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Final Report

CURING SYSTEMS AND CURING PROCEDURES WHICH IMPROVE
THE AGE RESISTANCE OF RUBBER

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OBJECT

The purpose of this investigation was to study non free sulfur curing systems for GR-S synthetic rubber which would yield vulcanizates of improved age resistance and which could be handled satisfactorily with present day processing machinery.

SUMMARY

The resistance to air-oven aging of GR-S vulcanizates cured with sulfur-bearing accelerators, with dicumyl peroxide and with dicumyl peroxide in combination with sulfur-bearing accelerators, has been studied. Some attention was given to the processing stability of the uncured compositions, and limited work was devoted to the suppression of blooming tendencies of certain vulcanizates.

It was found that vulcanizates cured with the peroxide and combinations of the peroxide with sulfur-bearing accelerators possessed excellent resistance to air-oven aging and no blooming tendency. The uncured compositions showed moderate resistance to precuring or decomposition at processing temperatures up to 250°F.

As a convenient basis for appraising the properties of the experimental compositions, two systems were selected as reference standards: I, a conventional formulation containing free sulfur and N-cyclohexyl-2-benzothiazyl sulfenamide, and II, a non-free sulfur system containing dipentamethylene-thiuram-tetrasulfide and 2-mercaptobenzothiazole.

Specific properties of five experimental systems were compared with I and II; namely: III, tetramethyl-thiuram-disulfide with dibenzothiazyl-dimethylthiol urea; IV, tetramethyl-thiuram-disulfide with 2-mercaptobenzothiazole; V, dicumyl peroxide; VI, dicumyl peroxide with tetramethyl-thiuram-disulfide; and VII, dicumyl peroxide with zinc dibutyl-dithiocarbamate.

The age resistance of the vulcanizates of the peroxide compositions, V, VI, and VII, was substantially greater than the vulcanizate of reference composition I and somewhat greater than that of vulcanizate II. The resistance to scorch, that is the processing stability as measured in minutes at 250°F, of the uncured compositions V, VI, and VII was about one-half that of composition I but several times longer than that of composition II. The values of the tensile strength of the unaged vulcanizates V, VI, and VII were slightly lower and the values of the per cent elongation were somewhat greater than those of vulcanizate I. The tensile properties of vulcanizate VII were the most nearly equivalent to those of I.

The vulcanizates of the sulfur-bearing accelerator compositions III and IV showed about the same tensile properties as vulcanizate II, but better resistance to aging than the latter product. The scorch resistance of the uncured compositions III and IV was about twice that of II.

Vulcanizates III and IV had a tendency to bloom. Results of preliminary experiments indicated that the blooming in vulcanizate III could be suppressed by the presence of a small amount of low molecular weight polyethylene wax.

On the basis of current market prices, the costs of the raw materials for experimental compositions III, IV, V, VI and VII would amount to some 2 - 6% more than for the conventional sulfur-accelerator system, I.

It was concluded that the excellent age resistance of the GR-S vulcanizates V - VII can justify the increase in material costs, and some limitation in processing conditions in the production of rubber items for military and mechanical goods applications where good age resistance is necessary.

INTRODUCTION

The need for improvement of the age resistance of rubber vulcanizates is of general importance, and that need is especially critical in the storage of military rubber items.

The age resistance of rubber vulcanizates is known to be influenced by the nature of the vulcanizing system, the products of the curing reactions, and the presence of inadvertant impurities such as metals. The commonly used curing system consisting of free sulfur in combination with small amounts of one or more accelerators has the advantages of being relatively inexpensive, and being relatively resistant to scorch or precuring at the moderately high temperatures used in processing before the final vulcanization stage. The conventional free sulfur based curing system has the limitation, however, of yielding products that fall short in resistance to aging.

The possibility that there may be other vulcanizing systems which have acceptable stability during processing and yield products having improved aging properties is of high interest. For example, use of combinations of the sulfur-bearing accelerators normally employed in the free sulfur system, but in the absence of added free sulfur, has given vulcanizates possessing improved age resistance. However, these combinations are more sensitive to scorch, and have a further disadvantage in cost since the use of the relatively larger amounts of these complex synthetic organic chemicals as the primary vulcanizing agent is more expensive.

Unfortunately, it appears that most of the curing systems that have been found to yield vulcanizates with improved aging qualities are not only relatively expensive but are also relatively more sensitive to precuring or decomposition in processing before the final vulcanization.

The problem is made more difficult by the continuing demand of the rubber industry for higher production rates, which in turn, with the present equipment and procedures, requires higher processing temperatures before the final vulcanization stage.

The Rock Island Arsenal has been following these trends and has been contributing in the developments over a number of years. The present study was undertaken to examine certain new vulcanizing systems which offered promise of yielding products of improved age resistance, and at the same time might meet the condition of, at least, a working compromise in cost and in stability during processing.

In the experimental work described below GR-S 1500, a copolymer of styrene and butadiene prepared at 41°F, was employed as the base rubber. Two compositions were selected as reference standards:

- I. a conventional sulfur vulcanization system, containing free sulfur in combination with a sulfur-bearing accelerator, and
- II. a non-free sulfur system comprising a combination of sulfur-bearing accelerators.

The age resistance of experimental vulcanizates has been compared with the age resistance of the vulcanizates of these two systems. Similarly, the tendencies of the experimental systems to scorch or decompose under processing conditions have been compared with the scorching tendencies of these reference compounds.

The experimental systems have comprised mainly,

- a. various combinations of accelerators commonly used with free sulfur but employed here in the absence of added free sulfur (as in reference compound II),
- b. systems containing dicumyl peroxide as the principal curing agent, and
- c. systems containing combinations of dicumyl peroxide with certain of the accelerators used in (a).

In brief, it has been found that several of these experimental compositions, particularly certain of those listed under (b) and (c) above, yielded vulcanizates possessing substantially improved resistance to air-oven aging compared to reference compositions I and II. They showed a moderate improvement in resistance to scorch or decomposition during processing, as compared with reference composition II but were still less resistant to scorch than the free sulfur reference composition I.

EXPERIMENTAL PART

Reference Compositions

GR-S 1500 with 50 PHR of medium abrasion furnace black (MAF) was used throughout the study. This mixture was further compounded with various vulcanizing agents, and in the subsequent sections of this report a particular composition shall be specified simply by identifying the nature and proportions of vulcanizing agents. In the production of GR-S 1500, 1.25 PHR of phenyl-β-naphthylamine (PBNA) are added by the manufacturer. In identifying the formulations PBNA will be specified only when an additional quantity of the material was used.

The components of the two compositions selected as standards for reference, mentioned in the Introduction, are as follows:

| Reference Composition I Free Sulfur + Accelerators | | Reference Composition II Accelerators | |
|---|-----------------|--|-----------------|
| Ingredient | Parts by weight | Ingredient | Parts by weight |
| GR-S | 100 | GR-S | 100 |
| MAF black | 50 | MAF black | 50 |
| Zinc oxide | 3 | Zinc oxide | 3 |
| Stearic acid | 1 | Stearic acid | 1 |
| PBNA | 1 | PBNA | 1 |
| Sulfur | 1.75 | DPMTS ^b | 1 |
| BTSCHA ^a | 1 | MBT ^c | 1 |

^a Benzothiazole-2-sulfenecyclohexylamide Or N-Cyclohexyl-2-benzothiazyl sulfenamide

^b Dipentamethylene-thiuram-tetrasulfide

^c 2-Mercaptobenzothiazole

Compounding and Curing

All batches were milled in a 3" x 8" two-roll 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" 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 was 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" (2 min.); and finally, (9) the mill

was opened and the batch withdrawn to give two uncured pads of approximately 6" x 6" x 0.1".

An electrically heated hydraulic press and a 6" x 6" x 0.080" 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 samples cured for 30 minutes at 307°F, and the cured pads were quenched in cold water.

Scorch Measurements

The scorch characteristics of the uncured compositions were determined by use of a shearing (scored) 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, as not entirely suitable for indicating the processing characteristics of the compositions containing dicumyl peroxide (DCP-40), since the peroxide tends to decompose without forming cross-links between the rubber molecules at 250°F. Another procedure was devised to indicate the behavior of uncured DCP-40 compositions 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, 230-250°F, for times up to three hours. After aging, 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 the uncured compositions.

Physical Property Measurements

Dumbbell specimens were cut from the 6" x 6" x 0.080" cured sheets by use of ASTM tensile die C (ASTM D 412-51T). Specimens for the tear measurements were prepared by use of ASTM Tear die C (ASTM D 624-54). The ultimate tensile strength, modulus, per cent elongation and tear resistance were measured by use of an automatic recording tensile testing machine. The values for the physical properties of the vulcanizates reported in succeeding tables are average values of four or more determinations.

Hardness was determined according to ASTM D-676-55T.

Dynamic properties were determined by use of a forced vibrator of the type designed by S. D. Gehman¹. The samples, 1 cm. diameter and 1 cm. high were formed in a special mold under the same conditions of curing as described above for the 6" x 6" x 0.080" sheets. The measurements were made at a frequency of approximately 60 cycles per second. The dynamic modulus E (kg/cm^2), the internal friction η (kilopoise), the heat buildup at constant amplitude H_x (calories/cycle), and the resilience R (per cent), are reported.

Aging Experiments

A mechanical convection oven was used for the aging experiments. The temperature variation of the oven at 212°F was within + 0.7°F. The conditions for most of the 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.

Reproducibility of Compounding, Curing and Aging Procedures

Since a maximum of only 200 g. of compounded rubber could be prepared at one time by use of the 3" x 8" mill it was desirable to establish the reproducibility of procedures in order that a large number of compositions could be studied.

In Table I the tensile properties of duplicate vulcanizates of the two standard compositions are recorded. The measurements were made with specimens from the cured sheets before and after aging in the mechanical convection oven at 212°F for 72 hours. The data for duplicate mixes listed in Table I show satisfactory agreement. Numerous other satisfactory checks on other duplicate compositions have been obtained.

TABLE I
REPRODUCIBILITY OF EXPERIMENTAL PROCEDURES

| Curing System ^a | Tensile, psi | | 300% Modulus, psi | | Elongation, % | | Hardness | |
|----------------------------|--------------|-------------------|-------------------|------|---------------|------|----------|------|
| | Orig. | Aged ^b | Orig. | Aged | Orig. | Aged | Orig. | Aged |
| 1.75 Sulfur + 1 BTSCHA | 2680 | 2920 | 2140 | -- | 400 | 250 | 68 | 74 |
| 1.75 Sulfur + 1 BTSCHA | 2870 | 2980 | 2170 | -- | 410 | 250 | 68 | 73 |
| 1 DPMTTS + 1 MBT | 2210 | 2380 | 1330 | 1830 | 470 | 380 | 66 | 67 |
| 1 DPMTTS + 1 MBT | 2230 | 2460 | 1340 | 1850 | 460 | 390 | 65 | 67 |

^aIn addition to the curatives listed, the compositions contained 1 part of stearic acid, 3 parts of ZnO, 1 part of PBNA and 50 parts of MAF black per 100 parts of GR-S 1500.

^bSpecimens were aged in air at 212°F for 72 hours.

PRESENTATION OF RESULTS

Sulfur-Bearing Accelerator Vulcanizing Systems

As mentioned in the Introduction, combinations of the sulfur-bearing 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:

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

Also, as previously mentioned, the first composition (a) was selected as a reference standard (reference composition II) for non-free sulfur vulcanizates since the Rock Island Arsenal had already developed considerable information regarding its properties.

The tensile and tear properties of these vulcanizates, measured before and after aging, are summarized in Table II. Table II also contains similar data for the free sulfur reference vulcanizate (reference composition I).

In Figures 1a and 1b the tensile properties of the vulcanizates from the second and third compositions, (b) and (c), are recorded. It may be seen from these curves that the optimum compositions are approximately:

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

By comparing the tensile properties of vulcanizates from these two optimum compositions, III and IV, with those of the free sulfur containing reference composition I, it may be seen that they possess lower values of tensile strength, 300% modulus and hardness, about the same tear resistance and considerably higher elongations. By making similar comparisons of vulcanizates of the optimum compositions, III and IV, with the non-free sulfur reference standard II, it may be seen that the physical properties are generally comparable, with the per cent elongations of vulcanizates III and IV being somewhat the higher.

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

TABLE II

PROPERTIES OF GR-S VULCANIZATES CURED WITH SULFUR-THIAZOLE AND THIURAM-THIAZOLE COMBINATIONS

| Curing System ^a | Tensile, psi | | Stress at 300% E, psi | | Elongation, % | | Hardness | | Tear, lb/in. at 77°F | |
|--------------------------------|--------------|-------------------|-----------------------|------|---------------|------|----------|------|----------------------|------|
| | Orig. | Aged ^b | Orig. | Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged |
| 1.75 Sulfur + (I) 1 BTSCHA | 2780 | 2950 | 2150 | -- | 410 | 250 | 68 | 74 | 260 | 170 |
| 1 DDMTTS + (II) 1 MBT | 2220 | 2420 | 1340 | 1890 | 470 | 390 | 65 | 67 | 280 | 210 |
| 1.5 TMTD + 1 DBTDMTU | 1970 | 2680 | 800 | 1270 | 650 | 610 | 63 | 65 | | |
| 1.75 TMTD + (III) 1 DBTDMTU | 2310 | 2650 | 950 | 1290 | 650 | 580 | 65 | 65 | 290 | 280 |
| 2 TMTD + 1 DBTDMTU | 2620 | 2830 | 1200 | 1620 | 610 | 320 | 64 | 69 | | |
| 3 TMTD + 1 DBTDMTU | 2970 | 2890 | 1750 | 2070 | 500 | 270 | 67 | 72 | | |
| 1 TMTD + 1 MBT | 970 | 2080 | 440 | 950 | 640 | 600 | 61 | 64 | | |
| 1.75 TMTD + (IV) 1 MBT | 2350 | 2730 | 1020 | 1440 | 610 | 550 | 66 | 66 | 280 | 270 |
| 2 TMTD + 1 MBT | 2580 | 2850 | 1200 | 1610 | 580 | 490 | 66 | 66 | | |

^aIn addition all systems contained 1 part of stearic acid, 3 parts of ZnO and 50 parts of MAF black per 100 parts of GR-S 1500.

^bSamples were aged in air for 72 hours at 212°F.

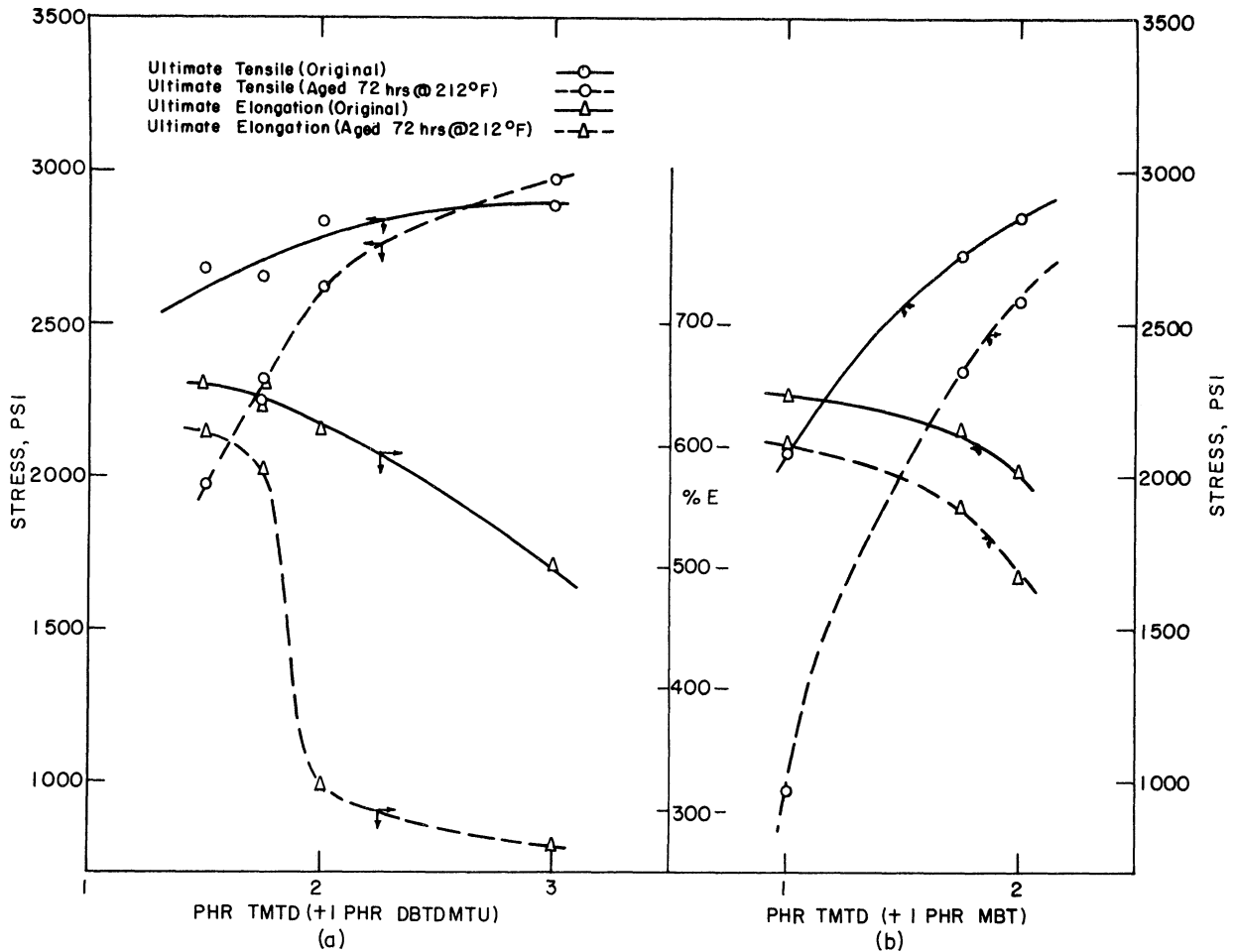


Fig. 1. Effect of concentration of sulfur-bearing accelerators on tensile properties of vulcanizates

The scorch resistance of these compositions shall be discussed in a later section.

Vulcanizates from compositions III and IV, that is tetramethylthiuram-disulfide in combination with dibenzothiazyl-dimethylthiol urea or 2-mercaptobenzothiazole exhibited a tendency to bloom, the blooming properties of the former being the more pronounced. It was learned through private communication² with a company which produces low molecular weight polyethylene waxes that the addition of such wax to rubber compositions might hinder or completely prevent blooming. A few vulcanizates of the composition III (TMTD with DBTMTU) were made with 2 PHR of the polyethylene wax. The products showed slightly lower tensile strength and slightly higher per cent elongation 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.

In summary, the properties of these non-free sulfur cured vulcanizates showed considerably greater resistance to air-oven aging, somewhat lower values of tensile strength and higher per cent elongation than the free sulfur-BTSCHA vulcanizates. Certain of the non-free sulfur vulcanizates showed a tendency to bloom. The blooming was controlled in one composition by the incorporation of 2 PHR of low molecular weight polyethylene wax.

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, such as systems based on peroxides. Much of the early work on various types of peroxides³ had not indicated much promise for commercial applications.

It happened that at the beginning of this project, however, the commercial availability of dicumyl peroxide was announced and the first information⁴ indicated that it possessed promising qualities for rubber vulcanization. Thus, it was of considerable interest to examine this material. (During the course of this work the successful vulcanizations of nitrile and Hevea rubbers with dicumyl peroxide was reported.²)

Rubber compounds containing dicumyl peroxide were prepared and vulcanized under the same conditions and with the same equipment as used in the preparation of the two standard vulcanizates. The physical properties of vulcanizates cured with various amounts of dicumyl peroxide (DCP-40 -- 40% dicumyl peroxide, 60% CaCO₃) are tabulated in Table III, the measurements having been made before and after aging.

Figures 2a and 2b show graphs of the tensile and elongation values of the vulcanizates versus the original DCP-40 concentration.

The original rubber compounds in Figure 2a contained only the PBNA originally present in the GR-S 1500 (1.25 PHR) while those in Figure 2b contained an additional PHR of PBNA. It should be noted that the concentration of DCP-40 corresponding to the maximum tensile value was shifted from approximately 1.75 to 2.5 PHR of DCP-40 by the addition of 1 PHR of PBNA. Thus, it was apparent that a portion of the PBNA and the DCP reacted.

The optimum DCP-40 vulcanizates had somewhat low values of tensile strength, per cent elongation, 300% modulus and tear resistance in comparison with those of the standard BTSCHA-sulfur cured vulcanizate (Table II), while the hardness values were comparable. These DCP-40 products had lower per cent elongation and tear resistance values than the DPMTTS-MBT reference composition II but otherwise the original physical properties were similar. After air-oven aging, however, the physical properties of DCP-40 cured vulcanizates were better than either the BTSCHA-sulfur or the DPMTTS-MBT cured standards.

The presence of ZnO and stearic acid with DCP-40 composition appeared to give vulcanizates with slightly improved ultimate tensile and elongation values compared to those obtained when only DCP-40 was used (Table III).

Thus, although the use of DCP-40 as a curing agent yields vulcanizates having somewhat lower tensile, elongation, 300% modulus and tear resistance values than those of the standard BTSCHA-sulfur cured vulcanizate, the excellent air-oven age resistance of these vulcanizates is striking.

TABLE III
 PROPERTIES OF GR-S VULCANIZATES CURED WITH DICUMYL PEROXIDE

| Curing System ^a | Tensile, psi | | Stress at %E, psi | | Elongation, % | | Hardness | | Tear, lb/in at 77°F | | |
|----------------------------|--------------|-------------------|-------------------|---------|---------------|------|----------|------|---------------------|------|-----|
| | Orig. | Aged ^d | Orig. | %E Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged | |
| 1 DCP-40 | 1710 | 1510 | 750 | 300 | 770 | 600 | 530 | 63 | 65 | 230 | 230 |
| 1.5 DCP-40 | 2260 | 2230 | 1420 | " | 1510 | 430 | 420 | 65 | 66 | 220 | 220 |
| 2 DCP-40 | 2280 | 2160 | 1650 | " | 1590 | 350 | 360 | 66 | 67 | 180 | 170 |
| 2.5 DCP-40 | 2220 | 2270 | 1370 | 200 | 1410 | 280 | 280 | 67 | 67 | | |
| 5 DCP-40 | 1830 | 1930 | 1160 | 100 | 1170 | 130 | 130 | 75 | 76 | | |
| 1.25 DCP-40 ^b | 1320 | 1130 | 550 | 300 | 530 | 610 | 550 | 58 | 60 | 230 | 230 |
| 2 DCP-40 ^b | 2210 | 2060 | 1260 | " | 1170 | 500 | 490 | 62 | 65 | 270 | 230 |
| 2.25 DCP-40 ^b | 2310 | 2190 | 1480 | " | 1430 | 450 | 410 | 65 | 65 | | |
| 2.5 DCP-40 ^b | 2320 | 2240 | 1730 | " | 1680 | 390 | 390 | 65 | 65 | 230 | 260 |
| 3.75 DCP-40 ^b | 2090 | 2290 | 1480 | 200 | 1460 | 280 | 280 | 69 | 70 | | |
| 5 DCP-40 ^b | 2000 | 2060 | 630 | " | 720 | 190 | 200 | 72 | 71 | | |
| 1.25 DCP-40 ^c | 990 | 870 | 390 | 300 | 390 | 640 | 620 | 58 | 60 | 200 | 200 |
| 2 DCP-40 ^c | 1930 | 2000 | 1030 | " | 1010 | 510 | 530 | 61 | 65 | 260 | 260 |
| 2.5 DCP-40 ^c | 2370 | 2290 | 1590 | " | 1540 | 430 | 410 | 65 | 66 | 230 | 260 |
| 3.75 DCP-40 ^c | 2320 | 2560 | 2210 | " | 2180 | 310 | 340 | 67 | 67 | | |
| 5 DCP-40 ^c | 2170 | 2350 | 1930 | 200 | 1970 | 210 | 220 | 72 | 72 | | |

^aAll systems contained 50 parts of MAF black per 100 parts of GR-S 1500.

^bThe curing systems contained 1 part of PBNA.

^cThe curing systems contained 1 PBNA + 3 ZnO + 1 stearic acid.

^dSamples were aged in air for 72 hours at 212°F.

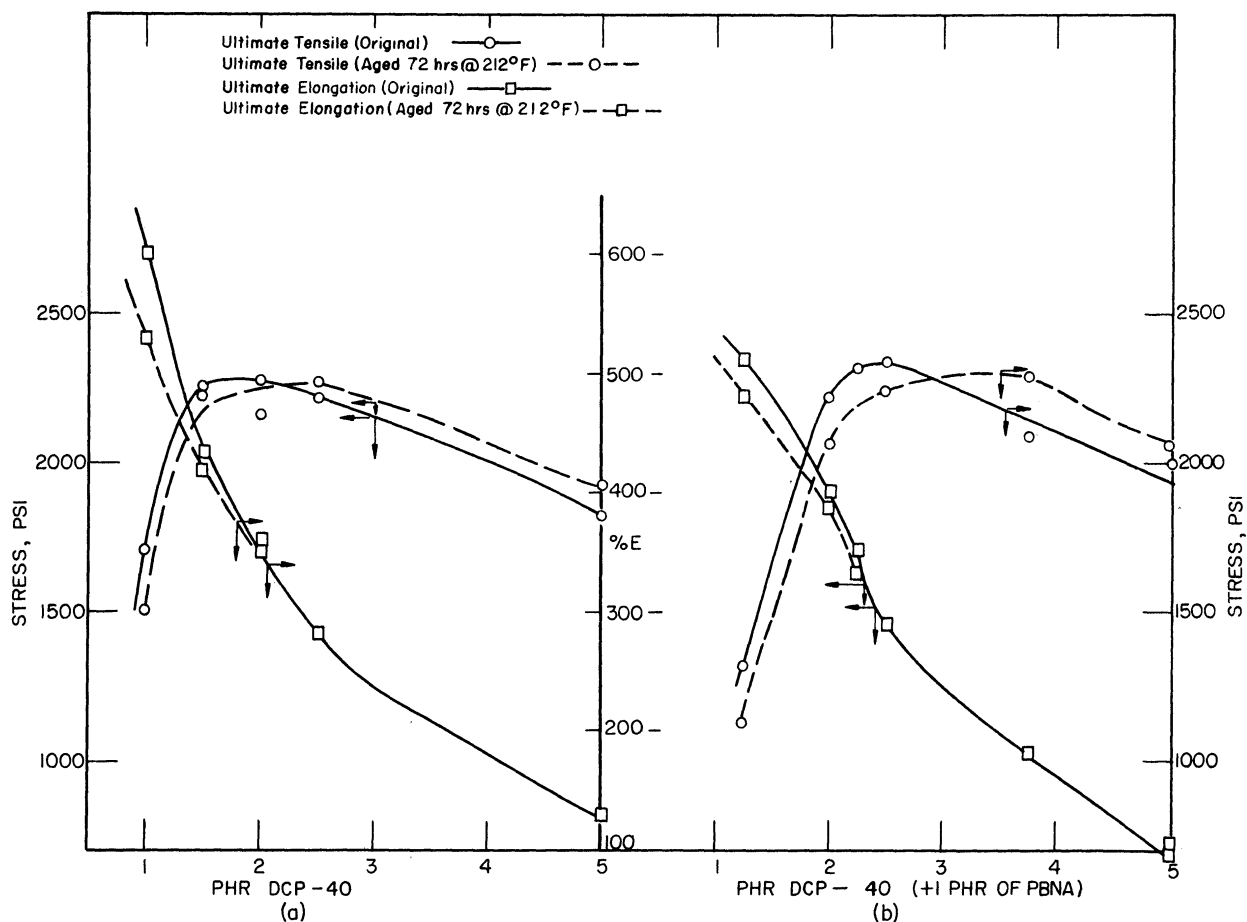


Fig. 2. Physical properties of GR-S 1500 vulcanizates cured with dicumyl peroxide

Effect of Oxygen-Containing Inhibitors on the Dicumyl Peroxide Curing System

It was noted above that there was some reaction between phenyl- β -naphthylamine and dicumyl peroxide during vulcanization. The surprising fact is, however, that the reaction is not dominant. That is to say, the vulcanization still took place. Therefore, it was of interest to carry out similar vulcanizations in the presence of oxygen-containing inhibitors, such as phenolic antioxidants.

The phenolic type materials, resorcinol, β -naphthol and hydroquinone were used in combination with DCP-40 and the results are summarized in Table IV. In these compositions the regular GR-S 1500 containing 1.25 PHR of PBNA was used with an additional PHR of PBNA. Therefore, the data listed in Table IV are actually for compositions including a combination of the oxygen- and nitrogen-containing inhibitors.

It may be seen in Table IV that the physical properties of the vulcanizates containing resorcinol and hydroquinone did not compare favorably with those of vulcanizates with PBNA alone (Table III). However, the properties of the composition containing β -naphthol were about equivalent to those of several of the vulcanizates listed in Table III. This study was very limited, and possibly the β -naphthol compositions should be examined

TABLE IV
EFFECT OF OXIDATION INHIBITORS ON THE DICUMYL PEROXIDE CURING SYSTEM

| Curing System | Tensile, psi | Elongation, % | 300% Modulus, psi | Hardness |
|--|--------------|---------------|-------------------|----------|
| 2.5 DCP-40 + 1 PBNA ^a + 0.75 Resorcinol | 1820 | 530 | 970 | 61 |
| 2.5 DCP-40 + 1 PBNA ^a + 0.3 β-Naphthol | 1990 | 440 | 1410 | 64 |
| 2.5 DCP-40 + 1 PBNA ^a + 0.5 Hydroquinone | 390 | 500 | 240 | 58 |

^aThe curing system contained an additional PHR of PBNA.

further with consideration to the facts that Braden et al⁶ noted that certain peroxides catalyze the decomposition of rubber, and Bolland and Ten Have⁷ observed that some phenolic substances inhibit the oxidation of olefins.

Dicumyl Peroxide - Sulfur-Bearing Accelerator Vulcanizing Systems

Turning to the third type of vulcanizing system mentioned in the Introduction, several sulfur-bearing accelerators were used in combination with dicumyl peroxide. 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)
 diphenylguanidine (DPG), and
- 3) 2,4-dinitrophenyl-dimethyl-dithiocarbamate (DNPDMDTC)

In brief, vulcanizates containing DCP-40 with members of the first group possessed the most desirable combination of physical properties; those from the second group appeared to have some less desirable properties, and those prepared with the product in the third group appeared to have the least desirable properties.

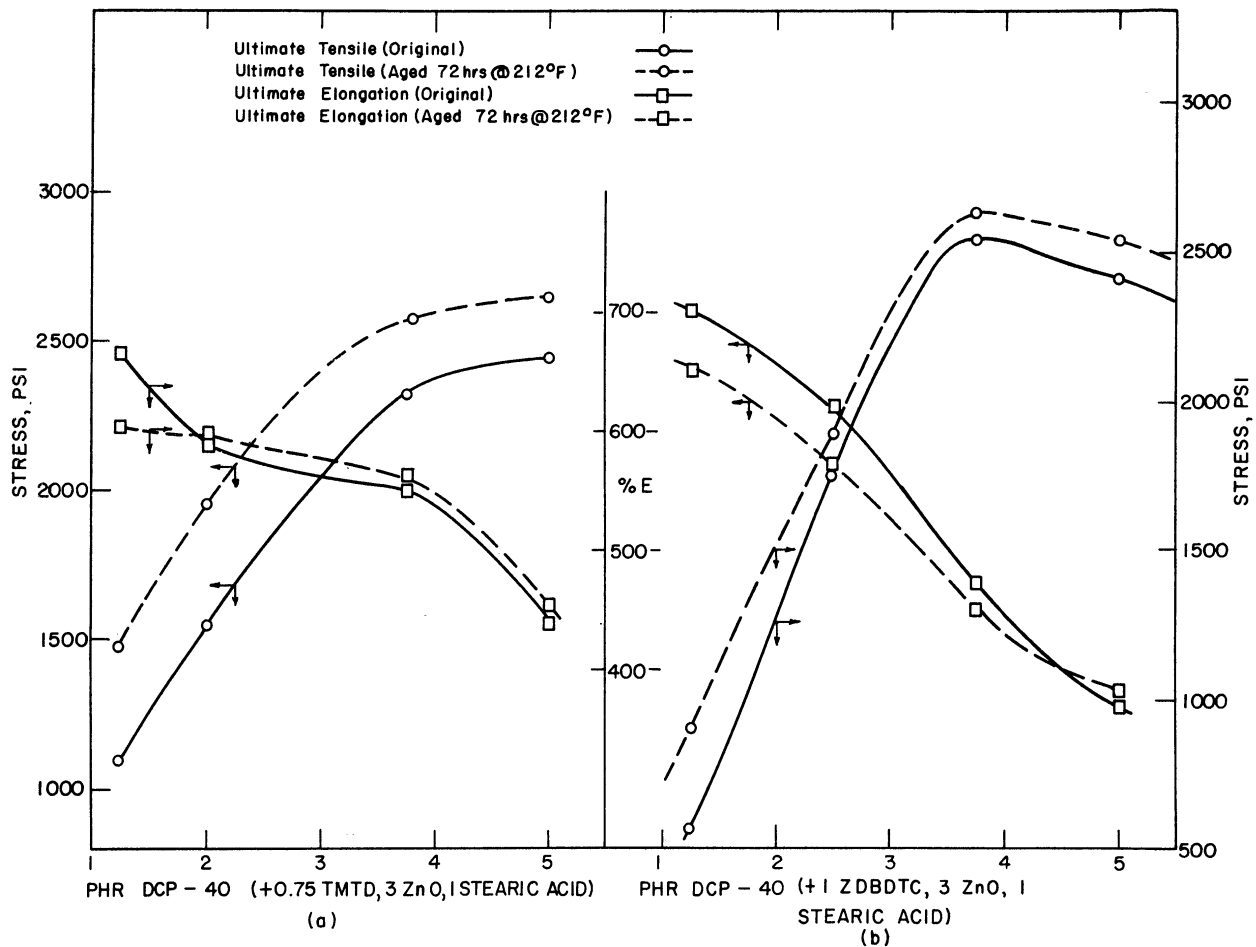


Fig. 3. Tensile properties of dicumyl peroxide - sulfur-bearing accelerator cured vulcanizates

Properties of the DCP-40-TMTD and DCP-40-ZDBDTC vulcanizates are shown in Figures 3a and 3b and Tables V and VI while the properties of the other combinations are recorded in Table VII.

The dicumyl peroxide - tetramethyl-thiuram-disulfide (DCP-40-TMTD) combination (Table V and Figure 3a) was improved by the presence of 1 additional PHR of phenyl- β -naphthylamine, 1 PHR stearic acid and 3 PHR zinc oxide. From Figure 3a it may be judged that the optimum proportions of the curing agents are 3.75 PHR DCP-40, 0.75 PHR TMTD, 3 PHR zinc oxide plus one additional PHR PBNA. On comparing the properties of this vulcanizate with those obtained from similar compositions containing DCP-40 as the only curing agent (Table III) it is apparent that the presence of the TMTD has caused some increase in tensile strength and a large increase in elongation with little effect on the aging properties and other physical properties.

Similar and somewhat more pronounced changes resulted from the presence of zinc dibutyl-dithiocarbamate with the DCP-40 (Figure 3b and Table VI). From Figure 3b, the optimum composition is 3.75 PHR DCP-40, 1 PHR ZDBDTC, 3 PHR ZnO, plus 1 additional PHR PBNA and 1PHR stearic acid. Again, by comparing the properties of this vulcanizate with those of a similar composition with DCP-40 as the only curing agent (Table III) it can be seen that the presence of the zinc dibutyl-dithiocarbamate has given considerably higher tensile and elongation values with little effect on the aging properties and other physical properties.

The tensile values for the aged vulcanizates in Figures 3a and 3b are higher than those for the original products, the effect being the more pronounced for DCP-40-TMTD compositions. The reasons for this effect are not clear but must be due at least in part to additional curing during the aging process. This effect shall be discussed further in the following section.

In summary, vulcanizates formed with combinations of dicumyl peroxide with tetramethyl-thiuram-disulfide or with zinc dibutyl-dithiocarbamate, possessed slightly lower tensile and tear values, somewhat higher values of per cent elongation, and markedly improved resistance to aging when compared with the standard free sulfur-BTSCHA (reference composition I) vulcanizate; when compared with the non-free sulfur vulcanizates (such as reference composition II), these vulcanizates showed improved physical and aging properties; and when compared with DCP-40 vulcanizates (with PBNA) they showed improved physical properties and equivalent age resistance.

TABLE V

PROPERTIES OF GR-S VULCANIZATES CURED WITH DICUMYL PEROXIDE-THIURAM COMBINATIONS

| Curing System ^a | Tensile, psi | | Stress at 300%E, psi | | Elongation, % | | Hardness | | Tear, lb/in. | |
|--------------------------------------|--------------|------|----------------------|------|---------------|------|----------|------|------------------|------|
| | Orig. | Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged |
| 2.5 DCP-40 + 3 TMTD ^b | 1070 | 1300 | 440 | 510 | 590 | 610 | 60 | 63 | 210 | 210 |
| 2.5 DCP-40 + .75 TMTD | 590 | 660 | 290 | 370 | 660 | 640 | 60 | 61 | 160 | 180 |
| 3.75 DCP-40 + .75 TMTD | 1120 | 1230 | 480 | 570 | 610 | 610 | 59 | 63 | 220 | 240 |
| 2.5 DCP-40 + .4 TMTD ^c | 1230 | 1300 | 510 | 600 | 610 | 600 | 61 | 65 | 220 | 260 |
| 3.75 DCP-40 + .4 TMTD | 1900 | 1990 | 920 | 1010 | 540 | 530 | 62 | 65 | 210 | 210 |
| 1.25 DCP-40 + .75 TMTD | 1100 | 1470 | 420 | 630 | 660 | 600 | 60 | 63 | 230 | 260 |
| 2 DCP-40 + .75 TMTD ^c | 1550 | 1840 | 650 | 830 | 600 | 590 | 60 | 64 | 280 | 290 |
| 3.75 DCP-40 + .75 TMTD | 2330 | 2570 | 1170 | 1290 | 550 | 560 | 62 | 66 | 210 | 210 |
| 5.0 DCP-40 + .75 TMTD | 2440 | 2640 | 1490 | 1650 | 440 | 450 | 65 | 68 | 180 ^d | 180 |

^a All systems contained 50 parts of MAF black per 100 parts of GR-S 1500.

^b The curing system contained 1 additional PHR of PBNA.

^c The curing system contained 1 additional PHR of PBNA + 3 ZnO + 1 stearic acid.

^d Samples were aged in air for 72 hours at 212°F.

TABLE VI

PROPERTIES OF GR-S VULCANIZATES CURED WITH DICUMYL PEROXIDE-DITHIOCARBAMATE COMBINATIONS

| Curing System ^a | Tensile, psi | | Stress at 300%E, psi | | Elongation, % | | Hardness | | Tear, lb/in. at 77°F | |
|------------------------------|--------------|-------------------|----------------------|------|---------------|------|----------|------|----------------------|------|
| | Orig. | Aged ^b | Orig. | Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged |
| 3.75 DCP-40 + 0.4 ZDBDTC | 2240 | 2330 | 1300 | 1390 | 470 | 470 | 65 | 66 | 180 | 200 |
| 3.75 DCP-40 + 0.75 ZDBDTC | 2170 | 2240 | 1150 | 1220 | 510 | 500 | 65 | 65 | 210 | 200 |
| 1.25 DCP-40 + 1 ZDBDTC | 570 | 910 | 240 | 390 | 700 | 650 | 61 | 62 | 180 | 210 |
| 2.5 DCP-40 + 1 ZDBDTC | 1750 | 1890 | 700 | 900 | 620 | 570 | 62 | 64 | 230 | 240 |
| 3.75 DCP-40 + 1 ZDBDTC | 2540 | 2630 | 1480 | 1610 | 470 | 450 | 65 | 66 | 180 | 200 |
| 5 DCP-40 + 1 ZDBDTC | 2410 | 2540 | 1900 | 2000 | 370 | 380 | 67 | 69 | 160 | 160 |

^aAll curing systems contained 1 part of PBNA, 3 parts of ZnO, 1 part of stearic acid, and 50 parts of MAF black per 100 parts of GR-S 1500.

^bSamples were aged in air for 72 hours at 212°F.

TABLE VII

PROPERTIES OF GR-S VULCANIZATES CURED WITH DICUMYL PEROXIDE--ACCELERATOR COMBINATIONS

| Curing System ^a | Tensile, psi | | Stress at 300%E, psi | | Elongation, % | | Hardness | | Tear, lb/in. at 77°F | |
|------------------------------|--------------|------|----------------------|------|---------------|------|----------|------|----------------------|------|
| | Orig. | Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged | Orig. | Aged |
| 3.75 DCP-40 + .4 MBT | 2280 | 2200 | -- | 2010 | 310 | 310 | 68 | 69 | 110 | 110 |
| 3.75 DCP-40 + .75 MBT | 2110 | 2210 | 1940 | 1860 | 310 | 330 | 68 | 68 | 130 | 130 |
| 3.75 DCP-40 + .2 DPG | 2360 | 2250 | 2060 | 1980 | 330 | 320 | 68 | 70 | 160 | 160 |
| 3.75 DCP-40 + .4 DPG | 2090 | 2180 | -- | -- | 270 | 280 | 69 | 71 | 140 | 150 |
| 3.75 DCP-40 + .75 DNPDMDC | 1360 | 1720 | 690 | 890 | 570 | 550 | 62 | 66 | 210 | 270 |
| 3.75 DCP-40 + .75 TBIM | 2460 | 2480 | 1480 | 1500 | 480 | 460 | 65 | 67 | 190 | 210 |

^aAll curing systems contained 1 additional part of PBNA, 3 parts of ZnO, 1 part of stearic acid, and 50 parts of MAF black per 100 parts of GR-S 1500.

^bSamples were aged in air for 72 hours at 212°F.

Effect of Curing Time on Various Dicumyl Peroxide Systems

Some evidence for post-curing during air-oven aging of dicumyl peroxide vulcanizates was noted above (see Figure 3a). It was of interest to examine the effect of curing time at 307°F on selected DCP-40 compositions. In Figures 4a, 4b and 4c variations of tensile properties with curing time are shown for vulcanizates containing DCP-40 and combinations of DCP-40 with tetramethyl-thiuriam-disulfide (TMTD) and with zinc dibutyl-dithiocarbamate (ZDBDTC).

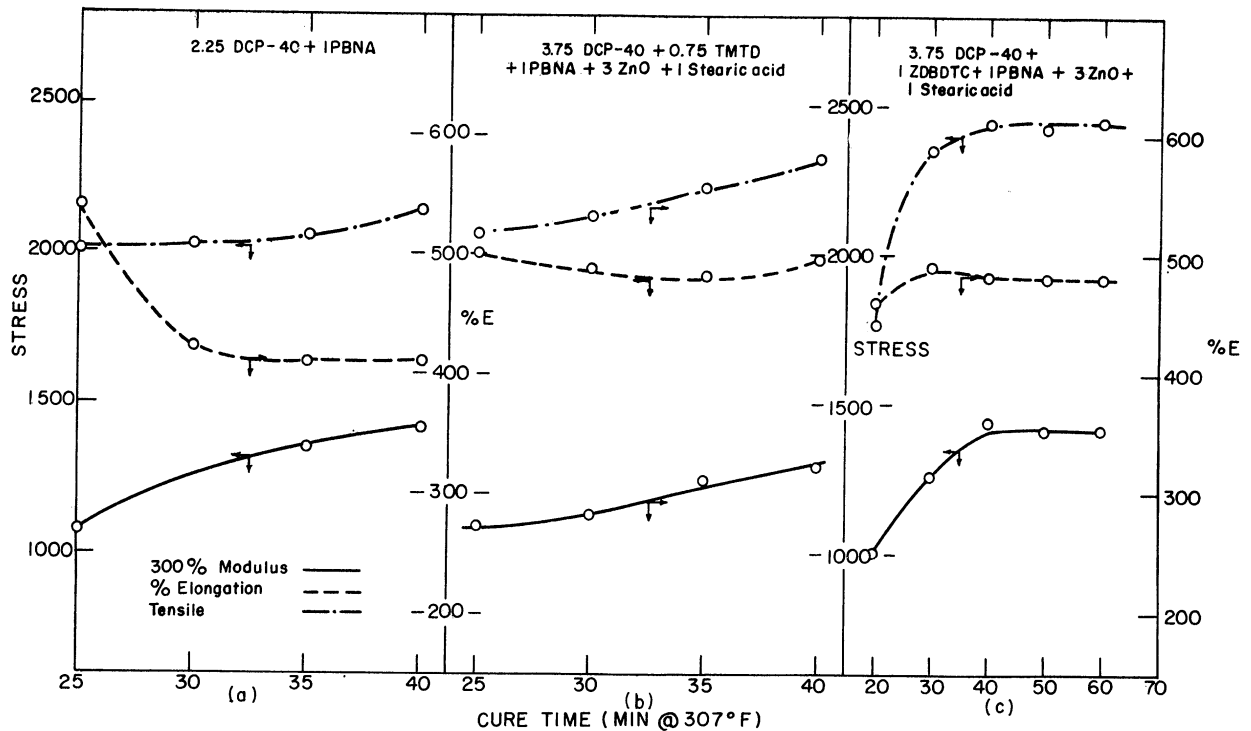


Fig. 4. Effect of curing time on tensile properties of dicumyl peroxide compositions

In Figures 4a and 4c it may be seen that the tensile properties of these vulcanizates are not greatly changed by curing at 307°F for periods longer than about 30 - 35 minutes. However, the values of the tensile strength and 300% modulus for the DCP-40-TMTD product, Figure 4b, appear to be rising at the 40 minutes point, and therefore, it seems likely that post-curing during aging can account for the behavior shown in Figure 3a.

Scorch Properties of Selected Vulcanizing Systems

As indicated in the Introduction, the weight of previous experience with non-free sulfur vulcanizing systems would immediately raise the question of processing stability for almost any non-free sulfur system under consideration.

Conventional scorch measurements were made according to the ASTM D 1077-55T procedure with a shearing disk type viscometer. The results are summarized in Table VIII.

The standard BTSCHA-sulfur compound had a high resistance to scorch as indicated by the time of 61 minutes required for a five unit rise of viscosity over the minimum value (t_5). The addition of 1 PHR of the retarder N-nitroso-diphenylamine (NNDPA) increased the t_5 value to 70 minutes. The non-free sulfur standard of DPMMTS + MBT had poor scorch resistance with a t_5 value of seven minutes; addition of 1 PHR of NNDPA to the compound resulted in a t_5 value of fourteen minutes.

The TMTD-MBT and the TMTD-DBTDMTU compounds had scorch values intermediate to the two standards; t_5 was 23 minutes for the former and 19 minutes for the latter. The compounds containing DCP-40 alone as the curing agent had t_5 values of 38 minutes for 3.75 PHR of DCP-40, and 62 minutes for 2.25 PHR of DCP-40. Compounds containing combinations of DCP-40 and sulfur-bearing accelerators had a wide range of scorch resistance as indicated by the t_5 values; DCP-40 + TMTD or DPG compounds had t_5 values of about 25 minutes while the DCP-40+ZBBDTC compound had a t_5 value of 40 minutes.

As mentioned in the Experimental Part, the conventional scorch test for the peroxide compositions is not entirely meaningful since some peroxide may undergo decomposition without causing vulcanization during the test. Therefore, the supplementary test described in the Experimental Part was used which involved heating sheets of the raw compound (as obtained directly from the mill) in a circulating air oven for periods up to three hours at temperatures in the range 230 - 250°F and then curing at 307°F during 30 minutes. The properties of three vulcanizates from compositions containing originally 2.25 and 2.50 PHR DCP-40 and 1 additional PHR PBNA are summarized in Table IX. It may be seen that the compositions tolerated preheating for about 30 minutes at 250°F and somewhat longer periods at the lower temperatures before changes in the physical properties of the vulcanizates were substantial.

As previously indicated, it is difficult to state what would be a satisfactory scorch resistance since the current industrial trend seems to be toward more severe processing conditions. While none of these experimental compositions have the scorch resistance of the conventional free sulfur compound (reference composition I, t_5 = 60 minutes), the several experimental compositions having stabilities of 20 - 40 minutes at 250°F could be used safely if their properties could justify some limitation in processing conditions.

TABLE VIII
SCORCH RESISTANCE OF SELECTED COMPOSITIONS^a

| Curing System | Scorch Time | | | | | |
|---|--|---|------------------------------|---|-----------------|--|
| | No Retarder t ₅ ^b | 1 PHR NNDA ^f t ₅ | t ₁₀ ^c | 1 PHR EDHMTM ^g t ₅ | t ₁₀ | 1 PHR NNDSBPPDA ^h t ₅ |
| 1 BTSCHA ^d + 1.75 Sulfur | 61 | 67 | 70 | 88 | | |
| 1.5 DPWTTSD + 1 MBT | 7 | 8 | 14 | 16 | | |
| 1.75 TMTD ^d + 1 MBT | 23 | 28 | 23 | 27 | 21 | 14 |
| 1.75 TMTD ^d + 1 DBTDMTU | 19 | 22 | | | | 16 |
| 2.25 DCP-40 ^e | 62 | 95 | | | | |
| 2.25 DCP-40 ^e | 54 | 70 | | | | |
| 3.75 DCP-40 ^e | 38 | 53 | | | | |
| 3.75 DCP-40 ^e + 0.75 TMTD | 26 | 33 | | | | |
| 5.00 DCP-40 ^e + 0.75 TMTD | 25 | 29 | | | | |
| 3.75 DCP-40 ^e + 1 ZBBDTC | 40 | 58 | | | | |
| 3.75 DCP-40 ^e + 0.75 MBT | 63 | 88 | | | | |
| 3.75 DCP-40 ^e + 0.4 DFG | 25 | 35 | | | | |

^aTest run at 250°F (ASTM Method D 1077-55T).

^bt₅ is the time in minutes for a 5 unit rise over the minimum.

^ct₁₀ is the time in minutes for a 10 unit rise over the minimum.

^dIn addition the system contained 1 part of stearic acid, 3 parts of ZnO, and 50 parts of MAF black per 100 parts of GR-S 1500.

^eIn addition the system contained 1 part of PBNA, 1 part of stearic acid, 3 parts of ZnO, and 50 parts of MAF black per 100 parts of GR-S 1500.

^fN-nitroso-diphenylamine

^g6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline

^hN,N'-disecbutyl-p-phenylenediamine

TABLE IX
STABILITY OF DICUMYL PEROXIDE COMPOSITIONS TO HEATING IN AIR

| Curing ^a System | Temp. F. | Tensile, psi | | | Elongation, % | | | Stress at 300% E, psi | | | Hardness | | | | | | | | | | |
|--------------------------------------|-------------|--------------|-------|-------|---------------|-------|-------|-----------------------|-------|-------|----------|-------|------|------|-----|-----|----|----|----|----|-----|
| | | Hours | Hours | Hours | Hours | Hours | Hours | Hours | Hours | Hours | Hours | Hours | | | | | | | | | |
| 2.25 DCP-40 + 1 PBNA | 250 | 0 | 1/2 | 1 | 2 | 3 | 0 | 1/2 | 1 | 2 | 3 | 0 | 1/2 | 1 | 2 | 3 | | | | | |
| | | 2380 | 2300 | 1770 | 1010 | ----- | 490 | 490 | 610 | 680 | ----- | 1240 | 1190 | 710 | 380 | --- | 65 | 65 | 62 | 60 | --- |
| | | 2270 | 2230 | 2140 | 1610 | 1670 | 400 | 420 | 460 | 510 | 510 | 1760 | 1570 | 1340 | 870 | 950 | 67 | 66 | 65 | 63 | 63 |
| 2.50 DCP-40 ^b + 1 PBNA | 230 | 0 | 1/2 | 1 | 2 | 3 | 0 | 1/2 | 1 | 2 | 3 | 0 | 1/2 | 1 | 2 | 3 | | | | | |
| | | 2130 | 2120 | 2080 | 1500 | 1510 | 500 | 520 | 560 | 590 | 600 | 1280 | 1130 | 950 | 780 | 740 | 63 | 63 | 63 | 63 | 62 |
| | | 2080 | 2080 | 2080 | 1500 | 1510 | 500 | 520 | 560 | 590 | 600 | 1280 | 1130 | 950 | 780 | 740 | 63 | 63 | 63 | 63 | 62 |

^a In addition all systems contained 50 parts of MAF black per 100 parts of GR-S 1500.

^b Compositions from a new supply of GR-S 1500. The new supply required 2.50 PHR DCP-40 to yield about the same state of cure as was obtained with the previous product and 2.25 PHR of DCP-40.

Aging of Selected Vulcanizates at Various Temperatures

Perhaps the answer to the question of whether these compositions can be used lies in the question of just how desirable are the aging properties of these products. To gain further information on this point, several of these compositions were subjected to air-oven aging at 212°F for periods up to 32 days at 250°F for 15 days and at 300°F for 12 hours. The results are summarized in Tables X, XI and XII.

Aging Studies at 212°F

The results at 212°F are shown graphically in Figures 5, 6, and 7, in which the values for per cent elongation, tensile strength and 300% modulus are plotted against time of aging. Inspection of these curves shows that the per cent elongation of the vulcanizates varied more regularly with time of aging than did the 300% modulus or tensile strength. Thus for discussion, attention may be concentrated on Figure 5.

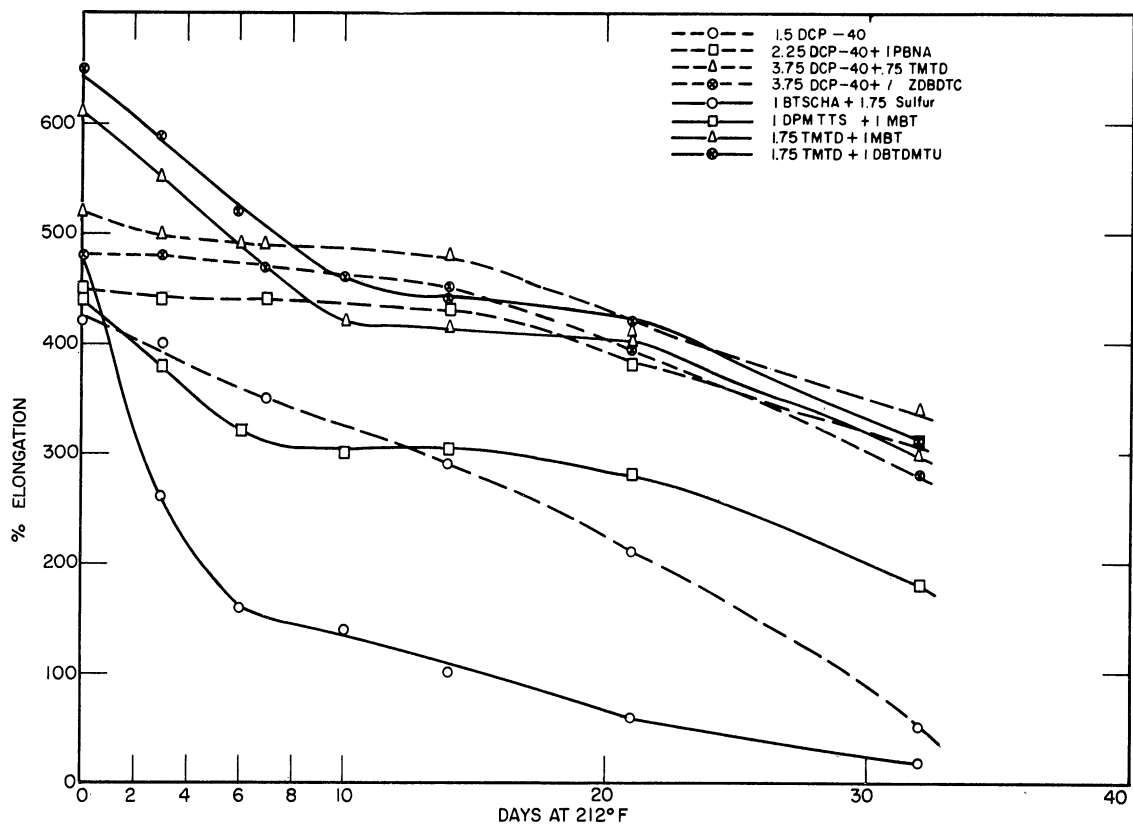


Fig. 5. Effect of extended air-oven aging at 212°F on the elongation of GR-S vulcanizates

TABLE X
EFFECT OF AGING AT 212°F ON SELECTED VULCANIZATES

| Curing System | Tensile, psi | | | Stress at 300% E, psi | | | Elongation, % | | | Hardness | | | | | | | | | | | | | | |
|---|--------------|-------------------|------|-----------------------|------|------|---------------|------|------|----------|------|------|-----|-----|-----|-----|-----|-----|----|----|----|----|----|----|
| | Orig. | Days ^c | | Orig. | Days | | Orig. | Days | | Orig. | Days | | | | | | | | | | | | | |
| | | 3 | 7 | | 14 | 21 | | 32 | 3 | | 7 | 14 | 21 | 32 | | | | | | | | | | |
| 2.25 DCP-40 ^a 1 PBNA | 2280 | 2170 | 2140 | 2120 | 2020 | 1760 | 1320 | 1300 | 1390 | 1510 | 1630 | 1710 | 450 | 440 | 440 | 430 | 380 | 310 | 64 | 66 | 66 | 67 | 68 | 69 |
| 3.75 DCP-40 ^b .75 TMTD + 1 PBNA | 2430 | 2620 | 2530 | 2420 | 2400 | 2270 | 1270 | 1450 | 1410 | 1490 | 1670 | 1920 | 520 | 500 | 490 | 480 | 410 | 340 | 65 | 66 | 67 | 69 | 69 | 70 |
| 3.75 DCP-40 ^b 1.0 ZBBDTC + 1 PBNA | 2310 | 2440 | 2400 | 2440 | 2380 | 1810 | 1330 | 1430 | 1510 | 1620 | 1720 | -- | 480 | 480 | 470 | 450 | 395 | 280 | 64 | 66 | 67 | 68 | 69 | 70 |
| 1.5 DCP-40 ^a 1.75 TMTD ^b 1 MBT + 1 PBNA | 2220 | 1970 | 1800 | 1620 | 1250 | 610 | 1550 | 1450 | 1500 | 1640 | -- | -- | 420 | 400 | 350 | 290 | 210 | 50 | 65 | 66 | 67 | 68 | 69 | 79 |
| 1.75 TMTD ^b 1 MBT + 1 PBNA | 2360 | 2720 | 2890 | 2700 | 2570 | 1950 | 1020 | 1440 | 1740 | 1910 | 1950 | 1950 | 610 | 550 | 470 | 415 | 400 | 300 | 66 | 66 | 66 | 67 | 69 | 70 |
| 1.75 TMTD ^b 1 DBTDMTU + 1PBNA | 2130 | 2680 | 2700 | 2480 | 2390 | 1890 | 900 | 1330 | 1470 | 1590 | 1750 | 1860 | 650 | 590 | 510 | 440 | 420 | 310 | 65 | 65 | 66 | 68 | 70 | 71 |
| 1 DBTMTS + 1 MBT + 1 PBNA | 2100 | 2400 | 2280 | 2200 | 1800 | 1330 | 1300 | 1890 | 2050 | 1960 | -- | -- | 440 | 380 | 310 | 310 | 280 | 180 | 65 | 67 | 68 | 69 | 70 | 72 |
| 1 BPSCHA + 1.75 Sulfur + 1PBNA | 2450 | 2550 | 2020 | 1750 | 1390 | 800 | 1430 | -- | -- | -- | -- | -- | 480 | 260 | 150 | 100 | 60 | 20 | 66 | 73 | 75 | 80 | 84 | 89 |

^aIn addition systems contained 50 parts of MAF black per 100 parts of GR-S 1500.

^bIn addition systems contained 1 part of stearic acid, 3 parts of ZnO, and 50 parts of MAF black per 100 parts of GR-S 1500.

^cDays aged in air at 212°F.

TABLE XI
EFFECT OF AGING AT 250°F ON SELECTED VULCANIZATES

| Curing System | Tensile, psi | | | Elongation, % | | | Stress at 300% E, psi | | | Hardness | | | | | | | | | | | |
|---------------------------------------|--------------|-------------------|------|---------------|------|------|-----------------------|------|-----|----------|------|------|-------|-------|----|----|----|----|----|----|----|
| | Orig. | Days ^c | | Orig. | Days | | Orig. | Days | | Orig. | Days | | | | | | | | | | |
| | | 1 | 3 | | 7 | 11 | | 15 | 1 | | 3 | 7 | 11 | 15 | | | | | | | |
| 1.75 DCP-40 ^a | 2130 | 1890 | 1320 | 410 | 1340 | 1320 | 420 | 370 | 290 | 60 | 20 | 1500 | 1330 | 1190 | -- | 65 | 65 | 66 | 82 | 93 | 97 |
| 2.5 DCP-40 + 1 PBNA | 2140 | 1890 | 1340 | 480 | 1050 | 1050 | 410 | 370 | 320 | 70 | 20 | 1550 | 1500 | 1300 | -- | 65 | 66 | 66 | 77 | 91 | 95 |
| 4.00 DCP-40 + .75 TMED + 1 PBNA | 2150 | 2200 | 2120 | 1820 | 460 | 270 | 510 | 510 | 470 | 270 | 40 | 1200 | 1220 | 1270 | -- | 63 | 65 | 69 | 71 | 81 | 92 |
| 4.00 DCP-40 + 1 ZDBDTC + 1 PBNA | 2350 | 2450 | 2380 | 660 | 950 | 280 | 480 | 480 | 460 | 150 | 20 | 1400 | 1480 | 1560 | -- | 65 | 66 | 69 | 71 | 89 | 92 |
| 1 BTSCHA + 1.75 Sulfur + 1 PBNA | 2920 | 2370 | 2120 | 1180 | 790 | 790 | 460 | 240 | 180 | 40 | 10 | 1840 | ----- | ----- | -- | 69 | 73 | 78 | 83 | 91 | 95 |
| 1 DPMETS + 1 MBT + 1 PBNA | 2090 | 2190 | 2090 | 1480 | 690 | 620 | 500 | 410 | 350 | 110 | 30 | 1260 | 1420 | 1710 | -- | 65 | 66 | 70 | 70 | 84 | 93 |

^a New supply of GR-S 1500. Systems contained 50 PHR of MAF black.

^b In addition systems contained 1 part of stearic acid, 3 parts of ZnO, and 50 parts of MAF black per 100 parts of GR-S 1500.

^c Days aged in air at 250°F.

TABLE XII
EFFECT OF AGING AT 300°F ON SELECTED VULCANIZATES

| Curing System | Tensile, psi | | Stress at 300% E, psi | | | Elongation, % | | | Hardness | | | | | | | | |
|--|--------------|--------------------|-----------------------|-------|-------|---------------|-------|-------|----------|-------|-------|-------|-----|-----|-----|----|----|
| | Orig. | Hours ^c | Orig. | Hours | | Orig. | Hours | | Orig. | Hours | | | | | | | |
| | | 9 | | 12 | 20 | | 9 | 12 | | 20 | 9 | 12 | 20 | | | | |
| 1.75 Sulfur + ^a 1 BTSCHA | 2930 | 560 | 2390 | ----- | ----- | 400 | 90 | 70 | 40 | 68 | 75 | 80 | | | | | |
| | | 750 | | ----- | ----- | | 410 | 310 | | 140 | 64 | 66 | 75 | | | | |
| | | 1340 | | 990 | 870 | | ----- | ----- | | 530 | 410 | 140 | 65 | 66 | 75 | | |
| 2.25 DCP-40 + ^b 1 PENA | 2300 | 990 | 1170 | 870 | ----- | 530 | 410 | 310 | 140 | 64 | 66 | 75 | | | | | |
| | | 1340 | | 990 | 870 | | ----- | ----- | | 530 | 410 | 140 | 65 | 66 | 75 | | |
| | | 1910 | | 1690 | 790 | | 1140 | 970 | | 1110 | ----- | 530 | 410 | 150 | 65 | 66 | 70 |
| 3.75 DCP-40 + ^a .75 TMTD + 1 PENA | 2200 | 1910 | 1140 | 970 | 1110 | 530 | 410 | 310 | 140 | 64 | 66 | 75 | | | | | |
| | | 2260 | | 2070 | 760 | | 1530 | 1300 | | 1290 | ----- | 470 | 460 | 140 | 65 | 66 | 70 |
| | | 2450 | | 2260 | 2070 | | 760 | 1530 | | 1300 | 1290 | ----- | 470 | 460 | 140 | 65 | 66 |

^a In addition these systems contained 1 part of stearic acid, 3 parts of ZnO, and 50 parts of MAF black per 100 parts of GR-S 1500.

^b This system also contained 50 parts of MAF black per 100 parts of GR-S 1500.

^c Hours aged in air at 300°F.

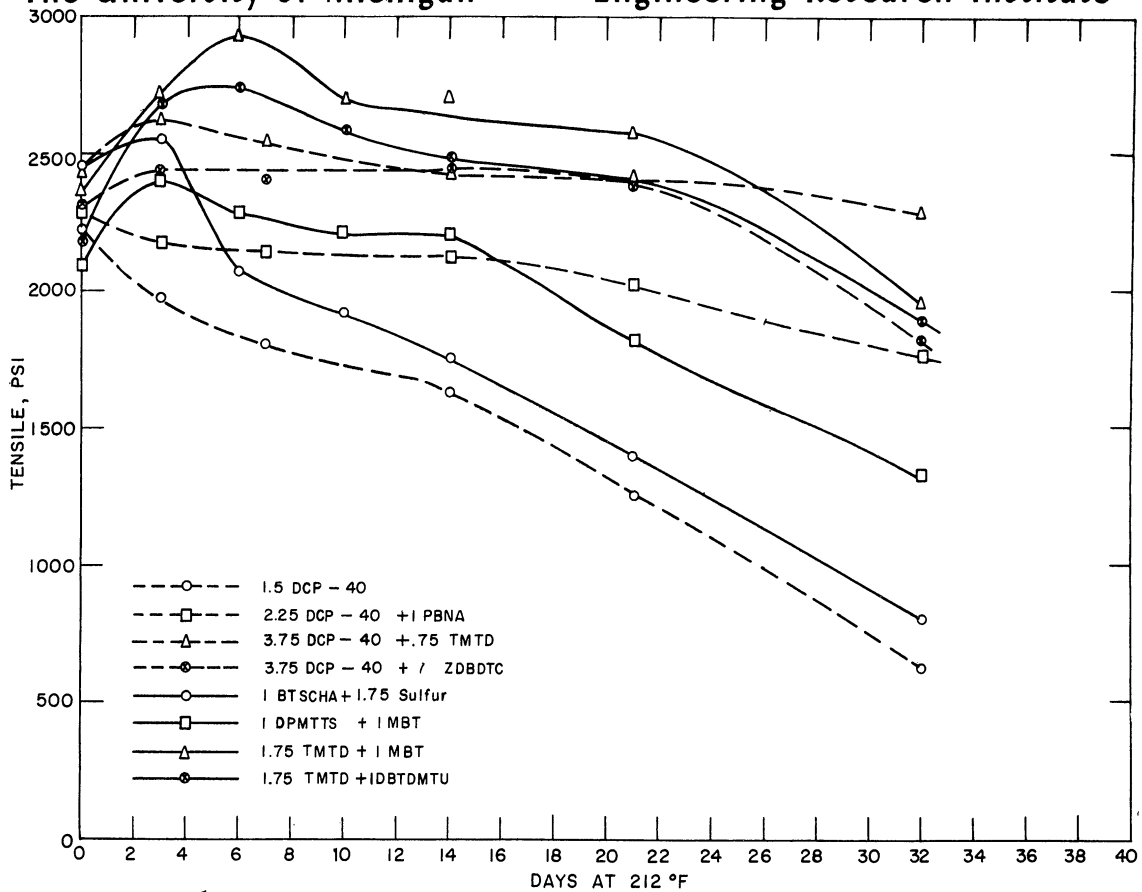


Fig. 6. Effect of extended air-oven aging at 212°F on the tensile strength of GR-S vulcanizates

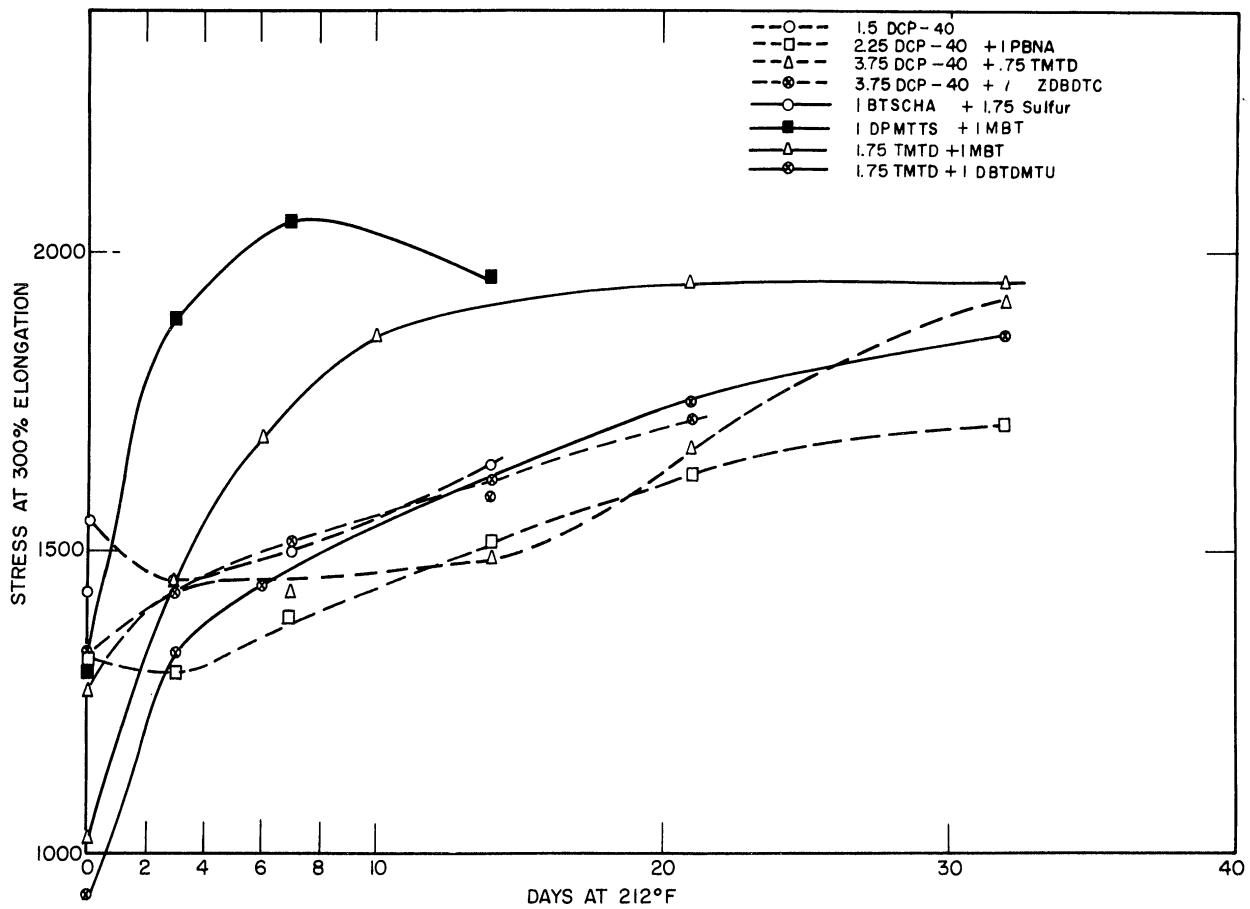


Fig. 7. Effect of extended air-oven aging at 212°F on the 300% modulus of GR-S vulcanizates

In Figure 5 it is interesting to note that the compositions which best resisted the effects of aging had been cured with:

- VI 3.75 PHR DCP-40 + 0.75 PHR TMTD + 1 (additional) PHR PBNA
- VII 3.75 PHR DCP-40 + 1 PHR ZDBDTC + 1 (additional) PHR PBNA, and
- V 2.25 PHR DCP-40 + 1 (additional) PHR PBNA.

During the first eight days of aging the vulcanizates formed with:

- III 1.75 PHR TMTD + 1 PHR DBTDMTU, and
- IV 1.75 PHR TMTD + 1 PHR MBT,

lost their very high elongations; but for the remainder of the 32-day aging period their values of per cent elongation were about the same as those for the members of the above group.

The values of per cent elongation for the reference composition II (DPMTTS + MBT) were, after an initial decrease, essentially constant for the 8th - 22nd day period.

The product formed with 1.5 PHR DCP-40 and without added PBNA showed a uniform and fairly rapid rate of loss of elongation throughout the whole 32 day period. The free sulfur containing reference composition I showed relatively poor aging properties.

The relatively poor aging properties of the vulcanizate formed with 1.5 PHR DCP-40 without added antioxidant as compared with those of the product formed with 2.25 PHR DCP-40 + 1 additional PHR PBNA indicates that sufficient PBNA can be added to give satisfactory antioxidant protection. At the same time, an additional amount of dicumyl peroxide must be employed. From these results it appears that 1 PHR of PBNA reacts with 0.75 PHR DCP-40 or 0.30 PHR of dicumyl peroxide. The remarkable fact is that the remainder of the two agents carry out their functions separately.

Aging Studies at 250°F

By reference to Figure 8 and Table XI it may be seen that air-oven aging for several days at 250°F represents severe conditions. The products prepared from:

- 4.00 PHR DCP-40 + 0.75 PHR TMTD + 1 (additional) PHR PBNA, and
- 4.00 PHR DCP-40 + 1.00 PHR ZDBDTC + 1 (additional) PHR PBNA,

showed the greatest resistance to aging. The reference composition II showed somewhat less resistance and the free sulfur reference composition I exhibited the least resistance. The per cent elongation for all of the compositions was essentially zero after 11 days at 250°F.

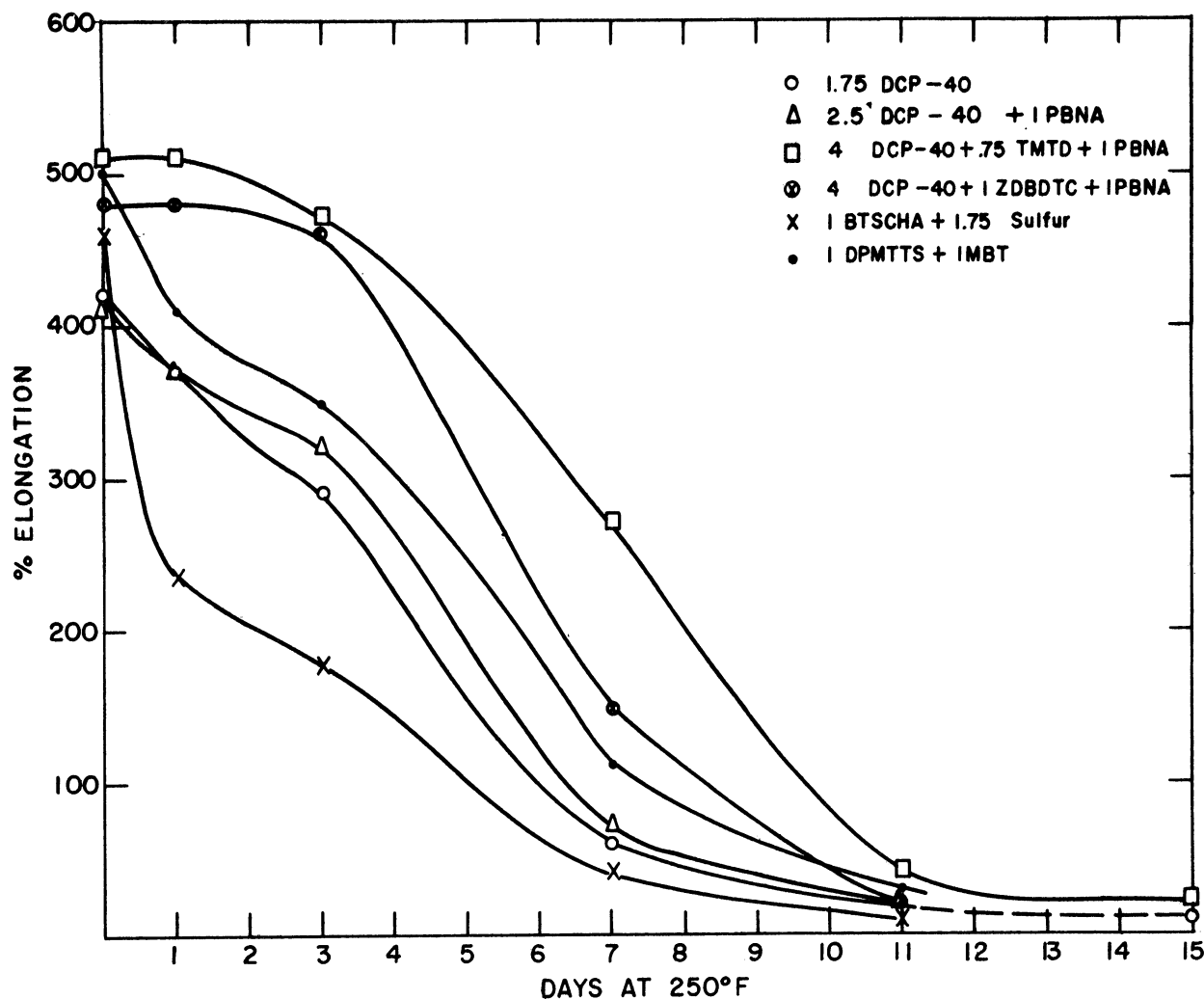


Fig. 8. Effect of aging at 250°F on elongation of selected vulcanizates

Aging Studies at 300°F

In Table XII the properties of the aged vulcanizates from three DCP-40 compositions and the reference composition I are recorded. Again, the dicumyl peroxide - sulfur-bearing accelerator formulations exhibited improved properties. The two vulcanizates prepared from,

3.75 PHR DCP-40 + 1 PHR ZDBDTC + 1 (additional) PHR PBNA, and
 3.75 PHR DCP-40 + 0.75 PHR TMTD + 1 (additional) PHR PBNA,

showed high resistance to aging at 300°F for some hours.

Thus, the resistance of these non-free sulfur vulcanizates, particularly those from compositions containing DCP-40 in combination with TMTD or ZDBDTC, is very striking and would justify some limitation in the processing temperatures used for BTSCHA-free sulfur compositions.

Dynamic Properties of Selected Vulcanizates

In order to more fully compare the properties of the various experimental vulcanizates with those of the reference compositions I and II, the dynamic properties were determined by use of a forced resonance vibrator¹. The quantities measured were E, the dynamic modulus in compression (kilograms/cm²), η , the internal friction (kilopoises), H_x, the heat build up (calories/cycle at the constant amplitude of 0.0164 cm.), and R, the resilience (per cent). The values obtained for the vulcanizates at 77°F are reported in Table XIII along with the estimated errors in the determination.

For purposes of orientation and comparison, values obtained by S.D. Gehman and colleagues⁸ for the dynamic properties of GR-S and Hevea gum and tread vulcanizates are listed below. These vulcanizates were cured with a sulfur plus accelerator system and contained 50 PHR of carbon black and thus the dynamic properties can be compared directly with those listed in Table XIII.

| | E kg/cm ² | η kilopoises | R % |
|-------------|-------------------------|----------------------|--------|
| GR-S Tread | 130 | 55 | 31 |
| Hevea Tread | 80 | 24 | 45 |
| GR-S Gum | 6 | 3 | 40-45 |
| Hevea Gum | 3 | 1 | 60 |

As may be seen, the dynamic properties listed in Table XIII agree rather closely with those of a conventional GR-S tread stock. There are, however, little differences in the dynamic properties among the experimental vulcanizates. This similarity of the dynamic properties of the experimental products is interpreted to mean that with the same elastomer, and the same type and amount of reinforcing carbon black, the several experimental vulcanizing systems have been cured to approximately the same level.

TABLE XIII
DYNAMIC PROPERTIES OF SELECTED VULCANIZATES AT 77°F

| Curing System | $\frac{E}{\text{kg./cm}^2}$ | η kilopoises | $\frac{H_x (x = 0.0164 \text{ cm.})}{\text{cal/cycle} \times 10^4}$ | $\frac{R}{\%}$ |
|--|-----------------------------|----------------------|---|----------------|
| 1 BTSCHA + 1.75 Sulfur ^a | 123 ± 2 | 48.8 ± 1.0 | 7.4 ± .2 | 39.1 ± 1.0 |
| 1 DPMTTS + 1 MBT ^a | 123 | 52.0 | 7.9 | 36.1 |
| 1.5 DCP-40 ^b | 123 | 50.1 | 7.6 | 37.5 |
| 2.25 DCP-40 + 1 PBNA ^b | 125 | 51.0 | 7.7 | 37.5 |
| 3.75 DCP-40 + 0.75 TMTD ^a + 1 PBNA | 122 | 52.2 | 7.9 | 36.2 |
| 5.0 DCP-40 + 0.75 TMTD ^a + 1 PBNA | 123 | 53.9 | 8.2 | 35.0 |
| 3.75 DCP-40 + 1 ZDBDTC ^a + 1 PBNA | 125 | 51.2 | 7.8 | 37.3 |
| 3.75 DCP-40 + 0.75 TBIM ^c + 1 PBNA | 123 | 50.1 | 7.6 | 37.5 |
| 3.75 DCP-40 + 0.75 MBT ^c + 1 PBNA | 127 | 50.1 | 7.6 | 38.7 |

^a In addition these systems contained 1 part of stearic acid, 3 parts of ZnO, and 50 parts of MAF black per 100 parts of GR-S 1500.

^b In addition these systems contained 50 parts of MAF black per 100 parts of GR-S 1500.

DISCUSSION OF RESULTS

As a convenient basis for appraising the results, aging data, scorch times and cost information for selected compositions are condensed in Table XIV.

Thus, composition VII (3.75 PHR DCP-40 and 1 PHR ZDBDTC) is the best of those listed; the unvulcanized compound has a 40 minute scorch value (t₅) and the vulcanizate has the best resistance to aging. The raw materials cost for this composition is approximately 5.6% greater than that for the free sulfur—BTSCHA compound.

Product V (2.25 PHR DCP-40 + 1 additional PHR PBNA) may be considered in second position; the aging properties of the vulcanizate are good, the raw compound may be safely heated in air at 250° for 30 minutes before serious decomposition occurs, and the cost of the raw materials is approximately 1.8% greater than that of the free sulfur—BTSCHA compound.

It may be possible that the results of the aging experiments at 212°F more nearly reflect the conditions of military storage than do the results of the aging experiments carried out at higher temperatures. Then compositions III - VII, inclusive, should be placed in position of approximately equivalent preference. The age resistance of the vulcanizates is good, and the scorch resistance values range from 20 to 40 minutes.

Some tensile and tear values for the vulcanizates I - VII are re-listed in Table XV. The tensile values of the unaged non-free sulfur vulcanizates are a little lower than that of the free sulfur—BTSCHA product. The tear value of the unaged vulcanizate VII is somewhat lower than the tear values of the other compositions. If, however, the comparisons are confined to the properties of the aged samples the non-free sulfur and the non-sulfur vulcanizates are superior in both tensile strength and tear resistance.

Thus, in view of the excellent aging properties of these vulcanizates, it is reasonable to suggest that they could be safely used with justification of the 2 - 6% additional materials costs for many rubber items, particularly in mechanical goods and military applications where good age resistance is necessary.

In completing this discussion brief attention may be given to each of several miscellaneous items of interest which should be considered in further work.

TABLE XIV
SUMMARY OF AGING, SCORCH AND COST DATA
FOR SELECTED VULCANIZATES

| Composition Number | Curing System | Elongation % | | | Scorch t ₅ , min. | Materials Cost, \$, 100 lbs. Compounded Rubber | Per Cent Cost Increase Over I |
|--------------------|---|--------------|---------------|--------------|------------------------------|--|-------------------------------|
| | | Unaged | Aged | | | | |
| | | | 32 days 212°F | 7 days 250°F | | | |
| I | 1 BTSCHA + 1.75 Sulfur | 400 | 20 | 40 | 70 | 19.05 | --- |
| II | 1 DPMTTS + 1 MBT | 460 | 180 | 110 | 130 | 20.05 | 5.3 |
| III | 1.75 TMTD + 1 DBTDMTU ^a | 630 | 300 | 110 | 270 | 20.10 | 5.5 |
| IV | 1.75 TMTD + 1 MBT ^a | 450 | 310 | 70 | 310 | 19.40 | 1.8 |
| V | 2.25 DCP-40 + 1 PBNA | 510 | 310 | 210 | 420 | 20.10 | 5.6 |
| VI | 3.75 DCP-40 + 0.75 TMTD + 1 PBNA ^a | | | | | | |
| VII | 3.75 DCP-40 + 1 ZDBDTC + 1 PBNA ^a | | | | | | |

^aAverage values are listed.

^bPreheated before curing in air oven at 250°F, see Experimental Part.

^cEstimated from market prices listed in Rubber Age 79, 870 (1956).

TABLE XV

EFFECT OF AGING ON TENSILE AND TEAR STRENGTH
OF SELECTED VULCANIZATES

| Composition Number | Tensile Strength, psi | | | Tear Strength, lbs/in. | |
|-----------------------|-----------------------|---------------|---------|------------------------|---------------|
| | Unaged | Aged at 212°F | | Unaged | Aged at 212°F |
| | | 7 days | 32 days | | |
| I | 2650 | 2020 | 800 | 260 | 170 |
| II | 2100 | 2280 | 1330 | 280 | 210 |
| III ^a | 2270 | 2790 | 1920 | 290 | 280 |
| IV ^a | | | | | |
| V | 2280 | 2140 | 1760 | 230 | 260 |
| VI ^a | 2370 | 2460 | 2040 | 190 | 200 |
| VII ^a | | | | | |

^a Average values are listed.

The question of the stability of DCP-40 compositions during processing still remains to be settled. The half-life of the product (in the absence of rubber) is listed by the manufacturer⁹ as 6 hours at 248°F. It was noted above that the DCP-40 raw rubber compound (which had been milled in air) could be heated at 250°F in air for 30 minutes without producing serious changes in the properties of the product after regular vulcanization (30 minutes, 307°F, essential absence of air). It is assumed that these data define the limitations of retaining the unvulcanized composition on a hot mill but do not bear directly on Banbury and extrusion operations carried out in the essential absence of air.

Mention has been made of the problem of bloom in vulcanizates of compositions III and IV and that the results of preliminary experiments showed promise for the use of low molecular weight polyethylene wax as a means of solving the problem. Further work might well include attention to the blooming tendency of these vulcanizates since the resistance to aging and scorch of the products represent an improvement over those of reference product II (DPMPTS + MBT). It is interesting that vulcanizates of compositions VI and VII containing DCP-40 showed no bloom.

The general results of this study are in accord with the view¹⁰ that vulcanizates formed from systems containing non-free sulfur and no sulfur are likely to have improved aging properties. The results may also be qualitatively related to estimates of the strengths of the different kinds of bonds constituting the cross-links. For example, Dogadkin and Torasova¹¹ list strengths of the probable cross-links formed in sulfur vulcanization as follows:

| Bond | Strength of Bond kcal | Possible Sources of Bond |
|----------|--------------------------|---|
| -C-C- | 62.7 | free radicals from peroxides, heat, light, etc. |
| -C-S-C | 54.5 | disulfides |
| -C-S-S-C | 27.5 | tetrasulfides |
| -C-Sn-C- | | free sulfur |

Possible sources of the different kinds of cross-links are also listed.

From this point of view then, the weaker the cross-link the more likely it may be broken to give active centers (presumably free radicals) which cause scission of the main chain as well as cross-linking and branching reactions. The overall results include shortening the trunk chains, more branching and crosslinking which, in turn, leads to decreasing tensile strength and elongation and increasing hardness and brittleness. Thus, according to this view, the vulcanizates from free sulfur and tetrasulfide combinations would be expected to be generally less stable than those from non-sulfur, and mono- and di-sulfide compositions.

The fact that phenyl- β -naphthylamine, a free radical inhibitor, can be used in combination with dicumyl peroxide, a free radical generator, has been emphasized. While there is some reaction between the two, a small increase in the proportion of each in the rubber composition leads to satisfactory vulcanization and a product with excellent aging qualities.

Possibly related to the above is the fact that certain nitrogen-sulfur-bearing vulcanization accelerators (Table XIV) in combination with dicumyl peroxide yield a vulcanizate with improved physical properties and equally good aging properties. Between the Rock Island Laboratory¹² and the members of the project, three suggestions have been made which may lead to an understanding of the situation, namely:

- 1) in each case, the unreacted portions of the nitrogen or sulfur-nitrogen compounds (remaining in the product after vulcanization) may act as inhibitors for aging in air;
- 2) in each case, the nitrogen- or the sulfur-nitrogen-compounds may induce the decomposition of the peroxide to yield free radicals by a process of lower activation energy than the thermal decomposition, resulting in a faster decomposition of the peroxide, but, at the same time, some wastage of peroxide; and
- 3) particularly in the latter case, the nitrogen-sulfur-bearing compounds might act as dispersing agents for the DCP-40. (The presence of ZnO and stearic had a beneficial effect on the DCP-40 vulcanizate.)

While the results summarized in this study do not afford a decision regarding the relative merits of these suggestions, certainly each suggestion is straightforward and should be considered in further study of the subject.

In conclusion, several peroxide and peroxide-sulfur-bearing accelerator combinations have been found to yield vulcanizates possessing excellent aging qualities, and good tensile properties. The processing stabilities of the unvulcanized compositions, while not equivalent to those of conventional free sulfur compositions, appear to be sufficient for practical application.

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