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AGING OF SOFT RUBBER GOODS

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By R. F. Tener, W. H. Smith, and W. L. Holt

ABSTRACT

In this investigation typical rubber compounds were prepared and subjected to different conditions of exposure, etc., in order to determine the influence of various factors, such as light, heat, oxygen, moisture, and the degree of vulcanization on the deterioration of rubber goods. The rate of deterioration was measured by tensile tests which were made at varying intervals of time. It was found that although all these factors contribute to deterioration, not all rubber compounds are affected the same. For instance, certain compounds were found to be resistant to heat but not to light, while in other compounds the reverse was true. Comparisons have been made between the results of accelerated aging tests and natural aging.

CONTENTS

I. INTRODUCTION

There is a tendency to ascribe the deterioration of rubber goods to oxidation influenced by such factors as light, heat, and humidity and by inherent factors, such as the degree of vulcanization and pigmentation. The purpose of the present preliminary study has been to separate, as far as possible, these different elements which contribute to the deterioration of rubber goods and to measure the effect of each factor independently.

II. PREVIOUS INVESTIGATIONS

In 1865 Spiller[1] showed the presence of oxygen in raw rubber which had become resinous. Miller [2] in the same year attributed deterioration of vulcanized rubber to oxidation.

Burghardt[3] stated that the destruction of india rubber, however brought about, is simply a greater or less degree of oxidation and that the percentage of oxygen present is a sure index of the amount of deterioration which rubber has undergone in a given time.

Thompson[4] exposed vulcanized rubber to sunlight for several months in each of the following: hydrogen, carbon dioxide, air, oxygen, and in a vacuum and found that only the rubber in oxygen or air suffered any change. Also no deterioration was shown for samples in hydrogen, carbon dioxide, or in a vacuum at the temperature of boiling water.

Henriques[5] showed that samples of pure rubber heated in absence of light absorbed oxygen very slowly while samples of vulcanized rubber absorbed it very rapidly, especially after being deprived of their free sulphur.

Herbst[6] isolated oxidation products similar in composition to Spiller's resin from a benzene solution of rubber through which air had been passed.

Ditmar[7] proposed an accelerated test in oxygen at 100° C. and assumed that oxygen was responsible for the deterioration in both accelerated and in natural aging.

Peachy[8] investigated the behavior of both raw and vulcanized rubber in oxygen and found that all of the degradation products contained oxygen.

Kirchhof,[9] from work similar to that of Peachy on raw and vulcanized rubber, obtained much the same results and indicated that the process was one of "autoxidation."

Gorter[10] showed that products containing oxygen were formed when raw rubber became tacky in air or oxygen while no changes occurred in an inert gas.

Eaton and Day [11] showed that samples increased in weight in storage and stated that it was practically certain that the increases in weight were due to oxidation.

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[1] J. Chem. Soc., London, **18**, p. 44; 1865.
[2] J. Chem. Soc., London, **18**, p. 273; 1865.
[3] J. Soc. Chem. Indust., **2**, p. 119; 1883.
[4] J. Soc. Chem. Indust., **4**, p. 710; 1885.
[5] Chemiker Zeitung, **21**, p. 415; 1897.
[6] Berichte der Deutschen Chemischen Gesellschaft, **39**, p. 523; 1906.
[7] Gummi-Zeitung, **20**, pp. 628, 945; 1906.
[8] J. Soc. Chem. Indust., **31**, p. 1103; 1912; **32**, p. 179; 1913; **37**, p. 55; 1918.
[9] Kolloid-Zeitschrift, **13**, p. 49; 1913.
[10] Le Caoutchouc et La Gutta-Percha, **12**, p. 8724; 1915.
[11] J Soc. Chem. Indust., **38**, p. 339T; 1919.

Stevens[12] exposed samples of rubber in moist air, dry air, and over kerosene, etc., and stated that acetone extract did not increase in samples exposed over kerosene and water, which showed that under these conditions the rubber was protected from oxidation and decomposition.

Tuttle[13] showed an increase in acetone extract for aged samples and attributed it to oxidation accelerated by light.

Bruni,[14] Marzetti,[15] and coworkers showed that the rate of deterioration was proportional to the rate of oxygen absorption, and that deterioration in warm oxygen gave the same oxygenated products that were found in naturally aged rubber.

V. Henri [16] concluded that ultra-violet light had no effect when samples were held in vacuum and that the effect obtained in air was oxidation promoted by light.

Ahrens [17] stated that light caused oxidation and oxidation caused tackiness.

Asano [18] exposed to light samples in vessels filled with carbon dioxide and, since oxygen was excluded in this case, stated that tackiness was due not to oxidation but to depolymerization.

Williams [19] stated that oxidation of rubber may take place in three ways (1) by deterioration throughout the rubber, (2) by the formation of a film on the surface of the rubber, and (3) by cracking or checking. He concluded that ozone was the active cause of cracking.

III. ACCELERATED AGING TESTS

The importance of the aging characteristics of rubber products has led to numerous proposed methods of making accelerated tests by which these characteristics can be determined. The method of Geer [20] has received more technical application than any other. In this test rubber compounds are subjected to a continuously renewed current of circulating air in an oven at 70° C. Twenty-four hours of this treatment is often considered equivalent to approximately six months of natural aging. This method or modifications of it are known to be in use by several important manufacturers of rubber goods.

The method of accelerated aging proposed by Bierer and Davis [21] consists in subjecting rubber compounds to the action of oxygen

[12] J. Soc. Chem. Indust., **39**, p. 251T; 1920.
[13] Rubber Age, **8**, p. 271; 1921.
[14] India Rubber J., **63**, p. 814; 1922.
[15] Rubber Age, **13**, p. 433; 1923.
[16] Le Caoutchouc et La Gutta-Percha, **7**, pp. 4371–4376; 1910.
[17] Chemiker-Zeitung, **34**, p. 266; 1910.
[18] Memoirs of the College of Engineering, Kyoto Imperial University, **3**, No. 10.
[19] Ind. and Eng. Chem., **18**, p. 367; 1926.
[20] India Rubber World, **55**, p. 127; 1916; India Rubber J., **61**, p. 1163; 1921; Rubber Age, **11**, p. 345; 1922.
[21] Ind. and Eng. Chem., **16**, p. 711; 1924; **17**, p. 860; 1925.

under a pressure of 300 lbs./in.^{2} in a bomb at 70° C. The effects produced are obtained much more rapidly than with the Geer test.

In the accelerated aging test of Marzetti [22] rubber compounds are subjected to oxygen at atmospheric pressure and a temperature of 77° C. This test is faster than that of Geer but consumes more time than that of Bierer and Davis. A temperature of 70° C. is used in the Geer and Bierer-Davis methods of accelerated aging, although Bierer-Davis have suggested 60° C. The more rapid effect produced by the Bierer-Davis method is due to a greater concentration of the oxygen, the active mass. They point out that this method is better than the Geer method in that the final product more closely resembles that obtained through natural aging.

Park [23] believes that natural aging presents more variables than are accounted for in the accelerated aging tests which have been proposed.

Asano [24] proposed "to keep a sample in an air oven at a constant temperature of 71° C. in a constant flow of air and expose it at the same time to an artificial ultra-violet light and examine the changes in stress-strain relation and in chemical composition after a certain interval of time."

A later accelerated test is that proposed by Jecusco [25] in which artificial light is used in conjunction with heat. He states that "the addition of light to heat in aging (1) broke down the stress in a few hours, (2) increased the acetone extract, (3) decreased the loss in weight, (4) changed the appearance of the aged sample, and (5) produced a red insoluble coating," and in conclusion says that "a great deal of work is necessary to supply a great many more facts."

The attitude of the Bureau of Standards toward an accelerated aging test of rubber goods represents the attitude of the consumer as well as that of the manufacturer. With respect to the consumer's point of view it is evident that different classes of rubber goods are subject to different conditions of environment during their period of usefulness. The tread and side walls of an automobile tire must suffer the added effects of light to which an insulation buried in a conduit is not subjected. A hot-water bottle must meet the condition of periods of elevated temperatures. The manufacturer has an added problem in the possible changes which may occur during shelf life before the material reaches the consumer.

The greater number of the above references point to oxidation being the cause of the deterioration of rubber goods. This opinion is not, however, held by all investigators although it is generally admitted that oxygen plays a part in deterioration of rubber. There is also a difference of opinion in regard to just what are the effects of light and heat, particularly the former, and it would seem that

[22] See footnote 15, p. 355.
[23] Kautschuk, pp. 57–61; 1926.
[24] See footnote 18, p. 355.
[25] Ind. and Eng. Chem., 18, p. 420; 1926.

much more work is desirable on effect of light. There is also a difference of opinion in regard to the value of accelerated aging tests and of those in use which are the better and which more nearly approach the conditions of natural aging. The tests referred to above are only a few of the many that have been proposed. Very few data are available on the use of light in accelerated aging tests.

In view of these differences of opinion in regard to the effect of different factors it was decided to try to isolate the variables and study each independently. Recognizing the fact that these variables could not be expected to act the same on all types of compounds four typical ones were chosen for the work. These represent the simplest compound—"a pure gum"—and three others, each of which contained a percentage of compounding materials, together with one of three common accelerators.

IV. RUBBER COMPOUNDS USED

Four compounds were chosen for the work and three different cures were made of each compound. "A" was a "pure gum" compound, "B" and "C" contained approximately 83 per cent rubber by volume. "B" was accelerated with the organic accelerator diphenylguanidine and "C" with an inorganic accelerator, litharge. "D" was a tire tread compound containing carbon black and reclaimed rubber.

The compositions of the compounds were as follows:

Compound A, light yellow in color	Parts by weight	Percentage by weight
Pale crêpe	90	90
Sulphur	10	10

Cured for periods of 2 1/4, 3 3/4, and 4 1/4 hours at 287° F. (142° C.).
This is a common test formula, although the percentage of sulphur is high, based on present-day commercial practice. The compound was included on account of its simplicity and possible theoretical value.

Compound B, light brown in color [1]	Parts by weight	Percentage by volume
Smoked sheet	100	83.00
Sulphur	4	1.47
Diphenylguanidine	.5	.25
Zinc oxide	4	.55
Whiting	50	14.73

Cured for periods of 20, 30, and 50 minutes at 287° F. (142° C.).

Compound C, gray in color [1]	Parts by weight	Percentage by volume
Smoked sheet	100	82.45
Sulphur	6	2.21
Litharge	10	.80
Whiting	50	14.54

Cured for periods of 15, 25, and 50 minutes at 287° F. (142° C.).

[1] Compounds B and C are stocks that were used by Bierer and Davis. See footnote 21 to text, p. 355.

Compound D, black in color	Parts by weight	Percentage by volume
Smoked sheet	100.00	60.41
Hexamethylene-tetramine	1.00	.41
Sulphur	6.53	1.74
Zinc oxide	18.75	1.92
Gas black	34.85	10.75
Mineral rubber	10.9	6.03
Palm oil	6.53	3.80
Reclaimed rubber	38.1	14.94

Cured for periods of 25, 50, and 90 minutes at 294° F. (146° C.).

The time and temperatures of curing the A and D compounds were selected to give an undercured compound, one of maximum tensile strength, and an overcured compound. These factors for the B and C compounds were the same as proposed by Bierer and Davis. In this report the three cures are designated by numerals 1, 2, and 3 designating the shortest, the medium, and the longest cures, respectively.

V. TEST CONDITIONS

Samples compounded and cured as indicated above were subjected to the following conditions:

1. Outdoor exposure.
2. Outdoor exposure with light excluded.
3. Laboratory storage conditions.
4. Outdoor exposure under glass.
5. Outdoor exposure under glass in a vacuum.
6. Outdoor exposure under slightly colored glass in a vacuum.
7. Dry air at 70° C.
8. Air humidified with water vapor at 70° C.
9. Air at room or normal humidity at 70° C.
10. Oxygen at 70, 80, and 90° C.
11. In commercial nitrogen at 70, 80, and 90° C.

A set of samples was exposed outdoors to represent natural aging. Another set was stored under laboratory conditions which represent conditions to which rubber is subjected on the manufacturers' shelves. In order to determine the effect of light a third set of samples was stored outdoors but light was excluded. To determine the effect of oxygen one set of samples was stored outdoors in glass tubes which were evacuated, but recognizing that these conditions were somewhat different from those of outdoor exposure a check set was stored in tubes not evacuated. Another set was stored in evacuated tubes colored with yellow varnish to exclude some of the shorter light waves. To examine the effect of modifications of the heat test one set of samples was exposed to heat by the regular method, a second set to humidified air, and in a third set the air was dried. To examine the test proposed by Marzetti [26] three sets of samples were

[26] See footnote 15, p. 355.

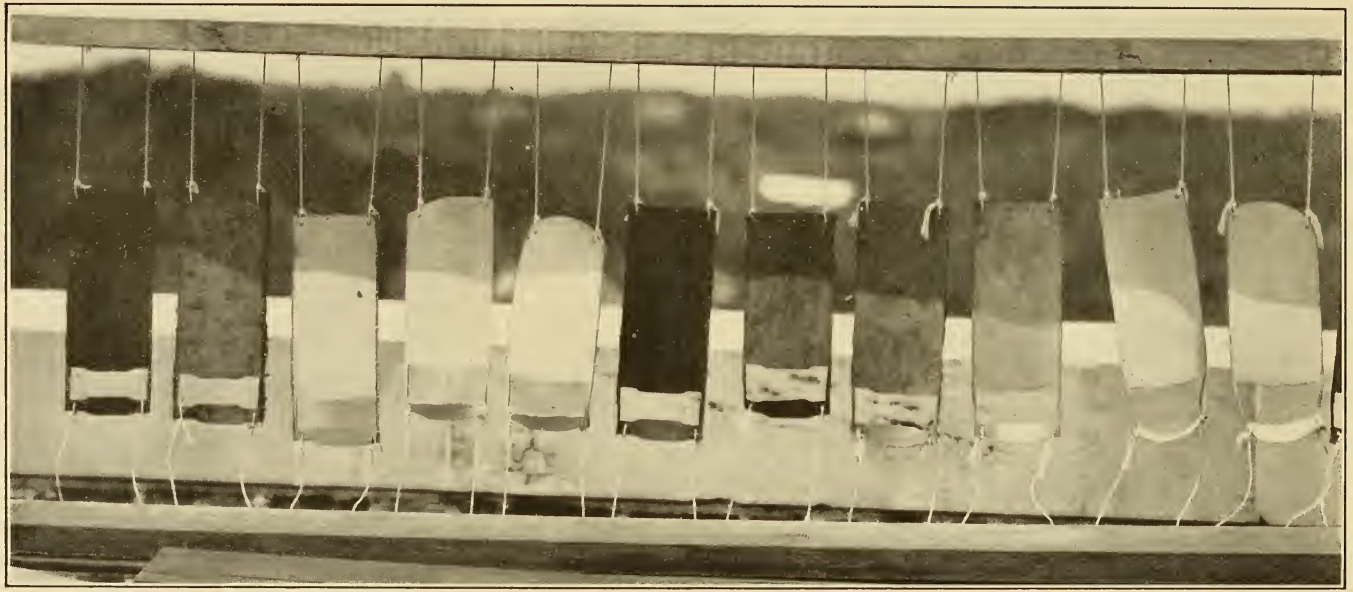

FIG. 1.—*Rack for holding samples during outdoor exposure*

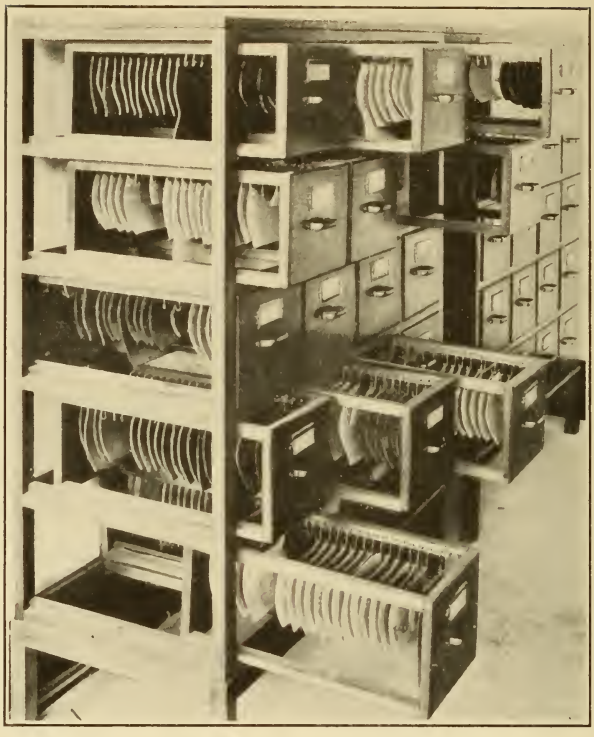

FIG. 2.—*Cabinet used for laboratory storage tests*

FIG. 3.—*Tubes used for exposing samples in a vacuum to sunlight*

exposed to the action of oxygen under normal pressure at temperatures of 70, 80, and 90° C., respectively. In order to determine if oxygen was the deteriorating agent three sets of samples were exposed to the action of nitrogen at 70, 80, and 90° C., respectively.

In all cases the degree of deterioration was measured by the tensile strength. In many cases the acetone extract and combined sulphur were determined to ascertain if the increases in acetone soluble material and combined sulphur were related to the physical deterioration of rubber.

The compounds were mixed in large batches and press cured in sheets approximately 5 by 15 inches by 0.070 inch thick. Before using any sheet samples cut from it were tested for tensile strength. Sheets in which these results were more than 4 per cent from the average were discarded. The original tensile was taken as the average of the results from all sheets of that kind.

All tests and analyses were made in accordance with the procedure described in Circular No. 232 [27] of the Bureau of Standards. The acetone extracts were, of course, corrected for free sulphur.

VI. METHODS AND APPARATUS

The effect of outdoor exposure was determined by suspending samples in a vertical position on a rack with the largest surfaces of the samples facing north and south. (See fig. 1.) The samples were placed on the rack during November, 1924 and their condition, at varying intervals until March, 1926, is indicated.

A similar series was placed in an open-end box on the roof. The interior of the box was blackened and a black cloth was placed over each end to exclude light but allow circulation of air. The temperatures of the air in this box and of that surrounding the samples under outdoor exposure were taken at intervals and found to be practically the same. The time of exposure for this series covered the same period as the series exposed to outdoor conditions.

The laboratory storage test was carried out in a filing cabinet as shown in Figure 2. The ends were closed with black cloth as in the previous test. The period of aging was the same as for outdoor exposure.

Samples of the same rubber compounds were placed in evacuated glass tubes and exposed on the roof from June, 1925, to May, 1926. (See fig. 3.) The tubes were approximately 2.5 m long, 3.5 cm in diameter, and 2 mm thick. An absolute pressure, which was never greater than 5 mm of mercury, was maintained in the tubes in the following way. The open end of each tube was closed by a special rubber cap which gripped the outside of the tube for a distance of

[27] United States Government Master Specification No. 59a for Rubber Goods.

about 3 cm. A capillary glass tube passed through the cap to a container of mercury. The vacuum was produced by the use of a pump which was connected to the mercury container. The samples in each tube were joined together and were prevented from touching the inner surface of the tube by paper clips. At the beginning of the exposure sulphur bloomed from the samples and collected on the interior of the tubes in such quantities that it was necessary to remove it occasionally during the first four months. After this the tubes remained clear. In this test an effort was made to prevent the effect of oxygen and determine the effect of sunlight.

Samples were also exposed in similar tubes coated with a spar varnish containing 3.6 mg per cc of an oil-soluble yellow dye. It was hoped in this way to exclude some of the ultra-violet light or light of short wave lengths. Spectral transmission measurements were made on samples of the clear and varnished glasses, but the similarity of the results obtained in exposure tests does not warrant drawing any conclusions from the specific characteristics of the glass.

For a direct comparison with these results samples were exposed in open glass tubes, both clear and coated with the varnish, respectively. This comparison of results from samples in a vacuum and under glass, and in air and under glass, should give evidence as to the effect of oxygen on the deterioration of rubber goods since all the other factors were approximately the same.

For the test in dry air at 70° C. the samples were placed in a container in an oven. Air from a pressure tank was passed very slowly through the container after having been dried by passing through sulphuric acid and calcium chloride. For air of normal humidity, or the humidity prevailing in the oven at the time the tests were made, the usual accelerated aging test was used; that is, by hanging samples in circulating air at 70° C. in an electric oven.

The above test was also carried out in humidified air. This was produced by placing an open pan of water in the oven. A comparison of the results of the above tests in dry air and in air containing different amounts of water vapor should give the effects of moisture on the deterioration of rubber at this temperature.

Considerable work has been reported on the effect of oxygen on rubber compounds at various temperatures and at increased pressures but very little data have been published on the tensile properties of rubber compounds when exposed to oxygen at various temperatures and at normal pressure. Such data should be interesting and valuable in the study of the aging properties of rubber. Marzetti [28] gives some data on tests made at a temperature of 77° C. In this investigation tests were made at temperatures lower, approximately the same, and higher than that used by Marzetti. An apparatus similar to the

[28] See footnote 15, p. 355.

one used for dry air, except that the drying train was omitted, was employed for these tests.

A comparison of results of tests in oxygen at 70, 80, and 90° C. should show the effect of an increase in temperature on the rate of deterioration. A comparison of the results of tests in air and oxygen at 70° C. should show the effect of increasing the concentration of oxygen. A comparison of the results in oxygen at the three temperatures given above with those in nitrogen at the same temperatures should show the effect of oxygen on rate of deterioration.

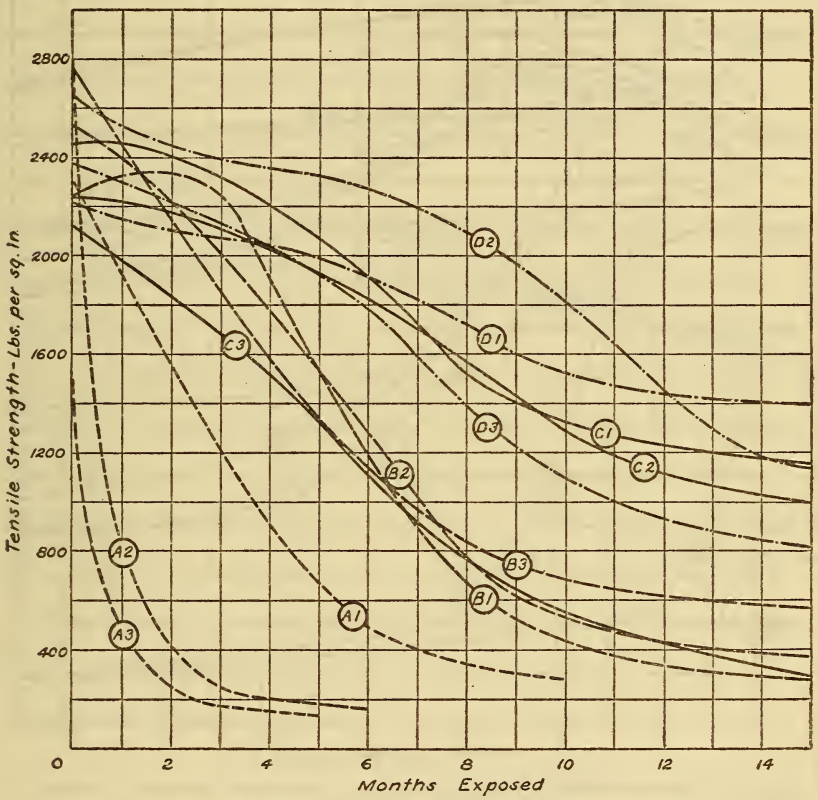

FIG. 4.—*Changes in tensile strength of rubber compounds exposed to weather*

In order to avoid the effects of oxygen and to determine the effect of heat samples were maintained in an atmosphere of nitrogen at various temperatures. The same apparatus was used as for oxygen.

VII. DISCUSSION OF RESULTS

1. RESULTS OF PHYSICAL TESTS

The curves in Figure 4 represent the history of a natural aging test when the compounds were exposed to outside weather conditions.

In Figure 5 results are shown from samples which were subjected to practically the same conditions as in Figure 4 except that light was

excluded. The deterioration of all the stocks was less rapid than when they were exposed to light. This was decidedly pronounced in the case of the B compound.

Figure 6 shows the results from samples aged under ordinary conditions of inside storage. In general, these results are similar to those from outside exposure with light excluded except that it appears that the laboratory conditions were less severe. The A1 compound behaved quite differently than it did under the conditions shown in

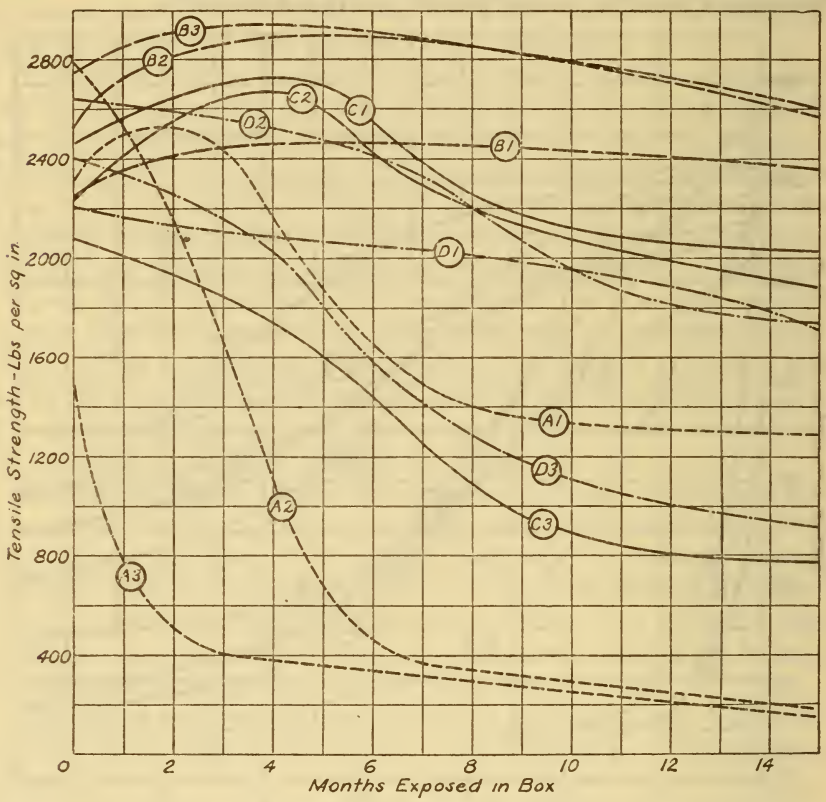

FIG. 5.—*Changes in tensile strength of rubber compounds exposed to weather but protected from sunlight*

Figure 5 in that the tensile strength continued to rise over a period of 15 months.

These three conditions of aging represent those to which rubber articles under normal usage might be subjected. The last two conditions; that is, laboratory storage and outdoor storage with light excluded, should have nearly the same effect. The characteristic effect of exposure to sunlight was surface cracking of certain of the compounds, particularly A and B. D showed no cracking. Without sunlight, as under the other two conditions, none of the stocks cracked to any extent.

In Figures 7 and 8 results are given for the compounds exposed in clear and colored glass evacuated tubes. The results are essentially the same whether the clear or colored glass was used. In practically all cases deterioration took place during the first three or four months. After that time the rate of deterioration became almost negligible. The A compound behaved in about the same manner as when exposed to the weather.

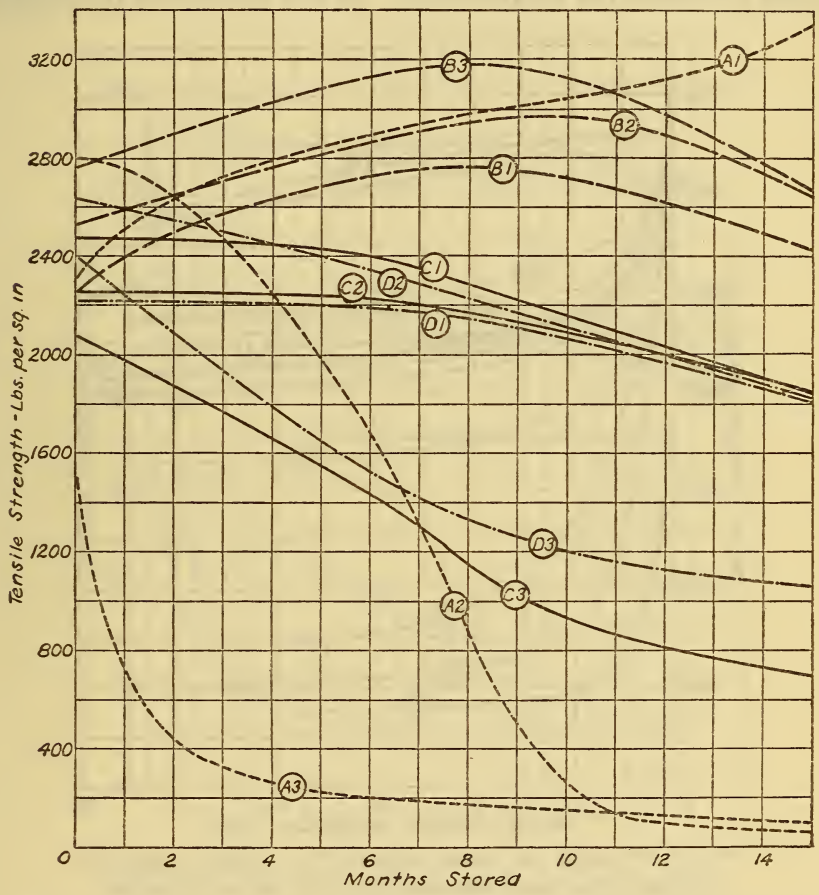

FIG. 6.—*Changes in tensile strengths of rubber compounds stored in laboratory protected from light*

In order to show a direct comparison between samples exposed in air and in a vacuum, Figures 9 and 10 are given—Figure 9 for A and B stocks and Figure 10 for C and D stocks. The added effect of air was very plainly shown on all stocks except the A stocks. It is most marked on the B compound. The D stock was least affected by light whether in a vacuum or in air.

These four tests all relate to the deterioration of rubber compounds when kept in a vacuum. It would be expected that the samples which were in the tubes containing air would deteriorate the same as those which were on the rack. (Fig. 1.) However, inasmuch as the two tests were not started at the same period of the year and as the presence of the glass tubes might cause higher temperatures than was the case with the samples on the rack, these air tube tests were made to parallel the vacuum tests. As was anticipated the samples

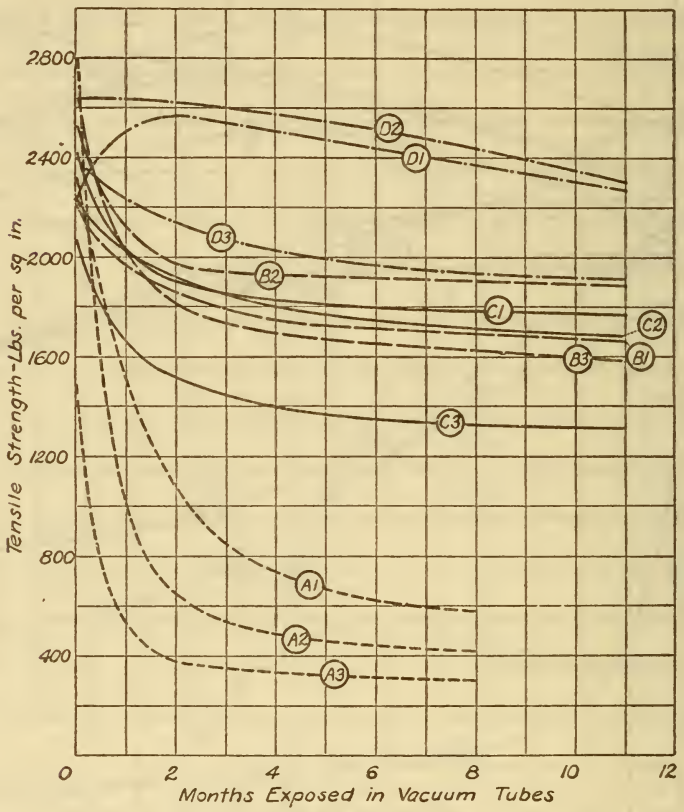

FIG. 7.—*Changes in tensile strengths of rubber compounds exposed in clear glass evacuated tubes to the action of sunlight*

in the tubes deteriorated at a faster rate due to a higher average temperature, but the different stocks showed, in general, the same aging characteristics as in the "rack" tests.

Figures 11, 12, and 13 show results of heat tests at 70° C. in dry air, in air of normal humidity, and in humidified air, respectively. The results are quite similar under all three conditions. The most consistent results are shown by the D stocks, in which there was a rapid deterioration regardless of moisture conditions. The B com-

pounds were least affected but the results are somewhat inconsistent with regard to the three cures. In the A1 stock and the C2 stock the deterioration was apparently retarded slightly by the presence of moisture, but, in general, the presence of moisture did not influence the results greatly.

Figures 14, 15, and 16 show the results of tests in oxygen at temperatures of 70, 80, and 90° C., respectively. The relative order of deterioration of the different samples was about the same at each

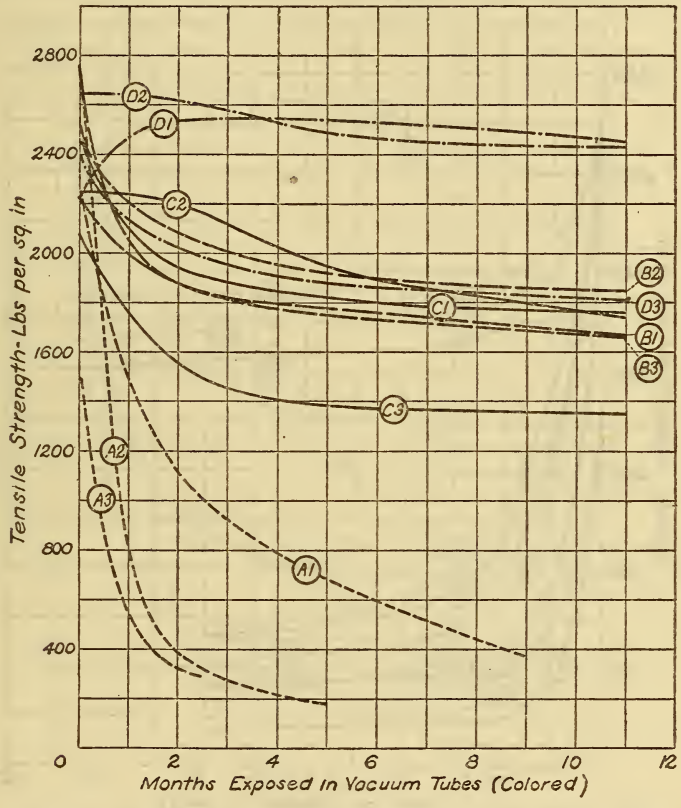

FIG. 8.—*Changes in tensile strength of rubber compounds exposed in colored glass evacuated tubes to the action of sunlight*

of these temperatures but there was a decided difference in the rate at which it took place, being much greater at 90° C. than at 70° C.

Figures 17, 18, and 19 show the results obtained from samples maintained at 70, 80, and 90° C. in nitrogen in place of oxygen. At temperatures of 70 and 80°, there was very little deterioration except for the A2, A3, and C3 compounds. At a temperature of 90° for the 15-day period the effect of heat began to show more plainly and all the stocks deteriorated to some extent. The deterioration was great-

est in the A and C compounds and least in the B compound. For a direct comparison between the effects of oxygen and nitrogen at 90° Figure 20 is shown which covers the same period of time (48 hours) as Figure 16. Aside from the A compound very little deterioration was apparent for this period in any of the compounds in nitrogen while in oxygen the deterioration in all the compounds was very rapid.

These nine tests might be referred to as "oven tests," as all the results were obtained by keeping samples in an oven under different

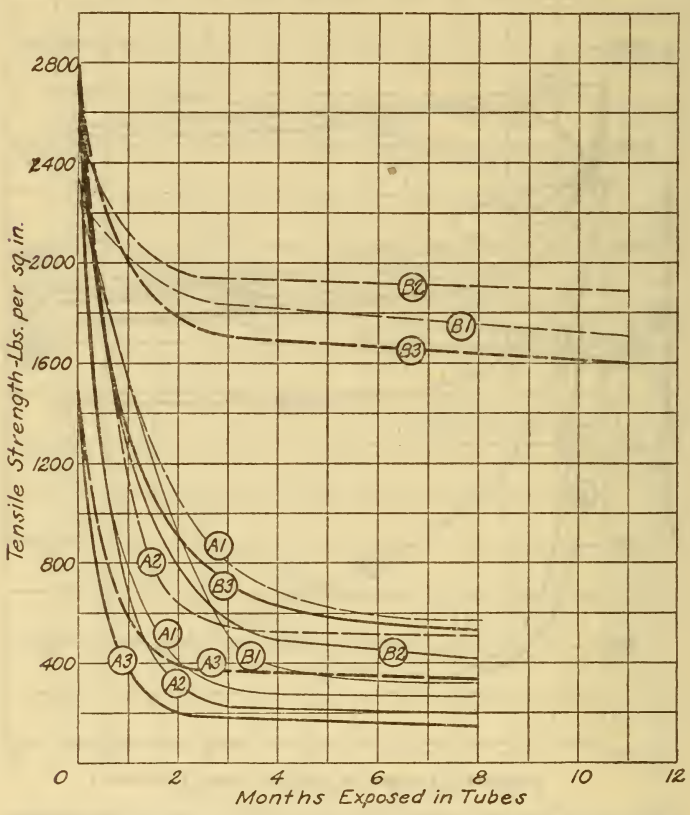

FIG. 9.—*Comparison of changes in tensile strengths of rubber compounds A and B exposed in clear glass evacuated and nonevacuated tubes to the action of sunlight*

Full lines show results in air. Broken lines show results in a vacuum.

conditions of humidity, temperature, and gaseous atmospheres. In contrast with the sunlight exposure tests no surface cracking of the samples was apparent in any of the oven tests. In general, there was a tendency for the different compounds to soften during the period of exposure. This was particularly true of the compounds containing litharge.

2. RESULTS OF CHEMICAL TESTS

The data from these tests are given in charts and show changes in acetone extract and combined sulphur resulting from the different test conditions. The data are given for periods of time at which some change was shown in physical properties, or, if there was no noticeable change in physical properties, at the end of the test period. If a sample deteriorated completely before the end of the test, the data are given at that time.

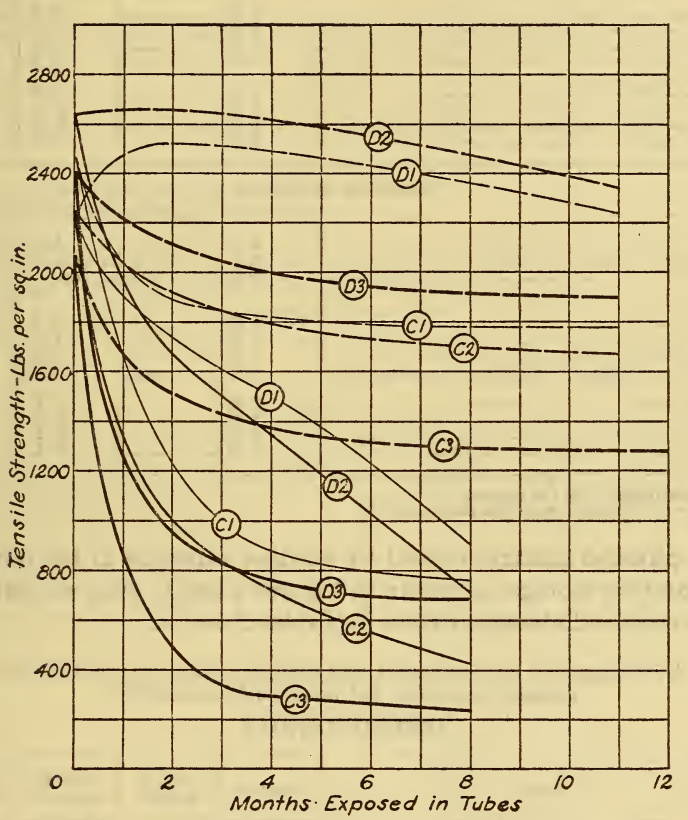

FIG. 10.—*Comparison of tensile strengths of rubber compounds C and D exposed in clear glass evacuated and nonevacuated tubes to the action of sunlight*

Full lines show results in air. Broken lines show results in a vacuum.

Table 1 shows changes in acetone extract and combined sulphur for samples subjected to outdoor exposure. All stocks except D1 showed an increase in acetone extract at or before the end of the 15-month period, but little change in combined sulphur was noted in any of the stocks except A1, A3, and C2 for corresponding periods of time.

TABLE 1.—*Changes in acetone extract and combined sulphur of rubber compounds exposed to outdoor conditions*

ACETONE EXTRACT

Stock	Original	After 2 months	After 8 months	After 15 months
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.84		6.90	
A2	2.82	3.90		
A3	3.04	3.80		
B1	2.2		7.77	
B2	2.13		7.24	
B3	2.07		6.53	
C1	1.72		2.39	3.97
C2	1.73		2.42	3.88
C3	1.68		3.55	
D1	8.77		N. I.	N. I.
D2	8.51		N. I.	8.82
D3	8.21		9.33	N. F. I.

COMBINED SULPHUR

A1	2.74		3.82	
A2	5.17	N. I.		
A3	5.4	6.00		
B1	.70		.99	
B2	1.03		N. I.	
B3	1.43		1.71	
C1	1.37		1.51	N. F. I.
C2	1.76		2.45	N F I.
C3	2.52		N. I.	
D1	1.85		N. I.	N. I.
D2	2.52		N. I.	N. I.
D3	3.36		N. I.	N. I.

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

The physical changes caused by outdoor exposure in the dark and by laboratory storage, as shown in Figures 5 and 6, were accompanied by the chemical changes shown in Tables 2 and 3.

TABLE 2.—*Changes in acetone extract and combined sulphur of rubber compounds exposed to weather, but protected from sunlight*

ACETONE EXTRACT

Stock	Original	After 2 months	After 8 months	After 15 months
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.84	3.04	N. F. I.	N. F. I.
A2	2.82		3.66	
A3	3.04	3.8		
B1	2.2			N. I.
B2	2.13			N. I.
B3	2.07			N. I.
C1	1.72			N. I.
C2	1.73			N. I.
C3	1.68		2.37	2.85
D1	8.77			N. I.
D2	8.51			8.79
D3	8.21		9.19	9.54

TABLE 2.—*Changes in acetone extract and combined sulphur of rubber compounds exposed to weather, but protected from sunlight*—Continued

COMBINED SULPHUR

Stock	Original	After 2 months	After 8 months	After 15 months
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.74		2.97	N. F. I.
A2	5.17		N. I.	
A3	5.4	N. I.		
B1	.70		.80	N. F. I.
B2	1.03			N. I.
B3	1.43			N. I.
C1	1.37			N. I.
C2	1.76			2.25
C3	2.52		2.79	N. F. I.
D1	1.85			N. I.
D2	2.52			N. I.
D3	3.36		3.54	N. F. I.

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

TABLE 3.—*Changes in acetone extract and combined sulphur of rubber compounds stored in laboratory, but protected from sunlight*

ACETONE EXTRACT

Stock	Original	After 2 months	After 8 months	After 15 months
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.84			3.56
A2	2.82		3.11	
A3	3.04	3.52		
B1	2.20			2.50
B2	2.13			2.24
B3	2.07			N. I.
C1	1.72			N. I.
C2	1.73			2.08
C3	1.68		2.49	3.24
D1	8.77			N. I.
D2	8.51			9.14
D3	8.21		8.33	10.11

COMBINED SULPHUR

A1	2.74			4.35
A2	5.17		N. I.	
A3	5.40	5.59		
B1	.70			N. I.
B2	1.03			N. I.
B3	1.43			N. I.
C1	1.37			1.60
C2	1.76			2.37
C3	2.52		2.72	N. F. I.
D1	1.85			N. I.
D2	2.52			N. I.
D3	3.36		3.50	N. F. I.

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

With the exception of the A compound and C3 and D3 stocks there was little change in acetone-soluble material. There were, in

general, small increases in combined sulphur in the C and the A compounds.

The results given in these three tables correspond with the physical results given in the first three sets of curves (figs. 4, 5, and 6) or what might be called normal usage tests.

Table 4 shows the increases in combined sulphur for the samples exposed in a vacuum. There was a slight increase in all compounds

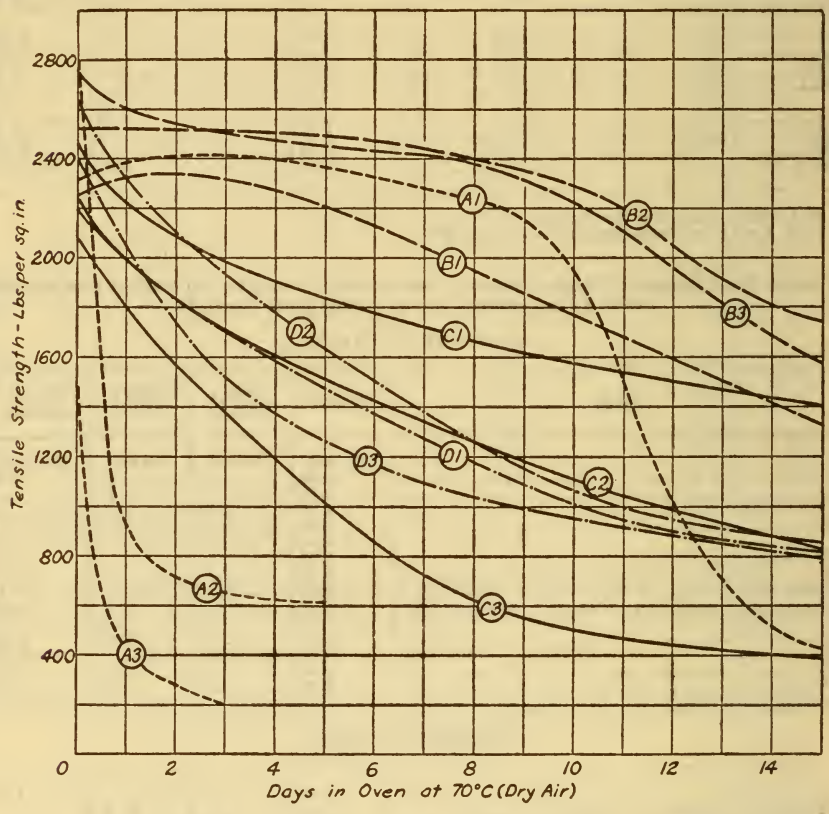

FIG. 11.—*Changes in tensile strengths of rubber compounds in circulated dry air at 70° C.*

except the D3. No increase in acetone extract could be detected in any of the compounds; if anything, there was a slight tendency for acetone-soluble material to decrease. Samples did not respond to the pyrrole test made in accordance with the procedure of Bruni and Pelizzola.[29]

[29] India Rubber J., 63, p. 415; 1922. The sample of rubber is heated with ammonium acetate and a pine shaving previously moistened with concentrated hydrochloric acid is held in the fumes above the sample. A crimson color indicates the presence of oxidation products. Samples of rubber which had been subjected to natural aging gave positive results.

TABLE 4.—*Changes in combined sulphur in rubber compounds exposed in clear glass evacuated tubes to the action of sunlight*

COMBINED SULPHUR

Stock	Original	After 1 month	After 3 months	After 5 months
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.74			3.16
A2	5.17		5.60	
A3	5.4	5.53		
B1	.70		.83	1.13
B2	1.03		1.18	1.43
B3	1.43		1.95	N. F. I.
C1	1.37		1.49	1.72
C2	1.76		1.84	1.97
C3	2.52		3.01	N. F. I.
D1	1.85			1.99
D2	2.52			2.71
D3	3.36			N. I.

N. I. = No increase over the original.
N. F. I. = No further increase over column to left.

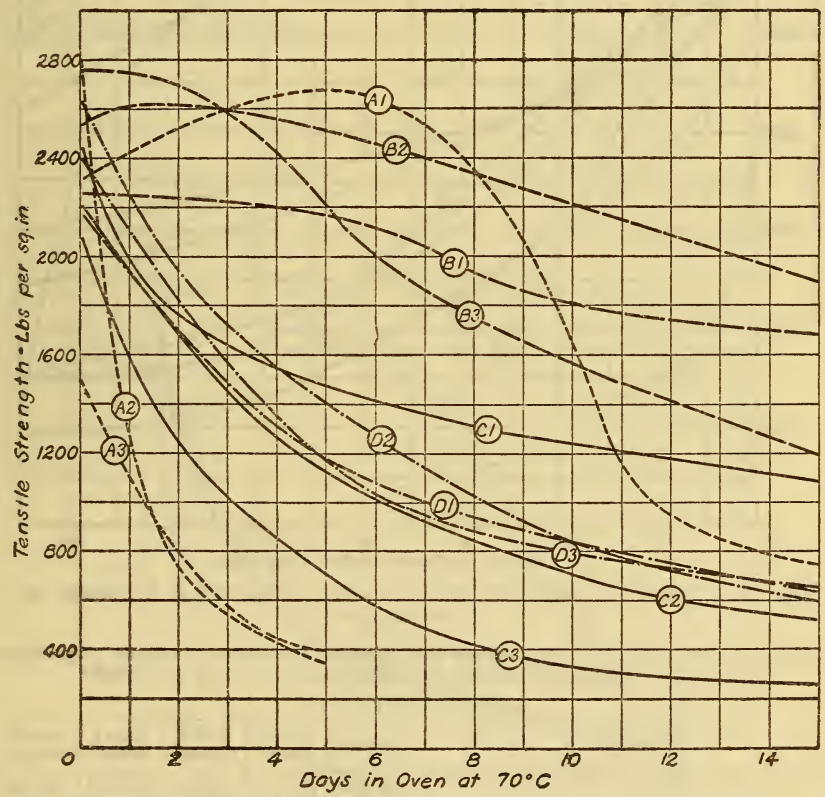

FIG. 12.—*Changes in tensile strengths of rubber compounds in circulated air at 70° C.*

Table 5 shows increases in acetone extract and combined sulphur for samples under glass but exposed to air. The table shows an increase in acetone extract in all cases except the A1, A3, and the D1 stocks. If the results shown in this table are compared with those in Table 1 certain inconsistencies appear which are not at present

explainable. The seasons of the year at which the tests were made, however, were different. Those given in Table 1 were started in November and those in Table 5 the following May. The samples under glass even at the same season of the year would naturally have a slightly higher temperature. The combined sulphur increased slightly in all stocks except the D3, A2, and A3 compounds. This agrees fairly well with the results shown in Table 1.

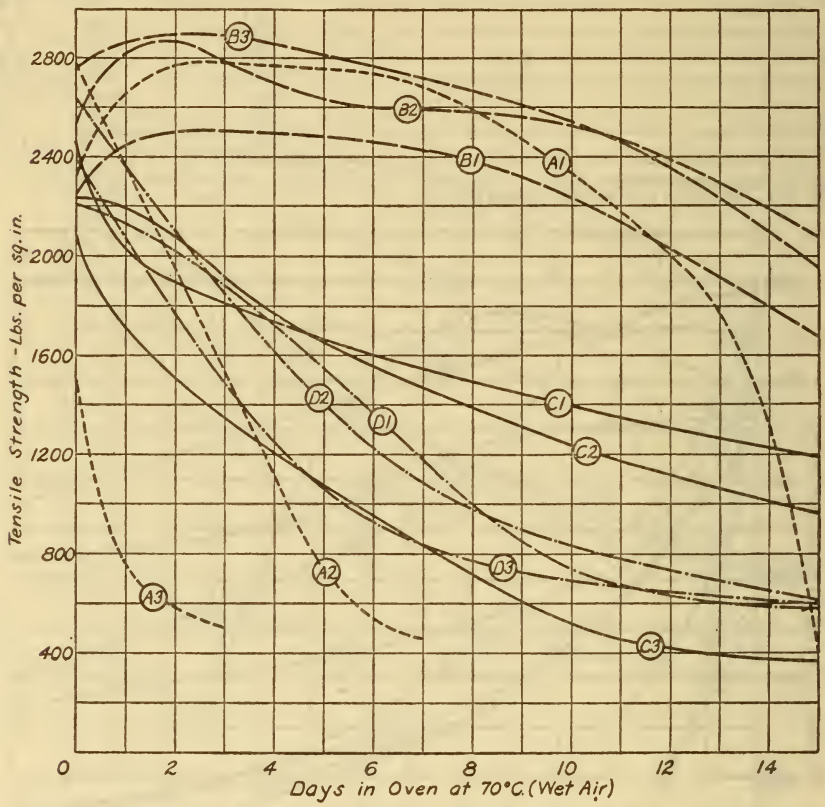

FIG. 13.—*Changes in tensile strengths of rubber compounds in circulated wet air at 70° C.*

TABLE 5.—*Changes in acetone extract and combined sulphur of rubber compounds exposed in clear glass tubes (not evacuated) to the action of sunlight*

ACETONE EXTRACT

Stocks	Original	After 1 month	After 3 months	After 5 months	After 8 months
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1	2.84	N. I.	N. I.	----------	----------
A2	2.82	3.51	----------	----------	----------
A3	3.04	N. I.	----------	----------	----------
B1	2.2	3.91	4.95	----------	----------
B2	2.13	4.19	5.5	----------	----------
B3	2.07	3.66	N. F. I.	----------	----------
C1	1.72	1.85	2.04	2.42	----------
C2	1.73	2.16	2.58	2.95	----------
C3	1.68	3.07	3.17	----------	----------
D1	8.77	----------	N. I.	N. I.	N. I.
D2	8.51	----------	8.94	N. F. I.	9.50
D3	8.21	----------	8.51	N. F. I.	10.33

TABLE 5.—*Changes in acetone extract and combined sulphur of rubber compounds exposed in clear glass tubes (not evacuated) to the action of sunlight*—Contd.

COMBINED SULPHUR

Stocks	Original	After 1 month	After 3 months	After 5 months	After 8 months
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1	2.74	2.94	N. F. I.	----------	----------
A2	5.17	N. I.	----------	----------	----------
A3	5.4	N. I.	----------	----------	----------
B1	.70	.98	N. F. I.	----------	----------
B2	1.03	1.37	1.72	----------	----------
B3	1.43	1.75	N. F. I.	----------	----------
C1	1.37	1.67	N. F. I.	N. F. I.	----------
C2	1.76	2.08	N. F. I.	N. F. I.	----------
C3	2.52	3.02	N. F. I.	----------	----------
D1	1.85	----------	2.18	N. F. I.	N. F. I.
D2	2.52	----------	2.67	2.82	N. F. I.
D3	3.36	----------	N. I.	N. I.	N. I.

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

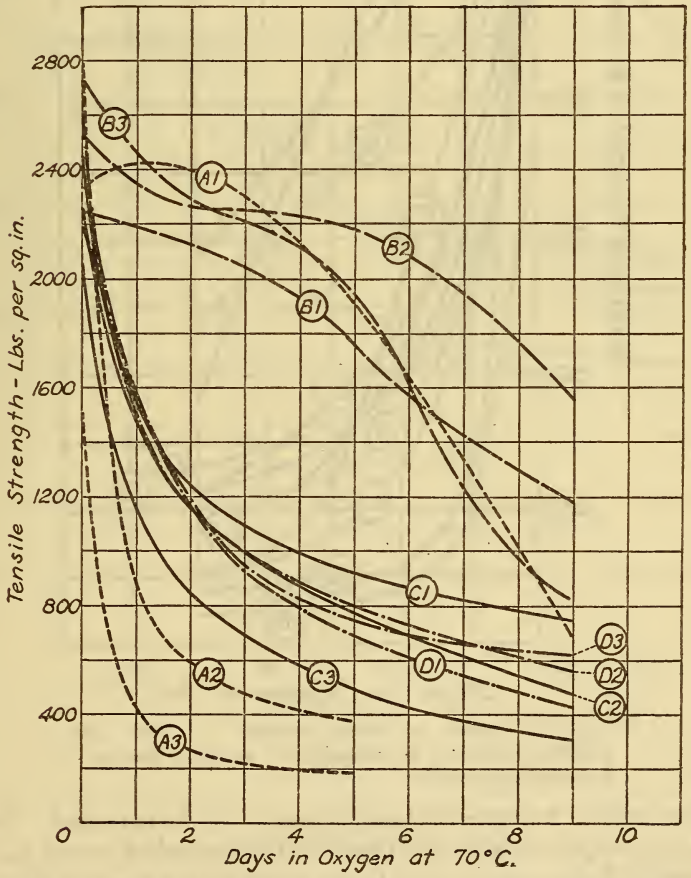

FIG. 14.—*Changes in tensile strengths of rubber compounds in oxygen at atmospheric pressure and at a temperature of 70° C.*

The results shown in these two tables correspond with the physical results given in Figures 7, 8, 9, and 10, or those obtained from "vacuum" tests. An increase in the acetone-soluble material of a rubber compound is attributed to oxidation, and, accordingly, when

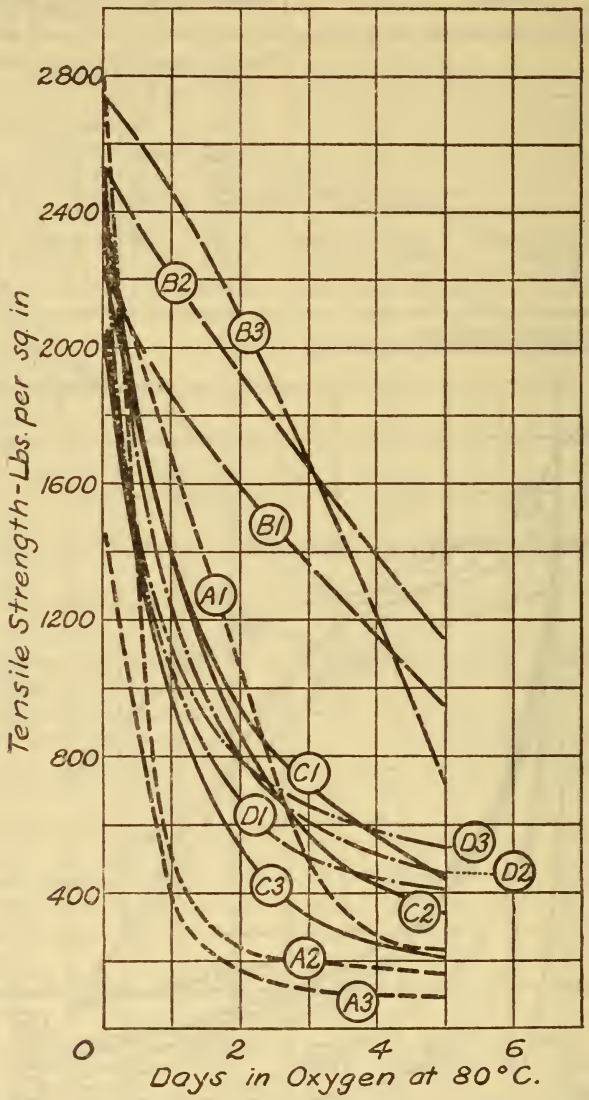

FIG. 15.—*Changes in tensile strengths of rubber compounds in oxygen at atmospheric pressure and at a temperature of 80° C.*

no air or oxygen was present no increase would be expected. On the other hand, an increase in combined sulphur or what would actually be increased vulcanization could take place in the absence of air.

The results of determinations of acetone extract and combined sulphur in compounds exposed to air at 70° C. are shown in Table 6,

D2, D3, C3, and B3 showed appreciable increases in acetone extract. The C compound showed an increase in combined sulphur. The other stocks showed very little change in combined sulphur.

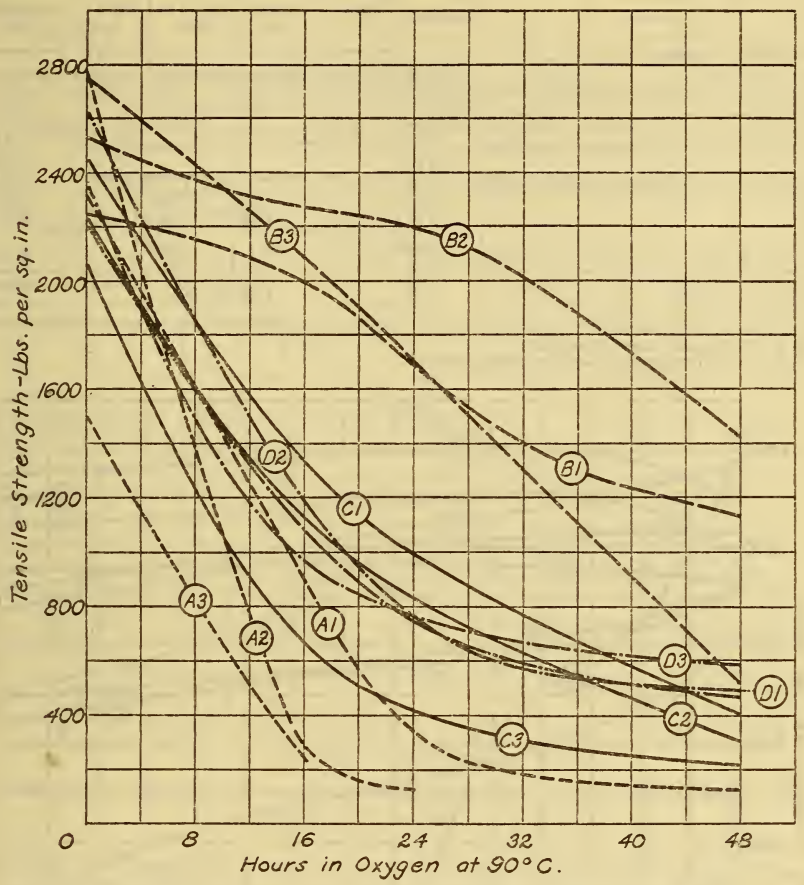

FIG. 16.—*Changes in tensile strengths of rubber compounds in oxygen at atmospheric pressure and at a temperature of 90° C.*

TABLE 6.—*Changes in acetone extract and combined sulphur of rubber compounds in circulated air at 70° C.*

ACETONE EXTRACT

Stock	Original	After 1 day	After 7 days	After 11 days	After 13 days	After 15 days
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1	2.84			N. I.	3.31	
A2	2.82		N. I.			
A3	3.04	N. I.				
B1	2.2					2.37
B2	2.13					2.63
B3	2.07					3.36
C1	1.72		N. I.	1.92		N. F. I.
C2	1.73		1.98	2.23		3.05
C3	1.68		2.32	3.32		
D1	8.77		N. I.	N. I.		
D2	8.51		8.74	9.17		
D3	8.21		10.01	No data.		

TABLE 6.—*Changes in acetone extract and combined sulphur of rubber compounds in circulated air at 70° C.*—Continued

COMBINED SULPHUR

Stock	Original	After 1 day	After 7 days	After 11 days	After 13 days	After 15 days
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1	2.74			3.26	3.50	
A2	5.17		5.28			
A3	5.4	5.95				
B1	.70					0.86
B2	1.03					N. I.
B3	1.43					1.66
C1	1.37		1.57	1.68		2.06
C2	1.76		1.89	2.09		2.78
C3	2.52		N. I.	2.80		
D1	1.85		2.07	N. F. I.		
D2	2.52		2.80	N. F. I.		
D3	3.36		3.58	No data.		

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

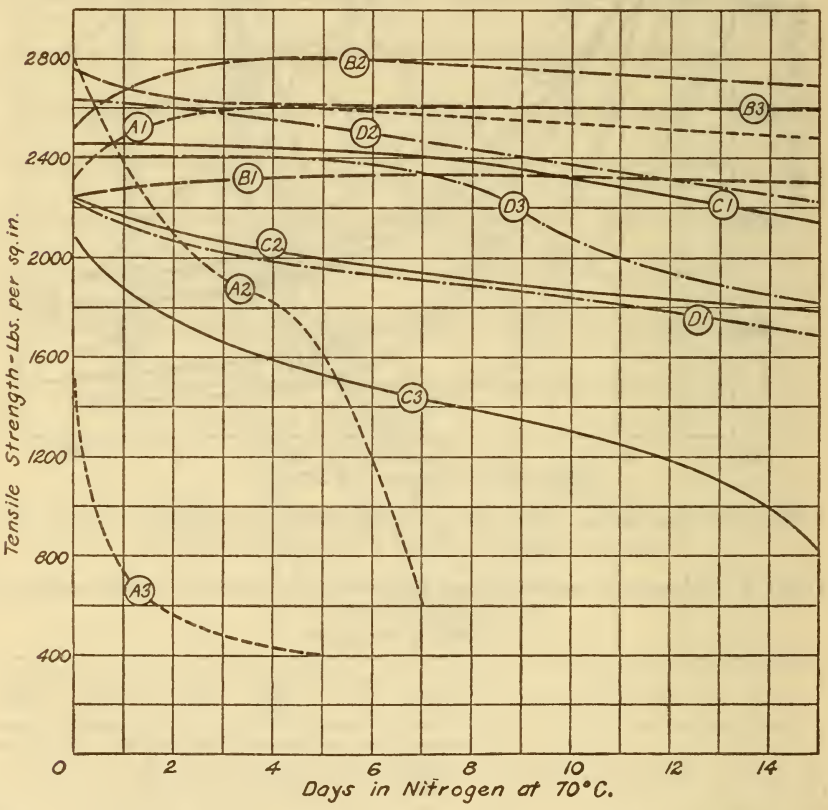

FIG. 17.—*Changes in tensile strengths of rubber compounds in commercial nitrogen at a temperature of 70° C.*

In oxygen at 70° C. (Table 7) all compounds except the B compound showed a considerable increase in acetone extract. B1 showed

no increase and B2 and B3 appreciable increases. The combined sulphur as a whole increased very little and in some cases not at all.

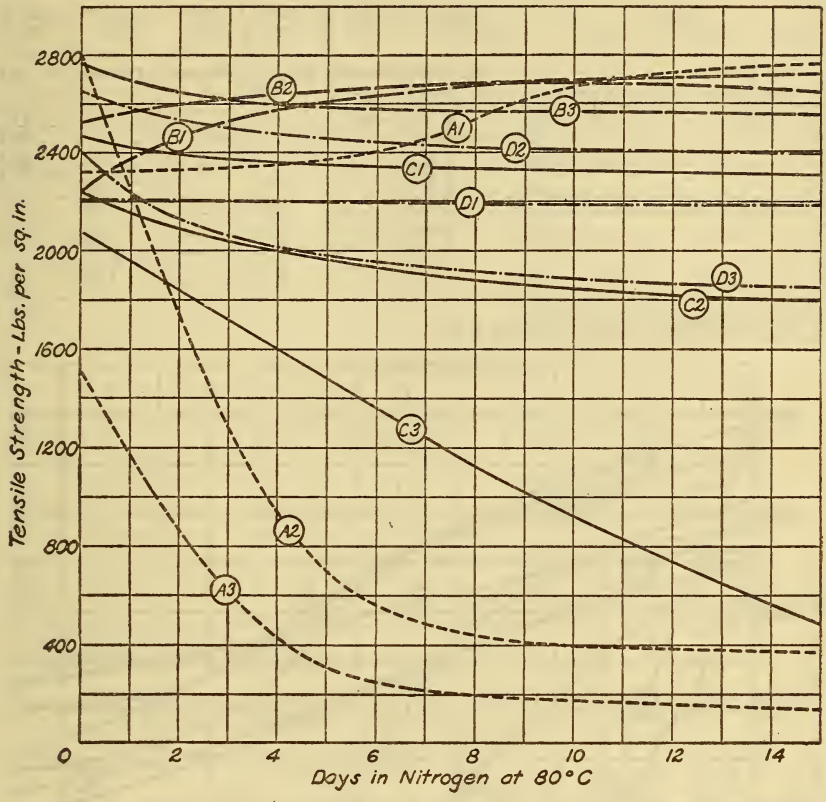

FIG. 18.—*Changes in tensile strengths of rubber compounds in commercial nitrogen at a temperature of 80° C.*

TABLE 7.—*Changes in acetone extract and combined sulphur of rubber compounds in oxygen at atmospheric pressure and at a temperature of 70° C.*

ACETONE EXTRACT

Stock	Original	After 1 day	After 3 days	After 5 days	After 7 days	After 9 days
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1	2.84		3.31			
A2	2.82	3.43				
A3	3.04	3.61				
B1	2.2					N. I.
B2	2.13					2.51
B3	2.07			2.30		3.63
C1	1.72		2.55		2.80	
C2	1.73		2.84		4.08	
C3	1.68		2.98		5.47	
D1	8.77		9.17		9.88	
D2	8.51		10.25		12.05	
D3	8.21		11.36		13.13	

TABLE 7.—*Changes in acetone extract and combined sulphur of rubber compounds in oxygen at atmospheric pressure and at a temperature of 70° C.*—Contd.

COMBINED SULPHUR

Stock	Original	After 1 day	After 3 days	After 5 days	After 7 days	After 9 days
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1	2.74		2.85			
A2	5.17	N. I.				
A3	5.40	N. I.				
B1	.70					N. I.
B2	1.03					N. I.
B3	1.43			1.60		N. F. I.
C1	1.37		N. I.		1.63	
C2	1.76		1.91		2.27	
C3	2.52		2.61		2.83	
D1	1.85		N. I.		2.01	
D2	2.52		2.72		N. F. I.	
D3	3.36		N. I.		3.50	

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

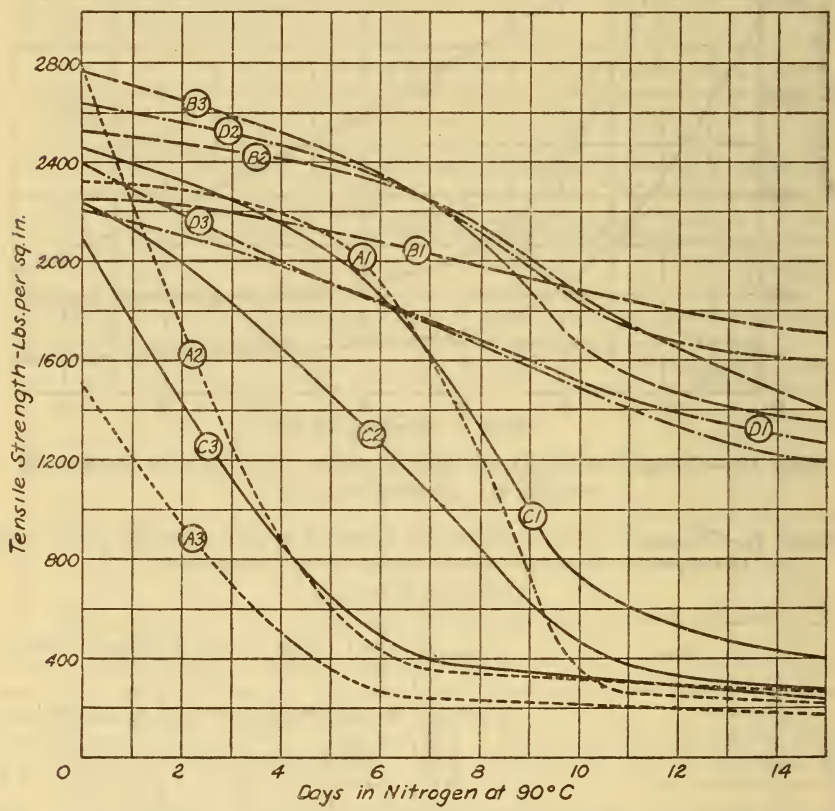

FIG. 19.—*Changes in tensile strengths of rubber compounds in commercial nitrogen at a temperature of 90° C.*

Tables 8 and 9 give changes in acetone extract and combined sulphur when the compounds were heated in oxygen at 80 and 90° C. The results are, in general, similar to those in Table 7, except that the effects are more pronounced.

TABLE 8.—*Changes in acetone extract and combined sulphur of rubber compounds in oxygen at atmospheric pressure and at a temperature of 80° C.*

ACETONE EXTRACT

Stock	Original	After 1 day	After 3 days	After 5 days
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.84		5.35	
A2	2.82	3.35		
A3	3.04	3.84		
B1	2.20			2.38
B2	2.13			3.33
B3	2.07			4.33
C1	1.72		4.62	
C2	1.73		3.91	
C3	1.68		5.19	
D1	8.77		11.79	
D2	8.51		11.93	
D3	8.21		11.41	

COMBINED SULPHUR

A1	2.74		3.18	
A2	5.17	N. I.		
A3	5.4	6.14		
B1	.70			N. I.
B2	1.03			N. I.
B3	1.43			1.60
C1	1.37		1.69	
C2	1.76		1.99	
C3	2.52		2.81	
D1	1.85		2.21	
D2	2.52		2.82	
D3	3.36		3.78	

N. I.=No increase over the original.
N. F. I.=No further increase over column to left.

TABLE 9.—*Changes in acetone extract and combined sulphur of rubber compounds in oxygen at atmospheric pressure and at a temperature of 90° C.*

ACETONE EXTRACT

Stock	Original	After 16 hours	After 24 hours	After 48 hours
	Per cent	*Per cent*	*Per cent*	*Per cent*
A1	2.84		4.13	
A2	2.82	5.23		
A3	3.04	6.63		
B1	2.20			2.55
B2	2.13			3.58
B3	2.07			4.42
C1	1.72		3.40	5.14
C2	1.73		4.02	5.59
C3	1.68		4.12	
D1	8.77		11.04	
D2	8.51		10.18	
D3	8.21		10.16	

COMBINED SULPHUR

A1	2.74		3.17	
A2	5.17	5.65		
A3	5.40	6.93		
B1	.70			0.84
B2	1.03			1.16
B3	1.43			1.69
C1	1.37		1.59	1.82
C2	1.76		1.97	2.16
C3	2.52		2.71	
D1	1.85		1.95	
D2	2.52		2.82	
D3	3.36		No data.	

The results given in these four tables correspond with the physical results given in Figures 12, 14, 15, and 16 or those obtained in oven tests. Increases in combined sulphur are more to be expected under these conditions than in some of the other tests because of the higher temperatures. It is the general opinion that the acetone extract does not usually increase materially in oven tests in air and these results, in general, check that opinion. The use of oxygen in place of air does, however, show a greater tendency to produce acetone soluble material for corresponding physical deterioration.

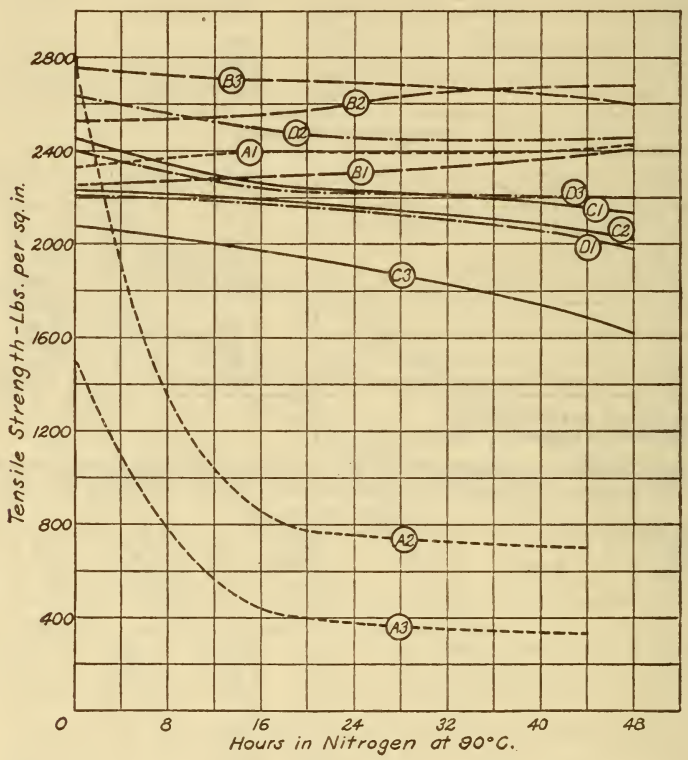

FIG. 20.—*Changes in tensile strengths of rubber compounds in commercial nitrogen at a temperature of 90° C.*

3. EFFECT OF DIFFERENT FACTORS

(*a*) OXIDATION.—It is generally recognized that oxygen plays an important part in the deterioration of soft rubber goods. These results bear out this belief. The effect of oxygen is shown by a direct comparison of Figures 14 and 17, 15 and 18, and 16 and 20, which show the deterioration due to oxygen at temperatures of 70, 80, and 90° C., respectively, when compared with nitrogen at the same temperatures. The effect of oxygen is also indicated by a study of the results shown in Figures 9 and 10, obtained from testing com-

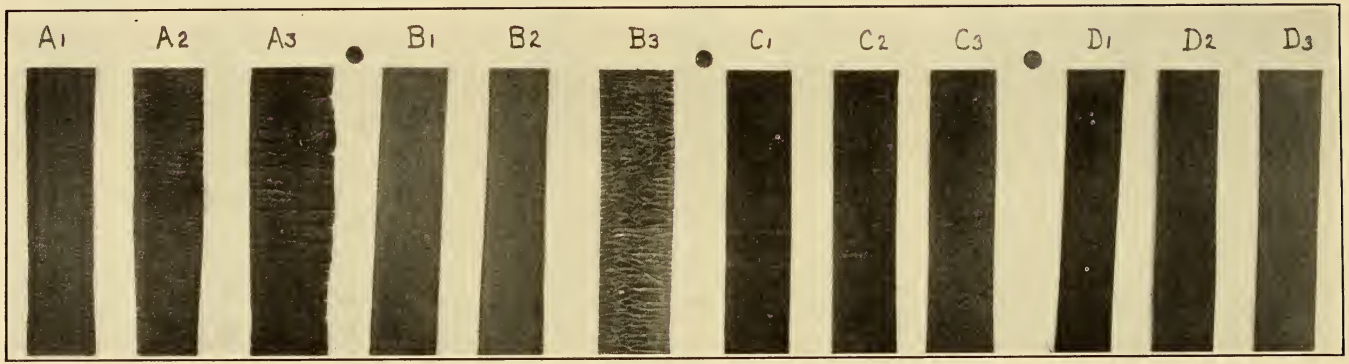

FIG. 21.—*Appearance of samples from vacuum tubes after exposure to sunlight*

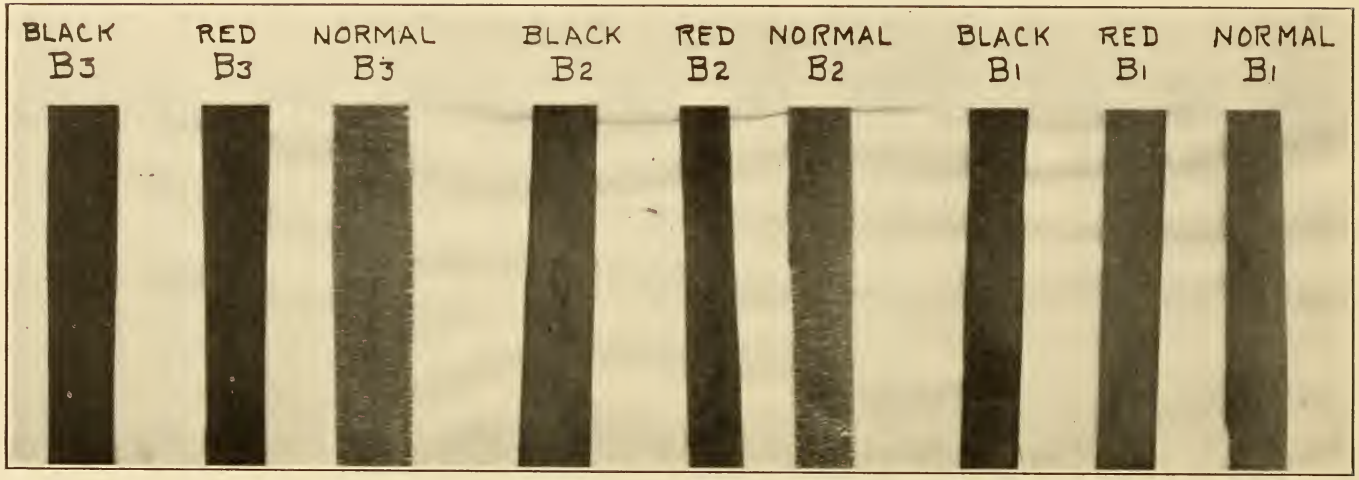

FIG. 22.—*Appearance of normal, red and black samples after outdoor exposure*

pounds which had been exposed in evacuated and nonevacuated tubes. It is also indicated by a comparison of Figures 17, 12, and 14, which show the results when samples were kept in nitrogen, air, and oxygen, respectively, at a temperature of 70° C. The rate of deterioration was greatest in oxygen, least in nitrogen, and intermediate in air.

(*b*) Light.—The effect of light is shown by a comparison of Figures 4 and 5. All compounds deteriorated more rapidly when exposed to light, but not all were affected to the same degree. The presence of light had little effect on the rate of deterioration on the D compounds, but has a very marked effect on the B compounds.

In Figures 7 and 8 it will be noted that deterioration took place in the absence of air when samples were exposed to sunlight. Examination of these samples showed that a hard brittle coating was formed on the surface of the samples, particularly on the A and B compounds. This coating, when once formed, seemed to decrease the rate of deterioration. The coating was insoluble in acetone, benzine, and other common organic solvents. It contained more combined sulphur than the interior portion of the sample which was still elastic. The following analysis (Table 10) represents the approximate combined sulphur on the inside and outside of the sample.

Table 10

Stock number	Combined sulphur	Stock number	Combined sulphur
B1 a	0.83	C3 c	2.78
B1 b	1.82	D1 a	1.97
B1 c	.69	D1 b	2.05
B2 a	1.23	D1 c	1.97
B2 b	2.05	D2 a	2.66
B2 c	1.00	D2 b	2.74
B3 a	1.80	D2 c	2.57
B3 b	2.87	D3 a	3.36
B3 c	1.50	D3 b	3.47
C3 a	2.93	D3 c	3.45
C3 b	3.17		

a=Total sample.
b=Surface of the sample.
c=Inside of the sample.

This coating was evidently different from that noted by Williams[30] which was soluble in alcohol and which resulted from oxidation.

The appearance of samples exposed in vacuum tubes is shown in Figure 21. The samples were under a slight tension when the photograph was taken and the presence of the coating is shown by the cracks. Apparently the A3 and B3 stocks were most affected. No checks were apparent in the D compound and the C3 stock showed only a slight checking.

(*c*) Heat.—The effect of heat is shown in Figures 17, 18, and 19. The C compound was probably the most sensitive to heat, particularly

[30] Ind. and Eng. Chem., 18, p. 367; 1926.

C3 which was affected at all temperatures. The deterioration was probably a result of continued vulcanization as litharge is known to be an active accelerator at comparatively low temperatures. The B compound was most resistant to heat. There seemed to be a critical temperature between 80 and 90° C. where all the compounds were noticeably affected.

The effect of heat is also shown in the presence of oxygen where the rate of deterioration increased greatly when the temperature was successively increased from 70 to 80 to 90° C. (See figs. 14, 15, and 16.)

(*d*) Degree of Vulcanization.—The effect of the degree of vulcanization was most marked in the A compound. It affected the deterioration to a considerable extent in the C compounds, and to a less extent in the B and D compounds. In general, the intermediate cures of the B, C, and D compounds aged better than the other cures though there were some exceptions. The under cure of the A compound deteriorated much less rapidly than either of the other cures.

(*e*) Color.—By a comparison of Figures 4 and 5 it can be seen that there was a marked difference in the rate of deterioration of the B compound in the presence and absence of sunlight, while in the case of the D stock there was little difference. In order to determine if any of this could be attributed to color, to one batch of the B compound was added 3 per cent of red iron oxide, and to another 2 per cent of carbon black. The three compounds, one without addition of coloring, one red and one black, were simultaneously exposed to sunlight for six months and tests made at intervals of two months to determine the deterioration of each.

The results show that during this period the rate of deterioration of the normal uncolored compound was about five times as great as that of the black and about twice that of the red. The quantities of coloring materials added to the compounds were not sufficient to affect appreciably the physical properties but exposure to light showed that the aging properties were greatly changed. The general appearance of these samples at the end of the six months' period is shown in Figure 22. The photograph was taken with the samples under slight tension in order to show the surface cracking.

VIII. ACCELERATED AND NATURAL AGING

In general, the deterioration in air and oxygen at elevated temperatures showed the principal difference to be in the rate of deterioration. If the tensiles of the C and D stocks are compared at the end of one day at 90° C., two days at 80° C., and four days at 70° C., the results will show that the rate of deterioration at 80° C. is approximately twice as rapid as at 70° C., and approximately twice as

rapid at 90° C. as at 80° C. The above does not apply to the A compound and only partially to the B compound.

A comparison of the results of accelerated tests with those in which the samples were protected from sunlight during aging (figs. 5 and 6) shows a comparatively close agreement in order of deterioration.

The statement that 24 hours in air at 70° C. is equivalent to approximately six months of natural aging in the absence of light seems to hold fairly well except for compounds A2, A3, and D3. When the results of accelerated tests (fig. 12) are compared with results shown in Figure 4, which represent compounds exposed to sunlight, there is no agreement. Taking the B and D compounds only, for example, the B compounds are decidedly the best aging when stored in the dark, while in sunlight the D compounds are decidedly the best. The B compounds, although showing excellent ability to resist aging in the dark, will not stand up in sunlight.

In speaking of "natural aging" it would accordingly seem necessary to state carefully the conditions of exposure.

IX. RELATION OF ACETONE-SOLUBLE MATERIAL TO THE DETERIORATION OF RUBBER GOODS

In the outdoor exposure tests the B stock deteriorated fastest and showed the greatest increase in acetone extract. The D stock deteriorated least as measured by physical tests and showed the smallest increase in acetone extract. The C stock stood intermediate both as to deterioration and increase in acetone-soluble material. There seemed to be no definite relation between the deterioration and the acetone extract in the A compound.

In the absence of sunlight, the B compound deteriorated least and showed no increase in acetone extract. The C and D stocks which deteriorated similarly showed corresponding increases in acetone extract. The A compound did not show increases in acetone-soluble materials corresponding with the deterioration physically.

When the compounds were heated in air, there was no very close agreement between the deterioration and the increase in acetone-soluble material except in the case of the B compound. When oxygen was used in place of air the relation between acetone-soluble material and deterioration seemed to be more comparable.

X. CONCLUSIONS

The results of these tests show that the deterioration of rubber is influenced by internal factors, such as the composition and state of vulcanization, and by external factors, such as heat, light, and oxygen. The effect of the degree of vulcanization is very marked in the case of the pure gum compound. When overcured it deterio-

rated rapidly regardless of external conditions. This characteristic would not necessarily be true of all compounds which contain a high percentage of rubber.

In the compounds containing accelerators the effect of the degree of vulcanization was not so marked.

External factors do not affect all rubber compounds in the same way. One compound may be very sensitive to sunlight while another may be very sensitive to heat.

The results obtained by accelerated aging tests do not agree in all cases with those obtained by so-called natural aging. They are most useful as a means of predicting the action of rubber compounds in storage.

Natural aging is usually accepted as the standard of comparison in determining the effect of an accelerated test. Outdoor weather conditions are far from constant at varying periods of the year. It is believed that a better standard might result if the varying factors which are present in an outdoor test were each standardized. Reproducible results might then be possible, and, if desired, one or more of the factors of an outdoor test might be eliminated.

Color influences the rate of deterioration in the presence of sunlight. These tests indicate that, in general, dark colored compounds are more resistant to effects of sunlight than light colored compounds.

Many compounds when exposed to sunlight deteriorate by checking or cracking on the surface; this, however, is not true of all compounds. The D compounds, which were black, showed very little, if any, checking due to sunlight while the lighter colored ones checked considerably. In the accelerated aging tests, or when stored in the dark, this condition was not apparent.

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