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CHANGE OF VOLUME OF RUBBER ON STRETCHING: EFFECTS OF TIME, ELONGATION, AND TEMPERATURE

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ABSTRACT

The change of volume on stretching was studied for four rubber compounds; two were pure gum, and one each contained 10 percent by volume of carbon black and whiting, respectively. Samples were made in the form of narrow molded rings. Measurements of the change with time up to about 20 minutes were made with a water-filled dilatometer; for longer periods a mercury-filled dilatometer was used. The whiting compound increased in volume on stretching, presumably on account of the formation of vacuoles around the coarse particles of filler. With the other compounds the volume remained constant up to an elongation of 200 or 300 percent, above which it decreased by an amount which was greater the higher the elongation, the lower the temperature, and the longer the time the rubber was kept stretched. The decrease was an approximately linear function of the logarithm of the time from a few minutes after stretching, to about 4 weeks, the duration of the experiment. The volume thermal expansivity of the stretched rubber was greater than that of the unstretched. Increased vulcanization of a given compound, in general, decreased the volume change on stretching. The results indicate that, in the absence of coarse fillers, Poisson's ratio for rubber is 0.5 or greater, the numerical value depending upon the composition, the temperature, the time after stretching, and other factors.

CONTENTS

I. INTRODUCTION

The present investigation was suggested by the work of Davey and his students,[1] who found that a time lag of a few seconds elapsed between the stretching of rubber and the development of the full intensity of the X-ray diffraction pattern. Feuchter [2] had previously shown that the volume of rubber decreased on stretching, and on the basis of these two observations one of the present authors predicted that a time lag would occur in the change of volume of rubber on stretching. When this time lag was looked for it was found without difficulty,[3] and seems to afford a simple, convenient means for studying the fibering or "crystallization" of stretched rubber. Incidental to studying this time lag observations were made as to the effect of composition, temperature, and elongation on the volume of stretched rubber.

The time lag has been recently observed in connection with the double refraction of stretched rubber, by Thiessen and Wittstadt,[4] and probably constitutes the effect which was dismissed by previous observers as "optical creep." [5]

The literature on rubber contains a wide range of values for the change of volume on stretching and for Poisson's ratio. Most of the data pertain to rubber-filler systems,[6] [7] which increase in volume on stretching because the formation of vacuoles around the coarse filler particles or aggregates increases the volume of the stretched rubber to a much greater extent than the fibering of the rubber phase decreases it.

Early investigators [8] who worked with rubber containing no fillers failed to observe any decrease in volume on stretching, probably for the reason that inhomogeneities such as sulphur crystals due to the relatively high percentage of sulphur used at that time led to the formation of vacuoles which masked the effect of fibering of the rubber phase.

II. PREPARATION OF SAMPLES

The samples used in the present investigation were molded rings which were made as thin as practical in the radial dimension so that when they were stretched the inside and the outside would have nearly the same elongation. The rings were approximately 1 mm in width, 4 mm in depth, and 100 mm in average circumference. The inside circumference was about 96.9 mm and the outside, 103.1 mm, hence when the rings were stretched by a relatively large amount the actual elongation of the rubber ranged from about 3 parts per 100 below to

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[1] M. F. Acken, W. E. Singer, and W. P. Davey. *X-ray study of rubber structure*, Ind. Eng. Chem. **24**, 54–57 (1932).
John D. Long, William E. Singer, and W. P. Davey. *Fibering of rubber. Time lag and its relation to structure*, Ind. Eng. Chem. **26**, 543–547 (1934).

[2] H. Feuchter, *The volume contraction with the formation of anisotropic rubber systems by stretching*, Gummi-Ztg. **39**, 1167–1168 (1925).

[3] BS Tech. News Bul. 201, p. 6 (Jan. 1934).

[4] Peter A. Thiessen and Werner Wittstadt. *Crystals and fused substances in stretched rubber*, Z. phys. Chem. **29B**, 359–362 (1935). English translation, Rubber Chem. Tech. **9**, 52–54 (1936).

[5] Wilfred E. Thibodeau and Archibald T. McPherson. *Photoelastic properties of soft, vulcanized rubber*, J. Research NBS **13**, 887–896 (1934) RP751.

[6] H. F. Schippel, *Volume increase of compounded rubber under strain*, J. Ind. Eng. Chem. **12**, 33–37 (1920).

[7] W. W. Vogt and R. D. Evans, *Poisson's ratio and related properties for compounded rubber*, Ind. Eng. Chem. **15**, 1015–1018 (1923).

[8] A summary of the early work is given by Whitby in Plantation Rubber and the Testing of Rubber, p. 486–501 (Longmans, Green and Co., London, 1920).

3 parts per 100 above the average elongation, which is the figure reported in the present work.

The mold used for making the rings consisted of a heavy metal plate containing cylindrical cavities. In each cavity a removable disk, 1 mm smaller in radius than the cavity, was fitted in such a way as to leave an annular space in which the ring was molded. By taking out this central disk a sample which had been vulcanized in the cavity could be removed without damage. Details of the mold are shown in figure 1.

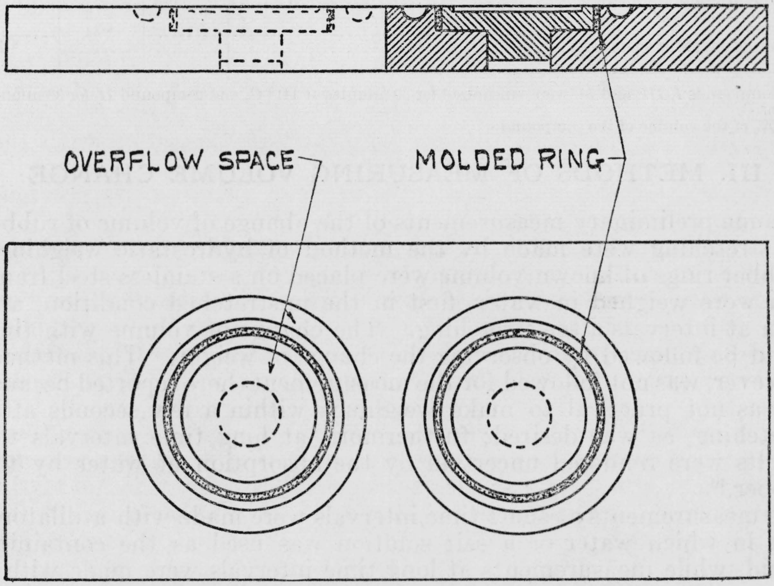

FIGURE 1.—*Mold for rubber test rings.*

The rings, after vulcanization, were carefully trimmed and inspected for flaws and inclusions before use. Those which were to be employed in the mercury-filled dilatometer were stored under mercury for some time to remove free sulphur and other constituents which might cause fouling.

Most of the work reported in this paper was done with two "pure gum" compounds which were vulcanized with mercaptobenzothiazole and tetramethylthiuram disulphide, respectively, as accelerators. These are compounds *I* and *II* in table 1. Compound *II* is identical with compound *B* which was used in photoelastic studies on rubber.[9] A few experiments were conducted with compounds *III* and *IV*, which contain 10 percent, by volume of whiting and carbon black, respectively.

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[9] See footnote 5.

TABLE 1.—*Composition of rubber compounds*

Ingredients	Compounds [a] (parts by weight)			
	I	*II*	*III*	*IV*
Smoked sheet rubber	100	----------	100	100
Pale crepe rubber	----------	100	----------	----------
Zinc oxide (Kadox)	1	1	5	5
Stearic acid	1	1	1	1
Mercaptobenzothiazole	1	----------	0.8	0.8
Tetramethylthiuram disulphide	----------	0.3	----------	----------
Sulphur	2	2	3	3
Whiting	----------	----------	[b] 34	----------
Carbon black (Micronex)	----------	----------	----------	[b] 22.5

[a] Compounds *I*, *III*, and *IV* were vulcanized for 30 minutes at 141° C, and compound *II*, for 30 minutes at 126° C.

[b] 10% of the volume of the compound.

III. METHODS OF MEASURING VOLUME CHANGE

Some preliminary measurements of the change of volume of rubber on stretching were made by the method of hydrostatic weighings. Rubber rings of known volume were placed on a stainless steel frame and were weighed in water, first in the unstretched condition, and then at intervals after stretching. The change of volume with time could be followed by observing the change of weight. This method, however, was not followed for the measurements here reported because it was not practical to make weighings within a few seconds after stretching, as was desired; furthermore, at long time intervals the results were rendered uncertain by the absorption of water by the rubber.[10]

The measurements at short time intervals were made with a dilatometer in which water or a salt solution was used as the containing liquid, while measurements at long time intervals were made with a mecury-filled dilatometer.

1. WATER-FILLED DILATOMETER FOR MEASUREMENTS AT THE SHORTER TIME INTERVALS

The apparatus which was used in measuring the change of volume at intervals from a few seconds to 20 or 30 minutes after stretching is illustrated in figure 2. It consisted essentially of a brass tube about ⅜ inch in diameter and 20 inches in length, connected by a side arm to a calibrated glass capillary tube. The brass tube was provided with stuffing boxes at each end, through which a 1-mm brass wire could be drawn back and forth. A ring-shaped sample could be stretched within the tube by means of a fixed hook attached at one end of the tube and a movable hook fastened to the brass wire.

In using the apparatus one or more rubber rings were mounted, unstretched, over the two hooks; the tube was then closed and filled with water or a salt solution to a convenient height on the glass capillary. The filling was facilitated by a second side tube which was provided with a stopcock. When the rubber rings were stretched by drawing the brass wire through the tube any change in the volume

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[10] When water is taken up by unstretched rubber the swelled rubber occupies almost, if not precisely, the same volume as the rubber and the water taken separately, but in the case of stretched rubber there appears to be an appreciable net loss of volume on swelling. The authors do not wish to report numerical data regarding this effect until further experiments have been conducted.

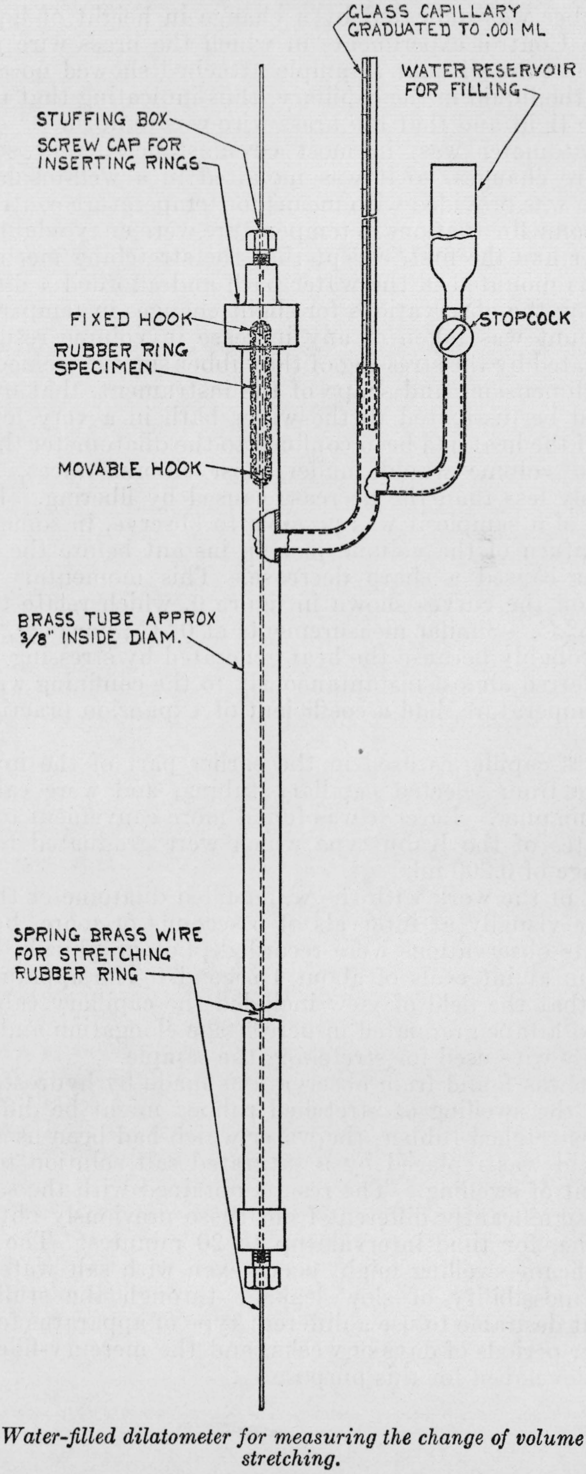

Figure 2.—*Water-filled dilatometer for measuring the change of volume of rubber on stretching.*

of the rubber was indicated by a change in height of liquid in the capillary. Control experiments in which the brass wire was drawn through the tube without a sample attached showed no appreciable motion of the liquid in the capillary, thus indicating that the stuffing boxes were tight and that the brass wire was uniform.

The dilatometer was, in most circumstances, very sensitive to temperature changes, so it was mounted in a well-insulated water bath which was provided with means for temperature control. Since, however, some fluctuations in temperature were unavoidable, a second dilatometer like the first, except that the stretching mechanism was absent, was mounted in the water bath and afforded a direct means of correcting the observations for slight changes in temperature.

No account was taken of any increase in volume resulting from heat generated by the stressing of the rubber since it seemed probable, from the dimensions and shape of the instrument, that most of this heat would be dissipated to the water bath in a very few seconds. But even if the heat had been confined to the dilatometer the resulting increase in volume would, under most circumstances, have been considerably less than the decrease caused by fibering. During the stretching of a sample it was possible to observe, in some instances, a slight upturn of the volume just an instant before the fibering of the rubber caused a sharp decrease. This momentary upturn is indicated on the curves shown in figure 6, which relate to observations at 25° C. Similar measurements at 0° C., however, showed no upturn, probably because the heat generated by stressing the sample was transferred almost instantaneously to the confining water which, at that temperature, had a coefficient of expansion practically equal to zero.

The glass capillaries used in the earlier part of the investigation were made from selected capillary tubing, and were calibrated in the usual manner. Later it was found more convenient to use capillary pipettes of the Kahn type which were graduated to 0.001 ml over a range of 0.200 ml.

In most of the work with the water-filled dilatometer the readings were made visually at intervals of 5 seconds or more, but in some experiments observations were recorded photographically on motion picture film at intervals of about 1 second. The apparatus was so arranged that the field of view included the capillary tubes, a stopwatch, and a tape graduated in percentage elongation and connected to the brass wire used for stretching the sample.

When it was found from observations made by hydrostatic weighings that the swelling of stretched rubber might be different from that of unstretched rubber, the water which had been used as a confining liquid was replaced by a saturated salt solution to minimize the amount of swelling. The results obtained with the salt solution were not significantly different from those previously obtained with water alone, for time intervals up to 20 minutes. The possibility that significant swelling might occur even with salt water, together with the possibility of slow leakage through the stuffing boxes, rendered it desirable to use a different type of apparatus for measurements over periods of days or weeks, and the mercury-filled dilatometer was developed for this purpose.

2. MERCURY-FILLED DILATOMETER FOR MEASUREMENTS AT THE LONGER TIME INTERVALS

The dilatometer in which mercury was used as a confining liquid is shown in figure 3. It consisted essentially of a heavy steel tube, closed at the ends by means of lapped steel disks, and connected through a steel capillary tube to a glass capillary. When the steel disks were lubricated lightly with stopcock grease and held securely in place by screw caps no leakage was observed under either vacuum or pressure. The steel capillary tube was provided with fins, as indicated in the figure, so that when the dilatometer was used at an elevated temperature the cemented glass-to-metal joint did not become hot enough to soften.

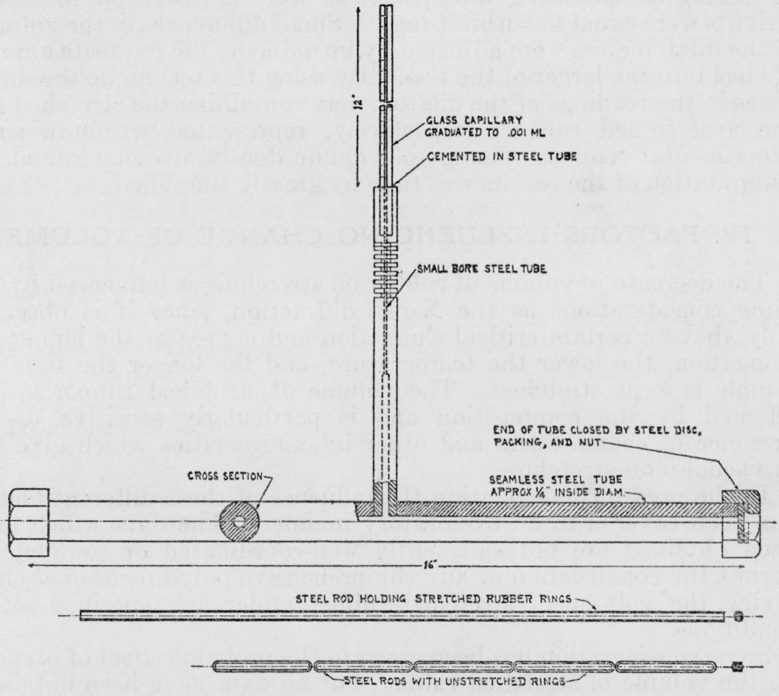

Figure 3.—*Mercury-filled dilatometer for measuring the change of volume of stretched rubber over long periods of time.*

Two methods were used for stretching the rubber rings. When the temperature at which the experiment was to be conducted differed appreciably from that of the room the rubber rings were slipped over hooks and placed, unstretched, in the steel tube. This was then brought to the desired temperature in an appropriate bath, after which it was removed quickly and wrapped in cloth to minimize temperature change. The rings were then stretched and the hooks fastened at the ends of the tube. When the temperature employed was that of the room the samples were stretched over a rod which was then slipped into the dilatometer tube.

The dilatometer tube, with the sample in place, was closed by means of the lapped steel disks, and was placed in a constant-temperature bath. The air was then evacuated through the capillary and the whole filled with mercury by means of a two-way stopcock to an appropriate height in the capillary. This operation, from the time the sample was stretched, required about 20 minutes, so the experiments with the mercury-filled dilatometer served to indicate only that part of the volume change which occurred after the 20 minutes. In order to obtain the total volume change, the portion which occurred during the first 20 minutes was obtained by means of the water-filled dilatometer described in a preceding section.

Tests were always made with duplicate mercury-filled dilatometers, one containing unstretched, and the other, stretched rubber. The rubber samples, which weighed about 1.2 g, were selected so as to have the same weight to within 1 mg, and the hooks or rods used for stretching or mounting the specimens were adjusted so that their weights were equal to within 1 mg.[11] Small differences in the volumes of the dilatometers were adjusted by introducing the requisite amount of steel into the larger of the two. By using this technique the differences in the readings of the dilatometers containing the stretched and the unstretched rubber, respectively, represented within a small experimental error the change of volume due to stretching, and the computation of the results was thereby greatly simplified.

IV. FACTORS INFLUENCING CHANGE OF VOLUME

The decrease in volume of rubber on stretching is influenced by the same considerations as the X-ray diffraction, since it is observed only above a certain critical elongation and is greater the higher the elongation, the lower the temperature, and the longer the time the sample is kept stretched. The volume of stretched rubber is also affected by the composition and is particularly sensitive to the presence of coarse fillers and other inhomogeneities which give rise to vacuoles on stretching.

In the present investigation the influence of these different factors has been covered in an exploratory manner. The data which have been obtained are not sufficiently well-coordinated or complete to permit the construction of any comprehensive polydimensional chart giving the volume of stretched rubber under any specified set of conditions.

Some consideration has been given to the probable effect of pressure on the volume of stretched rubber, but no data have been obtained.

1. COMPOSITION

As indicated previously, most of the work here described was done with two "pure-gum" compounds, but some measurements were made on compounds containing 10 percent, by volume, of whiting and of carbon black, respectively, which illustrate two contrasting types of behavior. When the samples containing whiting were stretched there was an increase in volume which was greater the higher the elongation. But when these samples were held in the stretched condition the volume decreased with time, indicating that two effects were operating in different directions. During the stretching the

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[11] This precise duplication was not necessary in the case of the two water-filled dilatometers because, with them, a very nearly constant temperature was maintained for each test, whereas in the present case the temperature was sometimes changed over a wide range in the course of a test.

rubber phase evidently pulled away from the filler particles and formed vacuoles of such magnitude as to cause a distinct increase in the volume of the sample as a whole, and to mask the decrease resulting from the fibering of the rubber phase. But when the sample was held in the stretched condition the fibering continued and caused a distinct decrease in the volume of the sample with time, as may be seen in figure 4. On releasing the sample the volume returned almost but not quite to the original volume, the slight increment, no doubt, resulting from the presence of small amounts of gas which prevented the complete collapse of the vacuoles.

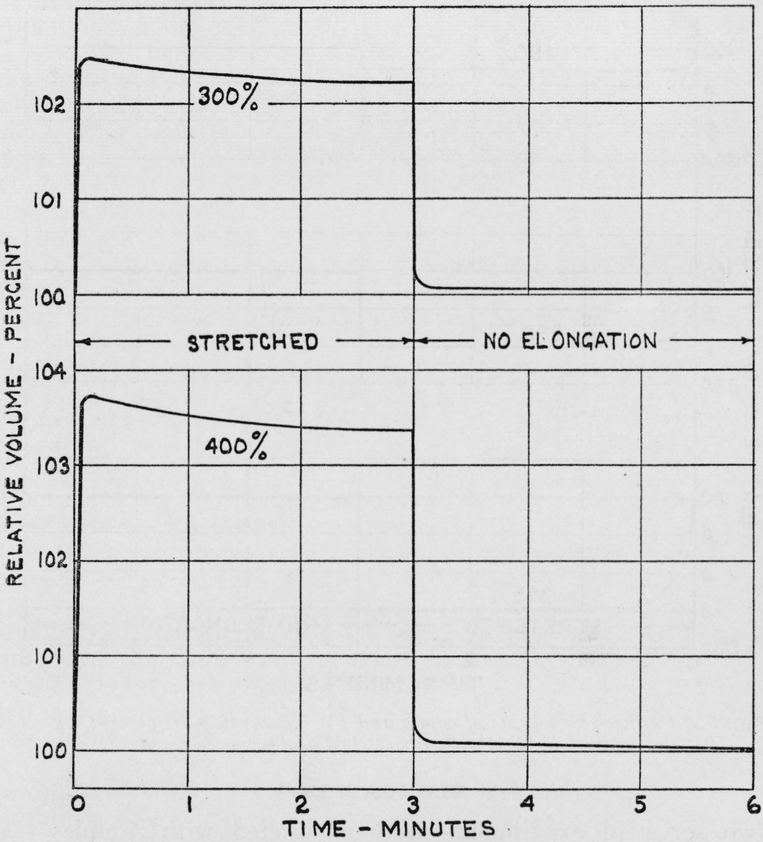

Figure 4.—*Changes in volume of compound III (containing 10 percent, by volume, of whiting) when stretched and when released.*

When the compound containing 10 percent of carbon black was stretched there was a decrease rather than an increase in volume, as is illustrated by the results shown in figure 5. This decrease became apparent at an elongation of 190 percent; this is somewhat lower than the elongation at which a decrease was observed with pure-gum rubber, a circumstance which is readily explained by the fact that the rubber phase in a compound containing filler is under greater actual elongation than that indicated by the stretch of the sample as a whole.

The fact that there was no increase in volume with the sample containing carbon black is an indication that the carbon black was present in such a state that no vacuoles were formed on stretching.

The relative behavior of the samples containing whiting and carbon black, respectively, suggests that the measurement of the change of volume on stretching may constitute a very simple and practical way of finding the nature and degree of dispersion of the filler in an unknown rubber compound.

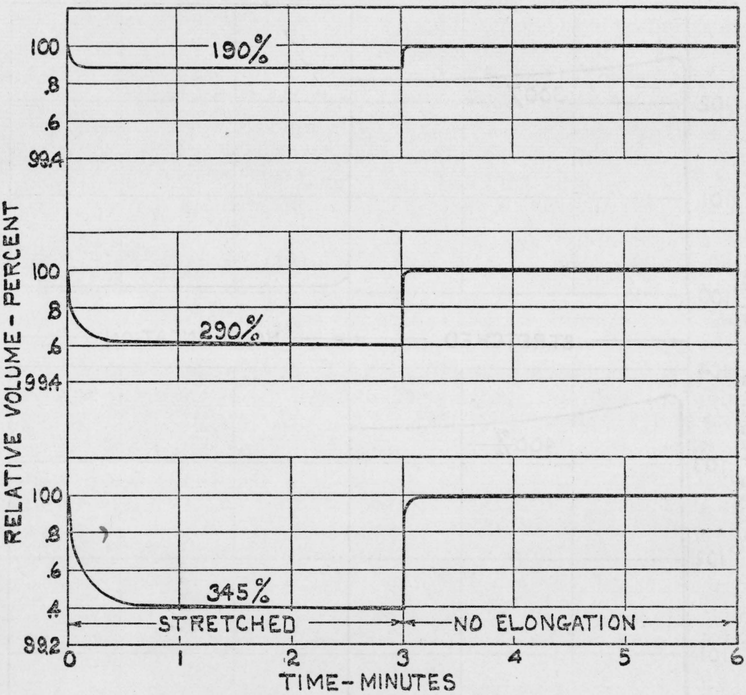

FIGURE 5.—*Changes in volume of compound IV (containing 10 percent, by volume, of carbon black) when stretched and when released.*

2. ELONGATION [12]

Two series of experiments were conducted with samples made from compound *II* to ascertain the effect of elongation on the change of volume during the first few minutes after stretching. In one series, the rubber was stretched to a given elongation and held at that elongation for 3 minutes, observations on the volume being made at frequent intervals. It was then released and observations again taken at intervals over a period of 3 minutes. The same procedure was repeated for successive different elongations.

In a second series of experiments the samples were stretched first to a relatively low elongation, 200 percent, and were held at this elongation for 3 minutes while observations were being made. Then, without release, the sample was stretched to successive higher elonga-

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[12] The term "elongation" is used throughout this paper to mean the amount of stretch. A sample stretched to twice its original length, for example, has an elongation of 100 percent.

tions, each for 3 minutes, until the maximum elongation had been reached. The process was then reversed by the same stepwise procedure.

The results of the first series of experiments are shown graphically in figure 6. At an elongation of 450 percent the volume decreased by about 0.1 percent in 3 minutes. At higher elongations the decrease became progressively greater and amounted to nearly 2 percent at an elongation of 725 percent. After the observations had been made at elongations up to 600 percent a second set of readings was made on the same sample at elongations of 550 and 600 percent, respectively. The results, which are indicated by large circles on the graph, are in practical agreement with the first set of observations. This, and other experiments of a similar character, indicated that the change of volume on stretching was not significantly affected by the previous stress history of the sample, provided that it had been allowed to retract completely from the previous stretching. This is in contrast to the stress-strain behavior which is markedly altered by the first few cycles of stressing.[13]

The results of the second series of experiments in which the samples were stretched by a stepwise procedure are shown in figure 7. The changes of volume at the different elongations were, in general, slightly greater than the changes which were observed when the samples were released between each two elongations.

When the sample was released in a stepwise manner the volume showed a decided lag, and at any elongation except zero it was less than the volume attained on stretching to the same elongation. At zero elongation, however, the original volume was resumed. It might be thought that the volume attained at any given elongation in the release cycle would represent the equilibrium or final value which would be attained if rubber were stretched initially to that elongation and held for a very long time. Experiments reported in a subsequent part of this paper, however, indicate that when rubber is held for a long time in the stretched condition the volume may reach lower values than those shown in figure 7, and still give no indication of having become constant.

After the sample which had been put through the stepwise cycle was released it was stretched directly to 600-percent elongation, at which it assumed a volume practically identical with that observed on stepwise stretching to the same elongation.

3. TIME

The change of volume of stretched rubber with time is of such basic significance that it has, of necessity, been considered simultaneously with each of the other factors studied. Some observations, however, were made over relatively long periods in order to determine the nature of the relation between volume and time, and to ascertain whether a constant state would be reached. In these experiments mercury-filled dilatometers were employed in conjunction with dilatometers filled with water, and the curves obtained with the two instruments were joined at a point 20 minutes after stretching, as was indicated in a previous section. The results of two experiments are

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[13] W. L. Holt, *Behavior of rubber under repeated stresses*, Ind. Eng. Chem. **23**, 1471–1475 (1931).

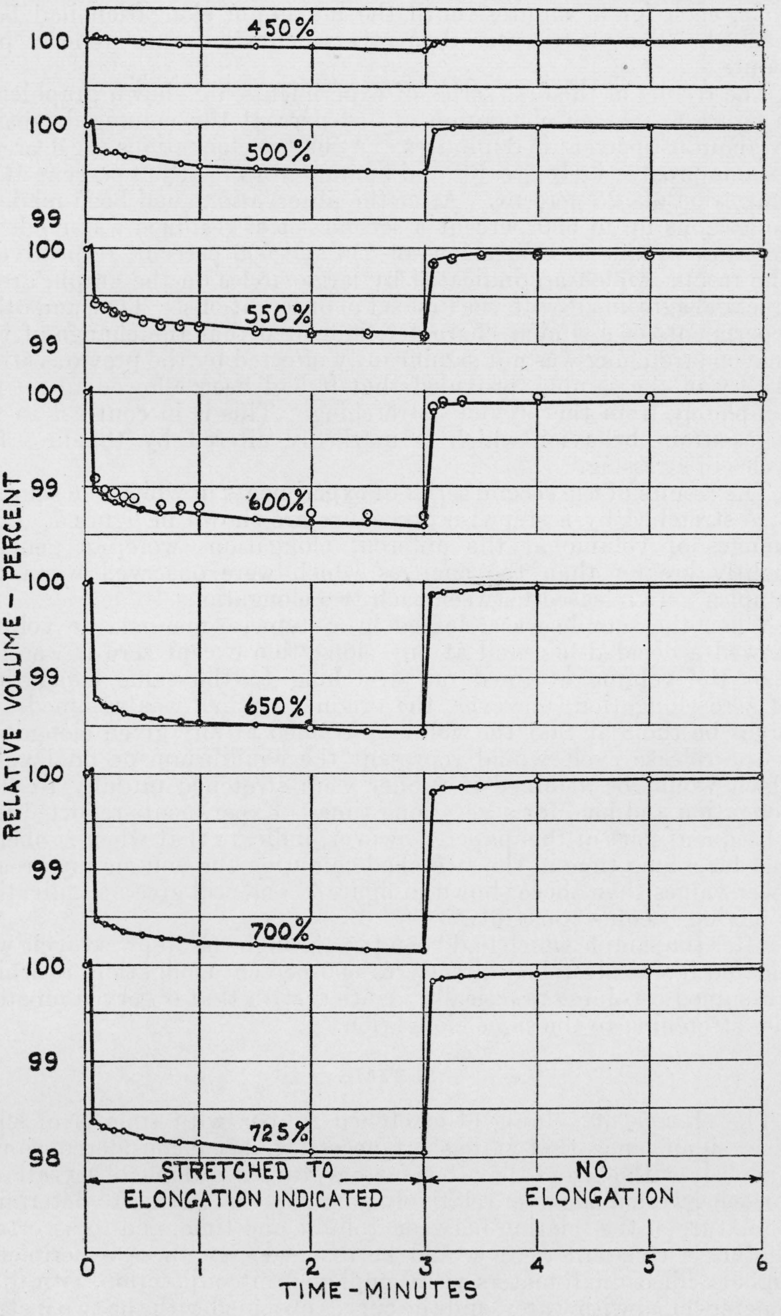

Figure 6.—*Change in volume of rubber on stretching to different elongations at 25° C.*

All tests were made on the same specimen which was stretched to the elongation indicated and held for 3 minutes, after which it was released and allowed to stand for 3 minutes before stretching to another elongation. The tests were made in the following order: —450-percent elongation, 500, 550, 600, 550 (second test), 600 (second test), 650, 700, and 725. The results of the second tests are indicated by the large circles.

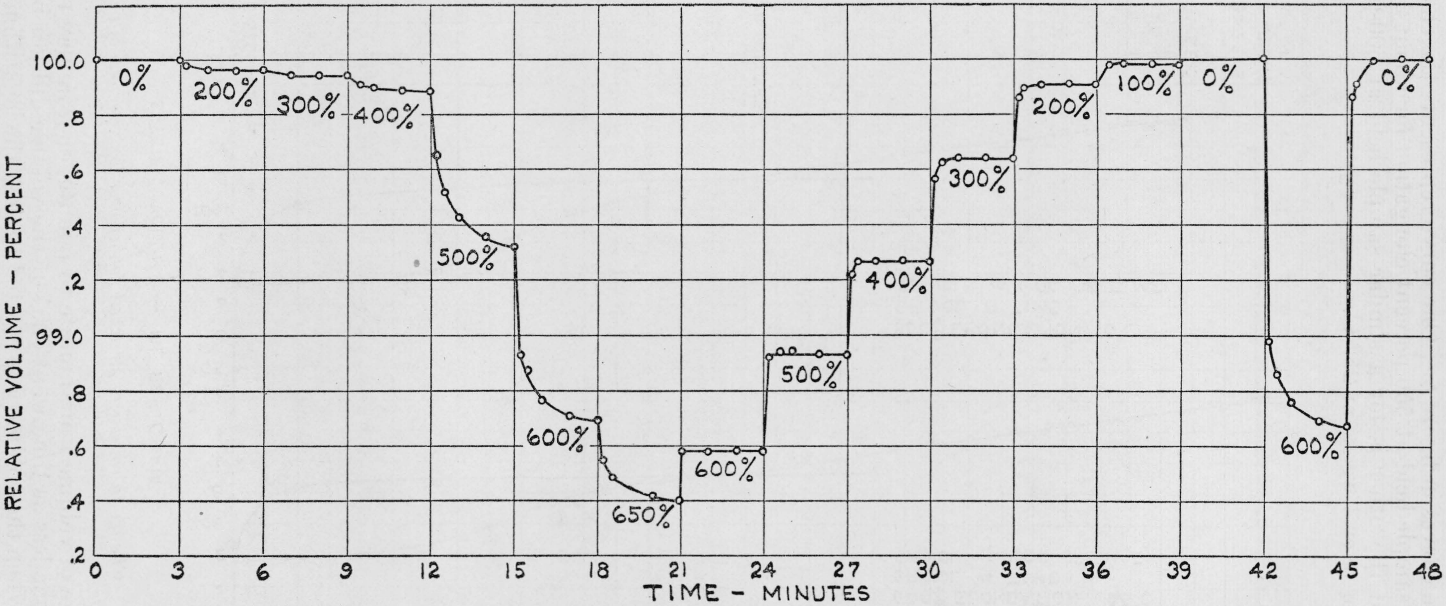

FIGURE 7.—*Change in volume of rubber when stretched and when released in a stepwise manner*

All tests were made on the same sample which was successively stretched (or released) and held at each of the elongations indicated for 3 minutes.

shown by the curves in figure 8. One curve represents the change of volume of a sample held at 550 percent elongation for about 2 weeks at 0° C., and the other is for a similar sample held at 600-percent elongation for over 3 weeks at 25° C.

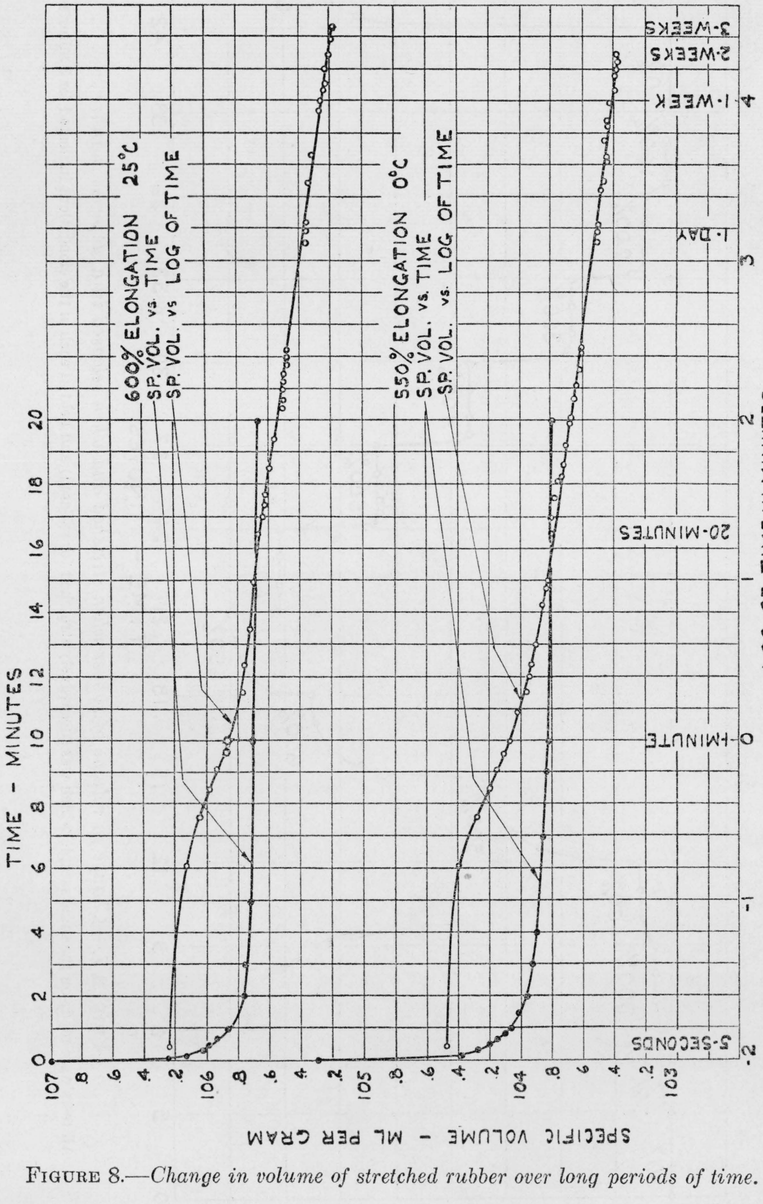

FIGURE 8.—*Change in volume of stretched rubber over long periods of time.*

The change of volume from minute to minute, or from day to day, rapidly became less as time went on, but the volume did not become constant. When the volume was plotted against the logarithm of the time the curves so obtained were approximately linear after the first few minutes, indicating that the change in the rubber was proceeding at a constant rate with respect to the *logarithm of the time*. There was no indication that any limiting volume was being approached. It appears that observations over a considerably longer period of time will be required to give any definite indication of the final or equilibrium volume of stretched rubber. The inflection of the logarithmic curve at one minute is, of course, a natural characteristic of the curve and does not indicate any discontinuity in the behavior of the rubber at that point.

4. TEMPERATURE

The effect of temperature on the change of volume was investigated at two intervals of time after stretching—one minute and several days. The former measurements were made by stretching samples of rubber in a water-filled dilatometer at different temperatures and noting the volume change at the end of one minute. In the latter measurements a mercury-filled dilatometer containing a given sample was subjected to a series of temperatures, and the change of volume with temperature noted.

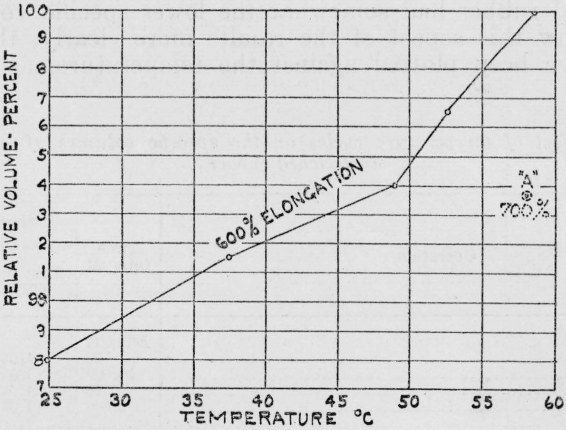

FIGURE 9.—*Change in volume of rubber when stretched to 600-percent elongation and held for 3 minutes at different temperatures.*

The same sample of compound *I* was used in all tests. After stretching to 600 percent at 58° C it was released and stretched to 700 percent with the result indicated by point *A*.

The results of the first series of experiments indicate that for a given elongation the change of volume becomes less the higher the temperature, a point ultimately being reached at which there is no change of volume on stretching. Typical results are shown in figure 9. At an elongation of 600 percent the change of volume ranges from 1.2 percent at 25° C to zero at 58° C. But when the same sample was stretched to 700 percent at 58° C there was a decrease in volume amounting to about 0.6 percent. The curve shown in figure 9 is simply a broken line connecting the observed points. The present data do not warrant any assumption as to the precise nature of the function.

In the second series of experiments a sample was stretched to 600-percent elongation at 25° C in a dilatometer with mercury as the confining liquid. A similar sample was mounted in another mercury-filled dilatometer of the same content as the first. After several days when the decrease in the volume of the stretched rubber from day to day had become very small the two dilatometers were carried through cycles of temperature between 25 and 0, −20, and 70° C, respectively. Duplicate samples of rubber were then taken and further observations were made, this time at temperatures of 25, 0, 100, and 25° C, respectively. The results computed in terms of specific volume are summarized in table 2, and are shown graphically in figure 10.

The specific volume of the stretched rubber was, at all temperatures, less than that of the unstretched rubber. It was anticipated that at 70° C the two samples would have the same specific volume, since the rubber underwent no change in volume when stretched to 600-percent elongation at temperatures above about 58° C. However, such was found not to be the case, and even at 100° C the stretched rubber had somewhat the lower specific volume. In order to show this aspect of the results more clearly, the specific volumes have been plotted against the temperature, as shown in figure 11.

TABLE 2.—*Effect of temperature cycles on the specific volumes of stretched and unstretched rubber*

Operation	Time interval	Specific volume	
		Stretched 600%	Unstretched
	Minutes		
Stretched at 25° C	20	1.0567	1.0700
Held at 25° C	30,000	1.0519	1.0700
Transferred to 0° C	20	1.0329	1.0530
Held at 0° C	2,800	1.0314	1.0530
Transferred to 25° C	----------	----------	----------
Held at 25° C	1,200	1.0519	1.0700
Transferred to −20° C	20	1.0179	1.0405
Held at −20° C	1,700	1.0158	1.0405
Transferred to 25° C	70	1.0519	1.0700
Transferred to 70° C	6	1.0949	1.1035
Transferred to 25° C	20	1.0536	1.0700
Held at 25° C	6,000	1.0526	1.0700
Transferred to 70° C after 8 cycles at 25 to 70° C	40	1.0935	1.1035
Transferred to 25° C	10	1.0542	1.0700
Held at 25° C	10,000	1.0521	1.0700

The curves for the stretched and the unstretched rubber, respectively, constitute two straight lines of different slopes which approach each other but lack somewhat of meeting at 100° C. The points indicating the specific volume of the stretched rubber at the different temperatures scatter somewhat because of changes with time and with the thermal history of the sample. The lower point at 25° C, for example, represents the volume after 30,000 minutes (about 3 weeks) at that temperature; the upper point represents the volume after a number of cycles, the last of which was from 70 to 25° C. The slopes of the curves indicate that the volume expansivity of the unstretched rubber is 0.00067, while that of the stretched rubber is approximately

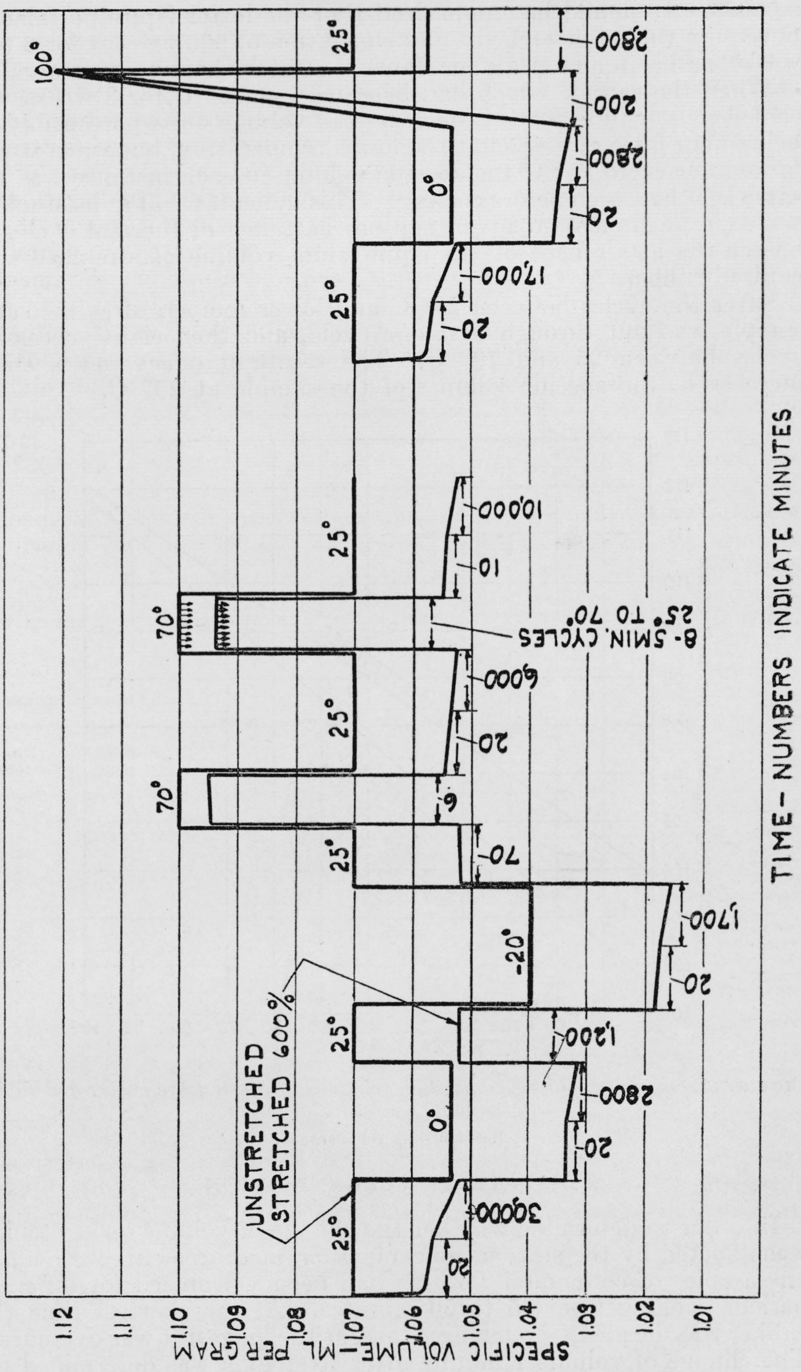

FIGURE 10.—*Specific volume-temperature-time relations for unstretched rubber and rubber stretched to 600-percent elongation.*

The two series of tests shown were conducted with two different samples of compound *I*.

0.00083. It should be emphasized that the latter figure pertains to pure-gum rubber stretched to an elongation of 600 percent for 2 to 4 weeks, and is in no sense a constant for stretched rubber in general.

When the sample which had been held at 25° C for 3 weeks was cooled to 0 or to −20° C it decreased in volume quite perceptibly on being kept for a day or so at the lower temperature, but when it was brought back to 25° C the specific volume in each instance was the same as it had been before cooling. This indicates that at least under some circumstances no advantage can be taken of thermal cycles to hasten the attainment of the equilibrium volume of stretched vulcanized rubber.

After the cycles between 25° C and lower temperatures the same sample was put through first one cycle, and then eight successive cycles between 25 and 70° C. The resultant effect was a small increase in the specific volume of the sample at 25° C.

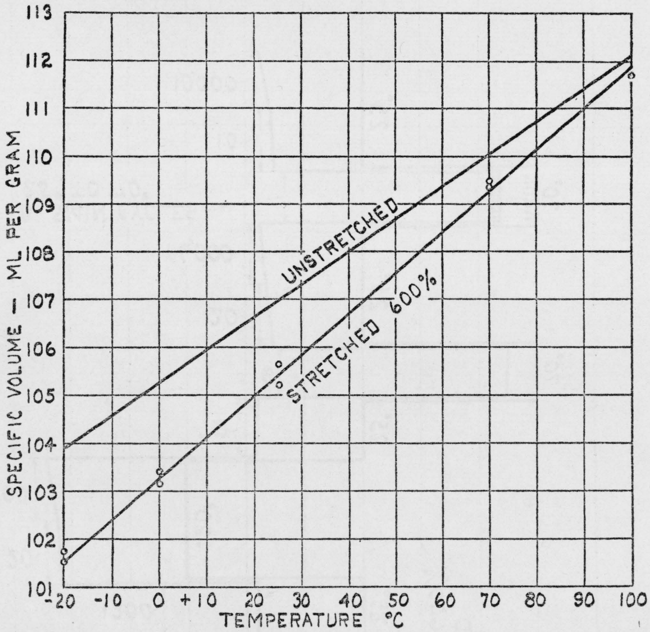

Figure 11.—*Specific volume-temperature relations for unstretched rubber and rubber stretched to 600-percent elongation.*

Based on data from figure 10.

5. STATE OF VULCANIZATION

In order to determine whether the change of volume on stretching was affected by the state of vulcanization, measurements were made on samples of compound *I* which had been vulcanized for different periods ranging from 15 to 60 minutes. At the shortest time the rubber was decidedly undercured, and at the longest it was overcured. The change of volume 1 minute after stretching was determined for each sample at a series of elongations, with results which are shown in figure 12. For any given sample the volume, above a certain critical elongation, was found to decrease in an approximately linear manner with increasing elongation. The curves for the different samples lie rather close together, and are roughly parallel, except that the curve for the sample having the 15-minute cure crosses some of the others. In general an increase in the time of vulcanization results in a decrease in the volume change at a given elongation. Also an increase in the time of vulcanization results in an increase in the elongation at which the change of volume first becomes apparent. The relative effect of the degree of vulcanization is likely to be much greater at low elongations than at high.

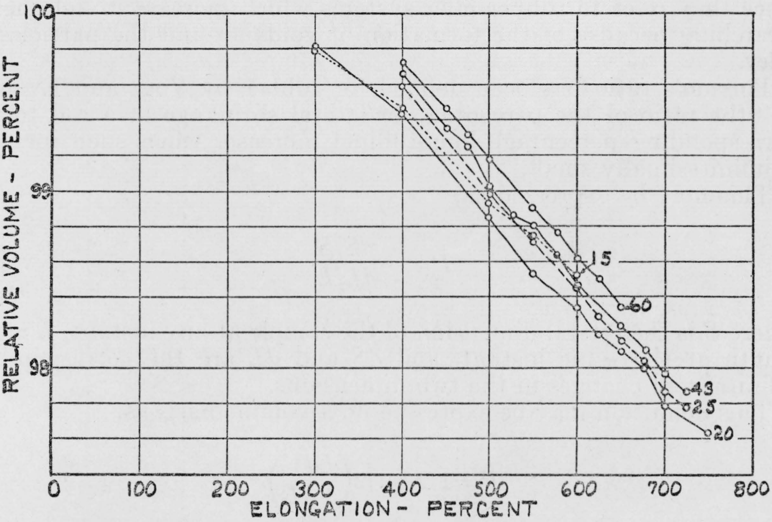

FIGURE 12.—*Effect of time of vulcanization on the change in volume of rubber when stretched to different elongations.*

Samples of compound *I* were vulcanized at 141° C for periods of from 15 to 60 minutes, as indicated on the curves. The change in volume was measured one minute after stretching.

6. OTHER FACTORS

The results which were obtained in the course of this work did not show as high an order of precision as the methods and apparatus were capable of giving. Variations were encountered between different lots of samples which were prepared at intervals over a period of 2 years. For instance, when different samples of compound *I* were stretched to 600-percent elongation at 25° C the decreases in volume observed ranged from 1.1 to 1.5 percent, with most of the values in the neighborhood of 1.2 percent. This variation is probably due, in part at least, to bloom and inhomogeneities in the rubber which would tend to cause an increase in volume on stretching. Some very erratic results which were obtained in the case of a compound vulcanized with 3 percent of tetramethylthiuram disulphide were traced by microscopic examination to particles of the accelerator which had crystallized out from the rubber. Inasmuch as the present investigation was exploratory in character, no critical study was made of the variations between different samples or different lots of rubber compound.

V. POISSON'S RATIO

Poisson's ratio for homogeneous rubber is precisely 0.5 at low elongations where there is no change of volume on stretching, and is greater than 0.5 at high elongations where the volume decreases on stretching. Inasmuch as this change in volume is dependent on the composition, the elongation, the temperature, and the time the sample is kept stretched, all of these factors must be specified in order to give significance to any numerical value for the ratio. Most of the values for Poisson's ratio which are given in the literature are less than 0.5 since they refer to rubber-filler systems which increase in volume on stretching because of the formation of voids around the particles of filler.

Poisson's ratio has been defined for rubber by Vogt and Evans [14] as "the ratio of the percentage of lateral shrinkage of a rod to the corresponding percentage longitudinal increase, when such increase is infinitesimally small."

This may be expressed as,

$$P=-\frac{dS/S}{dL/L}, \tag{1}$$

where S is the lateral dimension of the sample at any instant, L is the length at the same instant, and dS and dL are the corresponding infinitesimal changes in the two dimensions.

This definition may be expressed on a volume basis as,

$$P=1/2-1/2\left(\frac{LdV}{VdL}\right), \tag{2}$$

where the initial volume is taken as unity and V is the volume at any instant.[15]

For purposes of illustration, Poisson's ratio has been computed from data shown in figure 6. The relative volumes 3 minutes after stretching have been taken from the different curves shown in this figure and have been plotted against the elongation to give the curve shown in figure 13. The slope of this curve is dV/dL. The numerical values of the slope have been found at several points, as indicated on the graph, and have been used for the computation of the values of

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[14] W. W. Vogt and R. D. Evans, *Poisson's ratio and related properties for compounded rubber*, Ind. Eng. Chem. **15**, 1015–1018 (1923).

[15] Equation 2 can be obtained from equation 1 as follows:

$$V=KLS^2, \text{ where } K \text{ is a constant.} \tag{3}$$

Differentiating,

$$dV=2KLSdS+KS^2dL. \tag{4}$$

Dividing equation 4 by equation 3

$$dV/V=2dS/S+dL/L \tag{5}$$

Or

$$\frac{dV/V}{dL/L}=\frac{2dS/S}{dL/L}+1. \tag{6}$$

Combining equations 6 and 1,

$$P=1/2-1/2\left(\frac{LdV}{VdL}\right).$$

Poisson's ratio which are given in table 3. The slope is 0 up to 300-percent elongation, making the ratio 0.500 for this range. Between 400- and 500-percent elongation the slope increases rapidly and at the latter elongation the ratio reaches its maximum value of 0.527; at higher elongations it decreases somewhat and drops to 0.515 at 700 percent.

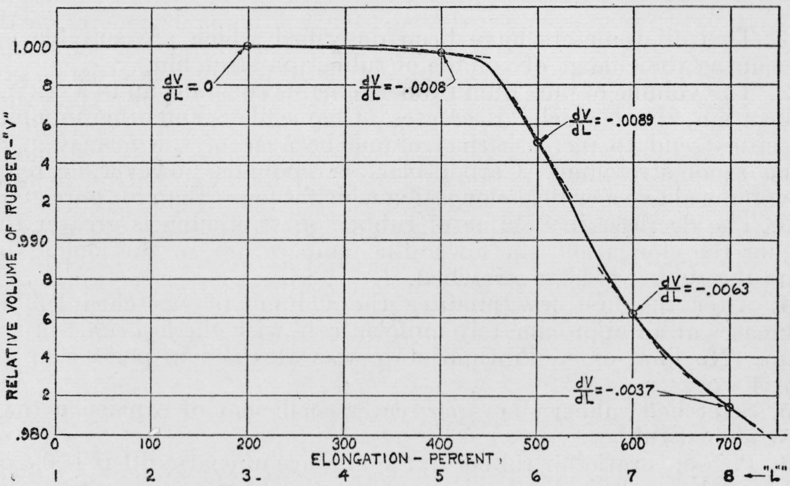

Figure 13.—*Elongation-volume relation for use in computing Poisson's ratio*

The data refer to samples of compound *II* stretched to the elongations indicated and held for 3 minutes at 25° C.

Table 3.—*Poisson's ratio for compound II stretched for 3 minutes at 25°* C

Elongation	Length, *L*	Volume, *V*	*dV/dL*	Poisson's ratio
Percent				
100	2	1.000	0.	0.500
200	3	1.000	0.	.500
300	4	1.000	0.	.500
400	5	0.9996	−.0008	.502
500	6	.995	−.0089	.527
600	7	.986	−.0063	.522
700	8	.9815	−.0037	.515

VI. INTERPRETATION OF RESULTS

Measurements of the volume changes associated with the stretching of rubber afford a simple, quantitative means of studying the fibering or crystallization which is the basis for the well-known contrast between the properties of unstretched and stretched rubber. The present investigation has been conducted from the standpoint of developing simple facts and relations and exploring the field. No attempt has, as yet, been made to coordinate the results of the volume measurements with theories of the molecular structure and the mechanism of stretching. One limitation of the present results from the standpoint of their utilization for purposes of basic theory is that none of the volume change measurements has been followed to any ultimate or equilibrium state. The change with time *on a logarithmic scale* proceeds at a rate which shows no significant diminution for the longest periods covered by the present work. There can, of course, be no full understanding of the process of fibering until the end product has been prepared and its properties measured.

VII. SUMMARY

1. Two dilatometers have been described which are suitable for measuring the change of volume of rubber on stretching.
2. The volume of pure gum rubber remains constant up to a critical elongation, above which it decreases. Coarse fillers and other inhomogeneities tend to increase the volume because of the formation of vacuoles on stretching. Carbon-black compounds, however, decrease in volume above a critical elongation which is lower than for pure gum.
3. The decrease in volume of rubber on stretching is greater the higher the elongation, the lower the temperature, or the longer the time the rubber is kept stretched.
4. After the first few minutes the volume of stretched rubber decreases at an approximately uniform rate with the *logarithm* of the time. No final or equilibrium state was attained in periods up to 3 or 4 weeks.
5. Stretched rubber shows a greater coefficient of expansion than unstretched rubber.
6. Poisson's ratio for rubber in the absence of coarse fillers is 0.5 or greater, the numerical value being a function of the composition, the elongation, the temperature, and the time after stretching.

WASHINGTON, August 26, 1936.