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LOW-TEMPERATURE ELASTIC BEHAVIOR OF FOURTEEN COMPOUNDED ELASTOMERS

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ABSTRACT

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Fourteen compounded elastomers, each one at three hardness levels, were studied in this investigation. These studies included modulus of rigidity, brittle temperature, Young's modulus at 10,000 psi, and relative stiffness of each compound. Graphical data are presented which illustrate the findings of these experiments.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (CONCLUDED)

TECHNICAL MEMORANDUM X-53137

LOW-TEMPERATURE ELASTIC BEHAVIOR OF FOURTEEN COMPOUNDED ELASTOMERS

SUMMARY

The viscoelastic behavior of polymers over a wide range of temperatures is particularly important in space vehicles where high functional reliability must be maintained. However, technical information in this area is conspicuously lacking in published literature, particularly for compounded elastomers of varying compositions designed for definite purposes.

Fourteen compounded elastomers, each one at three hardness levels, were studied in this investigation. These studies included modulus of rigidity, brittle temperature, Young's modulus at 10,000 psi, and relative stiffness of each compound. Graphical data are presented which illustrate the findings of these experiments.

INTRODUCTION

Numerous types of synthetic elastomers are used presently in space vehicles. Frequently, these materials are required to operate at low temperatures with characteristic elastic qualities during launch and/or flight of the vehicle. In various applications, the change in flexural characteristics of these elastomers at low temperatures is extremely important. Because it was recognized that high functional reliability of rubber parts must be maintained at the operating temperature, it became necessary to determine the low-temperature behavior of the several types of synthetic rubber available for the design of spacecraft.

The properties of 14 types of base polymers formulated into typical compounds were studied, each at three hardness levels, at sub-zero temperatures. These properties were: (a) torsional modulus of rigidity in psi from room temperature to temperatures below the "glassy state;" (b) relative stiffness at T_2, T_5, T_{10}, and T_{100} (the temperature at which the stiffness is 2, 5, 10, and 100 times the stiffness measured at room temperature); (c) brittle temperature (the temperature at which embrittlement was evidenced); (d) the temperature at which Young's modulus became 10, 000 psi.

Other phases of the investigation, such as hardness versus temperature relationship, second-order transition, and hardness versus elasticity relationship, are also reported; however, these items are not discussed as comprehensively as those previously mentioned.

Graphs, tables, and experimental findings, as well as methods used and application recommendations for each of the elastomers, are included in this report.

DISCUSSION

Technical information pertaining to the low-temperature properties of synthetic elastomers is conspicuously lacking in published literature. Several new elastomers, about which very little was known of their low-temperature properties, have come into existence during the last few years. Therefore, the object of this investigation was to determine the sub-zero properties of 14 types of synthetic elastomers and to present this information comprehensively in graphic form, thus providing a direct comparison between the several expressions in current usage which relate to and characterize the low-temperature behavior of elastomeric materials.

The properties investigated and the applicable test procedures were as follows:

(a) Modulus of rigidity - ASTM method D1053-58T

(b) Relative stiffness - ASTM method D1053-58T

(c) Young's modulus of 10,000 psi-ASTM method D1053-58T

(d) Brittleness temperature-ASTM D746-57T

At this point, it should be remembered that "modulus of rigidity" (also referred to as shear modulus or more commonly called "stiffness" as a function of temperature) is not to be confused with Young's modulus (modulus of elasticity). They may be compared, however, by the following equation:

$$E = 2G\,(1+P)$$

where E = Young's modulus

G = Shear modulus

P = Poisson's ratio.

Taking Poisson's ratio as 0.5 (assuming no volume change, the ratio of an isotropic material is exactly 0.5), the shear modulus is 1/3 Young's modulus; therefore, using the term "G" for "modulus of rigidity," we see where Young's modulus equals 3G.

Relative stiffness values (T_2, T_5, T_{10}, and T_{100}) simply signify the temperature at which the elastomer's stiffness or rigidity is 2, 5, 10, or 100 times the values recorded at room temperature.

To determine low-temperature serviceability of elastomers, by measurements of physico-mechanical characteristics, generates principal difficulties originating from relaxation phenomena caused by the supermolecular structure of cured or vulcanized elastomers and complicated by the presence of fillers and other extraneous materials. Almost all of the usual characteristic tests are methods developed for practical purposes in narrow temperature limits. The serviceability of compounded elastomers should be determined under conditions closely related to the actual conditions of use. It is fortunate, therefore, that even for highly compounded elastomeric samples a connection between mechano-elastic behavior and the transition states of the pure elastomer can be established.

In Table I, fourteen compounded elastomers used in this investigation are compiled. This table illustrates the base polymer and percentages of filler and plasticizer compounded therein to produce the desired Shore-A hardness.

Stress-strain curves were determined from the values obtained during studies of each of the compositions listed in this table. These curves are shown in FIG 1 through FIG 14 and illustrate the change in apparent moduli of rigidity (psi) to variations in temperature. The curves also contain points T_2, T_5, T_{10}, and T_{100} as well as point T_E 10,000, the temperature at which Young's modulus is 10,000 psi.

All graphs show the temperature range investigated for the particular compositions. At room temperature, the horizontal part of the rubbery plateau is recognizable, followed with decreasing temperature by the steep transition range, and, finally, the horizontal glassy range. In all of the samples studied, there was a steeper rise of the modulus of rigidity in those with tne lowest hardness at 26°C than in the corresponding samples of higher hardness.

The modulus of rigidity for given conditions does not necessarily permit a comparison of the elastic behavior of different elastomers. Only the complete curve of moduli over the range of interest characterizes the elastomer. Yet, if definite limits of elasticity can be set for a given purpose or application, e. g., E of 10, 000 psi, a comparison of different samples is possible (FIG 15).

The effect of stress upon a body is displacement from equilibrium. If a body were perfectly elastic, the stored energy would be momentarily and completely released when the stress was released. In the case of polymers, the result would be the return of chain elements to their original minimum position in the energy wells. Hooke's law ($\Delta l/l = S/E$) describes this relation. It is obvious with these considerations that to a certain point the elasticity of a body will improve with rising temperature for kinetic and thermo-dynamic reasons. However, there are no bodies known which are perfectly elastic. It was found that even the stress-strain behavior of vulcanized natural and synthetic rubbers does not obey Hooke's law in shear. An increase in shear-stress produces a more-than-proportional increase in shear-strain. Fillers aid vulcanized or cured elastomers to exhibit Hooke-behavior. With the exception of ZnO, they cause an increase of viscosity and other rheological effects and, thus, have a remarkable influence upon hardness. Of course, these effects are specific for individual elastomers and fillers. From Table I, it can be seen that in the hardness range of 60 to 90 Shore-A natural rubber compounds contain 31-54% filler. Nitrile-butadiene compounds contain 16-48% filler, and acrylic rubber compounds 22-40% filler.

Some of the compounded elastomers creep during hardness measurements, particularly those made from nitrile-butadiene, urethane, thiokol, and fluorinated vinylidene rubbers. Note, however, that values for hardness depend upon the method used. Generally, the indentation caused by a loaded point or sphere is determined after a standard period of time, and relaxation is neglected under such conditions. From Table II, it can be seen that samples of higher hardness show a higher absolute creep effect but a smaller relative one, obviously an effect of the extraneous materials and fillers. A comprehensive study of hardness measurements using different instruments has been made. Correlating factors for these are now being compiled for a later report.

In Table III, data are compiled for samples of 60 Shore-A hardness. The elastomers are listed with a rising T_E 10, 000, i.e., falling elasticity. G_r and G_g are approximate moduli of the horizontal rubbery and glassy plateaus, respectively. G_i is the modulus at the inflection point of the curves calculated from:

$$\text{Log } G_i = 1/2 (\log G_r + \log G_g)$$

Note that G_r, G_g, and E_i fluctuate approximately $\pm 30\%$ around an average value, whereas T_E 10, 000 rises from -73 to + 1°C.

The values of Si-28 are different from those of Si-31 (another silicone elastomer), but the difference in composition of the two samples is negligible. Neither rubber has reached Tg at -90°C; yet their elastic properties are different. FIG 16 through FIG 19 [illustrating values of natural, thiokol, fluorosilicone (LS), and Si-28] show further evidence of the dependence of hardness on temperature. Again, the behavior of Si-28 is abnormal. When temperatures at which no further change of hardness at falling temperatures occurs are compared with T_g, the relationship becomes obvious.

There is an excellent agreement between T_E 10, 000 and T_i for hardnesses between 30 and 60 Shore for seven of our elastomers. Therefore, it can be said that for these compounded elastomers the Young's modulus of 10, 000 psi is reached at the point of inflection of their corresponding temperatures. This is all the more remarkable since the temperatures at which this inflection occurs vary with types of elastomers and their hardnesses. For elastomers of higher hardness, the values show discrepancies between T_E 10, 000 and T_i. Here, the influence of great quantities of extraneous materials enters the picture. Also, it may be observed from Table III that the glass transition characteristics, T_g and G_g, are not solely responsible for low-temperature elastic behavior; this can be seen from a comparison of T_E 10,000 with T_g. Furthermore, there is no simple relationship apparent between T_E 10,000 and G_i or the brittle point.

CONCLUSIONS

The following conclusions are based upon the evaluation of all of the values obtained throughout this study. It is believed that these conclusions and the graphs and tables included herein make it easy for design and materials engineers to "custom" select an elastomer that will produce the reliability desired for low-temperature applications. It should be noted further that selective choice of fillers and other extraneous materials must be considered in compounding these elastomers, and, if changes in additives are possible without damaging other properties, improvements can be expected.

Properties of each of the formulations tested are summarized in this report so that each formulation may be studied on an individual basis.

ACRYLIC (Acrylic Ester Copolymer)

Low-temperature characteristics of this elastomer may be termed as "intermediate," or slightly below, when compared with the other compounds tested. The low hardness stocks of this compound tend to become stiff at a more rapid rate as they approach a certain temperature while the high hardness stock increases at a more gradual, uniform rate. The "curve pattern" of the 60 Shore-A stock is slightly irregular, compared with other 60 hardness compounds, particularly in the lower temperature regions.

a. 40 Shore-A

This 40 hardness stock begins to stiffen fairly slowly at the beginning of the cooling procedure and continues slow until the temperature reaches 0°C (+ 32.0°F). From this point, the stiffness increase becomes more rapid, reaching a relative value of T_{10} at -9°C (+15.8°F). This rapid rate continues as the temperature is lowered, reaching a relative value of T_{100} at -12°C (+10.4°F). Young's modulus of 10,000 is located between these relative values at -11°C (+12.2°F).

b. <u>60 Shore-A</u>

At +2°C (+35.6°F), the stiffness of this 60 hardness stock begins to increase at a more rapid rate, although not quite as rapidly as the 40 Shore-A stock. At -13°C (+8.6°F), a relative value of T_{10} is reached and increases to T_{100} at -29°C (-20.2°F). Young's modulus of 10,000 is found between these values, at -18°C (-0.4°F).

c. <u>80 Shore-A</u>

Characteristics of this 80 hardness compound are slightly different from those of lower hardness stocks, especially in the temperature region around 0°C (+32.0°F). In this region, no sharp increase in the stiffness rate is noted, and the sample continues to stiffen at a gradual increase. At -9°C (+15.8°F), a relative value of T_{10} is reached, increasing to T_{100} at -15°C (+5.0°F). Young's modulus is located very close to the T_{10} value and is also reported at -9°C (+15.8°F).

<u>BUTYL (Isobutylene-Isoprene Copolymer)</u>

Low-temperature characteristics of this elastomeric compound are very good, this being one of the better compounds tested. Properties of each hardness level vary to some extent. However, the 60 and 70 Shore-A stocks have slightly related properties. With this material, as with most of the compounds tested, the lower hardness levels indicate a rapid increase in stiffening at a certain point; whereas, the higher levels tend to stiffen more gradually and uniformly. This may be noted below by the properties of the three stocks studied.

a. <u>50 Shore-A</u>

Modulus of rigidity increases fairly slowly and uniformly during the cooling process until the sample temperature approaches -20°C (-4.0°F). At this temperature, a rapid increase in stiffness is observed with a relative value of T_{10} being at -27°C (-16.6°F). On further cooling, this stiffening rate is still very rapid and has reached a value of T_{100} at -31°C (-23.8°F). Young's modulus of 10,000 is observed between these two values at -29°C (-20.2°F).

b. 60 Shore-A

The rigidity of this hardness stock increases at a fairly uniform rate throughout the cooling process, with this rate becoming slightly more rapid at approximately -20°C (-4.0°F). A relative stiffness value of T_{10} is reached at -35°C (-31.0°F) and increases to a value of T_{100} at -43°C (-45.4°F). Young's modulus of 10,000 is located between these values at -38°C (-36.4°F).

c. 70 Shore-A

Stock of this hardness level begins to stiffen more quickly than the lower level compounds; however, the rate is not quite so rapid throughout the entire cooling period. The stiffness increase rate becomes more rapid at -15°C (+5.0°F) and has reached a relative modulus value of T_{10} at -34°C (-29.2°F). This value increases to T_{100} at -48°C (-54.4°F) with Young's modulus of 10,000 found just after the T_2 value at -35°C (-31.0°F).

HYPALON (Chlorosulfonated Polyethylene)

This elastomer, although not the poorest, is not considered one of the better compounds for low-temperature applications. Stiffness begins to increase fairly rapidly on compounds of 60, 70, and 80 Shore-A stock as the temperature approaches 0°C (+32° F). In the entire study, including all three hardness levels, there was only 7°C variation in Young's modulus of 10,000 and the relative modulus value T_{100}. Exact locations and other data of these studies are listed below for the stocks tested.

a. 60 Shore-A

This 60 hardness compound has slightly better low-temperature properties than stocks of the same elastomer in 70 and 80 hardness levels. During the cooling process, the stiffness begins to increase at a more rapid rate as the temperature approaches 0°C (+32° F) and reaches a relative modulus value of T_{10} at -13°C (+8.6°F). By further cooling, the sample reaches Young's modulus of 10,000 at -15°C (+5.0°F) and a relative value of T_{100} at -21°C (-5.8°F).

b. 70 Shore-A

Compounds of this 70 hardness stock also begin to stiffen at a more rapid rate as the temperature approaches 0°C (+32° F), and they reach a relative value of T_{10} at -7°C (+19.4°F). It is observed at this point that the "curve" pattern of the stiffness rate is increasing very rapidly, with Young's modulus of 10,000 being at -8°C (+17.6°F) and the relative value T_{100} at -16°C (+3.2°F).

c. <u>80 Shore-A</u>

Although an increase in the stiffening rate of this hardness stock is observed at approximately 0°C (+32° F), it is not so "sharp" as the rate of 60 and 70 hardness levels. The increase from room temperature (26°C) is gradual to this point (0°C) but then seems to speed up slightly, reaching a relative modulus value of T_{10} at -9°C (+15.8°F). Like the 70 hardness stock, Young's modulus of 10,000 is very close to this point, being noted at -10°C (+14.0°F). Further cooling indicates that this stiffness rate is still increasing, reaching a relative value of T_{100} at -14°C (+6.8°F).

<u>KEL-F (Copolymer of Vinylidene Fluoride and Chlorotrifluoroethylene)</u>

Low-temperature properties are fair but are not considered to be grouped with the "better" compounds tested. Characteristics are very similar for each hardness level tested except for the difference in initial modulus at room temperature. Each stock indicates a certain point at which a distinct increase in stiffness begins. Properties of each level tested are:

a. <u>60 Shore-A</u>

A rapid increase in stiffness occurs with this 60 hardness stock as the temperature approaches 0°C (+32 °F). From this point, a relative value of T_{10} is reached at -4°C (+24.8°F) and increases to T_{100} at -10°C (+14.0°F). Young's modulus of 10,000 is located between these relative values at -6°C (+21.2°F).

b. <u>70 Shore-A</u>

Low temperature properties of this 70 hardness stock are very similar to the 60 Shore-A stock except for slight variations of the relative values. A rapid increase in stiffness becomes evident as the temperature approaches 6°C (+42.8°F). At -2°C (+28.4°F), a relative value of T_{10} is reached and increases to T_{100} at -9°C (+15.8°F). Young's modulus of 10,000 is located between these relative values at -3°C (+26.6°F).

c. 80 Shore-A

With this 80 hardness stock, a rapid increase in stiffness begins as the temperature approaches +5°C (+41.0°F). At -1°C (+30.2°F), a relative value of T_{10} is reached, which increases to T_{100} at -8°C (+17.6°F). Young's modulus of 10,000 is reached at 0°C (+32.0°F), and here, again, is an example of this value being reached before the relative value of T_{10} in an 80 Shore-A stock.

LS (Methyl Trifluoropropyl Silicone)

Low-temperature properties of this compound were very good and, like the other silicones tested, indicated a distinct "point" at which a rapid increase in rigidity became evident. Characteristics of the 60 and 70 Shore-A stocks are very similar, indicating almost identical relative points at T_{10}, T_{100}, and Young's modulus of 10,000. The initial modulus of rigidity of the 80 Shore-A stock was considerably higher than the other levels tested and increased in stiffness at a slightly slower rate. Properties of each stock tested were:

a. 60 and 70 Shore-A

Except for a slight difference in initial modulus at room temperature (35 psi variation), the properties of these compounds were very much alike. A distinct, rapid increase in stiffness began to occur at -29°C (-20.2°F) with the 60 Shore-A stock compared to the same characteristic of the 70 Shore-A beginning at -25°C (-13.0°F). Each stock had a relative value of T_{10} at -34°C (-29.2°F). Only 1°C was noted in the difference of Young's modulus of 10,000 for these, the 60 Shore-A being at -31°C (-23.8°F) and the 70 Shore-A at -32°C (-25.6°F).

b. 80 Shore-A

The low-temperature properties of this stock were slightly different from those of the lower hardness levels although some similarity was evident in their "stiffness rate curve." Stiffening was gradual and slow during the cooling process until the temperature approached -30°C (-22.0°F). At this point, more response was noted to a temperature drop, with stiffness increasing at a much faster rate. A relative value of T_{10} was reached at -41°C (-41.8°F) and this increased to T_{100} at -49°C (-56.2°F). Young's modulus of 10,000 was located just before the T_{10} value which, as stated before, is not uncommon for most 80-90 Shore-A compounds at -40°C (-40.0°F).

NATURAL (Polyisoprene)

The low-temperature stiffness properties of this elastomer are very good, being second only to the methyl phenyl vinyl silicone. Characteristics vary with the hardness level of the compound due to the initial differences in their room temperature (26°C) moduli. Like the silicone elastomers, this compound also indicated a distinct point at which the stiffness begins to increase at a rapid rate. This is particularly noted in the low hardness stocks. Characteristics of this elastomer at various hardness levels are as follows:

a. 30 Shore-A

This compound, at room temperature (26°C), is very flexible and reacts slightly differently from harder stocks at lower temperatures. Practically no increase in stiffness is evident between room temperature and -38°C (-36.4°F); however, below this temperature, the modulus of rigidity increases very rapidly. The relative modulus value of T_{10} is reached at -44°C (-47.2°F) and increases in stiffness to T_{100} at -45°C (-49.0°F). Young's modulus of 10,000 is located at -44°C (-47.2°F), which is the same temperature observed for the T_{10} value. From these data, it is evident that once the stiffness begins to increase, the range in which the compound becomes completely rigid is only 6 or 7°C.

b. 60 Shore-A

The stiffness of this 60 Shore-A stock increases uniformly throughout its entire "curve" from room temperature, 26°C (+74.8°F), to the rigid or "freezing point." Modulus of rigidity begins to increase distinctly at 0°C (+32.0°F) and reaches a relative value of T_2 at -21°C (-5.8°F). The stiffness increase rate continues gradually from this point, reaching a relative value of T_{10} at -40°C (-40°F) and T_{100} at -52°C (-61.6°F). Young's modulus of 10,000 is located between the T_{10} and T_{100} values at -45°C (-49.0°F).

c. 90 Shore-A

Low-temperature characteristics of this 90 hardness stock are very similar to those of the 60 Shore-A compound except for a higher initial modulus at room temperature. Increase in stiffness (while cooling) is uniform and gradual, reaching a relative modulus value of

T_{10} at -40°C (-40.0°F). This value increases to T_{100} at -49°C (-56.2°F) with Young's modulus of 10,000 being at -38°C (-36.4°F).

Here, again, is another example of Young's modulus of 10,000 being reached before the relative value of T_{10} on a 90 Shore-A compound. This characteristic will be noted quite frequently throughout the entire series of tests.

NEOPRENE (Polychloroprene)

Low-temperature characteristics of this compound are considered "intermediate" when compared with the other elastomers tested. The 30 and 60 Shore-A stocks indicate a distinct point at which the stiffness begins to increase at a more rapid rate; whereas, the 90 Shore-A stock stiffens more gradually and uniformly throughout the test. A fairly large difference in initial modulus of rigidity is noted at room temperature (26°C, +78.8°F), ranging from 40 psi at the 30 hardness level to 650 psi at the 90 hardness level. The properties of each hardness level are indicated below.

a. 30 Shore-A

This 30 hardness stock increased in stiffness fairly slowly until the temperature approached -22°C (-7.6°F). At this point, a rapid increase in rigidity became evident as the temperature was lowered, reaching a relative value of T_{10} at -31°C (-23.8°F). This value increases to T_{100} at -33°C (-27.4°F) with Young's modulus of 10,000 also noted at this temperature.

b. 60 Shore-A

The stiffness increase is fairly slow with this 60 hardness stock until the temperature approaches -10°C. From this point, the stiffness rate begins to increase rapidly as the temperature is lowered and reaches a relative value of T_{10} at -18°C (-0.4°F). This value increases to T_{100} at -22°C (-7.6°F), with Young's modulus of 10,000 located between these two values at -19°C (-2.2°F).

c. 90 Shore-A

The stiffness increase of this 90 hardness stock is fairly gradual until the temperature approaches -18°C (-0.4°F). At this point, a relative value of T_{10} and Young's modulus of 10,000 are noted. At temperatures below this, the stiffness-increase rate is very fast, reaching a relative value of T_{100} at -23°C (-9.4°F).

NBR (Butadiene-Acrylonitrile)

This compound began to stiffen or become rigid at the highest temperature of any compound tested. In the three hardness levels, -13° C (+8.6°F) was the lowest temperature reached before a relative value of T_{100} was reached. On one of the levels studied (60 Shore-A), a relative value of T_{10} was observed before the temperature reached 0°C. Young's modulus was 10,000 with all levels of hardness at a minimum of -7°C (+19.4°F) and in one level was reached at +1°C (+33.8°F). Properties of each level tested were:

a. 40 Shore-A

This 40 hardness stock increased fairly slowly in stiffness until the temperature approached 5°C (+41.0°F). From this point, stiffening occurred fairly rapidly with a relative value of T_{10} reached at -3°C (+26.6°F), and this increased to T_{100} at -7°C (+19.4°F). Young's modulus of 10,000 was noted between these relative values at -5°C (+23.0°F).

b. 60 Shore-A

Although the curve "pattern" of this 60 hardness stock was similar to that of the 40 Shore-A, the relative modulus points plotted were recorded at a higher temperature than any compound of any hardness level tested. At +4°C (+39.2°F), a distinct increase was noted in the stiffness rate. At +2°C (+35.6°F), a relative value of T_{10} was reached and this increased to T_{100} at -1°C (+30.2°F). Young's modulus of 10,000 was between these values at +1°C (+33.8°F). It was noted from these data that this compound became very rigid in about 5°C after reaching +4°C (+39.2°F).

c. 90 Shore-A

Properties of this hardness level were quite different from those of the lower hardness levels in that the stiffness increase was more gradual throughout the test with no sharp increases in the stiffness curve "pattern." At -8°C (+17.6°F), a relative value of T_{10} was reached and increased to T_{100} at -14°C (+6.8°F). Young's modulus of 10,000 was located between these values at -10°C (+14.0°F) instead of below the T_{10} value, as was common with most of the other 90 hardness compounds tested.

SILICONE (Methyl Vinyl Polymer)

Low-temperature stiffness properties of this elastomer are very good but are not to be compared with methyl phenyl vinyl silicone rubber. The methyl phenyl vinyl compound reached the lowest temperature, without stiffening, of the entire series; whereas, this compound could be classed "in the middle of the group." Characteristics of the 60 and 80 hardness levels are very similar except for the initial modulus of rigidity at room temperature (26°C). Each hardness level tested indicated a distinct point at which the stiffness begins to increase at a more rapid rate; however, the 40 hardness stock has a very low initial stiffness at room temperature and tends to be less uniform in its increase as the temperature is carried below its relative value of T_{100}. Properties of each hardness tested are:

a. 40 Shore-A

This 40 hardness stock is very low in rigidity at room temperature (70 psi) and stiffens very slowly during the initial lowering of temperature. At -16°C (+3.2°F), the stiffness rate begins to increase very rapidly and reaches a relative modulus of T_{10} at -20°C (-4.0°F). From this point, the increase continues to be very rapid and reaches a value of T_{100} at -25°C (-13.0°F). Young's modulus of 10,000 is located just between these values at -22°C (-7.6°F).

b. 60 Shore-A

This 60 hardness stock, like the 40 Shore-A, begins to stiffen very fast as the temperature approaches -18°C (-0.4°F). The relative modulus T_{10} occurs at -23°C (-9.4°F) and increases to T_{100} at -30°C (-22.0°F). Young's modulus of 10,000 is found between these values at -25°C (-13.0°F).

c. 80 Shore-A

This 80 hardness stock also reaches a point at which the stiffness rate begins to increase more rapidly. This rate is not quite so fast as that indicated for the 40 and 60 hardness levels; however, the initial modulus is considerably higher (600 psi) and the "rapid increase" temperature is slightly higher than the other two levels. At -14°C (+6.8°F), the stiffness rate shows a distinct change, increasing in response to temperature change. At -22°C (-7.6°F), the relative modulus is T_{10} and increases to T_{100} at -32°C (-25.6°F). Young's modulus of 10,000 is at -21°C (-5.8°F) and, here again, is an example of this value being reached before the value of T_{10} on an 80 Shore-A compound.

SILICONE (Methyl Phenyl Vinyl Polymer)

The low-temperature stiffness properties of this type of silicone elastomer are excellent. Each of three hardness levels were subjected to extremely low temperatures before significant increase in stiffness could be noted. This was particularly observed in stocks of low hardness levels. One thing should be noted however; upon reaching the temperature at which an increase in stiffness becomes evident, the range at which complete rigidity occurs is very narrow from this point. More evidence of this characteristic is given in individual data of the three hardness levels tested.

a. 30 Shore-A

Low-temperature stiffness properties at this hardness level are very good. The compound was subjected to lower temperatures, without stiffening, than all other elastomers tested. No apparent stiffness increase is noted until the temperature of the sample approaches -70°C (-94°F). At -74°C (-101.2°F), a very rapid increase is noticed in the modulus of rigidity, and, at -81°C (-113.8°F), a relative stiffness value of T_{10} is reached. This value rapidly increases to T_{100} at -83°C (-117.4°F) with Young's modulus of 10,000 located between these values at -82°C (-115.6°F). It can be observed from these data that no gradual increase in stiffness is evident; rather, the compound becomes almost completely rigid in a range of 3-4°C once this "rapid increase point" is reached.

b. 60 Shore-A

Low-temperature properties at this hardness level are also very good and, like the 30 Shore-A stock, indicate a definite point at which the stiffness begins to increase rapidly. As the temperature of the sample approaches -60°C (-76.0°F), a significant increase in rigidity is observed, and a relative value of T_{10} is reached at -71°C (-95.8°F). This value increases to T_{100} at -75°C (-103.0°F) with Young's modulus of 10,000 recorded at -73°C (-99.4°F). This range in which the compound becomes very rigid is broader than that of the 30 Shore-A stock and begins at a higher temperature; however, the range of increase is still to be considered rapid in that the elastomer goes from a very flexible state to an almost completely rigid form in approximately 15°C.

c. <u>80 Shore-A</u>

The low-temperature characteristics of this stock are quite similar to those of 60 Shore-A hardness except for a higher initial modulus at room temperature (+26°C). No significant increase in stiffness is noted until the sample temperature approaches -56°C (-68.8°F); whereas, with the other hardness levels, a rapid increase in rigidity is detected. At -68°C (-90.4°F), the relative modulus reaches a value of T_{10} and increases to T_{100} at -73°C (-99.4°F). With this compound, Young's modulus of 10,000 is reached also at -68°C (-90.4°F); however, this closeness to the T_{10} value is not uncommon in compounds of the 80-90 Shore-A hardness levels. In essentially all of the studies conducted, Young's modulus of 10,000 is located between the relative values of T_{10} and T_{100} in compounds of 40 through 70 Shore-A hardness. At higher hardness levels (80-90 Shore-A), this value changes and is usually reached just <u>below</u> or at the relative value of T_{10}.

<u>SBR (Styrene Butadiene)</u>

Low-temperature properties of this elastomer are very good, particularly in the lower hardness compounds. Although the characteristics of this compound vary with the hardness levels, there is considerably more variation between the 60 and 90 Shore-A stocks than between the 60 and 30 hardness stocks. Although initial stiffening is gradual throughout the entire test on the 90 hardness stocks, a rapid increase occurs as the 30 and 60 hardness stocks reach a certain temperature. The following characteristics were noted of the various hardness levels studied.

a. 30 Shore-A

Initial modulus of rigidity is very low at this hardness level (85 psi) and increases gradually from room temperature (+26°C or +78.8°F) to approximately -36°C (-32.8°F) during the cooling process. At this point, the stiffness increase becomes more rapid and reaches a relative value of T_{10} at -41°C (-41.8°F). From this point, the rigidity increases very rapidly and reaches a relative value of T_{100} at -43°C (-45.4°F). Young's modulus of 10,000 is also observed at this temperature, and it can be noticed that the relative values of T_{10}, T_{100}, and Young's modulus of 10,000 all occur within a span of 2-3°C in this temperature range.

b. 60 Shore-A

Properties of the 60 hardness stock indicate a fairly high initial modulus of rigidity (185 psi) and a slightly more gradual increase in stiffness at extreme temperature conditions. Stiffness begins to occur at a more rapid rate at approximately -16°C (+3.2°F) and reaches a relative value of T_{10} at -33°C (-27.4°F). This value increases to T_{100} at -40°C (-40.0°F) with Young's modulus of 10,000 being located between the two at -34°C (-29.2°F).

c. 90 Shore-A

Low-temperature characteristics of the 90 hardness stock vary quite differently from those of lower hardness levels in such a manner that stiffness increase is gradual throughout the cooling range with no sharp increases in stiffness. The initial modulus of rigidity at room temperature is also fairly high (500 psi), and the "curve structure" or the stiffness pattern begins increasing immediately upon starting the cooling process. A relative stiffness value of T_{10} is noted at -14°C (+6.8°F),and this increases to T_{100} at -27°C (-16.6°F). Young's modulus of 10,000 is reached at -10°C (+14.0°F), which is a considerably higher point than the temperature at which this same value was observed for the 30 and 60 hardness stocks of this elastomer.

THIOKOL (Polysulfide)

This elastomer has very good low-temperature properties, particularly the lower hardness formulations. Modulus of rigidity increases gradually and uniformly during the cooling process; this characteristic is noted with all of the polysulfide compounds tested. Curve graphs, plotted with data from studies of this compound, illustrate there are no sharp breaks or sudden increases in stiffness at any point above its rigid or "freezing" temperature. Properties of each hardness tested are:

a. 60 Shore-A

Increase in rigidity begins gradually as the cooling process begins. A relative value of T_2 is present at -19°C (-2.2°F) and has increased to T_{10} at -39°C (-38.2°F). At -46°C (-50.8°F), a relative value of T_{100} has been reached with Young's modulus of 10,000 located between these latter two values at -43°C (-45.4°F). Little significant difference (2 or 3°C) may be noticed between the temperature of T_{100} and the rigid or "freezing" point.

b. 70 Shore-A

Although the "curve" appearance (when plotted on graph) of this stock is similar to the 60 hardness sample, the relative modulus and other values are quite different because of the initial stiffness at room temperature (26°C). For this formulation, a relative value of T_2 appears at -6°C (+21.2°F) and increases to T_{10} at -29°C (-20.2°F). Young's modulus of 10,000 is observed at -30°C (-22.0°F), and a relative value of T_{100} is reached at -38°C (-36.4°F). This is about 8°C higher than the same value for the 60 hardness sample.

c. 80 Shore-A

At this hardness level, the compound begins to stiffen immediately, reaching a relative modulus value of T_2 at -10°C (+14.0°F). This value increases to T_{10} at -33°C (-27.4°F) and to T_{100} at -44°C (-47.2°F). Young's modulus of 10,000 is noted at -30°C (-22.0°F); here again is an example of this value being approached before the relative value of T_{10}.

URETHANE (Polyurethane)

Low-temperature properties of this polyurethane elastomer are fairly good and, like the methyl vinyl silicone rubber, could be termed as "in the middle range" of all the compounds tested. Only two hardness levels of this compound (60 and 70 Shore-A) were available for testing during this study, and very little difference in properties is noted between the two. The stiffness rate begins to increase fairly rapidly for each stock as the temperature approaches -15°C (+5.0°F). At approximately -18°C (-0.4°F), a relative stiffness value of T_{10} is reached on each and increases to T_{100} at -23°C (-9.4°F). Young's modulus of 10,000 is very close for each stock, being at -20°C (-4.0°F) for the 60 Shore-A and at -19°C (-2.2°F) for the 70 Shore-A.

VITON-A (Copolymer of Vinylidene Fluoride and Hexafluoropropylene)

The low-temperature characteristics of this elastomer would probably be acceptable for some applications; however, where extreme conditions are anticipated, they would not be desirable. The initial stiffening varies considerably with the hardness level, especially in the higher regions. Compounds of 60, 70, and 90 Shore-A stock were tested for this study, and the following properties were noted:

a. 60 Shore-A

Although the initial modulus of rigidity for this 60 hardness stock is fairly low (150 psi), a very distinct increase in stiffness begins at approximately +5°C (+41.0°F). From this point, stiffness increases rapidly as the temperature is lowered. A relative modulus of T_{10} is noted at -4°C (+24.8°F) and increases to T_{100} at -9°C (+15.8°F). Young's modulus of 10,000 is at -6°C (+21.2°F) between the T_2 and T_{100} values.

b. 70 Shore-A

Very little difference is found between properties of this 70 hardness stock and those of the 60 hardness level except for the initial modulus of rigidity (285 psi). Stiffness increases gradually as the temperature is lowered until it approaches +6°C (+42.8°F). At this point, the modulus of rigidity increases very rapidly and reaches a relative value of T_{10} at -5°C (+23.0°F). At approximately this same point (-5°C), the properties show a Young's modulus of 10,000 and increase to a value of T_{100} at -9°C (+15.8°F).

c. 90 Shore-A

Low-temperature stiffness properties of this 90 hardness stock are somewhat different from those found in the lower levels. A high modulus of rigidity at room temperature (730 psi) and a more gradual stiffening throughout the entire cooling process are particularly noticed. Young's modulus of 10,000 is reached at -6°C (+21.2°F), and the relative value of T_{10} is noted at -10°C (+14.0°F). Here again is an example of where T_{10} is approached after Young's modulus of 10,000 with a 90 hardness sample. Stiffening from this point continues to increase gradually as the temperature is lowered and reaches a relative value of T_{100} at -17°C (+1.4°F).

TABLE I. FOURTEEN COMPOUNDED ELASTOMERS TESTED

ELASTOMER*	DESIGNATION NUMBER	SHORE A-2 HARDNESS	PERCENT IN COMPOUND			
			BASE POLYMER	FILLER	PLASTICIZER	CURING AGENT, ADDITIVES
Acrylic	RA 33240	40	82	12	1	5
Acrylic	RA 32460	60	73	22	1	4
Acrylic	RA 32680	80	64	31	1	4
Butyl	RA 25550	50	78	12	2	8
Butyl	RA 25660	60	68	24	1	7
Butyl	RA 25770	70	60	33	1	6
Hypalon	RA 32860	60	74	4	0	22
Hypalon	RA 30070	70	60	21	0	19
Hypalon	RA 30180	80	51	33	0	16
Kel-F	RA 27060	60	81	11	0	8
Kel-F	RA 27170	70	75	18	0	7
Kel-F	RA 27280	80	70	23	0	7
Natural	RA 22630	30	76	1	13	10
Natural	RA 22960	60	59	31	3	7
Natural	RA 23290	90	40	46	2	12
Neoprene	RA 23830	30	78	1	14	7
Neoprene	RA 24160	60	68	25	0	7
Neoprene	RA 24490	90	46	50	0	4
NBR	RA 30540	40	73	1	15	11
NBR	RA 30760	60	71	16	2	11
NBR	RA 31090	90	44	49	1	6
LS	RA 27760	60	98	0	0	2
LS	RA 27870	70	90	9	0	1
LS	RA 27980	80	76	23	0	1
Silicone (RA 31)	RA 31230	30	81	13	0	6
Silicone (RA 31)	RA 31560	60	57	38	0	5
Silicone (RA 31)	RA 31780	80	44	53	0	3
Silicone (RA 28)	RA 28340	40	72	23	0	6
Silicone (RA 28)	RA 28560	60	58	37	0	5
Silicone (RA 28)	RA 28780	80	44	53	0	3
SBR	RA 20330	40	67	13	12	8
SBR	RA 20660	60	66	26	0	8
SBR	RA 20990	90	46	48	0	6
Thiokol	RA 31860	60	70	26	2	2
Thiokol	RA 31970	70	61	36	2	1
Thiokol	RA 32080	80	53	44	2	1
Urethane	RA 33260	60	80	16	0	4
Urethane	RA 33370	70	67	28	0	5
Viton - A	RA 36360	60	79	0	0	21
Viton - A	RA 36470	70	61	26	0	13
Viton - A	RA 36690	90	41	50	0	9

* See Table of Contents

TABLE II

AVERAGE HARDNESS DROP* (IN SHORE-A2 POINTS) FROM 0 TO 30 SECONDS FOR THIRTEEN STANDARD RUBBER COMPOUNDS

COMPOUND	HARDNESS RANGE TESTED (SHORE)	AVERAGE DROP (POINTS) FROM 0-15 Sec.	15-30 Sec.	0-30 Sec.
Silicone (RA-28)	30 - 80	0.7	0.3	1.0
Butyl	50 - 70	1.3	0	1.3
Neoprene	30 - 90	1.4	0.2	1.6
Natural	30 - 80	1.5	0.7	2.2
Acrylic	40 - 80	1.8	0.8	2.6
LS	60 - 80	2.0	0.3	2.3
SBR	30 - 90	2.1	0.7	2.9
Hypalon	60 - 80	2.7	0.7	3.3
Kel-F	60 - 80	3.0	1.0	4.0
Thiokol	60 - 80	3.7	1.0	4.7
Urethane	60 - 70	4.0	1.0	5.0
Viton-A	60 - 90	4.5	1.0	5.5
NBR	40 - 90	10.7	2.0	12.7

* Average drop of the overall hardness range for all compounds tested.

TABLE III. CORRELATED DATA OF SHORE-A SAMPLES

Sample	Rubbery Plateau ≈ T_r	Rubbery Plateau ≈ G_r	Glassy Plateau ≈ T_g	Glassy Plateau ≈ $G_g 10^{-3}$	T_E 10,000	T_i	T_{br}	E_i
Silicone (RA 31)	+30	160	-120*	300	-73	-74	-□	6940
Natural	+10	155	-80	200	-45	-39	-56	5480
Thiokol	+40	160	-61	220	-43	-24	-34	5350
Butyl	0	170	-50	160	-38	-36	-33	3580
SBR	-8	186	-41	180	-34	-30	-49	5690
LS	+30	160	-65	250	-32	-12	-52	5910
Silicone (RA 28)	+30	125	-120*	150	-24	-23	□	4240
Urethane	+40	160	-47	250	-20	-20	-43	5470
Neoprene	+30	185	-46	200	-19	-18	-29	6000
Acrylic	+4	150	-18	200	-19	-14	-10	5480
Hypalon	+26	195	-	170	-15	-9	-57	5830
Kel-F	+30	135	-	170	-6	-5	-54	4790
Viton A	+40	140	-41	240	-6	-5	-36	5800
NBR	+30	92	-9	140	+1	-5	-8	3550

* - Given by producer
□ - Not yet reached at -90°C
T_r - Temperature at which rubbery plateau begins
G_r - Modulus (psi) at T_r
T_g - Temperature at which glassy state reached
G_g - Modulus (psi) at T_g
T_E 10,000 - Temperature at which E=10,000 psi
T_{br} - Temperature at which brittle point determined
T_i - Temperature at which curves invert
E_i - Young's modulus at T_i in psi

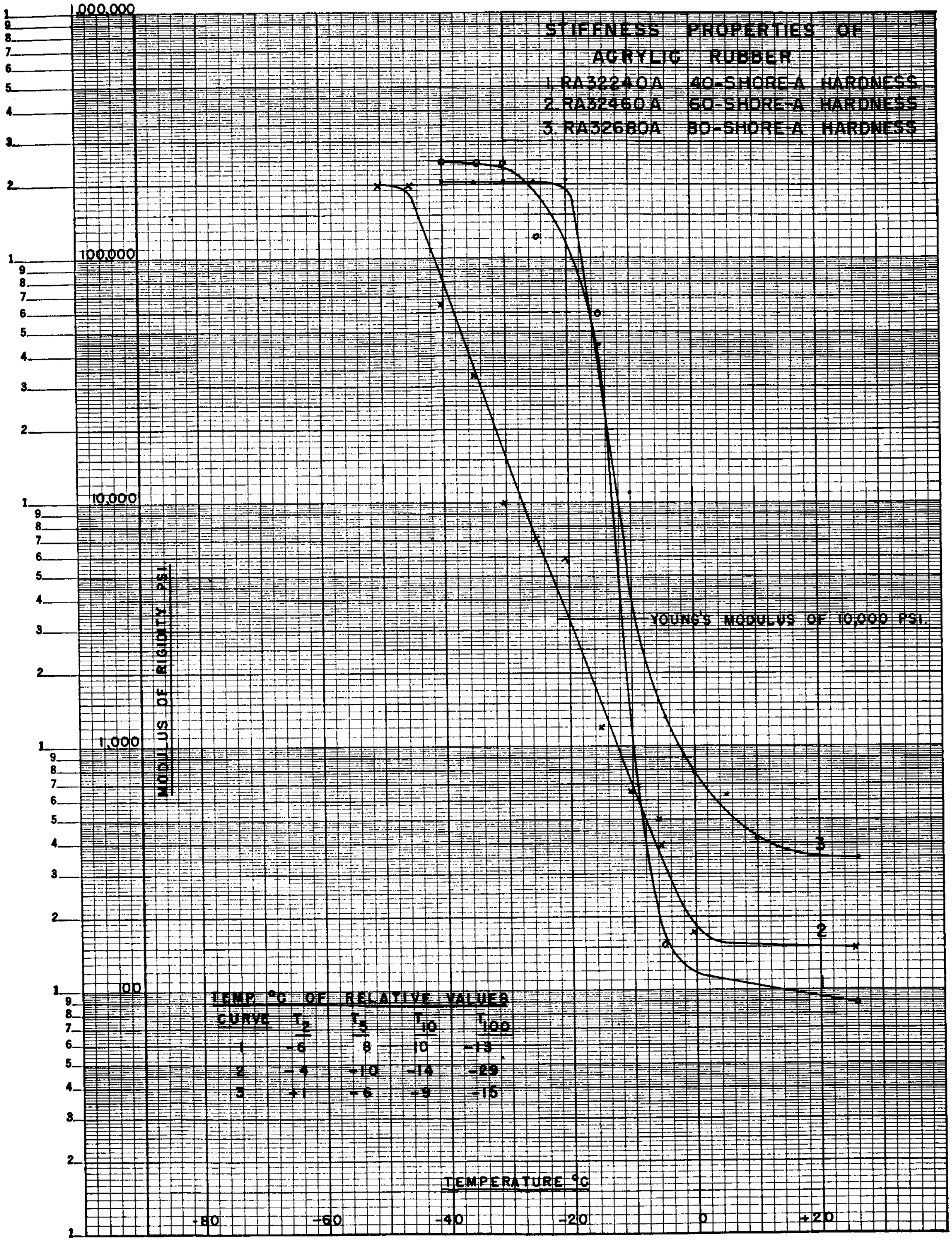


FIGURE 1. STIFFNESS PROPERTIES OF ACRYLIC RUBBER

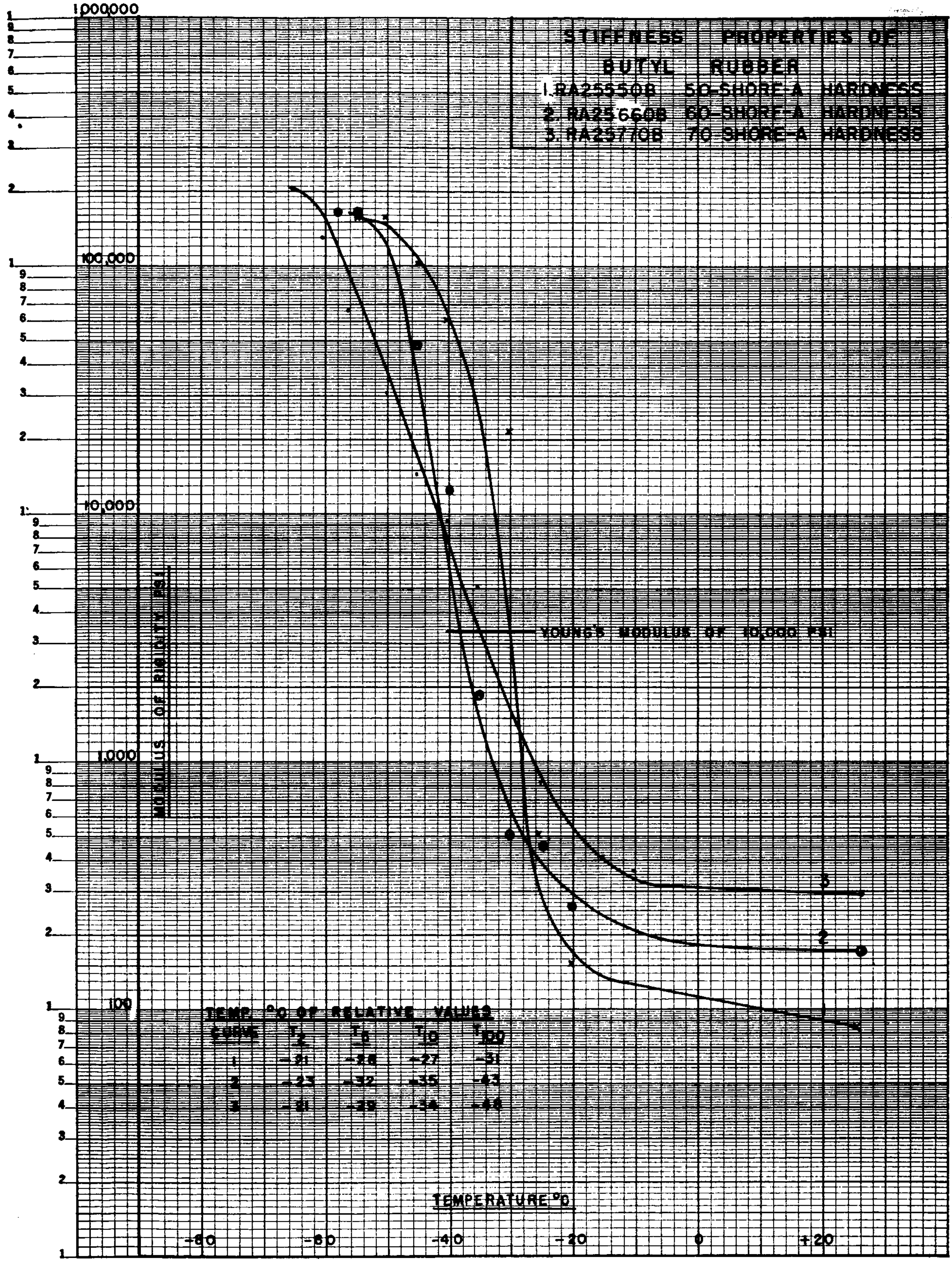


FIGURE 2. STIFFNESS PROPERTIES OF BUTYL RUBBER

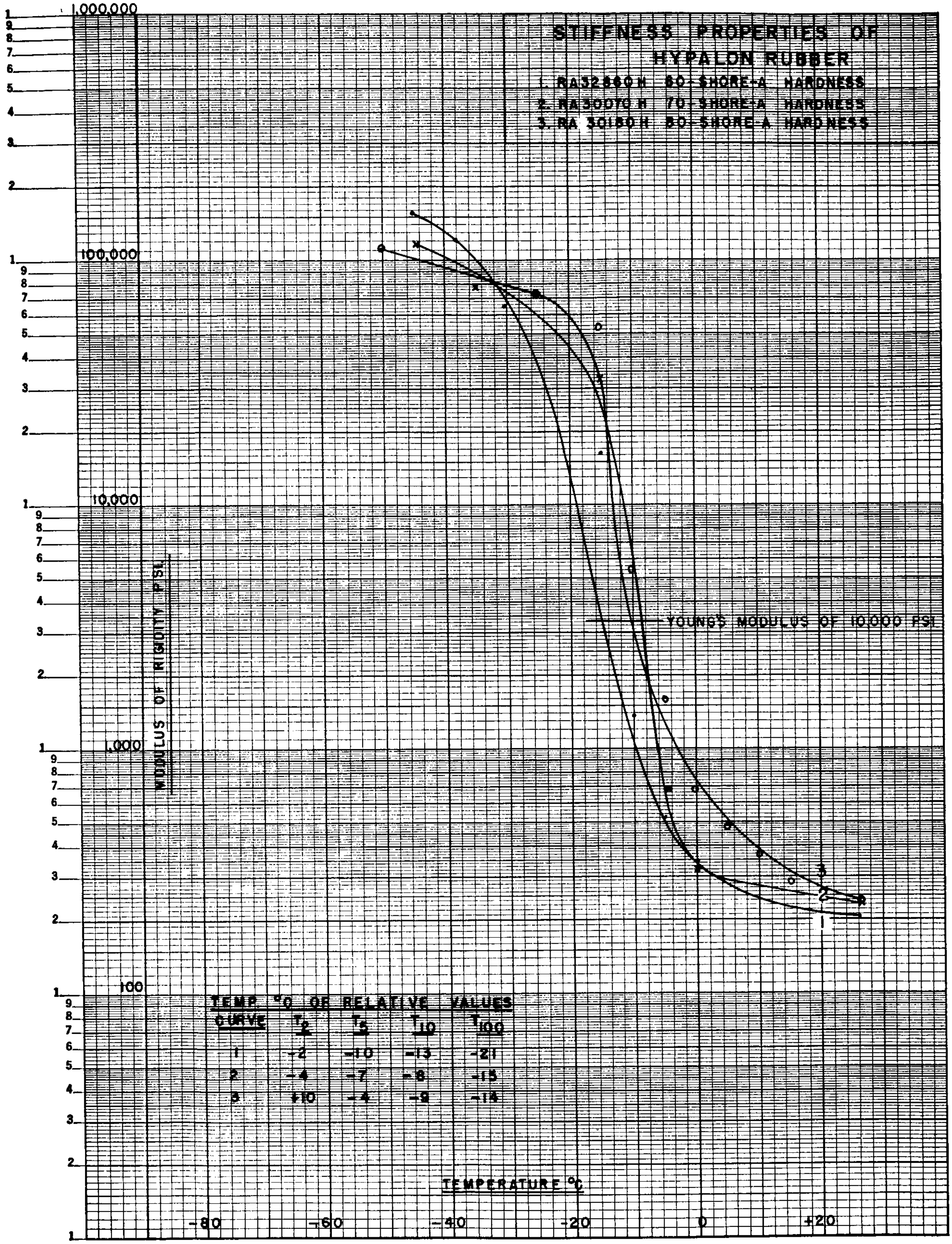


FIGURE 3. STIFFNESS PROPERTIES OF HYPALON RUBBER

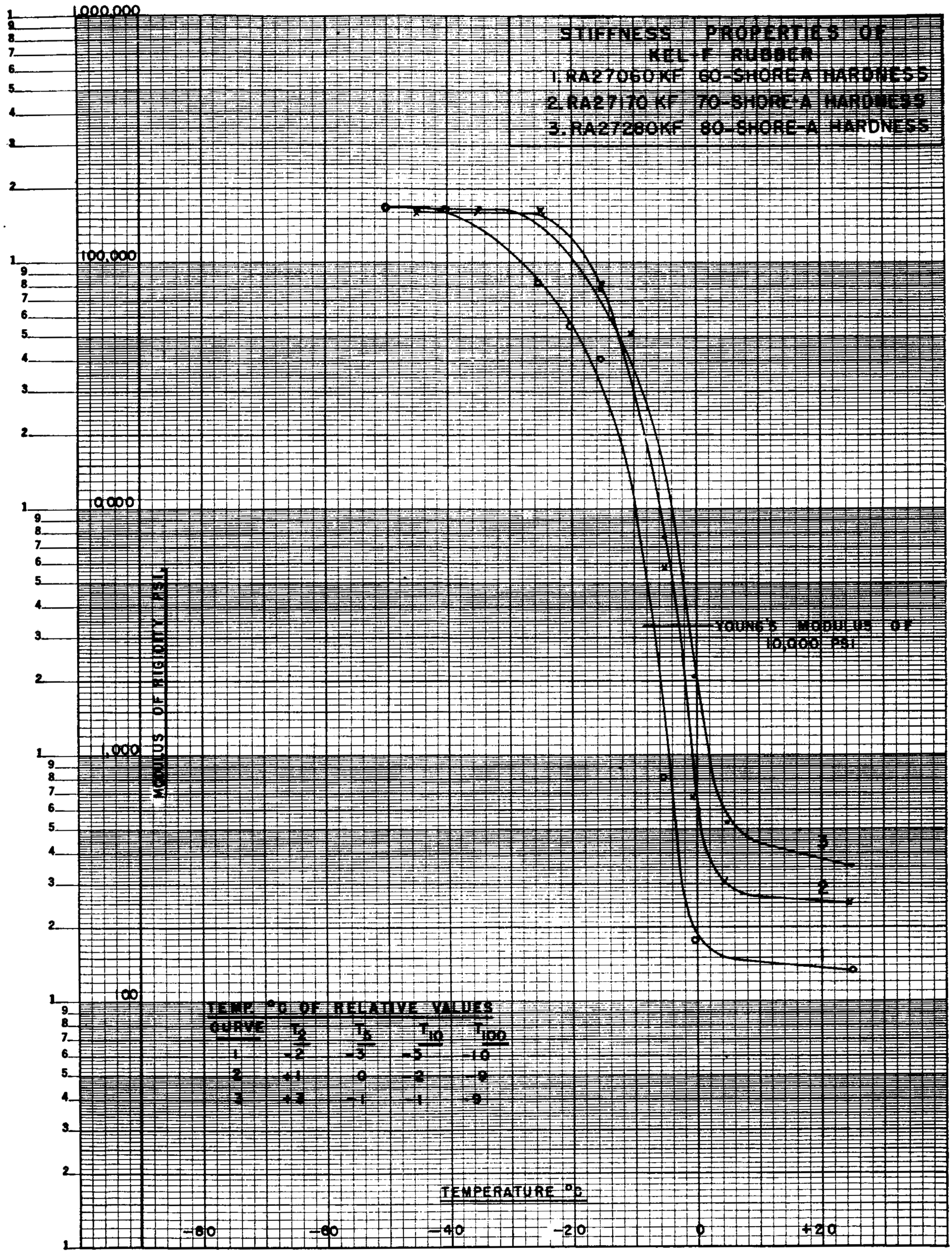


FIGURE 4. STIFFNESS PROPERTIES OF KEL-F RUBBER

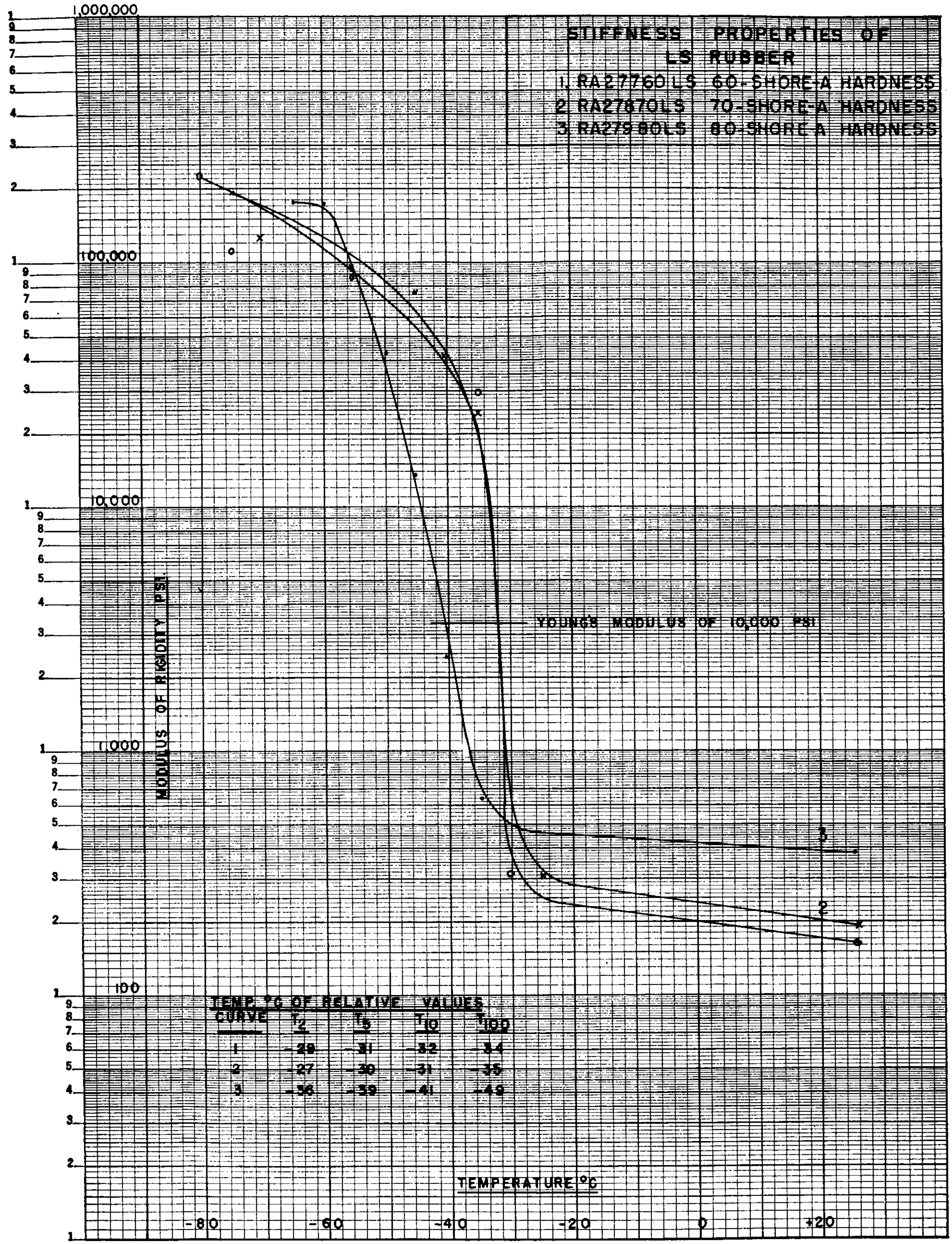


FIGURE 5. STIFFNESS PROPERTIES OF LS RUBBER

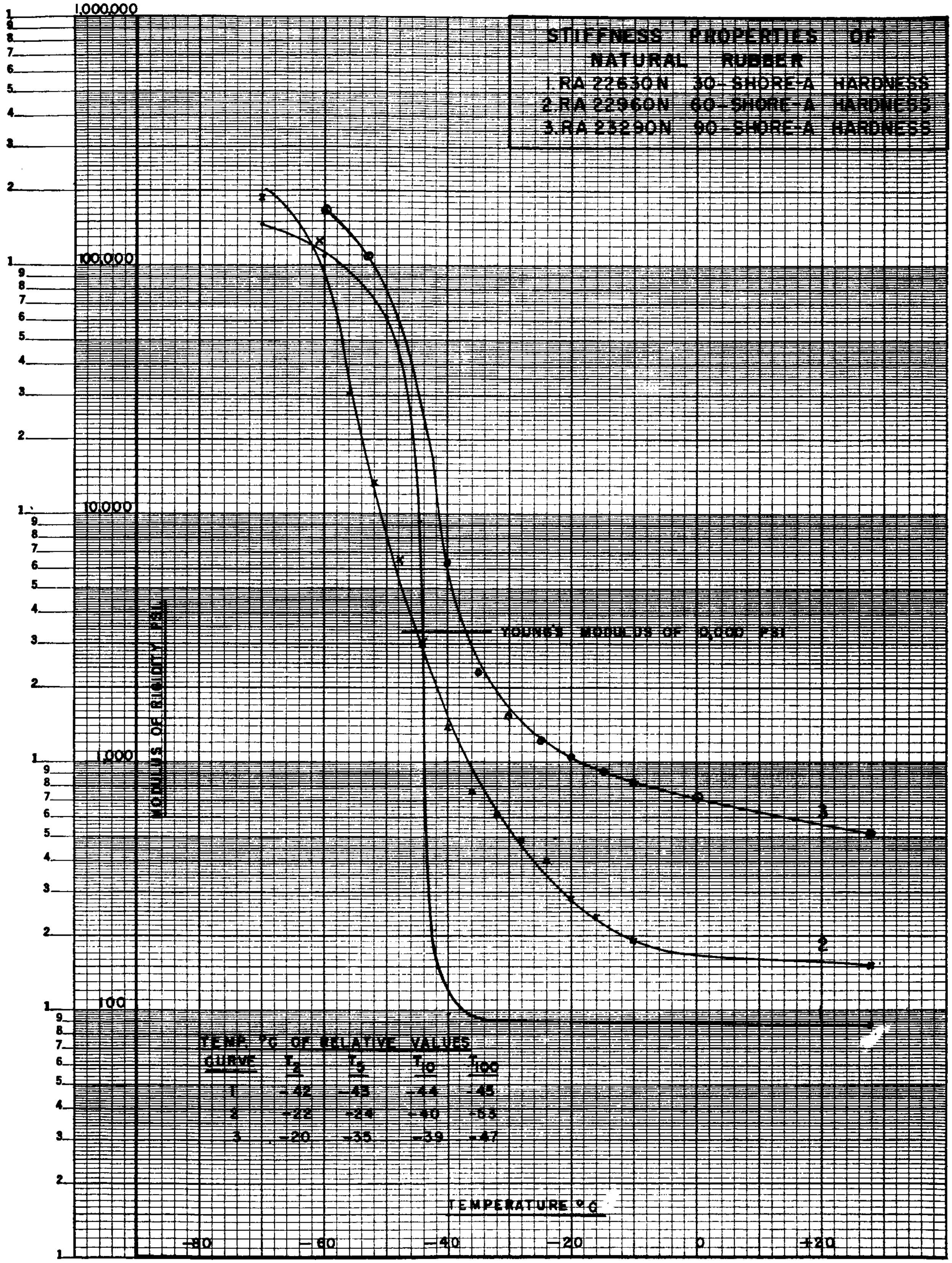


FIGURE 6. STIFFNESS PROPERTIES OF NATURAL RUBBER

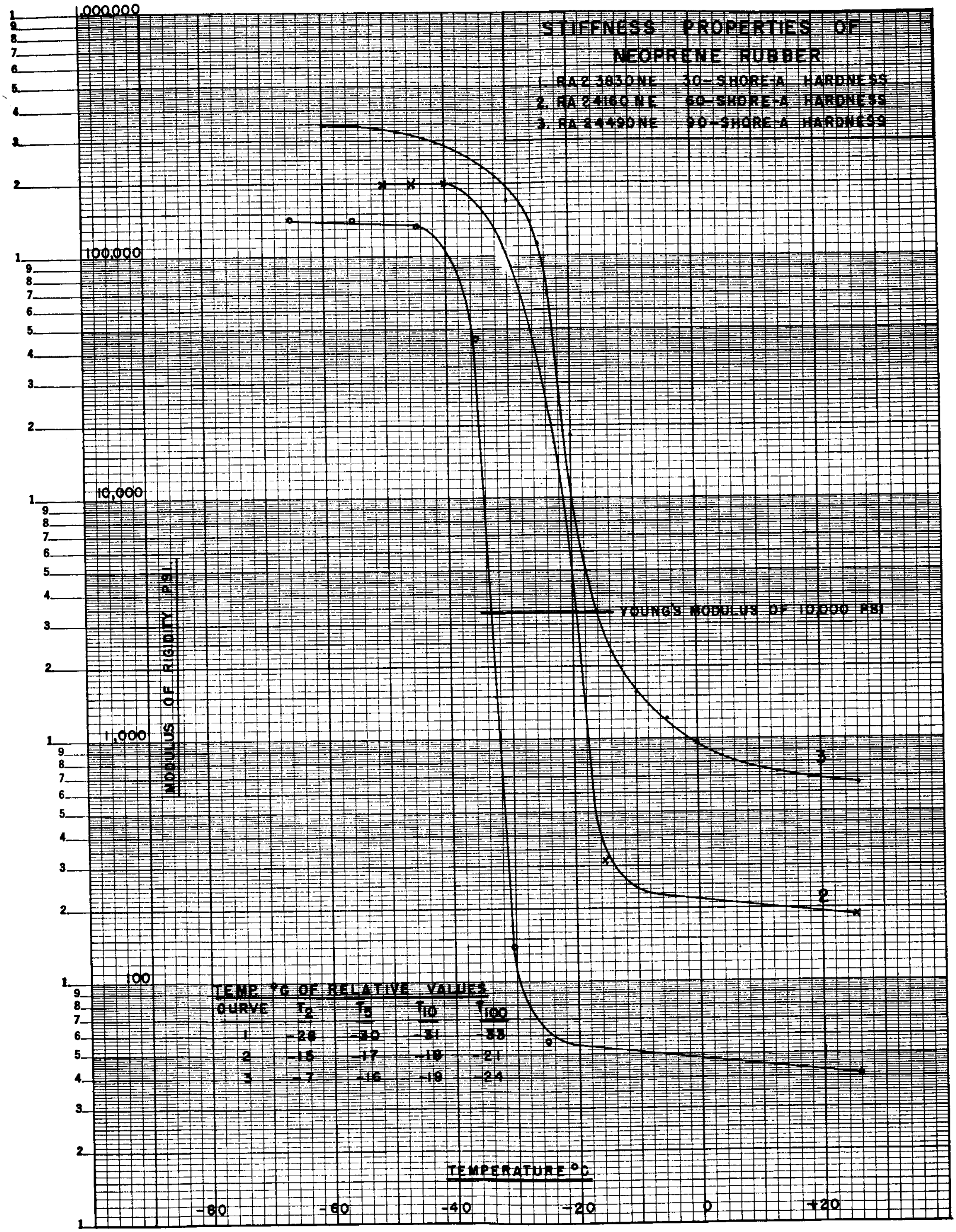


FIGURE 7. STIFFNESS PROPERTIES OF NEOPRENE RUBBER

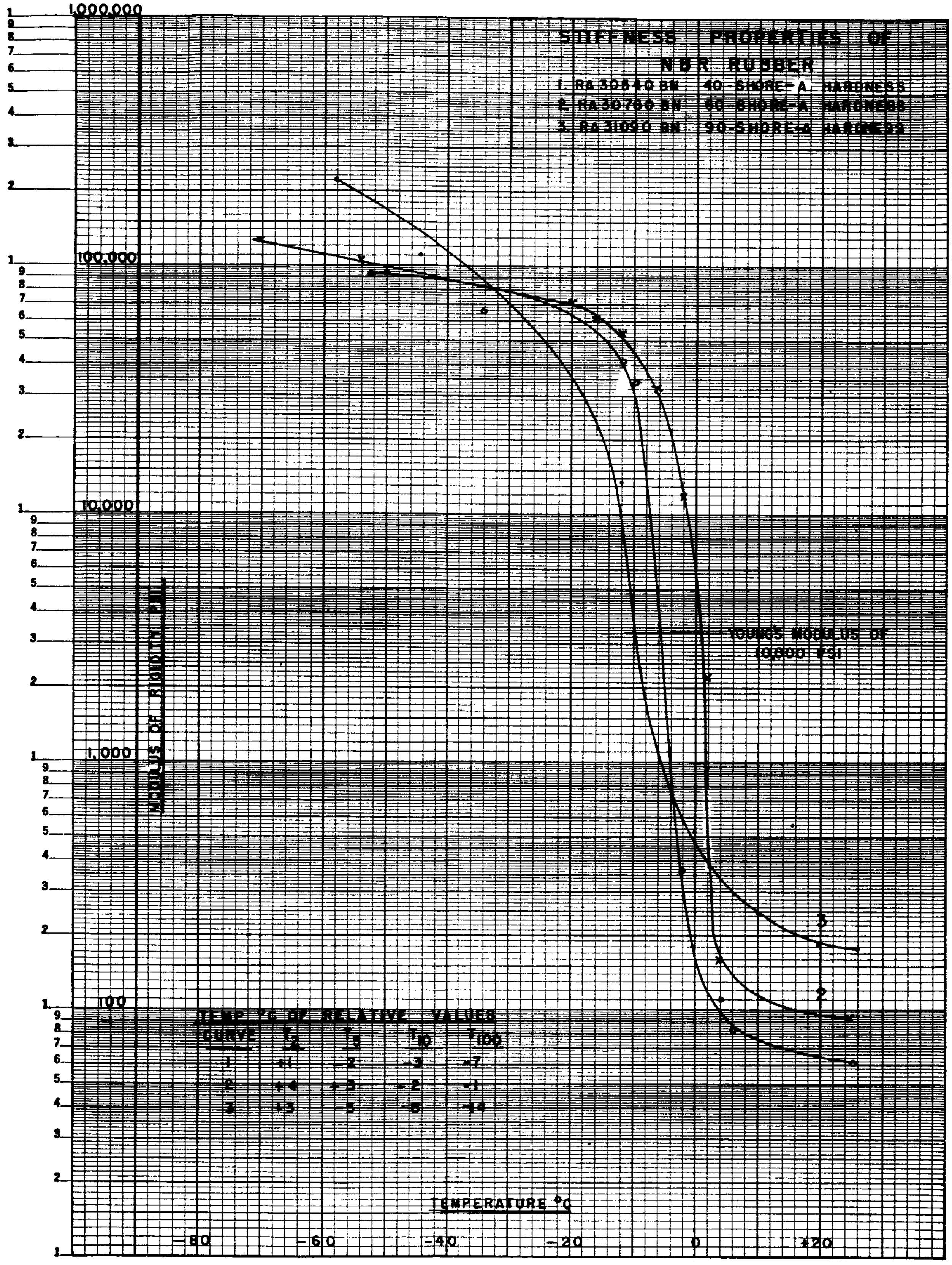


FIGURE 8. STIFFNESS PROPERTIES OF N B R RUBBER

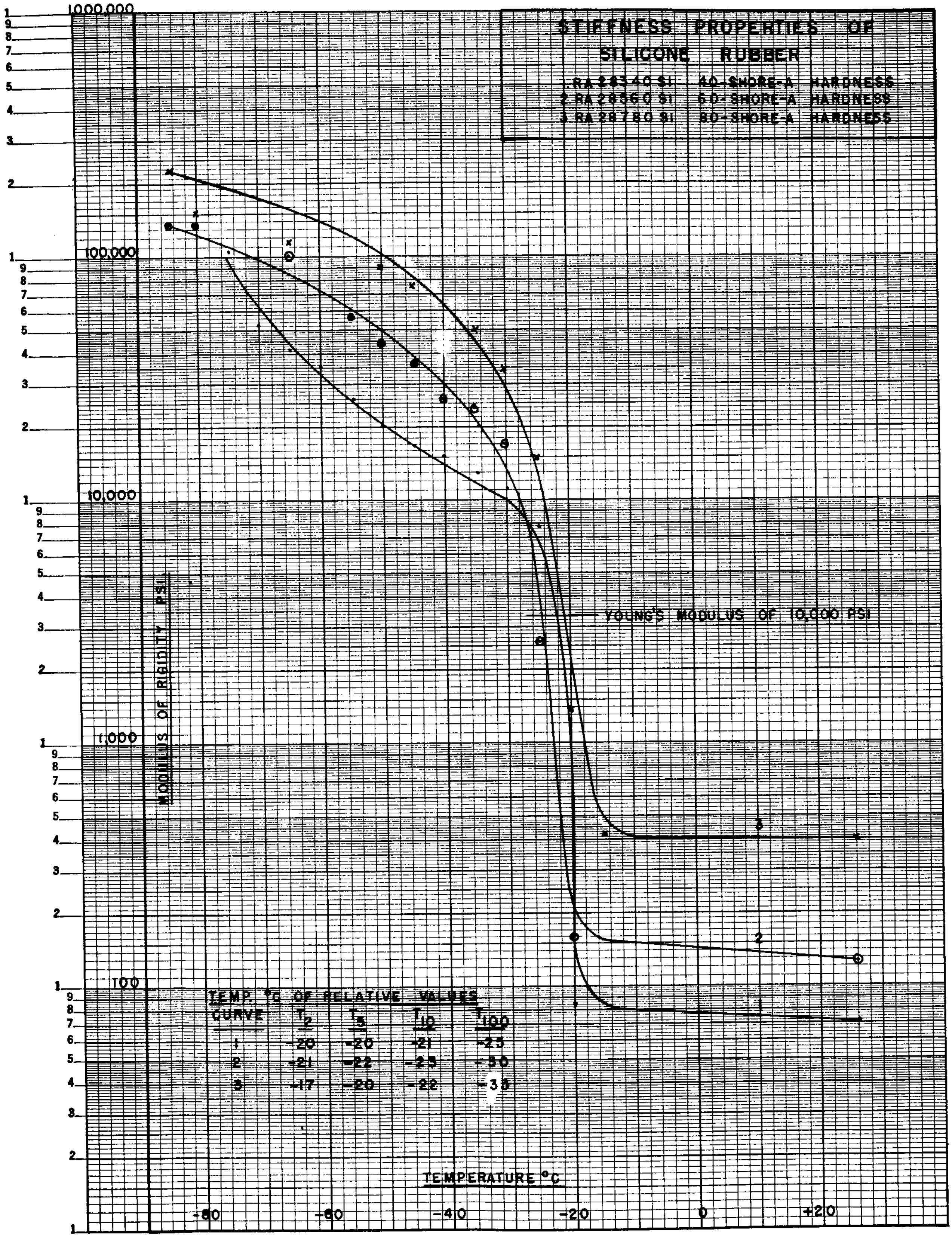


FIGURE 9. STIFFNESS PROPERTIES OF SILICONE RUBBER

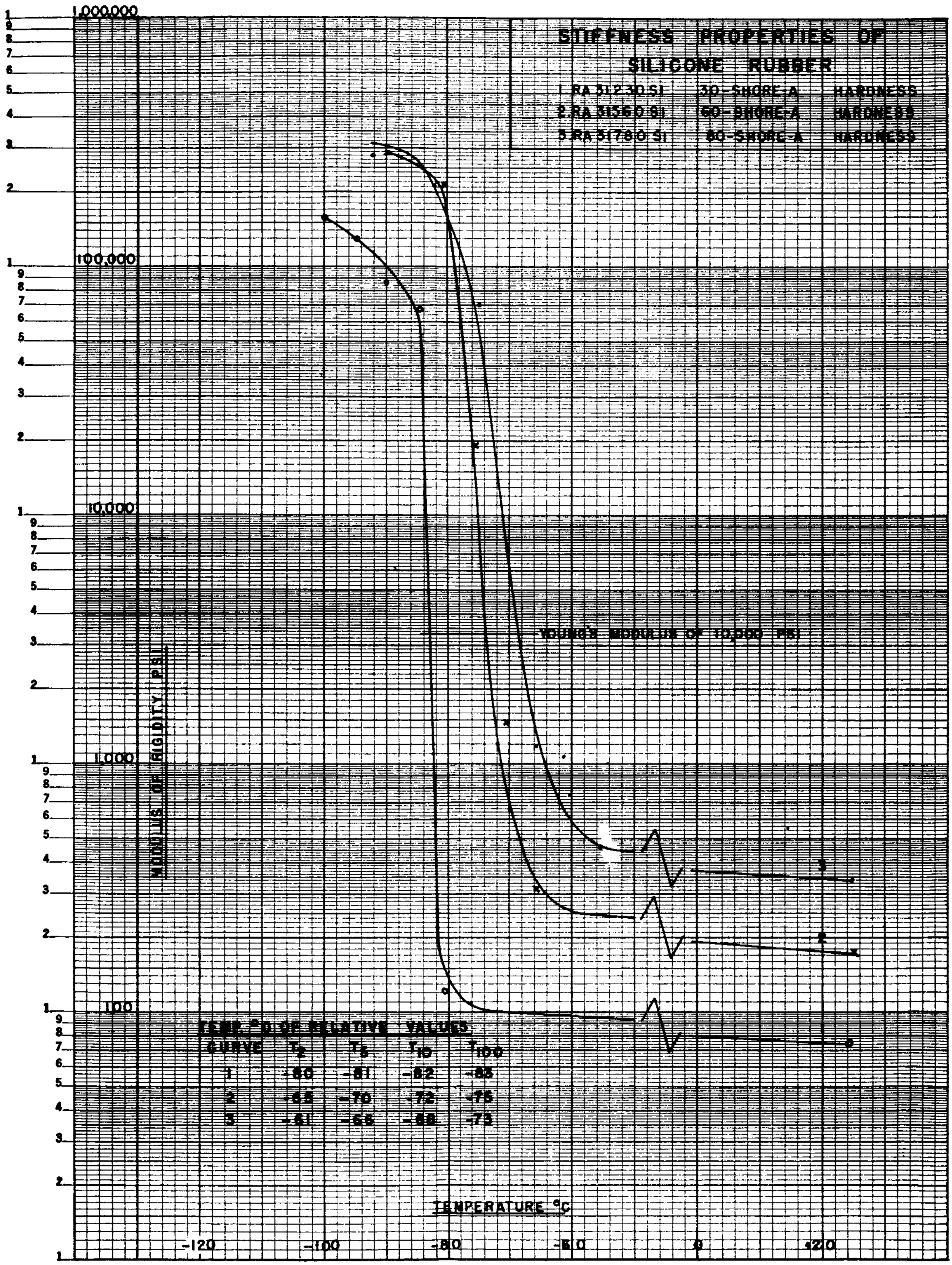


FIGURE 10. STIFFNESS PROPERTIES OF SILICONE RUBBER

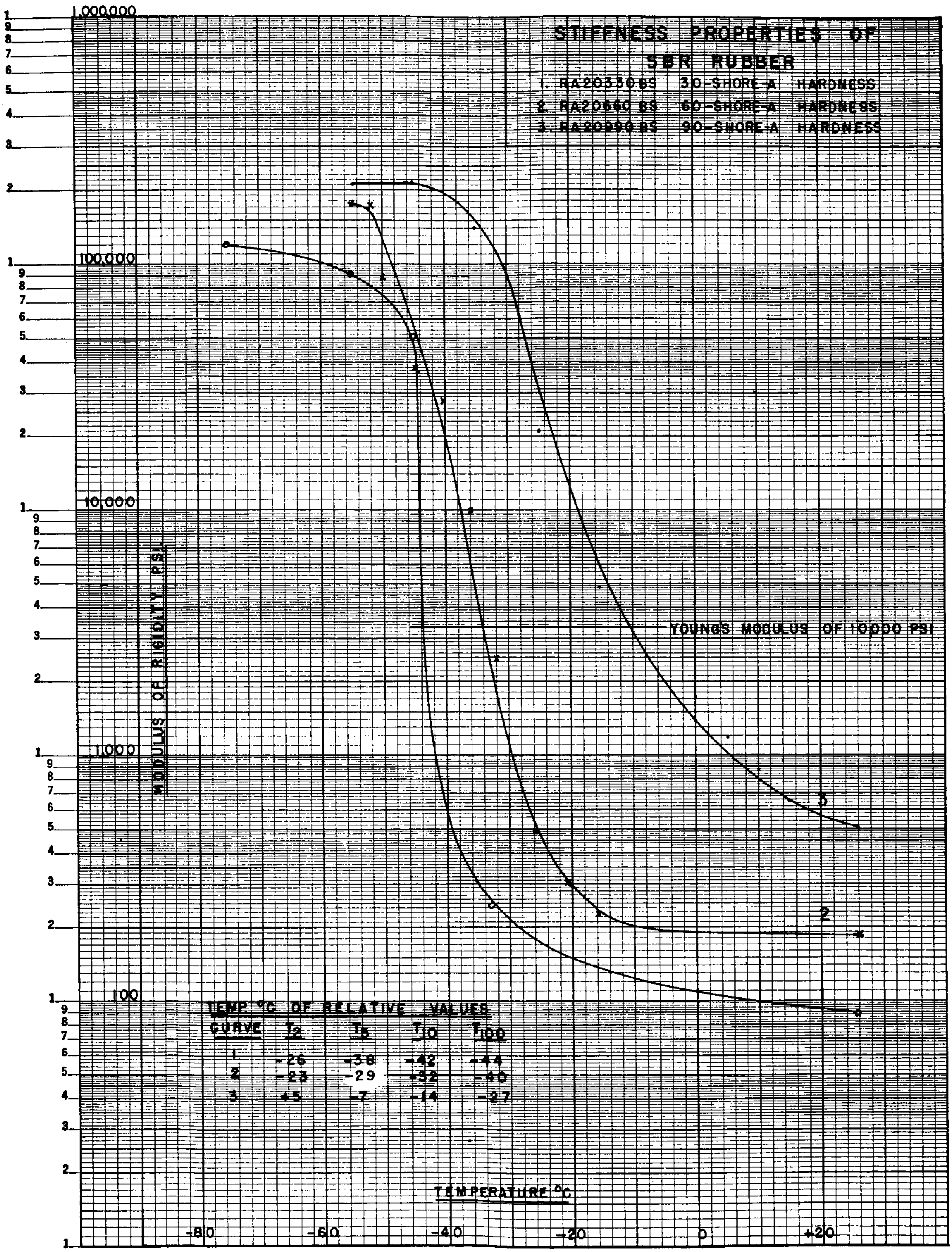


FIGURE 11. STIFFNESS PROPERTIES OF S B R RUBBER

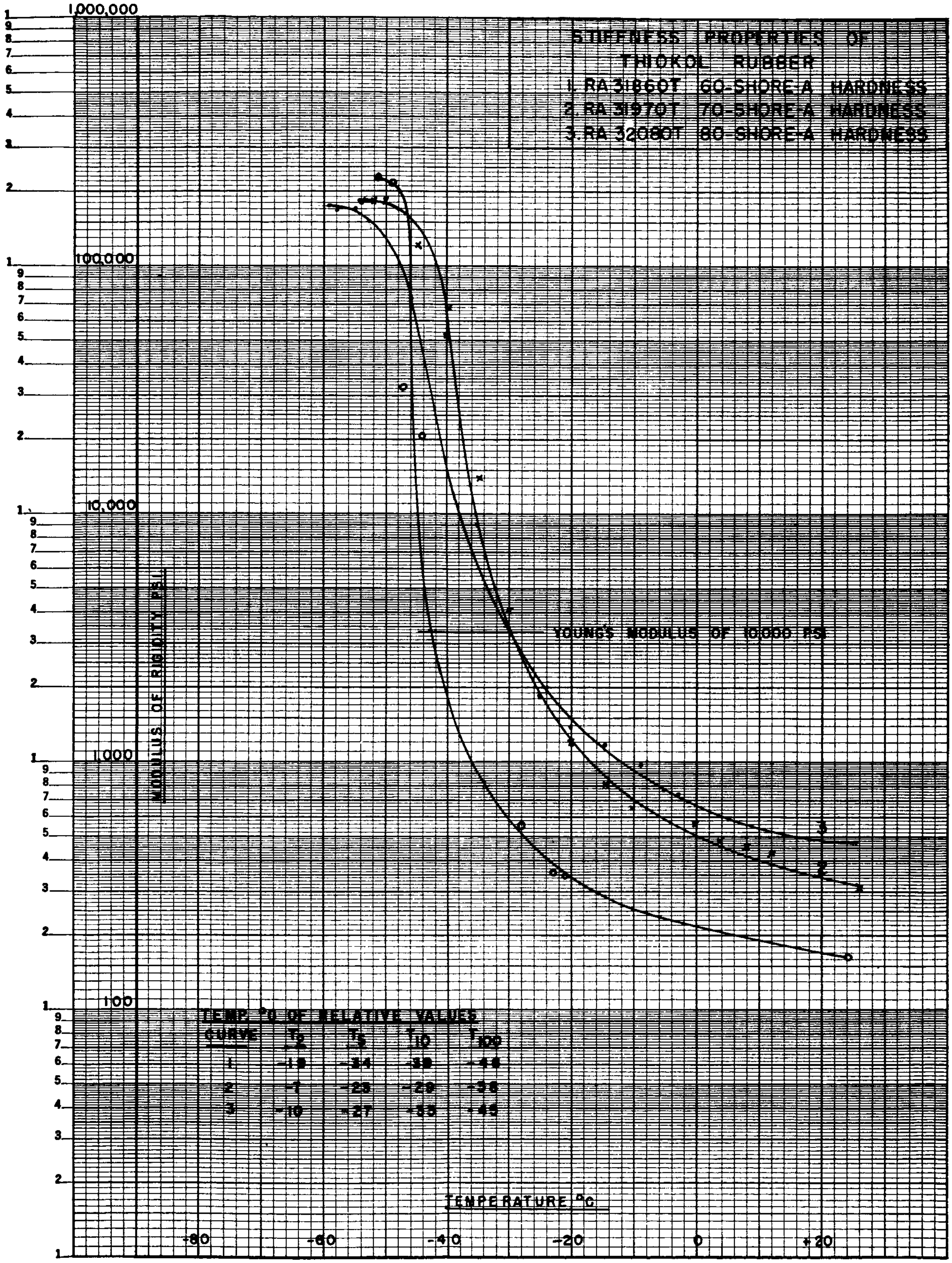


FIGURE 12. STIFFNESS PROPERTIES OF THIOKOL RUBBER

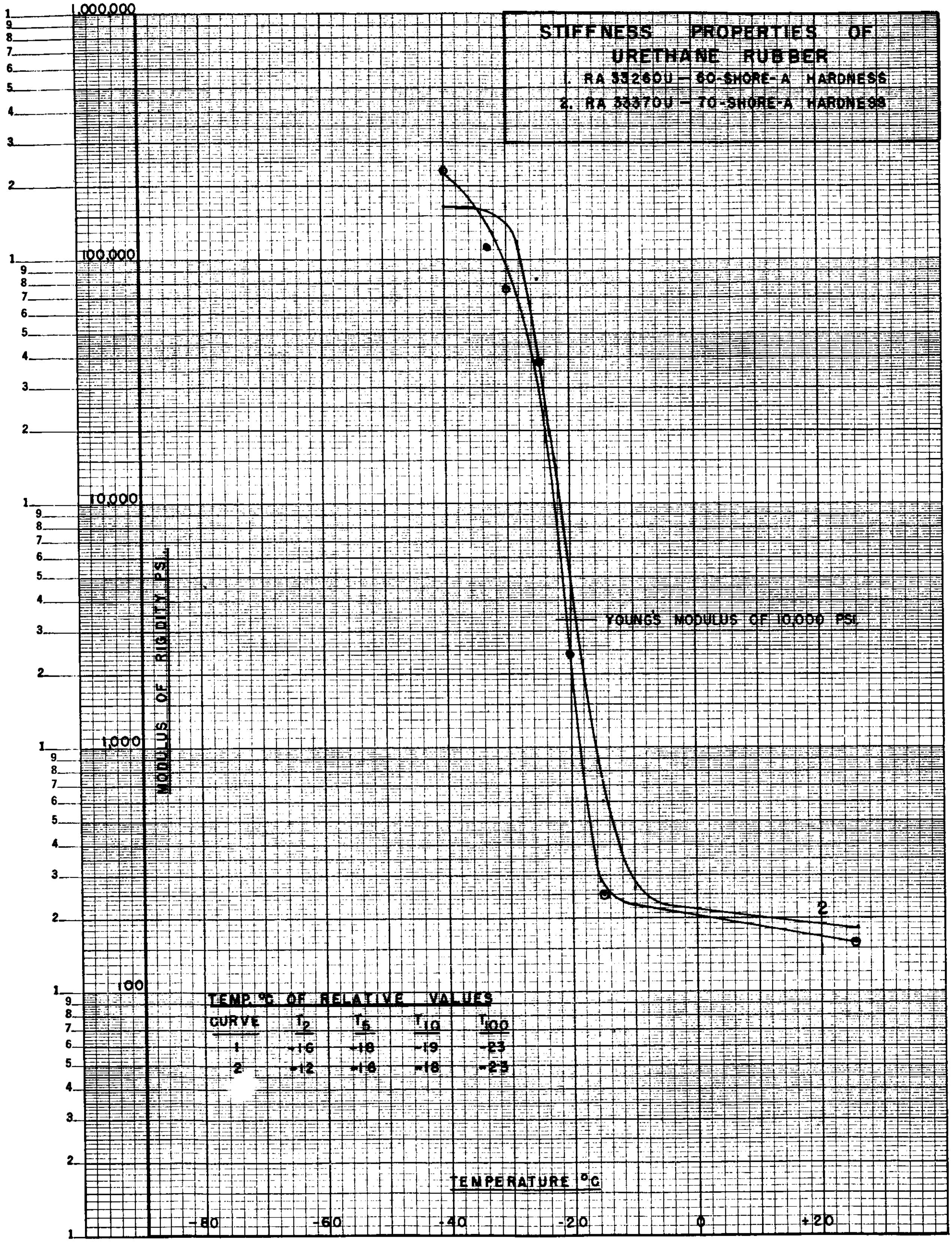
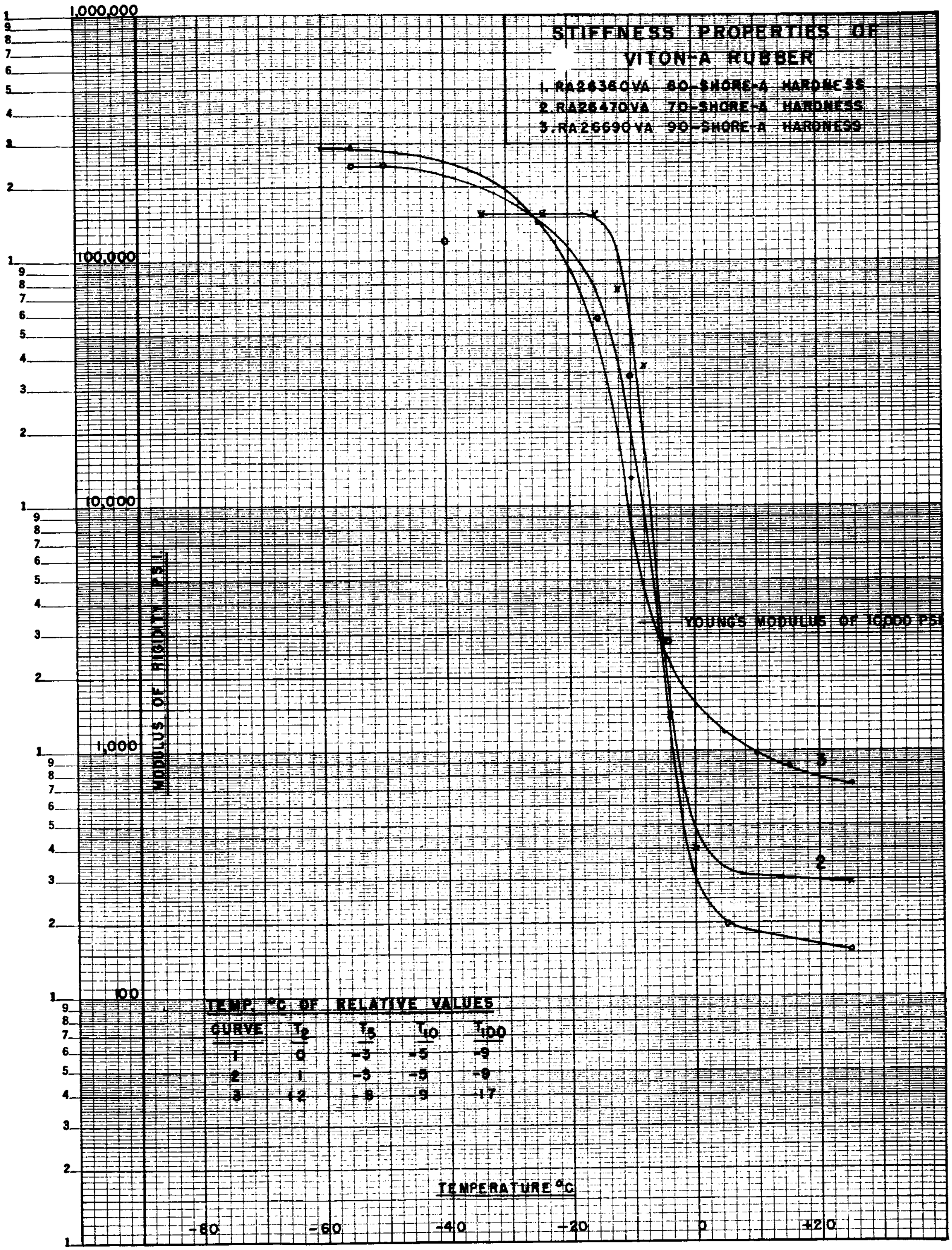


FIGURE 13. STIFFNESS PROPERTIES OF URETHANE RUBBER



CURVE	T_2	T_5	T_{10}	T_{100}
1	0	-3	-5	-9
2	1	-3	-5	-9
3	+2	6	-9	-17

FIGURE 14. STIFFNESS PROPERTIES OF VITON-A RUBBER

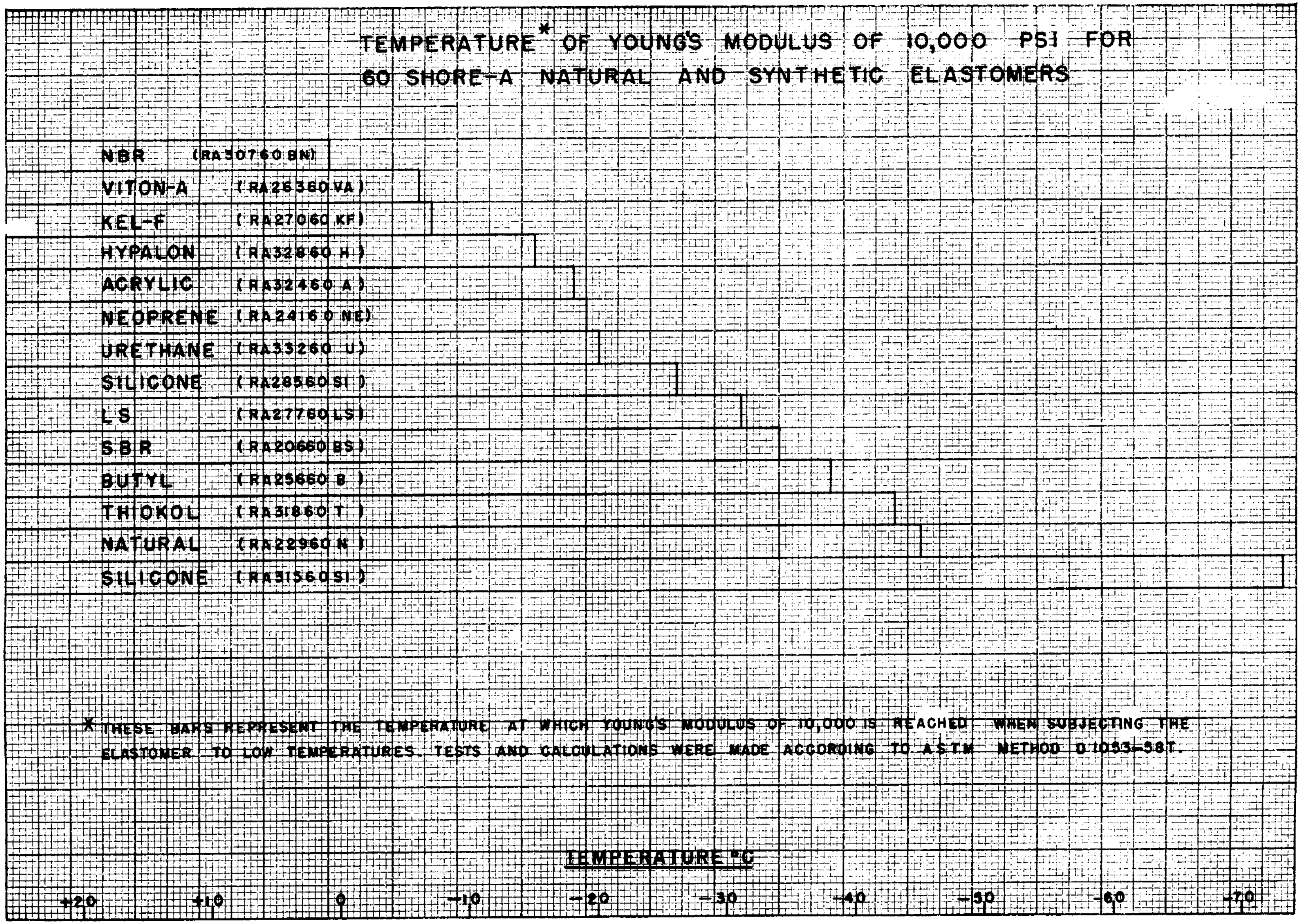


FIGURE 15. TEMPERATURE OF YOUNG'S MODULUS OF 10, 000 PSI FOR 60 SHORE-A NATURAL AND SYNTHETIC ELASTOMERS

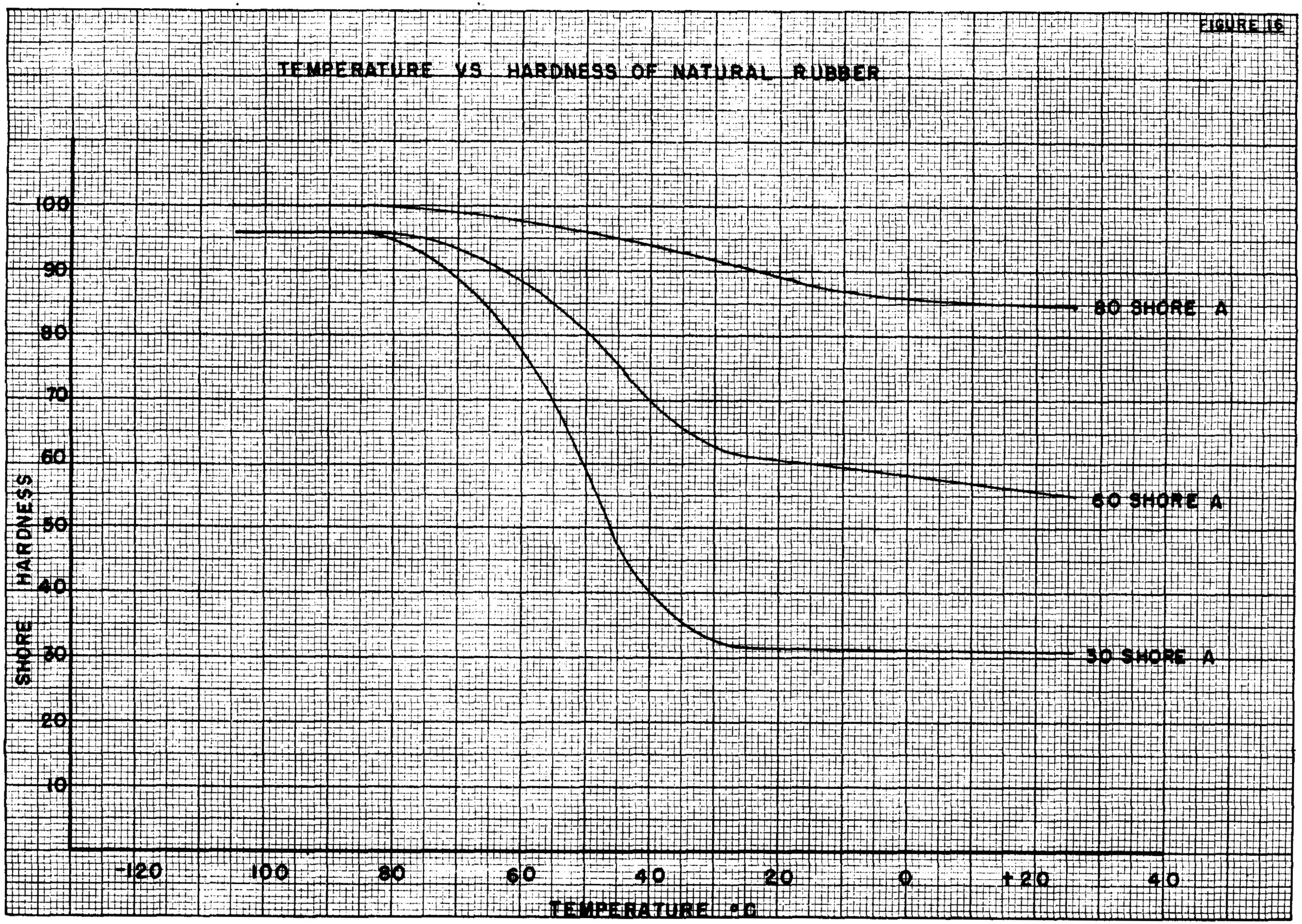


FIGURE 16. TEMPERATURE VS HARDNESS OF NATURAL RUBBER

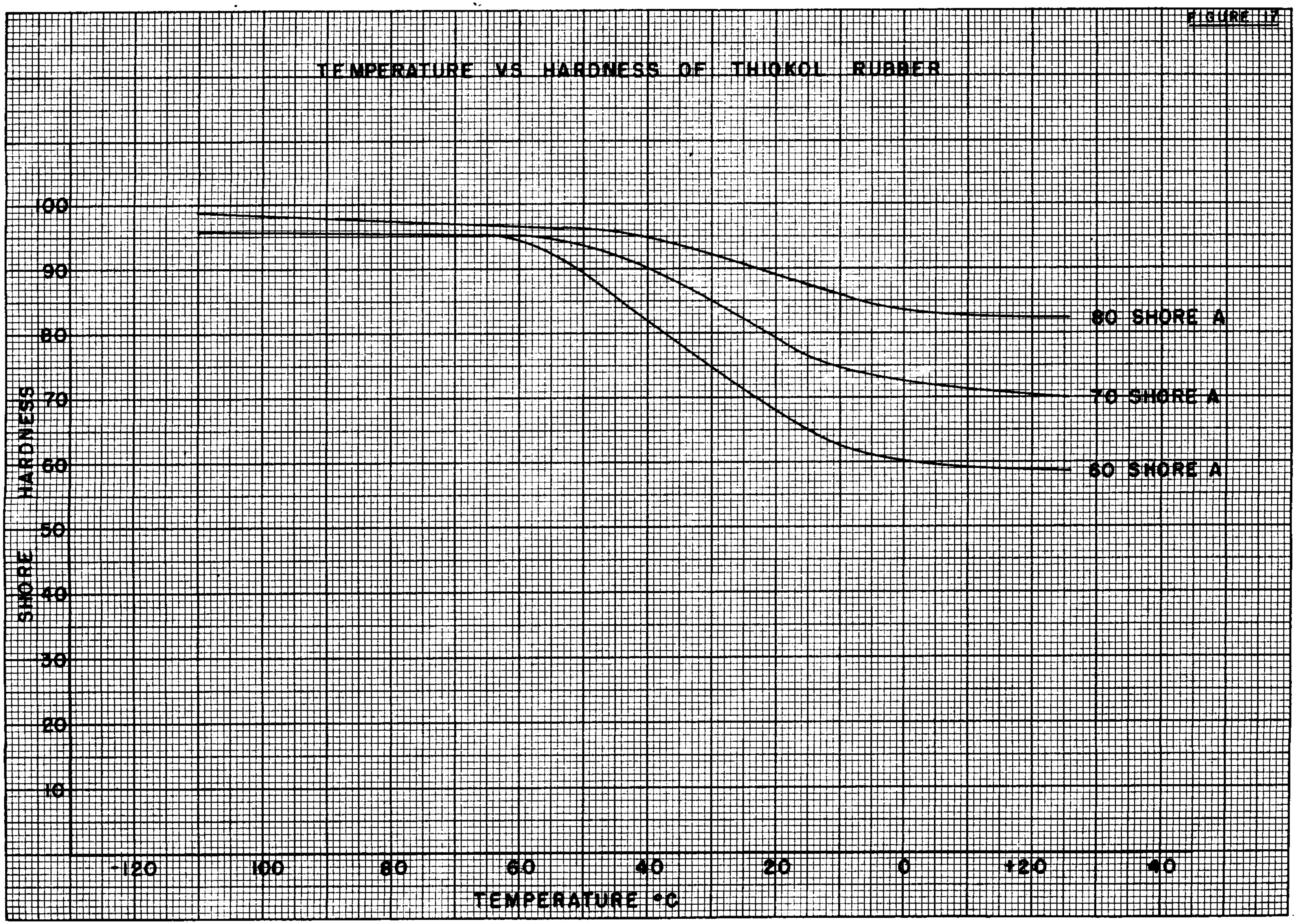


FIGURE 17. TEMPERATURE VS HARDNESS OF THIOKOL RUBBER

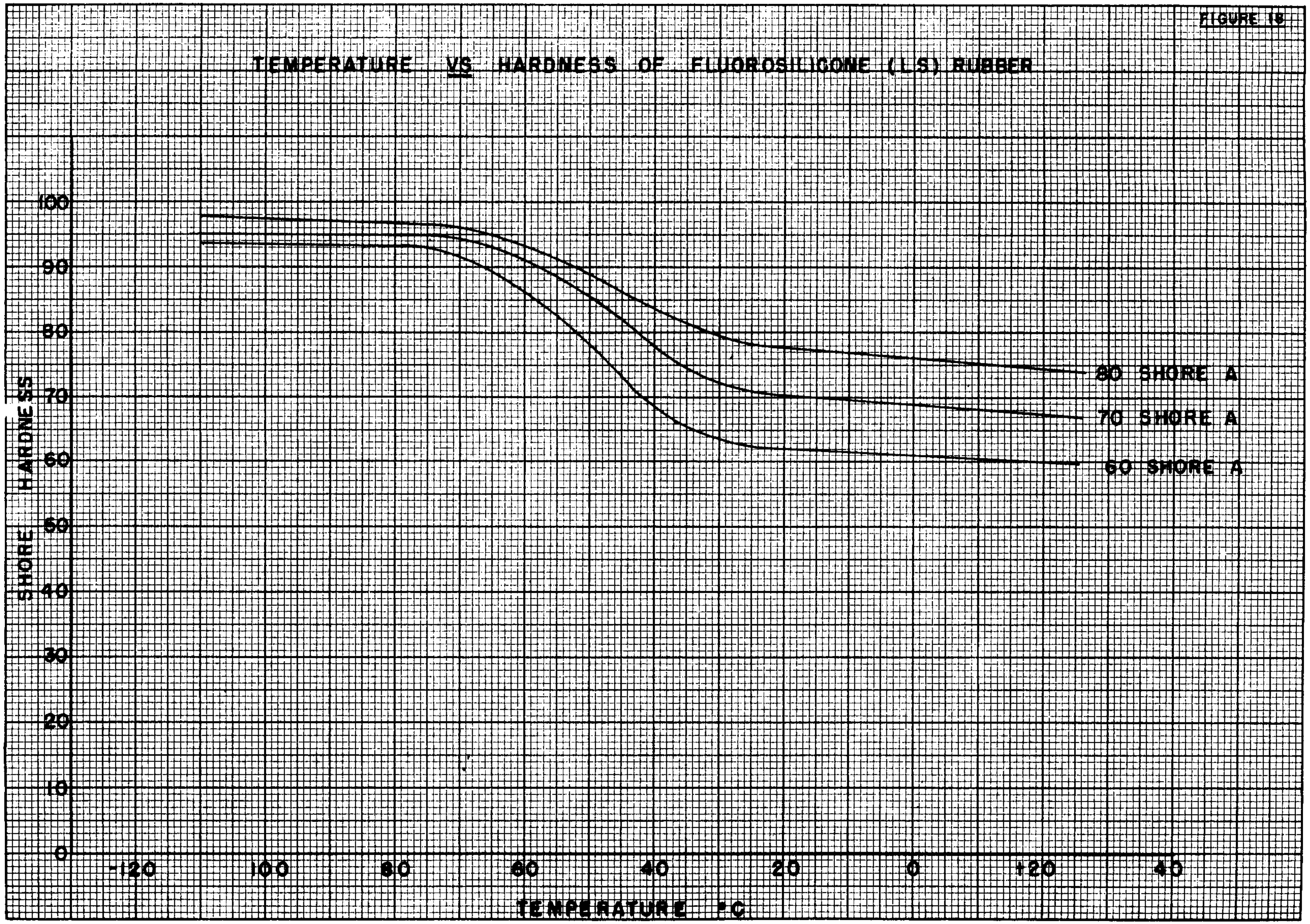


FIGURE 18. TEMPERATURE VS HARDNESS OF FLUOROSILICONE (LS) RUBBER

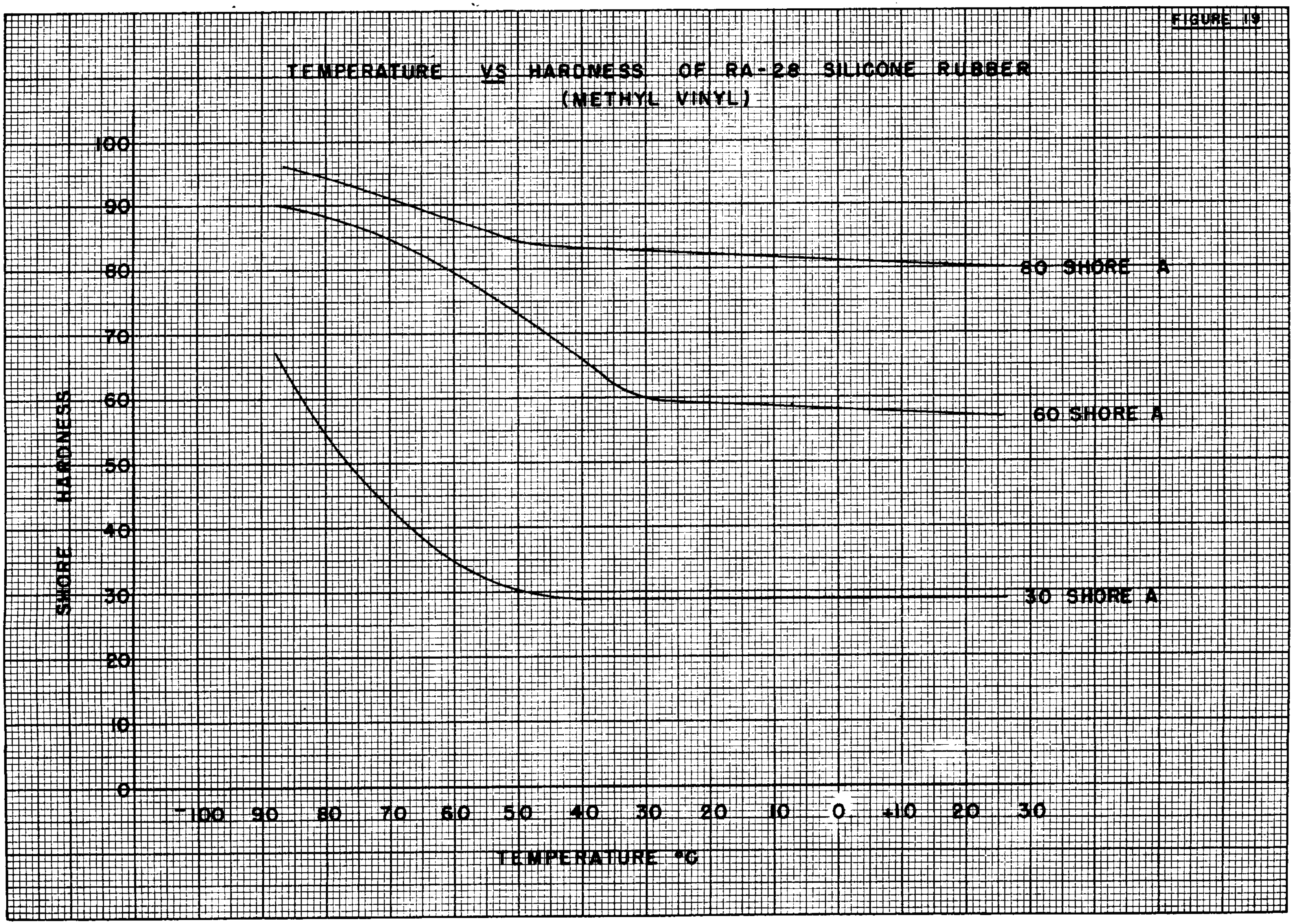


FIGURE 19. TEMPERATURE VS HARDNESS OF RA-28 SILICONE RUBBER (METHYL VINYL)

September 21, 1964 APPROVAL TM X- 53137

LOW-TEMPERATURE ELASTIC BEHAVIOR OF FOURTEEN COMPOUNDED ELASTOMERS

By

C. D. Hooper

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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