

*Thermal Conductivity of Soft Vulcanized Natural Rubber, Selected Values**

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Abstract

The published literature on the thermal conductivity of natural rubber has been assembled and the results critically evaluated. Best values of thermal conductivity as a function of temperature have been selected, and are presented in both graphical and tabular form. An attempt was made to consult all work that could significantly affect the choice of best values. Published papers were located with the aid of *Chemical Abstracts*, *Physics Abstracts*, the *Thermophysical Properties Retrieval Guide* and some other general sources. In addition, relevant references in the papers themselves were followed up until a substantially "closed system" had been generated, as shown by the fact that no new references were being turned up.

1. Introduction

Natural rubber is a complex material. Raw rubber in itself is a complex substance; in the process of manufacture it becomes still more complex. It is nearly always vulcanized, and compounding ingredients of certain classes are nearly always added. These treatments greatly modify and improve its properties. Among the ingredients that are nearly always added to raw rubber are a vulcanizing agent, an accelerator, one or more activators, an antioxidant, and a softening or lubricating agent. A great many but not all common types of rubber contain, in addi-

tion, various fillers; the amount of filler may be small or large.

Raw rubber has a low thermal conductivity, somewhat lower than that of the commoner compounding ingredients; the additives all, or nearly all, increase the thermal conductivity, k . There are not enough published data on any one composition of rubber to permit us to present selected values for a single composition; we must be content to lump together the data for rubbers of a range of compositions, and even in many cases to accept data for rubbers whose composition is only partially specified. Hence we have found it necessary to ignore the effect on k of small amounts of compounding ingredients, known or unknown. Variation in the amount and kind of such ingredients then contributes to the scattering of the results of different observers. We believe that this contribution is smaller than the scattering attributable to other causes. (By small amounts, we mean not more than about 5 parts of any single additive per 100 parts of raw rubber, and usually not more than 1 or 2 parts.)

The selected values tabulated in this paper refer to soft vulcanized natural rubber containing relatively small amounts of additives.

* This paper is the third in a series of critical evaluations of thermal-conductivity data. The previous studies dealt with Pyrex glass and polystyrene, and were issued respectively as Reports TC-1 (November 1962) and TC-2 (April 1964) of the Pioneering Research Division, Quartermaster Research and Engineering Center, U. S. Army, Natick, Mass.

II. Characterization of Rubber

Raw natural rubber is principally obtained by coagulating the latex of the rubber plant, *Hevea brasiliensis*. Raw rubber consists of rubber hydrocarbon (about 93 per cent by weight) and other natural constituents (about 7 per cent). These other constituents include moisture, fatty acids, sterols, esters, proteins, and materials that remain as ash on burning [40]. Natural rubber hydrocarbon consists of long chains of *cis*-polyisoprene. The monomer unit, isoprene, has the formula $CH_2:CCH_3CH:CH_2$. Monomer and other products are formed when the natural polymer is heated in the absence of air; conversely, isoprene can under the proper conditions be polymerized to form chains of the same structure as those occurring in natural rubber.

The molecular weight of rubber hydrocarbon probably is not an important factor in determining the thermal conductivity. A typical weight-average molecular weight for fresh polymer is 300,000, corresponding to a degree of polymerization of 4400; however, wide variations in molecular weight occur. In the process of manufacture the molecular weight is reduced. The action of oxygen is one of the important causes. A large part of the reduction in molecular weight takes place while the rubber is being milled.

Vulcanization. Unvulcanized (raw, crude) rubber has few commercial uses. Vulcanized (cured) rubber is ordinarily made by mixing sulfur, an accelerator, and a metallic oxide with raw rubber, and heating [41]. Vulcanization produces cross links between polymer chains, greatly improving the mechanical properties of the rubber for most applications. Soft vulcanized rubber is highly extensible, and after being stretched returns very nearly to its original length. There is a considerable variation in the amount of sulfur used in vulcanization. A typical amount in soft rubber is 2.5 parts per 100 parts of raw rubber. Hard rubber is made by greatly increasing the amount of sulfur; a typical amount is 47 parts of combined sulfur per 100 parts of raw rubber (this is 32 per cent of the combined weight of rubber plus sulfur).

A Typical Soft Rubber. A typical composition for soft vulcanized natural rubber is formula 2A of the American Society for Testing Materials [42]. This formula contains, in parts by weight: raw rubber, 100; sulfur, 2.5; benzothiazyl disulfide, 1; zinc oxide, 5; stearic acid, 1; and phenyl beta naphthylamine, 1. These compounding ingredients or their equivalent are likely to be found in almost all rubber samples. Sulfur is the vulcanizing agent; benzothiazyl disulfide (MBTS) is the accelerator, which promotes vulcanization and reduces the amount of sulfur required; ZnO is an activator that also im-

proves the mechanical properties of the rubber (an activator contributes to the efficiency of the accelerator); stearic acid is an activator that also acts as a softener and lubricant; and phenyl beta naphthylamine is an antioxidant. The major function of each compounding ingredient is the one given above; most compounding ingredients have additional beneficial effects on the rubber.

Typical Fillers. Among the compounding ingredients that are used in rubber only when the application demands it is carbon black, which is very widely used. Other often-used fillers are TiO_2 , $CaCO_3$, SiO_2 , and certain clays [43]. All these, including carbon black, harden the rubber, and most improve its resistance to abrasion. Carbon black is especially good at imparting abrasion resistance; TiO_2 imparts an attractive white color to rubber. Sometimes the principal function of a filler is to reduce cost.

Density. The density of a sample of rubber is sensitive to the amount of filler present. From the results of Scott [44], the density of a sample containing 2.5 parts by weight of bound sulfur per 100 parts of pure rubber, but without any other compounding ingredients, is found to be 0.927 g cm^{-3} . Additional compounding ingredients, especially zinc oxide, increase the density. Rubber made by standard formula 2A may be expected to have a density of about 0.97. Gengrinovich and Fogel [20] found 0.974 for their stock No. 1, which differs only slightly from standard formula 2A.

The Glass Transition. The glass-transition temperature of a plastic or rubberlike material is the temperature above which it is relatively soft, and below which it is relatively hard and brittle. Many of the properties of the material undergo changes at the glass-transition temperature, or more precisely, in a narrow temperature region. The glass-transition temperature can be determined in various ways; perhaps the most common method is to measure the thermal expansion and locate the temperature at which the expansion coefficient undergoes a large change. For soft vulcanized rubber, the glass-transition temperature is slightly above 200°K . This temperature is sensitive to the degree of vulcanization; hard rubber containing 47 parts by weight of bound sulfur per 100 parts of raw rubber has its glass transition at about 363°K [45]. A moderate peak or break in the curve of thermal conductivity versus temperature is to be expected at the glass transition in any plastic or rubberlike material. Soft rubber exhibits such a peak. A few observers have reported a large and somewhat erratic jump in the thermal conductivity of rubber at its glass transition, but these results are probably in error.

Crystallization, Stretching, and Orientation. Raw rubber can be caused to crystallize without difficulty; the process is most rapid at about 247°K (-26°C).

Soft vulcanized rubber, if not stretched, has almost no tendency to crystallize, and may be assumed to be amorphous. But when it is stretched to 3 or 4 times its original length, a substantial fraction of it crystallizes within a time as short as 1 second, and when it returns to its unstretched state, the crystallites disappear with comparable rapidity.

The presence of crystallites in stretched rubber should increase its thermal conductivity, since crystals are in general much better heat conductors than amorphous materials are. In addition, the stretching tends to orient the long axes of the polymer molecules in the direction of stretch. There is evidence that heat flows more readily in the direction of orientation of polymer molecules than at right angles to it. However, the experiments on rubber [21], [27] are less conclusive than the results on other polymers [33], [46]. Rubber was investigated above its glass transition; the other polymers were investigated below theirs; perhaps this has something to do with the problem. The selected values in the present paper refer to unstretched, uncrystallized rubber.

III. Effect of Compounding Ingredients

The effect of various compounding ingredients on the thermal conductivity of rubber was studied by Williams [31] and by Barnett [15]. The results were presented by assigning one value of k to pure rubber and another to each compounding ingredient. The value of k assigned to a compounding ingredient is not in general the true thermal conductivity of the ingredient in either solid or powder form, but simply an empirical constant appropriate to the particular calculation. The conductivity of a binary mixture of rubber and one other ingredient is then found by assuming that the conductivity (at a given temperature) is a linear function of the volume fractions of the two components, each multiplied by its assigned k -factor. The method may be extended if several additives are present. It must be used with caution, for the curves of k versus either volume fraction or weight fraction of additive usually are noticeably concave upward.

The effect on k of a few of the most important compounding ingredients will be briefly discussed. These are sulfur, zinc oxide, and carbon black. For convenience we will adopt the practice of the rubber industry and specify additives in parts by weight per hundred parts of raw rubber.

Sulfur. Sulfur has only a moderate effect on k ; some investigators have in fact found the same conductivity for raw rubber and for soft vulcanized rubber [15], [31]. However, we may compare soft and hard rubber; they differ primarily in the amount of combined sulfur present. Our selected value for soft

rubber at 25°C (298.15°K) is $0.000360 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ C}^{-1}$. The average of 9 published values for hard rubber, at or near room temperature, we found to be about 11 per cent higher. If we assume the soft rubber to contain 2.5 parts by weight of sulfur per 100 parts of raw rubber, and the hard rubber to contain 47 parts per 100 of rubber, the addition of 10 parts of sulfur to 100 parts of raw rubber will raise k by a little over 2 per cent.

Carbon Black and Zinc Oxide. Both carbon black and zinc oxide affect the thermal conductivity of rubber more than sulfur does. We have plotted and analyzed the published data for these two additives, and find that an addition of 10 parts by weight of carbon black per 100 parts of raw rubber may be expected to raise k by about 17 per cent, at room temperature and somewhat above. In the same temperature region, the same addition of ZnO may be expected to raise k by about 7 per cent. These values are presented as rough estimates only, and the curvature known to be present at high concentrations is simply ignored. However, within their limited accuracy, these values appear to be usable up to about 40 parts of carbon black per 100 parts of raw rubber. Kainradl [24] found large differences in the effects of different carbon blacks on k . The size and shape of the particles undoubtedly have some influence. There is evidence that graphite has a different effect from carbon black; it causes the curve of k versus composition to curve upward more steeply.

IV. Selection of the Values

As indicated earlier, the tables have been prepared to represent the thermal conductivity of soft, unstretched, vulcanized natural rubber with conventional amounts of compounding ingredients. Standard formula 2A of the ASTM, the composition of which was given in Section II of this report, is typical of the compositions for which the tables are intended. Before the tables are assumed to apply to any rubber suspected of having a substantially different composition, Sections II and III of this paper should be studied.

The selected values given in the tables are represented by the heavy master curve in Fig. 1. The available data were first plotted on a large-scale version of Fig. 1, and a tentative master curve was drawn. After study and revisions, the master curve shown in the figure was accepted. Table 1 was then prepared by reading values from the accepted master curve. These values were differenced, smoothed, and rechecked for consistency with the master curve before acceptance. Table 2 was derived from Table 1 and is consistent with it.

The selected values follow the general shape of the curve of results of Eiermann and Hellwege [1].

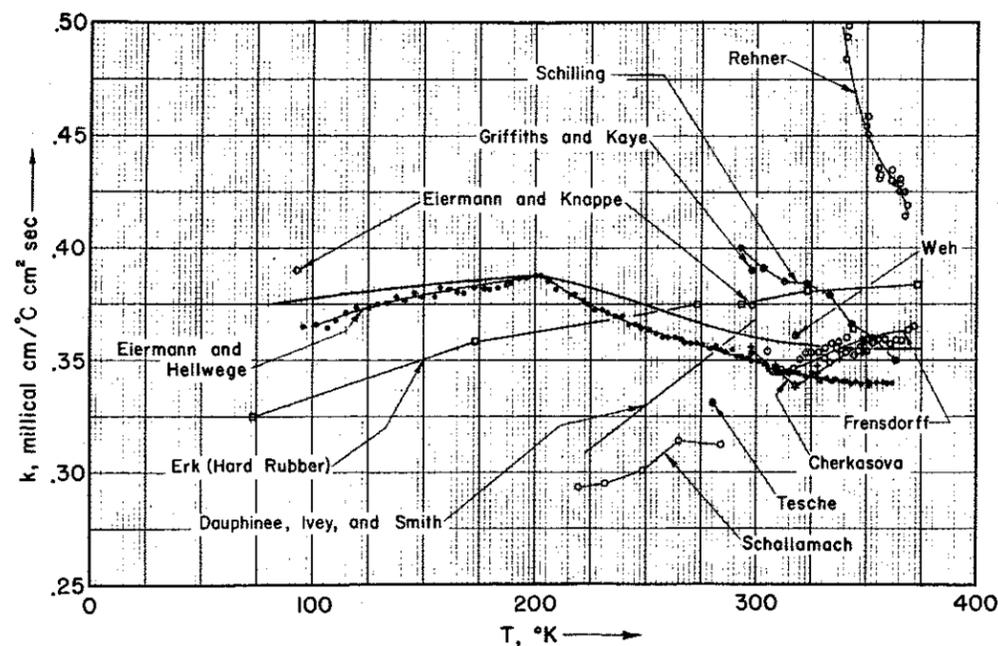


FIG. 1. THERMAL-CONDUCTIVITY DATA OF REF. [1] - [12]. ALL ARE FOR SOFT VULCANIZED NATURAL RUBBER EXCEPT THE DATA OF ERK, WHICH REFER TO HARD RUBBER. THE HEAVY LINE REPRESENTS THE SELECTED VALUES.

Thermal Conductivity of Soft Vulcanized Natural Rubber

TABLE 1		
T	k	Δ
$^{\circ}\text{K}$	$\frac{\text{cal cm}}{^{\circ}\text{K cm}^2 \text{ sec}}$	
80	0.000375	3
100	0.000378	2
120	0.000380	2
140	0.000382	2
160	0.000384	2
180	0.000386	2
200	0.000388	2
220	0.000383	-5
240	0.000378	-6
260	0.000372	-7
280	0.000365	-5
300	0.000360	-3
320	0.000357	-1
340	0.000356	-1
360	0.000355	0
380	0.000355	0

TABLE 2		
T	k	Δ
$^{\circ}\text{R}$	$\frac{\text{Btu in.}}{^{\circ}\text{R ft}^2 \text{ hr}}$	
150	1.09	1
200	1.10	1
250	1.11	1
300	1.12	1
350	1.13	-2
400	1.11	-2
450	1.09	-3
500	1.06	-2
550	1.04	-1
600	1.03	0
650	1.03	0
700	1.03	0

These authors made measurements by a quasistationary method [47], after establishing the validity of the method in separate experiments. The selected values in the neighborhood of the glass-transition temperature (about 202°K) are of necessity based almost entirely on the results of Eiermann and Hellwege. The sample used by these workers contained 2 per cent of sulfur. Since T_g is sensitive to combined-sulfur content, the temperature at which the peak in the k -curve occurs may be expected to shift up or down with variation in content of combined sulfur.

Eiermann and Knappe [2] give two values, one at liquid-air temperature, the other at room temperature, obtained by a steady-state method, to which considerable weight has been given. They undertook this particular investigation to clear up the uncertainty that had existed in the behavior of the thermal conductivity of rubber near and below the glass transition. Values obtained with the apparatus evacuated were erratic, and generally lower than those obtained when the apparatus was filled with helium gas. Their evidence seems conclusive that some previous workers obtained erroneous results because of poor thermal contact between the sample and the hot and cold plates. Hardening of the sample at the glass transition appears to greatly increase the possible errors from this source. The values from Eiermann and Knappe plotted in Fig. 1 are the average values obtained with helium gas surrounding the sample, so that good thermal contact was obtained.

Frensdorff [3] gives a valuable set of data covering the range 32 to 99°C. The reported values are of thermal diffusivity a ; the k -values must be computed from the a 's. A standard technique for making this computation for rubber was worked out and used in all cases where a , rather than k , was reported. This technique is described later.

The data of Cherkasova [4] are somewhat puzzling; they have a minimum in k at about 318°K. Cherkasova attributes this minimum to the completion of melting of a crystalline phase, and states that crystallization was produced by long storage at 20°C. Presumably the samples were unvulcanized; there is no statement on this point. Perhaps they were of the modification known as "stark rubber."

Schilling's [5] recent paper includes results for soft vulcanized rubber. His apparatus could be operated in various ways; the results we have plotted were probably obtained by a quasistationary technique.

Schallamach [6], and also Dauphinee, Ivey, and Smith [7], reported thermal-conductivity measurements over temperature ranges extending well below the glass transition. In both investigations the apparatus was evacuated to reduce heat exchange with the surroundings; and in both, the thermal conductiv-

ity was erratic and showed a steep drop at and below the glass transition. Eiermann and Knappe have, as mentioned above, explained this as due to poor thermal contact. We have accepted this explanation, and have therefore rejected all data of references [6] and [7] below about 220°K. Above that temperature, for Schallamach the plotted points are reproduced; but for Dauphinee, *et al.*, the points were so numerous and scattered that we have reproduced only the upper straight line that they gave, which we believe represents their more reliable data.

Rehner [8] reported a rather than k . The steep slope of his curve casts doubt on the reliability of the data.

The papers mentioned thus far are the only ones we have found that give data for soft rubber covering appreciable ranges of temperatures. A set of data for hard rubber, given by Erk [9], is included in Fig. 1 for comparison. Note that hard rubber shows no peak near 200°K, where the glass transition of soft rubber occurs. The glass transition of hard rubber may be expected to occur at about 363°K; however, Erk's data are too widely spaced to prove or disprove the existence of a peak in the k -curve in this region.

A number of papers not so far discussed contain only a single value of k ; a few contain more than one value but cover no appreciable temperature range. These papers have been evaluated, and the data from three [10-12] are given in the figure. In all three a steady-state hot-plate method was used. The rest of this group of papers were considered less reliable or less usable for various reasons. These remaining papers are listed in the second group of references, with numerical k -values and annotations.

To calculate values of k from values of thermal diffusivity, a , the equation $k = a\rho c_p$ is used, where ρ is density and c_p is specific heat at constant pressure. For density, we have used the values of Scott [44]. For specific heat, we have used a paper of Bekkedahl and Matheson [48], in which c_p is tabulated at 5-degree intervals. Above the range of the tables we used linear extrapolation.

The Thermal Conductivity at Higher Temperatures. The selected values of k in Table 1 extend from 80 to 380°K, and the master curve becomes nearly level at the upper end of this range. In a study of the resistance of various rubbers to high temperatures, Hayes, Smith, Kidder, Henning, Rigby, and Hall [49] made measurements and reported thermal-conductivity values for natural rubber at 100, 300, and 400 F (up to 478°K). A measurement at 500 F had to be discontinued because of deterioration of the sample.

The results are not plotted in Fig. 1, because the sample contained among the compounding ingredients 50 parts (on the rubber) of carbon black. Such an addition of carbon black raises the k -values by roughly

85 per cent. In the range of their measurements, Hayes, *et al.* found dk/dT negative, with a value of about 5×10^{-7} cal cm^{-1} sec^{-1} $^{\circ}\text{K}^{-2}$. It is reasonable to expect rubber without carbon black also to have dk/dT negative between 380 and 500 $^{\circ}\text{K}$ and, until additional measurements have been made, it is reasonable to use the value 5×10^{-7} given above for both soft and highly compounded rubber.

V. Reliability of the Tables

The tabulated values of k near and above room temperature are believed to be accurate to ± 8 per cent or better. At lower temperatures, where the data are scarcer, the uncertainty is perhaps 12 or 15 per cent. We attribute roughly half the uncertainty to errors in the experimental measurements, and half to differences in composition of the rubber.

Acknowledgment

We are indebted to Dr. Lawrence A. Wood of the National Bureau of Standards for a number of valuable suggestions.

Annotated References Containing Data Plotted in Fig. 1

- [1] K. Eiermann and K. H. Hellwege, "Thermal conductivity of high polymers from -180°C to 90°C ," *J. Polymer Sci.*, Vol. 57, 1962, p. 99-106. Their Fig. 1 contains 89 plotted points for rubber, from which values of T and k were read.
- [2] K. Eiermann and W. Knappe, "A simple plate apparatus for the determination of the thermal conductivity of plastics, with a contribution to the question of thermal contact at low temperatures," *Z. angew. Physik*, Vol. 14, 1962, p. 484-488. "Room temperature" has been taken to be 25°C ; "liquid-air" temperature, -180°C .
- [3] H. K. Frensdorff, "The thermal diffusivity of natural rubber," *J. Appl. Polymer Sci.*, Vol. 6, 1962, p. S28-S29. His Fig. 1 contains 33 "zerotime corrected" points, from which values of T and α were read.
- [4] L. N. Cherkasova, "Effect of structure on the thermal conductivity of polymers," *Russian, J. Phys. Chem.*, Vol. 33, No. 9, 1959, p. 224-226. Her Fig. 2 contains 16 plotted points, from which values of T and k were read.
- [5] H. Schilling, "Thermal conductivity of elastomer-filler systems at 20 to 90° ," *Kautschuk und Gummi*, Vol. 16, 1963, p. 84-87. Values of T and k at the ends of the interval of measurement are tabulated. The remaining values were read from Schilling's Fig. 1. The two curves for unfilled rubber appear to be duplicates. The 6 interior points of each were read and corresponding values were averaged.
- [6] A. Schallamach, "The heat conductivity of rubber at low temperatures," *Proc. Phys. Soc. (London)* Vol. 53, 1941, p. 214-218. His Fig. 2 contains 13 points, from which values of T and k were read. For reasons given in the text, we have rejected all except those for the 5 highest temperatures.
- [7] T. M. Dauphinee, D. G. Ivey, and H. D. Smith, "The thermal conductivity of elastomers under stretch

and at low temperatures," *Can. J. Research*, Vol. A 28, 1950, p. 596-615. No values of plotted points were read from the graphs; instead, the upper solid straight line of their Fig. 5 has been used.

[8] J. Rehner, Jr., "Heat conduction and molecular structure in rubberlike polymers," *J. Polymer Sci.*, Vol. 2, 1947, p. 263-274. The values in his Table I are extrapolations. We have therefore used his Fig. 2; it contains 18 points, from which values of T and α were read.

[9] S. Erk, "Physical properties, application and processing of synthetic materials," in *Der Chemie-Ingenieur*, Vol. 3, Pt. 2, A. Eucken and M. Jakob, Eds., (Akademische Verlagsgesellschaft, Leipzig, 1938), p. 360-386. On hard rubber.

[10] J. A. Weh, "Thermal conductivity of insulating materials," *Gen. Elec. Rev.*, Vol. 40, 1937, p. 138-140. The temperature of the measurement has been taken to be 45°C .

[11] E. Griffiths and G. W. C. Kaye, "The measurement of thermal conductivity," *Proc. Roy. Soc. (London)*, Vol. A 104, 1923, p. 71-98. We have accepted one k -value from their table 13, the value for 92 per cent rubber.

[12] O. Tesche, "Determination of the thermal conductivity of technical materials," *Z. techn. Physik*, Vol. 5, 1924, p. 233-236. We have accepted the third entry in his table, for "Gummi 90 per cent."

Containing Data Not Plotted in Fig. 1

These references contain the data judged to be less important than those in [1] - [12]. The arrangement is alphabetical. Each of the references in this group is followed by a brief annotation, in which the k -values reported in the paper are included. Numerical values given below are in cal $\text{cm}^{-1}\text{sec}^{-1}^{\circ}\text{C}^{-1}$.

[13] Amer. Soc. Testing Materials, "Tentative method of test for comparing the thermal conductivities of solid electrical insulating materials, Tentative Standard D325-30 T," *Proc. ASTM*, Vol. 30, I, 1930, p. 1224-1228. The use of standard specimens made from rubber was anticipated; with varying amounts of graphite added to increase the conductivity. For soft vulcanized rubber (no graphite), k is given as 0.000342; for an unspecified temperature, presumably at, possibly above, room temperature.

[14] W. Backes, "Contribution to the thermal conductivity of vulcanizates of natural and synthetic rubber," *Kautschuk und Gummi*, Vol. 9, 1956, p. WT257-260. Thermal diffusivity was measured, presumably near room temperature. We have averaged the two values for unmastered rubber without carbon-black filler, and computed k ; the result is $k = 0.000437$.

[15] C. E. Barnett, "Thermal properties of rubber compounds. I. Thermal conductivity of rubber and rubber compounding materials," *Ind. Eng. Chem.*, Vol. 26, 1934, p. 303-306. No numerical value is given for soft rubber, but we have read a value from the graph of k versus volume fraction of ZnO . At zero ZnO -content, $k = 0.00032$. Presumably this value is for room temperature. Presumably also it is for raw rubber, but Barnett states that raw and cured rubber have the same k -value.

[16] L. N. Clarke and R. S. T. Kingston, "Equipment for the simultaneous determination of thermal conductivity and diffusivity of insulating materials using a variable-state method," *Australian J. Appl. Sci.*, Vol. 1, 1950, p. 172-187. This paper gives $k = 0.000365$ at 25°C ; however the density of the rubber is 1.10 g cm^{-3} , so the sample must be considered to be outside our limits for soft natural rubber.

[17] C. Cuthbert, "Vulcanization: application of unsteady-state heat conduction theory," *Trans. Inst. Rubber Ind.*, Vol. 30, 1954, p. 16-32. A nonsteady-state method gave for rubber, $k = 0.000455$, and showed "no significant change with temperature over the range room temperature to 280°F ."

[18] L. Frumkin and Yu. Dubinker, "Investigation of the thermal conductivity of rubber," *Rubber Chem. Technol.*, Vol. 11, 1938, p. 359-371. Two values in this paper appear to fall within our limits for soft vulcanized natural rubber. These are the first value in table I: $k = 0.000431$; and the first value in Table IV: $k = 0.000355$. We cannot be sure of the temperature; the average temperature of the hot plate appears to have been 65°C .

[19] L. S. Frumkin and Yu. B. Dubinker, "The heat conductivity of rubber," *Rubber Chem. Technol.*, Vol. 13, 1940, p. 361-374. The curve for "pure mixture" in Fig. 9 of this paper gives the thermal diffusivity of soft vulcanized natural rubber (the English translation of the title of the paper is incorrect - it should be "thermal diffusivity," not "heat conductivity"). We have taken the value for diffusivity from this curve at a sphere-center temperature of 50°C , and have calculated from it a k -value of 0.000174. The mean temperature to be associated with this value is not given; a rough estimate is 55°C .

[20] V. I. Gengrinovich and V. O. Fogel, "Thermophysical characteristics of cured rubber stocks," *Rubber Chem. Technol.*, Vol. 32, 1959, p. 444-453. One value is given for soft vulcanized natural rubber (Stock No. 1): $k = 0.000314$. A nonsteady-state method was used. We estimate the temperature corresponding to this value to be 90°C .

[21] J. Hennig, "The thermal conductivity of stretched high polymers below and above the glass-transition temperature," *Kolloid Z. und Z. Polymere*, Vol. 188, 1963, p. 159-160. A comparison method was used; the reference sample was poly-CTFE with an accepted k of 0.000325. For soft vulcanized rubber unstretched, and also for stretched rubber perpendicular to the direction of stretch, k was found to be 0.00036 at 25°C .

[22] A. S. Herschel, G. A. Lebour, and J. T. Dunn, "Experiments to determine the thermal conductivities of certain rocks, showing especially the geological aspects of the investigations," *Brit. Assoc. Advancement Sci. Report of 49th Annual Meeting*, 1879, p. 58-63. For soft vulcanized natural rubber two values are given: for a gray "nearly pure" sample, $k = 0.00044$ at 46°C ; for a red sample, $k = 0.00034$ at 49°C .

[23] G. B. Hodgetts, "A method of measuring the thermal conductivity of wire coatings," *Brit. J. Appl. Phys.*, Vol. 13, 1962, p. 310-313. Insulated and uninsulated wires were immersed in running water and electrically heated; the temperature rises were calculated from the observed electrical resistances. The k -value found for a rubber insulation is 0.00033, at a temperature of about 30°C .

[24] P. Kainradl, "Method for the measurement of the thermal conductivity of vulcanizates. Effect of carbon blacks and fillers," *Gummi und Asbest*, Vol. 5, 1952, p. 44-46. A comparison method was used; the reference sample was hard rubber, whose k -value (not given) was known to 2.5 per cent. From his Fig. 2, at 0 per cent additive, we find $k = 0.000378$; it corresponds to a temperature of approximately 19°C .

[25] O. Krischer and H. Esdorn, "A simple, rapid process for the simultaneous determination of the thermal conductivity, heat capacity, and heat-penetration number of solid materials," *VDI Forschungsheft*, 450 (Suppl. to *Forsch. Gebiete Ingenieurw.* B 21), 1955, p. 28-39. A

nonsteady-state method was developed; for rubber it gave $k = 0.000508$ and $k = 0.000511$ at 24°C . As a check the same sample was measured in a conventional, two-plate apparatus; the result was $k = 0.000506$ at 28°C .

[26] A. Schallamach, "Heat conductivity of rubber at low temperatures," *Nature*, Vol. 145, 67 (1940). The first two values in this report we consider superseded by reference (6). However, the third value was obtained by a different method, by filling a rubber bag with liquid nitrogen, immersing it in liquid oxygen, and noting the rate of evaporation of nitrogen. The value of k found by this method at 83°K is 0.000010, a very low value.

[27] H. Tautz, "The variation of the thermal conductivity of rubber with stretching," *Kolloid Z.*, Vol. 174, 1961, p. 128-133. Heat flow took place along the two legs of a doubled thread of rubber under conditions not favorable to accurate measurement of k . From Fig. 2 we read off the two values of k at zero extension. The average is 0.000144; it corresponds to a temperature of 59°C .

[28] M. S. Van Dusen, "The thermal conductivity of heat insulators," *J. Am. Soc. Heating Ventilating Engrs.*, Vol. 26, 1920, p. 625-652. This contains an accurate measurement made by the guarded hot-plate method: $k = 0.000420$ at approximately 30°C . Unfortunately, the density (1.10 g cm^{-3}) is so high that the sample must be considered to be outside our limits for soft natural rubber.

[29] R. Vieweg and Fr. Gottwald, "Measurements of thermal diffusivity of plates of synthetic materials in a steam calorimeter," *Kunststoffe*, Vol. 32, 1942, p. 10-12. A sample with a thermocouple at its center is suddenly exposed to steam, and the rate of temperature rise is observed. Only one of the reported values, that for natural rubber of density 1.05 g cm^{-3} , falls within our limits. The value of k given by Vieweg and Gottwald for this sample is 0.00039; the corresponding temperature lies somewhere between room temperature and 100°C , say at 60°C .

[30] V. S. Volkenshtein and N. N. Medvedev, "Determination of the coefficients of thermal diffusivity and thermal conductivity of solid and liquid materials," *Inzhener-Fiz. Zhur., Akad. Nauk Belorus, S. S. R.*, Vol. 2, No. 10, 1959, p. 26-32. A nonsteady-state method was used, in which a reference material was required. For soft rubber, using gypsum as the reference material, they report $k = 0.00050$; when sand was the reference material, they found $k = 0.00036$. The temperature of measurement appears to be room temperature.

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The arrangement is alphabetical.

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Reprinted from "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," 1965, The American Society of Mechanical Engineers, 345 East 47th Street, New York, N. Y. 10017.