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MEASUREMENT OF DENSITIES OF SYNTHETIC RUBBERS*

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ABSTRACT

A method has been developed for preparing specimens of synthetic rubber in a form suitable for precise measurements of the density. The rubber is outgassed in a vacuum chamber, and while still under vacuum is molded into a sheet about $\frac{1}{16}$ in. (1.6 mm) thick. Specimens weighing between 1 and 2 g each are cut from this sheet and are employed for the measurement of the density by the method of hydrostatic weighings. The values obtained with different specimens from the same sample rarely differ from each other by more than 0.05 percent. Measurements are made soon after molding because some rubbers recover, and develop roughened surfaces and vacuoles which bring about a decrease in the apparent density.

Unvulcanized Buna S, prepared in a laboratory polymerization with a minimum quantity of materials other than butadiene and styrene, was found to have a density at 25° C of 0.9291 g/cm³. Corresponding values for butadiene-styrene copolymers produced on a commercial scale are as follows: Firestone Buna S, 0.9358; U. S. Rubber Co. Buna S, 0.9369; Standard Oil Co. (N.J.) Buna S, 0.9390; Chemigum IV, 0.9391; Hycar O.S.-20, 0.9385; and Hycar O.S.-30, 0.9303 g/cm³. The densities of other common varieties of synthetic rubber were found to be as follows: Neoprene CG, 1.2307; Neoprene E, 1.2384; Neoprene FR, 1.1406; Neoprene GN, 1.2290; Chemigum I, 1.0135; Hycar O.R., 0.9992; Perbutan, 0.9684; Thiokol RD, 1.0564; Thiokol A, 1.5983; Thiokol FA, 1.3298; and Butyl B-1.45, 0.9175 g/cm³.

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I. INTRODUCTION

For many purposes the density of a material need be known with an accuracy of only a few percent. For many materials the density of one sample may differ from that of another by this amount, and no useful purpose may be served by making more precise measurements on individual samples. In natural rubber, the densities of different samples have been shown, in a compilation¹ of 21 values, to lie, with two exceptions, between 0.905 and 0.919 g/cm³ at 25° C. The variations probably represent real differences in the samples and not accidental errors of observation. Since one can seldom know exactly the origin and subsequent treatment of a sample of natural rubber, there is little value in increasing the precision of measurement.

* L. A. Wood, *Values of the physical constants of rubber*, Proc. Rubber Tech. Conference London 1938, p. 933 (W. Heffer and Sons, Cambridge, England). Reprinted in Rubber Chem. Tech. 12, 130 (1939).

* Presented before the Rubber Division of the American Chemical Society in Buffalo, N. Y., on September 11, 1942, and published also in J. Ind. Eng. Chem. 34, 1291 (1942).

Synthetic rubbers, on the other hand, can be regarded as usually produced under conditions which are much better controlled and known. It is logical then to measure the density with greater precision and to hope to be able to ascribe significance to its variations from one sample to another. The present work is concerned with the development of a method for preparing specimens of synthetic rubber in a form suitable for precise measurements of the density, the actual measurement by the method of hydrostatic weighings, and a presentation of the results for most of the varieties of synthetic rubber now of commercial importance in the United States.

II. PREPARATION OF SPECIMENS

Samples of synthetic rubbers, as received from the manufacturer, were never found to be in a form suitable for precise measurements of the density. Even where there appeared to be no entrapped air and the surfaces seemed to be relatively smooth, molding produced specimens yielding higher and much more consistent values. Since a number of precautions are necessary in order to obtain good specimens, the method of preparation of specimens will be described in considerable detail. The ease of preparation of specimens was considerably affected by their rheological properties, and there was a wide difference between the different types of synthetic rubber in this respect. In many cases not all the precautions described were necessary.

The surface of the material was first examined for the presence of talc or other powders that might have been dusted on it. Vigorous scrubbing with a brush under running water usually removed the powders. This was followed by drying in a vacuum desiccator.

About 7 cm³ of the material was then sheeted out by several passes between warm mill rolls. The sheet, usually between 0.010 and 0.015 in. thick, was folded over itself several times and placed in a mold consisting merely of a sheet of metal with a single rectangular opening. The specimen and mold were sandwiched between aluminum sheets and placed in the vacuum chamber, a diagram of which is shown in figure 1. The chamber was made of steel, and included a movable piston of the same material, with about 3.5 mm clearance between chamber and piston. The piston was sealed by a toroidal rubber gasket, which did not slide on the piston or sidewalls, but rolled as the piston moved up or down. The gasket was about 100 mm in diameter and about 4 mm in diameter of section. Four springs at the corners of the plate at the top of the chamber exerted an upward force on the piston. They were so chosen that, when the chamber was evacuated, atmospheric pressure on the piston moved it downward about half its full stroke, compressing the springs. The chamber was then placed between the platens of the vulcanizing press and the platens were moved together sufficiently to make contact with the top of the vacuum chamber, and to compress the springs a little more, but not sufficiently to move the piston far enough to cause appreciable flow of the material. In this manner the material was heated for 1 or 2 hours at about 130° C under vacuum. Next the platens of the hydraulic press were brought somewhat closer together to cause some flow of the material. After several stages of increases of hydraulic pressure, the full force of 50 tons

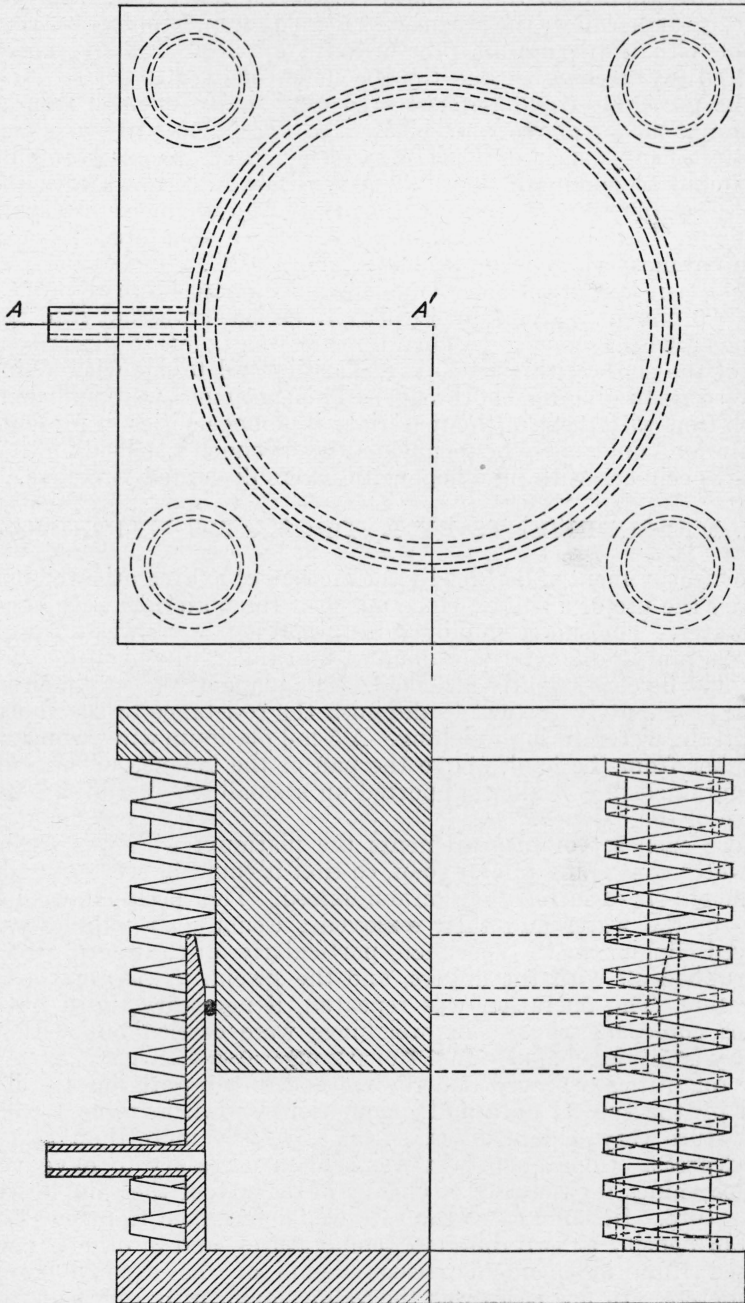


FIGURE 1.—*Vacuum chamber.*

Section *AA'* is shown at the lower left. The cross section of the rubber gasket is shown in black. The plates at the top and bottom of the chamber are 180 mm square. The diameter of the piston is 125 mm.

was finally applied to the vacuum chamber. After 1 or 2 hours to allow for further flow, the steam was turned off and the press allowed to cool with the hydraulic pressure still applied. Finally, air was admitted to the chamber and the specimen removed.

Some materials could be separated only with difficulty from the aluminum sheets above and below the specimen. In some cases mold lubricants, such as Carbowax, when used in small amounts, were found to eliminate this difficulty. Carbowax is water-soluble, and was readily removed from the surface of the specimens by washing. Chemigum I and some other materials were separated from the aluminum most easily when cooled to about 0° C.

The dimensions of the sheets made in this manner were about 60 by 60 by 1.6 mm (2.4 by 2.4 by $\frac{1}{16}$ in). Each sheet was cut into three specimens with scissors. In cutting, care was taken to discard portions of the sheet with surface irregularities and to cut with a single stroke so as to give a smooth edge. The specimens were sufficiently thin so that with most of the materials, inhomogeneities, if present in the interior, could easily be seen when the specimen was held up to the light. Specimens with inhomogeneities were discarded of course.

III. MEASUREMENTS BY HYDROSTATIC WEIGHINGS

The measurement of density by the method of hydrostatic weighings required the use of a sinker, since many of the materials were lighter than water. The sinker employed in the present work was a tin disk about 20 mm in diameter and about 4 mm thick, to which the specimen could be conveniently attached. The plane of the specimen was kept approximately vertical to diminish the resistance to the motion through the water during weighing. A 5-mil platinum wire suspended the sinker from the hook above the pan of the balance. The water was contained in a beaker supported on a small wooden bridge over the pan of the balance.

Before each set of measurements the platinum wire was washed with water containing talc or soap, so that it could be wetted readily and the effects of surface tension minimized. The specimen was next placed in the water and then removed. Usually air bubbles were observed clinging to the specimen, particularly on the edges. These were rubbed off with the fingers, and the specimen was replaced in the water. The operation was repeated, if necessary, until no air bubbles could be seen. The weighings were carried out with an ordinary analytical balance to 0.1 or 0.2 mg.

The quantities observed and the method of computation are illustrated by the typical data and calculations shown in table 1. The temperature very seldom differed from 25° C by more than two or three degrees. Consequently it was seldom necessary to have very accurate values for the rate of change of density of the sample with temperature. In some cases the rate was determined from measurements of density at two different temperatures, and in others it was obtained from independent measurements of the expansivity by dilatometers. In few cases was the value significantly different from $620 \times 10^{-6} \text{ g cm}^{-3} \text{ deg}^{-1}$, the value reported² for natural rubber.

²H. L. Curtis, A. T. McPherson, and A. H. Scott, *Density and electrical properties of the system, rubber-sulphur*, BS Sci. Pap. 22, 383 (1927) S560. Cf. L. A. Wood, *Values of the physical constants of rubber*, Prog. Rubber Tech. Conference London 1938, p. 933. (W. Heffer & Sons, Cambridge, England.) Reprinted in Rubber Chem. Tech. 12, 130 (1939).

TABLE 1.—Typical data and calculations

Quantity	Buna S	Neoprene GN
A. Weight of specimen.....	g.....	2.0577
B. Weight of sinker in water.....	g.....	11.1370
C. Weight of specimen and sinker in water.....	g.....	11.0497
D. Weight of specimen in water.....	g.....	— .0858
E. Loss of weight in water.....	g.....	1.2431
F. Specific gravity.....	g/cm ³	0.9310
G. Temperature.....	°C.....	26.6
H. Density of water at temperature G.....	g/cm ³	0.9966
I. Density of sample at temperature G.....	g/cm ³9279
J. Density of sample at 25° C.....	g/cm ³9289

A, B, C, and G were measured directly.
H was obtained from tables.
D=C-B.
E=A-D.
F=A/E.

I=JH.
J=I/[1+α(G-25)].
α=rate of change of density of the sample with temperature.

IV. RESULTS

The results of measurements of the densities of 18 different varieties of synthetic rubber are given in table 2. With the exception of the sample of Buna S described in the first footnote, they were all of commercial origin, and are considered to be typical of present-day

TABLE 2.—Values of density at 25° C

Type I. Chloroprene polymers and related polymers.

Type II. Butadiene copolymers.

A. Copolymers with styrene (Buna S type).

B. Other butadiene copolymers, chiefly copolymers with acrylonitrile.

Type III. Organic polysulfides.

Type IV. Isobutene copolymers.

Type	Name	Manufacturer	Density
I.....	Neoprene CG.....	E. I. du Pont de Nemours & Co.....	g/cm ³ 1.2307
I.....	Neoprene E.....	do.....	1.2384
I.....	Neoprene FR.....	do.....	1.1406
I.....	Neoprene GN.....	do.....	1.2290
IIA.....	Buna S ¹	Firestone Tire & Rubber Co.....	0.9291
IIA.....	Buna S ²	do.....	.9358
IIA.....	Buna S.....	U. S. Rubber Co. (Naugatuck Chemical Div.).....	.9369
IIA.....	Buna S.....	Standard Oil Co. (N. J.).....	.9390
IIA.....	Chemigum IV.....	Goodyear Tire & Rubber Co.....	.9391
IIA.....	Hycar O. S.-20 ³	B. F. Goodrich Co (Hycar Chemical Co.).....	.9385
IIA.....	Hycar O. S.-30 ⁴	do.....	.9303
IIA.....	Chemigum I.....	Goodyear Tire & Rubber Co.....	1.0135
IIA.....	Hycar O. R.....	B. F. Goodrich Co. (Hycar Chemical Co.).....	0.9992
IIA.....	Perbunan.....	Standard Oil Co. (N. J.).....	.9684
IIA.....	Thiokol RD.....	Thiokol Corporation.....	1.0564
III.....	Thiokol A.....	do.....	1.5983
III.....	Thiokol FA.....	do.....	1.3298
IV.....	Butyl B-1.45.....	Standard Oil Co. (N. J.).....	0.9175

¹ Prepared in a laboratory polymerization with a minimum quantity of materials other than butadiene and styrene. Analysis of this sample is said to give:

Ash.....	% 0.09
Free fatty acid.....	.51
Phenyl-beta-naphthylamine.....	.50
Acetone extract.....	4.01

Information contained in a private communication from J. N. Street.

² Contains about 4.5 percent of free fatty acid and 2 percent of phenyl-beta-naphthylamine. Ash content about 0.4 percent. Information contained in a private communication from J. N. Street.

³ "A special type of butadiene-styrene copolymer made by the process developed by the B. F. Goodrich Co. It is made from butadiene and styrene in the same ratio as is used in the manufacture of Hycar O. S.-30. It is stabilized with 2 percent of Stalite antioxidant." Information contained in a private communication from W. L. Semon.

⁴ "A butadiene-styrene copolymer of the type which will be made in the Government-financed plants. It contains not only the rubber hydrocarbon but approximately 4.5 percent of fatty acid. It is stabilized with 2 percent of Stalite anti-oxidant." Information contained in a private communication from W. L. Semon.

commercial production in the United States. Most of them were received during the spring and summer of 1942. The values shown are, in most cases, the means of the measurements on six different specimens, three cut from each of two moldings. Additional specimens were molded when any of the individual results differed from the mean by more than about 0.05 percent. In a few cases only four specimens were used, and in other instances more than six were made.

Unpublished observations made in this laboratory have shown that crystallization, with an accompanying increase of density, occurs at room temperature with Neoprene CG, Neoprene E, Neoprene GN, and Thiokol A. Consequently with these materials, care was taken to make the measurements of density as quickly as possible after the heating. All the measurements on Neoprene CG, which crystallizes most rapidly, were made within a half-hour after heating. Crystallization effects do not seem evident with any of the other varieties of synthetic rubber listed in table 2. However, it was found that a number of the synthetic rubbers showed elastic recovery effects which made it preferable to make the measurements soon after molding. This elastic "memory" led to the development of roughened surfaces and and sometimes to vacuoles, which brought about a decrease in the apparent density after a few days. The results under these conditions were always much less consistent than those obtained from observations made immediately after molding. The necessity for molding under vacuum did not seem to be as great for those materials in which the "memory" effects were small.

It should be noted that, although the values given represent the means of observations on a number of specimens, the specimens were made from only one sample of each variety. Consequently this work furnishes no information regarding the variation in density from different batches or runs of the same manufacturer. The method of measurement described here should be sufficiently precise to find application for this purpose, and might be used as a control method.

Grateful acknowledgment is made of the cooperation of the companies listed in table 2 in furnishing samples of synthetic rubber on which the observations were made. Especial thanks are due to J. N. Street for the preparation and analysis of the polymer described in the first footnote to table 2.

WASHINGTON, October 9, 1942.