212°F on ultimate elongation, tensile and stress at 300% elongation are summarized in Figures 5, 6 and 7. Figures 8 and 9 show the effect of air-oven aging at 250° and 300°F on the ultimate elongation of the various vulcanizates. A brief summary of these data is reported

in Table IV.

Aging Studies at 212°F

On inspection of the curves shown in Figures 5, 6 and 7, it can be seen that the per cent elongation of the vulcanizates varied more regularly with time of aging than did the stress at 300% elongation or the ultimate tensile strength. Thus, for purposes of discussion, attention may be concentrated on Figure 5.

It is interesting that the vulcanizates from the peroxide containing compositions VI, VII and VIII, showed the greatest resistance to change in per cent elongation throughout the 30 day period at 212°F. However, vulcanizates III and IV, from the sulfur-bearing accelerator combinations, showed equally good resistance after the first 10 days.

Vulcanizate V, produced by the action of 1.5 PHR DCP-40 (without additional PBNA), showed relatively poor resistance to aging, but vulcanizate VI formed from 2.25 PHR of DCP-40, with one addition PHR of PBNA showed excellent resistance. The age resistance of the vulcanizate formed from 3 PHR DCP-40 with 2 additional PHR of PBNA (not shown on the graph) was somewhat greater than that of vulcanizate VI; however, the product from 3.75 PHR DCP-40 with 3 additional PHR of PBNA (not shown on the graph) gave no further improvement in age resistance.

Aging Studies at 250°F

The per cent elongation values of the selected vulcanizates after air-oven aging for various times at 250°F are shown in Figure 8, and the tensile, elongation, stress at 300% elongation and hardness after aging for 7 days at 250°F are reported in Table IV. The data indicate that 250°F represents severe aging conditions, with the per cent elongation for all the aged vulcanizates being essentially zero after 11 days at that temperature.

The vulcanizates VII and VIII (cured with DCP-40 plus TMTD or ZDBDTC and including additional PBNA) had the greatest resistance to aging at 250°F. The order of decreasing age resistance of the remaining vulcanizates was: 1) accelerator cured reference vulcanizate II, 2) dicumyl peroxide cured vulcanizate VI, and 3) the sulfur plus accelerator cured standard vulcanizate I.

Aging Studies at 300°F

The curves in Figure 9 represent the change in elongation with the time of air-oven aging at 300°F, while Table IV lists the tensile, elongation, stress at 300% elongation and hardness after aging 12 hours at 300°F. Again, the vulcanizates cured with dicumyl peroxide plus accelerator combinations, VII and VIII, exhibited the greatest age and/or temperature resistance. These vulcanizates showed little change in elongation until after 9 to 12 hours in air at 300°F. Beyond that point the elongation decreased regularly to a value of approximately 150% at 20 hours.

Raw Materials Costs of Vulcanization Systems

In Table V the relative costs of the compositions I - VIII (excluding V) including the indicated vulcanizate agents and 50 PHR MAF carbon black are listed. It may be seen that raw materials costs of vulcanizate VI is 1.8% greater, and the other compositions are 5.2 - 5.8% greater than the cost of the sulfur-accelerator system.

DISCUSSION OF RESULTS

The results of this study are summarized in a qualitative fashion in TableVI, and are briefly discussed in the following paragraphs.

Physical Properties of Vulcanizates

It has been seen that physical properties of the unaged vulcanizates prepared by use of the peroxide-accelerator-PBNA system are essentially equivalent, though not identical, to those of the products cured with the free sulfur-accelerator system. Vulcanizates prepared by the action of dicumyl peroxide without accelerators, and vulcanizates produced by the accelerators combinations possessed somewhat lower tensile properties. However, heating of the uncured accelerator compositions for 30 minutes at 250°F followed by compression molding at 307°F for 30 minutes yielded sheets with high tensile strengths. The vulcanizates which had been cured with accelerator combinations showed a tendency to bloom. The presence of a small amount of polyethylene wax eliminated bloom in the one case tried. Vulcanizates from the peroxide systems showed no bloom.

Age Resistance of Vulcanizates

The age resistance of the vulcanizates produced from all of the non-free sulfur curing systems was substantially greater than those from the free sulfur-accelerator combination. The vulcanizates produced by the action of dicumyl peroxide in combination with accelerators were the most resistant to air-oven aging.

By reference to Table VI, a rough parallelism may be noted between the age resistance of vulcanizates and the strength of the probable cross-links as listed by Dogadkin and Torasova (13). On that basis it would appear

that C-C crosslinks should yield the strongest and most age resistant rubber. Then the question arises regarding the contribution of the accelerators (which contain sulfur and nitrogen) to the dicumyl peroxide vulcanization. Three possible functions of the sulfur-nitrogen bearing accelerators to the peroxide vulcanization are suggested: 1) the accelerators induce the decomposition of the peroxide allowing the process to take place at a lower activation energy and resulting in a more even distribution of crosslinks; (2) the decomposition produds of the sulfur-nitrogen bearing accelerators function as antioxidants; and (3) the accelerators act as dispersing agents for the peroxide in the rubber.

While the results of this study do not afford a decision regarding the relative merits of these suggestions, they do emphasize that further study of dicumyl peroxide vulcanization systems should include attention to other reducing and dispersing agents.

Processing Stability of Uncured Compositions

The results listed in Table VI show that compounds containing the conventional free sulfur-accelerator combination remain the most resistant to precuring or decomposition during processing. Compounds with the peroxide combinations are stable in air for 30 - 40 minutes at 250°F and for longer periods at lower temperatures. The accelerator compositions gave scorch values of 20 - 30 minutes. However, the heating of the uncured accelerator formulations from 0.5 to 2.0 hours at 250°F did not prevent curing by compression molding at 307°F.

Relative Costs of Raw Materials

The raw materials costs for compositions containing 50 parts of carbon black per hundred parts of rubber and the specified vulcanizing agents

are surprisingly similar. The DCP-40 + PBNA composition is 1.8% greater and the others are 5.2 - 5.8% greater than the cost of the free sulfur-accelerator combination.

Thus it is concluded that vulcanization systems for SBR based on dicumyl peroxide in combination with accelerators and phenyl-β-naphthylamine yield vulcanizates with satisfactory physical properties and excellent aging qualities, but they are somewhat more expensive and are less stable to processing than the conventional free-sulfur accelerator curing systems.

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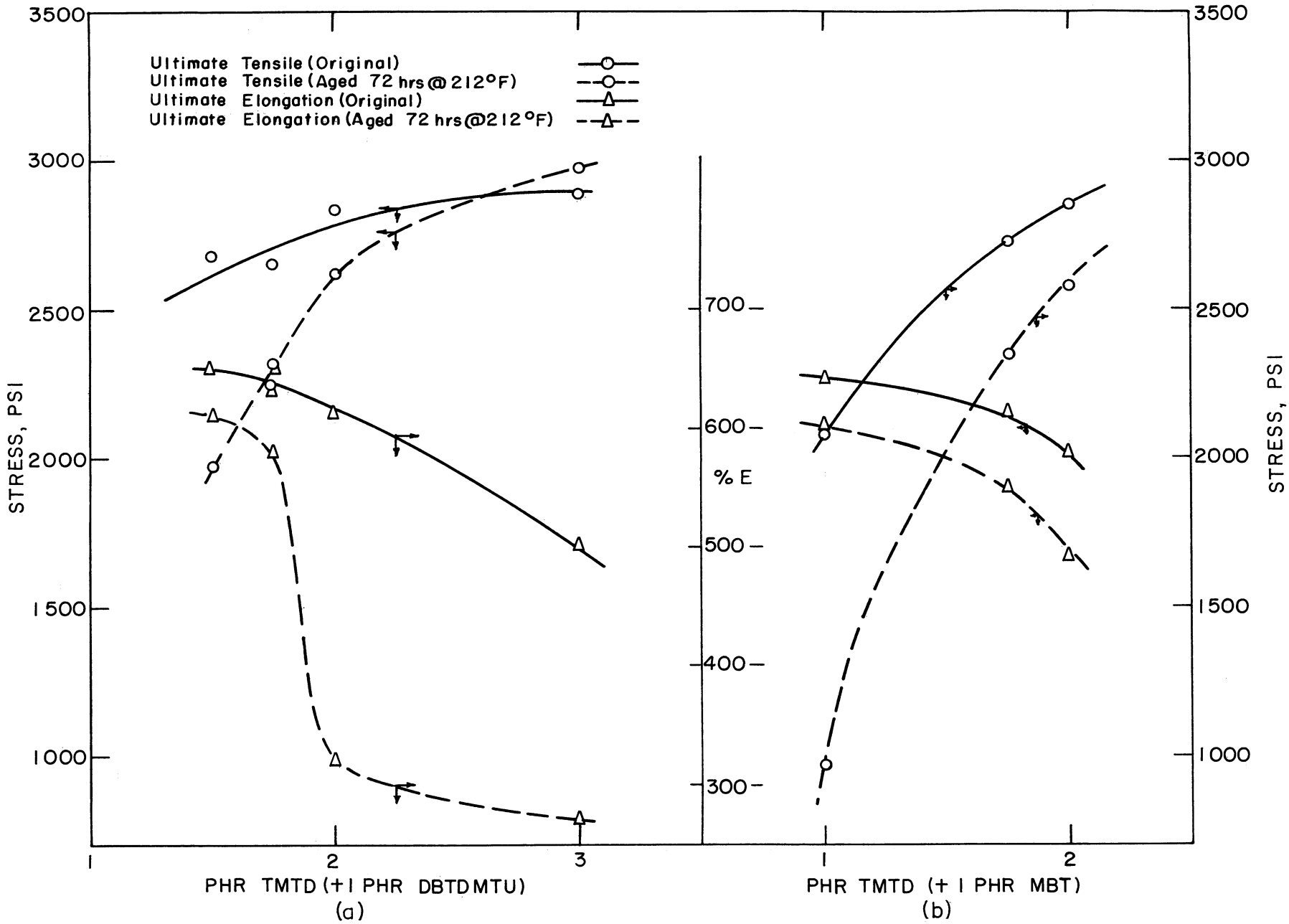

Fig. 1 Physical properties of SBR-1500 vulcanizates cured with accelerators.

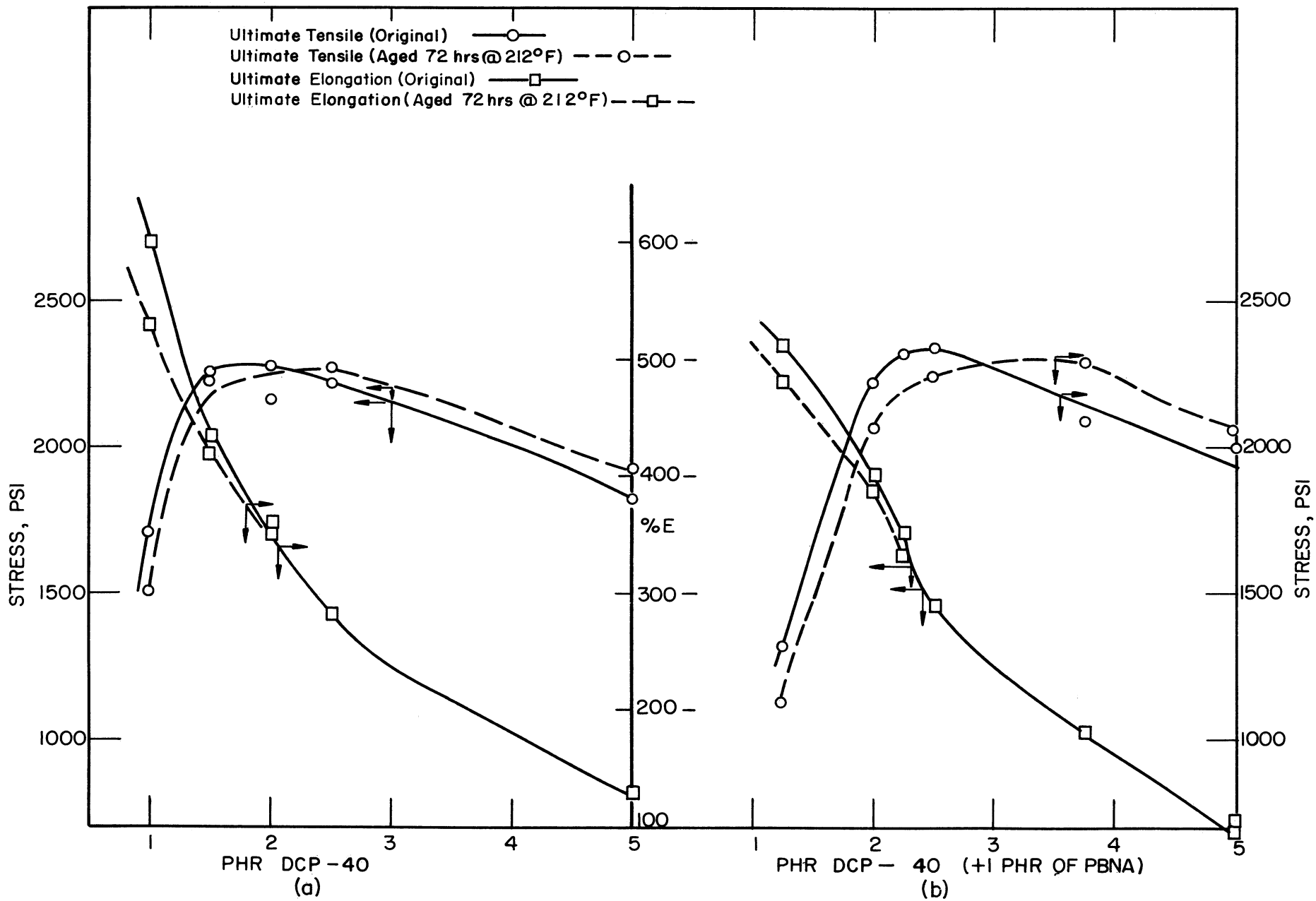

Fig. 2 Physical properties of SBR-1500 vulcanizates cured with dicumyl peroxide.

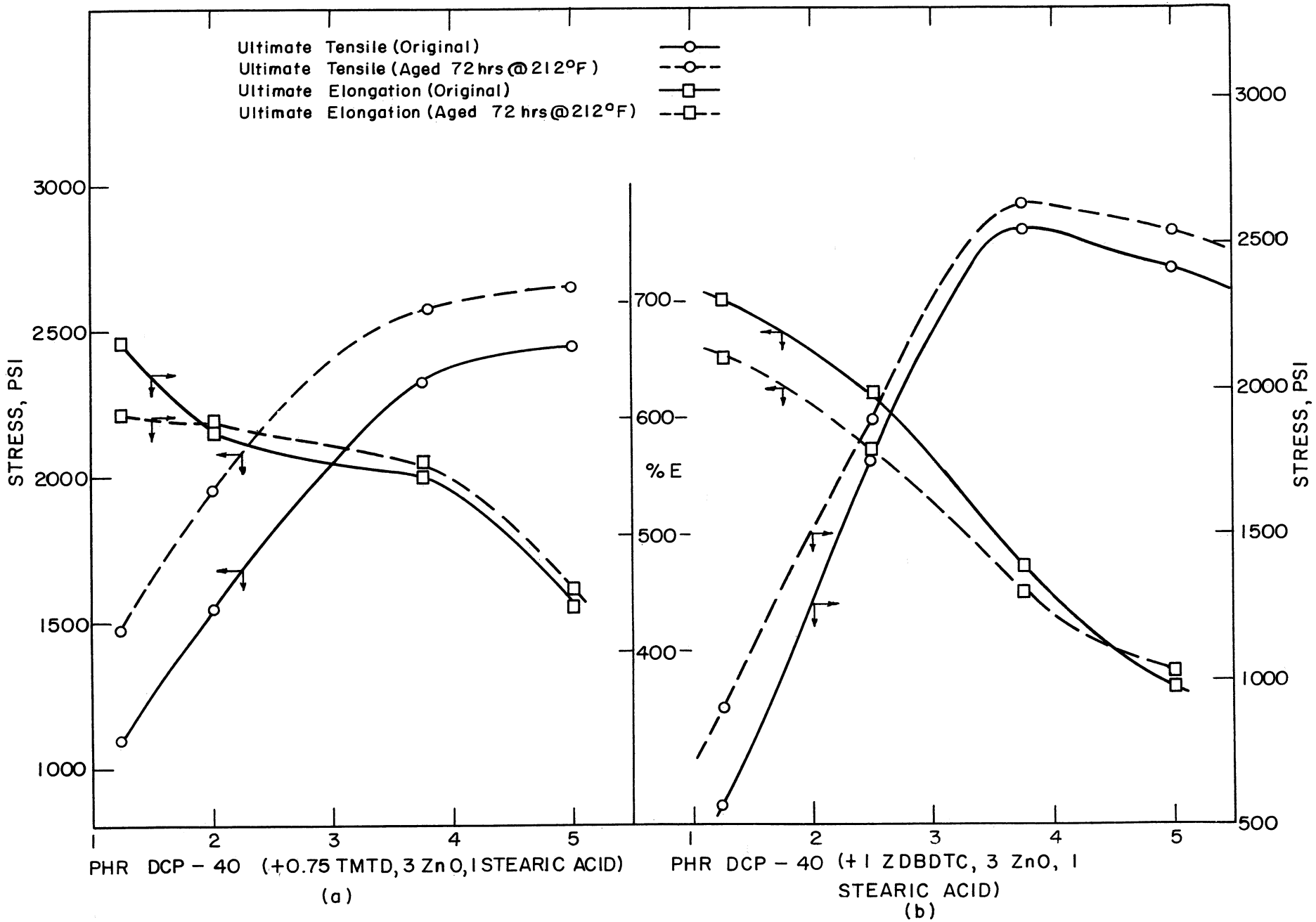

Fig. 3 Tensile properties of SBR-1500 vulcanizates cured with dicumyl peroxide-accelerator combinations.

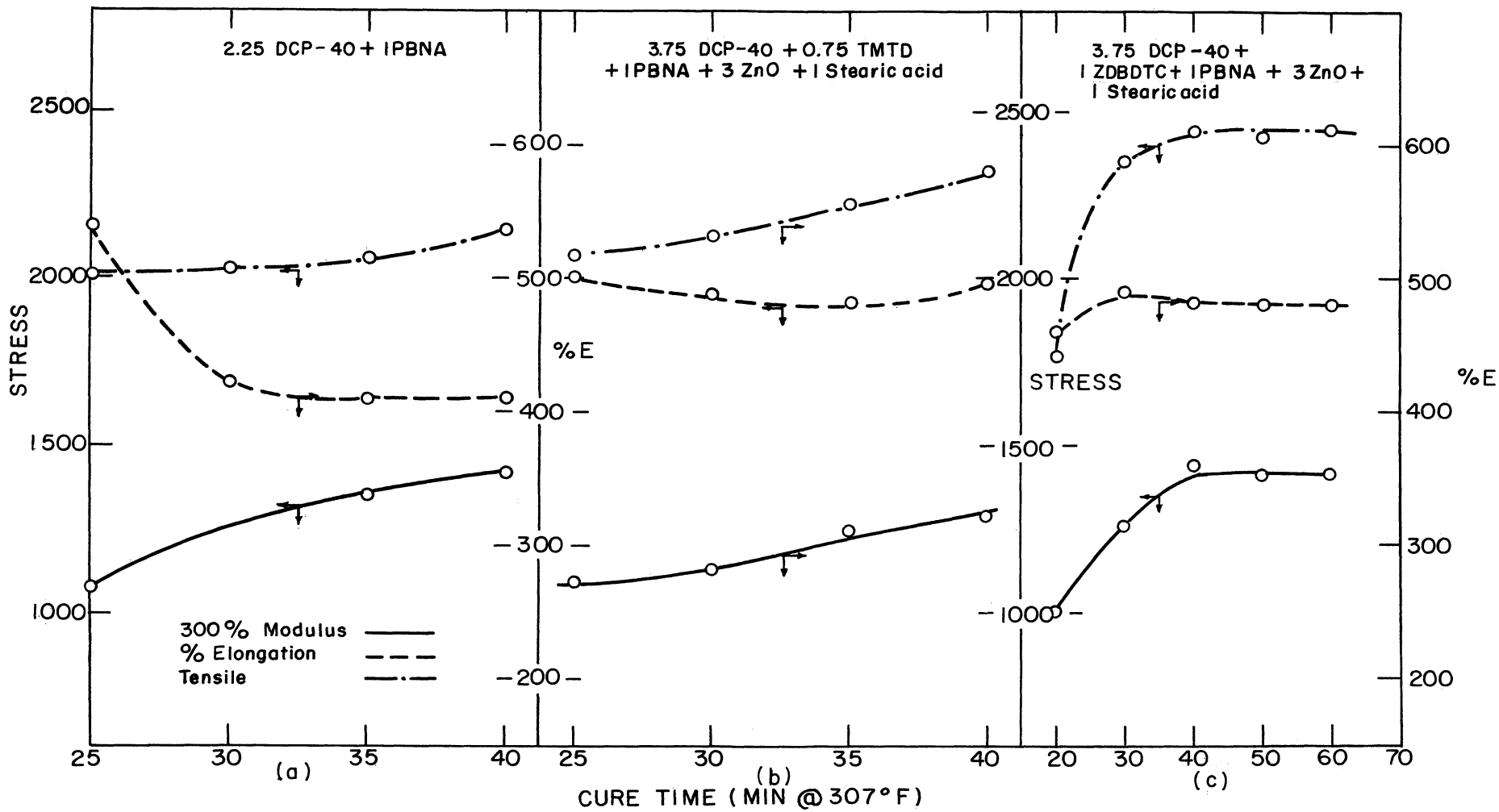

Fig. 4 Effect of curing time on tensile properties of SBR vulcanizates cured with systems containing dicumyl peroxide.

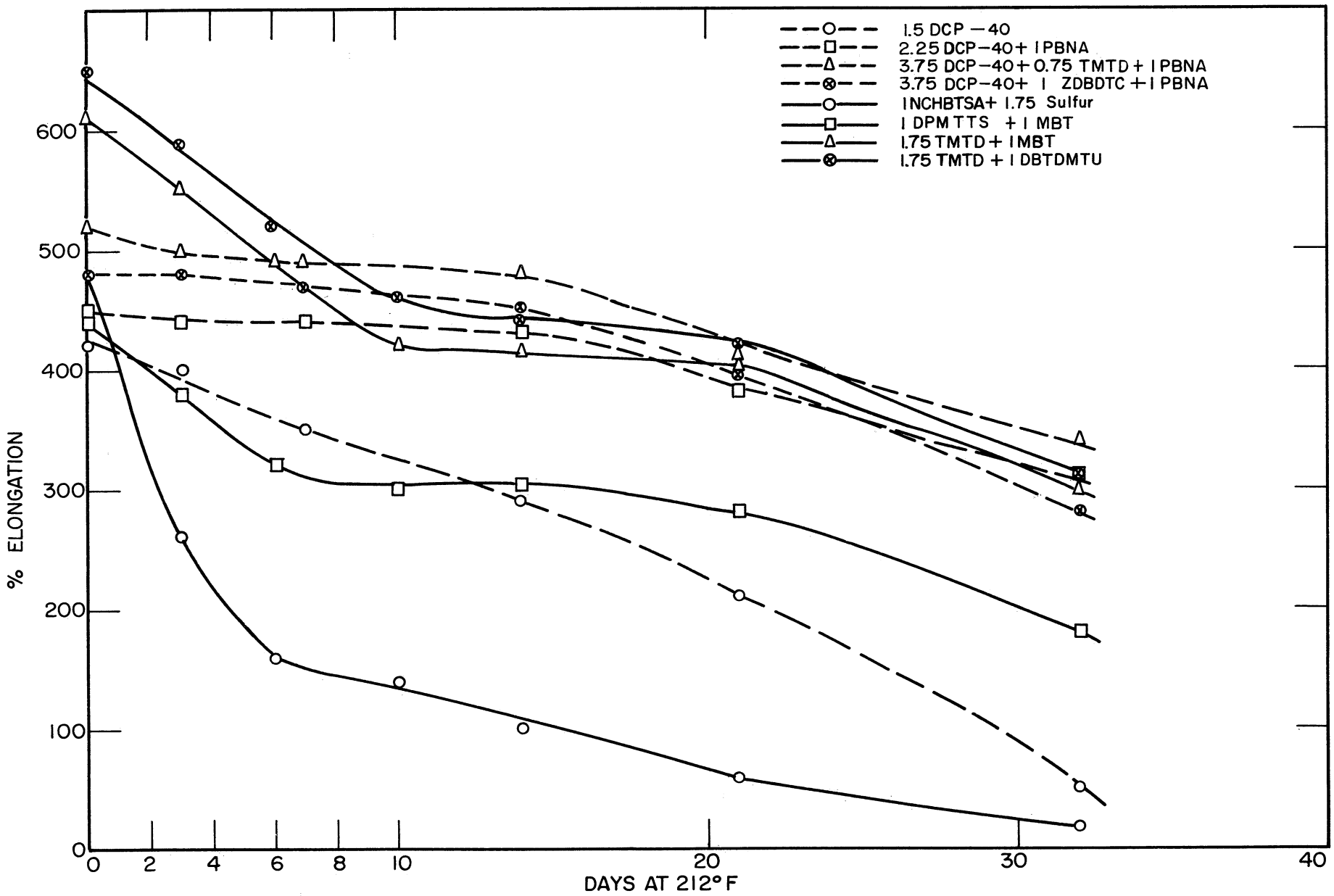

Fig. 5 Effect of extended air-oven aging at 212°F on the elongation of SBR vulcanizates.

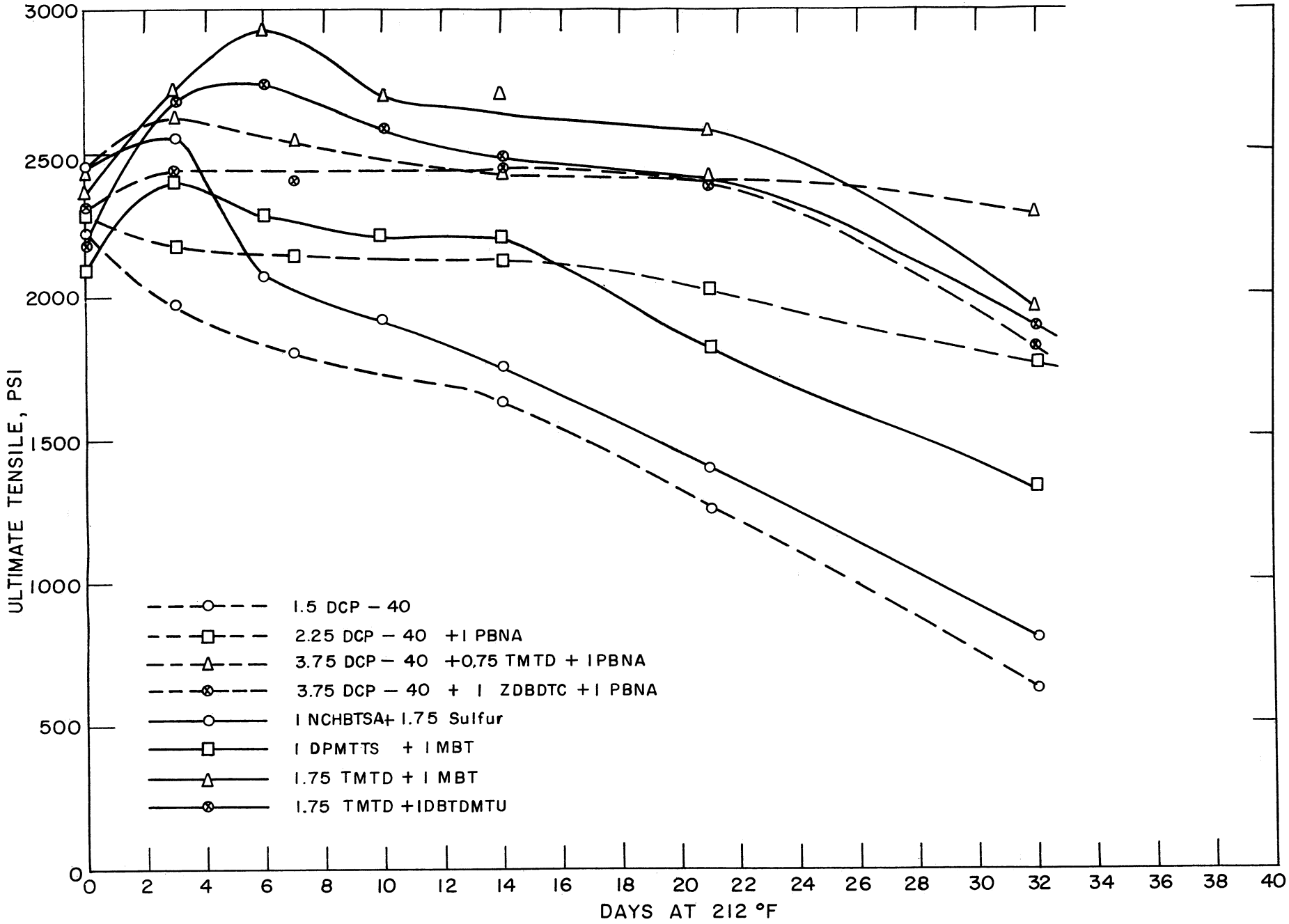

Fig. 6 Effect of extended air-oven aging at 212°F on the tensile strength of SBR vulcanizates.

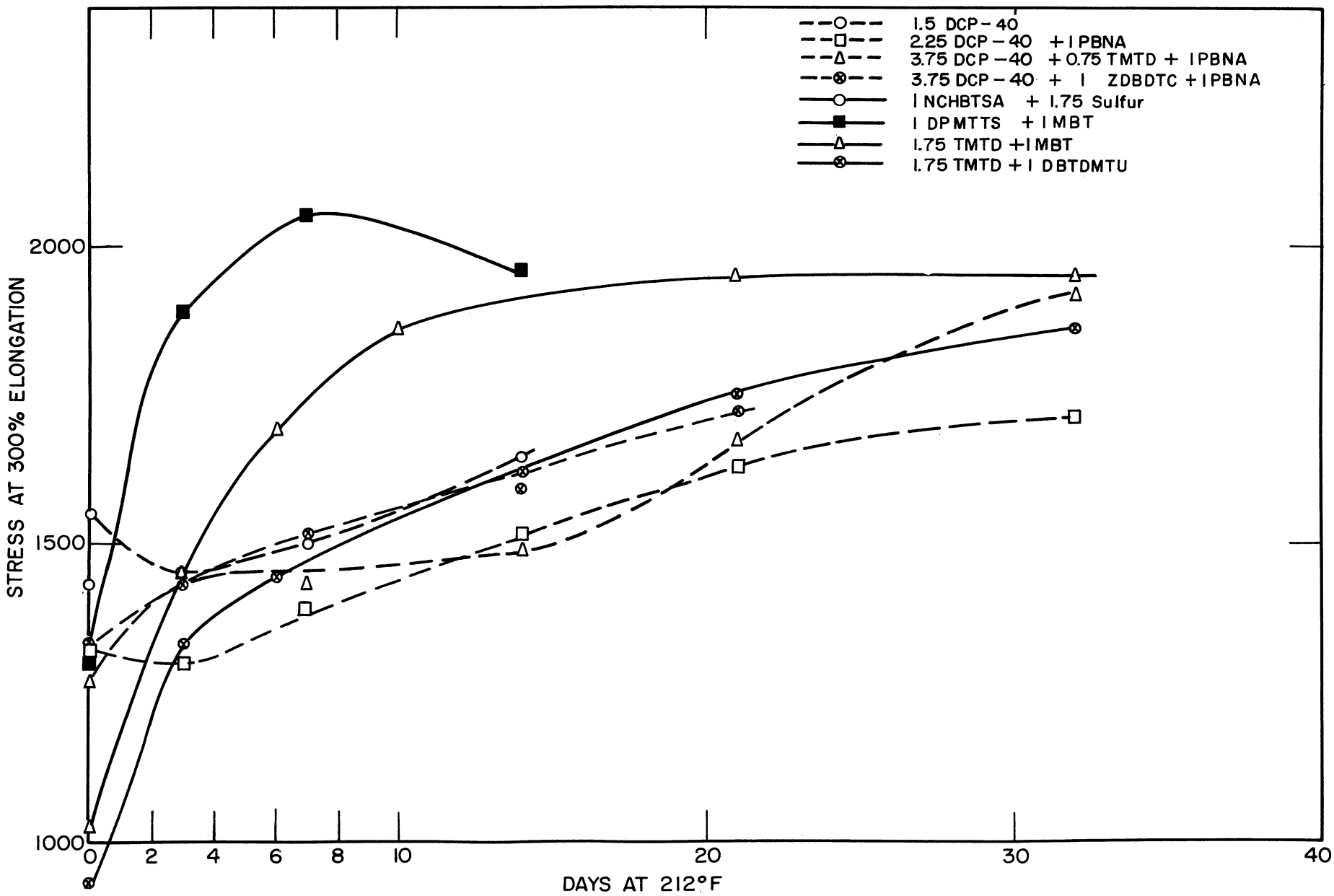

Fig. 7 Effect of extended air-oven aging at 212°F on the stress at 300% elongation of SBR vulcanizates.

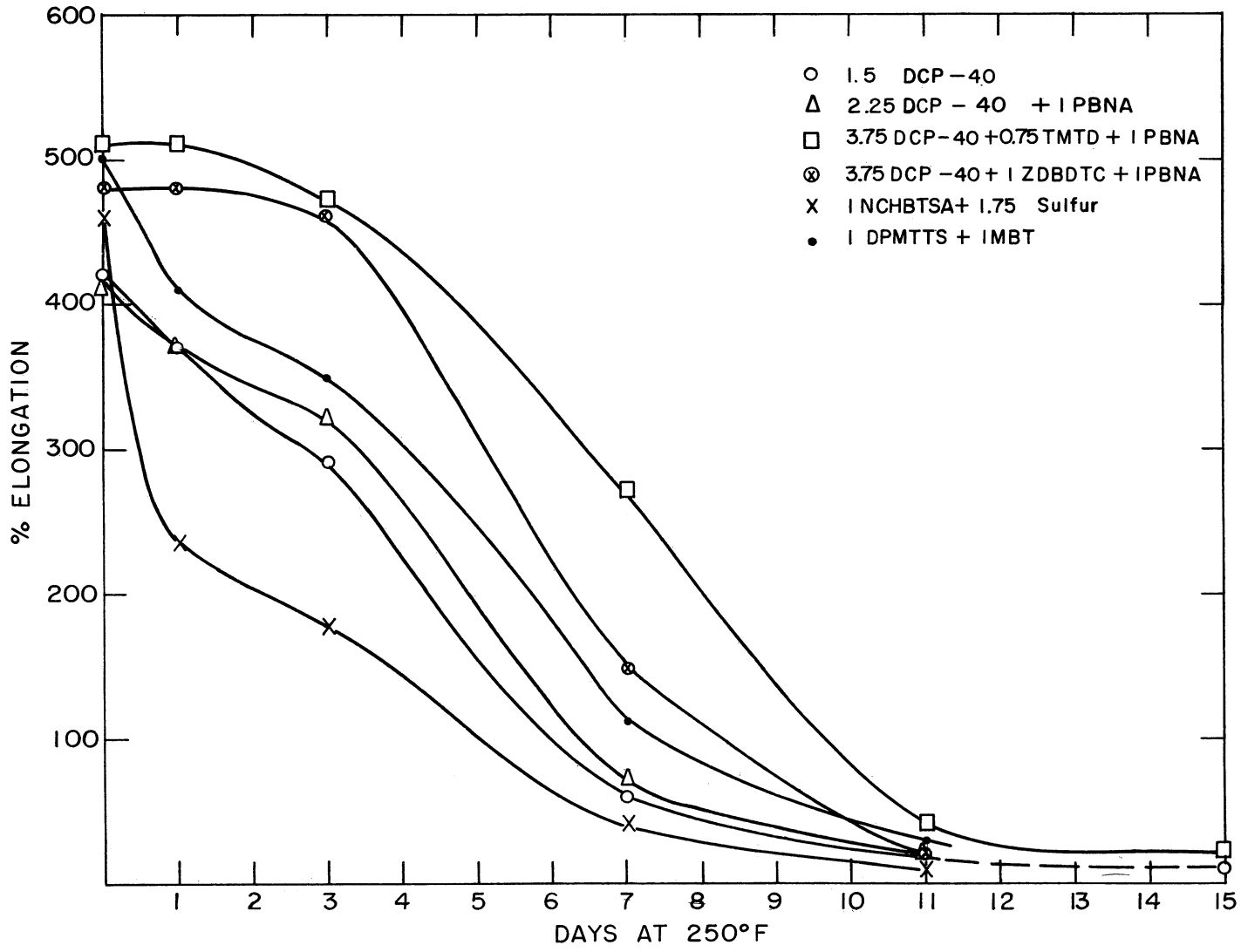

Fig. 8 Effect of air-oven aging at 250°F on elongation of selected SBR vulcanizates.

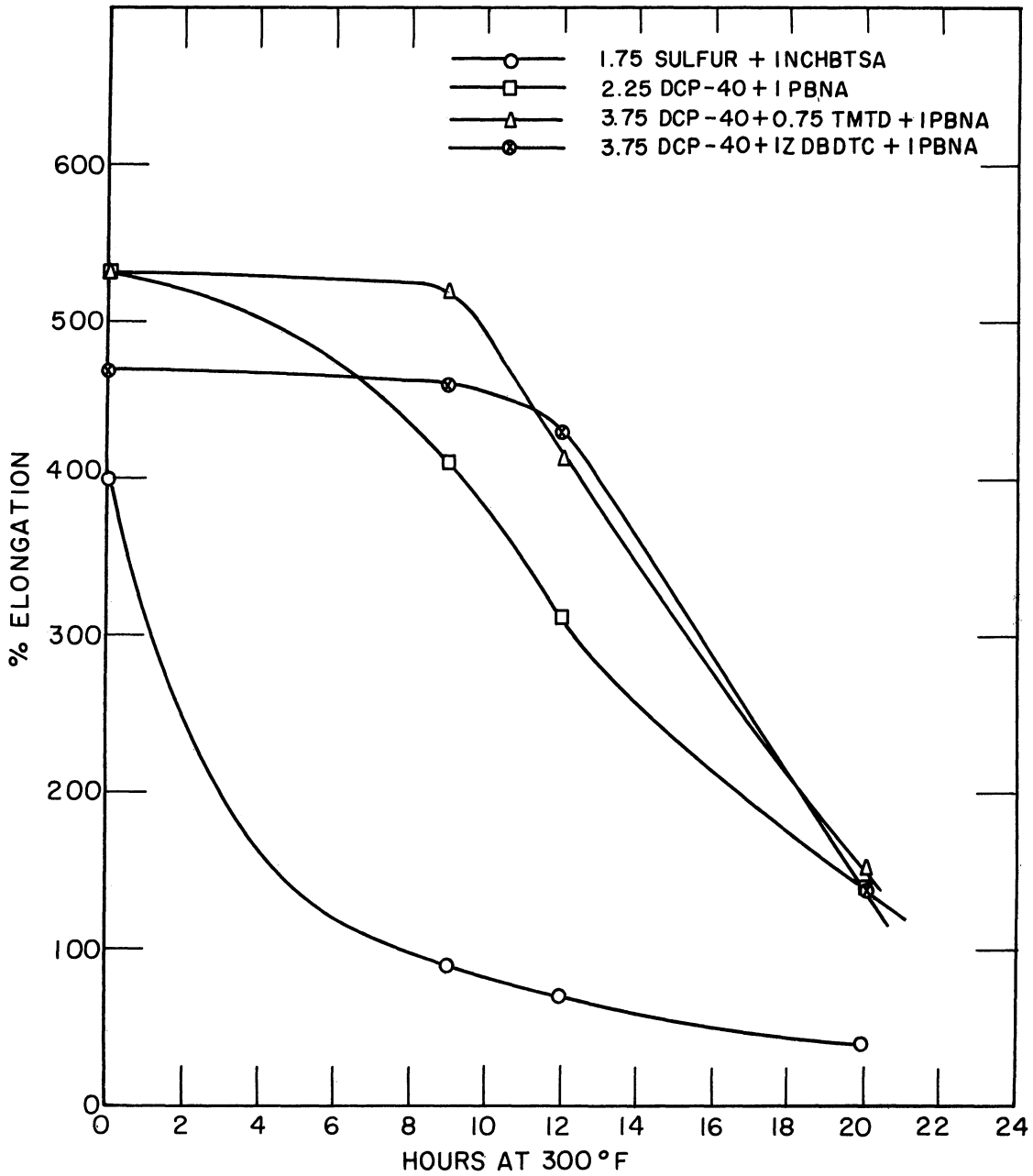

Fig. 9 Effect of air-oven aging at 300°F on elongation of selected SBR vulcanizates

COMPOSITIONS OF RUBBER COMPOUNDS

Ingredient	Code Name	Parts by Weight											
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
SBR 1500[a]		100	100	100	100	100	100	100	100	100	100	100	100
MAF carbon black[b]		50	50	50	50	50	50	50	50	50	50	50	50
Zinc oxide		3	3	3	3			3	3	3	3	3	3
Steraric acid		1	1	1	1			1	1	1	1	1	1
Phenyl-β-naphthylamine	PBNA	1	1	1	1		1	1	1	1	1	1	1
Sulfur		1.75											
N-cyclohexyl-2-benzothiazyl sulfenamide[c]	NCHBTSA	1											
Dipentamethylene-thiuram-tetrasulfide[d]	DPMTTS		1										
2-mercaptobenzothiazole[e]	MBT		1		1					0.4			
Dibenzothiazyl-dimethylthiol urea[f]	DBTDMTU			1									
Tetramethyl-thiuram-disulfide[g]	TMTD			1.75	1.75			0.75					
Dicumyl peroxide-40%-calcium carbonate 60%[h]	DCP-40					1.5	2.25	3.75	3.75	3.75	3.74	3.75	3.75
Zinc dibutyl-dithiocarbamate[i]	ZDBDTC								1				
Diphenylquanidine[j]	DPG										0.20		
2,4-dinitrophenyl-dimethyl-dithiocarbamate[k]	DNPDMDTC											0.75	
Tetrabutyl-thiuram-monosulfide[l]	TBTM												0.75

[a]Texas-U.S. Chemical Co., and Goodrich-Gulf Chemicals Inc.
[b]Philblack A, Phillips Chemical Co.
[c]Santocure, Monsanto Chemical Co.
[d]Tetrone A, E.I. du Pont de Nemours and Co.
[e]Captax, R. T. Vanderbilt Co.
[f]El Sixty, Monsanto Chemical Co.
[g]Methyl Tuads, R. T. Vanderbilt Co.
[h]DiCup 40C, Hercules Powder Co.
[i]Butyl Zimate, R. T. Vanderbilt Co.
[j]Monsanto Chemical
[k]Safex, Naugatuck Chemical
[l]Pentex, Naugatuck Chemical

TABLE II
PHYSICAL PROPERTIES OF SELECTED COMPOSITIONS AND VULCANIZATES

Composition Number	Curing System[a]	Tensile, psi		Elongation, %		Stress at 300% E., psi		Tear, lbs/in.		Durometer Hardness		Mooney Scorch, min.	
		Unaged	Aged[b]	Unaged	Aged[b]	Unaged	Aged[b]	Unaged	Aged[b]	Unaged	Aged[b]	t_5[c]	t_{10}[c]
I	1.75 Sulfur + 1 NCHBTSA	2450	2550	480	260	2150	----	260	170	68	74	61	67
II	1 DPMTTS + 1 MBT	2100	2400	440	380	1340	1890	280	210	65	67	7	8
III	1.75 TMTD + 1 DBTDMTU	2180	2680	650	590	950	1290	290	280	65	65	19	22
IV	1.75 TMTD + 1 MBT 1 MBAT	2360	2720	610	550	1020	1440	280	270	66	66	23	28
V	1.5 DCP-40	2220	1970	420	400	1550	1450	220	220	65	66	--	--
VI	2.25 DCP-40++ 1 PBNA	2280	2170	450	440	1430	1680	230	260	65	65	54	70
VII	3.75 DCP-40 + 0.75 TMTD + 1 PBNA	2330	2570	550	560	1170	1290	210	210	62	66	26	33
VIII	3.75 DCP-40 + 1 ZDBDTC + 1 PBNA	2540	2630	470	450	1480	1610	180	200	65	66	40	58
IX	3.75DDCP-40 + 0.4 MBT + 1 PBNA	2280	2200	310	310	2090	2010	110	110	68	69	--	--
X	3.75 DCP-40 + 0.2 DPG + 1 PBNA	2360	2250	330	320	2060	1980	160	160	69	70	--	--
XI	3.75 DCP-40 + 0.75 DNPDMDTC + 1 PBNA	1360	1720	570	550	690	890	210	270	62	66	--	--
XII	3.75 DCP-40 + 0.75 TMTM + 1 PBNA	2460	2480	480	460	1480	1500	190	210	65	67	--	--

a The rubber contained 1.25 PHR of PBNA. Only concentration of additional PBNA is shown in formulations.
b Samples were aged in an air oven at 212°F. for 72 hours
c t_5 and t_{10} represent the number of minutes required for a five and ten unit rise over the minimum.

TABLE III

STABILITY OF COMPOUNDED RUBBER TO HEATING IN AIR[a]

Composition Number	Curing System	Temp. °F.	Tensile, psi Hours 0	1/2	1	2	3	Elongation, % Hours 0	1/2	1	2	3	Stress at 300% E., psi Hours 0	1/2	1	2	3	Durometer Hardness Hours 0	1/2	1	2	3
VI	2.25 DCP-40 + 1 PBNA	250	2380	2300	1770	1010	--	490	490	610	680	--	1240	1190	710	380	--	65	65	62	60	--
	"	240	2270	2230	2140	1610	1670	400	420	460	510	510	1760	1570	1340	870	950	67	66	65	63	63
	"	230	2130	2120	2080	1500	1510	500	520	560	590	600	1280	1130	950	780	740	63	63	63	63	62
III	1.75 TMTD + 1 DBTDMTU	250	2150	2520	2340	2120	--	650	640	650	640	--	1300	1450	1400	1400	--	65	65	65	69	--
IV	1.75 TMTD + 1 MBT	250	2300	2480	2400	2110	--	600	580	580	570	--	1430	1580	1620	1570	--	65	65	65	67	--
VII	3.75 DCP-40 + 0.75 TMTD + 1 PBNA	250	2350	2310	2060	1980	--	510	550	580	500	--	1410	1250	1200	1170	--	65	65	65	69	--

[a]The compounded rubbers were heated in air at the designated temperatures and times after which the compounds were cured for 30 minutes at 307°F. and the physical properties of the resulting vulcanizates were measured.

TABLE IV

AIR-OVEN AGE RESISTANCE OF SELECTED VULCANIZATES AT 212, 250 and 300°F.

Composition Number	Curing System	Tensile, psi				Elongation, %				Stress at 300% E., psi				Durometer Hardness			
		Unaged	Aged			Unaged	Aged			Unaged	Aged			Unaged	Aged		
			32 days at 212°F.	7 days at 250°F.	12 hours at 300°F.		32 days at 212°F.	7 days at 250°F	12 hours at 300°F		32 days at 212°F.	7 days at 250°F.	12 hours at 300°F.		32 days at 212°F.	7 days at 250°F.	12 hours at 300°F.
I	1.75 Sulfur + 1 NCHBTSA	2450	800	1180	560	480	20	40	70	2150	--	--	--	68	89	83	77
II	1 DPMTTS + 1 MBT	2100	1330	1480	--	440	180	110	--	1340	1960	1710	--	65	72	70	--
III	1.75 TMTD + 1 DBTDMTU	2180	1890	--	--	650	310	--	--	950	1590	--	--	65	71	--	--
IV	1.75 TMTD + 1 MBT	2360	1950	--	--	610	300	--	--	1020	1910	--	--	66	70	--	--
V	1.5 DCP-40	2220	610	410	--	420	50	60	70	1550	1640	1190	--	65	79	82	--
VI	2.25 DCP-40 + 1 PBNA	2280	1760	480	990	450	310	70	310	1730	1510	1300	870	65	69	77	66
VVII	3.75 DCP-40 + 0.75 TMTD + 1 PBNA	2330	2270	1820	1690	550	340	270	410	1170	1490	1270	970	62	70	71	66
VIII	3.75 DCP-40 + 1 ZDBDTC + 1 PBNA	2540	1810	660	2070	470	280	150	430	1480	1620	1560	1300	65	70	71	66

TABLE V

COST OF MATERIALS FOR SELECTED COMPOSITIONS

Composition Number	Curing System	Materials Cost,[a] $/100 lbs. Compounded Rubber	Per cent Cost Increase Over Composition I
I	1.75 Sulfur + 1 NCHBTSA	19.05	--
II	1 DPMTTS + 1 MBT	20.05	5.2
III	1.75 TMTD + 1 DBTDMTU	20.16	5.8
IV	1.75 TMTD + 1 MBT	20.04	5.2
VI	2.25 DCP-40 + 1 PBNA	19.40	1.8
VII	3.75 DCP-40 + 0.75 TMTD + 1 PBNA	20.04	5.2
VIII	3.75 DCP-40 + 1 ZDBDTC + 1 PBNA	20.15	5.8

[a]The values listed were estimated from market prices listed in Rubber Age, 79 870 (1956).

TABLE VI

SUMMARY OF FINDINGS

Composition		Vulcanizates					Safe Processing Time 250°at Min.	Relative Materials Cost
					Crosslinks			
No.	Type	Tensile Properties	Bloom	Age Resistance	Type	Bond Strength k cal		
I	Free Sulfur + NCHBTSA	Excellent	No	Poor	$-c-s_m-c-$	27.5	60	100.0
II-IV	Accelerator Combinations	Fair	Yes	Good	-c-s-s-c- -c-s-c-	27.5 54.5	20-30	105.2-105.8
VI	DCP-40 + PBNA	Good	No	Very Good	-c-c-	62.7	30	101.8
VIII	DCP-40 + ZDBDTC + PBNA	Excellent	No	Excellent	?	?	40	105.8