THE INFLUENCE OF DEGREE OF CRYSTALLINITY ON THE THERMAL CONDUCTIVITY OF NYLON 66

by

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I. INTRODUCTION

The invention of the wheel and bearing was man's first step toward modern technology. These simple machines still play a key role in the complex mechanical world of today, even though the principle behind them, reduction of friction, is the same as it was 5000 years ago. Modern technology has improved details of design, precision of manufacture, lubricating media, and materials of construction. Of particular interest in recent years has been the application of materials with good antifriction characteristics but poor structural strength to bearings by utilizing a thin layer of such materials held in a strong sleeve.

One material recently used to large extent for bearing sleeve linings is nylon. Nylon is used in a wide range of bearing applications, from marine bearings to baby carriage bearings, as well as for gears and thread guides in textile spinning. Although ordinarily thought of as a textile fiber, nylon is commercially available in massive form as well, in which form it may be called a plastic. Its unusual hardness and toughness as well as its low coefficient of friction make it suitable as a bearing material in massive form. One drawback of nylon bearings is that nylon is a poor conductor of heat compared to the bearing metals. Nylon bearings tend to overheat in spots, and when this happens the material expands and softens so that the bearing freezes to the shaft.

There is a general principle which suggests a way of increasing the thermal conductivity of nylon. It is that the thermal conductivity of a substance in crystalline form is higher than that of the same substance in amorphous form. Since nylon is a mixture of crystalline and amorphous phases, an increase in the proportion of crystalline material should result in an increase in the thermal conductivity. The amount of crystalline material can be increased by annealing at a temperature below the melting point and by cold rolling. Both operations are commercially feasible. The expected increase in thermal conductivity would make possible the use of nylon bearings in many installations where it would be otherwise unsuitable. This investigation was undertaken to study these possibilities.

The purpose of this investigation was to determine the extent to which the degree of crystallinity of nylon can be increased by cold-rolling and annealing, and the change in thermal conductivity resulting from these treatments.

II. LITERATURE REVIEW

Survey of Plastic Bearing Materials

Schwartz[79] has given a practical criterion for judging bearing materials. From the user's point of view it is performance which counts--usability under adverse weather and loading conditions, durability, dependability, and low initial and maintenance costs. Tait[84] remarked that "the perfect, universal bearing material has yet to be found." Instead, the most suitable material for each application is used. Delmonte[35] stated that bearings made from plastics have their own particular applications, where they are better than metal bearings.

Properties of an Ideal Bearing. Schwartz[79] discussed the properties which an ideal bearing should have. He was speaking particularly of metallic bearings.

Modulus of Elasticity. The modulus of elasticity of a bearing material should be low so as to allow the material to deform under impact loads and to cushion the shock. More important, it should be low to allow foreign material to pass through the bearing without scoring either journal or bearing surface.

Fatigue Strength. The fatigue strength should be high so that repeated overloads do not cause failure. Fatigue is the most common cause of bearing failure. A recent trend is the use of thin sleeves of bearing material bonded to steel to provide more fatigue strength.

Melting Point. The melting point should be high enough so that there is no tendency for incipient fusion to take place at operating temperatures.

Corrosion Resistance. The corrosion resistance should be high so that acid oils and moisture will not damage the bearing. Corrosion is a serious difficulty for metallic bearings.

Compressive Strength. The compressive strength should be high enough so that the bearing material will not extrude under load. However, all bearing metals have sufficiently high compressive strength.

Wettability. It is very important that wettability be high so that a strong, tough oil film will form. However, laboratory tests have not indicated a direct relation between wettability and toughness of the oil film.

To give a general view of the importance of good bearing materials, Schwartz[79] stated that if full fluid lubrication could be maintained whenever the bearing was in use, inferior bearing materials would do. But under adverse operating conditions the best bearing materials must be used to offset the trouble encountered with poor lubrication.

Nylon as a Bearing Material. A comparison of the properties of nylon and babbit metal is given in Table I. Nylon is better than babbit metal (more like the ideal material) in modulus of elasticity, fatigue strength, and corrosion resistance. It is about the same in coefficient of friction and compressive strength. Data for wettability are not available. The allowable pressure on bearings depends upon the use of the bearing, but Karelitz[163] gives some allowable pressures for metallic bearings varying from 45 to 1800 pounds per square inch. Akin[1] in performance tests on plain nylon bearings found load limits of 550 pounds per square inch when running dry, 1040 pounds per square inch with water lubrication, and 1550 pounds per square inch with oil lubrication.

From Table I it is seen that nylon's most serious disadvantages are a low melting point and a low thermal conductivity. Schwartz[79] has indicated that this is a bad combination of disadvantages because of the nature of overheating of bearings. The bearings tend to overheat near the bearing surface, especially in spots where the fit is not perfect. A high conductivity is desirable so that heat may be conducted away from such spots, thus minimizing incipient fusion of the bearing material. A high conductivity is not desired for the purpose of conducting heat to the surroundings when flowing lubricant is used; the actual removal of heat from the bearing is then the function of the stream of lubricant.

TABLE I

Properties of Bearing Materials

	Modulus of elasticity, lb/sq in.	Fatigue strength	Melting point, °F	Corrosion resistance	Compressive strength, lb/sq in.	Thermal Conductivity, Btu/hr-sq ft-°F/ft	Static coefficient of friction against steel	Dynamic coefficient of friction - steel
Ideal Material[f]	low	high	medium	high	medium	high	low	low
White metal	12×10^6[a]	medium[f]	500-800[c]	medium[f]	2800-4400[c,j]	2.97	0.07-0.15[c,k]; 0.15-0.30[c,l]	0.005-0.01[c,k]
Nylon[i]	400×10^3[a,g]	high[a]	480[a]	excellent[a]	4900[a,h]	0.150	0.15[b,l]	0.04-0.2[b,l]

[a] DuPont Molding Powder, E. I. DuPont de Nemours Co., Arlington, New Jersey, 1950.

[b] Akin, R. B.: Nylon as a Bearing Material, India Rubber World, 120, 467-468 (1948).

[c] Smith, C. S.: "Mechanical Engineers' Handbook," (L. S. Marks, Editor), p. 668. McGraw-Hill Book Co., New York, N. Y., 1941. 4 ed.

[d] Seeley, F. B.: "Resistance of Materials," p. 25. John Wiley and Sons, New York, N. Y., 1947. 3 ed. Value quoted is for zinc metal.

[e] Tichvinski, L. M.: Properties and Performance of Plastic Bearing Materials, Mod. Plastics, 17, 5-54 (1940).

[f] Schwartz, C. E.: "Sleeve Bearing Materials," (R. W. Dayton, Editor), pp. 23-34. American Society for Metals, Cleveland, O., 1949. 1 ed.

[g] At 77 °F.

[h] At one per cent deformation.

[i] DuPont Formula FM10001.

[j] At 0.125 per cent deformation and 68 °F.

[k] Well-lubricated.

[l] Dry.

Tichvinski[86] stated that the Westinghouse Company developed one formulation of its graphited "Micarta" (laminated phenolic resin) to provide a plastic bearing material with higher thermal conductivity. He said that further increasing of the conductivity would be desireable, but it is not possible to approach the conductivity of the white metals.

Application of Bearings of Plastic Materials. Delmonte[35] described some applications where plastic bearings are superior to metals. Among them are steel rolling mills, where heavy loads and shocks are hard on bearings. Plastic bearings outlasted metal ones many times in such mills. For marine propeller-shaft bearings, plastics can stand the vibrating load and the corrosive action of the sea water. Large bearings can be made more cheaply from laminated phenolic resin than from any other material.

Comparison of Nylon and Phenolic Bearing Materials. The phenolic bearing materials are widely used, according to Delmonte[35], while use of nylon is only just beginning. Frequent news items[86,75], however, testify to the widespread interest in nylon bearings.

Nylon has several advantages over the laminated phenolics. Delmonte[35] said that its coefficient of friction is lower and its shock resistance is higher. In practice, phenolics are not run above 250 °F, while the duPont Company[67] reported that nylon bearings may be used at temperatures up to 325 °F. Nylon is chemically resistant to more substances than phenolic resins, being attacked or dissolved only by meta-cresol, formic acid, and molten phenol. It is not swelled by water as much as the laminated phenolics. It will

not impart odor or taste to foods, and is used in food handling machinery. Small bearings can be made more cheaply from nylon than from laminated phenolic resins since the nylon can be injection molded. For such small bearings, and where light loads are used, no lubrication is necessary. Nylon bearings and threadguides are a boon to the textile industry, since they are used without oil, eliminating the danger of ruining the fabric with oil. Nylon[67] bearings are usually molded from DuPont Company's formula FM10001.

Performance Tests on Nylon Bearings. Akin[1] has given data on the performance of nylon bearings. The allowable loads were found to be 550 pounds per square inch for bearings running dry, 1040 pounds per square inch with water lubrication, and 1550 pounds per square inch with oil lubrication. Certain peculiarities were noted; for example, the bearings tended to smooth as they were used, with resultant decrease in the dynamic coefficient of friction. When run in abrasive dust-laden atmosphere, the nylon surface absorbed the dust and was not worn by it.

Excessive loading resulted in overheating and seizure of the shaft by the bearing. This effect appeared to be due to the expansion of the heated plastic between its sleeve and the shaft. When the system was allowed to cool after seizure, the plastic remained stuck to the shaft, coming free from the sleeve, and was ruined. It was recommended that a larger clearance be provided for nylon than for metal bearings, and 0.003 inches was suggested.

A new design[75] for nylon bearings has been reported. A thin sheet of nylon is rolled into a cylindrical shape in the steel bearing support by press fitting or clamping methods. An expansion gap is left so that on heating, the plastic may expand laterally without closing up the space between the bearing and the shaft. This design is suitable for larger bearings than can be made by injection molding. Such a bearing is shown in Figure 1, drawn from the description of the new design.

Theory of Thermal Conduction in Non-metallic Solids

Fourier's Law. Fourier's law is a mathematical definition of thermal conductivity. It was stated by McAdams[66]:

$$dQ/d\theta = -kA(dt/dx) \qquad (1)$$

where

Q = the quantity of heat flowing, Btu

θ = the time in which heat flows, hours

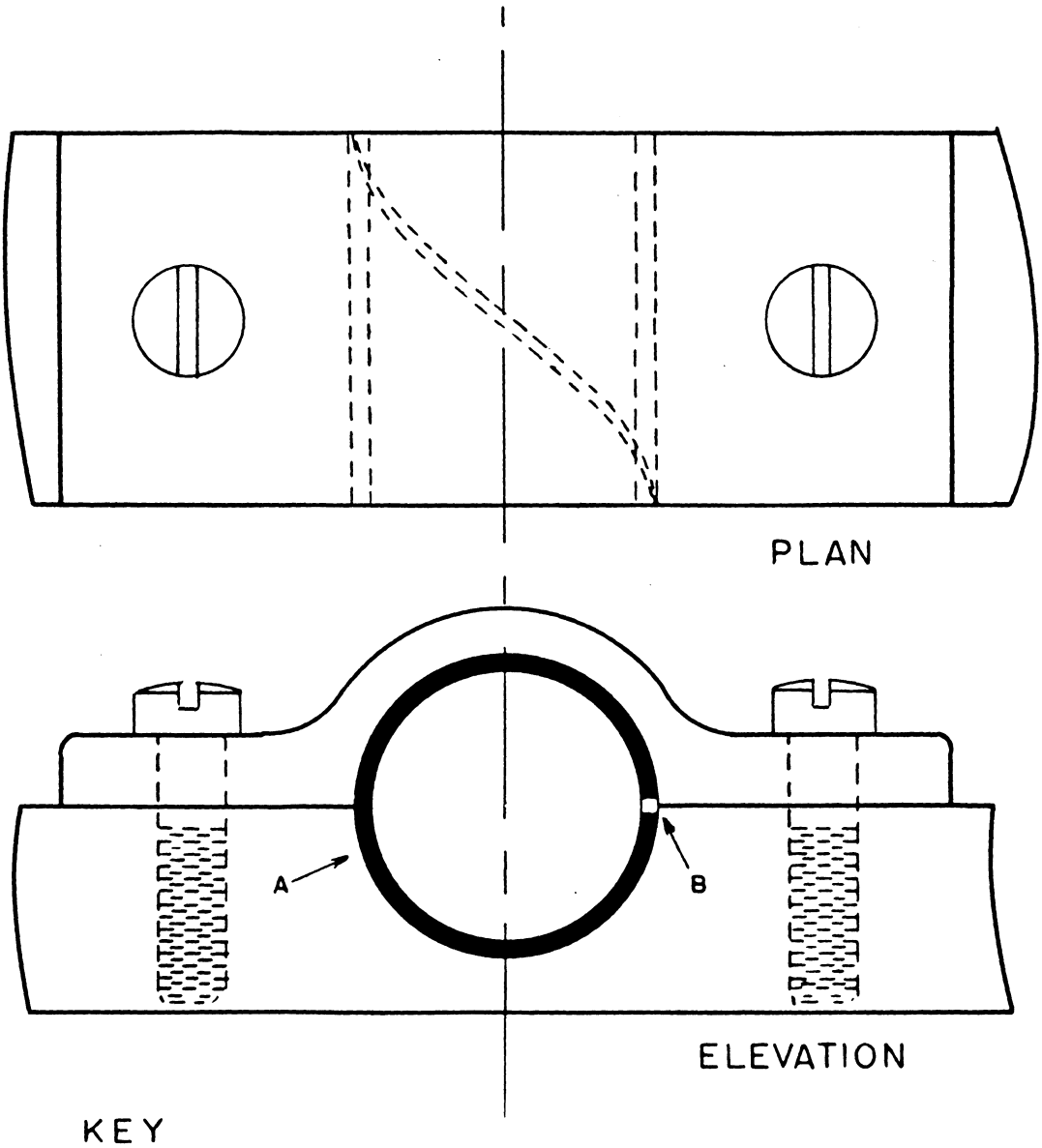
A = the area through which heat flows, taken at right angles to the direction of flow, square feet

t = temperature, ^{o}F

x = length of path of heat flow, feet

k = thermal conductivity, Btu per hour - square foot - ^{o}F per foot.

In words, the rate of heat flow is proportional to the area and the temperature gradient.



KEY

A- NYLON LINER

B- EXPANSION GAP

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

SLEEVE BEARING WITH NYLON LINER

SCALE: NONE
DRAWN BY RHS DATE MAR 27, 1952
CHECKED BY RHS DATE MAR 27, 1952
APPROVED BY RAF DATE MAR 27, 1952

FIGURE 1
FILE NO. 52
CASE NO. 599

Austin[4] pointed out that the Fourier equation does not give any basis for assuming a priori that k is independent of any variable. This matter must be determined by experiment. It is usual to think of k as a constant in the use of the integrated form of the equation:

$$q = \frac{A}{x} k (t_1 - t_2) \qquad (2)$$

where

q = rate of heat flow, Btu per hour.

The assumptions made in integrating are that k is independent of temperature, which is in general not true, and of heat flow, which on the basis of present evidence is substantially correct but not a proven fact. The following list gives the factors which seem likely to have an influence on thermal conductivity:

Factors Affecting Thermal Conductivity.

- Chemical Composition
  - Influence of Molecular Structure in Pure Compounds
  - Influence of Impurity in Solid Solution
- Physical Texture
  - Porosity
    - Total Void Space
    - Size and Shape of Pores
    - Size and Shape of Grains

Presence of a Vitreous or Liquid Phase

Total Amount of Phase

Distribution of Phase

Anisotropy and Directional Effects

Temperature

Pressure, Stress or Strain

Heat Flow

Thermodynamic Relation Between k and Cv. Austin[5] derived a thermodynamic relation between k and Cv, the heat capacity at constant volume of a substance, and showed that k is proportional to Cv.

Experiment showed that the relation holds as a first approximation for vitreous silica and other glasses, but it fails completely for pore-free crystalline solids. Data showing the proportionality between thermal conductivity and specific heat for vitreous silica are given in Table II.

The Crystalline and Amorphous States of Matter. Confusion will be avoided if the terms crystalline and amorphous are explained here. They refer to ideal states of matter, and real substances are usually not strictly amorphous or crystalline, according to Glasstone[49]. Solid crystals contain flaws in the regular ordering of their molecules, according to Oldham and Ubbelohde[70], and Glasstone[49] stated that even liquids exhibit some local order. That is, the molecules tend to arrange themselves in regular directions with respect to their neighbors, in the same way as molecules in crystals.

TABLE II

Data Showing Proportionality Between Thermal Conductivity and Specific Heat for Vitreous Silica

Temperature, °C	True C_p, gm-cal per gm x 10^3	k, cgs units	Ratio, C_p/k
200	227	3.50	65
400	260	4.25	61
600	275	5.00	52
800	286	5.75	50

Austin, J. B.: Factors Influencing the Thermal Conductivity of Non-metallic Materials, "Symposium on Thermal Insulating Materials," p. 6. American Society for Testing Materials, Philadelphia, Pa., 1939. 1 ed.

Because of this difficulty, Nichols[69] defined a crystalline polymer as one having a well-defined x-ray diffraction pattern. Again, from the point of view of thermal conductivity Austin[7] stated that a substance may be considered amorphous if the ratio Cp/k is approximately constant for that substance. He mentioned as an example the refractory substances composed of an aggregate of fine crystalline particles oriented at random. Such substances are silica brick, fireclay, and porous alumina brick, for which Cp/k is a constant.

Kinetic Theory of Thermal Conduction. Rehner[74] stated in 1947 that "no physical molecular theory of thermal conductivity exists at the present time." However, Debye[34] had formulated a kinetic theory of thermal conduction in non-metallic crystals in 1914.

Debye assumed that the heat is transferred not only from molecule to molecule as it is in gases, liquids, and amorphous solids, but also by a conduction of the lattice as a whole. Debye's reasoning was explained simply by Jakob[62]. According to him, the phenomenon which is observed as heat is the evidence of thermal vibrations of the molecular particles. The speed of a single vibration passing through quartz, that is the acoustic velocity, would be 15,000 to 20,000 feet per second. But the rate of heat flow is very small compared with this. It must be that some disturbances retard the passage of the thermal energy. Of this idea Bragg[25] said, "The advancing heat wave in a crystal

has to fight its way toward the cold end through a fog of waves which it produces itself."

As Austin[7] put it, Debye "considers the solid to be a system of coupled resonators in which long-wave oscillations are superimposed on the atomic or molecular motions. These 'thermoelastic' waves, which can develop properly only in crystals, have a wave length somewhat greater than the distance between lattice points, are not purely harmonic, and may be disturbed by the heat flow itself. They are also scattered, distorted, or disturbed by imperfections in the lattice and suffer a decrease in intensity on this account."

Jakob[62] further stated that each bond in the crystal is an oscillator with very high natural frequency. For crystalline silica bonds the frequency is 30×10^{12} vibrations per second. There are 55×10^{9} oscillators per centimeter, but the rate of heat flow is only 0.02 centimeters per second. Hence the oscillators appear to be slightly damped or loosely coupled. They are in the right position for the maximum amplitude transfer only once in a million times.

The Debye Equation. The Debye[34] equation derived from the assumptions in the previous section is:

$$k = \frac{1}{4} l w_s d C_v \qquad (3)$$

where

l = the distance the wave travels before its amplitude is reduced to 1/e of its original value, e being the base of natural logarithms, feet

w_s = the rate of propagation of the waves, number per hour

d = the density of the crystal, pounds per cubic foot

C_v = the specific heat at constant volume, Btu per hour - pound - ^oF.

Effect of Complexity of Crystal Structure. An attempt was made by Eucken(42) to check the validity of the Debye equation. He found that observed values differed from calculated ones by as much as a factor of ten. But the equation leads to certain qualitative deductions which are substantially correct, according to Austin(7). For example, other things being equal, the highest thermal conductivity should be found in a substance of simple molecular structure crystallizing in a lattice of high symmetry, and the conductivity should decrease with increasing complexity of molecular structure and of crystal lattice. The measured conductivities given in Table III support this deduction.

That a change in lattice structure greatly affects the thermal conductivity of a diatomaceous-earth brick was found by Nakai(68). The change in lattice structure was detected by x-ray diffraction measurements and true density measurements.

TABLE III

Data Showing Decrease in Thermal Conductivity With Increasing Complexity of Molecular Structure

Substance	Temperature, °C	k, Cal x 10^{-3}/sq cm - sec - °C/cm
Sodium Floride	0	25
Calcium Carbonate	0	11
Potassium Alum	0	4.7
Vitreous Silica	0	3.3
Naphthalene	35	0.79
a-Naphthol	35	0.57
b-Naphthol	35	0.59
Naphthyl Salicylate	35	0.45
Naphthylamine	35	0.36

Austin, J. B.: Factors Influencing the Thermal Conductivity of Non-metallic Materials, "Symposium on Thermal Insulating Materials," p. 8. American Society for Testing Materials, Philadelphia, Pa., 1939. 1 ed.

Austin[7] analysed the significance of factors other than lattice structure affecting thermal conductivity from the theoretical viewpoint of the Debye equation and on the basis of experimental evidence. Some of his conclusions are mentioned below.

Polar Structure of the Molecule. In dealing with crystalline compounds, Austin[8] pointed out the general rule that when the component atoms have the same electron shells the conductivity is high, and furthermore that the smaller these shells are, the higher is the conductivity. The few meager experimental observations available are consistent with this view, which focuses attention on the polar structure of the molecule and on the strength of molecular binding, both of which factors must have some influence on heat conduction. The substances which have been studied are the alkali halides and refractories such as silicon carbide.

Purity. Austin[9] clarified some of Eucken's[42] work on the influence of purity on thermal conductivity. Austin states the general rule that foreign atoms in the lattice should be sources of vibration disturbances, and thus the presence of small amounts of impurities should cause large decreases in conductivity. Substances in solid solution may be considered impurities. Also larger amounts of the second substance should cause less effect because the disturbed lattice becomes less sensitive to further additions.

Data have been presented by Austin[9] to show that these generalizations are valid, and that they follow the analogous rule for electrical conductivity.

Compressibility or Hardness. Austin[11] continued to examine Eucken's[40] consideration of the effect of the variables in the Debye equation. If ($lC_v d$) is approximately constant, the conductivity should vary with w_s, the rate of propagation of the thermoelastic waves. But it can be shown, Austin[11] stated, that w_s is inversely proportional to $\sqrt{Xd}$, where X is the compressibility of the crystal and d the density. Eucken[42] arbitrarily selected alkali halides for which ($lC_v d$) is approximately constant, those of the series of salts which showed maximum conductivity. He found that k is proportional to hardness, which is a related quantity to $\sqrt{Xd}$. Austin[11] verified that k is proportional to hardness. He also measured $\sqrt{Xd}$ for these substances, and found k inversely proportional to $\sqrt{Xd}$, as predicted from the Debye equation.

Melting Point. Austin[10] criticized the suggestion of Eucken[40] that in any group of substances the order of increasing melting point is also the order of increasing thermal conductivity. The relation holds only in special cases.

Another suggestion by Eucken[40] was that the thermal conductivity of most crystalline substances is the same at the melting point. Austin[10] found that, as far as data are available, the rule seems to hold approximately, and it is at least true that

conductivities of crystalline substances approach each other at the melting point. It is hard to obtain data to prove this generalization because values at the melting point must be obtained by extrapolation.

Thermal Anisotropy of Crystals. The phenomenon of anisotropy of thermal conduction of single crystals was described by Worthing[91]. The relative conductivity of the crystal along the major axes is observed by coating a cut face with paraffin. When a point source of heat is applied to the surface, the wax melts in the shape of an ellipse. The conductivity is found to be proportional to the length of the axes of the crystal, according to this author.

Austin[17], in disagreement, stated that the conductivity is not necessarily a maximum along the longest crystal axis, but may be a minimum. Crystals may be either thermally positive or thermally negative, according to whether the conductivity is a maximum or minimum along the major optical axis. At an angle to the major axis, the following relation holds:

$$k_\theta = k_\perp + (k_\parallel - k_\perp) \cos^2\theta$$

where

k_θ = the conductivity in the given direction, Btu per hour - square foot - ^oF per foot

$k_\parallel$ = the conductivity in the direction of the principal axis, Btu per hour - square foot - ^oF per foot

$k_\perp$ = the conductivity perpendicular to the axis, Btu per hour - square foot - ^oF per foot

θ = the angle between this axis and the given direction, degrees.

For triclinic crystals the optical axes are not mutually perpendicular and there is no axis of symmetry. The conductivity is then different in all directions. But the thermal axes are nevertheless mutually perpendicular, and an isotherm is an ellipsoid of revolution. The thermal axes do not coincide with the optical axes.

Two-phase Aggregates. The most common kind of two-phase aggregate is a dispersion of a crystalline phase and an amorphous phase, according to Russell[77]. He has recognized two varieties, one where the crystalline phase is continuous and one where the amorphous phase is continuous. His equations were derived for porous brick.

A single equation derived by Eucken and discussed by Austin[14] covers both cases. It is:

$$k_b = k_u \frac{1 + 2V_d \frac{1 - Q}{2Q + 1}}{1 - V_d \frac{1 - Q}{2Q + 1}} \qquad (5)$$

where

k_b = conductivity of the aggregate, Btu per hour - square foot - ^oF per foot

k_u = the conductivity of the continuous phase, Btu per hour - square foot - ^oF per foot

k_d = the conductivity of the discontinuous phase, assumed to be in the form of spherical particles embedded in the other phase, Btu per hour - square foot - ^oF per foot

V_d = the amount of the dispersed phase expressed as a fraction of the total volume, dimensionless

Q = the ratio k_u / k_d, dimensionless.

The equation agrees with those of Russell, which are plotted in Figure 2.

Austin[15] pointed out effects of differences in the ratio k_s/k_a, the conductivities in the crystalline and amorphous phases respectively. In Figure 2, for Q greater than one the phase with higher conductivity (the crystalline phase) is continuous, and for Q less than 1.0 the phase with lower conductivity (the amorphous phase) is continuous. The first case refers to particles of glass embedded in a crystalline medium, and the second refers to crystalline

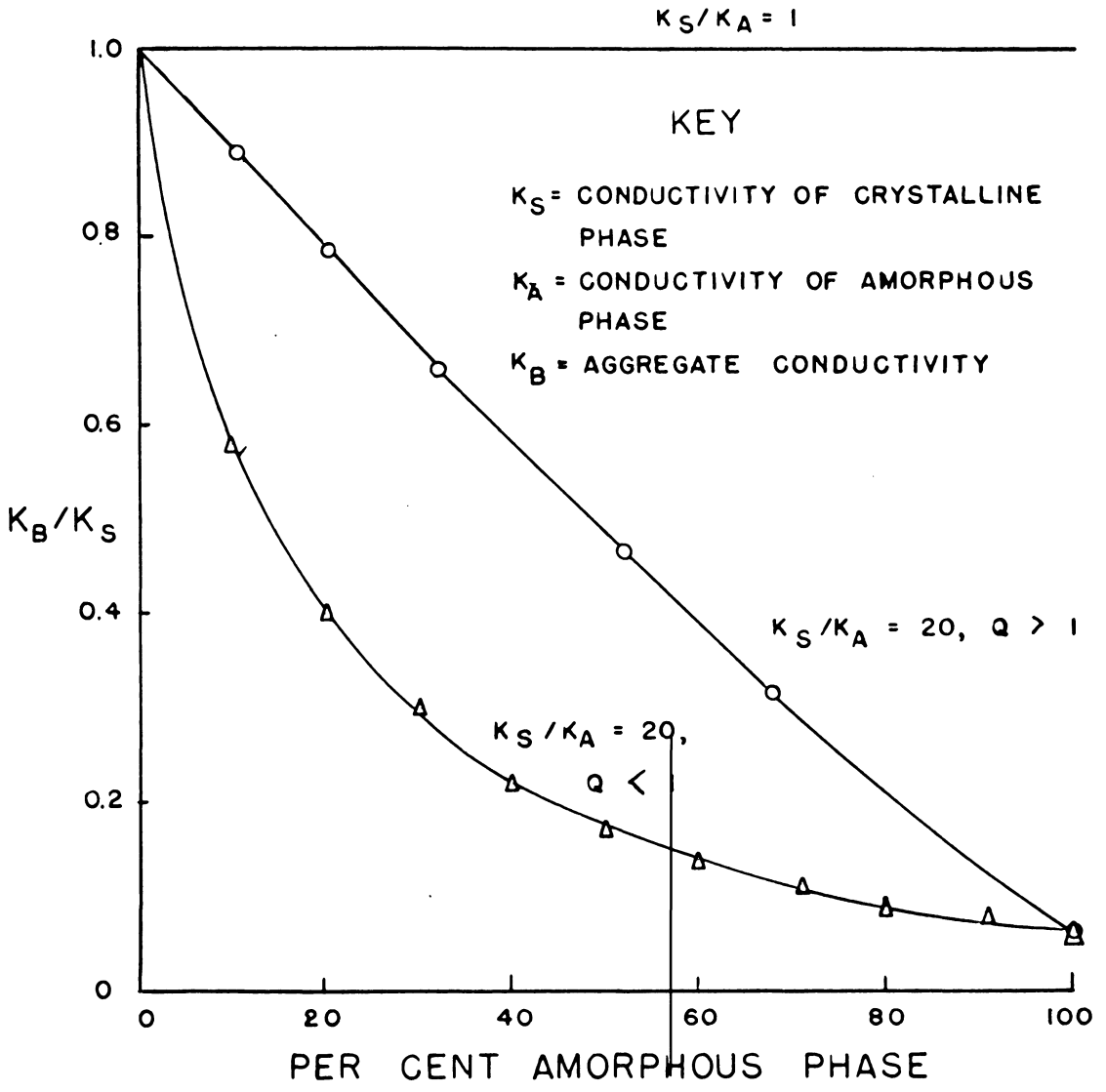


FIGURE 2. VARIATION OF THERMAL CONDUCTIVITY OF AGGREGATE WITH COMPOSITION

AUSTIN, J. B.: "SYMPOSIUM ON THERMAL INSULATING MATERIALS," P. 17. AMERICAN SOCIETY FOR TESTING MATERIALS, PHILADELPHIA, PA., 1939. 1 ED.

areas embedded in a glass. Furthermore, when k_s/k_a is 1.0 there is no variation of aggregate conductivity with composition. But when the ratio is near 1.0, variation is sensitive to small changes in k_s/k_a. For values of the ratio greater than 20 the curves are only slightly depressed downward, and the curve for 100 would be close to that for 20, that is the conductivity of the aggregate is little affected by changes in the ratio k_s/k_a.

Figure 3, after Austin[16], shows the change in behavior of the conductivity of an aggregate of silica and glass with changing composition as a function of temperature. The upper curve shows the characteristic behavior of a crystalline material, with a high conductivity at low temperatures and decreasing with increasing temperatures, though not so rapidly as the temperature goes up. The lower curve shows the straight-line temperature increase characteristic of glasses. Intermediate curves show the gradual transition from crystalline behavior to amorphous.

A few experimental results are available for the conductivity of two-phase aggregates of solid and glass. Table IV compares results of Austin[18] on the conductivity of portions of brick from an open-hearth furnace, the pores of which had become filled with slag, with the values calculated by Eucken's equation 5. The agreement is good.

Summary. The thermal conductivity of amorphous substances is approximately porportional to heat capacity at constant volume. It increases linearly with temperature. The conductivity of

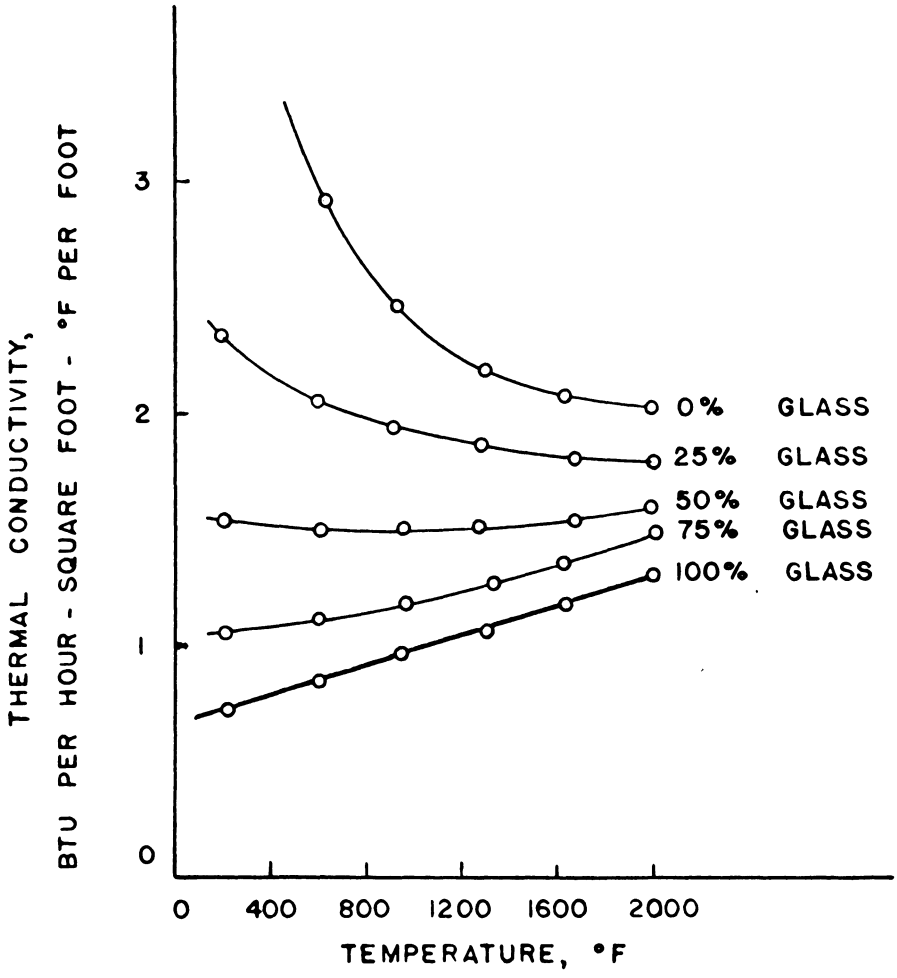


FIGURE 3. THERMAL CONDUCTIVITY OF SILICA CONTAINING DIFFERENT AMOUNTS OF GLASS

AUSTIN, J. B.: "SYMPOSIUM ON THERMAL INSULATING MATERIALS," P. 20. AMERICAN SOCIETY FOR TESTING MATERIALS, PHILADELPHIA, PA., 1939. 1 ED.

TABLE IV

Thermal Conductivity of Iron Oxide-bearing Silica Brick Compared with Data of Eucken

Mean Temperature, °C	k, values of Pierce and Austin[1] Cal x 10^{-3}/sq cm - sec - °C/cm	k, values of Euken[2] Cal x 10^{-3}/sq cm - sec - °C/cm
1100	7.6	8.2
1370	5.8	7.6

(1) Austin, J. B., and R. H. H. Pierce, Jr.: A Comparison of the Thermal Expansion of Used Silica Brick from an Insulated and an Uninsulated Open-Hearth Furnace Roof, J. Am. Cer. Soc., 19, 276 (1936).

(2) Eucken, A.: "Die Wärmeleitfähigkeit keramischer feuerfester Stoffe," VDI Forschungsheft 353, Forsch. Geb. Ingen. B3, (March -April, 1932); Austin, J. B.: Factors Influencing the Thermal Conductivity of Non-metallic Solids, "Symposium on Thermal Insulating Materials," p. 32. American Society for Testing Materials, Philadelphia, Pa., 1939. 1 ed.

crystalline materials may be several times that of the same substance in amorphous form, but the conductivities of two forms of the same substance approach each other at the melting point.

Simple molecules in a crystal lattice of high symmetry have the highest conductivities, while crystals of low symmetry show anisotropy of conductivity. Small amounts of impurities in a crystal decrease the conductivity markedly.

Other things being equal, conductivity is proportional to hardness.

Equations are available for finding the conductivity of an aggregate of glasses and crystals when the conductivities of the two phases are known.

Thermal Conductivity of Polymers

The data and theory available on the thermal conductivity of polymers are even more sparse and unsatisfactory than those for non-polymeric substances. A few values of conductivity for a number of plastics are given in Table V. The investigations which have been made on the subject are reviewed below, but they are so incomplete that they barely indicate the nature of the problem of determining what influences the thermal conductivity of polymers.

Conductivity of Amorphous Rubbers. Rehner[74] attributed relatively small, though "technologically important" differences among thermal conductivities in amorphous rubbers to structural and chemical differences. But he suggested that the conductivity

TABLE V

Thermal Conductivity of Some Plastic Materials

Material	Thermal conductivity,[1] Cal x 10^{-4}/sq cm - sec - ^{o}C/cm
Phenol-formaldehyde molding compound, no filler	3 - 6
Melamine-formaldehyde molding compound,	
asbestos filler	13 - 17
cellulose filler	8.4
Analine-formaldehyde resin, no filler	2.6
Cellulose acetate molding compound	4 - 8
Cellulose nitrate	3.1 - 5.1
Vinylidene chloride molding compound	3.0
Methyl methacrylate molding compound	4 - 7
Polystyrene and its copolymers	1.8 - 3.3
Polyethylene	6.0 - 8.0
Nylon compression molding compound	6.5

(1) Property Chart No II, "Modern Plastics Encyclopoedia," Plastics Catalogue Corp., New York, N. Y., 1948.

is determined mainly by chain-valence forces that are usually of the same general nature (carbon-to-carbon single and double bonds.)

Directional Effects. Although no investigation has been made on the anisotropy of conductivity of a crystalline polymer, Wooster[90] proposed that conductivity should be greater along the chains than across them.

Conductivity of Glasses over the Softening Range. The thermal conductivities of glassy and liquid glucose were measured over the temperature range -70 to 80 °C by Greene and Parks[52]. The data indicated that the conductivity varied about five per cent at the softening or transition region, giving a relative maximum, but the authors concluded that there was no important irregularity in this range.

For rosin and phenolphthalein in amorphous form, the thermal conductivity was found by Kuoshinski[64] to be constant over the softening range.

Effect of Plasticizer. The effect of plasticizer on the thermal conductivity of polymethyl methacrylate was measured by Caress[29]. He found the values 5.0 calories per square centimeter - second - °C per centimeter for the plasticized polymer and 3.5 for the unplasticized polymer.

Analogy Between Conduction in Liquids and Rubbers. An attempt was made by Rehner[74] to draw an analogy between the theory of thermal conductivity in liquids and in rubbers. He reasoned that polymers in amorphous form resemble liquids in their molecular

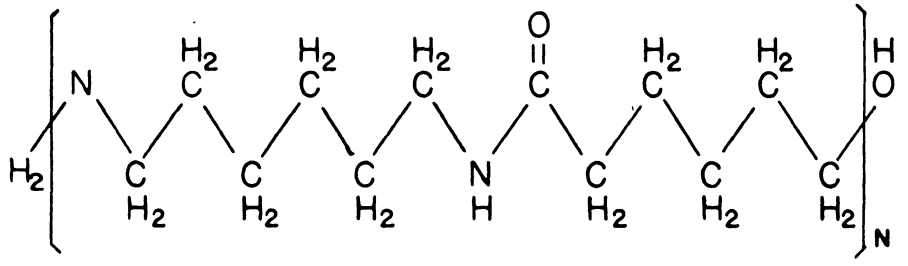
arrangement. He therefore tried to apply to rubbers the Bridgeman equation, which relates acoustic velocity and conductivity for liquids. He found that it did not give results agreeing with his measured data.

He attributed this to the fact that rubbers are more complicated in molecular structure than liquids, since they contain extraordinarily long molecules. The difference is further accentuated in the extreme case of a crystalline polymer by the fact that such substances exhibit anisotropy of conductivity, a phenomenon which does not occur in liquids.

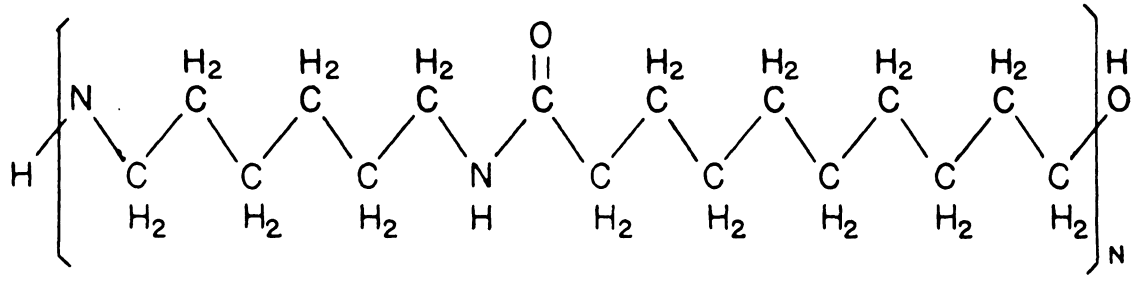
Thermal Conductivity of Nylon 66. The duPont Company[36] reported the thermal conductivity of its nylon compression molding compound to be 0.15 Btu per hour - square foot - ^{o}F per foot. Modern Plastics Encyclopoedia[73] reported the conductivity of the same material to be 0.16 Btu per hour - square foot - ^{o}F per foot.

The term nylon 66 refers to polyhexamethylene adipamide. Schmidt and Marlies[78] explained the numerical designation of the various nylons. The first number represents the number of carbon atoms in the diamine, and the second the number of carbon atoms in the dicarboxylic acid that form the monomer. Figure 4 shows the structural formulas for nylon 66 and 610.

Summary. The values of thermal conductivity available for plastic materials are both sparse and unreliable. Values in the literature usually do not specify completely the material to which they refer. Manufacturers report values for their products identifying them by trade name but not by formulation.



POLYHEXAMETHYLENE ADIPAMIDE, NYON 66



POLYHEXAMETHYLENE SEBACAMIDE, NYLON 610

FIGURE 4. STRUCTURAL FORMULAS OF NYLON 66 AND 610

BUNN, C. W., AND E. V. GARNER: THE CRYSTAL STRUCTURE OF TWO POLYAMIDES, PROC. ROY. SOC. LOND., A189, 41, (1947).

No theory has been developed which relates conductivity to molecular structure or physical state.

Nylon in the Crystalline State

That samples of solid nylon containing crystalline regions can be prepared has been shown by many investigators[27,21,32]. An understanding of the chemistry of crystalline nylon and of the physical microscopic nature of the crystal is helpful in understanding the nature of thermal conduction in crystalline nylon.

Intermolecular Forces in Nylon. Baker[20] stated that the strongest intermolecular forces in any chain polymer occur in nylon, and these are due to the dipoles and accompanying hydrogen bonding arising from the presence of the peptide linkage in the chain (see Figure 4). A discussion of hydrogen bonding is given by Pauling[71].

In their infra-red absorption investigations of nylon, Elliot, Ambrose, and Temple[38] determined that the presence of a single fairly broad band at a wave number of about 3280 per centimeter indicates that the degree of hydrogen bonding for bonds having this wave number is very considerable, and probably nearly complete.

The index of normal hydrogen bonds is defined by Champetier and Aelion[31] as the number of hydrogen bonds per 100 covalent bonds. The index number is 28 for nylon 66.

According to Mark[65], in addition to the bonds between the peptide linkages, other forces act between the paraffinic parts of

the chains. These forces, said to be due to the dispersion effect, are the result of electrical fluctuations within the atoms or molecules. When two atoms are close together these fluctuations are more likely to be in phase than out of phase, as may be shown by statistical methods. The result is an electrostatic attraction.

Crystalline Constitution of Nylon. Nylon does not crystallize in large single crystals, as do non-polymeric substances. According to Freund and Mark[45], some polymers such as nylon can exist as two-phase systems containing crystalline and amorphous regions. The crystalline state, as in non-polymeric substances, consists of a three-dimensional lattice. The atoms are fixed and the only movement they can exhibit is regular vibration. No crystalline faces can be seen in nylon because the crystalline areas are too small, of the order of 500 Angstrom units. Other investigators[80,47,45] have estimated the crystalline areas to be 1000 Angstroms in diameter.

Mechanism of Crystallization of Nylon. Evidence of the crystallization of nylon was reported by Baker and Fuller[21]. They plotted time-temperature cooling curves and found a halt in cooling at one point. The melt became cloudy as it solidified during the halt in cooling. They called this point the melting point and noted that the temperature at which it took place depended on the rate of cooling. Nine degrees supercooling before solidification was observed in one test.

Because the molecular weights of the individual molecules vary widely, the melting point should be a range, yet the stiffening was sudden. The authors referred to Oldham and Ubbelohde[70] for explanation. The latter compared the solidification to gelation, and called it a "cooperative setting-up." They proposed the following mechanism: as soon as some of the dipoles line up, they produce an electrostatic field which tends to speed the orientation of the rest of the molecules.

Induction of Crystallinity in Nylon. Carothers[33, 21] was the first successfully to induce crystallinity in nylon. He found that this was possible only when the sample possessed a high molecular weight.

Baker[20] pointed out that the percentage of crystalline material present, called degree of crystallinity, is greater when the sample is cooled slowly or annealed at temperatures somewhat below the melting point. Conversely, sudden quenching of the melt results in a nearly amorphous solid which, on the basis of extrapolated rate measurements, will retain its glass-like character for as much as forty years. His conclusions were based on measurements of x-ray fiber patterns of nylon samples.

Bergman, Fankuchen, and Mark[23] arrived at the same conclusions by the same method. They also noted that the effect of a more drastic treatment was to overshadow milder, previous treatment. Also, the effect of stretching nylon fibers was to increase the degree of crystallinity as well as to orient the molecule axes parallel to each other.

Freund and Mark[45] stated that for fibers the extent of ordered arrangement in which crystalline, amorphous, and mesomorphous regions occur is increased by stretching at constant temperature and cooling at constant stress. Conversely, it is decreased by swelling with solvents at constant temperature and heating at constant stress.

Schmidt and Marlies[78] pointed out that orientation of nylon molecules may be induced not only by stretching but also by unidirectional rolling.

Effect of Degree of Crystallinity on Physical Properties of Nylon. Large differences in the physical properties of nylon are due to differences in the amount of crystalline material present, stated Baker[20]. He attributed this fact to the difference in the position of the attractive centers in the two states. In the crystalline state the molecules are lined up with dipole next to dipole so that the cohesive forces are greater. Figure 5, for example, shows the relation of modulus of elasticity to quenching temperature. The nylon quenched at lower temperatures has a lower degree of crystallinity.

That unoriented molecules are present in samples of nylon fibers which are considered crystalline is shown by the phenomenon of retraction after stretching, according to Baker[20]. Alfrey[3] pointed out that the long chain molecules may pass through a number of crystallites, but exist in a kinked or coiled form in the amorphous regions. It is this kinking which gives rise to elasticity and

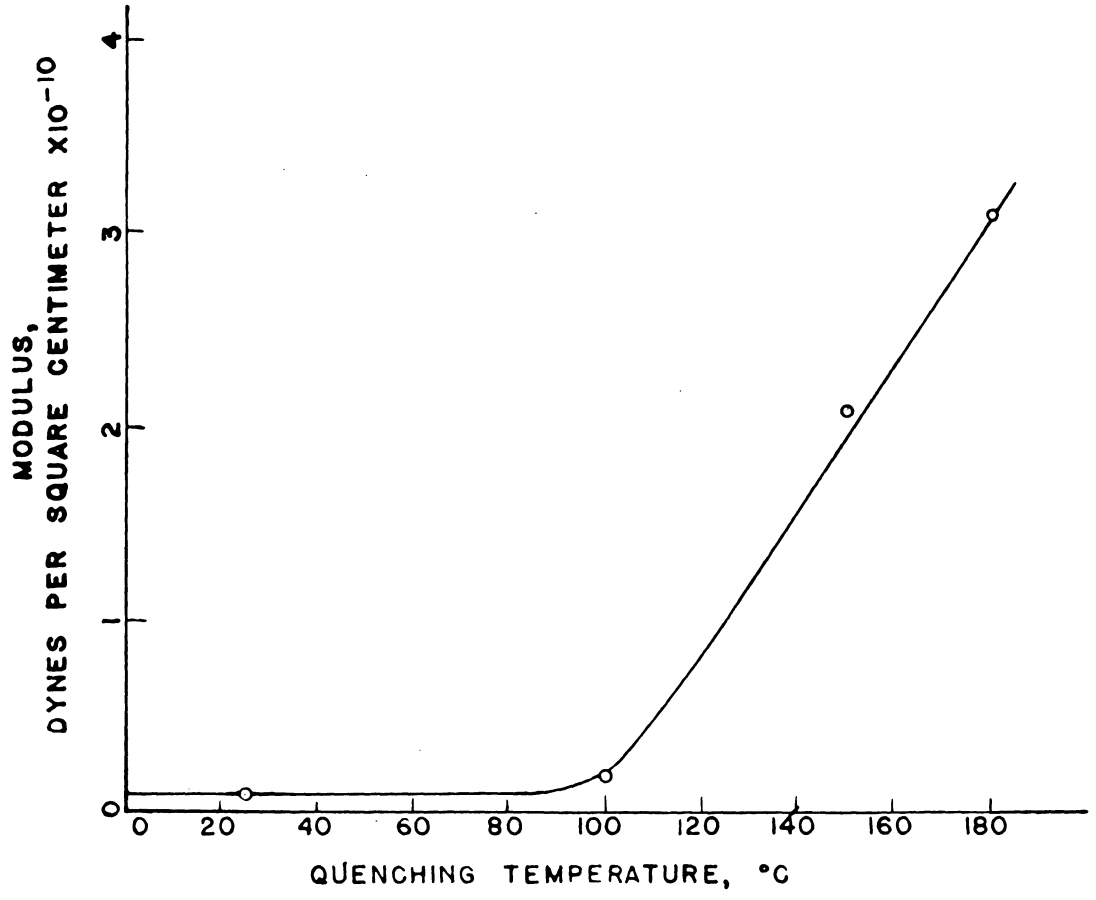


FIGURE 5. STIFFNESS OR HARDNESS OF NYLON 610 QUENCHED FROM MELT AT VARIOUS TEMPERATURES

BAKER, W. O. : NATURE OF THE SOLID STATE OF CHAIN POLYMERS, "ADVANCING FRONTS IN CHEMISTRY" (S. B. TWISS, EDITOR), P. 119. RHEINHOLD PUBLISHING CORP., NEW YORK, N. Y., 1945. 1 ED.

resilience. Conversely, that nylon is elastic indicates that it contains an amorphous phase.

Crystal Chemistry. It has long been recognized, according to Goldschmidt[51], that many properties of crystals are not accounted for on the basis of the classical chemistry of the component atomic particles alone. For example, there is no direct relation between the chemical valences of the particles that make up the crystal and the form of the resulting crystal. Rather, the external symmetry of the crystal depends on the arrangement of the neighboring atoms, or their coordination. The atomic distances, which may be thought of as the radii of the spherulitic atoms, limit the number of atoms of one kind which can cluster about atoms of another kind, hence limit the coordination of the atoms. For the sake of illustration, a table of the limits of atomic radii for given coordination numbers is given in Table VI.

Goldschmidt[51] further pointed out two facts. One is that polar ions, which are nonspherical, may act as units in the crystal lattice just as atoms do, and in this case the coordination relation is unsymmetrical. This situation may give rise to a layer structure. The other fact is that the cohesive properties also depend on atomic radii. For example, hardness is greater when the atomic distances are small and consequently the valence forces are large.

Since a knowledge of the chemistry of nylon alone does not allow a prediction of its crystal structure, other information is needed.

TABLE VI

Packing of Spheres About a Central Sphere

Number of surrounding spheres, x	Arrangement of spheres	Limit of radius A/radius x
2	Opposite	---
3	Equilateral triangle	0.15
4	Tetrahedron	0.22
4	Square	0.41
6	Octahedron	0.41
8	Cube	0.73

Goldschmidt, V. M.: Crystal Chemistry and X-ray Research, Ergb. tech. Roentgenkunde, 2, 151-182 (1931).

This information is provided by x-ray diffraction pattern photographs, which indicate the positions of the atoms in the crystal molecule.

X-ray Fiber Patterns. Fibering is defined by Sproull[82] as the preferential orientation of crystals due to plastic deformation of the substance. Bunn[27] stated that the fiber pattern is formed when an x-ray beam is allowed to impinge on a thread of material perpendicular to its major axis and the resulting reflections expose a photographic film. A fiber pattern of nylon 66 is shown in Figure 6.

According to Bunn[27], each ring in the diffuse x-ray pattern of a non-fibered polymer represents a reflection from a particular type of crystal plane. When the sample is stretched, the crystals become oriented and the diffuse rings resolve themselves more or less into spots.

Definitions. It is convenient to define a number of terms to describe fiber patterns. Equatorial reflections, which may be spots or arcs, are those which lie on a horizontal line through the center of the diffraction diagram, according to Baker[20]. They are characteristic of the arrangement of the molecule axes in the crystal and the separation between them. Meridian spots are those that lie on a vertical line through the center of the diagram. They represent spacings between layers of x-ray scattering centers which are perpendicular to the fiber axis. Layer-line spots, according to Baker[20], and Baker and Fuller[21] are reflections lying on either side of

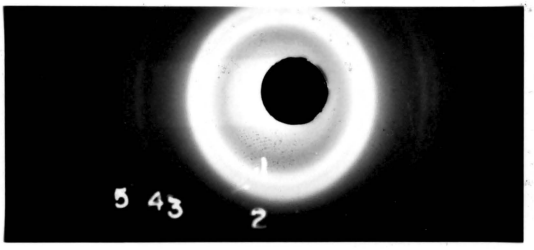


Figure 6. X-ray Diffraction Pattern of Nylon FM10001.

the vertical axis of the diagram. They represent the fiber identity period, which is the distance between repeating elements in the crystal. The fiber period is an inverse function of the distance of the reflections from the target at the center of the diagram.

Analysis of Fiber Patterns. Bunn[27] stated that the fiber period, which is obtained from the layer lines, gives certain distances within the molecule along the chain axis, for chain-type polymers. Nylon has a long fiber period corresponding to the length of the monomer and a shorter one corresponding to the distance between carbon atoms. The short fiber period is similar to that for low molecular weight hydrocarbons, which indicates that the molecular packing in nylon is essentially paraffinic. The equatorial reflections, which represent relations between the chains, are very similar to those of the hydrocarbons. But Bunn warns that one cannot be certain about the crystal structure until the fiber period, the unit cell dimensions, and finally the probable position of every crystal atom have been fixed. The first two steps are accomplished by measuring the positions of the reflections from the crystal planes, and the last step is accomplished by measuring their intensities.

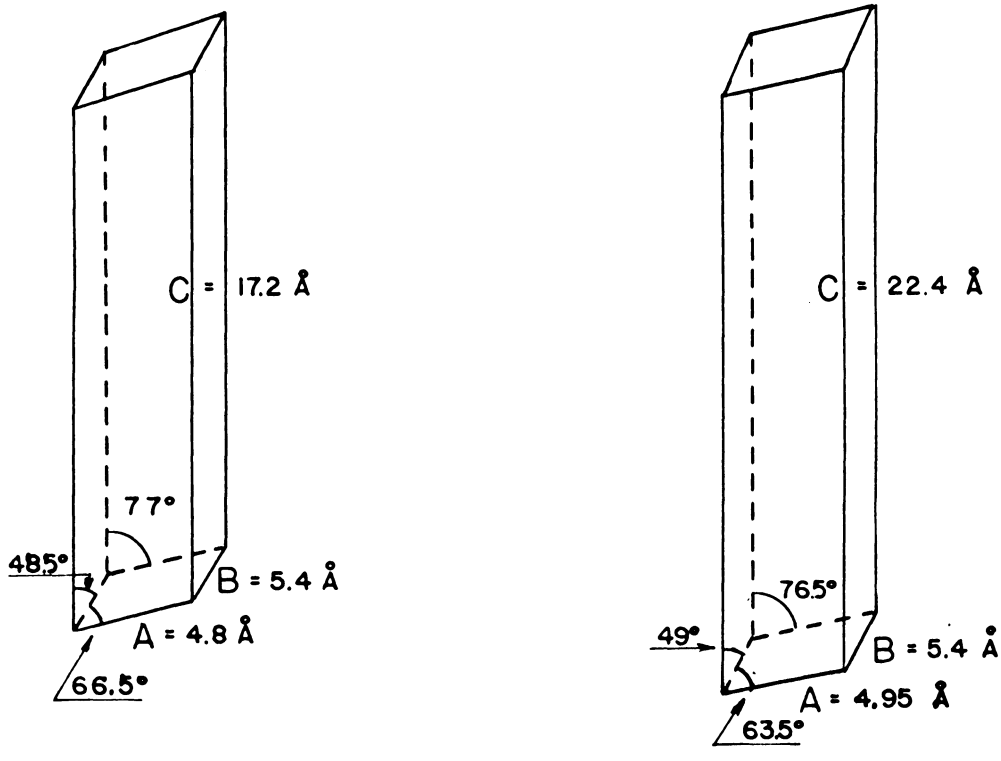
Fuller[47] stated that the breadth of the reflections show the size of the crystal regions, which are usually 500 Angstroms long in nylons.

Analysis of Two Nylons by X-ray Diffraction. Bunn and Garner[28] have described the crystal structure of nylon 66 and nylon 610 from their x-ray diffraction pattern investigations. Copper Kα radiation was used on cylindrical films.

Shape of the Molecule. The fiber period, or length of the recurring crystal unit, was 17.2 Ångstroms for nylon 66 and 22.4 Ångstroms for nylon 610. This agrees with the calculated length which the monomeric unit should have; hence the chains must be fully extended in planar zig-zag form.

Unit Cell. All the spots on the fiber pattern could be explained only on the assumption that the unit cell is of triclinic form. Taking the height, or long axis as the c axis, the unit cell dimensions are as shown in Figure 7. A representative of the orientation of a nylon 66 chain in its unit cell is shown in Figure 8. Nylon 610 is similar. The plane of the chain is in or near the 010 face and parallel to the 120 face. The oxygen atom is on the same level as the nitrogen-hydrogen group. The oxygen atom is not in the plane of the carbon chain, but lies back near the 010 face. The orientation of the chain in the cell was found by calculating the atomic positions from the x-ray pattern, by a trial and error method. The interatomic distances were assumed to be those of the monomer.

Ecochard[38] found by the Brill method that the six crystal parameters of nylon 66 fiber are a,b,c: 5.00, 4.17,



NYLON 66

NYLON 610

FIGURE 7. THE UNIT CRYSTAL CELLS OF NYLON 66 AND NYLON 610

BUNN, C. W., AND E. V. GARNER: THE CRYSTAL STRUCTURES OF TWO POLYAMIDES, PROC. ROY. SOC. LOND., A189, 30-68 (1949).

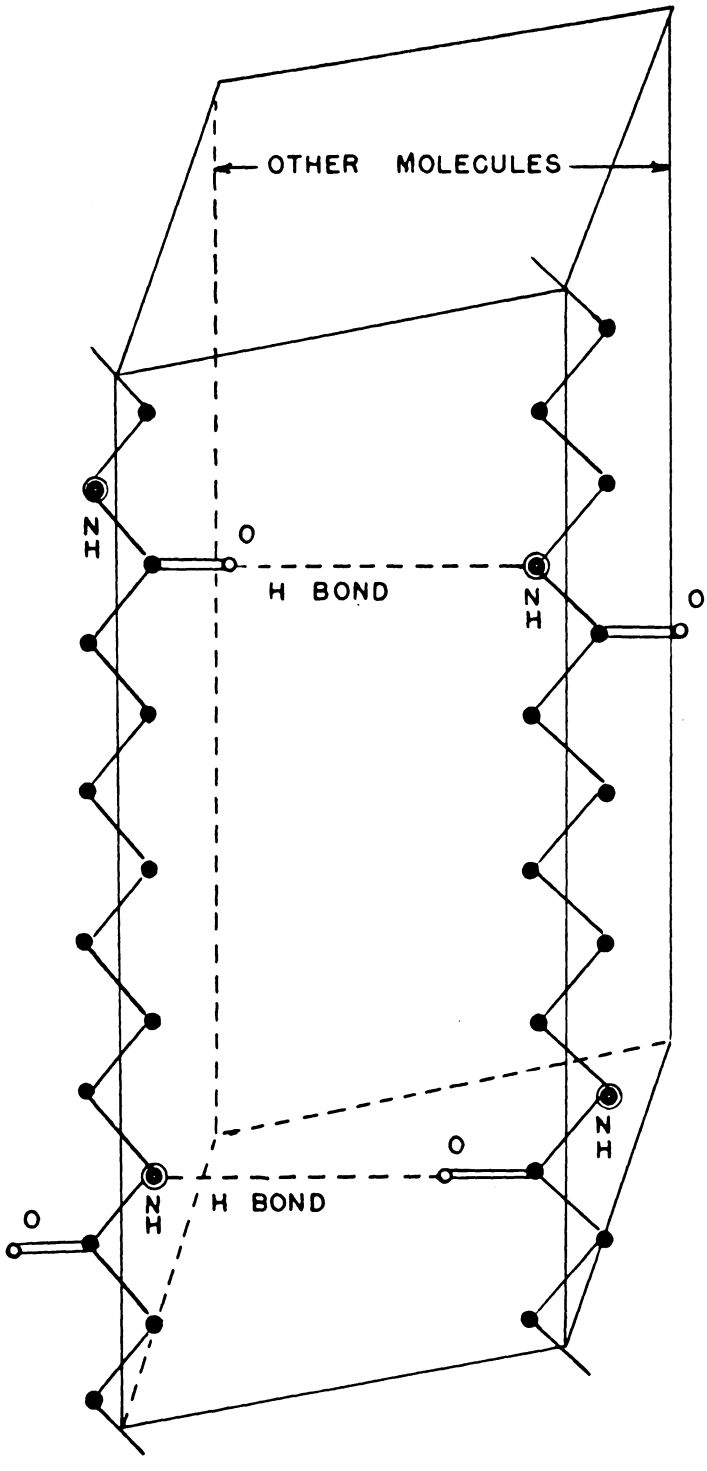


FIGURE 8. THE UNIT CRYSTAL CELL OF NYLON 66 SHOWING POSITIONS OF MOLECULAR CHAINS

BUNN, C. W., AND E. V. GARNER: THE CRYSTAL STRUCTURES OF TWO POLYAMIDES, PROC. ROY. SOC. LOND., A189, 45 (1947).

and 17.3 Angstroms; alpha, beta, gamma: 81.11, 76.23, and 63.08 degrees respectively. These values differ somewhat from those of Bunn and Garner.

Crystal Orientation. In a stretched fiber, all crystals have their c axes parallel to the fiber axis, according to Bunn and Garner[28].

If an undrawn fiber is pressed, the c axes align in a direction perpendicular to the fiber axis along the direction of greatest flow during pressing. Experiment has shown that a further alignment also takes place so that the 010 plane of the unit cell becomes parallel to the plane of the sheet. These conditions define four possible positions for the unit cell in a rolled or pressed sheet.

In support of Bunn and Garner[28], Elliot, Ambrose, and Temple[39] have found striking differences between the infrared absorption by rolled and stretched sheets of nylon, indicating different orientation resulting from these two treatments. There was no dichroism in the stretched sheets, so the orientation was unidirectional, parallel to the direction of the stretch. In rolled sheets, planar orientation of the "plate-like" nylon crystals was observed, with the 010 planes parallel to the sheets. Dichroism was observed, and the carboxyl bonds lay within the plane of the sheet.

Distortions and Thermal Vibrations. Referring to Bunn and Garner[28] again, the observed intensities of some of the

reflections are in some disagreement with the calculated values. It was explained that this is due to the fact that the thermal vibrations of the molecules are strongly anisotropic, which is certain to be true of a triclinic crystal. This results in slight distortion from the regular zig-zag form first postulated.

The strongest forces, the hydrogen bonds, lie in the 010 plane; therefore, thermal vibrations are greatest perpendicular to the 010 plane and least in it. The infra-red absorption evidence of Elliot, Ambrose, and Temple[39] supports this statement. Other movements are also possible, according to Bunn and Garner[28]: a sinuous movement of the whole chain, and a torsional movement of the individual atoms, as well as vibration of the atoms.

Opacity. The individual crystallites are too small to be seen, so that opacity is due to the presence of aggregates of crystallites. These are spherulitic in shape, and may be seen under a microscope with crossed nicol prosms as black crosses.

Orientation on Pressing. It is expected that the larger dimension will set itself in the plane of the sheet. Also, compressibility is greater along the a axis than perpendicular to it, which is why the 010 plane aligns parallel to the plane of the sheet.

Change in Crystal Form on Heating. Brill[26] has investigated the change in crystal form which takes place on heating nylon 66. He found that two main equatorial reflections in the x-ray pattern

move closer together as the temperature rises and finally fuse at 160 °C. "Every fusion of interferences signifies an increase in symmetry," and Brill found that at this temperature the a and b axes become equal in length. The transition is to a hexagonal crystal system. On cooling, the form changes back at 140 °C.

Fuchino, Tanaka, and Yasui[46] have likewise reported a change in the crystal structure of nylon at high temperatures. An increase in crystallinity was also found to take place at 200 °C.

Glatt[50], in infra-red studies of nylon 610, found that some of the hydrogen bonds rupture at 200 °C, which is below the melting point (260 °C.) This allows the rotational movements and realignments to take place which have been inferred from x-ray data for nylon 610, as well as for nylon 66.

Structure and Physical Properties of Massive Nylon. Clark, Mueller, and Stott[32] studied the physical properties and crystalline nature of massive nylon. They determined that, with few exceptions, the statements made above for nylon fibers hold equally well for massive nylon. Their work is discussed below.

Effect of Annealing on Diffraction Rings. With annealing there was in general a shifting apart of the two most prominent x-ray diffraction rings, and improvement in definition. This shifting was taken as an indication that the amount of crystallinity had increased. In this respect large samples (two-inch rod) showed less effect of annealing than small ones (0.028-inch

strip.) This difference was due to the fact that the large samples cooled more slowly after molding.

In Table VII are given the camera angle differences between the two rings for samples annealed at various temperatures, and the length of time of annealing after which no further widening of the space between the lines was observed.

Patterns Taken at Elevated Temperatures. Brill[26], working with nylon fibers, found that the two prominent lines fuse when the sample is annealed at 160 °C. This was taken to indicate that a transition from triclinic to hexagonal crystal form had taken place. Clark, Mueller, and Stott[32] found a shift toward fusion of the lines, but did not find actual fusion of the lines at 160 °C. They stated that this was because Brill's fibers were highly oriented to start with whereas their strips were not.

Cold Rolling and Annealing. Clark, Mueller, and Stott[32] cold-rolled strips of nylon 0.027 inches thick down to 0.011 inches and then heated them 30 minutes in silicone fluid at 250 °C. The heating produced more diffraction spots, showing that some recrystallization had taken place. This result agrees with the work of Brill[26] on nylon fibers.

Hardness. Clark, Mueller, and Stott[32] found that the hardness of samples increased whenever there was evidence of increased crystallinity.

Microscopic Examination. When the surfaces of annealed samples were polished, graininess was visible under a

TABLE VII

Relation of Time of Annealing of Nylon 66 to Changes in Crystalline Constitution as Shown by X-ray Diffraction

Annealing temperature, °C	Camera angle difference between two lines, degrees	Time after which no change, min
Unannealed	2.70	—
150	2.88	30
200	3.07	3
235	3.50	2
100[a]	3.05	60

[a] Annealed in water.

Clark, G. L., M. H. Mueller, and L. L. Stott: Structure and Physical Properties of Massive Nylon, Ind. Eng. Chem., 42, 831 (1950).

microscope. This was because the polishing wore away the soft material between the grains.

It was concluded that the size of the grains depends on the size of the sample. Fewer nuclei, and hence fewer grains are formed in large samples which crystallize slowly on annealing.

Density. The densities of three commercial slabs of nylon reported by Clark, Mueller, and Stott[32] are given in Table VIII, with densities of drawn and undrawn fibers reported by Black and Dole[24] for comparison. Clark, Mueller, and Stott[32] stated that the differences between the densities of the three slabs was not significant.

Summary. The forces which bind nylon molecules together in crystals are hydrogen bonds and the dispersion effect. Nylon has a definite melting point. The degree of crystallinity may be substantially increased by annealing, stretching, and rolling, while the latter two operations also orient the crystals. All nylon samples contain crystalline and amorphous phases. Degree of crystallinity has a marked effect on the physical properties of nylon. It may be expected to affect thermal conductivity, since this is greater for crystalline substances than amorphous, although no correlation has been made of these properties in nylon.

Thermal vibrations in nylon crystals are strongly anisotropic, and are greatest perpendicular to the 010 plane, which contains the hydrogen bonds. Therefore thermal conductivity is expected to be least in a direction normal to a rolled sheet, due to the orientation

TABLE VIII

Density of Various Nylon Samples

Sample	Density at 25 °/4 °C
Undrawn filament[1]	1.1339
Drawn filament[1]	1.1384
Drawn, annealed filament[1]	1.1564
Highly annealed filament[2]	1.166
Slab 1/4 x 4 x 10 inches[3]	1.142
Slab 1/8 x 4 x 10 inches[3]	1.140
Slab 1/4 x 2 x 10 inches[3]	1.172

(1) Black, C. E., and M. Dole: Density of Nylon Filaments, J. Poly. Sci., 3, 358 (1948).

(2) Rosenbaum, C. K.: Personal Communication, June 4, 1951. Wilmington, Del.

(3) Clark, G. L., M. H. Mueller, and L. L. Stott: Structure and Physical Properties of Massive Nylon, Ind. Eng. Chem., 42, 831 (1950).

of the crystals and the effect of molecular binding on thermal conductivity.

The lattice form of nylon 66 changes at 160 °C, and consequently a change in thermal conductivity is expected at that temperature.

Test Methods

Measurement of Thermal Conductivity. The American Society for Testing Materials[83] has defined thermal conductivity of a homogeneous material as "the rate of heat flow, under steady conditions, through unit, area, per unit temperature gradient in the direction perpendicular to the area of heat flow." It is calculated by means of the following equation:

$$k = \frac{qL}{A(t_1 - t_2)} \qquad (6)$$

where

k = thermal conductivity, Btu per hour - square foot - °F per inch

q = rate of heat flow, Btu per hour

L = length of path of heat flow (thickness), inches

A = actual area normal to the path of heat flow (flat surface), square feet

t_1 = temperature of the hot surface, °F

t_2 = temperature of the cold surface, °F.

Disagreement Among Reported Values of Conductivity. Austin[4] stated two causes for the confusing lack of agreement among the values given in the literature for the thermal conductivity of many non-metallic materials. First, there is no standard accepted method of test, but each investigator chooses the one apparatus among many which appeals to him the most, and usually varies the design to suit his convenience. The American Society for Testing Materials[83] stated that it is not possible to fix one design suitable for all needs.

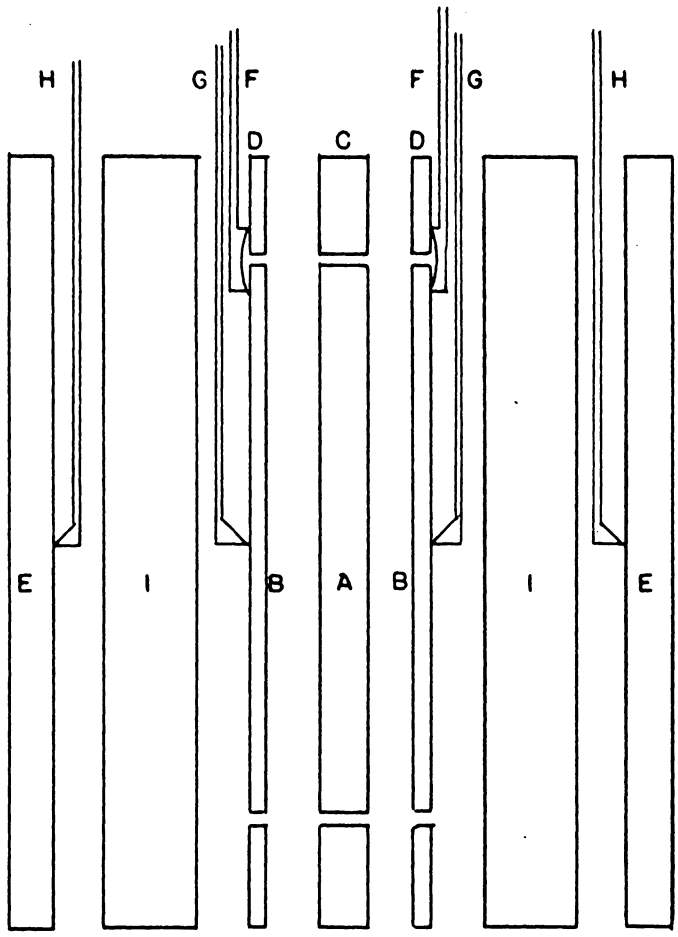
According to Austin[4], there is a second reason for the lack of agreement of values reported for thermal conductivity. He stated that there has been almost invariably an improper, or even inaccurate characterization of the sample studied. Many of the factors which influence the conductivity have not been measured or considered. He gives firebrick as an example, and it may be noted that conductivities of whole classes of plastics are often reported, such as "nylon," without specifying actual chemical composition, molecular weight, or previous physical treatment, as in Modern Plastics Encyclopoedia[73].

Experimental Errors in Measurement of Conductivity. Vierweg and Gottwald[87] studied the problem of determining thermal conductivity to find the most common experimental errors. They found that preliminary treatment, especially drying, has great influence on conductivity. Also, the greatest liability to error is due to taking measurements when the system is not in a steady state.

Summary of Methods of Measuring Thermal Conductivity. Ingersoll and Zobel[61] summarized the methods of measuring thermal conductivity of solids. Modern methods usually measure both temperature and heat flow directly, by thermocouples and measurement of electrical power used in the heat source.

ASTM Guarded Hot Plate Method C177-45. "The Standard Method of Test for Thermal Conductivity of Materials by Means of the Guarded Hot Plate," American Society for Testing Materials[83] Designation C177-45, is applicable to homogeneous flat slabs of materials with conductivity less than 0.4 Btu per hour - square foot - °F per foot. An accuracy of one per cent should be obtained when the specifications and procedure of the test are followed. The method makes use of the guarded hot plate apparatus illustrated diagramatically in Figure 9. The apparatus is in sandwich form with heat flowing from the central electrical heaters outward through the sample to the cooling units, in both directions. A guard heater with separate electric power adjustment is provided to minimize edge losses. Heat flow is measured by measuring the electric power input, and temperature difference is measured by means of surface thermocouples.

Accuracy of the Guarded Hot Plate Method. Griffiths[53] showed that the edge losses in a conductivity measuring unit similar to the one described above, but without the guard heater, could be reduced sufficiently to allow a one per cent accuracy in



KEY

HEATING UNIT

- A- CENTER HEATER
- B- CENTER SURFACE PLATES
- C- GUARD HEATER
- D- GUARD SURFACE PLATES

E- COOLING UNITS

F- DIFFERENTIAL THERMOCOUPLES

G- HEATING UNIT SURFACE THERMOCOUPLES

H- COOLING UNIT SURFACE THERMOCOUPLES

I- TEST SAMPLES

FIGURE 9. GUARDED HOT PLATE DIAGRAM

STANDARD METHOD OF TEST FOR THERMAL CONDUCTIVITY OF MATERIALS BY MEANS OF THE GUARDED HOT PLATE, DESIGNATION C177-45, "ASTM STANDARDS 1949," PART III, P. 304. AMERICAN SOCIETY FOR TESTING MATERIALS, PHILADELPHIA, PA., 1949.

the value of thermal conductivity. This was done by measuring the heat flow twice, once by measuring the electrical power dissipated and once by measuring the heating of the cooling water.

The effect of contact resistance was also determined by Griffiths(53). This was done by varying the applied pressure from 23 to 61 pounds per square inch, and by varying the thickness of the sample, and comparing the resulting conductivities obtained under these conditions. For materials which were not too hard the contact resistance could be reduced so that an accuracy in the thermal conductivity of less than one per cent could be obtained. For metals it was necessary to use films of mercury or vaseline and subtract the resistance of the films from the result.

Modified National Bureau of Standards Hot Plate. A modified "National Bureau of Standards Type Guarded Hot Plate" which fulfills the requirements of Method C177-45 was described by the American Society for Testing Materials(54).

Good heat distribution is provided by symmetric winding of resistance wire on an asbestos cement sheet 1/8 to 1/4 inch thick. There is a 1/16-inch separation between the center and guard heaters. The resistance wires fit into notches in the edges of the asbestos plates. The notches are half as deep as the plates are thick, except that the notches on the outer edge of the guard heater are one fourth the cement sheet thickness.

To provide electrical insulation between the resistance wires and the copper face plates, the heater is covered with sheet mica 0.008 inches thick and asbestos papers 0.022 inches thick.

Face plates of copper are screwed on both sides of the heater. The plates are 1/8 to 1/4 inch thick, and the screws are of brass, either number 6-32 or 8-32. The face plates must be polished with fine emery cloth on a smooth surface. Variations over ninety per cent of the surface should be nil with maximum variations on any portion of the surface not exceeding 0.003 to 0.005 inches, no depression to contain over one per cent of the total surface area.

Measurement of the Degree of Crystallinity of Nylon. A method of measuring the degree of crystallinity of nylon is suggested by Hermans'[58] statement that the density of an organic substance is directly proportional to the percentage of crystalline material present. Mathematically,

$$\text{Degree of Crystallinity} = \frac{d - d_a}{d_x - d_a} \times 100 \qquad (7)$$

where

d = density of sample

d_a = density of substance in amorphous form

d_x = density of substance in crystalline form.

Hermans[56] used this relation to determine the crystallinity of cellulose. Results agreed within a few per cent with values found by

the sorption of water method. The latter method gave results which agreed within five per cent with the values found by x-ray diffraction measurements, in another experiment by Hermans and Weidinger[60].

Density of a Crystal. The density of a crystal can be calculated from the dimensions of the unit cell as measured by x-ray diffraction, according to Hermans[56].

$$d_x = \frac{M\,n}{V\,N} \qquad (8)$$

where

d_x = density of the crystal, grams per cubic centimeter

M = molecular weight of the substance, grams per mol

n = primitiveness of the unit cell

V = volume of the unit cell, cubic centimeters

N = Avogadro's number, 6.023×10^{23} molecules per mol.

Measurement of the Density of a Solid. Bauer[22] stated that a buoyancy method using hydrostatic weighing with the analytical balance gives the best results for determining the density of large homogeneous samples of a solid. An accuracy of plus or minus 0.001 in the density may be attained by this method.

Difficulties are caused by cracks and bubbles in the sample and the presence of trapped air or moisture on its surface. Remedies are the boiling of the liquid under low pressure 10 to 15 minutes, adding wetting agents, and inspecting the sample for cracks under the microscope. The liquid chosen should have

a low viscosity and surface tension and the buoyant effect of air must be corrected for. The procedure used should result in the cancelling out of the effect of surface tension.

Hermans[57] pointed out that the liquid used must be indifferent to the sample, that is it must be unabsorbed by it. DuPont Company[36] reported that nylon when immersed in water absorbed 3.5 per cent by weight of water in one day, and when immersed in ethyl acetate, carbon tetrachloride, or toluene absorbed less than 0.2 per cent by weight of the liquid in one week.

Nylon also absorbs water from the air. Under exposure to air at 50 per cent relative humidity, it will contain as much as 1.5 per cent water by weight.

Hermans's Measurement of Cellulose Density. Hermans[59] determined the density of cellulose fibers by a buoyancy method. Particular care was taken to dry the sample because cellulose absorbs moisture from the air. In one method the sample was dried in a stream of air at 100 °C. In another it was dried 36 hours over phosphorous pentachloride in vacuo.

Density of Nylon. The most nearly amorphous sample of Nylon FM10001 which has been examined at duPont Company[76] was prepared by shock-cooling and had a density of 1.111 at 25 °C compared to water at 4 °C. The most completely annealed sample had a density of 1.166.

Characterization of Nylon by Solution Viscosity. The characterization of nylon samples as to molecular weight is conveniently done by measuring a dependent quantity, stated Schmidt and Marlies[78]. Viscosity of high-polymer solutions is easy to measure and is strongly dependent on molecular weight.

Flory's Relation. Schmidt and Marlies[95] further stated that the best equation relating solution viscosity to molecular weight is the empirical one given by Flory[43,44]:

$$[n] = K_w M_v^a \qquad (9)$$

where

$[n]$ = intrinsic solution viscosity

K_w = an empirical constant

a = an empirical constant

M_v = the viscosity-average molecular weight, grams per mol.

By definition,

$$[n] = \lim_{c \to 0} \left(\ln \; n_r/c \right) \qquad (10)$$

where

c = concentration of solution, grams per 100 milliliters of solution

n_r = relative viscosity, viscosity of solution relative to viscosity of solvent, consistent units.

The viscosity-molecular weight relationship is not a closed subject, according to Schmidt and Marlies[78], and many of the molecular weights reported in the literature are now known to be wrong. Because of this uncertainty, high polymers are now often characterized by their intrinsic solution viscosities alone.

Viscosity of Nylon 66 in Formic Acid. Taylor[85] determined the relation of molecular weight of nylon 66 to its intrinsic viscosity in 90 per cent formic acid solution and found it can be expressed by the relation:

$$M_n = 13{,}000[\eta]^{1.39} \qquad (11)$$

where

M_n = the number average molecular weight.

Since the viscosity is only a relative measure of molecular weight, the absolute measurement of molecular weight was made by means of end-group titrations over a range of molecular weight from 5000 to 25000. An Ubbelohde viscosimeter with enlarged receiving reservoir was used.

In determinations of the molecular weight distribution of nylon 66, Taylor[85] found that the ratio of number to viscosity average molecular weight approaches 2.1.

III. EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was to determine the extent to which the degree of crystallinity of nylon can be increased by cold-rolling and annealing, and the change in thermal conductivity resulting from these treatments.

Plan of Experimentation

The plan of experimentation comprised three phases of work. The first phase consisted of constructing apparatus for cold-rolling nylon, for annealing nylon, and for measuring the thermal conductivity of nylon. The second phase consisted of working out methods of test for determining the density, degree of crystallinity, intrinsic solution viscosity, and thermal conductivity of nylon. The third phase consisted of making these tests.

The specific program of testing required the following steps and determinations:

I. Rolling nylon. Two samples five inches square, to be rolled from a thickness of 0.260 inches to 0.130 inches

II. Density measurement of nylon samples. Duplicate determinations.

Samples:

A. Cast, as received

B. Dried to constant weight over phosphorous pentoxide

C. Dried to constant weight at 130 °C

D. Annealed at 240 °C for 1/2 hour, 2 hours, 2 days

E. Rolled to half thickness

F. Rolled to half thickness and annealed two hours at 240 °C

III. X-ray diffraction patterns

A. Camera: powder camera

Samples:

1. Annealed one hour at 230 °C

2. Quenched from melt in water at 15 °C

B. Camera: flat cassete, fixed sample

Samples:

1. Cast, as received

2. Annealed two hours at 240 °C

3. Rolled to half thickness

4. Rolled to half thickness and annealed two hours at 240 °C

IV. Intrinsic solution viscosity of nylon in 90 per cent formic acid. Temperature 25 °C. Duplicate determinations.

Concentrations:

A. 0.0 grams per 100 milliliters

B. 0.2 grams per 100 milliliters

C. 0.4 grams per 100 milliliters

D. 0.6 grams per 100 milliliters

E. 0.8 grams per 100 milliliters

V. Moisture content. Duplicate determinations.

Samples:

A. Cast nylon, as received

B. Nylon rolled to half thickness, annealed two hours at 240 °C and left in room two weeks

VI. Thermal conductivity at 80 °F and at 185 °F. ASTM method C177-45. Duplicate determinations.

Samples:

A. Cast nylon, as received

B. Rolled to half thickness

C. Rolled to half thickness and annealed two hours at 240 °C

Materials

Formic Acid. Reagent grade, 87-90 per cent, code No. 1067. Manufactured by General Chemical Co., New York, N. Y. Used as solvent for nylon in determining degree of polymerization of nylon.

Naphthalene. Flakes. Obtained from Phipps and Bird Inc., Richmond, Va. Used for calibrating thermocouples at temperature of condensing naphthalene.

Nitrogen Gas. Water-pumped; one cylinder required. Obtained from Southern Oxygen Co., Roanoke, Va. Used to provide inert atmosphere for annealing nylon.

Nylon Slab. Cast slab 1/4 inch by 4-3/16 inches by 36 inches, duPont formula FM10001. Obtained from the Polymer Corp., Reading, Pa. Used as sample for experimental work.

Prussion Blue Oil Paste. Obtained from Industrial Engineering Department Shop. Used on flat surface to compare with heater and cooling blocks.

Silicone Resins. Formulas DC 804 and DC 801. Manufactured by Dow-Corning Co. A two-to-three mixture thinned with 25 per cent toluene used to insulate thermocouples.

Sodium Sulfate. Decahydrate, USP crystals. Manufactured by Merck and Co., Rahway, N. J. Used in test for anisotropy of thermal conductivity of nylon.

Apparatus

The individual items of apparatus which were procured for this investigation are first listed. Items which were assembled or constructed in the laboratory are then described.

Aluminum Foil. "Reynolds Wrap," general purpose aluminum foil. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used to cover heater while hardening the resin in thermocouple slots and to wrap nylon samples for protection during annealing.

Asbestos Shingle. Building construction shingle, 12 inches by 12 inches by 1/4 inch thick. Manufactured by Johns-Manville Co., Philadelphia, Pa. Used as core for resistance heaters and for resistors in water bath control circuit.

Asbestos Welding Cloth. Nominal thickness 1/16 inch, non-wire filled. Manufactured by Johns-Manville Co., Philadelphia, Pa. Used to hold together the guarded heater and to insulate the core from the copper face plates.

Balance. Analytic, "Chainomatic," capacity 100 gm, one-mg graduations with vernier for tenth mg. Manufactured by Sederer Kohlbusch Inc., Jersey City, N. J. Used for determining density of nylon and for weighing various samples.

Balance. Heavy duty, triple beam, capacity 111 gm, sensitivity 0.01 gm. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for weighing viscosimeter.

Brass Screws. Machine screws, No 6-32, 3/4-inch long; one gross required. Obtained from Noland Co., Roanoke, Va. Used to assemble the guarded hot plate.

Bronze castings. Cast from pattern made to specifications by Mr. Hale Sweeney of the Industrial Engineering Department, Virginia Polytechnic Institute; two required. Cast by Salem Foundry and Machine Works, Salem, Va. Used in constructing guarded hot plate.

Calorimetric Thermometer. Mercury, range 66-95 ^{o}F, with 0.1-^{o}F graduations, catalogue No L5498. Calibration curve furnished. Manufactured by the Parr Instrument Co., Moline, Ill. Used with calorimeter.

Can. Solvent can, five gal capacity. Obtained from Chemical Engineering Stockroom. Used to construct water bath.

Carboy. Glass, five gal capacity. Obtained from Chemical Engineering Stockroom. Used to contain distilled water for calorimeter calibration tests.

Circulating Pump. Electrically driven centrifugal pump, capacity 3/4-gal water per min against seven-foot head, motor rating 1/10 hp, 110 v, 60 cy, ac, 1725 rpm. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to circulate cooling water to guarded hot plate.

Copper Tubing. Dead soft, seamless, 3/8-inch outside diameter; 30 feet required. Manufactured by National Copper and Smelting Co., Cleveland, O. Used for water bath cooling coil and for carrying circulating water to guarded hot plate.

Copper Tubing. Dead Soft, seamless, 5/16-inch outside diameter; two feet required. Manufactured by National Copper and Smelting Co., Cleveland, O. Used for nipples in rubber tubing connections.

Counter. Hand tally, with reset, range 999 units, catalogue No 27-397. Obtained from Phipps and Bird Inc., Richmond, Va. Used to count revolutions of wattmeter disk.

Double Plug Outlet. Standard wall outlet, rating 250 v; four required. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used in electric circuits.

Double Plug Outlet Face Plates. Plastic; four required. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used with double plug outlets.

Electric Heating Plate. "Autemp" heater, rating 450 w, 115 v, ac, with temperature regulator. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to heat distilling flask in calibrating thermocouples at the temperature of condensing naphthalene.

Esso Waterpump Grease. Manufactured by Esso Standard Oil Co., Bayway, N. J. Used to lubricate circulating pump.

Fisher Unitized Constant Temperature Bath. Water bath consisting of the following items: thermostat, catalogue No 15-444-10; jar and base unit 15-444-5; motor stirrer 15-444-15; 500-watt immersion heater 15-444-20. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to maintain viscosimeter at temperature of 25 °C plus or minus 0.05 °C.

Flat Surface. Steel plate, one surface finished true. Borrowed from the Industrial Engineering Department Shop. Used to compare with heater and cooling block surfaces.

Fuse. Rating ten amp, 115 v, standard base; one required. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used to protect water bath circuits.

Fuses. Rating two amp, Buss glass tube fuse, model No AGA2; five required. Manufactured by Bussman Manufacturing Co., St. Louis, Mo. Used to protect heater circuits.

Galvanometer. Light-beam type, sensitivity 0.031 microamp per mm deflection, balancing resistance 12000 ohms, resistance 332 ohms, period 3.0 sec, catalogue No 2420A, serial No 765436. Manufactured by Leeds and Northrup Co., Philadelphia, Pa. Used with potentiometer.

Gasket Compound. "Palmetto" asbestos sheet, 1/16-inch thick. Manufactured by Johns-Manville Co., Philadelphia, Pa. Used as gaskets between cover plates and cooling blocks of guarded hot plate.

Heater Face Plates. Copper, 1/8-inch thick, five by five inches square; two required. Cut from copper sheet by Lloyd Electric Co., Roanoke, Va. Used in constructing heater.

Immersion Heaters. "Aminco Lolag" flexible type, copper sheath, rating 500 w, catalogue No 3-404; two required. Manufactured by American Instrument Co., Silver Spring, Md. Used to heat water bath.

Knife Switches. "Trumble" double-pole, double-throw, rating 250 v; two required. Obtained from Virginia Polytechnic Institute Electric Service Department. Used to connect ammeter into center and guard heater circuits.

Lightnin' Agitator. Model L, propeller-type with extendable shaft, serial No 514897, rating 110 v, 60 cy, single-phase, ac. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to stir water bath.

Machine Bolts. Steel, 1/4-inch N. C. 20, 3/4 inch long; 15 required. Obtained from Noland Co., Roanoke, Va. Used to bolt cover to annealing pan.

Machine Bolts. Steel, 3/8-inch N. C. 16, 6-1/2 inches long; four required. Obtained from Noland Co., Roanoke, Va. Used to bolt guarded hot plate together.

Machine Bolts. Steel, 3/16-inch N. C. 24, 1-1/4 inches long; 22 required. Obtained from Noland Co., Roanoke, Va. Used to fasten binding post plates to zone box.

Mica Sheet. Five by seven inches, 0.004 inches thick, catalogue No 89285-D; three required. Obtained from Central Scientific Co., Chicago 13, Illinois. Used to hold together guarded heater and to insulate core from face plates.

Meter. Amperes, ac, style No 528, model No 250, with two ranges: 0-15 amp, 0.5-amp graduations; 0-5 amp, 0.1-amp graduations. Manufactured by the Weston Electrical Instrument Co., Newark, N. J. Used to compare current flowing through center and guard heaters.

Meter. Volts, ac, style No 528, model No A8269, with two ranges: 0-150 v, 5-v graduations; 0-15 v, 0.5-v graduations. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure potential across the center heater of the guarded hot plate.

Meter. Volts, dc, style No 489, model No 62580, with three ranges: 0-150 v, 2-v graduations; 0-7.5 v, 0.1-v graduations; and 0-3 v, 0.05-v graduations. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure storage battery emf.

Meter Terminals. Signal Corps, push-button contact; four required. Obtained from US Army Surplus. Used as meter terminals on panelboard.

Micrometer. Machinist's micrometer, one-inch opening, 0.001-inch graduations. Manufactured by Reed Small Tool Works, Worcester, Mass. Used to measure nylon sample thickness and in constructing rolls.

Motor Rheostat. Field type, sliding contact, rating 125 v, 0.26 ohm, 10.4 amp, catalogue No CR8000-B1, serial No 2240001 G45. Manufactured by General Electric Co., Schnectady, N. Y. Used to control temperature of muffle furnace.

Muffle Furnace. Hoskins Electric Furnace, type FD204C, serial No 34928, rating 110 v, 30.9 amp. Equipped with thermoelectric pyrometer, range 22-1200 °C, 25-°C graduations. Manufactured by Hoskins Manufacturing Co., Detroit, Mich. Used to heat annealing pan containing nylon.

Oxygen-bomb Calorimeter. Model No 13051, serial No 1215. Manufactured by the Parr Instrument Co., Moline, Ill. Used without bomb to calibrate wattmeter.

Pilot Light. Electric bulb, rating 7-1/2 w, 115 v. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used to indicate "on" position of water bath relay.

Pilot Light Socket. Wall type, plastic, standard base, rating 250 v. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used with pilot light.

Plywood Board. Five ply, four feet by three feet by 1/2 inch. Obtained from New River Lumber Co., Blacksburg, Va. Used as panelboard.

Polishing Cloth. "Blitz Cloth," impregnated. Manufactured by Auburn Specialties Co., Auburn, N. Y. Used to clean surfaces of guarded hot plate.

Potentiometer. "Rubicon High Precision," with three ranges: 0-1.6 v, 0-0.16 v, and 0-0.016 v, with graduations of 0.00005, 0.000005, and 0.0000005 v respectively; three sensitivities; catalogue No 2780. Manufactured by the Rubicon Co., Philadelphia, Pa. Used to measure thermocouple emf's.

Pressure Reducing Valve. Hoke-Phoenix oxygen valve, Model No 630, with tank pressure gage and flow gage, departmental No 3X277. Manufactured by the Hoke Co., New York, N. Y. Used to control flow of nitrogen gas from pressure cylinder to annealing pan.

Receptacle Box. Standard style; one required. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used to contain double plug outlet.

Rectifier. "Aminco Rectran," copper-oxide rectifier, input 115 v, ac, output 10 v, dc, catalogue No 4-465; two required. Manufactured by

the American Instrument Co., Silver Spring, Md. Used as actuating power source for thermoregulator, and for light-beam galvanometer.

Relay. "Silent Power Relay," mercury solenoid switch, six v, dc, actuating voltage, 115 v, ac, controlled voltage, catalogue No 4-371A. Manufactured by the American Instrument Co., Silver Spring, Md. Used to operate water bath automatic heater.

Relay Housing. Catalogue No 4-380. Manufactured by the American Instrument Co., Silver Spring, Md. Used to house relay.

Resistors. Sliding contact type R9, serial Nos 91859 and 93284. Manufactured by the National Electric Controller Co., Chicago, Ill. Used to balance power input to center and guard heaters.

Scraping Tool. Flat-ended chisel, steel. Borrowed from the Industrial Engineering Department Shop. Used to scrape heater and cooling block surfaces.

Standard Weston Cell. "Eplab Students' Cell," emf 1.0185 v, serial No 402775. Manufactured by the Eppley Laboratories, Inc., Newport, R. I. Used to standardize potentiometer.

Steel Box. All welded, open top, 16 inches long, 12 inches high, 10 inches wide, wall thickness 1/8 inch. Obtained from Chemical Engineering Stockroom. Used to contain guarded hot plate.

Storage Battery. "Gould Televel," lead, three cells, six v. Obtained from US Army Surplus. Used as source of emf for balancing potentiometer.

Thermocouple Wire. Chromel, No 28 B. and S. gage, bare, from spool No 60988-1. Manufactured by Leeds and Northrup Co., Philadelphia, Pa. Used to make thermocouples and for leads to cold junction.

Thermocouple Wire. Constantan, 1938 calibration, No 30 B. and S. gage, enamel insulated, from spool No 64200-2. Manufactured by Leeds and Northrup Co., Philadelphia, Pa. Used to make thermocouples and for leads to cold junctions.

Thermometers. Mercury, range 30-300 °F, two-°F graduations, catalogue No 14-990; two required. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for general thermometric purposes.

Thermoregulator. "Quickset Bimetallic Thermoregulator," range -77 to 177 °C, catalogue No 4-235. Obtained from American Instrument Co., Silver Spring, Md. Used to regulate water bath temperature.

Timer. "Time-it," range 9999.9 sec, 0.1-sec graduations, 110-v, 60-cy, ac power supply required. Manufactured by the Precision Scientific Co., Chicago, Ill. Used for timing various tests.

Toggle Switches. Standard wall type, rating 250 v; two required. Obtained from Virginia Polytechnic Institute Electric Service Department. Used to connect bath heaters.

Toggle Switch Double Face Plate. Plastic. Obtained from Virginia Polytechnic Institute Electric Service Department. Used with toggle switches.

Toggle Switches. Radio type, rating 250 v. Obtained from Central Scientific Co., Chicago, Ill. Used as thermocouple selectors.

Valve. Needle valve, 3/8-inch, brass. Obtained from Noland Co., Roanoke, Va. Used to regulate flow of circulating water to one cooling block, for equalizing heat flow through both directions of the guarded hot plate.

Valves. Globe valves, 3/8-inch, brass; three required. Obtained from Noland Co., Roanoke, Va. Used to regulate flow of bath cooling water, pump priming water, and flow of circulating water to one cooling block.

Viscosimeter. Modified Ostwald type, conforming to specifications of ASTM[96] Tentative Method of Test for Kinematic Viscosity, designation D445-46T, size 100, serial No B182. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to measure solution viscosity of nylon samples.

Voltage stabilizer. Rating 1.0 KVA, 60 cy, 95-130 v line, 115/120/125 v output, output voltage variation plus or minus 2.0 per cent at unity power factor, catalogue No 68G955. Manufactured by General Electric Co., Fort Wayne, Ind. Used to stabilize voltage for guarded hot plate heater.

Watt-hour Meter. Single phase, 115-v, serial No 103-x-385. Manufactured by the Westinghouse Electric and Manufacturing Co., Pittsburgh, Pa. Modified, calibrated, and used to measure electric power input to center heater of guarded hot plate.

Wire. Nichrome resistance, No 22 B. and S. gage, bare. Obtained from Leeds and Northrup Co., Philadelphia, Pa. Used to construct guarded heater and various resistors.

Wire. Copper, No 12 B. and S., plastic insulated, for indoor use. Obtained from Virginia Polytechnic Institute Electric Service Department. Used for wiring 115-v electric circuits.

Wire. Nichrome resistance, size 0.0063 inches, 16.89 ohms per ft, grade E. Manufactured by Wilbur B. Driver Co., Newark, N. J. Used as load for wattmeter calibrations.

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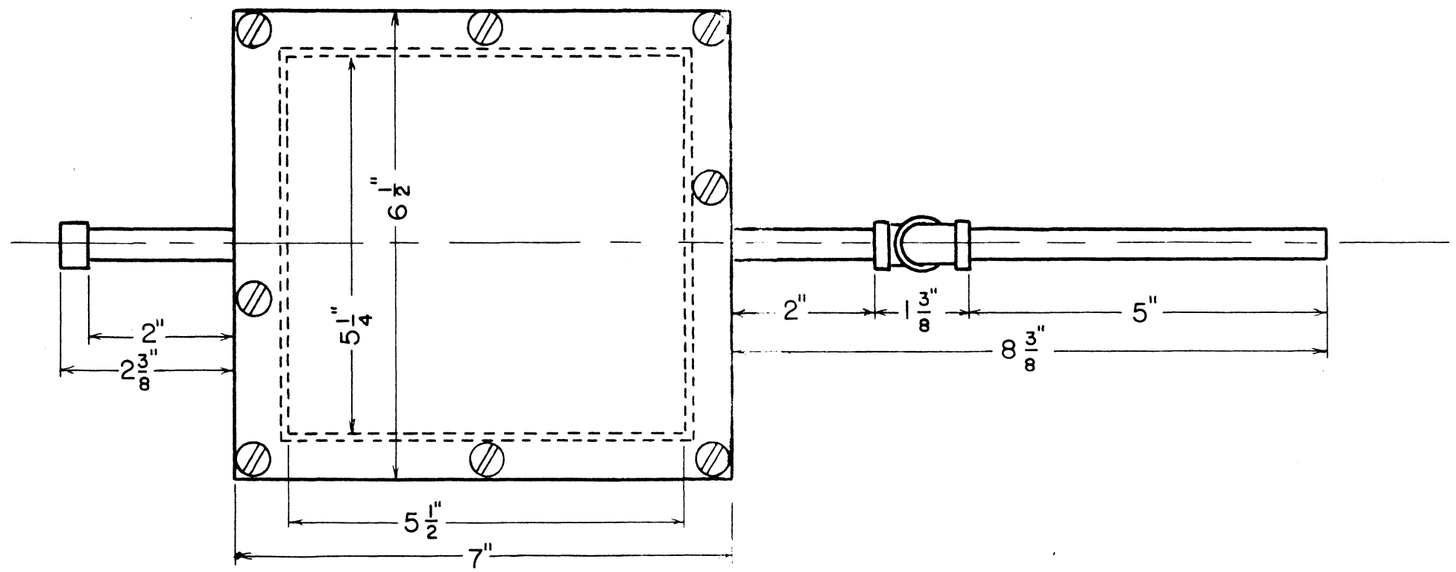
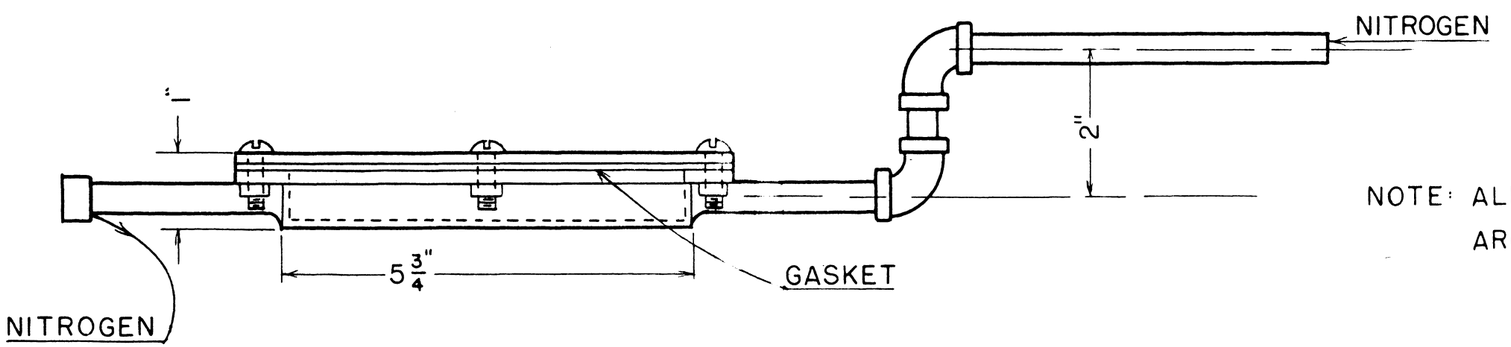
Figure 10. Covered Annealing Pan





MATERIALS

1 ANGLE IRON 1/2" X 1/2" X 1/8", 11-1/4" LONG
1 STEEL PLATE 1/8" THICK, 7" X 6-1/2"
1 STEEL PLATE 1/8" THICK, 5-1/2" X 5-1/4"
1 PIECE BLACK IRON PIPE 1/8" NOM., 11" LONG
2 BLACK IRON ELLS 1/8" NOM.
1 BLACK IRON CAP 1/8" NOM.
8 MACHINE SCREWS 1/4" N.C.-20 WITH NUTS
1 PALMETTO GASKET, 1/16" NOM., 6-1/2" X 7"

NOTE: ALL JOINTS ARC-WELDED

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COVERED ANNEALING PAN

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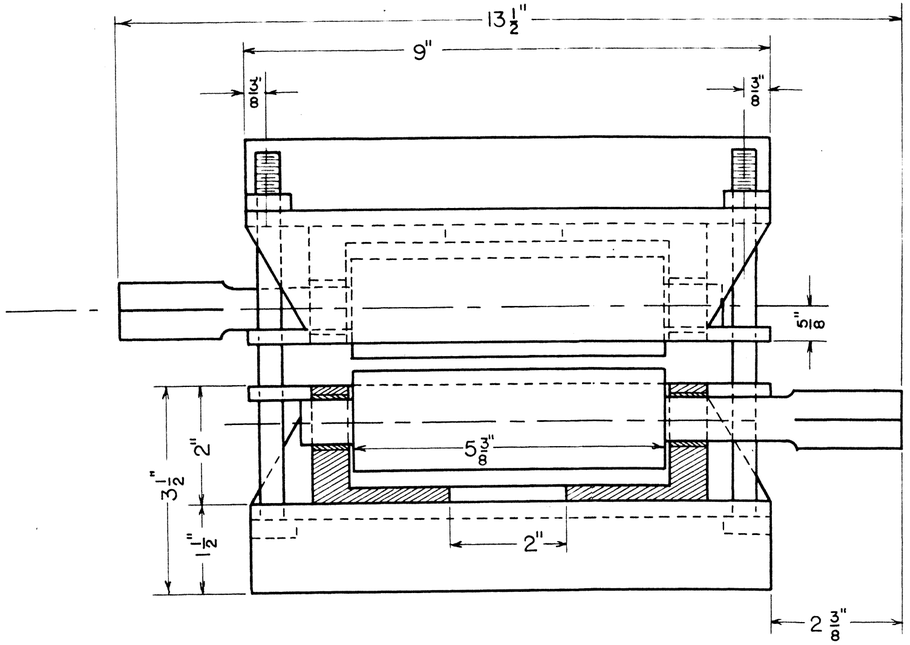
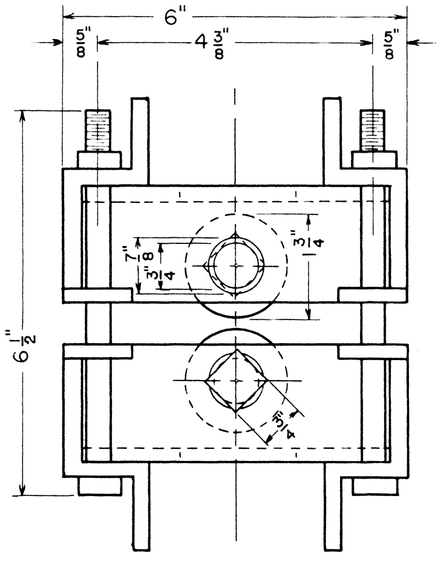
FIGURE 10
FILE NO. 52
CASE NO. 599

Figure 11. Rolls Assembly



FRONT ELEVATION

NOTE: ALL JOINTS
ARC-WELDED



SIDE ELEVATION

MATERIALS

2 PIECES STEEL SHAFT 2" DIA, 8" LONG

2 PIECES ANGLE IRON 2" X 2" X 1/4", 25" LONG

4 PIECES ANGLE IRON 1-1/2" X 1-1/2" X 1/4", 9" LONG

4 STEEL BARS 2" X 3/8", 6" LONG

8 WEBS, 1/4" STEEL, RIGHT TRIANGLES 1-1/8" X 1-3/4"

8 WEBS, 1/4" STEEL, RECTANGLES 1-1/8" X 1-1/4"

8 MACHINE BOLTS, 3/8" N.C 16, 6-1/2" LONG, WITH NUTS

2 PIECES STEEL BAR STOCK 3/4" X 3/4", 2-1/2" LONG

2 PIECES COPPER PIPE 3/4" I.D., 3/8" LONG

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ROLLS ASSEMBLY

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FIGURE 11
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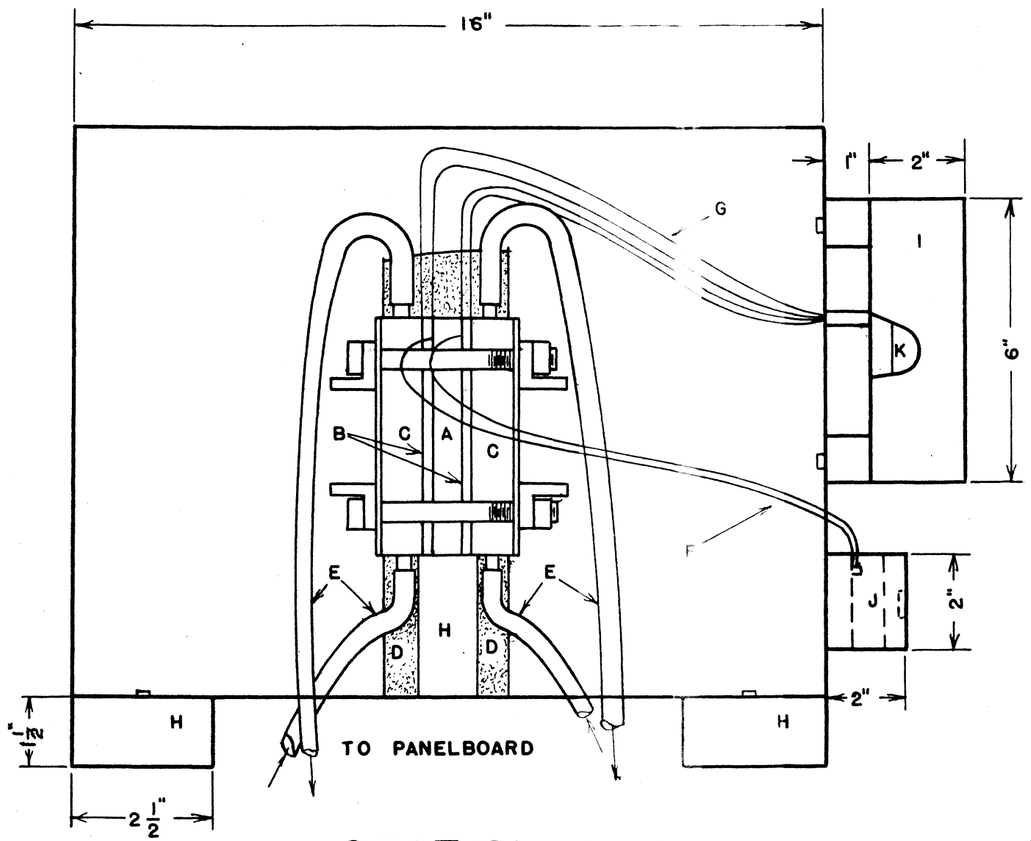
Guarded Hot Plate. A guarded hot plate was constructed in the laboratory to measure the thermal conductivity of nylon. It is shown in Figure 12. It was made according to the requirements of the American Society for Testing Materials Standard Method of Test for Thermal Conductivity of Materials by Means of the Guarded Hot Plate, ASTM Designation C177-45[83]. The ASTM method does not give detailed instructions concerning the design of the apparatus, but sets down a few essential requirements. Further suggestions are given in a pamphlet published by the Society[54], but some leeway is left to the experimenter's judgment.

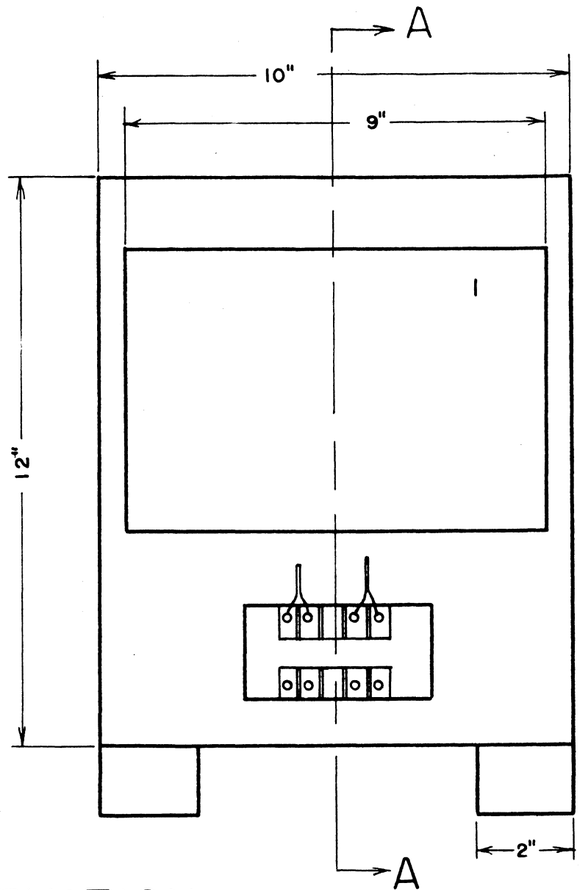
Electric Heater. The heater was of the design called "Modified National Bureau of Standards Heater" in the ASTM pamphlet[54]. It consisted of two parts, a square center heater, surrounded by an annulus-shaped guard heater to control edge temperature. The center heater was 3.5 inches square and the guard heater was 5.0 inches square with a 1/16-inch separation between the two. The heater is shown in Figure 13.

Heating Elements. The heating elements of the heater were formed by winding No. 22 nichrome resistance wire on cores of asbestos shingles 1/4-inch thick in the arrangement shown in Figure 14. The dimensions of the cores were the same as those of the heaters. First, the corrugations on the shingle were ground off. Notches in the edges of the cores were sawed to space the wires. The wires rested directly on the surface of the

Figure 12. Guarded Hot Plate Assembly



SECTION A-A



ELEVATION

KEY

A- HEATER
B- NYLON SAMPLES
C- COOLING BLOCKS
D- MAGNESIA INSULATION
E- RUBBER TUBES
F- HEATER LEADS
G- THERMOCOUPLE LEADS
H- WOODEN SUPPORTS
I- ZONE BOX
J- HEATER TERMINALS
K- THERMOCOUPLE CABLE EXIT (CABLE NOT SHOWN)

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GUARDED HOT PLATE ASSEMBLY

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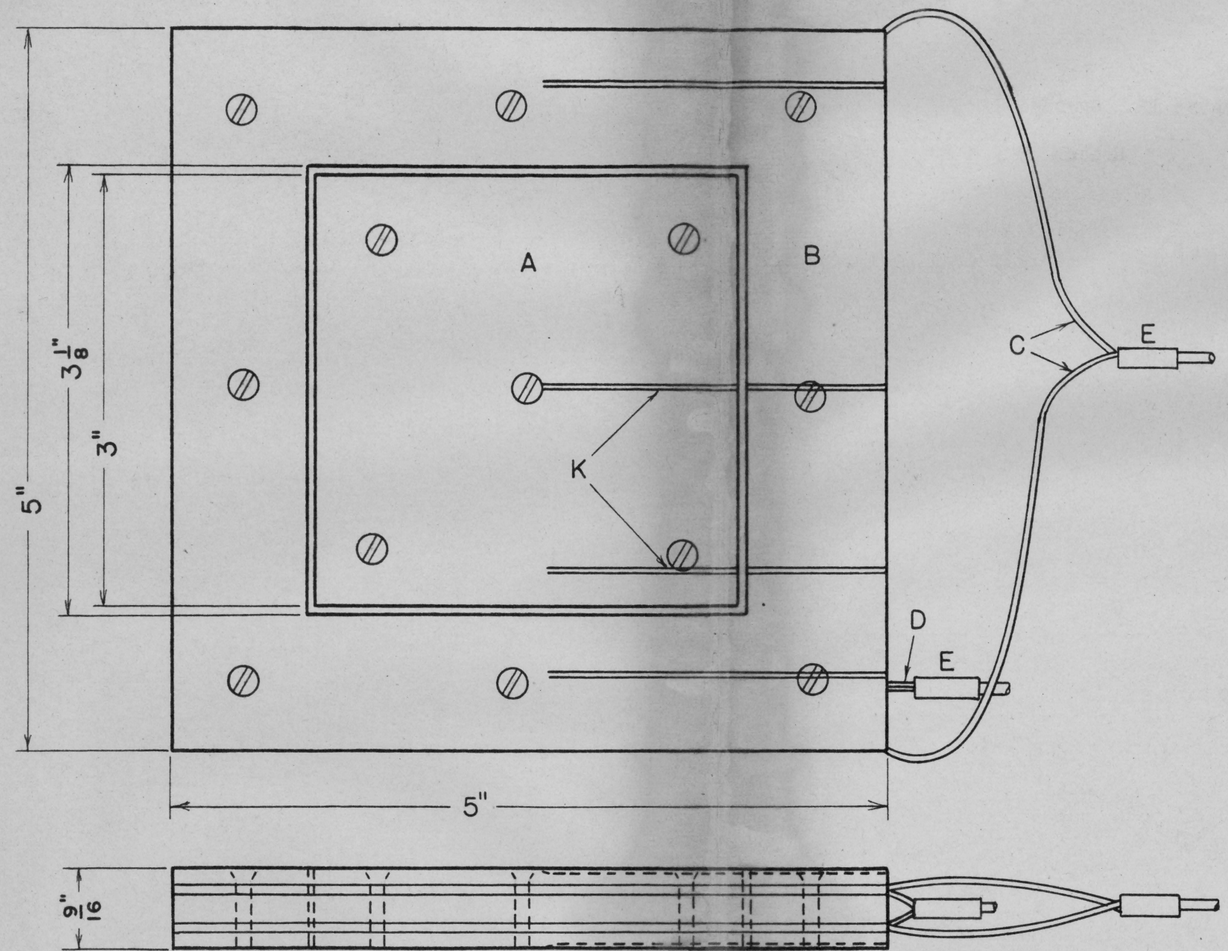
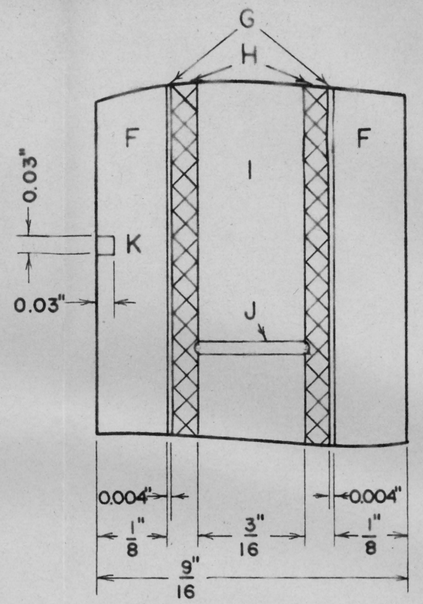
FIGURE 12
FILE NO. 52
CASE NO. 599

Figure 13. Guarded Hot Plate Heater





DETAIL
EDGE VIEW
SCALE: 1" = 1/4"

KEY

A- CENTER HEATER
B- GUARD HEATER
C- CENTER HEATER LEAD WIRES
D- GUARD HEATER LEAD WIRES
E- CERAMIC SPAGETTI
F- COPPER FACE PLATES
G- MICA SHEETS
H- ASBESTOS CLOTH
I- TRANSITE BOARD HEATER CORE
J- A RESISTANCE WIRE
K- THERMOCOUPLE SLOT

MATERIALS

2 COPPER SHEET 1/8" THICK, 5" X 5"
1 TRANSITE BOARD 3/16" THICK, 5" X 5"
1 TRANSITE BOARD 3/16" THICK, 3" X 3"
2 MICA SHEETS 0.004" THICK, 5" X 5"
2 PIECES ASBESTOS CLOTH 0.04" NOM. THICKNESS, 5" X 5"
13 BRASS MACHINE SCREWS, NO. 6-32

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GUARDED HOT PLATE HEATER

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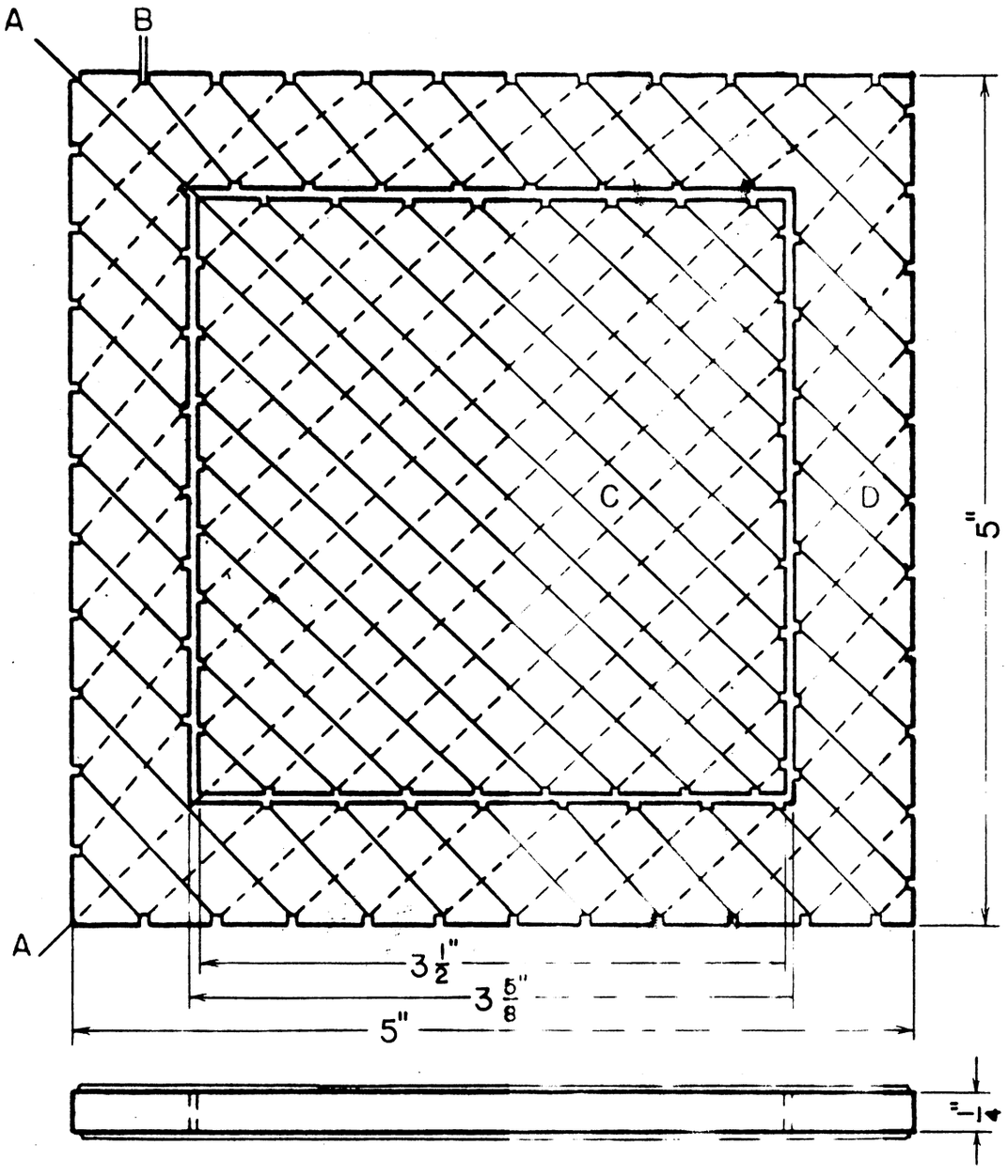
FIGURE 13
FILE NO 52
CASE NO 599

Figure 14. Heater Cores



KEY

A- CENTER HEATER LEADS

B- GUARD HEATER LEADS

C- CENTER HEATER

D- GUARD HEATER

MATERIALS

1 ASBESTOS SHINGLE 1/4" THICK, 5" X 5"

1 ASBESTOS SHINGLE 1/4" THICK, 3-1/2" X 3-1/2"

17 FT NO. 22 B&S NICHROME RESISTANCE WIRE

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HEATER CORES

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FIGURE 14
FILE NO. 52
CASE NO. 599

cores so that the force developed when the heater was screwed together would bear on them, improving heat transfer from the wires. Ninety-two inches of wire were wound on the center heater, with an additional 2.6 inches serving as leads through the guard heater.

Copper Face Plates. Copper face plates were cut from 1/8-inch copper sheet by Lloyd Electric Company, Roanoke, Va.

Heater Assembly. Screw holes were drilled in one face plate, and this was used as a template for drilling holes in the other parts of the heaters. A piece of asbestos welding cloth of 1/16-inch nominal thickness and five inches square was placed over each side of the wound cores, and these were covered by a piece of mica sheet 0.004 inches thick. The face plates were then set in place and the assembled heater screwed together with 13 No. 6-32 brass screws. The heads were countersunk so that they projected 0.005 inch from one side of the heater, and the screw holes in the face plate on the other side were tapped. The screws were then tightened uniformly.

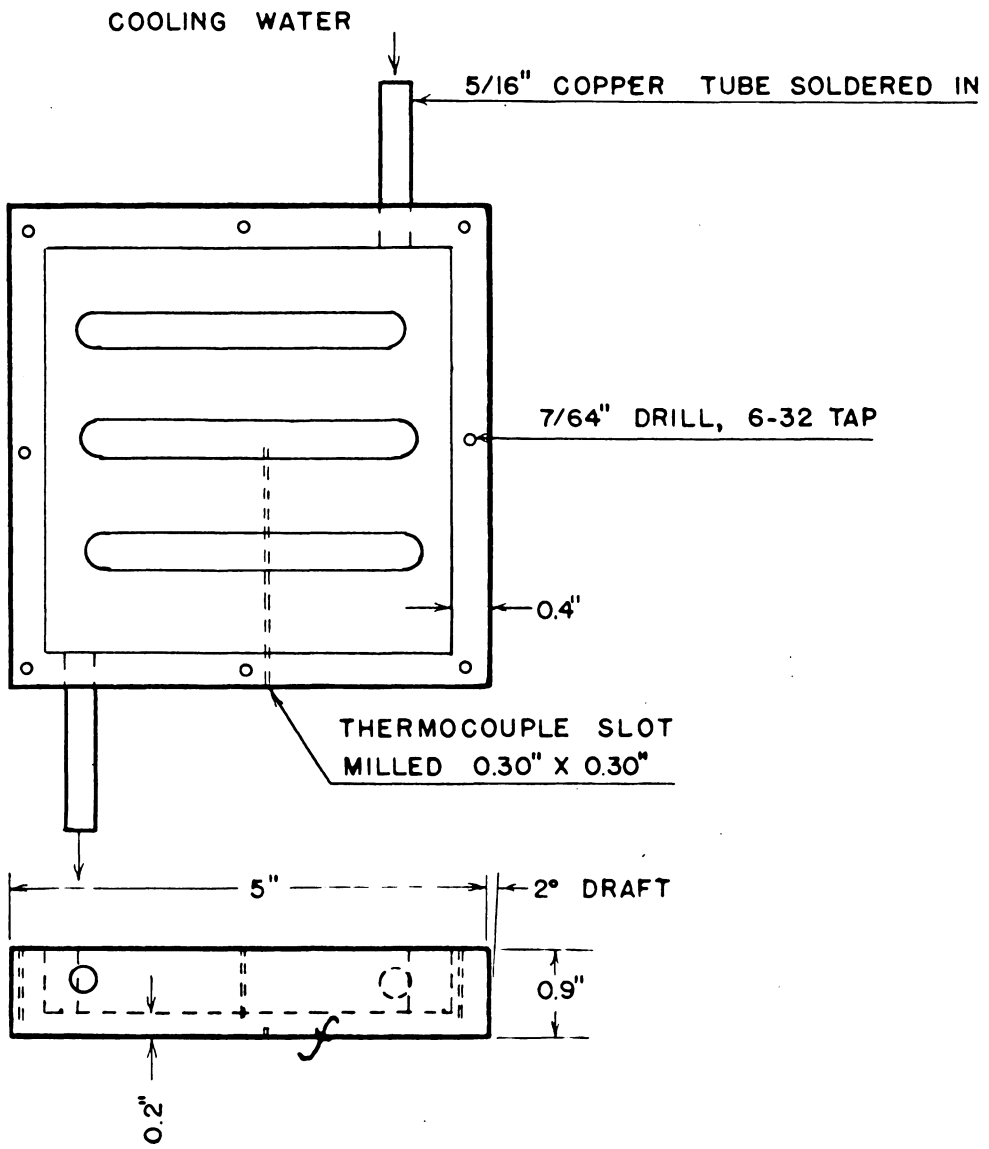
The assembled heater consisted of two separate heaters in one unit, a center and guard heater, held in place by the asbestos cloth and the mica sheets. This method of assembly provided sufficient rigidity.

Finishing Heater Surfaces. The two surfaces of the assembled heater were finished by scraping with a chisel and by lapping with

valve grinding compound, testing for flatness by comparison with a flat surface borrowed from the Industrial Engineering Department Shop. When finished, over 90 per cent of the surface of the heaters lay in a true plane within 0.001 inch, with no depression having an area greater than one per cent of the total or a depth (except screw slots) greater than 0.003 inches.

Thermocouple Slots. Slots for the thermocouple wires were milled in the heater surfaces by inserting a lathe tool in an arbor and feeding the work underneath the rotating tool by means of the lathe cross-feed. The slots were 0.030 inches deep and 0.030 inches wide. They are shown in Figure 14.

Cooling Blocks. The cooling blocks were cast of bronze by the Salem Foundry from a pattern made by Mr. Hale Sweeney of the Industrial Engineering Department, VPI. A cooling block is shown in Figure 15. The baffles in the hollow part of the blocks were provided to distribute the water flow. Nipples cut from 5/16-inch copper tubing were soldered into two opposite edges of the blocks so that rubber tubing could be connected to them to feed the circulating water through the blocks. Both faces of the blocks were turned down on the lathe, and the flat face was polished in the same way at the heater surfaces. The water spaces were closed over by covers constructed from 1/8-inch steel sheet screwed into place with eight 6-32 brass screws. A gasket was sealed in place under the cover with "Permatex" gasket-sealing compound.



MATERIAL OF CONSTRUCTION: CAST BRONZE

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COOLING BLOCK

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FIGURE 15
FILE NO. 52
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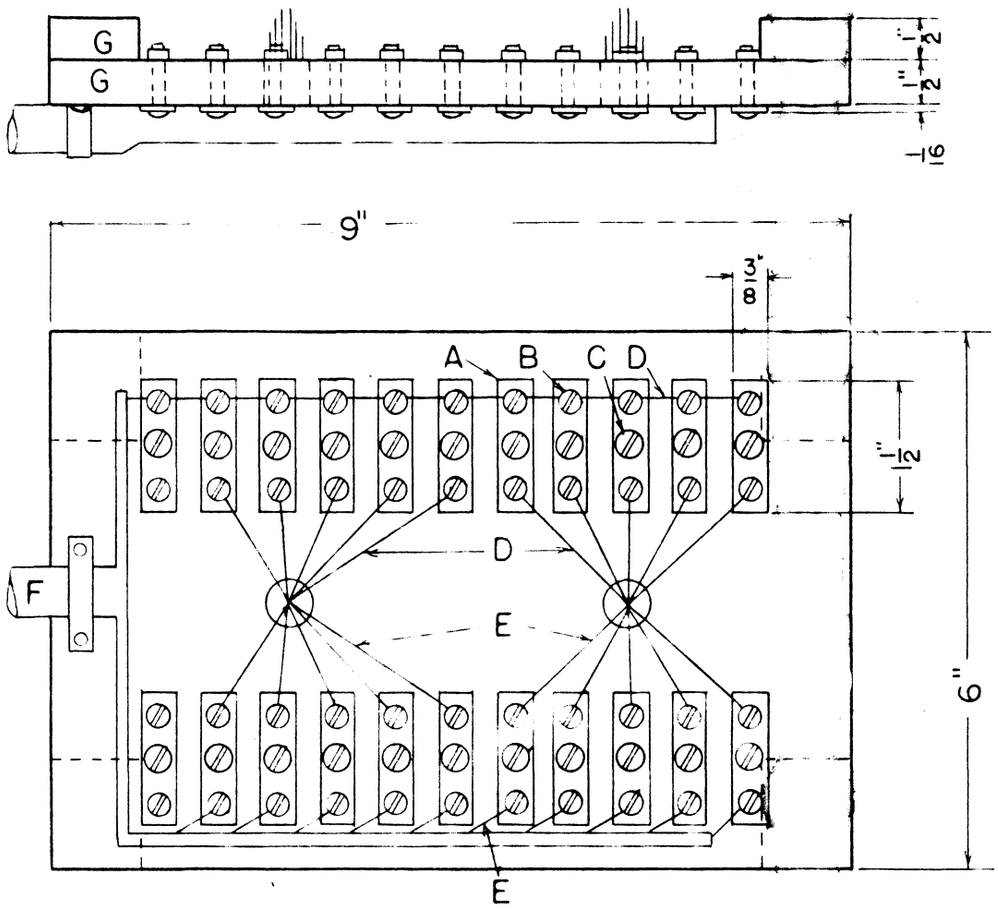
Page 101 is missing from all copies of this piece

It is shown in Figure 12 with the hot plate in position and with rubber hoses, thermocouples, and heater lead wires in place.

Zone Box. The zone box shown in Figure 16 was constructed to facilitate connecting the thermocouple wires to the lead wires, and to protect the connections from temperature differences due to air currents. Two rows of ten pieces of copper 3/8 by 2 by 1/16-inch were screwed to a piece of transite board which was bolted to the hot plate box. Two holes 7/16-inch in diameter were drilled in either end of these copper pieces and tapped with a 6-32 tap. Brass screws size 6-32 were screwed into the holes as binding posts. Each screw was fitted with a copper washer. The binding posts were numbered.

Thermocouple Cable. A lead-wire cable was constructed from thermocouple wire. It consisted of a common constantan wire and ten chromel wires, connected to the binding posts in the zone box and leading to the thermocouple selector switches, as shown in Figure 17. Each wire in the cable was wrapped with friction tape, the bundle of wires in the cable was wrapped with aluminum foil as shielding from stray magnetic fields, and the resulting cable was wrapped with friction tape. The aluminum foil was grounded to the water pipe, as was the zone box cover, the guarded hot plate box, and the selector switch box. The cable passed behind the panelboard to the selector switch box.

Figure 16. Zone Box



KEY

A - COPPER CONTACT PLATE
B - BINDING POST
C - MACHINE SCREW
D - CONSTANTAN THERMOCOUPLE WIRE
E - CHROMEL THERMOCOUPLE WIRE
F - LEAD WIRE CABLE
G - TRANSITE BOARD

MATERIALS

44 BRASS MACHINE SCREWS, NO 6-32, WITH COPPER WASHERS
22 STOVE BOLTS, 3/16"- N.C. 24, WITH NUTS
1 PIECE TRANSITE BOARD, 9" X 6" X 1/2"
4 PIECES TRANSITE BOARD, 1" X 1-1/4" X 1/2"
22 PIECES SHEET COPPER, 1-1/2" X 3/8" X 1/16"

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ZONE BOX

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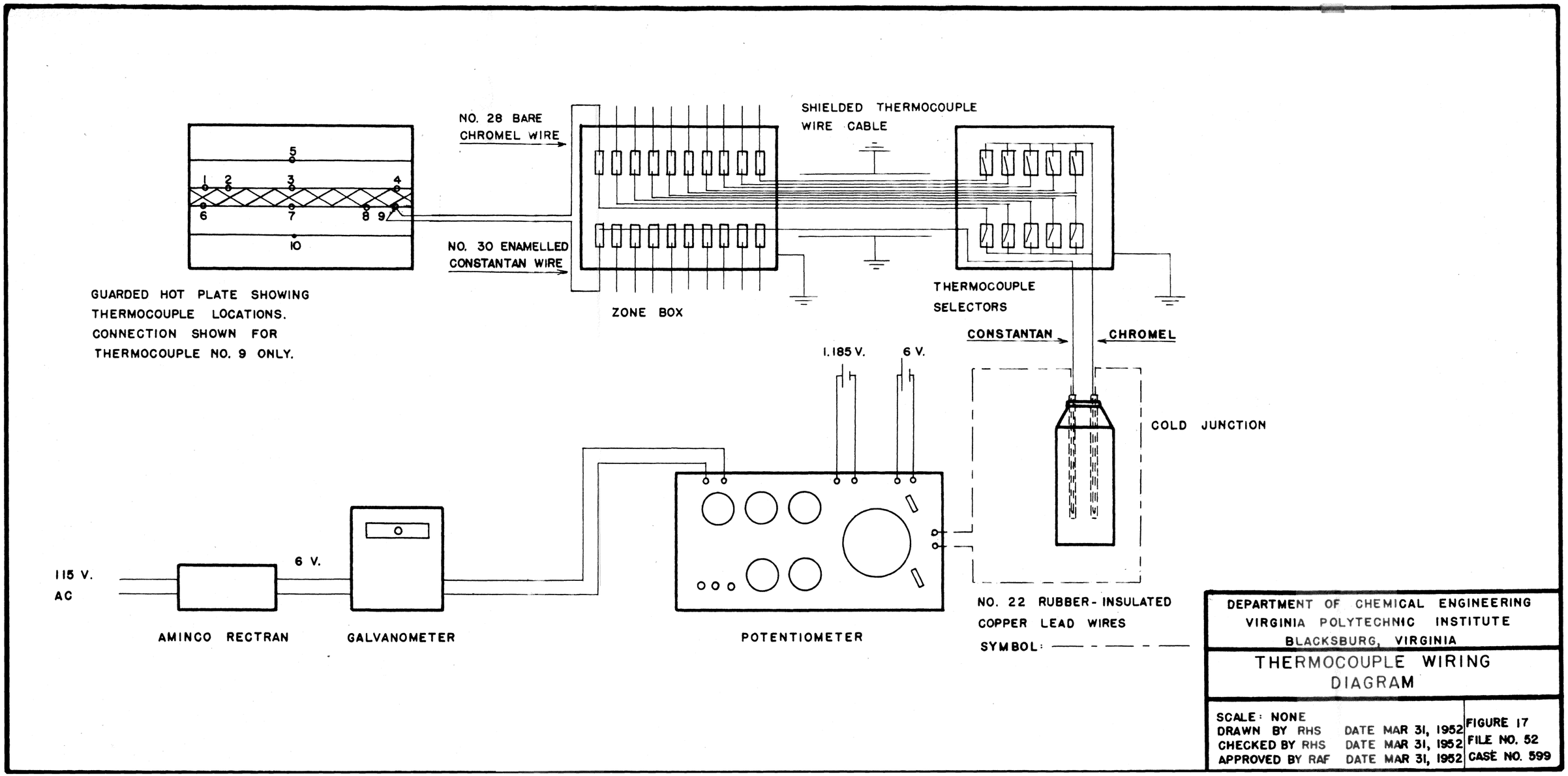
FIGURE 16
FILE NO. 52
CASE NO. 599

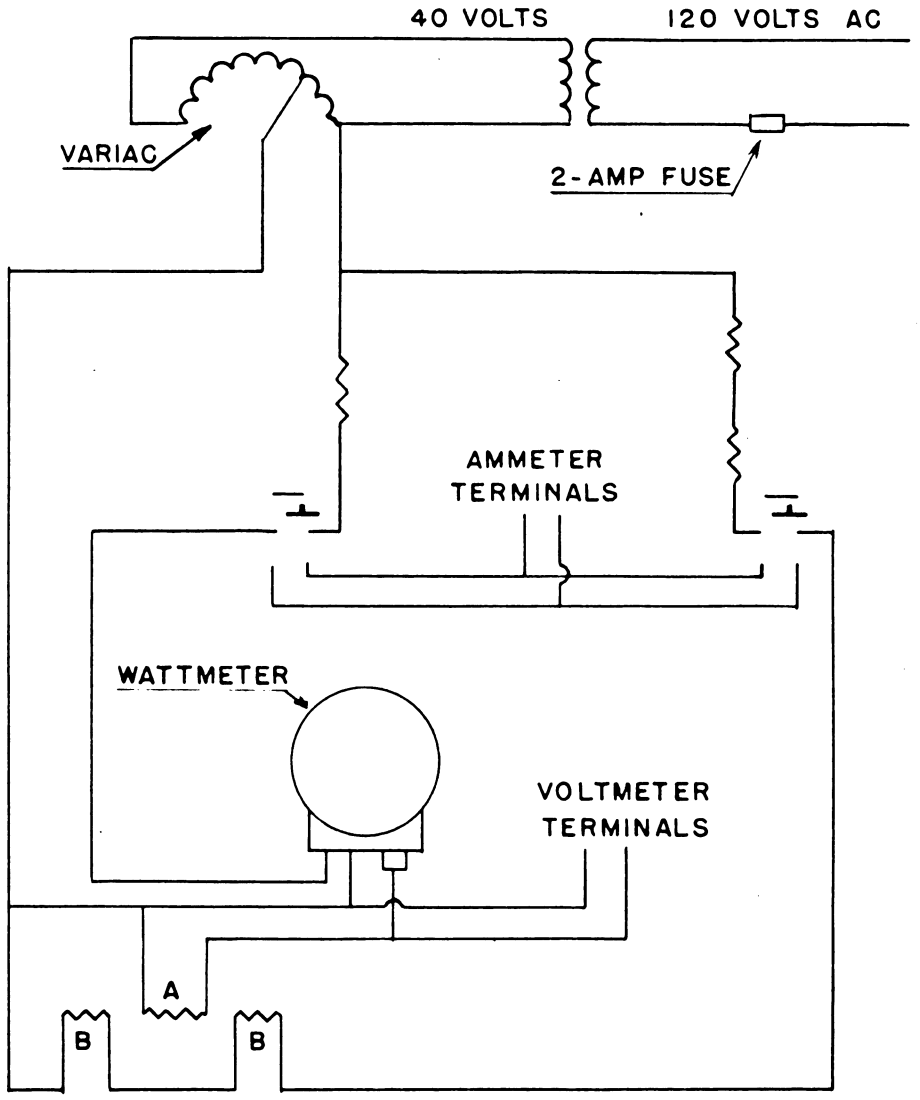
Figure 17. Thermocouple
Wiring Diagram



Selector Switch Box. The selector switches consisted of ten toggle switches mounted on a steel plate 1/8-inch thick, which was bolted to the panelboard. A grounded sheet steel cover was screwed to the back of the panelboard to protect the connections from drafts and magnetic fields. Two binding posts were provided so that the chromel and constantan wires leading to the cold junction could be disconnected there.

Emf Measuring Equipment. The remainder of the thermocouple circuit consisted of equipment for measuring the thermocouple emf's. Included were a cold junction, a potentiometer, a galvanometer, a six-volt storage battery, and a standard cell, connected as shown in Figure 17.

Hot Plate Heater Circuit. The hot plate heater circuit was assembled in the laboratory as shown in Figure 18. Alternating current at 120 volts from the voltage regulator in room 24 was supplied to a transformer which reduced the voltage to 40 volts. A Variac connected to the secondary of the transformer gave control of the voltage from zero to 40 volts, supplying both the center and guard heater circuits. A resistor was provided in each of these circuits to regulate the current and hence the temperature of the center and guard heaters separately, and an arrangement of two double-pole double-throw knife switches shown in the figure made it possible to measure the current through either heater with an ammeter for the coarse adjustment of the heater temperatures. A voltmeter measured the potential across the center heater at the outlet on the panelboard.



KEY

A - CENTER HEATER

B - GUARD HEATER

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HOT PLATE HEATER CIRCUIT

SCALE: NONE		FIGURE 18
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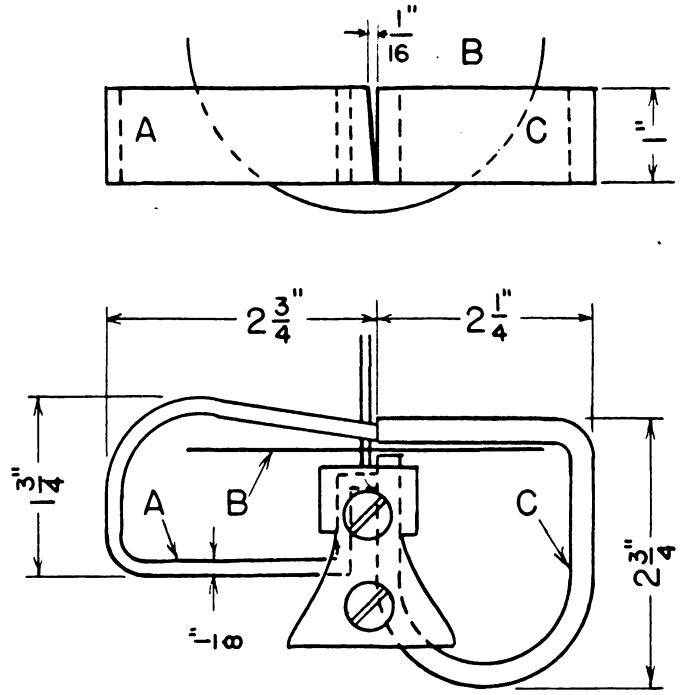
A double plug outlet was mounted on the panelboard. The two parts of the outlet were electrically separated from each other by sawing in half the live side connector and insulating the two halves from each other with friction tape. The top outlet was used for the center heater and the bottom one for the guard heater. Connection was made from the outlets to binding posts on the guarded hot plate box with lamp cord.

The electric power supplied to the center heater was measured by means of a watt-hour meter converted for use at voltages from nine to 40 volts. This was done by removing the gear train and one of the magnets, and partially shunting the magnetic circuit of the other magnet using a piece of soft iron. The arrangement of the shunt is shown in Figure 19. A mark was made on the meter disk so that the number of revolutions in a given time could be counted.

Water Bath. A water bath was assembled in the laboratory from equipment constructed in the laboratory and from purchased equipment.

The bath container was constructed from a five-gallon painted solvent can. The can was placed on an angle-iron stand on the floor under the bench and insulated with one inch of lagging. A cooling coil made from 20 feet of 3/8-inch copper tubing was fixed inside the can. The water line was connected to the coil through a valve on the panelboard, and the outlet led to the sink. (See Figure 20.) Two 500-watt heaters were fixed in the can with their terminals projecting through the side. One of these heaters was controlled by a mercury relay switch actuated by a bimetallic thermoregulator dipping into



KEY

A- SOFT IRON SHUNT

B- WATTMETER DISK

C- PERMANENT MAGNET

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WATTMETER DETAIL WITH MAGNETIC SHUNT

SCALE: 1" = 2"		FIGURE 19
DRAWN BY RHS	DATE APR 4, 1952	FILE NO. 52
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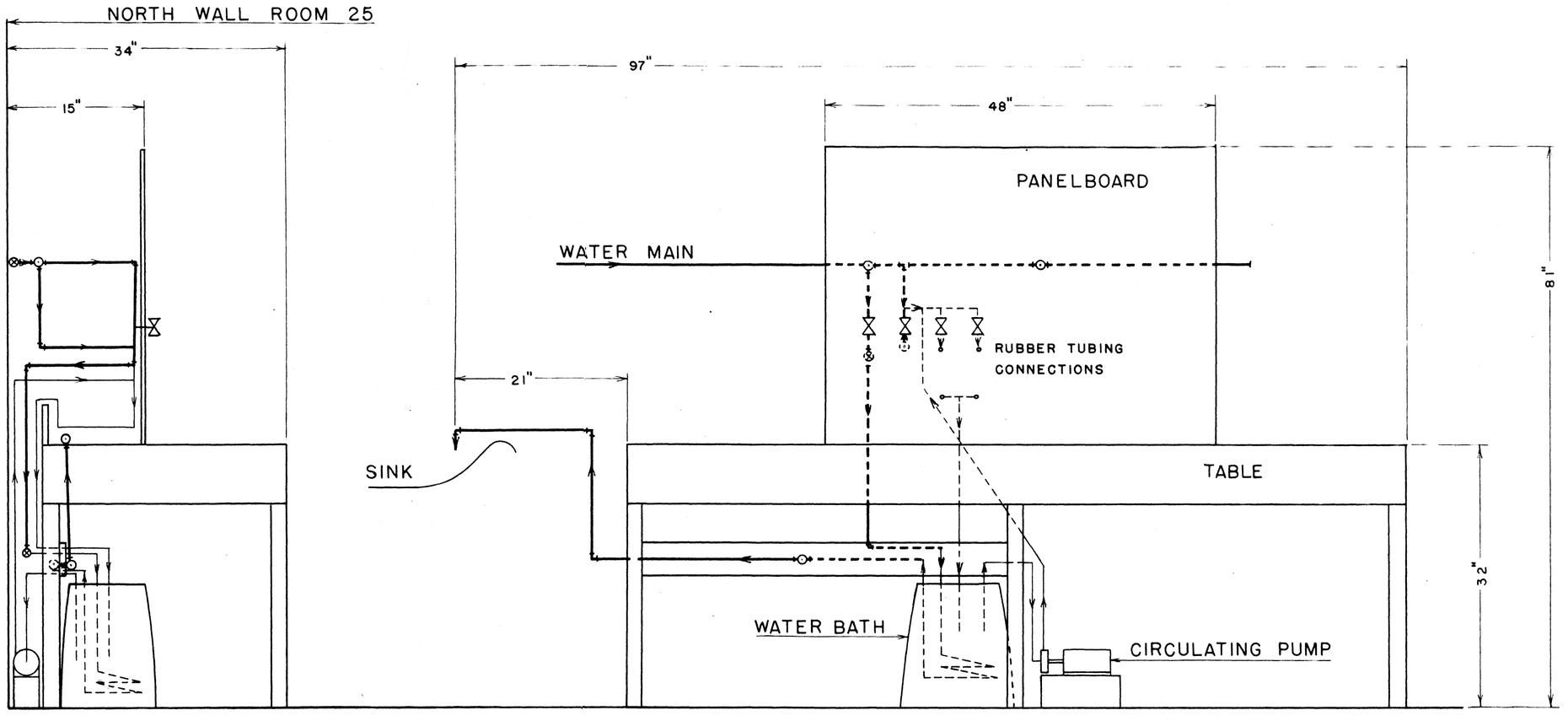
APPROVED BY RAF	DATE APR 4, 1952	

Figure 20. Piping Diagram



KEY

3/8" GALVANIZED IRON WATER PIPE

3/8" COPPER TUBE

MATERIALS

15' OF 3/8" GALVANIZED IRON PIPE

13 - 3/8" GALVANIZED IRON ELLS

2 - 3/8" GALVANIZED IRON TEES

2 - 3/8" GALVANIZED IRON UNIONS

3 - 3/8" BRASS GLOBE VALVES

1 - 3/8" BRASS NEEDLE VALVE

35' OF 3/8" COPPER TUBING

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PIPING DIAGRAM

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FIGURE 20
FILE NO. 52
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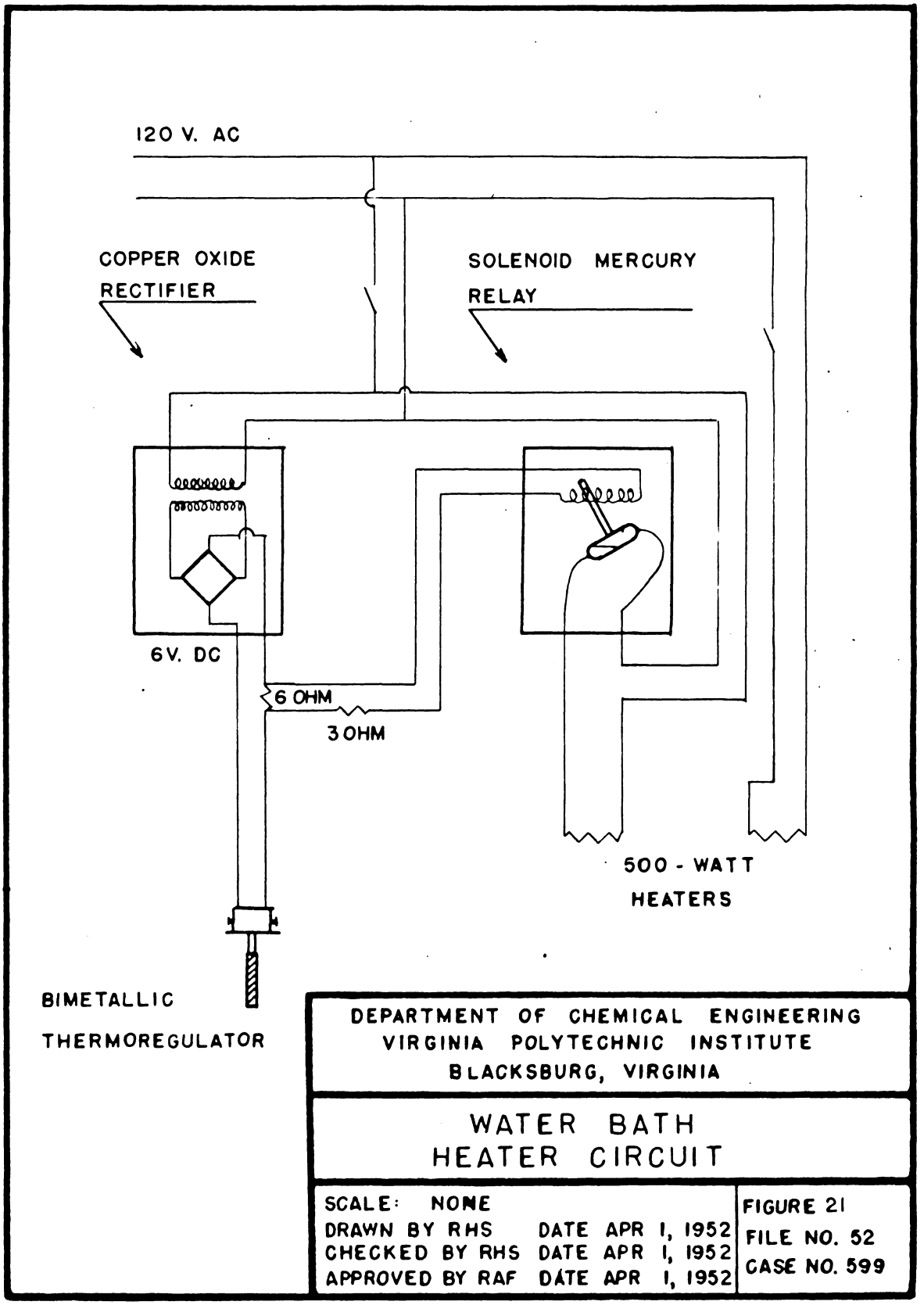
the water in the can. The other auxiliary heater was controlled by a toggle switch on the panelboard. The electric circuit diagram for the center bath heaters is shown in Figure 21.

A "Lightnin'" propeller-type agitator was mounted on a bracket fixed to the bench and dipped into the bath.

Circulating Water System. A system for circulating water from the bath through the two cooling blocks was assembled in the laboratory. A piping diagram for the circulating water system is shown in Figure 20.

A 0.1-horsepower centrifugal pump was mounted on a block of wood and placed behind the water bath can. The suction connection, a 3/8-inch copper tube, dipped into the water in the bath. A 3/8-inch copper tube from the pressure side of the pump led to a four-arm manifold on the panelboard. The manifold was constructed by silver-soldering together sections of 3/8-inch copper tubing. Three valves were connected to the manifold, a globe valve and a needle valve each controlling flow through nipples of 5/16-inch copper tubing on the front of the panelboard, and a globe valve connected to the water line for filling the water bath and priming the pump. The guarded hot plate cooling blocks were connected to the copper nipples with rubber tubing. Similar nipples on the panelboard were connected to a copper tube drain which lead back to the bath.

An arrangement was made to use cooling water direct from the water line instead of from the water bath. The incoming water was



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WATER BATH HEATER CIRCUIT

SCALE: NONE	FIGURE 21
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CHECKED BY RHS DATE APR 1, 1952	CASE NO. 599
APPROVED BY RAF DATE APR 1, 1952	

led through a rubber tube from a valve on the water line to a metal tee, and then to each cooling block. The outlet streams flowed through two rotameters to the sink.

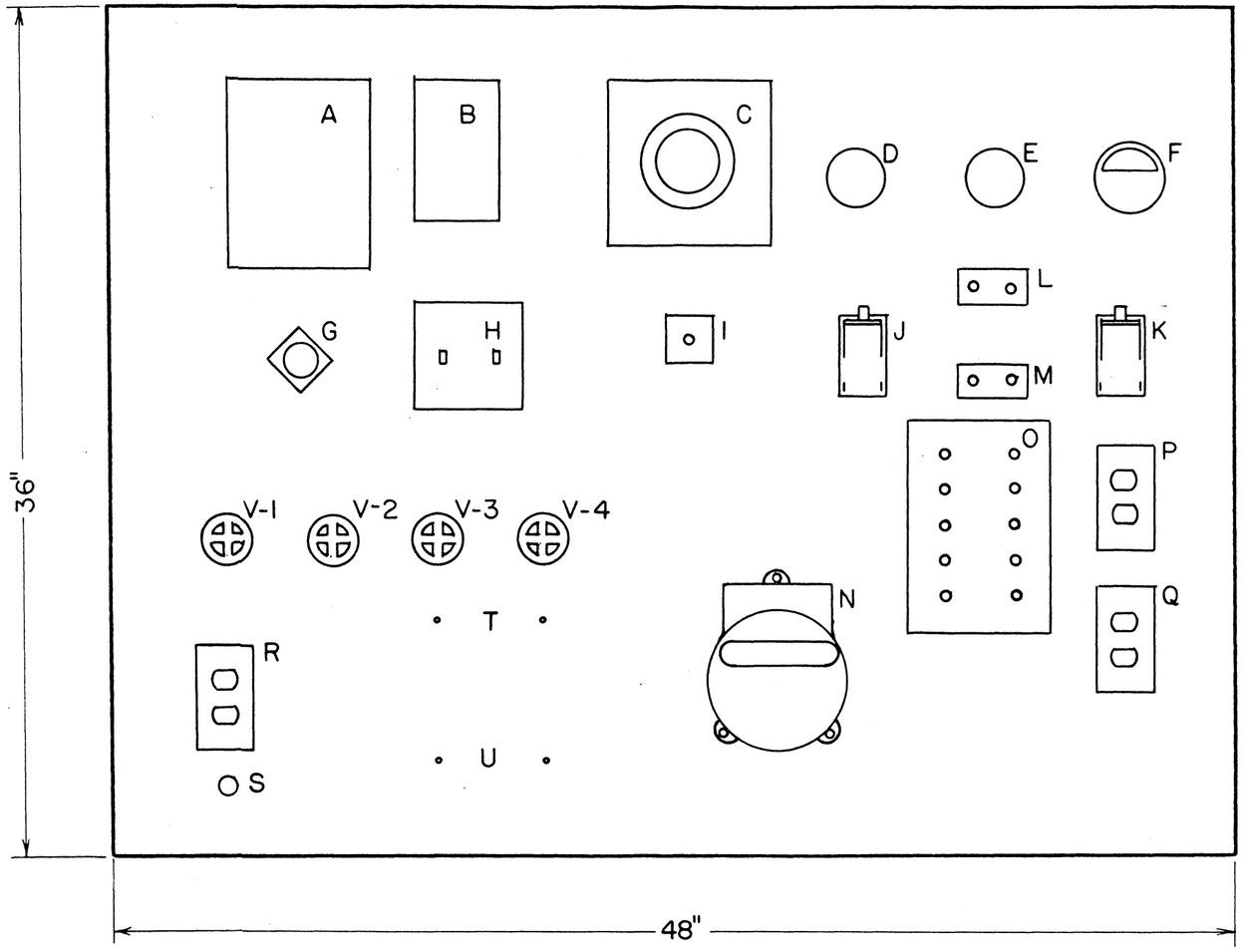
Panelboard. A panelboard was constructed in the laboratory and mounted on the bench. On it were mounted the control instruments. Figure 22 is an elevation of the panelboard. The instruments were wired from the back of the panelboard, and all connections were soldered so that no loose connections could develop during testing operations.

The front of the panelboard was sanded and painted with shellac. The back was painted black.

Thermocouple Calibration Equipment. Equipment was constructed to calibrate the thermocouples at the ice point, at the steam point, and at the temperature of condensing naphthalene vapors. Crushed ice in a vacuum bottle was used for the ice point. The thermocouples were inserted in a three-millimeter glass tube with one end sealed, dipping four inches into the ice. A hypsometer was constructed for determining the steam point. It is shown in Figure 23. The steam was drawn from the process steam line through a needle valve. A distilling flask with reflux air condenser was used for the naphthalene point determination.

Sling for Density Measurements. To measure the density of samples of nylon, the left-hand pan of an analytic balance was replaced with a wire sling (shown in Figure 24). The sling was constructed of No 22 nichrome wire, with copper weights attached to it. The lower sling,

Figure 22. Panelboard Elevation



KEY

A- MERCURY RELAY
B- AMICO RECTRAN
C- VARIAC
D- CENTER HEATER RESISTOR
E- GUARD HEATER RESISTOR
F- CENTER HEATER VOLTMETER
G- BATH HEATER PILOT LIGHT
H- BATH HEATER SWITCHES
I HOT PLATE CIRCUIT MAIN SWITCH
J- AMMETER CUT-IN FOR CENTER HEATER
K- AMMETER CUT-IN FOR GUARD HEATER
L- AMMETER TERMINALS
M- VOLTMETER TERMINALS FOR CENTER HEATER
N- WATTMETER
V-1- BATH COOLING WATER
V-2- PUMP PRIMER
V-3, V-4- CIRCULATING WATER
O- THERMOCOUPLE SELECTOR
P- 120-VOLT OUTLET
Q- 6-VOLT OUTLET
R- HEATER OUTLETS
S- THERMOCOUPLE CABLE ENTRANCE
T, U- NIPPLES

PANELBOARD MATERIAL OF CONSTRUCTION: 1/2" PLYWOOD

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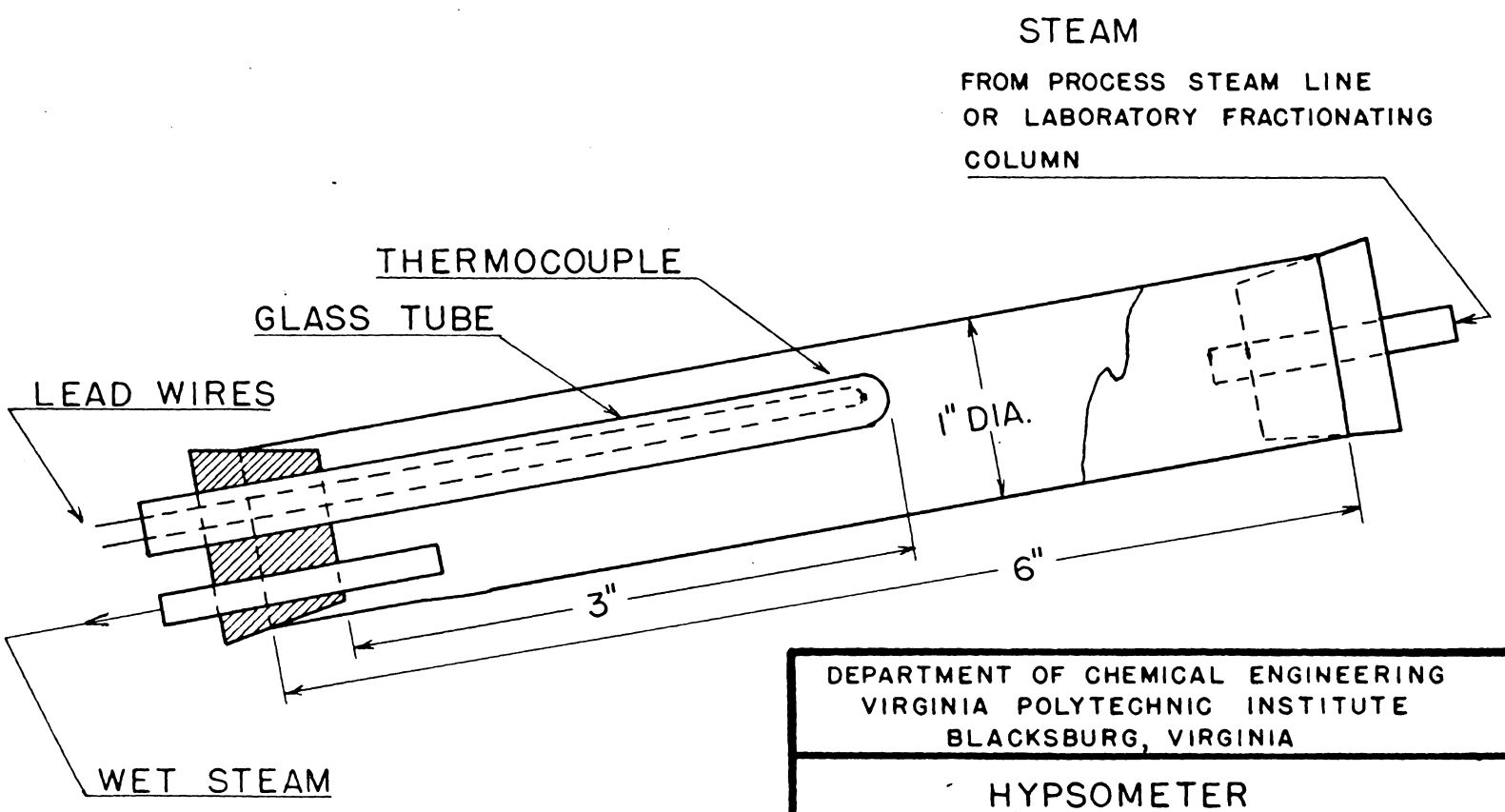
PANELBOARD ELEVATION

SCALE: 1" = 6"
DRAWN BY RHS DATE APR 1, 1952
CHECKED BY RHS DATE APR 1, 1952
APPROVED BY RAF DATE APR 1, 1952

FIGURE 22
FILE NO. 52
CASE NO. 599



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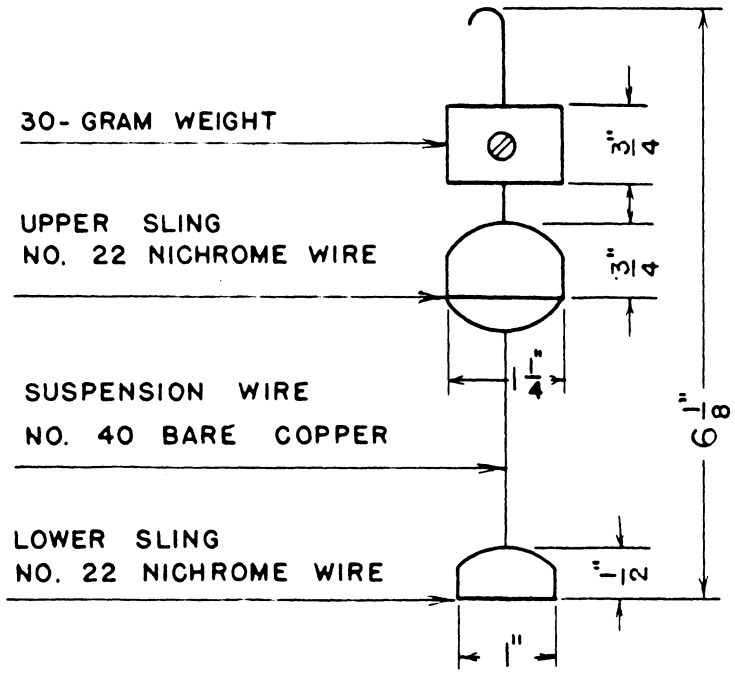
HYPSOMETER

SCALE: FULL		FIGURE 23
DRAWN BY RHS	DATE APR 24, 1952	FILE NO. 52
CHECKED BY RHS	DATE APR 24, 1952	CASE NO. 599
APPROVED BY RAF	DATE APR 24, 1952	



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BALANCE SLING

SCALE: 1" = 2"
DRAWN BY RHS DATE MAR 31, 1952
CHECKED BY RHS DATE MAR 31, 1952
APPROVED BY RAF DATE MAR 31, 1952

FIGURE 24
FILE NO. 52
CASE NO. 599

which dipped into an evaporating dish filled with water, was suspended from the upper one by means of a piece of No 40 bare copper wire that had been cleaned with hydrochloric acid and distilled water.

Method of Procedure

The plan of experimentation was carried out according to the following method of procedure.

Annealing Nylon Samples. Samples of both the original cast Nylon FM10001 and of nylon rolled to half its thickness were annealed in order to increase the degree of crystallinity. Tests were made to determine the effect of length of time of annealing on the degree of crystallinity.

Samples of from three to six grams were sawed from the slab of cast nylon and the edges trimmed with a knife. For each test, a sample was placed in the pan of the annealing apparatus and the cover screwed down. The pan was placed in the muffle furnace, the stream of nitrogen turned on, and the nitrogen pressure adjusted to 1/2-inch of water with the pressure-regulating valve on the cylinder. The furnace was turned on and the rheostats adjusted until the temperature reached 240 plus or minus ten ^{o}C. The oven was maintained at that temperature for the length of time of the test. The electric current was then shut off and the furnace allowed to cool. Then the gas stream was turned off.

Samples of the unrolled nylon were annealed for one hour, three hours, and two days at 240 °C to determine the optimum length of time of annealing, that is, the time after which no further change in density took place.

Samples of rolled nylon were annealed two hours at 240 °C to determine the effect of annealing on degree of crystallinity.

The samples used for making x-ray diffraction patterns and for thermal conductivity measurements were annealed two hours at 240 °C.

Determining the Degree of Crystallinity by the Density Method. The density of nylon samples was determined in order to measure the degree of crystallinity by the method described by Hermans[57]. This method assumes a linear relationship between degree of crystallinity and density. The standard laboratory buoyancy procedure for density described by Bauer[22] was used. The degree of crystallinity was calculated from the density.

Samples of nylon were weighed first in air and then in water using an analytic balance and the sling shown in Figure 24. The tare weight was first determined. The weight of a sample weighing from three to six grams was taken in air by placing it in the top sling, and then in water by placing it in the bottom sling. Weighings were made to the nearest tenth milligram. To assure that the surface of the sample was wetted, a drop of dilute liquid detergent was placed in the water in one test. The immersed sample was also inspected for adhering air bubbles. At least two samples were tested for each determination.

To determine that a measurable quantity of water was not absorbed by the nylon during the immersion, which lasted from three to five minutes, the sample was wiped, allowed to dry a few minutes, and again weighed in air.

Since nylon can absorb as much as three per cent water by weight, it was decided to determine the effect of moisture content on the density. Samples of the unrolled nylon were dried in a desiccator containing phosphorous pentoxide for two months and the density measured. Samples heated ten hours in the annealing oven at 130 ^{o}C to drive off moisture were also measured. It was not necessary to so dry the annealed samples, since they had already been heated more drastically.

Finally, the true densities of nylon unrolled and unannealed, unrolled but annealed, rolled but unannealed, and rolled and annealed were taken.

Rolling Nylon. An attempt was made to roll a nylon sample with the rollers constructed in the laboratory (Figure 11). A sample two inches wide and four inches long was clamped between the rolls, tightening the four bolts. The rolls were then turned with monkey wrenches, but they slipped and would not draw in the nylon. It was decided that larger rolls would have to be used. In order to calculate the minimum roll size, tests were made on deforming the sample by tightening down the rolls on the sample with the bolts.

It was found that the minimum deformation necessary to produce a permanent deformation was 0.030 inches.

Badger and McCabe[19] stated that for crushing rolls to nip a solid object the following relation must hold:

$$\tan a = u$$

where

a = angle of nip, degrees

u = coefficient of friction, dimensionless.

Akin[1] reported that the coefficient of friction of nylon against steel is 0.15, but to provide a factor of safety u was taken to be 0.1. The angle of nip was therefore five degrees 45 minutes.

From the geometry of the rolling operation Badger and McCabe[19] showed that the following relation must also be fulfilled:

$$\cos a = \frac{r + d}{r + R}$$

where r =

r = radius of the roll, inches

R = half the thickness of the largest possible particle, inches

d = half the thickness of the product, inches.

$$\cos (5^{\circ}\ 45') = \frac{r + (0.130 - 0.030)}{r - 0.130}$$

$$r = 5.8 \text{ inches}$$

The actual rolling of the samples used in density determinations and in thermal conductivity determinations was done at Radford Arsenal, Radford, Va., under the supervision of Mr. Rochford using even-speed calendars heated with water at 75 °C. Ten passes through the calendars were used to reduce the thickness from 0.260 to 0.122 inches.

Determining Chemical Constitution of Nylon FM10001. The nylon sample used in the tests, which was cast from duPont Nylon FM10001, was identified chemically as nylon 66 by means of x-ray diffraction analysis. A powder pattern (Figure 6) was made in a cylindrical camera. The developed film was indexed by laying it along a steel millimeter rule provided with a sliding pointer and vernier. This apparatus was set on top of a piece of ground glass lighted from beneath. The pointer was placed on the center of each line in turn, and the index distances read from the millimeter rule. The d-spacings of the crystal planes were calculated from the camera dimensions and the Bragg[82] diffraction law. The relative intensities of the lines were recorded as very strong, strong, medium, weak, or very weak.

The d-spacings and the intensities of the lines were compared with those reported by Bunn and Garner[28] for nylon 66. Bunn and Garner did not give d-spacings directly, but named the diffracting planes by Miller indices, hkl. The d-spacings corresponding to

these planes were calculated from the triclinic spacing formula given by Sproule[82], using the unit cell dimensions reported by Bunn and Garner[28] for nylon 66.

The x-ray diffraction pattern was made under the same conditions used by Bunn and Garner. The method is described below.

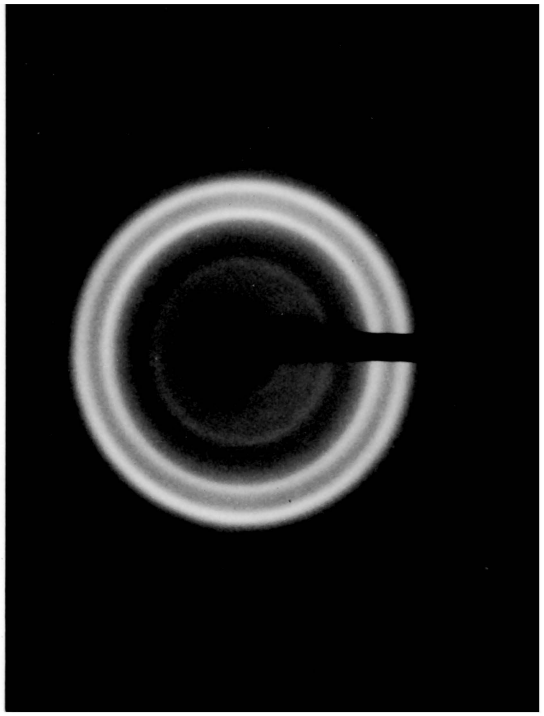
X-radiation and Exposure of Film. Copper Kα radiation was used from an x-ray tube using 35 kilovolts plate potential and 15 milliamperes plate current. The exposure lasted 45 minutes. Non-screen x-ray film was used, developed seven minutes in x-ray film developer.

Loading and Arranging the Camera. The sample was prepared by cutting a sliver of nylon from the sample 0.02 inches square and 0.25 inches long. This was mounted with wax in the holder of a cylindrical powder pattern camera. The cover and collimator were fixed in place, and the sample was watched while being rotated in the camera by hand. Any adjustments necessary to center it in the x-ray beam were made. Holes were punched in a strip of film to allow the primary x-ray beam to pass through, and the film was mounted in the camera. A nickel filter was placed over the collimator and a florescent screen over the beam exit tube. Lead shields were placed around the camera and the tube was excited. The camera position was adjusted until the spot on the screen appeared brightest. The sample was then rotated at a rate of one rotation per minute during exposure.

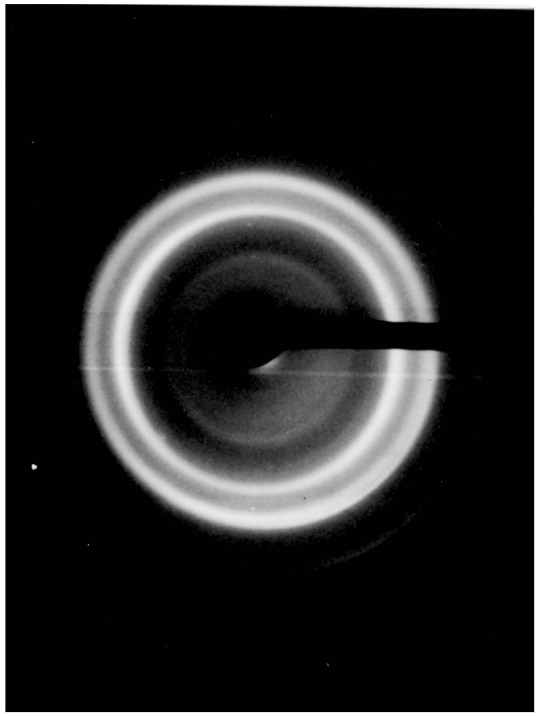
Checking Degree of Crystallinity. X-ray diffraction patterns were made of four samples of nylon to check the results of the density determinations of degree of crystallinity. (See Figures 25 and 26.) A sample of the original cast nylon as received, a sample annealed at 240 °C for two hours, a sample cold-rolled at Radford Arsenal, and a sample both rolled and annealed were tested in this way. The method of making the diffraction patterns was the same as that described above, except that the exposure time was shortened to one-half hour, and a piece of film five inches square held in a flat cassette was used. The sample was mounted directly on the end of the collimator with wax, taking care that the wax did not lie in the x-ray beam. The sample-to-film distance was five centimeters. A hole was punched in the upper right-hand corner of the film, looking down the beam, to identify the sample orientation. The samples were mounted with the direction of rolling parallel to the equator of the film, and with the plane of the sample sheet perpendicular to the x-ray beam. The beam-catcher was adjusted to intercept the undiffracted primary beam.

Contact prints were made from the resulting films on number five contrast paper. Qualitative deductions were made from the patterns concerning the effects of annealing and cold-rolling on the degree of crystallinity and orientation of the molecules in the nylon.

Calibrating Thermocouples. Each thermocouple was calibrated at the ice point, at the steam point, and at the temperature of condensing naphthalene vapors.

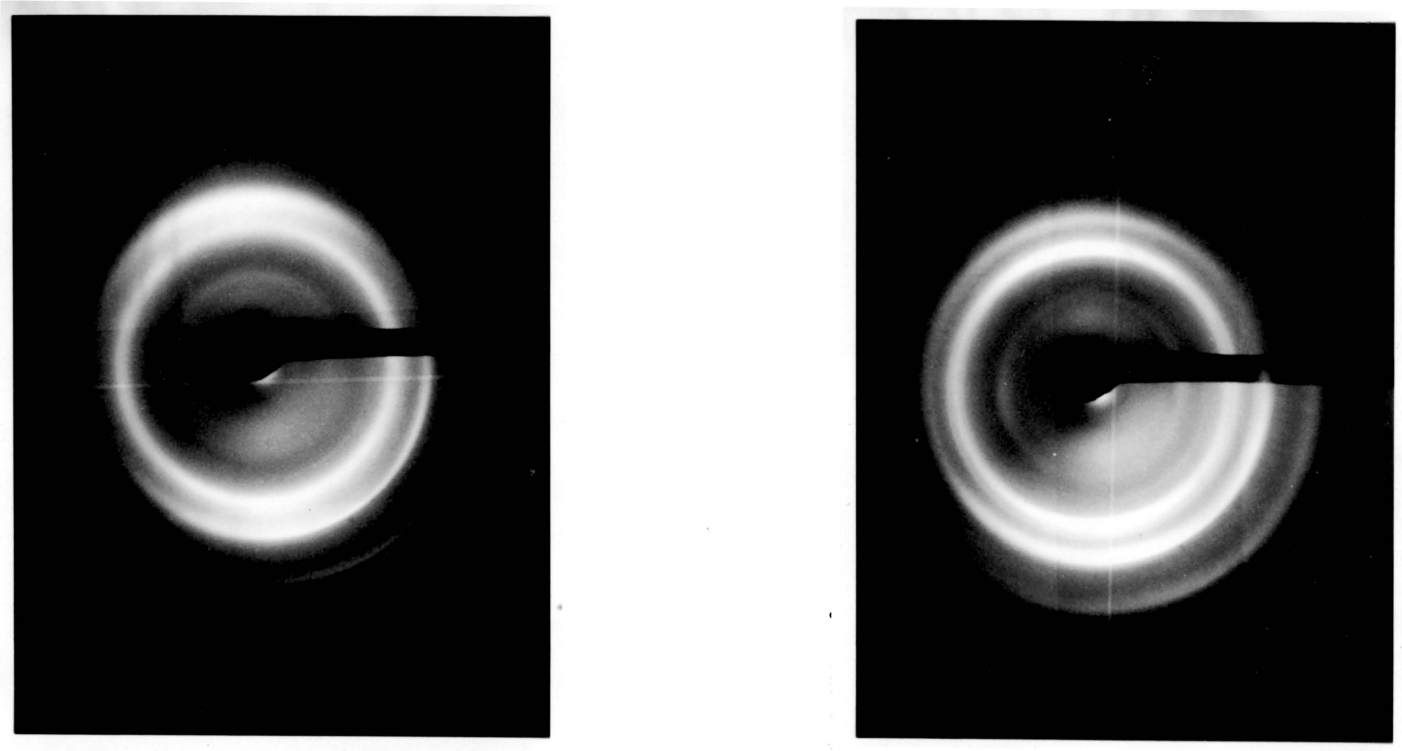


a. Nylon as Received



b. Nylon Annealed

Figure 25. X-ray Diffraction Patterns of Nylon 66 as Received and Annealed Two Hours at 240 °C.



a. Nylon Rolled

b. Nylon Rolled and Annealed

Figure 26. X-ray Diffraction Patterns of Nylon 66 Rolled to Half Thickness and Annealed Two Hours at 240 °C.

For the calibration at the ice point, the thermocouples were inserted individually into a glass tube for a depth of four inches, and the tube immersed in a vacuum bottle containing ice for five minutes, at which time the emf as measured by the potentiometer was constant. The thermocouples were connected to the potentiometer through the same circuit later used for the temperature measurements in the guarded hot plate. The emf was measured to the nearest microvolt. Two sets of tests were made on the thermocouples, which agreed within three microvolts.

For the calibrations at the steam point and at the naphthalene point, the thermocouples were inserted in a glass tube held in a stream of condensing vapors, as shown in Figure 23. The glass tube was covered with a wrapping of aluminum foil to prevent errors due to radiation of heat.

Process steam was used for the steam point determination, but it was dewatered by passing it through a separator consisting of a glass bottle with inlet and outlet tubes. A check was made on the steam point using steam from boiling distilled water. The steam was generated in a flask and passed through a glass fractionating column to eliminate any entrainment or superheat.

Calibration of Wattmeter. The wattmeter was calibrated in terms of Btu per rotation of the wattmeter disk by measuring the thermal energy produced in a resistance wire from the electrical energy which the wattmeter measured. The thermal energy was measured by determining the rise in temperature of water in a calorimeter when heated

by the resistance wire. Duplicate determinations were made at voltages applied to the load of 9, 12, 15, and 30 volts.

A piece of No 36 nichrome resistance wire four inches long was used as heat generating resistance. The wire was soldered to No 20 copper leads and immersed in the water in the calorimeter. The leads were plugged into the center heater outlet on the panelboard, so that the power was supplied by the hot plate heater circuit, Figure 18.

A plot was made of the temperature of the water in the calorimeter by reading the calorimetric thermometer at frequent intervals from two minutes before to two minutes after the period of heating, and the temperature rise was extrapolated to the mid-time of heating to correct for losses to the surroundings. The number of rotations of the disk during heating was counted using a hand tally. Distilled water was used in the calorimeter, and the weight of water used was measured on a balance of ten kilograms capacity.

Determining Calorimeter Constant. The calorimeter constant was determined by mixing two portions of water at unequal temperatures in the calorimeter and noting the temperature after mixing.

The can was weighed empty. Into it was placed about one liter of distilled water the temperature of which had been adjusted to about three degrees below room temperature. The weight of the can and water was then taken. A glass carboy fitted with a syphon and filled with distilled water at a temperature three ^{o}F above room temperature was placed on the bench so that it was at a higher level

than the calorimeter. The calorimeter stirrer was started and the cover put in place. For five minutes the temperatures in the calorimeter and in the carboy were taken every 30 seconds using the same calorimetric thermometer, stirring the water in the carboy each time. Then about a half-liter of water was run out of the carboy syphon to equalize the temperature of the syphon and the water, and one liter of the water from the carboy was run into the calorimeter can through a hole in the calorimeter cover. The temperature of the water in the calorimeter was then taken every 20 seconds for two minutes, and finally the filled calorimeter can was again weighed. This test was repeated twice.

Determining the Thermal Conductivity of Nylon. The thermal conductivity of nylon samples was determined using the guarded hot plate. Duplicate determinations of the conductivity of unrolled nylon slabs 0.260 inches thick and of slabs 0.148 inches thick rolled and annealed were made at mean temperatures of 80 and 185 °F.

Since the slab of nylon used for this investigation was only 4-3/16 inches wide, and test samples for thermal conductivity tests were required to be five inches square, the samples were pieced. The sawed edge of the added piece was planed flat with a jack plane so that it fitted against the main piece.

To prepare for a conductivity test at 80 °F, the samples were inserted in the guarded hot plate with the thermocouples in place. The bolts were tightened down gradually, making sure that the samples, the parts of the guarded hot plate, and the thermocouple wires remained

in place. Finally the bolts were uniformly tightened. They were screwed down firmly, holding the wrench near the head so as not to tighten them too much.

The assembled guarded hot plate was next placed on a piece of wood in the steel box with the thermocouple and heater wires at the top (see Figure 12), and with the water inlet nipples on the bottom side and the outlet nipples on the top side. The rubber tubes were connected to the appropriate nipples, the heater leads were screwed to their binding posts, and the thermocouple wires were screwed one by one to their binding posts, noting the correspondence of position of thermocouples in the guarded hot plate to the number of the selector switch to which each was connected. Cardboard baffles were put in place against the ends of the guarded hot plate, and loose magnesia insulation was poured into the space between these baffles so that it covered the sides of the guarded hot plate about two inches deep. To force the insulation under the guarded hot plate, it was stirred with a rubber tube out of which was flowing a gentle stream of air from the air line.

The water inlet tubes were connected to the valve on the water main, and the outlet tubes were connected to rotameters discharging into the sink. The water flow rate was adjusted to 0.6 gallons per minute in each cooling block.

The voltage stabilizer was turned on, and the voltage across the center heater adjusted to 12 volts in the case of the sample 0.260 inches thick and 15 volts in the case of the rolled sample. By means

of the variable resistors in the center and guard heater circuits and the ammeter, the current flowing through the center and guard heaters was roughly equalized. The storage battery leads were plugged into the potentiometer so that the battery would have time to reach a steady emf. The guarded hot plate was then allowed to approach steady state for two hours.

The vacuum bottle was filled with crushed ice and the two glass tubes containing the constantan-to-copper and chromel-to-copper junctions inserted through the rubber stopper into the ice for a depth of four inches. Water was poured into the vacuum bottle to a depth of two inches. As the ice melted during the test it was replaced and enough water poured out so that the ice could not float and leave water in the bottom which might rise above 32 ^{o}F. The emf values of the thermocouples were measured and recorded, standardizing the potentiometer against the standard cell as necessary.

Adjustments were made in the current flowing through the center and guard heaters by means of the variable resistors as necessary to equalize the temperatures of the center and guard heaters. The center heater applied voltage was adjusted to either 12 or 15 volts each time the resistors were adjusted, depending on whether the thick sample or the thin sample was being tested. The apparatus was allowed to approach steady state again for another half-hour, when the adjustment was repeated as necessary. When the guard and center heater thermocouple emf values agreed to within 15 microvolts, the water flow rates were adjusted if necessary to equalize the temperature

drop through the two samples as indicated by the thermocouple emf values. Since the samples varied in thickness by a few thousandths of an inch, it was not possible to obtain identical temperature drops across both samples, but the emf values of thermocouples on the two sides of the heaters were adjusted to within ten microvolts. The cold side emf values then disagreed with each other by less than 30 microvolts. The system was considered to be in steady state when the heater thermocouple emf values agreed to within ten microvolts (corresponding to 0.3 ^{o}F) and remained constant to within ten microvolts over a period of one-half hour. During this steady-state period the wattmeter was read three times by counting the number of rotations of the disk over a period of about four minutes.

The thickness of the sample was measured after the test by applying a micrometer in ten places and averaging the measurements.

The conductivity was calculated from the temperature drop across the samples measured by the thermocouples during the steady-state period, the heat flow as measured by the wattmeter, the area of the center heater measured with a rule, and the average thickness of the two samples measured with a micrometer.

In the case of conductivity determinations at 185 ^{o}F, the test was begun by first filling the water bath and turning on the water bath heaters, since cooling water for these tests was supplied from the water bath rather than from the water main. The thermoregulator was adjusted so that the bath reached a temperature of 155 ^{o}F. The rubber tubes were connected to the appropriate lines on the panelboard, and

the stirrer and pump started. After this, the test was conducted in the same way as for the tests at 80 °F.

Test for Anisotropy of Conductivity. A rough test was made to determine whether the conductivity of the rolled nylon was the same in two directions. The method used was suggested by Worthing[91]. The surface of a nylon slab was coated with a paste of damp sodium sulfate and a point source of heat applied to the center of the coated section of the slab. As the nylon was heated, the sodium sulfate passed through its transition temperature and lost ten molecules of water of crystallization. The liberated water then dissolved some of the sodium sulfate, and the end effect was observed as a melted elliptical ring around the heat source. The two major axes were measured with a rule.

The heat source was a short length of No 22 nichrome wire which fitted snugly into a hole drilled into the slab perpendicular to the plane of the slab. An electric current of four amperes from the panelboard circuit was passed through the wire.

Two tests were made on a sample which had been rolled from 0.260 inches to 0.122 inches thick, and two tests were made on a similar sample which had been annealed after rolling.

Determining Solution Viscosity of Nylon. The intrinsic solution viscosity of nylon was determined in order to characterize the molecular weight of the sample used. A modified Ostwald viscosimeter, size 100, was used, employing the method of Taylor[85]. The technique

recommended by the American Society for Testing Materials[97] was used, except for the method of filling the viscosimeter.

The method of filling the viscosimeter used made it unnecessary to empty the viscosimeter between each test. A stock solution of nylon was made by dissolving two grams of nylon, weighed to the nearest 0.3 milligram, in 80 milliliters of 90 per cent formic acid. The nylon sample was first dried in an oven overnight at 130 °C and cooled in a desiccator over phosphorous pentoxide.

The lower bulb of the viscosimeter was half filled with solvent by drawing the formic acid into it through the wide arm with suction. The weight of the filled viscosimeter was determined to the nearest 0.01 gram. The efflux time was determined. One and a half grams of the stock solution were pipeted into the wide arm, the contents mixed by shaking, and the apparatus again weighed. The efflux time was then determined again. Two further portions of the stock solution were pipeted in, mixed, the viscosimeter weighed and the efflux times again taken.

The viscosimeter was drained and rinsed four times with five-milliliter portions of formic acid. It was refilled with a volume of formic acid greater than that of the largest volume of nylon solution used, namely 14 grams, and the efflux time again measured. This was repeated for an intermediate volume of the solvent. The viscosimeter was drained, dried by drawing air through it with an aspirator, and weighed. The complete test procedure was repeated using a second stock solution.

From the data taken the relative viscosity of the nylon solutions was determined as a function of the concentration by taking the ratio of efflux time of solution to efflux time of solvent for each concentration. Corrections were applied for variations in density between the solutions of different concentrations and the solvent, and for the difference in head due to the difference in volume of sample used in each test. The latter correction was an empirical one based on the measured variation of efflux time of solvent with volume of solvent used.

The determinations were carried out in a room with good cross-ventilation to remove the obnoxious formic acid vapors. Care was taken to prevent the solvent from coming in contact with the skin. By mixing the solutions in the viscosimeter itself the amount of handling of the formic acid was minimized.

Data and Results

Nylon Density, Degree of Crystallinity, and Thermal Conductivity. As the principal result of this investigation, the thermal conductivity of nylon 66 was decreased from 0.172 to 0.130 Btu per hour - square foot - ^{o}F per foot by cold-rolling to half the original thickness and then annealing two hours at 240 ^{o}C. This treatment also increased the density from 1.1387 to 1.1499 at 25 $^{o}/4$ ^{o}C, and increased the degree of crystallinity from 21.2 to 30.8 per cent. The relation between physical treatment, degree of crystallinity, and thermal conductivity of nylon 66 is summarized in Table IX.

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The effect of physical treatment on the density and degree of crystallinity of nylon 66 is summarized in Table X. Table X also contains information on the density and degree of crystallinity of nylon samples for which the thermal conductivity was not determined. By drying, the density of the nylon as received was reduced from 1.1398 to 1.1387 at 25 °/4 °C. The density was practically the same whether dried over phosphorous pentoxide or dried by heating in air. By annealing unrolled samples two days at 240 °C the density and degree of crystallinity were increased to 1.1449 at 25 °/4 °C and 26.2 per cent, while by annealing rolled samples the density and degree of crystallinity were increased to 1.1499 at 25 °/4 °C and 30.8 per cent.

Tables XI to XXV contain data and intermediate calculated quantities which were used in calculating the results presented in Tables IX and X. Table XI shows the densities of nylon samples determined by the method of buoyancy in water, together with the weighings made to determine the densities. The thermocouple calibrations at fixed points are summarized in Table XII. The average calibrations are included for use in computations, and the individual values to indicate precision of measurement. Tables XIII to XXIII are logs for wattmeter calibration tests at voltages of 9, 12, 15, and 30 volts. The time records were needed for calculating the heat loss from the calorimeter to the surroundings during the test. The wattmeter calibration results are summarized in Table XXIV. The data of this table are not graphed because the thermal conductivity

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TABLE XI

Quantities Measured in Determining the Effect of Physical Treatment on the Density of Nylon Samples[a]

Sample No	Treatment	Wt in air, gm	Wt in water, gm	Temp, °C	Water density, referred to 4 °C [b]	Density of Sample at 25 °/4 °C
1	Untreated	6.0827	0.8014	22	0.99770	1.1411
2	Untreated	5.1700	0.6812	22	0.99770	1.1411
3	Untreated	5.5757	0.7182	22	0.99770	1.1373
4	Dried over P_2O_5 2 months	4.3146	0.5512	28	0.99623	1.1387
5	Dried over P_2O_5 2 months	3.9957	0.5102	28	0.99623	1.1387
6	Heated 3 hrs at 130 °C	6.0653	0.7891	25	0.99044	1.1386
7	Heated 3 hrs at 130 °C	5.1442	0.6718	25	0.99044	1.1392
8	Heated 3 hrs at 130 °C	5.5465	0.7294	25	0.99044	1.1404
9	Heated 1 hr at 180 °C, 10 hrs at 130 °C	6.0509	0.7870	25	0.99044	1.1385
10	Heated 1 hr at 180 °C, 10 hrs at 130 °C	5.1401	0.6683	25	0.99044	1.1384
11	Heated 1 hr at 180 °C, 10 hrs at 130 °C	5.5434	0.7226	25	0.99044	1.1389
12	Annealed 2 days at 230 °C	4.9132	0.6636	25	0.99044	1.1450
13	Annealed 2 days at 230 °C	4.4385	0.5977	25	0.99044	1.1445
14	Rolled to half thickness	3.5589	0.4339	26.5	0.99669	1.1350
15	Rolled to half thickness, annealed 2 hrs at 240 °C	3.4190	0.4747	25	0.99044	1.1501
16	Rolled to half thickness, annealed 2 hrs at 240 °C	3.8092	0.5272	25	0.99044	1.1496

[a] Determined by the buoyancy method using water.

[b] Densities of water from "Handbook of Chemistry and Physics" (C. D. Hodgman, Editor), p. 1721. Chemical Rubber Publishing Co., Cleveland, O., 1949. 31 ed.

TABLE XII

Thermocouple Calibration at Fixed Points

Couple No	Emf in ice-water mixture, 32.0 °F	Emf against thermometer at 79.14 °F	Emf in condensing steam,[a] 207.8 °F	Emf in condensing naphthalene,[a] 419.2 °F
	microvolts	microvolts	microvolts	microvolts
1	-34	1495	6150	14468
2	-24	1498	6153	14462
3	-31	1524	6151	14465
4	-29	1520	6153	14476
5	-28	1497	6151	14472
6	-30	1517	6144	14464
7	-30	1495	6151	14475
8	-30	1492	6149	14468
9	-32	1493	6156	14467
10	-33	1494	6158	14467
Average	-30	1503	6152	14469

[a] Fixed point temperatures calculated from equations in "Handbook of Physics and Chemistry," p. 1850. Chemical Rubber Publishing Co., New York, N. Y., 1949. 31 ed.

TABLE XIII

Wattmeter Calibration Log for Test 1a[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
6670	70.17	--
6750	70.18	--
6830	70.19	--
6870	70.20	--
6960	70.20	--
7010	70.20	--
7020	-----	0
7034	-----	1
7043	70.27	--
7048	-----	2
7065	70.35	--
7076	-----	4
7088	70.45	--
7104	-----	6
7116	70.55	--
7133	-----	8
7149	70.60	--
7161	-----	10
7215	70.95	--
7232	-----	15
7246	-----	16
7278	71.20	--
7288	-----	19
7305	71.30	--
7317	-----	21
7347	71.45	--
7388	-----	26
7411	71.70	--
7430	-----	29
7445	-----	30
7462	71.90	--
7502	-----	35
7517	72.10	--
7573	-----	39
7583	72.35	--
7628	-----	43
7642	-----	44
7660	72.65	--
7698	-----	48
7713	72.85	--
7727	-----	50
7769	-----	53
7780	73.10	--
7796	73.15	--
7820	73.25	--
7848	73.35	--
7854	-----	59
7870	73.43	--
7882	73.48	--
7896	73.52	--
7911	73.60	--
7937	73.68	--
7967	-----	67
7982	73.82	--
7996	73.82	--
8025	73.82	--
8100	73.83	--

[a] Applied emf 15.0 volts, 1980 grams water in calorimeter.

TABLE XIV

Wattmeter Calibration Log for Test 1b[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
8120	68.35	--
8220	68.36	--
8310	68.37	--
8360	68.38	--
8380	-----	0
8394	-----	1
8405	68.45	--
8418	68.50	--
8445	68.60	--
8472	68.70	--
8577	69.10	--
8696	69.55	--
8825	70.05	--
8966	70.60	--
9059	70.95	--
9169	71.40	--
9273	71.60	--
9377	72.20	--
9467	72.55	--
9506	72.70	--
9515	72.73	--
9537	-----	82
9550	72.85	--
9700	72.85	--

[a] Applied emf 14.7 volts; 1980 grams water in calorimeter.

TABLE XV

Wattmeter Calibration Log for Test 1c[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
1975	67.90	--
2043	67.91	--
2095	67.92	--
2157	67.94	--
2190	67.95	--
2200	-----	0
3045	-----	75
3071	71.91	--
3127	71.91	--
3150	71.91	--

[a] Applied emf 14.7 volts; 2070 grams water in calorimeter.

TABLE XVI

Wattmeter Calibration Log for Test 2a[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
9763	69.35	--
9900	69.36	--
9960	69.36	--
0000	-----	0
0016	-----	5
0050	70.00	--
0109	-----	34
0134	71.13	--
0158	71.13	--
0214	71.13	--
0294	71.14	--

[a] Applied emf 30.0 volts; 2083 grams water in calorimeter.

TABLE XVII

Wattmeter Calibration Log for Test 2b[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
0330	67.59	--
0409	67.60	--
0430	-----	0
0480	--	18
0497	68.60	--
0512	68.90	--
0519	-----	32
0554	-----	45
0570	69.95	--
0579	-----	54
0607	-----	64
0625	70.95	--
0638	-----	75
0649	71.45	--
0679	-----	90
0697	72.15	--
0711	72.16	--
0739	72.16	--
0780	72.16	--

[a] Applied emf 30.0 volts; 2078 grams water in calorimeter.

TABLE XVIII

Wattmeter Calibration Log for Test 2c[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
0886	68.27	--
1000	68.28	0
1028	-----	10
1065	-----	25
1136	-----	55
1152	70.85	--
1188	71.50	--
1247	72.60	--
1285	-----	115
1300	73.45	--
1417	73.45	--

[a] Applied emf 30.0 volts; 2075 grams water in calorimeter.

TABLE XIX

Wattmeter Calibration Log for Test 2d[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
1430	68.95	--
1520	68.95	--
1580	68.95	--
1610	-----	0
1748	-----	50
1880	-----	98
1902	73.95	--
1920	73.94	--
1960	73.94	--

[a] Applied emf 30.0 volts; 2072 grams water in calorimeter.

TABLE XX

Wattmeter Calibration Log for Test 3a[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
3220	68.87	--
3320	68.89	--
3370	68.90	--
3400	-----	0
3429	-----	1
3458	-----	2
3547	-----	5
3606	-----	7
3813	-----	14
3991	-----	20
4139	-----	25
4880	-----	50
4905	71.80	--
4977	71.81	--
5071	71.82	--
5276	71.85	--
5430	71.86	--

[a] Applied emf 9.0 volts; 2068 grams water in calorimeter.

TABLE XXI

Wattmeter Calibration Log for Test 3b[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
5440	71.80	--
6270	71.89	--
6300	-----	0
6684	-----	13
7391	-----	37
7775	-----	50
7800	74.66	--
7880	74.66	--
8060	74.66	--

[a] Applied emf 9.0 volts; 2069 grams water in calorimeter.

TABLE XXII

Wattmeter Calibration Log for Test 4a[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
8080	70.36	--
8140	70.37	--
8560	71.47	--
8670	70.50	--
8690	-----	0
9131	-----	27
9373	-----	41
9696	-----	60
9716	73.87	--
9950	73.88	--
9975	73.89	--
0010	73.90	--

[a] Applied emf 11.8 volts; 2067 grams water in calorimeter.

TABLE XXIII

Wattmeter Calibration Log for Test 4b[a]

Time, sec	Temperature, °F	Wattmeter disk revolutions, No
0000	70.80	--
0100	70.82	--
0140	70.83	--
0215	70.85	--
0240	-----	0
1202	-----	60
1221	74.11	--
1390	74.12	--

[a] Applied emf 12.0 volts; 2065 grams water in calorimeter.

TABLE XXIV

Wattmeter Calibration

Applied emf, volts	Heat power, Btu/rev
9.0	0.256
12.0	0.254
14.7	0.246
30.0	0.245

TABLE XXV

Nylon Thermal Conductivity Test Conditions

of Guarded Hot Plate at Steady State

Test No	Time of day, P. M.	Emf of Couple 1, v x 10^6	Emf of Couple 2, v x 10^6	Emf of Couple 3, v x 10^6	Emf of Couple 4, v x 10^6	Emf of Couple 5, v x 10^6	Emf of Couple 6, v x 10^6	Emf of Couple 7, v x 10^6	Emf of Couple 8, v x 10^6	Emf of Couple 9, v x 10^6	Emf of Couple 10, v x 10^6	Wattmeter disk speed^{-1}, sec/rev
1[a]	10:20	2526	2533	2529	2527	930	2535	2539	2525	2522	882	13.5
	10:35	2513	2510	2507	2510	921	2518	2518	2500	2507	875	----[c]
	10:50	2503	2495	2492	2501	923	2509	2504	2489	2498	876	13.4
2[a]	9:15	2206	2206	2204	2212	929	2212	2217	2205	2204	920	16.5
	9:50	2205	2207	2207	2202	926	2212	2221	2207	2204	917	16.6
	10:00	2204	2205	2205	2202	927	2212	2218	2206	2201	920	----[c]
3[a]	4:00	2245	2242	2240	2240	938	2251	2226	2235	2248	928	15.5
	4:25	2231	2227	2227	2222	905	2232	2208	2218	2229	902	15.2
	4:50	2232	2228	2229	2226	922	2235	2213	2224	2234	920	15.6
	5:20	2244	2242	2242	2236	924	2245	2227	2237	2243	923	----[c]
4[a]	4:40	6135	6132	6127	6128	4614	6137	6115	6132	6134	4628	15.1
	5:20	6133	6128	6123	6125	4617	6132	6111	6126	6129	4632	15.2
5[a]	4:35	6158	6162	6155	6152	4625	6150	6157	6159	----[d]	4648	15.0
	5:00	6160	6165	6158[c]	6155[c]	4630[c]	6152	6158	6162	----[d]	4653[c]	15.0[c]
	5:15	6159	6153	----	----	----[c]	6151	----[c]	6160	----[c]	----[c]	----[c]
6[b]	10:10	2653	2655	2652	2658	1116	2656	2659	2660	2660	1105	10.04
	10:40	2663	2663	2659	2672	1139	2669	2669	2671	2673	1126	10.09
	10:55	2662	2663	2659	2673	1141	2670	2670	2671	2673	1126	10.10
7[b]	7:30	1980	1967	1963	1972	962	1980	1974	1968	1977	936	----[c]
	7:50	1990	1982	1979	1982	965	1987	1985	1983	1984	938	15.4
	8:30	1983	1977	1975	1976	960	1983	1985	1979	1980	933	15.3
8[b]	10:25	6540	6545	6527	6545	4832	6551	6553	6559	6556	4835	10.10
	10:35	6540	6545	6526	6549	4823	6553	6553	6559	6559	4829	10.00
	10:45	6537	6537	6520	6547	4818	6556	6547	6552	6553	4825	----[c]
9[b]	4:10	5766	5766	5768	5761	4622	5781	5774	5778	5765	4635	14.9
	4:45	5752	5750	5753	5746	4607	5766	5759	5763	5752	4614	14.9

[a] Sample as received; average thickness 0.260 inches.

[b] Sample rolled and annealed; average thickness 0.148 inches.

[c] Measurement not taken.

[d] Measurement rejected due to negative deviation of 30 x 10^{-6} volts.

tests, in which the calibrations were used, were made at two of the calibrated points and interpolation was not necessary.

Finally, the nylon thermal conductivity test conditions of the guarded hot plate at steady state are presented in Table XXV. This table is a record of the emf values of the ten thermocouples on the surfaces of the nylon samples for a steady-state period of at least a half-hour during the conductivity tests. The averages of the emf values of the thermocouples on the hot and on the cold sides of the samples were used to determine the temperature drop across the samples in the conductivity tests. The individual emf values are given to indicate to what extent uniformity of temperature was attained in the guarded hot plate. The positions of the thermocouples are indicated in Figure 17.

The average values of the thermal conductivity test conditions together with measured conductivities for the individual tests are presented in Table XXVI, so that the individual results may be compared for precision.

Physical Changes Caused by Rolling and Annealing. Several further tests were made to determine the nature of the physical changes caused by rolling and annealing. X-ray diffraction patterns of four samples of nylon indicated that the molecules in the rolled samples were considerably oriented in one direction. Figures 25a and 25b are the diffraction patterns of cast nylon 66 and of the same sample annealed two hours at 240 °C. Figures 26a and 26b are

TABLE XXVI

Average Values of Thermal Conductivity Test Conditions Together with Measured Conductivities for Individual Tests

Test No	q, Btu/hr	emf, microvolts	t, °F	k, Btu/hr-sq ft-°F/ft	Mean t, °F
1	66.33	1612	49.03	0.168	85
2	53.48	1285	39.08	0.168	81
3	57.47	1313	39.93	0.178	81
4	58.42	1505	41.82	0.172	181
5	59.01	1518	42.18	0.173	183
6	85.13	1538	46.78	0.128	84
7	57.66	1030	31.33	0.129	77
8	83.07	1723	47.87	0.130	191
9	59.40	1144	31.78	0.131	176

the diffraction patterns of nylon 66 rolled to half its thickness and of the same sample annealed two hours at 240 °C.

That the thermal conductivity of rolled nylon is greater in the direction of rolling than in a direction perpendicular to it was shown by observing that sodium sulfate decahydrate spread on a slab of nylon heated at one point melted in the shape of an ellipse. The dimensions of the axes of the ellipses formed in four tests are presented in Table XXVII.

Further Characterization of Nylon Samples. The nylon samples used in the thermal conductivity tests were further characterized by determining the chemical composition, the moisture content, and the degree of polymerization.

Nylon FM10001 was identified as nylon 66 by x-ray diffraction analysis. An x-ray diffraction pattern of Nylon FM10001 is presented in Figure 6. Table XXVIII, which shows the indices of arcs of the same diffracted rings on opposite sides of the primary x-ray beam, served to orient the pattern with respect to the arbitrarily placed index rule. In Table XXIX are listed the indices of the diffractions used in calculating the corresponding interplanar crystal spacings. The spacings calculated from the data of Bunn and Garner[28] for nylon 66 are shown for comparison, together with the Miller indices of the diffracting crystal planes. The relative intensities of the observed diffractions are listed; they are the same as those reported by Bunn and Garner[28].

The untreated nylon had a moisture content of 0.56 per cent. The rolled and annealed nylon had a moisture content of 0.28 per

TABLE XXVII

Anisotropy of Thermal Conductivity of Nylon 66 Rolled Slab

Test No	Treatment	Dimension A,[a] inches	Dimension B,[b] inches
1	Rolled[c]	0.69	0.66
2	Rolled[c]	0.69	0.50
3	Rolled and annealed[d]	0.69	0.59
4	Rolled and annealed[d]	0.72	0.66

[a] Major axis of ellipse of melted sodium sulfate on surface of slab.

[b] Minor axis of ellipse of melted sodium sulfate on surface of slab.

[c] Cold-rolled to half thickness.

[d] Annealed two hours at 240 °C.

TABLE XXVIII

Scale Readings for Determining Center Line Index for Annealed Nylon FM10001 Powder Pattern

Line set	Side of hole	Index, mm
1	Right	202.3
1	Left	182.1
2	Right	203.9
2	Left	180.4

TABLE XXIX

X-ray Diffraction Pattern Measurements

Used to Identify Nylon FM10001

Line No	Index, mm	Diffraction angle, degrees	Measured d-spacing, Å	hkl[a]	Calculated d-spacing, Å	I_m
1	182.1	10.1	4.34	100	4.35	vs
2	180.4	11.8	3.71	010 110	3.70	vs
3	173.2	19.0	2.34	$\bar{1}10$ 210	2.31	w
4	171.7	20.5	2.17	200	2.07	w
5	169.3	22.9	1.96	$\bar{2}27$ $\bar{1}17$	1.92	vw

[a] hkl are the Miller indices of strong lines found by Bunn, C. W., and E. V. Garner: The Crystal Structure of Two Polyamides, Proc. Roy. Soc. Lond., A189, 66 (1947).

cent after exposure to the air for two weeks, at the time of the thermal conductivity tests.

The degree of polymerization of the nylon was 148. The degree of polymerization was calculated from the intrinsic solution viscosity in 90 per cent formic acid, which was 2.53. The efflux times of nylon solutions of various concentrations used for calculating the relative viscosities of the solutions are presented in Table XXX. The weights of solutions and of solute are included for calculating concentrations, and the densities of solutions are included for correcting efflux times for the effect of differences in density of solutions. The relation of efflux time of pure formic acid to quantity of acid used in the viscosimeter is presented in Table XXXI together with correction factors used to correct the efflux times of nylon solutions for differences in head due to differences in quantity of solution contained in the viscosimeter. The data of Table XXXI are presented graphically in Figure 27. Intermediate steps in the viscosity calculations are summarized in Table XXXII. The graph of Figure 28 is an extrapolation of viscosities to zero concentration for determining the intrinsic solution viscosity.

TABLE XXX

Test Conditions for Determining Relative Viscosities of Nylon Solutions at Various Concentrations

Test No	Total wt solvent, gm	Wt solution added, gm	Wt solute, gm	Calculated density[a] of solution, at 25 °/4 °C	Efflux time, sec	Corrected efflux[b] time, sec
1	14.46	1.74[c]	0.0378	1.222	130.5	130.0
2	15.41	2.69[c]	0.0584	1.224	155.0	153.0
3	16.39	3.67	0.0796	1.226	174.7	170.5
4	11.52	0.23[d]	0.0063	1.221	88.5	89.6
5	11.96	0.68[d]	0.0188	1.222	104.3	105.2
6	12.73	1.47[d]	0.0405	1.224	132.1	131.0
7	13.39	2.15[d]	0.0593	1.225	154.4	115.0
8	13.94	2.76[d]	0.0761	1.226	173.2	176.6

[a] Calculated on assumption that no increase in volume takes place on dissolving nylon.

[b] Corrected for difference in head by applying factor from Figure 29; corrected for density by applying ratio of density of solution to density of formic acid, 1.220 at 25 °/4 °C, from "Handbook of Physics and Chemistry," (C. D. Hodgman, Editor), p. 785. Chemical Rubber Publishing Co., New York, N. Y., 1943. 27 ed.

[c] Solution of 2.0880 grams nylon in 96.3 grams formic acid.

[d] Solution of 2.004 grams nylon in 72.51 grams formic acid.

TABLE XXXI

Determination of Static Head Corrections for Viscosity Determinations

Test No	Wt solvent, gm	Efflux time, sec	Correction Factor[a]
1	11.30	78.9	1.015
2	12.73	80.0[b]	1.000
3	13.75	81.0	0.988
4	18.64	84.9	0.942

[a] Ratio of actual to standard efflux time.

[b] Standard efflux time.

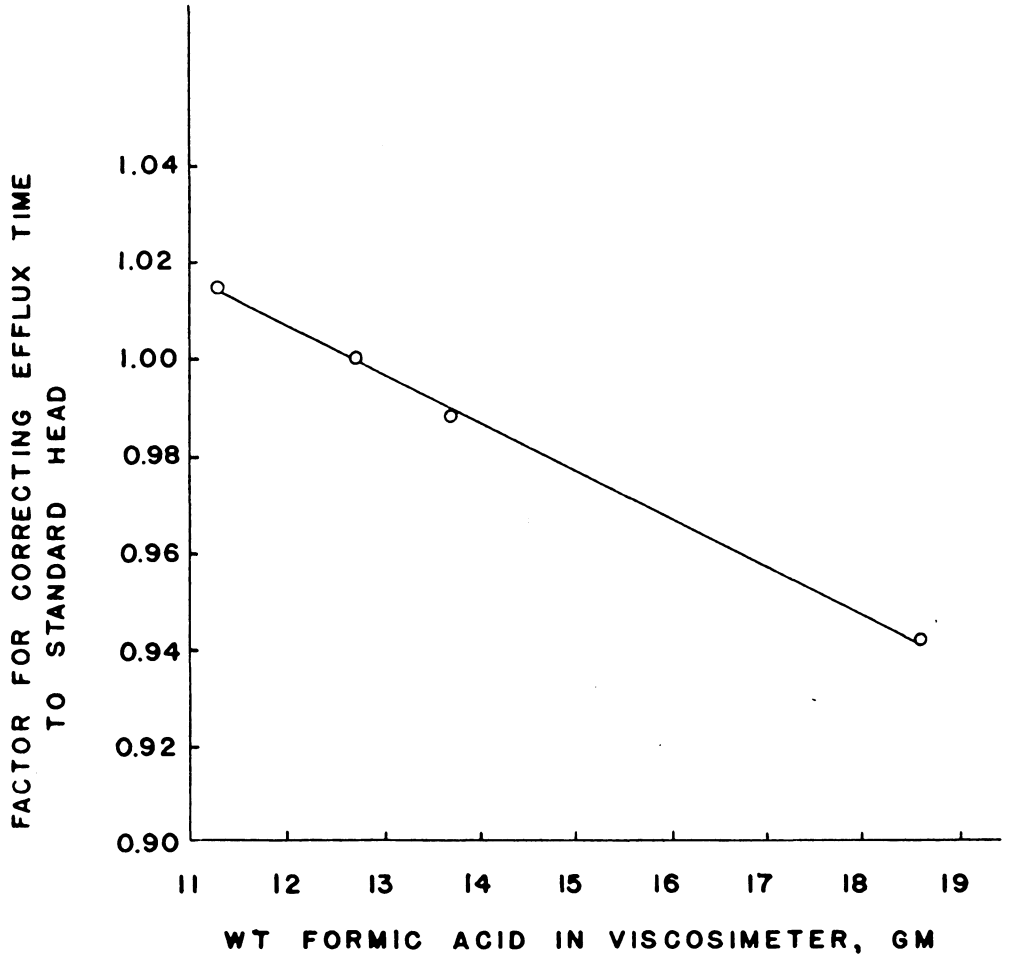

FIGURE 27. HEAD CORRECTION FACTOR FOR VISCOSIMETER EFFLUX TIME

TABLE XXXII

Intermediate Steps in Viscosity Calculations

Test No	η_r	c, gm/100 ml	η_{sp}/c 100 x ml/gm
1	1.627	0.214	2.93
2	1.913	0.311	2.94
3	2.130	0.398	2.84
4	1.120	0.0448	2.68
5	1.315	0.1290	2.44
6	1.639	0.261	2.45
7	1.939	0.363	2.59
8	2.205	0.448	2.69

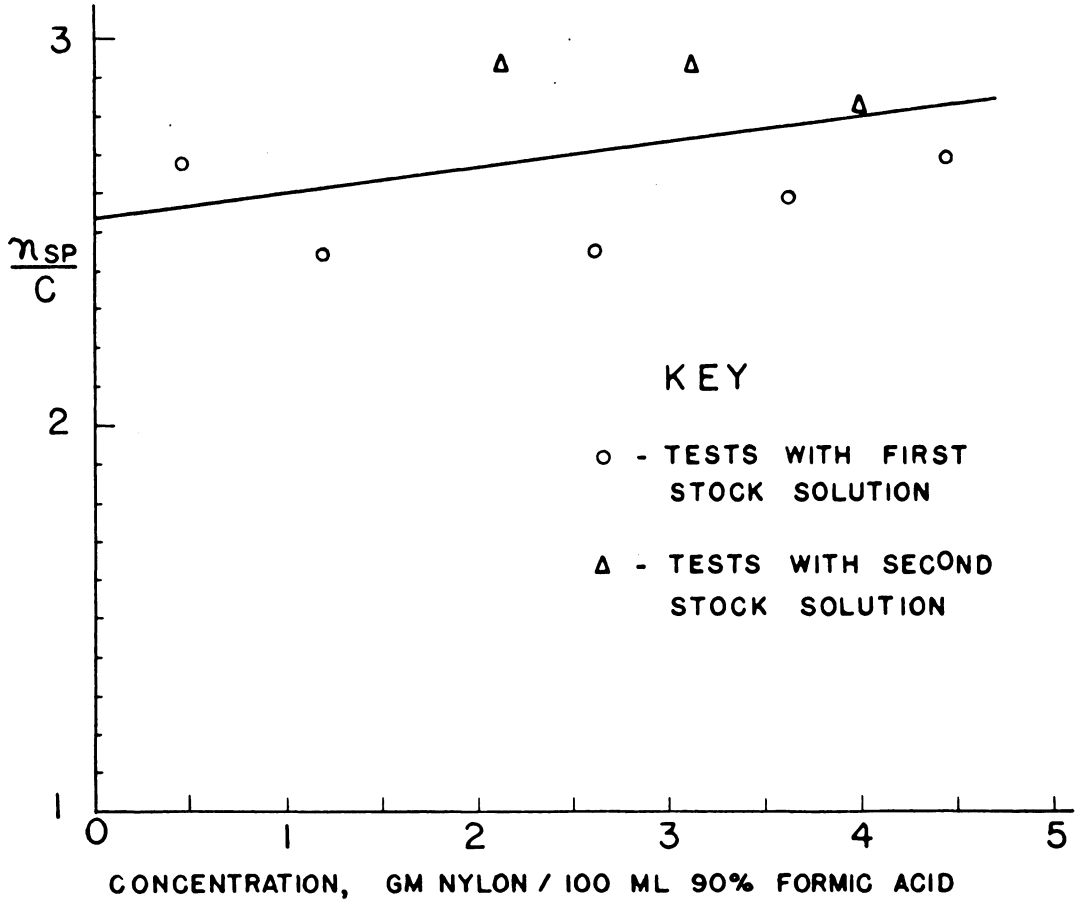

FIGURE 28. GRAPH FOR DETERMINING INTRINSIC SOLUTION VISCOSITY OF NYLON 66

Sample Calculations

Density of Nylon. The calculation of the density of nylon samples is illustrated with data for Sample 1 from Table XI:

$$d = \frac{W_a \, d_w}{W_a - W_w}$$

where

d = density of sample at 25 °/4 °C

W_a = weight of sample in air, gm

W_w = weight of sample in water, gm

d_w = relative density of water[54] at the temperature of the test compared to the density of water at 4.0 °C.

$$d = 4.3146 \text{ gm} \times 0.99623 \; / \; (4.316 - 0.5512) \text{ gm}$$

$$= 1.1387 \text{ at } 25 \text{ °/4 °C}$$

The corrections for the buoyant effect of air and for the thermal expansion of nylon for determinations at temperatures a few degrees different from 25 °C were negligible.

Degree of Crystallinity of Nylon. The degree of crystallinity of nylon was calculated from Hermans'[55] relation. Sample 1 of Table XI is again used as an example:

$$D.\ C.\ = \frac{d - d_a}{d_c - d_a} \times 100$$

where

D. C. = percentage crystalline material present in sample

d = density of sample at 25 °/4 °C

d_c = density of crystal, reported by Bunn and Garner[28] as calculated from x-ray diffraction data, 1.24 at 25 °/4 °C

d_a = density of amorphous nylon, assumed to be the density of the least dense sample of nylon 66 ever obtained by the DuPont Company[76] research laboratory, 1.111 at 25 °/4 °C.

D. C. = (1.1387 - 1.111) / (1.24 - 1.111) x 100

= 21.2 per cent

Wattmeter Calibration. The wattmeter calibration calculation is illustrated with data from the log of Test 1a, Table XIII. The temperature rise of the calorimeter due to electric power input measured by the wattmeter was determined by extrapolating the temperature rise during the actual period of heating to the mid-time of heating in order to correct for cooling losses. The following relation was used:

$$\Delta t' = \theta (r_1 + r_2) / 2$$

where

$\Delta t'$ = cooling temperature correction to be added to observed temperature rise, ^{o}F

θ = actual time of heating period, sec

r_1 = rate of cooling during period preceeding heating, found by inspection of the calibration log, Table XIII, $^{o}F/sec$

r_2 = rate of cooling during period following heating, $^{o}F/sec$.

For Test 1a, both r_1 and r_2 were zero, so $\Delta t'$ was zero.

The calibration factor R was calculated from the following relation:

$$R = \frac{(C + W)(\Delta t + \Delta t')}{n}$$

where

R = calibration factor, Btu/wattmeter disk revolution

W = weight of water used in calorimeter, lb

C = water equivalent of calorimeter, 0.19 lb

Δt = observed rise in temperature of calorimeter during heating, ^{o}F

$\Delta t'$ = cooling correction factor, ^{o}F

n = number of revolutions of wattmeter disk during test.

$$R = (0.19 + 4.36)\text{lb} \times (3.62 + 0.00)\ ^{o}F / 67\ \text{rev}$$

$$= 0.246\ \text{Btu/rev}$$

Thermal Conductivity of Nylon. The thermal conductivity of nylon samples was determined from the relation:

$$k = \frac{q\,L}{A\,\Delta t}$$

where

k = thermal conductivity, Btu/hr - sq ft - ^{o}F/ft

q = heat flux, Btu/hr

L = thickness of sample, ft

A = heat transfer area, sq ft

Δt = temperature drop across sample, ^{o}F.

Data from Test 1, Table XXV, are used in the following illustration. The heat flux was calculated from the measured average wattmeter disk speed according to the relation:

$$q = \frac{R \times 3600}{S}$$

where

R = calibration factor, Btu/rev

3600 = conversion factor, sec/hr

S = average reciprocal wattmeter disk speed, sec/rev.

$$q = \frac{0.254 \text{ Btu/rev} \times 3600 \text{ sec/hr}}{13.45 \text{ sec/rev}}$$

$$= 68.0 \text{ Btu/hr}$$

The thickness of the sample was measured with a micrometer, taking the average of ten readings on each of the two samples. The thickness was 0.0233 feet.

The temperature drop through the sample was calculated from the emf values of the thermocouples shown in Table XXV. The average emf of all the readings for Test 1 of all the thermocouples on the hot side of the sample was taken, and the average of those on the cold side. The temperature drop was calculated from the relation:

$$\Delta t = \frac{\Delta E \ \Delta t'}{\Delta E'}$$

where

Δt = temperature drop across sample, ^{o}F

ΔE = difference between average emf of the thermocouples on hot and cold sides of samples, μv

$\Delta E'$ = difference between average emf of thermocouples at 32.00 and 79.14 ^{o}F from Table XII, for Tests 1 through 5. In the case of Tests 6 through 9, the $\Delta E'$ between the thermocouple emf's at 79.14 and 207.8 ^{o}F was used.

$\Delta t'$ = temperature difference corresponding to $\Delta E'$, 79.14 - 32.00 ^{o}F in the case of Tests 1 through 5. In the case of Tests 6 through 9, $\Delta t'$ was 207.8 - 79.14 ^{o}F.

$$\Delta t = 1612 \mu v \times 47.14 \ ^{o}F \ / \ 1533 \mu v$$
$$= 49.03 \ ^{o}F$$

The heat transfer area A was the area of the center heater measured to the midpoint of the separation between it and the guard heater. It was 0.1760 square feet, counting both sides.

Inserting these quantities into the definition of thermal conductivity we have:

$$k = \frac{68.0 \text{ Btu/hr} \times 0.0233 \text{ ft}}{0.1760 \text{ sq ft} \times 49.03 \ ^{\circ}\text{F}}$$

$$= 0.168 \text{ Btu/hr - sq ft - } ^{\circ}\text{F/ft}$$

A summary of the intermediate quantities found in the calculation of k for each test is given in Table XXVI.

Identification of Nylon FM10001. From the camera geometry the diffraction angles corresponding to the five lines observed for Nylon FM10001 in Figure 6 were calculated:

$$\theta = \frac{(I - S_w)}{D} \times \frac{360}{\pi}$$

where

θ = diffraction angle, degrees

I = index of the center of the right-hand hole, the average of the four indices of lines of Table XXVIII, 192.2 mm

S_w = index of the line, mm

D = camera diameter, 55.8 mm

For line 1, the index from Table XXVIII was 169.3 millimeters. The diffraction angle for this line was then:

$$\theta = (192.2 - 169.3) \text{ mm} \times 360 \ ^{\circ}/55.8 \text{ mm} \times 3.1416$$

$$= 22.9 \ ^{\circ}$$

The interplanar crystal spacing for the first line of Table XXIX was calculated from the Bragg[82] spacing formula:

$$d = 1.5408 / 2 \sin \theta$$

where

d = interplanar spacing, Å

1.5408 = wavelength of Kα radiation used, 1.5408 Å.

$$d = 1.5408 \text{ Å} / 2 \sin 22.9^{\circ}$$

$$= 1.98 \text{ Å}$$

The spacings of the observed lines were compared with the spacings of the five most intense lines observed by Bunn and Garner[28] for nylon 66. Bunn and Garner reported only the Miller indices of the lines, hkl in Table XXIX, and the corresponding spacings were calculated from these using the unit cell dimensions of nylon 66 and the triclinic spacing formula[82]. This formula is:

$$d_{hkl} = \frac{1}{\sqrt{\dfrac{\frac{h}{a}\begin{vmatrix} h/a & \cos\gamma & \cos\beta \\ k/b & 1 & \cos\alpha \\ l/c & \cos\alpha & 1 \end{vmatrix} + \frac{k}{b}\begin{vmatrix} 1 & h/a & \cos\beta \\ \cos\gamma & k/b & \cos\alpha \\ \cos\beta & l/c & 1 \end{vmatrix} + \frac{l}{c}\begin{vmatrix} 1 & \cos\gamma & h/a \\ \cos\gamma & 1 & k/b \\ \cos\beta & \cos\alpha & l/c \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}}}$$

where

hkl = Miller indices of the line, 227

α , β, γ = unit cell angles, from Bunn and Garner[28], 48.5, 77.0, and 63.5 ^{o} respectively.

a, b, c = unit cell dimensions, from Bunn and Garner[28], 4.9, 5.4, and 17.2 $\mathring{A}$ respectively.

To simplify explication, call this expression:

$$d_{hkl} = \frac{1}{\sqrt{\dfrac{\frac{h}{a}\Delta_1 + \frac{k}{b}\Delta_2 + \frac{l}{c}\Delta_3}{\Delta}}}$$

For nylon 66, $\cos\alpha = 0.662$, $\cos\beta = 0.225$, and $\cos\gamma = 0.446$. For line 227,

$$\Delta_1 = \begin{vmatrix} 2/4.9 & 0.446 & 0.225 \\ 2/5.4 & 1 & 0.662 \\ 7/17.2 & 0.662 & 1 \end{vmatrix} = 0.141$$

Similarly, $\Delta_2 = 0.0051$, $\Delta_3 = 0.147$. Also,

$$\Delta = \begin{vmatrix} 1 & 0.446 & 0.225 \\ 0.446 & 1 & 0.662 \\ 0.225 & 0.662 & 1 \end{vmatrix} = 0.444$$

Then

$$d_{227} = \frac{1}{\sqrt{\dfrac{\dfrac{2 \times 0.141}{4.9} + \dfrac{2 \times 0.0051}{5.4} + \dfrac{7 \times 0.147}{17.2}}{0.444}}}$$

$$= 1.92 \text{ Å}$$

Intrinsic Solution Viscosity of Nylon 66. The viscosities of nylon solutions were determined in terms of time of efflux from the viscosimeter and were not converted to viscosity units.

Since the nylon solutions of various concentrations were made up by pipetting quantities of a concentrated solution into the solvent in the viscosimeter, the total quantity of solution in the viscosimeter was not constant, and the hydraulic head differed among the tests. To correct for this effect, the efflux time of the solvent was measured using different amounts of solvent and a correction factor plotted to convert the efflux time for each determination to values corresponding to an arbitrarily chosen standard head. The correction factors were plotted and read from Figure 27. The graph was drawn from the data of Table XXXI.

The efflux times were also corrected for difference in density due to difference in concentration of the solution. The densities, shown in the fifth column of Table XXX, were calculated from the relation:

$$d = d_f (1 + W_n / W_s)$$

where

d = density of solution at 25 °/4 °C

d_f = density of formic acid, 1.220 at 25 °/4 °C[55].

W_n = weight of nylon dissolved, gm

W_s = weight of formic acid, gm.

For Test 1, Table XXX:

$$d = 1.220\ (1 + 0.0378/14.46)$$

$$= 1.222 \text{ at } 25\ ^{\circ}/4\ ^{\circ}C$$

Applying both correction factors, the corrected efflux time for Test 1 was:

$$Tc = T\ F\ \frac{d}{d_f}$$

where

Tc = corrected efflux time, sec

T = measured efflux time, sec

F = correction factor for head, read from Figure 27, where weight of solvent = 14.46 gm.

$$Tc = 130.5 \text{ sec} \times 0.981 \times (1.222/1.220)$$

$$= 130.0 \text{ sec}$$

The remaining steps in the viscosity calculation are summarized in Table XXXII. The relative solution viscosity is defined as:

$$\eta_r = Tc / Ts$$

where

η_r = relative solution viscosity, and the other symbols have their previous meanings.

For Test 1:

$$\eta_r = 130.0 \text{ sec} / 80.0 \text{ sec}$$

$$= 1.627$$

The concentrations were calculated from the data of the second and fourth columns of Table XXX:

$$c = 100 W_n / W_s \times d_f$$

where

c = concentration, gm nylon / 100 ml formic acid

W_n = weight of nylon dissolved, gm

W_s = weight of formic acid solvent, gm

d_f = density of formic acid at 25 °/4 °C[55].

$$c = 100 \times 0.378 / 14.46 \times 1.220$$

$$= 0.214 \text{ gm nylon} / 100 \text{ ml formic acid}$$

The last column in Table XXXII was calculated from the relation:

$$\eta_{sp} / c = (\eta_r - 1)/c$$

where

η_{sp} = specific viscosity of nylon in formic acid, dimensionless, and the other symbols have their previous meaning.

$$\eta_{sp} / c = (1.627 - 1) / 0.214 \text{ gm}/100 \text{ ml}$$

$$= 2.93 \text{ ml} \times 100/\text{gm}$$

Finally, the intrinsic solution viscosity is defined by:

$$[\eta] = \lim_{c \to 0} (\eta_{sp} / c)$$

where

$[\eta]$ = intrinsic solution viscosity, ml x 100/gm, taken as the y-intercept of Figure 28, 2.53 ml x 100/gm.

Degree of Polymerization. The degree of polymerization was calculated from the relation recommended by Taylor[85]:

$$\overline{Mn} = 13{,}000[\eta]^{1.39}$$

where

$\overline{Mn}$ = number average molecular weight, gm/mol.

$$\overline{Mn} = 13{,}000\ (2.53)^{1.39}$$

$$= 48{,}100 \text{ gm/mol}$$

The degree of polymerization is the molecular weight divided by the weight of the monomer. The weight of the monomer is 326.17 grams per mol. The degree of polymerization was:

$$\text{Degree of Polymerization} = 48{,}100 \text{ gm/mol} / 326.17 \text{ gm/mol}$$

$$= 148.$$

IV. DISCUSSION

Discussion of Results

The purpose of this investigation was to determine the extent to which the thermal conductivity of nylon 66 could be increased by cold-rolling and annealing, and a number of theoretical considerations indicated that the increase would be large enough to be of technical importance. Yet the experimental results showed that the conductivity was not increased by such treatment; rather, it was decreased from 0.172 to 0.130 Btu per hour - square foot - ^{o}F per foot. It will be worthwhile to reconsider the theory concerning thermal conductivity to discover the meaning of the unexpected results. But first the results will be discussed in the light of the conditions of the tests and of the results of previous workers in order to establish what was determined and how reliable the determinations were. Then the theory, and finally the applications of the results will be discussed.

Effect of Cold-rolling and Annealing on the Density and Degree of Crystallinity of Nylon 66. The results of the determination of the effect of cold-rolling and annealing on the density and degree of crystallinity of nylon 66 were in agreement with results of previous

investigators. Black and Dole[24] showed that drawing and annealing increased the density of nylon filaments from 1.1339 to 1.1564 at 25 °/4 °C. (See Table VIII.) In this investigation the density of nylon slab was increased by cold-rolling and annealing from 1.1387 to 1.1499 at 25 °/4 °C. Evidently the cast nylon used in this investigation was more highly crystalline than the undrawn filament, as would be expected since the larger sample would cool from the melt slower and crystallize more completely. The effect of cold-rolling was less than the effect of drawing, again because the sample used was larger and the macroscopic stresses set up in the nylon caused it to begin to crack before the same amount of microscopic alignment of the molecules had taken place.

Bunn and Garner[28] showed qualitatively, by inspection of x-ray diffraction patterns, that rolling and annealing increased the degree of crystallinity of nylon filaments. The present results based on density measurements showed that cold-rolling and annealing nylon slabs increased the degree of crystallinity from 21.2 to 30.8 per cent.

Clark, Mueller, and Stott[32] showed that annealing increased the density of nylon slabs. Their results are suspect, however, since they reported (see Table VIII) a density of 1.172 at 25 °/4 °C for one cast, untreated nylon slab, which was greater than the density of the most completely drawn and annealed sample of nylon 66 ever prepared by the duPont research laboratories[76], 1.166 at 25 °/4 °C.

An original feature of this investigation was the measurement of the degree of crystallinity of nylon by the density method which Hermans[58] used for cellulose. The only other similar work is that of Clark, Mueller, and Stott[32], who obtained a relative measure of degree of crystallinity by measuring the distance between the two strong diffraction rings of nylon 66 and assuming that a decrease in the distance between the rings indicated an increase in degree of crystallinity. By this method they found that annealing increased the degree of crystallinity of nylon slabs. In the present investigation it was found that annealing increased the degree of crystallinity of nylon slabs from 21.2 to 26.5 per cent.

The values of density and degree of crystallinity which have been reported in this investigation are not identical to those of any other investigator. This fact does not indicate disagreement but only indicates that the samples used have undergone somewhat different physical treatment. Of especial significance for determining the degree of crystallinity and density are the conditions under which the sample was formed, as pointed out by Clark, Mueller, and Stott[32]. The rate of cooling of the nylon from the melt is of particular importance. Since the sample of nylon used in this investigation was a cast slab bought from the Polymer Corporation, Reading, Pa., the exact conditions under which it was formed are not known. This fact does not invalidate the results on the effect of degree of crystallinity on thermal conductivity, however.

Thermal Conductivity of Nylon 66. The values of thermal conductivity of nylon 66 determined in this investigation are an improvement over previously published data in accuracy, due to the method of test used, and in reliability, due to the more complete characterization of the sample. The conductivity of "nylon" listed in Modern Plastics Encyclopoedia[73] was 0.16 Btu per hour - square foot - °F per foot. DuPont Company[36] reported the conductivities of its various nylon formulations, giving that of FM10001 as 0.15. It is presumed that these are average values. They were obtained using ASTM Method[96] D325-31T, a comparative method for which an accuracy of ten per cent is claimed. In this investigation the ASTM Method[83] C177-45 was used, which is an absolute method for which ASTM claims an accuracy of one per cent.

In this investigation the thermal conductivities of two samples of nylon 66 were determined. A slab of cast nylon having a density of 1.1387 at 25 °/4 °C and a degree of crystallinity of 21.2 per cent had a thermal conductivity of 0.172 Btu per hour - square foot - °F per foot. After having been cold-rolled from a thickness of 0.260 inches to 0.122 inches and annealed two hours at 240 °C, the conductivity measured in a direction perpendicular to the plane of the slab was 0.130 Btu per hour - square foot - °F per foot. Other variables which might affect the thermal conductivity are subsequently discussed.

Effect of Other Variables on the Thermal Conductivity of Nylon 66. Other variables which might affect thermal conductivity and which were allowed for in this investigation for the first time are the degree of polymerization, the previous physical treatment of the sample, the chemical composition, the temperature, and the moisture content.

Degree of Polymerization. The effect of degree of polymerization was not studied. Instead, the degree of polymerization of the nylon as received was determined by measuring its intrinsic solution viscosity, and it was assumed that the degree of polymerization was not affected by cold-rolling and annealing. The intrinsic solution viscosity of the nylon as received was found to be 2.53, which corresponds to a degree of polymerization of 148, calculated from Taylor's[85] formula. As was pointed out by Carothers[30, 33], the degree of polymerization of nylon is determined substantially by the purity of the reactants, since this determines the extent of the polymerization reaction. Also, cold-rolling and annealing would not degrade the polymer significantly. They are mild treatments compared to the severe chemical treatments which degrade cellulose when it is made into paper, for example.

Chemical Constitution. The chemical constitution of the Nylon FM10001 used in this investigation was determined by x-ray diffraction analysis. Five lines were observed on a powder pattern, and the interplanar spacings for these lines agreed

very well with the interplanar spacings calculated for the five strongest lines reported by Bunn and Garner[28] for nylon 66. (See Figure 6 and Table XXIX.) The relative intensities of the lines also agreed, so it is assured that the lines were nylon 66 lines.

There remains the possibility that the sample contained some small amounts of other nylons for which no lines appeared. There are two reasons why this is unlikely: in the first place, if the sample were such a mixture it would crystallize less readily than pure nylon 66, and the density would have been lower than that of nylon 66 both before and after annealing. Actually, the density was of about the same magnitude as densities found by others for nylon 66 filaments (see Tables VIII and X). In the second place, Nylon FM10001 is duPont Company's[36] most widely used molding compound, and it is reasonable that this substance is simply nylon 66, the substance used in making textiles[80]. If it is a mixture, it would have to be purposely mixed and not an accidental mixture, since the reactants used in manufacturing nylon are highly purified in order to obtain a polymer with a high degree of polymerization. The reasons for this procedure have been explained by Coffman[33].

Moisture Content. Vierweg stated that moisture content may have an important effect on thermal conductivity of non-metals. Moisture content determinations on the unrolled nylon

showed that it contained 0.56 per cent water, and the rolled and annealed nylon, after standing in air two weeks, contained 0.3 per cent water.

Temperature. Within experimental error, the conductivity of the nylon was shown to be the same at 80 °F and 185 °F.

Physical Treatment. The results of this investigation show that previous physical treatment may have a significant effect on the thermal conductivity. This effect will be discussed in the next section from the theoretical point of view.

Theory of Thermal Conduction in Nylon 66. If it is granted that cold-rolling and annealing did increase the density and degree of crystallinity of the nylon, as the results of this investigation show (see Table IX), several theoretical considerations indicate that the thermal conductivity should likewise have increased.

The Debye Equation. The Debye equation is:

$$k = \frac{1}{4} w \, l \, C_v \, d$$

where

k = thermal conductivity, Btu per hour - square foot - ^{o}F per foot

w = rate of propagation of the thermal waves, feet per hour

l = distance a wave travels before being reduced to 1/e of its original intensity, feet

C_v = specific heat, Btu per pound - ^{o}F

d = density, pounds per cubic foot.

Density. The Debye equation predicts that the thermal conductivity of substances is proportional to their density, other things being equal. There is no experimental evidence for this prediction, but if it is correct, it is of application to the problem of this investigation: since the rolled and annealed nylon had a higher density than the untreated nylon (see Table IX), the former should have a higher conductivity. Other principles also have bearing on this problem, however, and will subsequently be discussed.

Degree of Crystallinity. A principle following from Debye's reasoning in developing the Debye equation is, according to Bragg[25], that the more orderly the array of molecules the less interference there should be between the thermal waves and

hence the greater should be the conductivity. Eucken[42] showed this to be true for silica. Therefore, the rolled and annealed nylon should have a higher conductivity than the untreated nylon on account of its higher degree of crystallinity.

Phase Boundaries. Austin[7] stated that phase boundaries have a thermal resistance because they are sources of interferences to the thermal waves. Clark, Mueller, and Stott[32] showed that differences in the degree of crystallinity of nylon samples resulting from different physical treatment after forming are due to differences in the average grain size rather than in the number of crystalline regions. Therefore, the rolled and annealed nylon should have less phase boundary surface per unit crystal volume, but more boundary surface per unit sample volume. It cannot be decided from these principles whether this effect would result in higher or lower conductivity.

Hardness. Austin[10] showed both from the Debye equation and by experiment that there is a relation between hardness and thermal conductivity. Other things being equal, harder substances have higher conductivities. Clark, Mueller, and Stott[32] showed that the hardness of nylon 66 increases with degree of crystallinity. Baker[20] plotted the modulus of elasticity of nylon 610 samples versus the temperature of quenching from the melt, which is a direct function of degree of crystallinity. His plot is reproduced in Figure 5. Since the hardness of nylon depends on the

degree of crystallinity, the thermal conductivity should be greater for samples with a greater degree of crystallinity.

Chemical Forces and Anisotropy of Conductivity. Since there are several indications that crystalline nylon should have a higher conductivity than amorphous nylon, the lower conductivity found experimentally needs explaining. The reason lies in the fact that the thermal conductivity was measured through the thickness of the sample slab, and there is reason to believe that nylon exhibits anisotropy of conductivity.

Orientation Produced by Cold-rolling. In order for a substance to be anisotropic, it must differ in physical character in different directions. The x-ray diffraction patterns of Figures 25 and 26 show that the rolled samples exhibit considerable orientation of the crystallites, while no orientation is evident for the unrolled samples. The evidence for this fact is that the diffraction rings for the unrolled samples are complete circles, while the rings for the rolled samples are arcs of circles. The two kinds of orientation that take place on rolling of nylon have been described by Bunn and Garner[28]: the long crystal axes, which contain the polymer molecule chains, line up in the direction of rolling, and one crystal plane tends to lie flat in the plane of the rolled sheet.

Orientation of Chemical Bonds. The significant thing about the orientation of nylon crystallites is that it results

in different kinds of chemical bonds being oriented in different directions to the extent the crystals are so oriented. Baker[20] stated that there are three kinds of bonds in nylon: the primary valence bonds between the atoms along the molecule chain, the hydrogen bonds between the peptide linkages on adjacent chains, and the other secondary forces between the paraffinic parts of the chains.

Strength of Chemical Bonding and Thermal Conductivity. Austin[9] showed by a study of the conductivity of inorganic compounds that those with the strongest bond forces have the highest conductivities. Schmidt and Marlies[94] have stated the approximate strengths of these bonds in polymers in terms of calories of energy required to rupture one gram-mol of such bonds. The values are:

Primary bonds	50,000 to 200,000 calories
Hydrogen bonds	5,000 to 10,000 calories
Secondary valence bridges	500 to 5,000 calories

Bunn and Garner[28] showed by x-ray diffraction that the strongest bonds (primary valence bonds) tend to lie in the direction of rolling, and that the next strongest bonds (hydrogen bonds) tend to lie in a direction perpendicular to the direction of rolling and in the plane of the sheet. These conclusions have been confirmed by Glatt[50] by infrared absorption studies. Therefore, to the extent that orientation occurs, only the weakest bonds (secondary valence bridges)

remain in a direction perpendicular to the plane of the sheet. But the thermal conductivity should be lowest in the direction in which the weakest bonds lie, through the sheet, the direction in which the thermal conductivity was measured. The conductivity should be higher in the direction in which the hydrogen bonds lie, and highest in the direction of the primary bonds, the direction of rolling.

This argument is in agreement with Rehner[74], who postulated that the conductivity of polymers is mainly due to the primary bonds along the molecular chains. For the same reason anisotropy of conductivity in polymers should be greater than for non-polymers because of the greater difference in bond strength in different directions.

Tests for Anisotropy of Conductivity. A good way to check these theoretical conclusions would be to saw up the sheet of nylon into strips, turn the strips on edge, and clamp them together so that the direction of rolling would be across the plane of the resulting sample. The sawed surfaces could then be finished in a milling machine, and the conductivity measured in the direction of rolling. Time did not permit this to be done, so instead a simple test was used to check the rolled sample for anisotropy in a qualitative way. A point heat source was applied to the sheet and the melting of sodium sulfate paste (90 ^{o}F) spread on the surface was observed. Since the salt melted more rapidly in the direction of rolling, it was concluded that

the conductivity is indeed greater in this direction than in the perpendicular direction, in which the hydrogen bonds tend to lie. The conductivity should be even less in the direction through the sheet, the direction in which it was measured using the guarded hot plate apparatus. The previous test for anisotropy using sodium sulfate could not be adapted for use in this direction since the sheet was only 1/8-inch thick. The sodium sulfate would have been melted by radiation from the hot wire rather than by conduction through the nylon.

Conclusions. The thermal conductivity of the rolled and annealed nylon was lower than that of the original cast sample not because it had a higher degree of crystallinity, but because the molecules were oriented in the rolled sample. The thermal conductivity of the rolled sample was measured in the direction which contained the lowest concentration of strong bonds.

It is believed that there is a relation between degree of crystallinity of nylon and thermal conductivity, but that the effect of degree of crystallinity was masked by the effect of anisotropy due to orientation of the molecules. The effect of degree of crystallinity could be shown by measuring the thermal conductivity of rolled annealed nylon in three directions and averaging the results. The resulting "direction-average" thermal conductivity would be greater for samples with higher degree of crystallinity and would be independent of anisotropic effects.

Practical Applications of the Results. One practical result of this work is an indication of the amount of variation which may occur between the conductivities of individual polymer samples which have received different physical treatment, and an indication of the reliability of the average values of conductivity of polymers which have been published. The applicability of the results is not limited to nylon; for example, a polyethylene extruded tubing is known to possess a high degree of crystallinity and considerable orientation in the direction of extrusion. It might be expected that this product would have a thermal conductivity through its thickness of about half the conductivity of unoriented polyethylene.

On the other hand this investigation, in pointing out the importance of the primary bonds in determining thermal conductivity, supports Rehner's[74] belief that conduction in polymers is mainly molecular conduction, rather than conduction by whole crystal lattices, and hence most polymers, which have similar bonds between the atoms in the chain molecules, should have conductivities of about the same magnitude, provided they are not oriented.

The results are not without significance for the original application which was considered in beginning this investigation: the improvement of nylon for use in bearings. Schwartz[79] stated that in bearings cooled by flow of lubricant a high conductivity is desired not for conducting heat away from the bearing surface through the sleeve, but for conducting heat away from hot spots set up in the bearing by uneven local stresses. The operation of cold-rolling,

by increasing the conductivity in a direction in the plane of the sheet, might reduce the amount of such spot-overheating. This effect could still be of importance even though the increase in conductivity in one direction would be obtained at the expense of the other directions, especially if the rolling and annealing proved to toughen the nylon.

Practical Observations Concerning Rolling and Annealing. From observations made while handling the rolled nylon, it was seen that rolled nylon would not be satisfactory for use in bearings unless it was annealed after rolling. The rolled samples were not perfectly flat, but were dish shaped (due to a slight difference in the speed of the rolls), with a concavity of 3/8-inch for a sheet five inches square. When one such sample was placed in a hydraulic press to flatten it with heat and pressure, it cracked under the strain. Unrolled nylon is so tough and elastic that it would have withstood such deformation easily, but the rolled nylon was already stressed. Two other samples were annealed before being flattened in the press, and they then withstood the strain.

That the rolled samples contained stresses before annealing was shown by viewing them with transmitted polarized light through an analyser lens: 15 fringe lines were counted following the contour of the sheet, showing that the sample was under tension circumferentially and under compression radially. When a sample measuring 5-1/8 by 5-1/8 inches was annealed one-half hour at 240 °C, it shrank

to 4-1/4 by 4-7/8 inches and the thickness increased from 0.122 to 0.148 inches. The direction of greatest shrinkage was the direction of rolling. The resulting sample showed rounded ridges several thousandths of an inch high and 1/4-inch wide. The density of the rolled sample was 1.1350 at 25 °/4 °C, and after annealing it had increased to 1.1499 at 25 °/4 °C. Evidently some of the internal strains were released on heating by a partial reformation of the sample toward its shape before rolling.

A comparison of the x-ray diffraction patterns of Figure 26 shows that some microscopic reformation took place on annealing the rolled sample. The crystallites in the rolled nylon were so much oriented that the outer of the two diffraction rings in Figure 26a is not complete but has become two separate arcs. After heating, the outer ring in Figure 26b is again complete, more nearly as in Figure 25 (taken before rolling), though the rings are still thicker at top and bottom than at the sides, showing that considerable orientation remained after annealing.

The observations on rolling and annealing nylon show that nylon liners for sleeve bearings could be formed from rolled annealed sheets by heating them to 130 °C and wrapping them around a mandril.

Technique of Thermal Conductivity Measurement

Details of the technique of measuring thermal conductivity which were not explained in the ASTM Method C177-45 or in the

procedure will be discussed. Certain precautions which were taken will be treated first, after which some experimental difficulties and the steps which were taken in attempting to overcome them will be described.

Preliminary Remarks Concerning Apparatus. It is believed that the guarded hot plate design recommended by the American Society for Testing Materials[54] is based on sound principles and is a good design from the point of view of workability. A few refinements will be proposed.

By mounting most of the controlling apparatus on a panelboard compactness was attained which resulted in saving of motion for the operator and allowed the measurements to be taken in an unhurried manner.

The particular electric circuits and controls used were almost completely automatic once they had been adjusted. This meant that the operator could concentrate his efforts on the adjustments themselves without being concerned with any disrupting vagaries of the equipment.

The thermocouple lead wires were shielded by wrapping them with aluminum foil which was grounded to the water pipe. In this way they were protected from stray magnetic fields arising from the fluctuating currents in adjacent wires, particularly the lead wires to the water bath heater, which would have caused induced currents and interfered with measurement of the thermocouple emf values.

Assembly of Guarded Hot Plate Apparatus. Nothing is said in the ASTM Method C177-45 concerning the method of assembling the guarded hot plate apparatus. It was found to be best to clamp the guarded hot plate together with samples and thermocouples in position and then insert it on its edge in the box as shown in Figure 12. This method of assembly had a number of advantages:

1. By placing the guarded hot plate on its edge instead of on its end any air bubbles in the cooling water stream were able to pass up through the cooling blocks and out the exit tubes at the top. There were sufficient air bubbles in the water stream so that if they had been held up in the cooling blocks they would have prevented good contact between the cooling water and the metal of the blocks, thus lowering heat transfer between the water and the cooling blocks.

2. By assembling the guarded hot plate outside the box instead of inside the box the insertion of thermocouples and alignment of the samples with the heater was facilitated. It was possible to tighten down the bolts slowly, stopping occasionally to adjust the position of the samples and to make sure that the thermocouple wires were in the slots in the heater rather than being caught between the sample and the heater surfaces.

3. With the guarded hot plate bolted firmly together it could be handled without fear of the component parts slipping out of place. At the same time it could be readily taken apart to insert a different set of samples to be tested.

Insulation of Thermocouple Wires. The thermocouple wires had to be insulated both within the guarded hot plate and along the length where they passed from the guarded hot plate to the binding posts in the zone box.

The portions of the thermocouple wires outside the guarded hot plate were insulated by painting them with silicone resin and baking the resin on by heating in the infra-red oven for one hour. The resin had a tendency to rub off as the wires were handled, causing short-circuits. The insulation was repaired from time to time by repainting them with black enamel. For future use the thermocouple wires should be replaced by cloth-insulated wires.

Cloth insulation would be too bulky to use for the thermocouple wires within the guarded hot plate. Instead, the wires within the slots on the heater surfaces were insulated by filling the slots, with wires in place, with silicone resin and hardening the resin by heat. This treatment had to be repeated every time the guarded hot plate was taken apart because the wires pulled loose from the slots. A better way to insulate the wires was used for the thermocouples on the cold side of the samples. Two pieces of asbestos paper 0.015 inches thick were inserted against the surfaces of the cooling blocks and the thermocouples sqeezed between the paper and the nylon sample. It was found that the thermocouple sank mainly into the paper and sank very little into the sample. The two wires leading to each thermocouple bead were insulated from each other simply by keeping them separated. This method of mounting thermo-

couples for measuring sample surface temperatures is suggested in the ASTM Method[83]. It was not used for insulating the thermocouples on the hot side of the sample because the thermocouples there had to serve two purposes: they measured the nylon surface temperature and they measured the temperature distribution on the heater surfaces. To use asbestos paper insulation, it would have been necessary to provide the same thermocouples in the heater surface slots as well as two more thermocouples placed between the sample surface and asbestos paper. It is recommended that this be done in future work with the apparatus. It was not done in this investigation because it would have required installing four new thermocouple selector switches as well as a new thermocouple cable containing four additional wires. Time did not permit this to be done.

Critique of Thermocouple Temperature Measurements. There was one difficulty in the use of the thermocouples to measure the surface temperature of the samples. The thermocouples did not agree to within one tenth of a degree, and this was thought to be due to shorting of the thermocouple wires in the slots caused by imperfect insulation. In a number of the tests one thermocouple read distinctly lower temperatures than the rest. It was not the same thermocouple which disagreed in all the tests, and in some tests all the thermocouples agreed to within a few tenths of a degree. In Test 5 of Table XXV, Thermocouple 9 read so much lower than the others that it was left out in the calculation of the temperatures.

These facts indicate that the fault was not due to the nature of the thermocouples but to the insulation, which was formed anew for each test and might be sound in one test and faulty in another. Errors resulting from such difficulty would be negative, since a short-circuit would result in an effective junction being formed near the edge of the guarded hot plate, where the temperature would be lower than at the center. In fact, whenever one thermocouple disagreed with the others, it read a lower temperature.

That such short-circuits existed at all casts some doubt on the reliability of all the thermocouple readings. The justification for assuming that the thermocouples indicated the true temperature of the surfaces was that in every test at least seven of the eight thermocouples on the heater surfaces agreed within a few tenths of a degree, whereas the one thermocouple that did not agree differed from the others by as much as one degree. It is believed that the thermocouples on the cold side of the samples were not subject to this error since they were insulated with the asbestos paper. This hypothesis could not be checked since only one thermocouple was used on the cold side of each sample. (The ASTM Method specified that two be used.) One assurance that the thermocouples on the cold sides were reading correctly was that the two thermocouples, one on the cold side of each sample, agreed except for a difference that was proportional to the difference in thickness of the samples. For future work it is recommended that two thermocouples be used on the cold side of each sample.

Guard Resistor too Coarse. It was found that the guard resistor was too coarse to allow close adjustment of the temperature of the guard heater relative to the center heater. This difficulty was partially remedied by making a six-ohm fixed resistor from No 22 nichrome wire wrapped on transite board and wiring it parallel with the variable resistor to increase its sensitivity. It was then possible to make the required adjustments, but still with time-consuming difficulty. The resistor should be replaced with one having more turns.

Actual and Possible Errors

Two classes of errors will be recognized in this discussion: accidental and systematic. Accidental errors will be considered as errors which cause deviation among several measurements of the same quantity but tend to cancel out when a large number of measurements are averaged. Systematic errors will be considered as errors resulting from some inherent difficulty in the system which produces the same error of the same sign for every measurement of a quantity. The average deviation of the results from their mean will be calculated, and an attempt will be made to estimate the magnitude of both accidental and systematic errors.

Thermal Conductivity Measurement. The accurate measurement of thermal conductivity has been the subject of years of experiment by many investigators[53, 89, 72]. The American Society for Testing Materials claims that an accuracy of one per cent can be attained by the use of its Method C177-45, which was the method used in this investigation.

Air Film Resistance. If the sample and metal surfaces are not perfectly smooth and flat, there will be an air film between them, over part of their surfaces. Such an air film would introduce a thermal resistance and cause a negative systematic error. However, the surfaces were finished according to the ASTM requirements and should therefore have been free from air spaces. Nylon is elastic enough so that although the thickness of the samples varied by 0.003 inches, the nylon conformed to the shape of the face plates. The samples were clamped in place tightly enough so that the outline of the heater screws was impressed on the samples. Air film resistance was eliminated on the cold side by placing the thermocouple directly against the sample under asbestos paper, as recommended by ASTM. The Method C177-45[83] provided that this precaution need be taken only when the sample is as hard as ordinary metals or has a conductivity in excess of 1.0 Btu per hour - square foot - ^{o}F per foot.

To obtain an indication of the effect of air film resistance, a sample calculation will be shown assuming an air film of 0.0002 inches. The relative resistance of the film can be calculated assuming that heat transfer through the film takes place by conduction only.

$$\frac{1}{U} = \frac{L}{k} + \frac{L_a}{k_a}$$

where

U = over-all coefficient of heat transfer, Btu per hour - square foot - ^{o}F

L = sample thickness, 0.0125 feet

k = thermal conductivity of sample, 0.15 Btu per hour - square foot - ^{o}F per foot

L_a = air film thickness, 0.000017 feet

k_a = air conductivity[93], 0.016 Btu per hour - square foot - ^{o}F per foot.

$1/U = 0.0125/0.15 + 0.000017/0.016 = 0.083 + 0.0011$ Btu per hour - square foot - ^{o}F per foot.

The air film resistance would be 1.5 per cent of the sample resistance.

Length of Time of Test. The timer could be read to within 0.4 seconds out of 400 seconds duration of test, which accounted for a 0.1 per cent accidental error.

Uncertainty in Thickness of Sample. The rolled sample varied in thickness by 0.003 inches. This fact resulted in an uncertainty in effective thickness of the sample for heat transfer. The measurements of sample thickness at individual points were accurate to within a few ten-thousandths of an

inch. The average deviation of the measurements of sample thickness from the mean was 1.0 per cent.

Wattmeter Calibration and Heat Flow. The average deviation of the wattmeter calibrations from the mean was 0.3 per cent. The wattmeter was calibrated using a calorimeter. A calibration chart was provided with the calorimetric thermometer. The greatest deviation of the thermometer was 0.02 °F, and the accidental error, or uncertainty in reading the thermometer was 0.02 °F. The total heat loss from the calorimeter to the surroundings was 0.05 °F, and the uncertainty in this quantity was 0.01 °F. The uncertainty in weighing the water was five grams out of 2000, or 0.25 per cent. These accidental errors added up to about 0.3 per cent, the same as the average deviation among wattmeter calibrations. Evidently accidental vagaries of wattmeter performance due to mechanical causes did not contribute to the accidental error.

The only possible systematic error was that of the calorimeter constant determination, which was four grams of water. This contributed another 0.2 per cent to the uncertainty in wattmeter calibration, making a total uncertainty of 0.5 per cent.

Unequal Heat Flow. One inherent difficulty of this method for measuring conductivity is that when the heat flow is not the same through the two samples, the conductivity becomes indeterminate. This effect is illustrated by a calculation:

Suppose that one sample was thicker than the other by 0.002 inches, which was actually the case. The heat flow would be greater through the thinner one by 0.002/0.15 or 1.7 per cent. This fact would be reflected in a difference in temperature drop through the samples, and actually such difference amounted to an average of 0.7 ^{o}F on all the tests. To consider this effect, the conductivity can be calculated on the basis of one of two assumptions.

If the heat flow is assumed to be the same through the two samples, it is reasonable to calculate the conductivity separately through each sample and average the results.

$$k_1 = \frac{1}{2} \times \frac{q\, L_1}{A\ \Delta t_1} \qquad \text{and} \qquad k_2 = \frac{1}{2} \times \frac{q\, L_2}{A\ \Delta t_2}$$

where

k = thermal conductivity, Btu per hour - square foot - ^{o}F per foot

q = total heat flow, Btu per hour

L = sample thickness, feet

A = individual heat transfer area, square feet

Δt = measured temperature drop, ^{o}F

Subscripts 1 and 2 refer to the two samples in the guarded hot plate.

Using typical values:

k_1 = 1/2 x 59.4 x 0.148 / 0.08798 x 35.4 = 0.1448

Btu per hour - square foot - ^{o}F per foot

k_2 = 1/2 x 59.4 x 0.150 / 0.08798 x 35.2 = 0.1440

Btu per hour - square foot - ^{o}F per foot

Average k = 0.1444

Assuming that heat flow is different through the two samples it is better to use an average temperature drop and thickness to calculate the average conductivity for the two samples:

$$k = \frac{q\, L}{A\ \Delta t} = 59.4 \times 0.149 \,/\, 2 \times 0.09798 \times 34.8$$

= 0.1445 Btu per hour - square foot - ^{o}F per foot

The value of the thermal conductivity for this example may be 0.1445 or 0.1444 Btu per hour - square foot - °F per foot, depending on which assumption is used in the calculation. The discrepancy would be greater for samples with greater difference in thickness, but was not significant in this determination.

A method has been described by Weh[89] for measuring thermal conductivity using only one sample. The sample is protected from heat loss from the bottom surface by a guard heater. The error resulting from using Weh's apparatus would probably be greater than the error in the present method, since minor fluctuations in the guard heater temperature would have a large effect on the apparent conductivity. It is better to obtain two samples as nearly the same thickness as possible.

Edge Losses. Edge losses were minimized by use of a guard edge heater and by use of two inches of loose insulation packed against the outside of the guard heater. The ASTM Method[83] requires that the guard heater be within 0.1 °F of the center heater, but the temperatures could only be measured to within 0.3 °F. The difference between the guard and center heater temperatures was too small to be measured, so this error was neglected.

Thermocouple Calibration Error. The probable accidental potentiometer error in measuring the thermocouple emf values was

two microvolts, or 0.06 °F, based on reproducibility of the tests. The potentiometer was sensitive to 0.5 microvolts, but the galvanometer was not so sensitive. The error of 0.06 °F was the personal error involved in reading the galvanometer.

The uncertainty in the temperatures of the fixed points at which the thermocouples were calibrated was due to the uncertainty in measuring the atmospheric pressure, and amounted to 0.2 °F corresponding to an uncertainty in barometric pressure of 3.0 millimeters mercury. The uncertainty in barometric pressure was arbitrarily assumed to be the difference in pressure read from the barometers in the Physics Laboratory and in the Unit Operations Laboratory, which are on the same floor level. The ice point was at least as accurate. The calorimetric thermometer used was accurate to within 0.2 °F. All of these calibration errors were sources of a systematic error in the temperature measurements.

The thermocouple emf values at fixed points were reproducible within 0.2 °F, and agreed with each other within 0.3 °F. When mounted in the guarded hot plate at room temperature they agreed within 0.1 °F, probably because they were at more nearly the same temperature, so it was decided to use the same average thermocouple calibration for all the thermocouples. The probable error in the thermocouple calibrations, including all the effects mentioned, was 0.3 °F maximum.

Error in Temperature Measurements. Aside from the error in calibrating the thermocouples, there was also a disagreement among the thermocouples. The amount of disagreement varied from test to test. In many tests all the thermocouples on one face agreed within 0.1 °F, which is the limit imposed by the ASTM Method. In almost every test there were one or two thermocouples which disagreed with the others by as much as 0.3 °F, as shown in Table XXV. This error is probably negative, caused by the short-circuiting of the thermocouple wires near the edge of the heater, for the thermocouples which were in greatest disagreement. This effect tends to mask and make uncertain any actual temperature variations of the surface temperature. Probably the actual variations are of the order indicated by the amount of agreement of thermocouples in the best of the tests, about 0.1 or 0.2 °F. Considering all errors, the temperature error is probably about 0.8 °F at the most.

Possible Temperature Fluctuations. The thermocouple readings were taken at intervals of 15 to 30 minutes. There was no guarantee that fluctuations did not occur between the times when these measurements were taken, although all the observations agreed.

Area of Sample. The heat transfer area linear dimensions were measured with a rule to within 0.05 inches. Several measurements were taken and averaged, since the center heater

was not a perfect square. The resulting error in length of a side was 0.05/3.5 = 1.5 per cent.

Error in Thermal Conductivity Values. The effect of the individual errors on the values of thermal conductivity can be found by differentiating the definition of thermal conductivity:

$$dk = \frac{L\,dq}{A\,\Delta t} + \frac{q\,dL}{A\,\Delta t} + \frac{q\,L\,dA}{A^2\,\Delta t} + \frac{q\,L\,d(\Delta t)}{A\,(\Delta t)^2}$$

$$= 0.0125 \times (59.4 \times 0.005)/0.176 \times 34.8$$
$$+ 59.4 \times (0.002/12)/0.176 \times 34.8$$
$$+ 59.4 \times 0.0125 \times (3.5 \times 0.05/144)/(0.176)^2 \times 34.8$$
$$+ 59.4 \times 0.0125 \times 0.8/0.176 \times (34.8)^2$$
$$= 6.0 \times 10^{-4} + 1.6 \times 10^{-3} + 8.4 \times 10^{-4} + 2.8 \times 10^{-3}$$
$$= 0.0058 \text{ Btu per hour - square foot - } ^{\circ}\text{F per foot}$$

In per cent, this error is:

$$(0.0058/0.130) \times 100 = 4.5 \text{ per cent}$$

where

0.130 = thermal conductivity of rolled nylon, Btu per hour - square foot - $^{\circ}$F per foot, from Table IX.

The thermal conductivities calculated from the data of separate tests are listed in Table XXVI. The average deviation of these values for each test condition was 1.0 per cent. The actual error may be as much as 4.5 per cent, including systematic errors and assuming that errors do not cancel out.

This analysis of errors indicates that to improve the accuracy of measurement the thickness of the sample and the temperature drop should be measured more accurately. Methods for accurately measuring the thickness of compressible samples under known pressures have been described by Griffiths[53]; they were not used because of time limitations. By using separate thermocouples for measuring the surface temperature of the sample the temperature error could be reduced from 0.8 ^{o}F to as little as 0.4 ^{o}F.

Nylon Density. The density of nylon was determined by weighing six-gram samples in air and in water.

Weighing Error. The weights were calibrated against the balance rider, so that the error in weighing was the personal error in making the weighings. This error was 0.0003 grams, the reproducibility of the weighings.

Cracks and Bubbles. The samples were inspected for cracks and bubbles, and none were found. The edges were trimmed with a knife to remove saw burrs.

Air Film. Precautions were taken in the procedure to insure that no air bubbles or film clung to the surface of the samples.

Surface Tension. The weights in air and in water were both taken with the lower sling in water, so that the effect of surface tension was the same in both weighings and in the tare weighing, and cancelled out.

Water Sorption. After immersion in water for five minutes the samples were found to have absorbed 0.0003 grams of water.

Density of Water. The density was expressed relative to the density of water at four °C. To make this conversion the actual water temperature was measured by keeping a thermometer in the balance case with the water for several hours. The temperature was recorded to the nearest 0.5 °C, which corresponded to a possible error of 0.01 per cent in the density.

The average deviation of the density measurements from the mean was 0.22 parts per thousand. This error is consistant with the estimates that have been made for the individual errors. It is believed that the densities are accurate to within 0.22 parts per thousand.

Degree of Crystallinity. In determining the degree of crystallinity the following relation was used:

$$D.\ C. = \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100$$

where

D. C. = degree of crystallinity, per cent

ρ = density of sample at 25 °/4 °C

ρ_a = density of amorphous nylon at 25 °/4 °C

ρ_c = density of nylon 66 crystal at 25 °/4 °C.

For the purpose of this investigation, this equation was considered to be the definition of degree of crystallinity.

If the crystalline and amorphous nylon are considered to be real, pure phases, then the assumption underlying the equation is that there is no volume change on "mixing" the crystalline and amorphous phases, and the degree of crystallinity is a linear function of density.

The density of amorphous nylon was taken to be that of the most strongly quenched sample ever prepared by the duPont[76] research laboratories, 1.111 at 25 °/4 °C. Undoubtedly this sample still contained some crystalline material, but it was assumed to be amorphous. From a general knowledge of the effect of heat treatment on the degree of crystallinity, the author estimates that it contained less than five per cent crystalline material.

The absolute values of degree of crystallinity may be in error by as much as ten per cent. In this investigation the values of degree of crystallinity were used to show the effect of physical treatment on changes in degree of crystallinity. The errors due to uncertainty in density of amorphous and of crystalline nylon would have about the same effect on the apparent degree of crystallinity of all samples, and only the uncertainty due to error in determining density affects such comparisons. This error is:

$$d(D.\ C.) = \frac{d\rho}{(\rho c - \rho a)} \times 100$$

$$= (0.00022 \times 1.1387/1.24 - 1.111) \times 100$$

$$= 0.19 \text{ per cent}$$

Annealing Temperature. A check of the pyrometer on the oven used to anneal the nylon samples was obtained in one test when the temperature as indicated by the pyrometer rose to 265 °C. It was found that the nylon had melted. In another test the nylon did not melt when the pyrometer read 250 °C. Since the melting point of nylon 66 is 260 °C according to Baker[21], the pyrometer was correct within about ten degrees in measuring the actual temperature of nylon.

In the test in which the nylon melted the oven was hotter than 260 °C for only about ten minutes, which indicates that there was little time lag in the heating of the nylon.

Recommendations

Further Investigations. The following recommendations are made concerning future work on the thermal conductivity of plastic materials.

1. In reporting the thermal conductivity of polymers which exhibit microcrystallinity, it is recommended that it be determined whether there was any orientation of the molecules in the samples tested, and that the density be reported. If there was orientation, the method of forming of the samples should be described as well as subsequent physical treatments, or the degree of orientation

should be determined by photometer measurements on x-ray diffraction patterns.

2. It is recommended that the thermal conductivity of rolled annealed nylon 66 be determined in the direction of rolling and also in the direction perpendicular to the direction of rolling but in the plane of the sheet in order to prove conclusively that there is a relation between bond strength and thermal conductivity in polymers. A good method would be to saw up a sheet of rolled annealed nylon into strips, turn the strips on edge, and clamp them together so that the direction of rolling would be across the plane of the resulting sample. The sawed surfaces should be finished in a milling machine.

3. It is recommended that tests be made to attempt to further increase the degree of crystallinity and orientation of nylon by subjecting the rolled annealed nylon sheet to a further rolling and annealing operation.

4. It is recommended that the effect of degree of crystallinity on the thermal conductivity of nylon 66 be determined separately from the anisotropic effect which results from cold-rolling. This should be done by measuring the thermal conductivity of rolled annealed nylon in three directions and averaging the results.

5. It is recommended that the effect of degree of polymerization and of moisture content on the thermal conductivity of nylon 66 be determined.

6. It is recommended that thermal conductivity measurements be made on oriented and unoriented polyethylene in order to obtain further data on the relation between bond strength and thermal conductivity.

Application. It is recommended that performance tests be made on nylon bearings made from rolled annealed nylon in order to determine:

1. Maximum load

2. Performance characteristics

3. Physical changes in the nylon caused by operation of the bearing that might affect thermal conductivity, such as changes in degree of crystallinity or orientation.

Improvements in Present Work. The following recommendations are made for improvement of the present work or for carrying out similar investigations on the thermal conductivity of nylon:

1. It is recommended that the density of amorphous nylon be determined in order to standardize the measurements of degree of crystallinity by the density method. Since it may not be possible to prepare pure amorphous nylon, it is recommended that the degree of crystallinity of one sample of nylon be determined by photometer measurements of an x-ray diffraction pattern of nylon according to the method described by Hermans[60]. The density of the sample should then be measured and the density of amorphous nylon as defined by the following relation should be calculated:

$$d_a = \frac{d - d_c\,(D.\,C.)/100}{1 - (D.\,C.)/100}$$

where

d_a = density of amorphous nylon at 25 °/4 °C

d_c = density of nylon crystal at 25 °/4 °C

d = density of sample at 25 °/4 °C

(D. C.) = degree of crystallinity of sample as determined by x-ray diffraction, per cent.

2. It is recommended that the variable guard heater used in the thermal conductivity measurement be replaced with a resistor of ten ohms resistance and 500 turns, provided with a smooth-sliding contact.

3. It is recommended that larger rolled samples be used in measuring the thermal conductivity so that it will not be necessary to piece them. Sheets six inches square would be large enough so that after the shrinking process which accompanies annealing they would still be larger than five inches square.

4. It is recommended that the degree of orientation of the nylon samples used in this investigation be determined by use of a photometer on the x-ray diffraction patterns in order to determine more specifically the relation between bond strength and thermal conductivity by allowing for the effect of degree of orientation.

5. It is recommended that the following precautions be followed in the use of the Standard Method of Test for Thermal Conductivity

of Materials by Means of the Guarded Hot Plate, ASTM Designation C177-45:

a. The guarded hot plate should be placed on its edge with water exit tubes up during operation to allow air in the water to escape; or, the cooling blocks described in an ASTM[54] pamphlet which are constructed by soldering a coil of copper tubing to a flat slab of bronze should be used.

b. The enamel-insulated thermocouple wires should be replaced with cloth-insulated wires.

c. An additional thermocouple should be provided on the cold face of each sample to check the temperature and comply with the ASTM requirements.

d. Two additional thermocouples should be provided on the hot side of each sample in order to measure the sample surface temperature independently of the heater surface temperatures. It is further recommended that these thermocouples be insulated from the heater face plates by use of two sheets of asbestos paper 0.015 inches thick.

e. The thickness of the samples should be measured while being compressed at the pressure used in the guarded hot plate by the method described by Griffiths[53].

Limitations

Effect of Cold-rolling and Annealing on Density and Degree of Crystallinity of Nylon 66. The following limitations applied

to investigations of the effect of cold-rolling and annealing on the density and degree of crystallinity of nylon 66:

1. Only one slab of cast nylon was used for the tests. The rate at which it cooled from the melt in the casting process was a limitation, but was not known. The slab measured 4-3/16 by 36 by 1/4 inches, and was cast from DuPont Company's FM10001 molding compound by the Polymer Corporation.

2. The nylon was characterized by an intrinsic solution viscosity of 2.53 in 90 per cent formic acid. A degree of polymerization of 148 was indicated.

3. The effect of only one condition of rolling was studied. The samples for all tests were rolled from a thickness of 0.260 inches to 0.122 inches by passing them through uniform-speed calendars ten times. The calendars were warmed with water at 75 °C.

4. In determining the effect of annealing on density, samples were annealed at temperatures of from 180 °C to 240 °C and for periods of from one-half hour to two days.

5. Orientation of nylon molecules was detected by inspection of x-ray diffraction patterns, but no quantitative measure of orientation was used.

6. In calculating the degree of crystallinity of nylon 66 from the density, the density of amorphous nylon was assumed to be 1.111 at 25 °/4 °C and of crystalline nylon 1.24 at 25 °/4 °C.

Effect of Density and Degree of Crystallinity on Thermal Conductivity. The following limitations applied to investigations of the effect of density and degree of crystallinity on the thermal conductivity of nylon 66.

1. The thermal conductivities of only two samples of nylon were determined. One was the original cast nylon, and the other was prepared from the original nylon by cold-rolling from a thickness of 0.260 inches to 0.122 inches and then annealing for two hours at 240 °C.

2. The density of the first sample was 1.1387 at 25 °/4 °C, and of the second sample 1.1499 at 25 °/4 °C.

3. The degree of crystallinity of the first sample was 21.2 per cent and of the second sample 30.8 per cent.

4. The ASTM Method C177-45, Standard Method of Test for Thermal Conductivity of Materials Using the Guarded Hot Plate, was used.

5. The thermal conductivity was measured in only one direction, perpendicular to the plane of the sheet and perpendicular to the direction of rolling.

6. The moisture content of the first sample was 0.56 per cent, and of the second sample 0.30 per cent.

7. The thermal conductivity was measured at two mean temperatures for each sample, 80 °F and 185 °F.

V. CONCLUSIONS

The following conclusions were reached from tests made on nylon 66 slab characterized by an intrinsic solution viscosity of 2.53 in 90 per cent formic acid, indicating a degree of polymerization of 148.

Microcrystalline Properties of Nylon Slab

Samples of nylon were annealed for two hours at 240 °C and rolled from a thickness of 0.260 to 0.122 inches. The density of amorphous nylon was assumed to be 1.111 at 25 °/4 °C and that of crystalline nylon to be 1.24 at 25 °/4 °C.

1. By annealing, the density of nylon was increased from 1.1387 to 1.1448 at 25 °/4 °C.

2. By annealing, the degree of crystallinity of nylon was increased from 21.2 to 26.2 per cent.

3. By rolling and annealing, the density of nylon was increased from 1.1387 to 1.1499 at 25 °/4 °C.

4. By rolling and annealing, the degree of crystallinity of nylon was increased from 21.2 to 30.8 per cent.

5. The nylon crystallites were oriented by the rolling operation.

6. The degree of orientation of rolled nylon was decreased by annealing.

Effect of Rolling and Annealing on the Thermal Conductivity of Nylon 66

The thermal conductivities of cast nylon and of nylon rolled from 0.260 to 0.122 inches in thickness and annealed two hours at 465 °F were determined by using ASTM Method C177-45, the Guarded Hot Plate Method. Anisotropy of conductivity was detected by observing the melting of sodium sulfate decahydrate paste spread on four nylon sheets and applying a point heat source to each sheet.

1. The thermal conductivity of nylon measured in a direction perpendicular to the plane of the sheet was decreased by rolling and annealing from 0.172 to 0.130 Btu per hour - square foot - °F per foot.

2. The thermal conductivity of nylon was the same at mean temperatures of 80 °F and 185 °F.

3. The thermal conductivity of rolled nylon in the plane of the sheet was higher in the direction of rolling than in a direction perpendicular to the direction of rolling.

4. The average deviation from the mean of the individual test values of thermal conductivity of nylon was 1.0 per cent, and an analysis of errors showed that the actual error was less than 4.5 per cent.

VI. SUMMARY

The use of massive nylon as a material for bearing liners is limited by its low melting point (260 °C) and its low thermal conductivity (0.172 Btu per hour - square foot - °F per foot). This combination of defects results in the formation of hot spots at points of stress, and since the material does not conduct away the heat from such spots rapidly enough, the nylon tends to expand and stick to the shaft. If it were not for this difficulty, more use would be made of nylon bearings, since it has excellent resistance to corrosive substances such as sea water and is capable of resisting repeated mechanical shock.

The purpose of this investigation was to determine the extent to which the degree of crystallinity of nylon could be increased by cold-rolling and annealing, and the change in thermal conductivity resulting from these treatments.

A survey was made of the literature on the thermal conductivity of nylon in particular and non-metallic solids in general, of the internal structure of nylon, of the effect of physical treatment on the internal structure and physical properties of nylon, and on test methods.

The duPont Company reported the thermal conductivity of its nylon molding compounds, and stated that an average value for Nylon FM10001 is 0.15 Btu per hour - square foot - °F per foot.

Austin and Eucken agreed in stating that on theoretical and experimental evidence the thermal conductivity of an inorganic compound is in general higher when the substance is in crystalline form than when it is in amorphous form. Jakob stated that in non-metallic solids heat is conducted by transfer of vibrations from molecule to molecule, and that in crystals heat is also conducted by a wave-like vibration of the lattice as a whole. Austin stated that the thermal conductivity of inorganic compounds is dependent on the strength of chemical bonding in the compounds. Rehner suggested that the thermal conductivities of organic polymers are all of about the same magnitude since heat is conducted mainly along the molecular chains, which contain primary valence bonds of about the same strength.

Many investigators have shown that nylon is microcrystalline in nature, containing crystalline regions about 1000 Angstroms in diameter imbedded in a matrix which is essentially a supercooled liquid. Thus nylon is a two-phase system. The density of nylon has been investigated repeatedly and has been shown to be a measure of the degree of crystallinity. The degree of crystallinity is defined as the percentage of crystalline material present. Direct comparison of the reported densities has not been possible because the samples tested have not been completely characterized as to previous physical treatment. It has been shown that the method of forming affects the density, and samples which have been cooled slowly from the melt have a smaller number of crystal nuclei and

a higher degree of crystallinity. Annealing, stretching, solvent swelling, and rolling increase the density and degree of crystallinity, and more drastic physical treatment tends to cancel out the effect of previous milder treatment.

Bunn and Garner have established the crystal form and crystal parameters of nylon 66 and 610 and demonstrated the nature of the orientation that takes place on cold-rolling and annealing. The nylon molecules tend to lie in the plane of the rolled sheet in the direction of rolling.

The experimental part of the work consisted of testing methods of increasing the thermal conductivity of nylon, measuring the thermal conductivity, and determining the changes in internal structure which caused the changes in conductivity.

The thermal conductivities of two samples of nylon 66 were determined. One was a slab of cast nylon 1/4-inch thick. The other was prepared from the first by cold-rolling it to half the original thickness and then annealing for two hours at 240 °C.

To determine the effect of physical treatment on the internal structure the density and degree of crystallinity were determined and x-ray diffraction patterns of the samples were made.

The material which was tested, nylon 66, was a practically pure chemical compound. It is known as polyhexamethylene adipamide, and is the most common nylon of commerce.

Standard laboratory procedures were used in all the tests. The thermal conductivity was measured using the ASTM Method

C177-45, the guarded hot plate method. In this method two sheets of nylon five inches square were sandwiched between an electrical heater and two brass cooling blocks. The quantity of heat which flowed through the samples under the temperature difference set up by the apparatus was measured by measuring the electric power input to the heater. The temperature drop across the samples was measured by means of thermocouples. The sample thickness and area were measured, and from these quantities the thermal conductivity was calculated.

The density was determined by weighing six-gram samples in air and in water, according to the standard method.

The degree of crystallinity was calculated from the density of dried samples by assuming a linear relationship between density and degree of crystallinity. This method of calculation was worked out by Hermans for cellulose, but has never before been used for nylon.

The results of this investigation showed that when nylon slab was rolled and annealed, the degree of crystallinity was increased, confirming the conclusions of previous investigators. On the other hand, the thermal conductivity was affected mainly by an orientation of the molecules produced by rolling rather than by the change in degree of crystallinity. Because of an orientation of the molecules in the direction of rolling, the nylon thermal conductivity became anisotropic. The conductivity was apparently increased in the direction of rolling at the expense of the other directions. These results support Rehner's hypothesis that the thermal conductivity of polymers is mainly dependent on the strength of the primary

bonds in the molecular chain, and that thermal conduction in polymers is mainly molecular conduction, not lattice conduction. This hypothesis was questioned at the beginning of the investigation, but the results seem to confirm it.

Rolled nylon would be superior to cast nylon for use in bearings since it could better conduct heat away from hot spots. The lower conductivity in the direction through the thickness of the liner would not be a drawback in bearings provided with fluid lubrication since the heat generated by friction is not conducted away through the walls but is carried away by the lubricant. The nylon would have to be annealed after rolling to eliminate residual strains caused by rolling which make it brittle, even though annealing caused some decrease in the degree of orientation of the molecules, with accompanying decrease in the effect of anisotropy of conductivity.

The following conclusions were reached from tests made on nylon 66 slab characterized by an intrinsic solution viscosity of 2.53 in 90 per cent formic acid, indicating a degree of polymerization of 148.

Microcrystalline Properties of Nylon Slab

Samples of nylon were annealed for two hours at 240 °C and rolled from a thickness of 0.260 inches to 0.122 inches. The density of amorphous nylon was assumed to be 1.111 at 25 °/4 °C and that of crystalline nylon to be 1.24 at 25 °/4 °C.

1. By annealing, the density of nylon was increased from 1.1387 to 1.1449 at 25 °/4 °C.

2. By annealing, the degree of crystallinity of nylon was increased from 21.2 to 26.2 per cent.

3. By rolling and annealing, the density of nylon was increased from 1.1387 to 1.1499 at 25 °/4 °C.

4. By rolling and annealing, the degree of crystallinity of nylon was increased from 21.2 to 30.8 per cent.

5. The nylon crystallites were oriented by the rolling operation.

6. The degree of orientation of rolled nylon was decreased by annealing.

Effect of Rolling and Annealing on the Thermal Conductivity of Nylon 66

The thermal conductivities of cast nylon and of nylon rolled from 0.260 to 0.122 inches in thickness and annealed two hours at 240 °C were determined by using ASTM Method C177-45, the Guarded Hot Plate Method. Anisotropy of conductivity was detected by observing the melting of sodium sulfate decahydrate paste spread on four nylon sheets and applying a point heat source to each sheet.

1. The thermal conductivity of nylon measured in a direction perpendicular to the plane of the sheet was decreased by rolling and annealing from 0.172 to 0.130 Btu per hour - square foot - °F per foot.

2. The thermal conductivity of nylon was the same at mean temperatures of 80 °F and 185 °F.

3. The thermal conductivity of rolled nylon in the plane of the sheet was higher in the direction of rolling than in a direction perpendicular to the direction of rolling.

4. The average deviation from the mean of the individual test values of thermal conductivity of nylon was 1.0 per cent, and an analysis of errors showed that the actual error was less than 4.5 per cent.

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