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SOME ALDEHYDEAMINE ACCELERATORS

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ABSTRACT

As part of the search for better accelerators for rubber vulcanization, a study is undertaken of some aldehydeamines with the purpose of correlating molecular structure with the physical properties imparted to the product. Six compounds synthesized for the study were evaluated in comparison with mercaptobenzothiazole (Captax) and the heptaldehydeaniline condensation product (Hepteen Base) with regard to tensile strength, tensile stress at 500% elongation, ultimate elongation, oven aging, oxygen-bomb aging, compression set, free sulfur, and hardness. None possessed the oxygen-resistant property of Captax. In the presence of an antioxidant however, N,N'-dibenzylidene ethylene diamine compared favorably with standard accelerators. It was found to act efficiently alone, as well as in various combinations with one or more of the compounds, Captax, benzothiazyldisulfide (Altax), and zinc dimethyl dithiocarbamate (Methyl Zimate).

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem No. C06-18R.

SOME ALDEHYDEAMINE ACCELERATORS

INTRODUCTION

The first artificial vulcanization accelerators were inorganic. Basic lead carbonate was patented by Goodyear (8) as early as 1844. Litharge, lime, and magnesia were used universally through the early period of the rubber industry.

The first step away from the metallic accelerators was the use of ammonia by Rowley (20) in 1881, but it was not until 1906 that Oenslager (15) observed the accelerating effect of aniline, for which discovery he was awarded the Perkin Medal about a quarter of a century later. He asserted that the activity of nitrogen-containing accelerators was related to the presence of amino nitrogen. Kratz, Flower and Coolidge (10) assumed that the activity hinged on the temporary change of valence of the nitrogen from 3 to 5 with the temporary addition of sulfur. The fact, they claimed, that p-phenylenediamine was twice as powerful as aniline, supported their proposed theory. Acetaldehydeammonia and hexamethylenetetramine were some of the original members of the early aldehydeamine group of accelerators. Since then, numerous investigators (6,11,12,17,19,21, to cite a few) have presented to the rubber world a large number of compounds of this type.

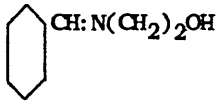
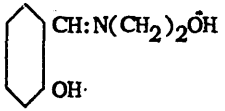
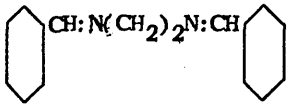
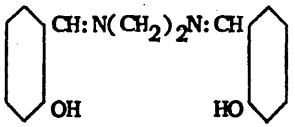
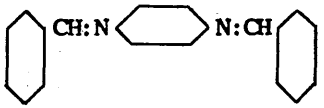
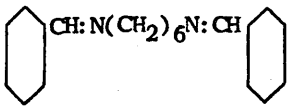
The present investigation has a two-fold purpose: (a) to correlate differences in molecular structure of the accelerators to variations in physical properties which they impart to vulcanized rubber, and (b) to discover accelerators better than existing ones. Thus far six compounds have been synthesized for this investigation. They are shown in the tabulation on page 2.

These compounds were evaluated and compared with Captax (mercaptobenzothiazole) and Hepteen Base (heptaldehyde-aniline condensation product) with regard to tensile, tensile stress at 500% elongation, ultimate elongation, durometer hardness, free sulfur, compression set, oven aging, and oxygen-bomb aging of the vulcanized rubber. The data presented are based on averages.

TEST PROCEDURES

Tensile Properties

Tensile strength, ultimate elongation, and tensile stress at 500% elongation were determined as recommended by A.S.T.M. procedures (2). A

Accelerator No.	Name	Structural Formula	Physical State	M.P.	B.P.
1	N-Benzylidene ethanolamine		Viscous, pale yellow liquid		128-130°C/ 4mm
2	N-Salicylidene ethanolamine		Viscous, dark yellow liquid		158-159°C/ 4mm
3	N,N'-Dibenzylidene ethylene diamine		Colorless needles (from ethyl alcohol)	52.4-53.4°C	
4	N,N'-Disalicylidene ethylene diamine		Fine, yellow crystalline flakes (from ethyl alcohol)	126-127°C	
5	N,N'-Dibenzylidene p-phenylene diamine		Silvery leaves (from ethyl alcohol)	139.7-140.7°C	
6	N,N'-Dibenzylidene-1,6-hexane diamine		White needles (from ethyl alcohol)	31-32°C	

minimum of six specimens, Type C, was used for each stock. The tests were performed in a room maintained at 76±2°F and 50% relative humidity.

Hardness

Hardness was determined by two durometer methods -- Shore A (instantaneous) and Rex -- according to A.S.T.M. procedures (4) on ½-inch thick samples. Hardness was taken at 76±2°F and 50% relative humidity on the day following the vulcanization of the samples.

Compression Set

Compression set measurements were run in duplicate according to A.S.T.M. procedures (1), method B, using samples ½-inch by 1-1/8-inch in diameter, under 40% constant deflection. Specimens were cured five minutes longer than the corresponding tensile sheet cures. The test assembly was placed in a controlled Aminco oven for 22 hours at 70°C. Thickness of the test specimens was taken at 76±2°F, 30 minutes after their removal from the clamps.

Free Sulfur

Determination of free sulfur on vulcanized samples was done in triplicate according to the method of Oldham, Baker, and Craytor (16). This is an elaboration of the original Bolotnikov and Gurova procedure. (5)

Oven Aging

Accelerated aging by the oven method followed A.S.T.M. procedures (3). Six tensile specimens, Type C, of each stock were placed in the oven for 96 hours at 70±1°C. Tensile strength and ultimate elongation were determined on the day following the removal of the specimens from the oven.

Oxygen-Bomb Aging

Six A.S.T.M. tensile specimens (Type C) of each stock were placed in oxygen bombs for 48 hours at 70±1°C with an oxygen pressure of 140 psi. The temperature was maintained by a thermostatically controlled circulating oil bath. Stocks were aged separately to avoid the effects of migration. The A.S.T.M. specification of 96 hours, 300 psi of oxygen pressure at 70°C was not followed in this instance. A preliminary aging test of 96 hours with an oxygen pressure of 140 psi and a temperature of 70°C had proved to be too severe; the specimens after aging were unfit for testing. Hence, the time of aging was reduced to 48 hours. Tensile strength and ultimate elongation were determined on the day following the removal of the specimens from the bomb.

EXPERIMENTAL METHODS

To evaluate these six compounds as accelerators, a range of cures was necessary to determine the amount of each accelerator and the time and temperature of cure, that is, the combination giving the optimum cure. Tensile strength was used as the standard criterion. With this information

at hand, a compound of high initial tensile strength was chosen for use in combination with one or two other accelerators already well established. The use of one accelerator only in any given formulation is here referred to simply as "single acceleration," while the use of a combination of two or three compounds is called "double acceleration" and "triple acceleration" respectively.

Basic formulation of the masterbatch was as follows:

Smoked sheet	100.0	parts by weight
Philblack 0	30.0	"
Zinc Oxide	5.0	"
Stearic acid	3.0	"
Sulfur	3.0	"
	141.0	

A masterbatch which contained all the ingredients except the accelerators was mixed on an 8 by 16-inch mill. The masterbatch was divided into smaller batches to which the accelerators were added as desired using a 6 by 12-inch mill. This same masterbatch was also the basic formulation for evaluation and comparison for double and triple acceleration.

SINGLE ACCELERATION

Table 1 gives the results of the range of cures for each accelerator singly.

The results of this range of cures are also shown in Figure 1, and Table 2 gives the formulations derived from the range of cures of stocks to be used in evaluation and comparison of the eight accelerators based on optimum cures.

The results of the tests based on optimum cures are given in Table 3.

The results on initial tensile strength, initial tensile stress at 500% elongation, tensile strength after oven aging, and tensile strength after oxygen-bomb aging are presented in Figure 2. Based on initial tensile strength, the best three stocks were 3, 7 and 8. With the exception of 5, none of the stocks, including one accelerated by Hepteen Base, possessed the oxygen-resistant property of Captax. In view of this fact, it was desirable to determine the effect of the inclusion of an antioxidant (Neozone A) in the three best stocks. Assuming that the presence of an antioxidant had very little effect, if any, on the rate of cure, the following stocks were formulated for this purpose:

Stock No.	Cure (Min/°F)	Master-batch	Neozone A (Phenyl Alpha-Naphthalamine)	Accelerator 3	Captax	Hepteen Base
9	30/300	141.0	2.0	2.5	-	-
10	15/300	141.0	2.0	-	1.5	-
11	30/300	141.0	2.0	-	-	0.5

Table 1

Accelerator	Parts of Accelerator Per 100 Parts of Rubber	Cure Time at 300°F (Minutes) 10	15	20	25	30	40	45	50	60	70	75	90
N-Benzylidene ethanolamine	0.	-	-	-	-	-	-	740	-	920	-	980*	1010
	1.0	-	1380	-	-	1760	-	1790	-	1610	-	-	-
	1.5	-	1740	-	-	2230	-	2340	-	2250	-	-	-
	2.0	-	2050	-	-	2620	-	2750	-	2660	-	-	-
	2.5	-	2260	-	-	3150	-	3350	-	2980	-	-	-
	3.0	-	2620	-	-	3980*	-	3710	-	3530	-	-	-
	3.5	-	2580	-	-	3690	-	3490	-	3200	-	-	-
	Note: 0 parts accelerator was the masterbatch.												
N-Salicylidene ethanolamine	0.5	-	970	-	-	1360	-	1500	-	1530	-	-	-
	1.0	-	1280	-	-	1850	-	2230	-	2150	-	-	-
	1.5	-	1670	-	-	2090	-	2420	-	2260	-	2140	-
	2.0	-	-	-	-	2680	-	3190	-	2990	-	2470	-
	2.5	-	-	-	-	3000	-	3420	-	3200	-	2740	-
	3.0	-	-	-	-	3470	-	3690*	-	3450	-	2980	-
	3.5	-	2210	-	-	3440	-	3560	-	3330	-	-	-
N,N'-Dibenzylidene ethylene diamine	0.5	-	1450	-	-	2270	-	2210	-	2030	-	1880	-
	1.0	-	2790	-	-	3450	-	3500	-	3070	-	-	-
	1.5	-	3170	-	-	3930	-	3450	-	-	-	-	-
	2.0	-	3450	-	-	4240	-	4120	-	-	-	-	-
	2.5	-	3820	-	-	4390*	-	4210	-	-	-	-	-
	3.0	-	3980	-	-	4310	-	4200	-	-	-	-	-
N,N'-Disalicylidene ethylene diamine	0.5	-	-	-	-	1380	-	1470	-	1260	-	1180	-
	1.0	-	-	-	-	1730	-	2120*	-	2020	-	1790	-
	1.5	-	-	-	-	1760	-	2050	-	1950	-	1860	-
	2.0	-	-	-	-	1640	-	1980	-	1800	-	1630	-
N, N'-Dibenzylidene p-phenylene diamine	2.0	-	-	-	-	1320	-	1540	-	1850	-	1800	-
	2.5	-	-	-	-	1690	-	2060	-	2380	-	2190	-
	3.0	-	-	-	-	1960	-	2070	-	2470	-	2390	-
	3.5	-	-	-	-	2010	-	2480	-	2820*	-	2800	-
	4.0	-	-	-	-	1970	-	2550	-	2600	-	2610	-
N,N'-Dibenzylidene-1,6-hexane diamine	2.0	-	1980	-	-	3070	-	3150	-	2650	-	-	-
	2.5	-	2470	-	-	3580	-	3560	-	3000	-	-	-
	3.0	-	2660	-	-	3790*	-	3620	-	3160	-	-	-
	3.5	-	2710	-	-	3760	-	3680	-	2990	-	-	-
Captax	0.5	-	2840	3050	3150	3150	-	-	-	-	-	-	-
	0.75	-	3490	3760	3730	3630	-	-	-	-	-	-	-
	1.0	-	3880	3890	3920	3810	-	-	-	-	-	-	-
	1.25	3470	4110	4040	4090	3970	-	-	-	-	-	-	-
	1.5	3920	4200*	4190	4100	-	-	-	-	-	-	-	-
	1.75	4080	4170	3840	3920	-	-	-	-	-	-	-	-
	2.0	4050	4170	3910	3930	-	-	-	-	-	-	-	-
Hepteen Base	0.2	-	-	1380	-	1600	1500	-	1390	-	-	-	-
	0.3	-	-	2360	-	2850	3120	-	3210	-	-	-	-
	0.4	-	-	3370	-	4050	4040	-	4070	-	-	-	-
	0.5	-	-	3820	-	4370*	4440	-	4150	-	-	-	-
	0.6	2620	-	4190	-	4330	4450	-	-	-	-	-	-

*Optimum cure

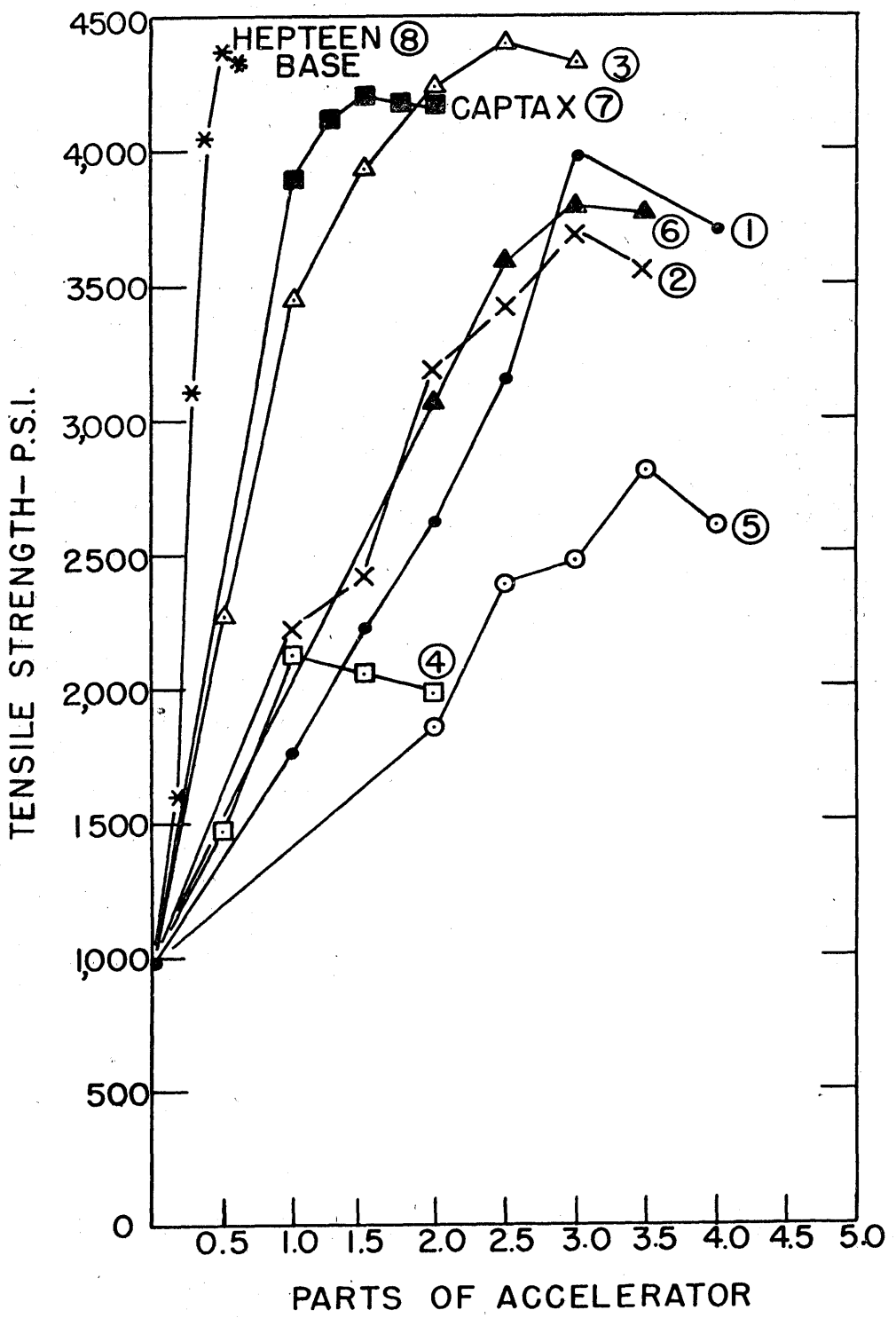


Figure 1-Range of Cures for Single Acceleration

Table 2

Stock No.	Cure Min/°F	Composition of Stock												
		Smoked Sheet	Philblack 0	Zinc Oxide	Stearic Acid	Sulfur	#1 Accelerator	#2 Accelerator	#3 Accelerator	#4 Accelerator	#5 Accelerator	#6 Accelerator	Captax	Hepteen Base
M.B.	75/300	100.0	30.0	5.0	3.0	3.0	-	-	-	-	-	-	-	-
1	30/300	100.0	30.0	5.0	3.0	3.0	3.0	-	-	-	-	-	-	-
2	45/300	100.0	30.0	5.0	3.0	3.0	-	3.0	-	-	-	-	-	-
3	30/300	100.0	30.0	5.0	3.0	3.0	-	-	2.5	-	-	-	-	-
4	45/300	100.0	30.0	5.0	3.0	3.0	-	-	-	1.0	-	-	-	-
5	60/300	100.0	30.0	5.0	3.0	3.0	-	-	-	-	3.5	-	-	-
6	30/300	100.0	30.0	5.0	3.0	3.0	-	-	-	-	-	3.0	-	-
7	15/300	100.0	30.0	5.0	3.0	3.0	-	-	-	-	-	-	1.5	-
8	30/300	100.0	30.0	5.0	3.0	3.0	-	-	-	-	-	-	-	0.5

Table 3

Stock No.	Initials							After Oven Aging		After Oxygen-Bomb Aging	
	Tensile Strength, psi	Tensile Stress at 500 % Elongation, psi	Ultimate Elongation, %	Durometer Hardness Shore A	Durometer Hardness Rex	Free Sulfur, %	Compression Set, %	Tensile Strength, psi	Ultimate Elongation, %	Tensile Strength, psi	Ultimate Elongation, %
M.B.	980	--	440	35	40	0.759	56.4	1320	400	200	300
1	3980	3320	560	38	45	0.445	52.3	3770	500	300	310
2	3690	3130	540	43	50	0.225	41.4	2660	410	300	310
3	4390	3720	590	47	55	0.330	48.9	4010	480	580	300
4	2120	--	490	37	45	0.507	50.6	1420	320	570	310
5	2820	2560	520	38	45	0.016	59.5	2620	450	1780	410
6	3790	3110	570	45	50	0.288	53.5	3380	400	1570	340
7	4200	3370	570	47	55	0.303	30.2	3980	510	2120	450
8	4370	3860	570	43	50	0.361	54.2	2820	440	170	310

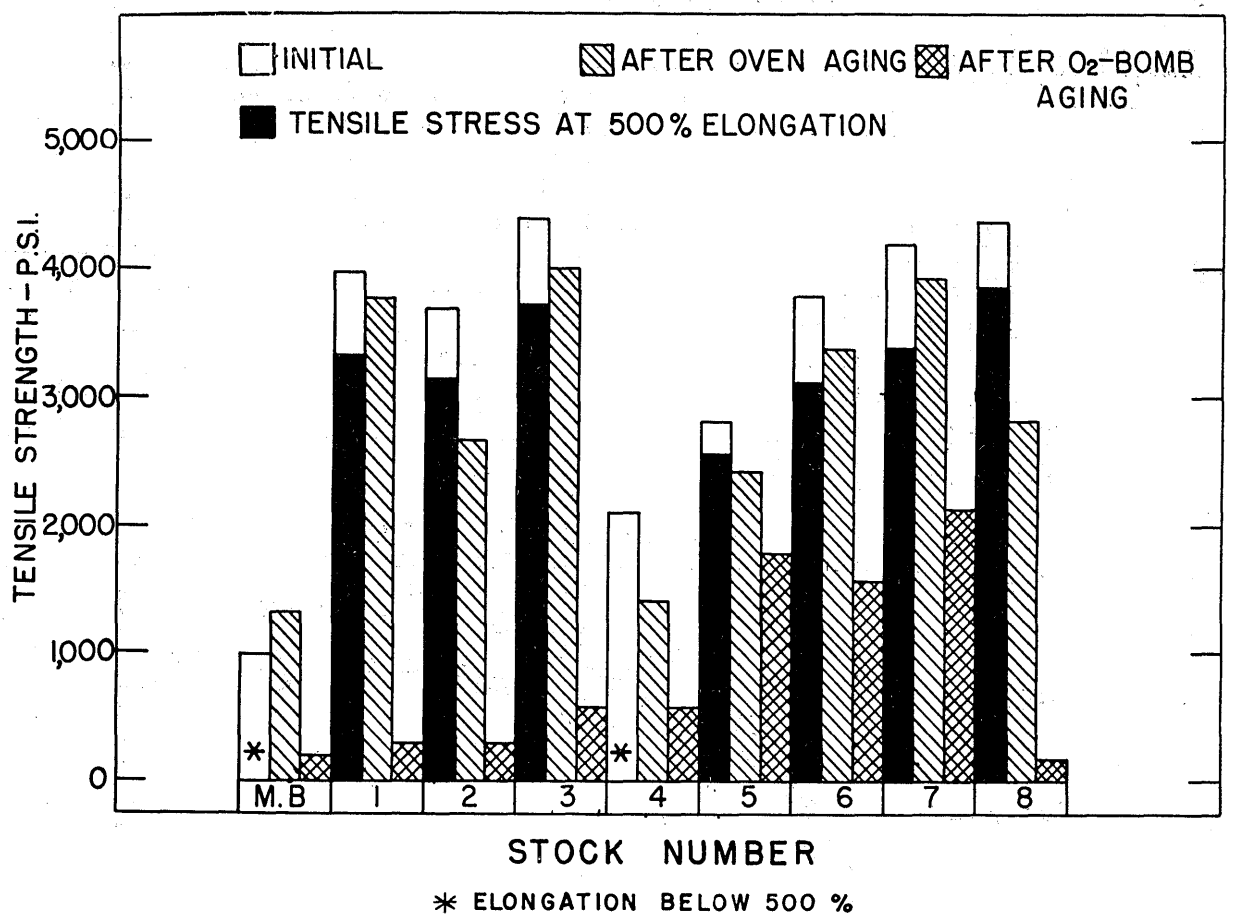


Figure 2-Tensile Properties of Stocks without an Antioxidant

The same tests were repeated on stocks 9, 10, and 11, and the results are shown in Table 4 on p. 12.

The inclusion of Neozone A in stocks 9, 10, and 11 improved the resistance to oxygen deterioration. In the presence of an antioxidant, N,N'-dibenzylidene ethylene diamine (accelerator 3) was as good as, if not better than, Captax or Hepteen Base as a primary accelerator. In view of this, an antioxidant was included in the formulations for evaluation of accelerator 3 in double and triple acceleration in various combinations with Captax, Altax (benzothiazyl disulfide), and Methyl Zimate (zinc dimethyl dithiocarbamate), all well known standard accelerators.

DOUBLE ACCELERATION

Accelerator 3 was tested and compared with Captax and Altax for double acceleration. The selection of accelerator 3 for this and triple acceleration was due primarily to the high initial tensile strength of its stock. However, this does not exclude the other accelerators from future evaluation, for some of them showed promise of possessing desirable qualities. Accelerator 5, for example, seemed to have antioxidant property. A range of cures was run to determine the optimum cure for various accelerator combinations. In any dual

combination of accelerators for experimental determinations, one must remain constant, the other variable. Formulations and results of the range of cures for double acceleration are given in Table 5 on p. 12.

The results of the range of cures are shown graphically in Figure 3. The formulations of stocks to be tested for double acceleration were:

Stock No.	Cure (Min/°F)	Master-batch	Neozone A	Captax	Accelerator 3	Altax
12	5/287	141.0	2.0	0.75	1.0	-
13	15/287	141.0	2.0	0.75	-	1.0
14	5/287	141.0	2.0	-	1.25	1.0

Results of these stocks are given in Table 6 on p. 13.

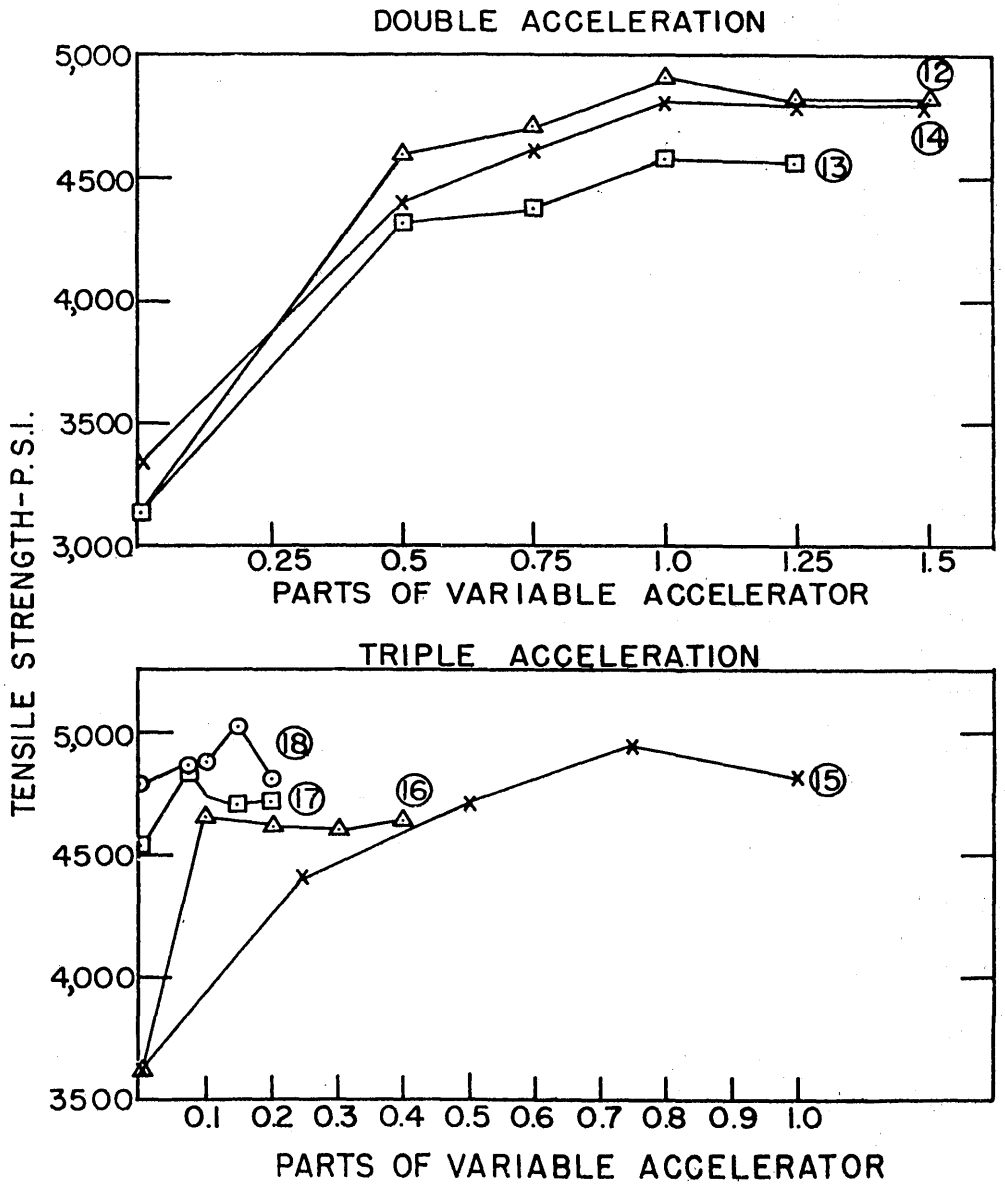


Figure 3-Range of cures for Mixed Accelerations

TRIPLE ACCELERATION

Accelerator 3 was evaluated for triple acceleration in various combinations with Captax, Altax, and Methyl Zimate. When running a range of cures for any given combination of accelerators, the amount of one accelerator is variable, the others remain constant. Results of the range of cures for triple acceleration are given in Table 7 on p. 13.

The results of this range of cures are shown graphically in Figure 3. Formulations of stocks for triple acceleration were:

Stock No.	Cure (Min/°F)	Master-batch	Neozone A	Captax	Altax	Accelerator 3	Methyl Zimate
15	10/274	141.0	2.0	0.75	0.5	0.75	-
16	10/274	141.0	2.0	0.75	0.5	-	0.1
17	5/274	141.0	2.0	0.75	-	1.25	0.075
18	5/274	141.0	2.0	-	0.5	1.25	0.15

Results of the tests for triple acceleration are given in Table 8 (p.13).

ANALYSIS OF DATA

Tensile Strength

In Figure 2 are plotted the tensile strengths of single-accelerated and unaccelerated stocks. The highest tensile strengths were given by stocks accelerated by accelerator 3, Hepteen Base, and Captax; the lowest was obtained by accelerator 4. Double- and triple-accelerated stocks had definitely higher tensile strength than single-accelerated stocks, as shown in Figure 4. Within the past twenty years it has been found by numerous investigators (13) that a combination of accelerators is capable of producing in the vulcanizate properties which any single accelerator would not be able to produce. The use of mixed acceleration is a general practice today.

Tensile Stress

Tensile stress was determined at 500% elongation for unaged stocks only, and the results are plotted in Figures 3 and 4. Stocks 3, 8, and 7, in that order, have the highest tensile stress at 500% elongation for single acceleration. Stocks 14 and 18 had the highest values for double and triple acceleration respectively.

Aging Properties

Of all the stocks without an antioxidant, those accelerated by accelerator 5 and Captax (Figure 3) possessed the highest oxygen resistance after oxygen-bomb aging with 62.8% and 50.5% retention of their initial tensile strength, respectvely. However, the former had comparatively low initial tensile strength. Stocks 3 and 8 have high initial tensile strengths but have retained of that initial strength only 13.2% and 3.8% respectively after

Table 4

Stock No.	Initials							After Oven Aging		After Oxygen-Bomb Aging	
	Tensile Strength, psi	Tensile Stress at 500% Elongation, %	Ultimate Elongation, %	Durometer Hardness Shore A	Durometer Hardness Rex	Free Sulfur, %	Compression Set, %	Tensile Strength, psi	Ultimate Elongation, %	Tensile Strength, psi	Ultimate Elongation, %
9	4220	3560	560	47	55	0.309	47.4	4040	490	3270	470
10	4010	3450	550	48	55	0.314	38.2	3600	460	2690	430
11	4180	3820	520	47	55	0.241	52.2	3960	470	3210	460

Table 5

Composition (Parts per 100 parts of rubber)					Cure Time, 287°F (Minutes) Tensile Strength - Psi												
Masterbatch	Neozone A	Captax	N, N'-Dibenzylidene Ethylene Diamine	Altax	2	3	5	7	10	15	20	30	40	50	60	70	80
141.0	2.0	0.75		-	-	-	-	-	1500	-	2560	3120	3040	2860	-	-	-
141.0	2.0	0.75	0.50	-	-	-	3950	-	4600	4730	4560	-	-	-	-	-	-
141.0	2.0	0.75	0.75	-	-	-	4620	-	4710	4630	4260	-	-	-	-	-	-
141.0	2.0	0.75	1.00	-	3020	4060	4910*	4720	4660	-	-	-	-	-	-	-	-
141.0	2.0	0.75	1.25	-	3260	4260	4820	4820	-	-	-	-	-	-	-	-	-
141.0	2.0	0.75	1.50	-	3660	4300	4820	4840	-	-	-	-	-	-	-	-	-
141.0	2.0	0.75	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
141.0	2.0	0.75	-	0.50	-	-	1370	-	3030	3990	4320	-	-	-	-	-	-
141.0	2.0	0.75	-	0.75	-	-	1980	-	3650	4380	4410	-	-	-	-	-	-
141.0	2.0	0.75	-	1.00	-	-	2530	-	3970	4580*	4640	-	-	-	-	-	-
141.0	2.0	0.75	-	1.25	-	-	2370	-	4080	4560	4460	-	-	-	-	-	-
141.0	2.0	-	1.25	-	-	-	-	-	-	-	-	2290	2530	3020	3330	3340	3310
141.0	2.0	-	1.25	0.50	-	3240	4020	-	4410	4340	-	-	-	-	-	-	-
141.0	2.0	-	1.25	0.75	-	3610	4370	-	4610	4440	-	-	-	-	-	-	-
141.0	2.0	-	1.25	1.0	-	4250	4810*	-	4510	4090	-	-	-	-	-	-	-
141.0	2.0	-	1.25	1.25	-	4400	4800	-	4440	4170	-	-	-	-	-	-	-
141.0	2.0	-	1.25	1.50	-	4680	4810	-	4240	4210	-	-	-	-	-	-	-

*Optimum cure

Table 6

Stock No.	Initials							After Oven Aging		After Oxygen-Bomb Aging	
	Tensile Strength, psi	Tensile Stress at 500% Elongation, psi	Ultimate Elongation, %	Durometer Hardness Shore A	Durometer Hardness Rex	Free Sulfur, %	Compression Set, %	Tensile Strength, psi	Ultimate Elongation, %	Tensile Strength, psi	Ultimate Elongation, %
12	4910	3110	670	48	55	0.879	81.1	4780	530	4370	610
13	4580	2950	650	44	50	0.853	56.1	4630	580	4010	570
14	4810	3530	610	47	55	0.816	83.6	4340	420	4570	590

Table 7

Composition (Parts per 100 parts of rubber)						Cure Time, 274°F (Minutes) Tensile Strength, Psi								
Masterbatch	Neozone A	Captax	Altax	N-N'-Dibenzylidene Ethylene Diamine (Accelerator 3)	Methyl Zimate	3	5	7	10	15	20	25	30	35
141.0	2.0	0.75	0.50	-	-	-	-	-	-	1710	2160	3170	3610	3480
141.0	2.0	0.75	0.50	0.25	-	-	1840	-	3740	4410	4580	-	-	-
141.0	2.0	0.75	0.50	0.50	-	-	3340	-	4720	4770	4720	-	-	-
141.0	2.0	0.75	0.50	0.75	-	-	4340	-	4950*	4800	4510	-	-	-
141.0	2.0	0.75	0.50	1.00	-	-	4370	-	4820	4360	4420	-	-	-
141.0	2.0	0.75	0.50	-		-	-	-	-	1710	2160	3170	3610	3480
141.0	2.0	0.75	0.50	-	0.10	-	3010	4220	4640*	4640	-	-	-	-
141.0	2.0	0.75	0.50	-	0.20	2890	4610	4460	4240	-	-	-	-	-
141.0	2.0	0.75	0.50	-	0.30	3580	4610	4520	3930	-	-	-	-	-
141.0	2.0	0.75	0.50	-	0.40	4640	4330	4020	3440	-	-	-	-	-
141.0	2.0	0.75	-	1.25	-	-	3500	-	4530	4320	4000	-	-	-
141.0	2.0	0.75	-	1.25	0.075	4330	4830*	-	4380	4310	-	-	-	-
141.0	2.0	0.75	-	1.25	0.10	4740	4680	-	4330	4140	-	-	-	-
141.0	2.0	0.75	-	1.25	0.15	4790	4700	-	4180	4120	-	-	-	-
141.0	2.0	0.75	-	1.25	0.20	4720	4390	-	4150	3850	-	-	-	-
141.0	2.0	-	0.50	1.25	-	-	2320	-	4350	4780	4720	4700	-	-
141.0	2.0	-	0.50	1.25	0.075	2850	4330	-	4860	4730	-	-	-	-
141.0	2.0	-	0.50	1.25	0.10	4020	4730	-	4870	4510	-	-	-	-
141.0	2.0	-	0.50	1.25	0.15	4700	5020*	-	4610	4400	-	-	-	-
141.0	2.0	-	0.50	1.25	0.20	4910	4800	-	4250	4190	-	-	-	-

*Optimum cure

Table 8

Stock No.	Initials							After Oven Aging		After Oxygen-Bomb Aging	
	Tensile Strength, psi	Tensile Stress at 500% Elongation, %	Ultimate Elongation, %	Durometer Hardness Shore A	Durometer Hardness Rex	Free Sulfur, %	Compression Set, %	Tensile Strength, psi	Ultimate Elongation, %	Tensile Strength, psi	Ultimate Elongation, %
15	4950	3590	650	50	55	0.686	69.3	4680	520	4410	560
16	4640	3400	630	43	50	0.874	70.3	4450	540	4060	560
17	4830	3330	630	54	60	0.502	73.4	2960	310	4320	560
18	5020	3630	630	55	60	0.408	70.5	4260	410	4400	570

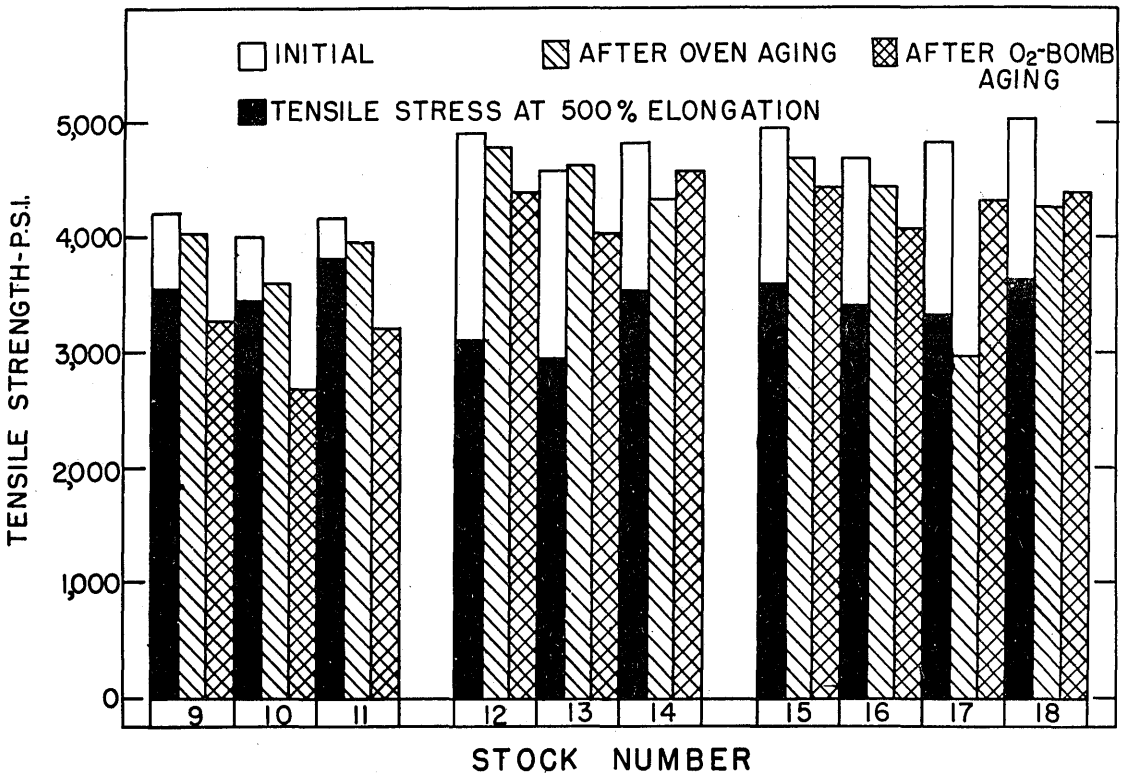


Figure 4-Tensile Properties of Stocks Containing an Antioxidant

oxygen treatment. The effect of an antioxidant is shown in the oxygen-resistant property of stocks 9 to 18 inclusive. This is plotted in Figure 4. All the stocks showed a general tendency to be resistant to oven aging, as shown in Figures 3 and 4. Stocks accelerated by accelerator 3 in the presence of Neozone A proved to be equally if not more resistant to oven aging and oxygen-bomb aging than Captax.

Ultimate Elongation

Figure 5 shows the ultimate elongation for initials after oven aging and after oxygen-bomb again for all stocks. For initials, double- and triple-accelerated stocks had higher ultimate elongation than the single-accelerated stocks. Stock 3 had the highest ultimate elongation for single acceleration, while stocks 12 and 15 had the highest values for double and triple acceleration respectively.

Durometer Hardness

Shore A (instantaneous) and Rex hardnesses of unaged stocks are plotted in Figure 6. Stocks 3, 7, and 6 were the hardest for single-accelerated stocks. Double and triple acceleration had a tendency to harden the vulcanizates.

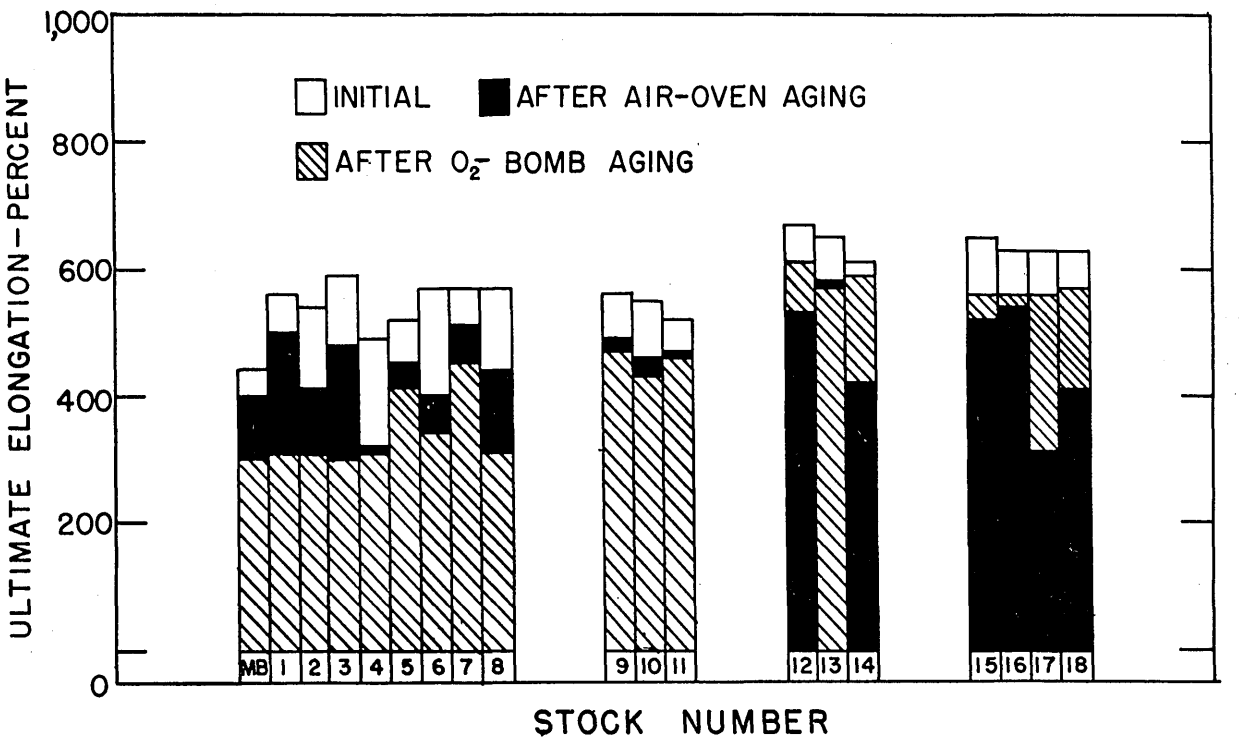


Figure 5-Ultimate Elongation of All Stocks

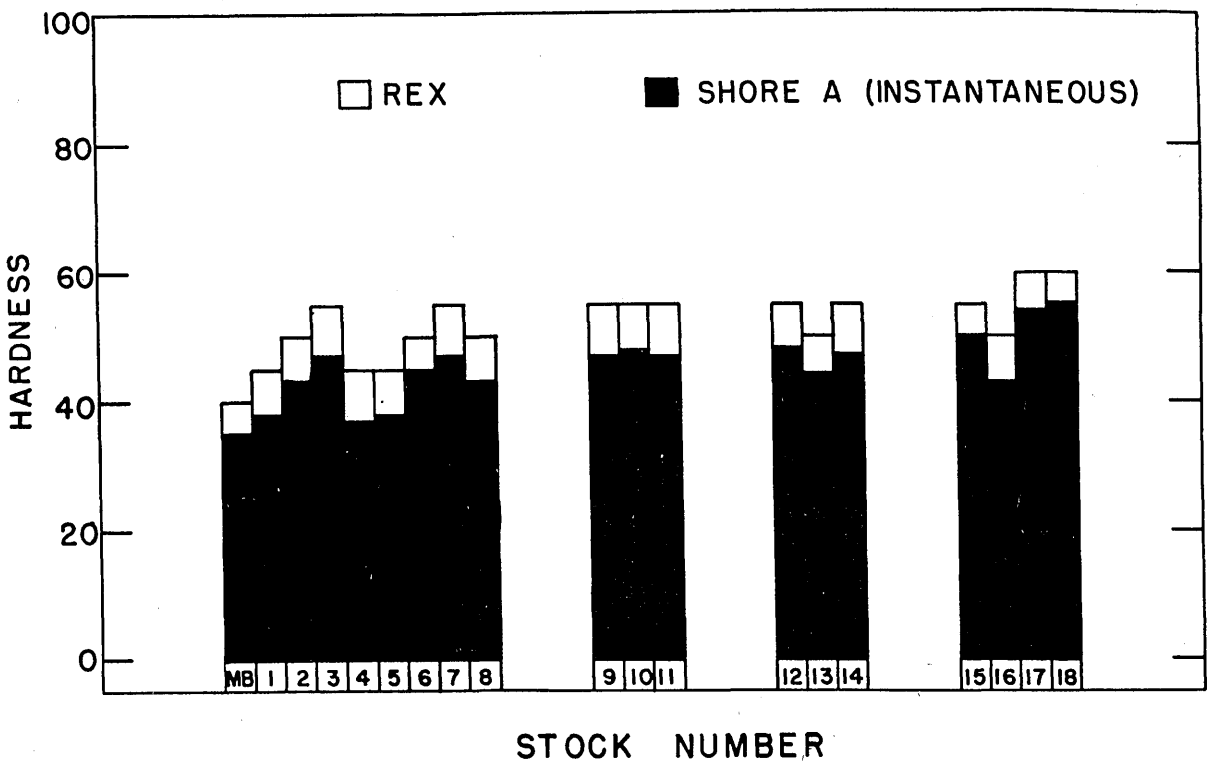


Figure 6-Durometer Hardness of Unaged Stocks

Compression Set

In Figure 7 are plotted the compression set values of all the stocks. In single acceleration, the stock accelerated by Captax was outstandingly superior to the others. Compression set values for double- and triple-accelerated stocks were much higher than those for the single-accelerated

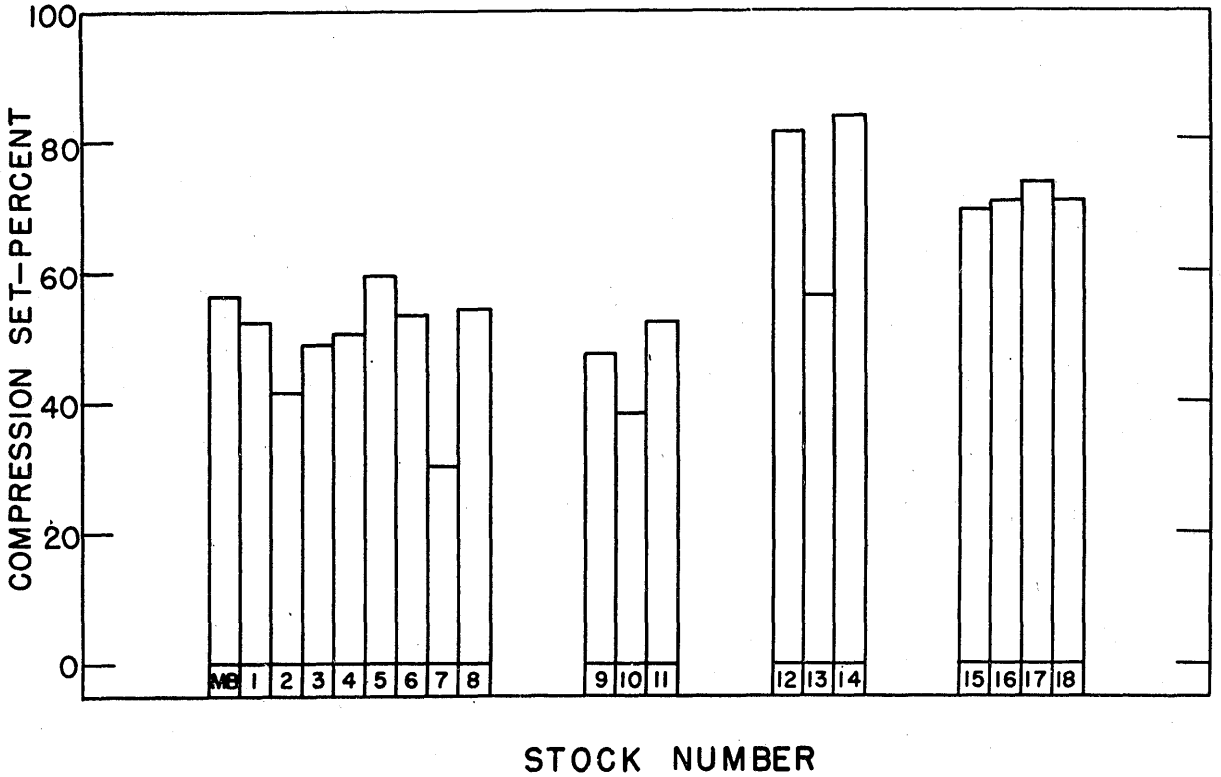


Figure 7-Compression Set of All Stocks

specimens. Generally, the optimum cure does not give the minimum compression set values, as stated by Morris and co-workers (14). However, these values can be used for comparative purposes.

Free Sulfur

Figure 8 shows the free sulfur content of all stocks. For single-accelerated and unaccelerated stocks, the masterbatch (MB) had the highest free sulfur content. Stock 4 was nest best. Stock 5, which had the highest percent retention of initial tensile strength after oxygen-bomb aging, had the lowest free sulfur content. Double- and triple-accelerated stocks had higher values than single-accelerated stocks. It is generally believed by some investigators (9) that free sulfur is available for further vulcanization. It has been asserted also that there is a relationship between the free sulfur at optimum cure of a vulcanizate and its aging properties. However, Yamazaki and Okumura (24) claimed that the amount of free sulfur is not a reliable criterion for predicting the aging characteristics of a vulcanizate. Nevertheless, free sulfur, along with the tensile-modulus and T-50 methods, has its importance in the determination of the optimum cure of a given stock.

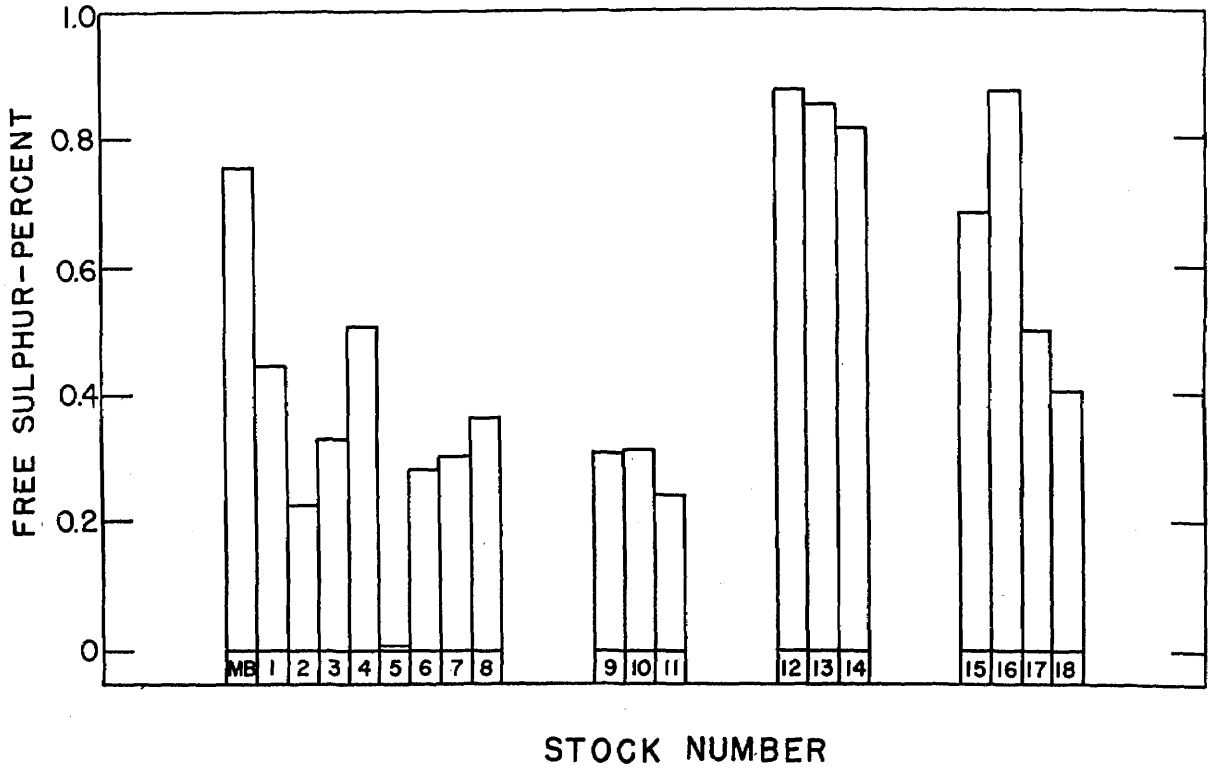


Figure 8-Free-Sulphur Content of Unaged Stocks

DISCUSSION OF RESULTS

It is interesting to note the correlation of molecular structure differences of accelerators 1 to 6 inclusive to the variations in physical properties of the vulcanized rubber. Comparing accelerators 1 and 2, the former produced the higher tensile stock; another pair for comparison is accelerators 3 and 4, with 3 proving the better of the two. It will be noted that in both cases the only difference in molecular structure of the pairs is the presence of the hydroxyl group in the ortho position of the benzene ring. Evidently the -OH group attached to the benzene ring has a retarding effect on acceleration. Phenol (7), for example, has been found to have such an effect.

Another interesting basis of comparison within a homologous series is the variation in the number and form of the saturated carbon atoms connecting the double-bonded nitrogen atoms in accelerator 3 which is composed of two methylene groups. Accelerator 6 has six methylene groups, and accelerator 5 has a benzene ring in the corresponding position. Increasing the number of methylene groups from two to six decreases the accelerating efficiency as shown in the corresponding decrease in tensile strength values. Furthermore, replacing the aliphatic with an aromatic structure, although unsaturated, reduces the efficiency of acceleration both in time of cure and with regard to tensile properties.

Peachey (18) emphasized not only the effect of certain groups, but also that of the position of these groups in the molecule. He cited the nitroso bases which are powerful accelerators and pointed out that the isomeric nitrosoamines, in which the nitroso group is not attached directly to the nucleus, are inert. Spence (22) found that certain compounds which contain groups in the para position are more active than their ortho or meta isomers. He cited the relative activities of the isomeric phenetidines as an example.

Other investigators (10) also have mentioned the superior activity of the para over the ortho or meta compounds. Twiss and Brazier (23) found that p-phenylene diamine was much more active than the meta compound.

Work is being continued in this Laboratory toward correlation of structure and position of groups with relative acceleration activity.

SUMMARY

A study of some aldehydeamine accelerators for rubber vulcanization has been undertaken, and there appears to exist a correlation between molecular structure of an accelerator and the physical properties imparted to vulcanized rubber. Certain active groups within the molecule have a definite effect on the accelerating activity of a compound. Taking the structure of accelerator 3, $\phi CH{=}N(CH_2)_2N{=}CH\phi$, for reference, the following modifications have a retarding effect on the efficiency of acceleration:

1. Addition of an -OH group in the ortho position of the benzene rings. This is shown in accelerator 4 and in the case of accelerator 2 as compared to accelerator 1.

2. Substitution of a benzene structure for the $-(CH_2)_2$. This is shown in accelerator 5.

3. An increase from 2 to 6 in the number of CH_2 groups connecting the two double-bonded nitrogen atoms. This is shown in accelerator 6.

Six compounds synthesized in this Laboratory were evaluated and compared with Captax and Hepteen Base with regard to tensile strength, tensile stress at 500% elongation, ultimate elongation, oven aging, oxygen-bomb aging, compression set, free sulfur, and hardness. None of the compounds was found to possess the oxygen-resistant property of Captax. However, in the presence of an antioxidant (Neozone A), N,N'-dibenzylidene ethylene diamine (accelerator 3) compared favorably with Captax and Hepteen Base. It was found to act efficiently in single acceleration, as well as in double and triple acceleration in various combinations with mercaptobenzothiazole (Captax), benzothiazyldisulfide (Altax), and zinc dimethyl dithiocarbamate (Methyl Zimate), all well known standard accelerators.

Being continued in this Laboratory is the study directed toward improving the accelerating activity of N,N'-dibenzylidene ethylene diamine (accelerator 3) by modifying the form and position of active groups in the molecule.

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