THERMAL ANISOTROPY AND CONDUCTIVITY STUDIES OF NYLON 66

by

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I. INTRODUCTION

The development of nylon from a laboratory curiosity to a recognized product of industry has brought a new and economical material of construction to the engineer and designer. While nylon is best known to the consuming public as a textile fiber and as a material for bristles, the plastics industry also recognizes it as a superior plastic material in massive form. It has been used to advantage in some applications where metals have been traditionally employed, and it is conceivable that its usefulness may be further extended in this and in other fields.

Nylon lends itself to many applications because of its outstanding toughness, abrasion-resistance, form-stability at higher temperatures, strength in thin sections, lightness in weight, and chemical resistance. These properties make it a satisfactory bearing material and, in some applications, it is superior to metallic bearings. However, the disadvantages of low melting point and low thermal conductivity prevent nylon from being used more extensively as a bearing material. Therefore, a study of methods for increasing nylon's thermal conductivity in order that it may dissipate heat more readily would be desirable.

A previous investigation of the effect of change in crystallinity brought about by rolling and annealing on the thermal conductivity of nylon 66 indicated that it exhibits anisotropy of conductivity and that its thermal conductivity depends not only on the degree of crystallinity, but also on other primary physical factors related to its molecular structure. Accordingly, further work in the light of these results is needed to determine the extent to which the thermal conductivity of nylon can be increased. This investigation was undertaken to study these factors.

The purpose of this investigation was to determine the relationships of anisotropy of thermal conductivity, bond strength, degree of crystallinity, molecular orientation, and the changes resulting from rolling-annealing treatment of nylon 66.

II. LITERATURE REVIEW

In making a rational study of the thermal properties of nylon, an extensive literature survey was carried out prior to the experimental portion of this investigation in order to acquaint the author with the established principles of physics and chemistry bearing on the subject. Since in some cases specific information on nylon was not available, it became necessary to interpret known facts about other materials and draw inferences by analogy. The survey is presented under the headings: Theory of Thermal Conduction in Non-metallic Solids, Anisotropy of Thermal Conductivity, Thermal Conductivity of Polymers, Nylon in the Crystalline State, and Test Methods.

Theory of Thermal Conduction in Non-metallic Solids

In dealing with heat conduction in non-metallic solids, much emphasis must be placed on the factors which influence their thermal conductivity. Also a correlation of these factors with kinetic and thermodynamic relationships is desirable. Although no specific information is available which applies to nylon, the following discussion proves helpful in obtaining an understanding of the generalized theory of thermal conduction in any non-metallic solid.

Fourier's Law. Fourier's law is a mathematical definition of thermal conductivity. It was stated by McAdams(51):

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

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, °F

x = length of path of heat flow, feet

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

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

Austin(2) pointed out that the Fourier equation does not give any basis for assuming that k is independent of any variable. This fact 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 = the 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. Also the differential dt/dx in the Fourier equation (Equation 1) gives the true temperature gradient, that is, the tangent of the temperature distribution curve at the point at which the plane A is selected. It is, therefore, the temperature gradient at a point which has but one temperature and it is the conductivity characteristic of that temperature. Unfortunately, the temperature gradient is not a quantity which can be easily determined by direct measurement because in practice it is not easy to determine the true temperature gradient at a point. What is almost always measured is a finite temperature drop over a finite interval of length, which is represented by $\Delta t/\Delta x$, and this is used in the Fourier equation instead of dt/dx.

Factors Affecting Thermal Conductivity. In a general survey of the work done by many investigators, Austin(3) outlined and discussed the factors which may influence the thermal conductivity of non-metallic materials. The general plan was to evaluate the effect of a change in each variable taken singly when all others were held sensibly constant. The following factors were listed:

- Chemical Composition
    - Molecular Structure in Pure Compounds
    - Impurities in Solid Solutions

- 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 C_v. Austin(3) derived a thermodynamic relation between k and C_v, the heat capacity at constant volume of a substance, and showed that k is proportional to C_v. 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.

The Crystalline and Amorphous States of Matter. According to Glasstone(37), the terms crystalline and amorphous refer to ideal states of matter, and real substances are usually not strictly amorphous or crystalline. Solid crystals contain flaws in the regular ordering of their molecules, according to Oldham and Ubbelohde(53). Glasstone(37) further 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. Because of this difficulty, Nichols(52) defined a crystalline polymer as one having a well-defined x-ray diffraction pattern.

Kinetic Theory of Thermal Conduction. Rehner(56) stated in 1947 that "no physical molecular theory of thermal conductivity exists at the present time." Debye(4), however, 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(48). 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 was believed that some disturbances retard the passage of the thermal energy. Bragg(20) stated "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."

Debye(4) considered "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 scattered, distorted, or disturbed by imperfections in the lattice and suffer a decrease in intensity on this account." According to Debye's consideration, the thermoelastic waves set up heat flow throughout the crystal as each successive wave impinges upon a lattice point. Because of the heat flow, the lattice expands and causes the lattice points to shift about by means other than their natural translational, vibrational, and rotational motions. It is their natural shifting about in the lattice that causes distortions and scattering of the advancing thermoelastic waves.

Jakob(48) 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 55×10^7 oscillations per centimeter. But the rate of heat flow is only 0.02 centimeters per second. Hence the oscillations appear to be slightly damped or loosely coupled. They are in the proper position for the maximum amplitude only once in a million times.

The Debye Equation. The Debye(4) equation derived from the preceding assumption is:

$$k = 1/4\ l w_s \rho C_v \tag{3}$$

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, waves per hour

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

C_v = the specific heat at constant volume, Btu per hour - pound - °F.

Effect of Complexity of Crystal Structure. An attempt was made by Eucken(4) 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. The equation, however, leads to certain qualitative deductions which are substantially correct, according to Austin(4). For example, other things being equal, the highest value of l, and consequently 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.

Austin(4) analyzed 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. In dealing with crystalline compounds, Austin(5) pointed out the general rule that when the component atoms have the same electron shells the conductivity is high, and also 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 heat substances which have been studied are the alkali halides and refractories such as silicon carbide.

Purity. Eucken's(33) work on the influence of purity on thermal conductivity was clarified by Austin(6). Austin stated 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 has been presented by Austin(6) to show that these generalizations are valid, and that they follow the analogous rule for electrical conductivity.

Compressibility or Hardness. Eucken's consideration of the effect of the variables in the Debye equation was also examined by Austin(8). If (lC_vd) is approximately constant, the conductivity should vary with w_s, the rate of propagation of the thermoelastic waves. It was shown by Austin that w_s is inversely proportional to $\sqrt{Xd}$, where X is the compressibility of the crystal and d the density. Eucken(34) arbitrarily selected alkali halides for which (lC_vd) 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(8) 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. The suggestion of Eucken's(32) that in any group of substances the order of increasing melting point is also the order of increasing thermal conductivity, was criticized by Austin(7). The relation holds only in special cases. Another suggestion by Eucken(32) was that the thermal conductivity of most crystalline substances is the same at the melting point. Austin(7) 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 difficult to obtain data to prove this generalization because values at the melting point must be obtained by extrapolation.

Two-phase Aggregates. The most common type of two-phase aggregate is a dispersion of a crystalline phase and an amorphous phase, according to Russell(58). He has identified two variations, one where the crystalline phase is continuous and one where the amorphous phase is continuous. He derived equations for porous brick.

A single equation derived by Eucken and discussed by Austin(9) covers both cases. It is:

$$k_b = k_u \frac{1 + 2V_d \frac{1 - Q}{2Q + 1}}{1 - V_d \frac{1 - Q}{2Q + 1}} \qquad (4)$$

where

k_b = conductivity of the aggregate, Btu per hour - square foot - ^{o}F per foot

k_u = the conductivity of the continuous phase, Btu per hour - square foot - ^{o}F 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 - ^{o}F per foot

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

Q = the ratio k_u/k_d, dimensionless.

The equation agrees with those of Russell, which are plotted in Figure 1, page 13.

Austin(10) pointed out effects of differences in the ratio k_s/k_a, the conductivities in the crystalline and amorphous phases, respec-

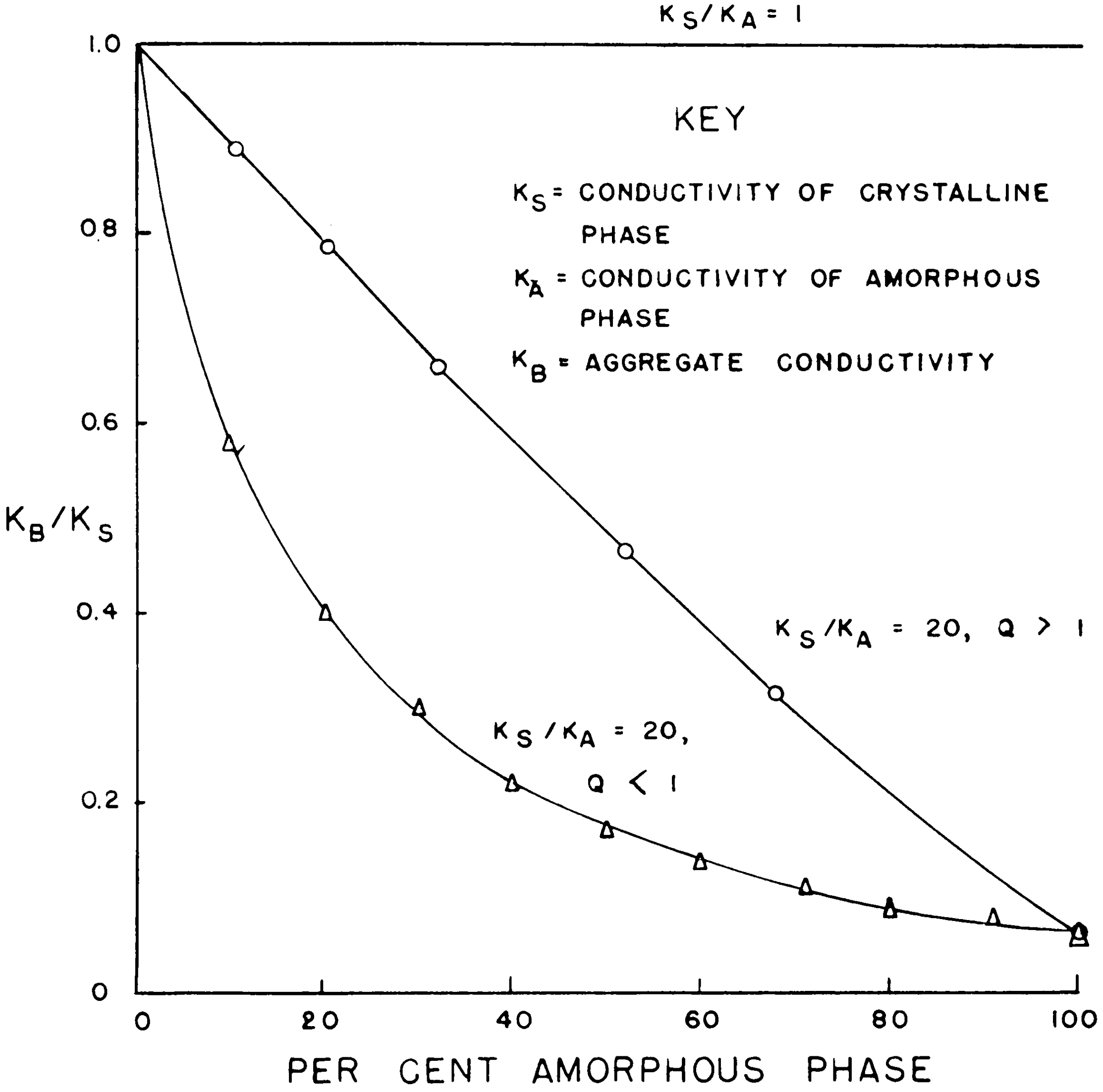


FIGURE 1. VARIATION OF THERMAL CONDUCTIVITY OF AGGREGATE WITH COMPOSITION

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

tively. In Figure 1, page 13, for Q greater than one the phase with higher conductivities (the crystalline phase) is continuous. The first case refers to particles of glass embedded in a crystalline medium and the second refers to crystalline areas embedded in glass. Also 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 2, page 15, presented by Austin(11), 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 temperature 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.

Anisotropy of Thermal Conductivity

The phenomenon of anisotropy of thermal conductivity of single crystals was first described by Worthing(80). He stated that the Swiss physicists A. A. de LaRive and de Candolla were the first investigators to present evidence of the fact that anisotropic bodies

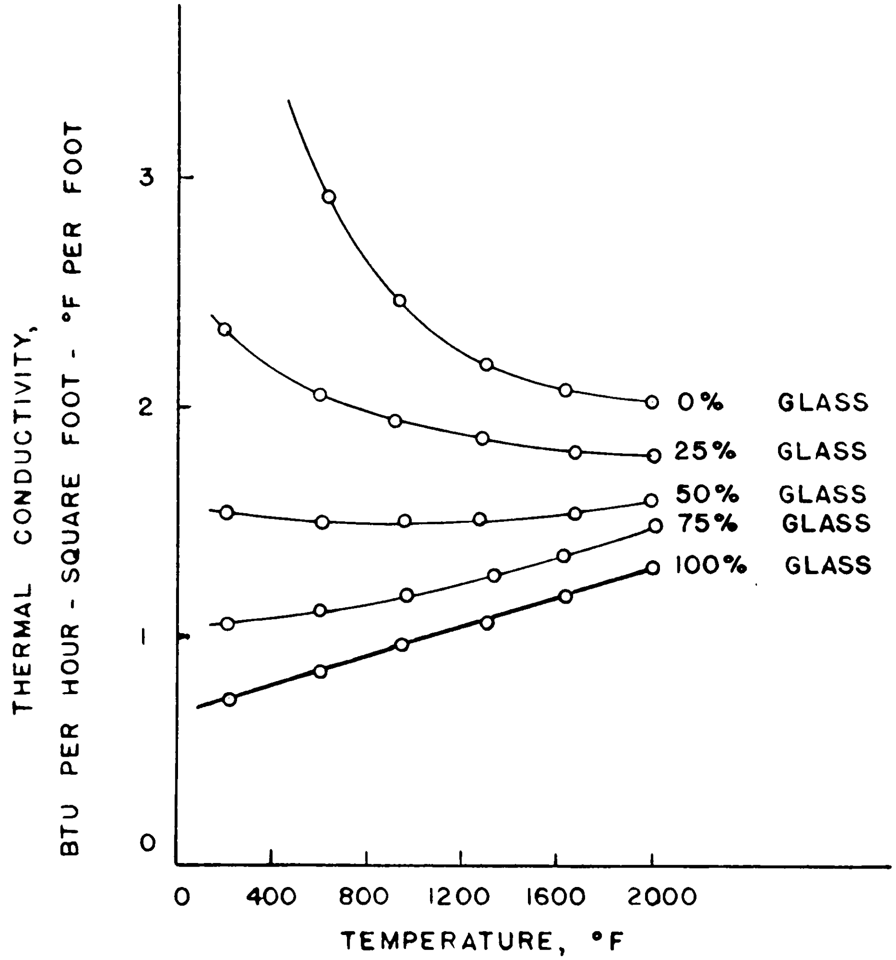


FIGURE 2. THERMAL CONDUCTIVITY OF SILICA CONTAINING DIFFERENT AMOUNTS OF GLASS

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

possess different thermal conductivities for different directions of measurement. Their results stemmed from an investigation involving wood.

Definitions. The properties of a crystal such as tensile strength, elasticity, heat conduction, electric conductance, rate of transmission of light, and rate of solution may be different along the different axes of a crystal. Such a crystal is called anisotropic. An isotropic crystal is one which has the same properties in all directions.

Single Crystals. Worthing(80) stated that mathematical theory predicts and experimental evidence verifies that the isothermal surfaces surrounding a point source of heat within a crystal should be ellipsoidal. If the crystal is isotropic, these surfaces are spherical. If the crystal is uniaxial, the surfaces are ellipsoids of rotation symmetrical with respect to the crystal axis. If the crystal is biaxial, all three axes of the ellipsoidal isothermal surfaces differ in magnitude. A case in point is the triclinic crystal, optical axes of which are not mutually perpendicular. There is no axis of symmetry and the thermal conductivity is different in all directions. The thermal axes are still mutually perpendicular, however, and an isotherm is an ellipsoid of revolution. The thermal axes do not coincide with the optical axes. It has been deduced that the thermal conductivities of the crystal along the three main axes vary directly as the squares of the lengths of those main unit cell axes.

Austin(12), in disagreement, stated that the conductivity could be either a maximum or a minimum along the longest axis. When the thermal conductivity is a maximum in the direction of this axis, the crystal is said to be thermally positive; when it is a minimum, the crystal is negative. At an angle to the major axes, the following relation holds:

$$k_\theta = k_\perp + (k_\parallel - k_\perp) \operatorname{Cos}^2\theta \qquad (5)$$

where

k_θ = the thermal conductivity in the given direction, Btu per hour - square foot - $^\circ$F per foot

$k_\parallel$ = the conductivity in the direction of the principle axis, Btu per hour - square foot - $^\circ$F per foot

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

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

Naturally Deposited Diatomaceous Earth. Austin(13) explained the anisotropic effect of single crystals by giving the example of the refractory material, naturally deposited diatomaceous earth, which paradoxically has in general fewer crystalline attributes than any other refractory material. It has a distinct layered or "grained" structure. This material has an appreciably greater thermal resistance to flow normal to the plane of the layers than it does to flow in the plane of the layers. In this respect it resembles an optically uniaxial crystal. The behavior is not at all surprising since a block of the material is in effect a macroscopic crystal composed of layers of diatom skeletons which have a crude resemblance to atom planes.

A more striking example stated by Austin(14) was the thermal conductivity of expanded mica granules. Although no data on singular granules are available, the thermal conductivity in a direction normal to the plane of the flakes must be very much less than the conductivity in the plane of the flakes. This marked anisotropy is usually masked by the fact that, as commonly used, the granules are oriented at random. However, if the granules were oriented in some way, marked anisotropy would be the result.

Evidence of Anisotropy of Thermal Conductivity in Bismuth. Experiments performed by Lownds, Perrot, and Jaeger and discussed by Kaye and Roberts(49) have shown that the thermal conductivity of bismuth crystals in different directions differs considerably. Kaye and Roberts stated that the results obtained by the above mentioned workers were incapable of furnishing conclusive evidence since they used the method of measuring the ratio of the axes of the elliptical figures formed by applying a point source of heat to a crystal surface coated with paraffin. This ratio, which gave the square root of the ratio of the thermal conductivities in the two directions parallel and perpendicular to the trigonal axis of bismuth, afforded no information as to the absolute value of either of the conductivities.

Jaeger and Diesselhorst(49) measured the thermal conductivity of a bismuth rod which was assumed to consist of a random arrangement of aggregations of small crystals possibly held together by intercrystalline layers of unknown structure and indefinite extent. The value they obtained was 0.0193 c. g. s. units at 18 °C.

Kaye and Roberts(49) measured the thermal conductivity of single crystals parallel and perpendicular to the trigonal axis and found the values to be 0.0159 and 0.0221 c. g. s. units, respectively. In comparing their results with that of Jaeger and Diesselhorst, they reasoned that the reciprocals of conductivities, or resistivities, were additive and noted that the value at right angles to the axes of symmetry must be multiplied by a factor of two.

Using the relation

$$1/k = 1/3\ (1/k_{\parallel} + 2/k_{\perp}) \qquad (6)$$

where

k = the mean thermal conductivity of the material,

$k_{\parallel}$ = the thermal conductivity parallel to the trigonal axis,

$k_{\perp}$ = the thermal conductivity at right angles to the trigonal axis,

they found the mean thermal conductivity of the crystal to be 0.0195 c. g. s. units at 18 °C. Agreement of this figure with that of Jaeger and Diesselhorst indicated that, in the case of bismuth metal in the aggregate, the distribution of the constituent small crystals is random, and that the effect of such inter-crystalline layers on the thermal conductivity is not appreciable.

Anisotropy of Conductivity in Wood. An interesting example of anisotropy of thermal conductivity was reported by Griffiths and Kaye(40) following an investigation of the conductivities of wood timber. Conductivity measurements were made on ash timber with heat flow parallel to the grain of the wood (fibers), across the grain (perpendicular to the fibers) and radial to the annual rings, and across the grain and tangential to the annual rings. The thermal conductivity with the grain was found to be roughly twice that of either of the "traverse" conductivities and of the two latter directions, the "radial" conductivity was usually approximately five to ten per cent greater than the "tangential" conductivity.

These results might be anticipated if it is noted that in the direction of the grain the heat finds virtually an unbroken path of flow, because the annual rings consist of rings running longitudinally through the wood in continuous cylindrical bands concentric with the axis of the tree. Also when heat flow takes place across the grain and radially to the annual rings, the path of heat flow, although largely obstructed by the fibers lying across the path, is supplemented by the medullary rays which consist of bands of honeycomb-like cells radiating from the center of the tree and interconnecting the annual rings. In the case of heat flow across the grain and tangential to the annual rings, the path of heat flow is obstructed by both the fibers of the wood and the medullary rays; the result being a lower value of the conductivity than in either of the previous instances.

Austin(13), in agreement stated that anisotropic conduction appears to be a characteristic of any grain-like structure and that the conductivity along the grain or layers is greater than that across the grain.

Thermal Conductivity of Polymers

The data and theory in published literature on the thermal conductivity of polymers are very meager. The investigations which have been made on the subject are reviewed below, but are so incomplete that they do not fully indicate the factors which influence the thermal conductivity of polymers.

Conductivity of Amorphous Rubbers. Rehner(56) attributed relatively small though "technologically important" differences among thermal conductivities in amorphous rubbers to structural and chemical differences. He suggested on the basis of general consideration that thermal conductivity is related to the strength of the interatomic binding forces of the material in question. High values of the binding forces in metals would result in high values of thermal conductivity, while the relatively low values in organic polymers are considered not only to result in correspondingly low thermal conductivity, but also in asymmetry of crystalline structure. Accordingly, the conductivity along the main valence chain should differ from that between the chains, and a highly oriented polymer, therefore, should be anisotropic in this property.

Directional Effects. Although no quantitative investigation has been made on the anisotropy of conductivity of a crystalline polymer, Wooster(79) proposed that the conductivity should be greater along the chains than across them. Snow(69) made qualitative tests on thin slabs of rolled and rolled-annealed nylon 66 by measuring the two major axes of an elliptical ring formed by applying a point source of heat to a coating of sodium sulfate on the sample. For the rolled sample, he reported the length of the major elliptical axis as 0.69 inches while the minor axis was 0.58 inches long. Rolled-annealed samples had lengths of axes equal to 0.71 and 0.62 inches for the major and minor axes respectively.

Analogy Between Conduction in Liquids and Rubbers. Rehner(56) attempted to draw an analogy between the theory of thermal conductivity in liquids and in rubbers. He suggested that polymers in amorphous form resemble liquids in their molecular arrangement. He tried to apply the Bridgeman equation to rubbers, which relates acoustic velocity and conductivity for liquids. He found that it did not give results agreeing with his measured data. He explained his results by stating that rubbers have a more complex molecular structure as compared to liquids.

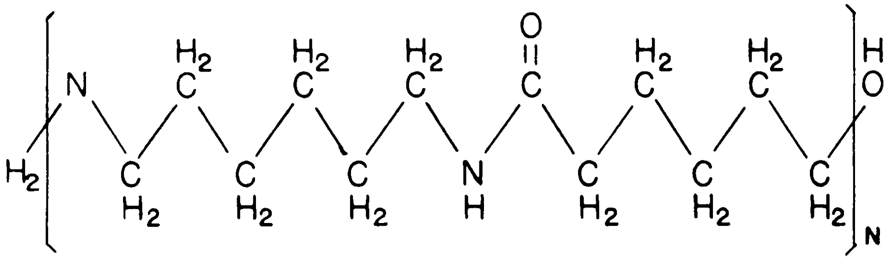
Thermal Conductivity of Nylon 66. The du Pont Company(29) has reported the thermal conductivity of its nylon compression molding compound (nylon FM10001) to be 0.15 Btu per hour - square foot - °F per foot. Modern Plastics Encyclopedia(55) reported the same material to have a value of 0.16 Btu per hour - square foot - °F per foot. These values were obtained using ASTM Method(76) D325-31T, a comparative method for which an accuracy of ten per cent is claimed.

The term nylon 66 refers to polyhexamethylene adipamide. Schmidt and Marlies(60) explained the numerical designation of the various nylons. The first number represents the number of carbon atoms in the diamine, and the second number represents the number of carbon atoms in the dicarboxylic acid that forms the monomer. Figure 3, page 24, shows the structural formulas for nylon 66 and nylon 610.

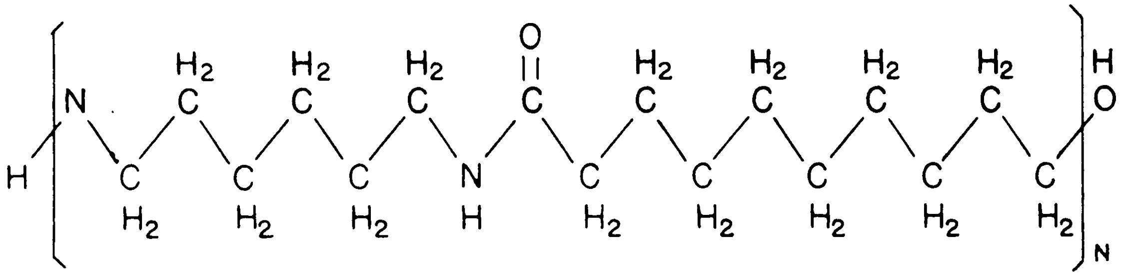
Nylon in the Crystalline State

It has been shown by many investigators(16, 22, 27) that solid nylon containing crystalline regions can be prepared. An understanding of the chemistry of crystalline nylon and the nature of its unit crystal is of importance in studying the nature of thermal conduction in crystalline nylon.

Crystalline Constitution of Nylon. Nylon does not crystallize in large single crystals as is the case of non-polymeric substances.



POLYHEXAMETHYLENE ADIPAMIDE, NYON 66



POLYHEXAMETHYLENE SEBACAMIDE, NYLON 610

FIGURE 3. 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).

According to Freund and Mark(35), 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(35, 36, 61) have estimated the crystalline areas to be 1,000 Angstroms in diameter.

Intermolecular Forces in Nylon. Baker(15) 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 3, page 24). A discussion of hydrogen bonding is given by Glasstone(37) and Conant and Blatt(26).

In their infra-red absorption investigations of nylon, Elliott, Ambrose, and Temple(31) 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(24) as the number of hydrogen bonds per 100 covalent bonds. The index number is 28 for nylon 66.

According to Mark(50), 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.

Schmidt and Marlies(59) have stated the approximate strengths of the bonds found in polymers in terms of the 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 bonds	500 to 5,000 calories

Mechanism of Crystallization in Nylon. Evidence of the crystallization of nylon was reported by Baker and Fuller(16). Time-temperature cooling curves were plotted and a halt in cooling at one point was found. The melt became cloudy as it solidified during the halt in cooling. This point was called the melting point. It was 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 solidification was sudden. Oldham and Ubbelohde(53) compared the solidification to gelation, and called it a "cooperative setting-up." The following mechanism was proposed: 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(16, 25) was the first to induce crystallinity in nylon successfully. He found that this was possible only when the sample possessed a high molecular weight.

Baker(15) stated that the percentage of crystalline material, 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(18) 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 and cause parallel orientation of the molecule axes.

Freund and Mark(35) stated that for fibers the extent of ordered arrangement in which crystalline, amorphous, and meso-morphous 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.

Effect of Degree of Crystallinity on Physical Properties of Nylon. Baker(15) stated that large differences in the physical properties of nylon are due to differences in the amount of crystalline material present. 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.

According to Baker(15), the fact that unoriented molecules are present in samples of nylon fibers which are considered crystalline is shown by the phenomenon of retraction after stretching. Alfrey(1) 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. This fact was verified by Schmidt and Marlies(60). It is this apparent kinking which gives rise to elasticity and resilience. The fact that nylon is elastic indicates that it contains an amorphous phase.

Crystal Chemistry. Snow quoted the statements of Goldschmidt(39), 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. Instead, the external symmetry of the crystal depends on the arrangement of the adjacent 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, and hence limit the coordination of the atoms.

Two other facts were pointed out by Snow in reference to Goldschmidt(39). One was that polar ions, which are nonspherical, may act as units in the crystal lattice in the same manner as atoms do, and in this case the coordination relation is unsymmetrical. This situation may give rise to a layer structure. The other fact was 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 does not allow a prediction of its crystal structure, other means must be resorted to. Further information is provided by x-ray diffraction patterns, which indicate the positions of the atoms in the crystal molecule.

X-ray Fiber Patterns. As defined by Sproull(74), fibering is the preferential orientation of crystals due to plastic deformation of the substance. Bunn(22) 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 (FM10001) is shown in Figure 4, page 30.

According to Bunn(22), each ring in the x-ray pattern of a nonfibered polymer is diffuse and represents a reflection from a particular

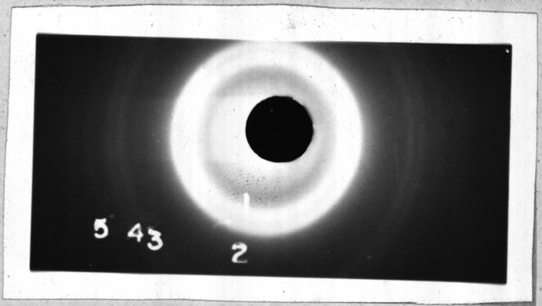


Figure 4. X-ray Diffraction Pattern of Nylon FM10001.

Snow, R. H.: The Influence of Degree of Crystallinity on the Thermal Conductivity of Nylon 66, p. 54. Unpublished M. Sc. Thesis, Library, Va. Poly. Inst., Blacksburg, Va., (1952).

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. Baker(15) defined equatorial reflections as spots or arcs which lie on a horizontal line through the center of the diffraction diagram. 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 were defined by Baker(15) and Baker and Fuller(16) as reflections lying on either side of the vertical axis of the diagram. They represent the fiber identity period, which is the distance between repeating elements in the distance of the reflections from the target at the center of the diagram.

Analysis of Fiber Patterns. Bunn(22) 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 is essentially paraffinic. The equatorial reflections, which represent relations between the chains, are very similar to those of hydrocarbons. Bunn warned however 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 have been fixed. The first steps are accomplished by measuring the positions of the reflections from the crystal planes, and the last step is accomplished by measuring their intensities.

Baker and Fuller(16) stated that the breadth of the reflections shows 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(23) have described in detail the crystal structure of nylon 66 and nylon 610 from their x-ray diffraction pattern investigations. Copper Kα radiation was used on cylindrical films.

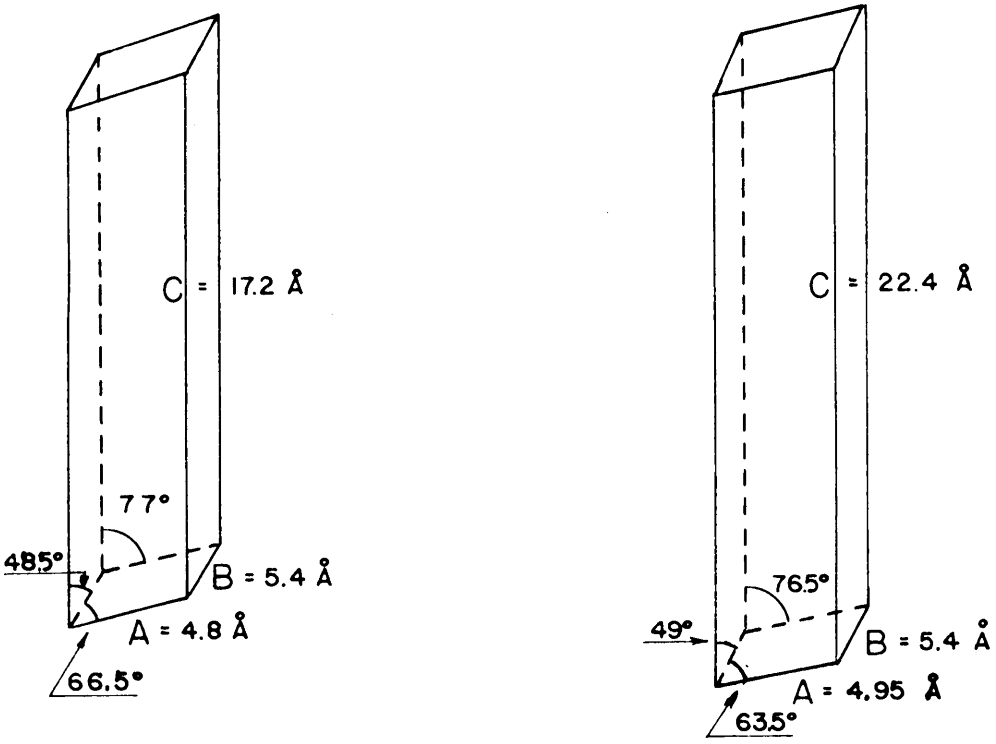
Shape of the Molecule. The fiber period, or length of the recurring crystal unit, was 17.2 Angstroms for nylon 66 and 22.4 Angstroms for nylon 610. This agrees with the calculated length which the monomeric unit should have; hence the chains must be fully extended in planar zig-zag form.

Unit Cell. All spots could be satisfactorily 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 shown in Figure 5, page 34. A representation of the orientation of a nylon 66 chain in its unit cell is shown in Figure 6, page 35. Nylon 610 is similar. The plane of the chain is in or rear 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.

Crystal Orientation. In a stretched fiber, all crystals have their c axes parallel to the fiber axis, according to Bunn and Garner(23). 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 suggest four possible positions for the unit cell in a rolled or pressed sheet.

In support of the results of Bunn and Garner(23), Elliot, Ambrose, and Temple(31) have found striking differences between



NYLON 66

NYLON 610

FIGURE 5. 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., <u>A189</u>, 30- 68 (1949).

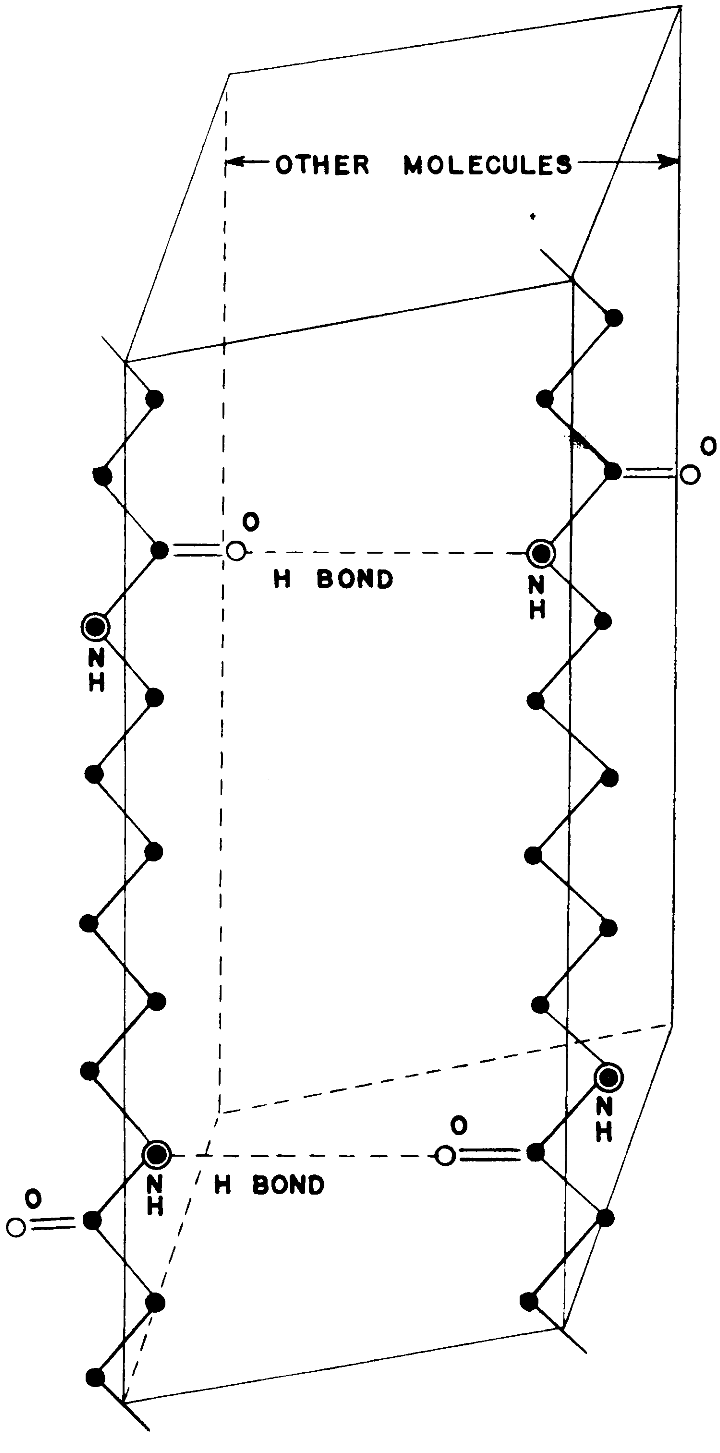


FIGURE 6. THE UNIT CRYSTAL CELL OF NYLON 66 SHOWING POSITIONS OF MOLECULAR CHAINS

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

the infra-red 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 stretch. Dichroism is the quality of showing two colors in the infra-red absorption spectra, as of some crystals when viewed from different angles. 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. Bunn and Garner(23) noted that 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(31) supports this statement. According to Bunn and Garner, other movements are possible: 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 prisms 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(21) 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. He stated that every fusion of interferences signifies an increase in symmetry and found that at this temperature the a and b axes become equal in length. The transition is to a hexagonal crystal system and on cooling, the form changes back at 140 °C.

Glatt(38) performed infra-red studies on nylon 610 and found that some of the hydrogen bonds rupture at 200 °C, which is below the melting point (260 °C). This allows 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(25) studied the physical properties and crystalline nature of massive nylon. They determined that, with few exceptions, the statements made for nylon fibers hold equally well for massive nylon. Their work is discussed below.

Effect of Annealing on Diffraction Rings. Upon annealing there was in general a shifting apart of the two most prominent x-ray diffraction rings and improvement in definition. Snow(71) observed the same effect with annealed nylon 66. 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.

Patterns Taken at Elevated Temperatures. Brill(21), 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(25) 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(25) cold-rolled strips of nylon 0.027 inch thick down to 0.011 inch and then heated them 30 minutes in silicone fluid at 250 °C. The heating produced more diffraction spots, showing that some recrystallisation had taken place. This result agrees with the work of Brill(21) on nylon fibers. Snow(72) reported an increase in degree of crystallinity of nylon slabs from 21.2 to 26.5 per cent by rolling and annealing. His x-ray diffraction patterns showed that the two outer diffraction rings had separated and become two separate arcs and thicker at top and bottom than on the sides. He concluded that the nylon crystallites were oriented by the rolling operation, but annealing of the rolled samples tended to decrease the degree of orientation.

Hardness. Clark, Mueller, and Stott(25) 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 microscope. This was because the polishing wore away the soft material between the grains.

It was concluded that the size of the grain 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(25) are given in Table I, page 41, with densities of drawn and undrawn fibers reported by Black and Dole(19) for comparison. Clark, Mueller, and Stott(25) stated that the differences between the densities of the three slabs was not significant. The most nearly amorphous sample of nylon FM10001 which has been examined at du Pont Company(57) 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. Snow(68) reported a density of 1.1396 for nylon slabs with no treatment and a value of 1.1387 after the sample had been dried over phosphorus pentoxide for two months. A sample which had been annealed for two days at 230 °C had a density of 1.1449, while a rolled sampled annealed for two hours at 240 °C was reported as having a density of 1.1499.

Effect of Degree of Crystallinity on Thermal Conductivity of Nylon 66. Snow(70) studied the thermal conductivity of nylon 66 as a function of internal structure. Measurements of thermal conductivity were made according to the ASTM method C177-45, the Guarded Hot Plate Method. The thermal conductivity of nylon measured in a direction perpendicular to the

TABLE I

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
Slab 1/4 x 4 x 10 inches(2)	1.1420
Slab 1/8 x 4 x 10 inches(2)	1.1400
Slab 1/4 x 2 x 10 inches(2)	1.1720
Highly quenched sample(3)	1.1110
Highly annealed sample(3)	1.1660
X-ray crystal density(4)	1.2400

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

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

(3) Rosenbaum, C. K.: Personal Communication, June 4, 1951. Wilmington, Del. (To R. H. Snow, Va. Poly. Inst., Blacksburg, Va.)

(4) Bunn, C. W. and E. V. Garner: The Crystal Structure of Two Polyamides, Proc. Roy. Soc. Lond., A189 39-68 (1947).

plane of the sheet was decreased by rolling and annealing from 0.172 to 0.130 Btu per hour - square foot - °F per foot. He indicated that this change occurs at mean temperatures of 80 °F and 185 °F. He explained that the thermal conductivity was affected mainly by an orientation of the molecules in the direction of rolling rather than by the change in crystallinity. Because of this apparent orientation, he concluded that the nylon thermal conductivity became anisotropic. This result tends to support Rehner's(56) 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.

Test Methods

Measurement of Thermal Conductivity. The American Society for Testing Materials(75) 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:

$$k = \frac{qL}{A\,(t_1 - t_2)} \qquad (7)$$

where

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

q = rate of heat flow, Btu per hour

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

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(2) 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(75) stated that it is not possible to fix one design for all needs.

According to Austin(2), 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 Encyclopedia(55).

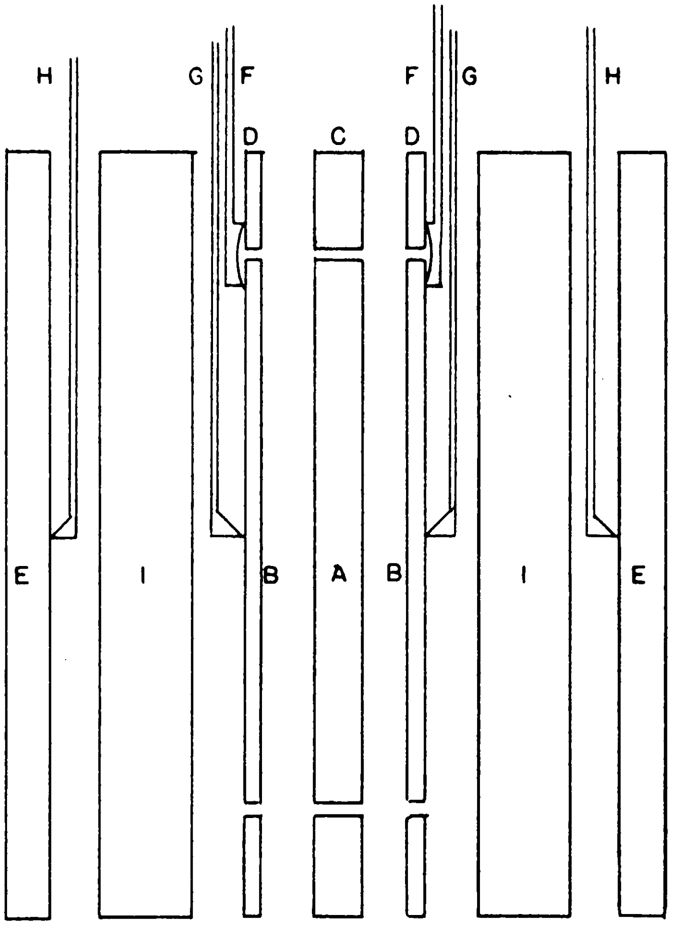
Experimental Errors in Measurement of Conductivity. Vierweg and Gottwald(77) studied the problem of determining thermal conductivity to find the most common experimental errors. They found that preliminary treatment, especially drying, has great influence on conductivity. Also, the greatest liability 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(47) 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 in the heat source.

A method has been described by Weh(78) for measuring thermal conductivity using only one sample. The sample is protected from heat loss from the bottom surface by a guard heater. He has estimated the error in his apparatus to be plus or minus ten per cent.

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(75) 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 7, page 46. 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 and Kaye(40) 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 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.



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 7. 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 effect of contact resistance was also determined by Griffiths and Kaye(40). 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.

Somers and Cyphers(73) stated that thermal conductivity measurements made by the guarded hot plate method are subject to error from heat loss by convection at the exposed edges of the sample. The departure from unidirectional heat flow is caused by the relative amount of heat lost to the guard ring section from the center heater. A mathematical model was developed based on specifications correlating the dimensions of test samples and limiting hot plate dimensions as specified in the ASTM designation C177-45(75). Analytical solutions were obtained to show the maximum errors for square and round samples. For square samples, the following relation was developed. This relation is plotted graphically in Figure 8, page 49:

$$k/k_{exp.} = \varphi (y_1/y_o)\ (z_o/y_o) \qquad (8)$$

where

y_1 = center heater dimension, inches

y_o = center heater dimension plus guard heater dimension, inches

z_o = sample thickness dimension, inches

k = true thermal conductivity, consistent units

k_{exp}. = observed experimentally determined thermal conductivity, consistent units

φ = a function, dimensionless.

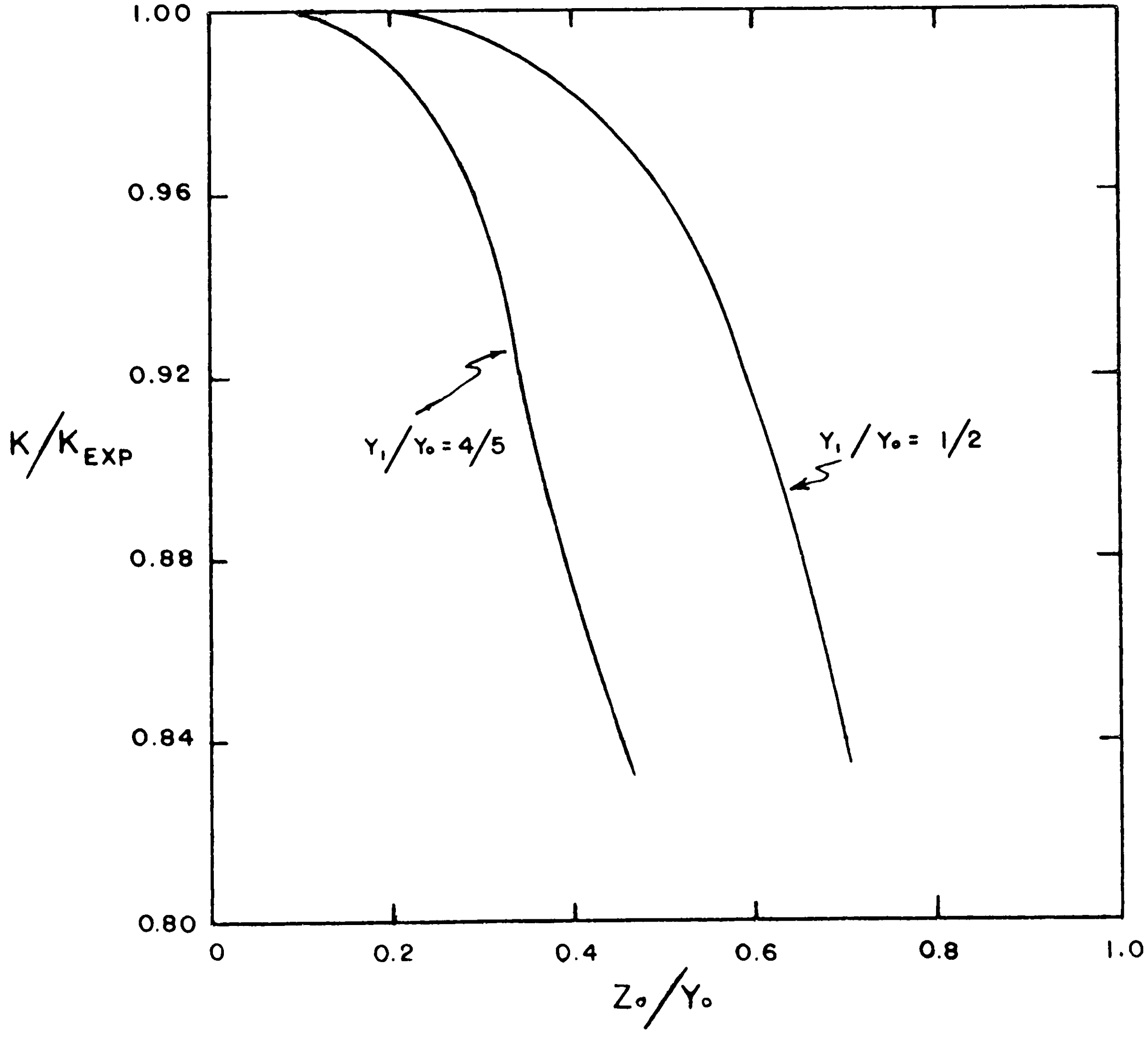


FIGURE 8. RELATION BETWEEN RATIOS OF K/K_{EXP}, Y_1/Y_0, AND Z_0/Y_0

SOMERS, E. V. AND J. A. CYPHERS; ANALYSIS OF ERRORS IN MEASURING THERMAL CONDUCTIVITY OF INSULATING MATERIALS, REV. SCI. INST., 22, 8-583 (1951).

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(41).

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 inch thick and asbestos papers 0.022 inch 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 inch, 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'(44) statement that the density of an organic substance is directly proportional to the percentage of crystalline material present. This method was used by Snow(67) to determine the crystallinity of nylon. Mathematically,

$$\text{degree of crystallinity} = \frac{d - d_a}{d_x - d_a} \times 100 \qquad (9)$$

where

d = density of sample

d_a = density of substance in amorphous form

d_x = density of substance in crystalline form.

Hermans(42) 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(46).

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(42).

$$d_x = \frac{Mn}{VN} \qquad (10)$$

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(17) 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(43) pointed out that the liquid used must be indifferent to the sample, that is it must be unabsorbed by it. Du Pont Company(29) 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(30). Under exposure to air at 50 per cent relative humidity, it will contain as much as 1.5 per cent by weight.

Hermans' Measurement of Cellulose Density. Hermans(45) 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 phosphorus pentachloride in vacuo.

Annealing of Nylon. Snow(66) has discussed a method for annealing relatively small samples of nylon for testing purposes. Samples of nylon were placed in a steel pan with cover and gasket in which the samples could be heated under an atmosphere of nitrogen. A small water-filled manometer was used to measure the nitrogen pressure. A positive pressure of 1/2-inch of water was maintained in the annealing pan during the heating period.

III. EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was to determine the relationships of anisotropy of thermal conductivity, bond strength, degree of crystallinity, molecular orientation, and the changes resulting from rolling-annealing treatment of nylon 66.

Plan of Experimentation

The plan of experimentation consisted of three phases of work. The first phase consisted of modifying and performing maintenance on existing apparatus for measuring the thermal conductivity of nylon. The second phase of work was that of working out methods for determining the thermal conductivity of nylon along three axes. The third phase consisted of making tests on samples of nylon 66 subjected to various physical treatments.

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

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

II. Density measurement of nylon samples. Quadruplicate determinations.

Method: weighing in air and in water

Samples:

A. Cast, as received

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

III. Thermal conductivity at 80 °F. ASTM method C177-45. Quadruplicate determinations.

Samples:

A. Cast nylon, as received
   1. Perpendicular to the plane of the sheet
   2. Perpendicular to the main dimension, but in the plane of the sheet
   3. In the direction of the main axis, but in the plane of the sheet.

B. Rolled to half thickness and annealed two hours at 240 °C.
   1. Perpendicular to the plane of the sheet
   2. Perpendicular to the direction of rolling, but in the plane of the sheet
   3. In the direction of rolling and in the plane of the sheet.

Materials

Formic Acid. Reagent grade, 87-90 per cent, code No 1067. Manufactured by General Chemical Co., New York, N. Y. Used as adhesive agent for cementing nylon strips together in determining thermal conductivity of nylon.

Naphthalene. Flakes. Practical grade. Obtained from Eastman Kodak Co., Rochester, N. Y. Used for calibrating thermocouples at temperature of condensing naphthalene.

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

Nylon Slab. Slab, cast by a special transfer molding process, 1/4 inch by 4-3/16 inches by 36 inches, du Pont formula FM10001 (nylon 66); three required. Obtained from the Polymer Corporation, Reading, Pa. Used as sample for experimental work.

Apparatus

The individual items of apparatus which were procured for this investigation are first listed. Assembled items are then described.

Aluminum Foil. "Reynolds Wrap", general purpose aluminum foil. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used to wrap nylon samples for protection during annealing and to shield thermocouple cable.

Asbestos Paper. Thickness, 0.002 inch, non-wire filled. Manufactured by Johns-Manville Co., Philadelphia, Pa. Used to insulate and protect thermocouples in the guarded hot plate.

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

Calorimetric Thermometer. Mercury, range 66-95 °F, with 0.05 °F graduations, catalogue No L5498. Manufactured by the Parr Instrument Co., Moline, Ill. Used to calibrate thermocouples at room temperature and used with calorimeter.

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

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 steam and naphthalene.

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 distilled water at temperature of 100 °F plus or minus 0.05 °F in calibrating calorimeter.

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 12,000 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.

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, range, 0-30 v, 1-v graduations. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure storage battery emf.

Micrometer. Machinists' micrometer, one-inch opening, 0.001-inch graduations. Manufactured by Central Tool Co., Auburn, Rhode Island. Used to measure thickness of nylon samples.

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.

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, 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.

Rectifier. "Aminco Rectran," copper-oxide rectifier, input 115 v, ac, output 6 v, dc, catalogue No 4-460; one required. Manufactured by the American Instrument Co., Silver Spring, Md. Used as actuating power source for light-beam galvanometer and to "trickle charge" storage battery.

Standard Weston Cell. "Eplab Students' Cell," emf 1.0185 v, serial No 431250. 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. Used to contain guarded hot plate.

Storage Battery. "Gould Televel," lead, three cells, six v. Obtained from Virginia Department of Highways, Richmond, Virginia. Used as source of emf for balancing potentiometer.

Torque Wrench. "Craftsman," 19-inch lever arm, capacity, 150 foot-lbs, serial No RF15. Obtained from Sears, Roebuck Co., Chicago, Ill. Used to tighten bolts on guarded hot plate.

Thermocouple Wire. Copper, 1938 calibration, No 30 B. and S. gage, enamel insulated. 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 junction.

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

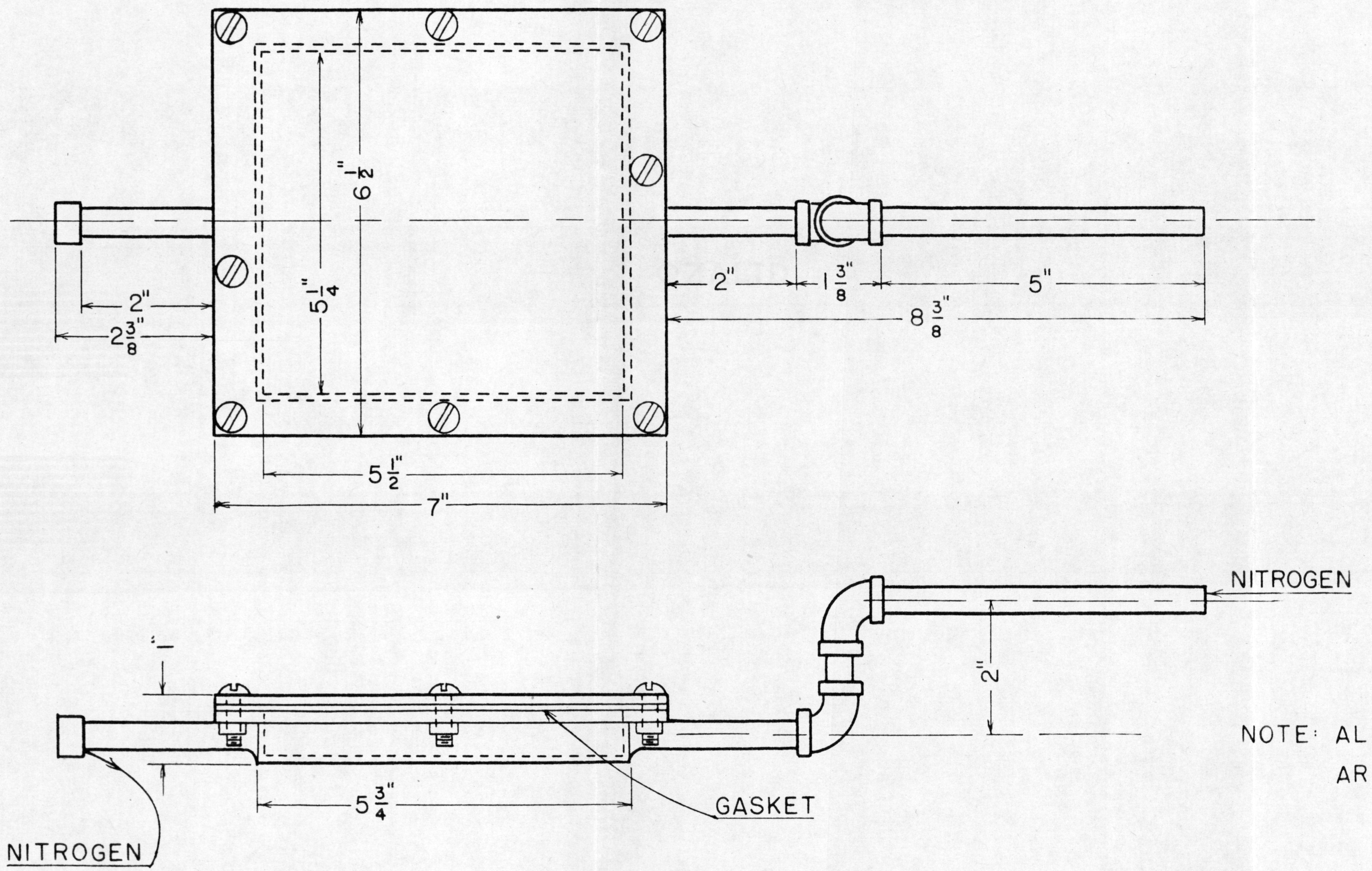
Transformer. "Sola," constant voltage type, input range, 95-125 v, 60 cy, ac, rating, 120 watts, output, 115 v, catalogue No 30806, serial No G2113. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to stabilize voltage for guarded hot plate heater.

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

Nylon Annealing Apparatus. Constructed in the laboratory by R. H. Snow(62). The apparatus consisted of a steel pan with cover and gasket in which the sample of nylon could be heated under an atmosphere of nitrogen. The covered pan is shown in Figure 9, page 62. The pan was heated in an electric muffle furnace supplied with a thermoelectric pyrometer for measuring the temperature and a hand operated rheostat for regulating the temperature. To provide for a flow of nitrogen through the pan, opposite ends of the pan were provided with sections of 1/8-inch pipe to serve as an inlet and outlet. The exit pipe was loosely capped so that a positive pressure of the gas could be maintained in the pan. To measure the pressure, a manometer was constructed. It consisted of a glass bottle containing one inch of water into which a glass tube was dipped. The bottle was connected to the nitrogen line with rubber tubing.

Guarded Hot Plate. Constructed in the laboratory by R. H. Snow(63) to measure the thermal conductivity of nylon. It is shown in Figure 10, page 63. 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.



NOTE: ALL JOINTS
ARC- WELDED

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"

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COVERED ANNEALING PAN

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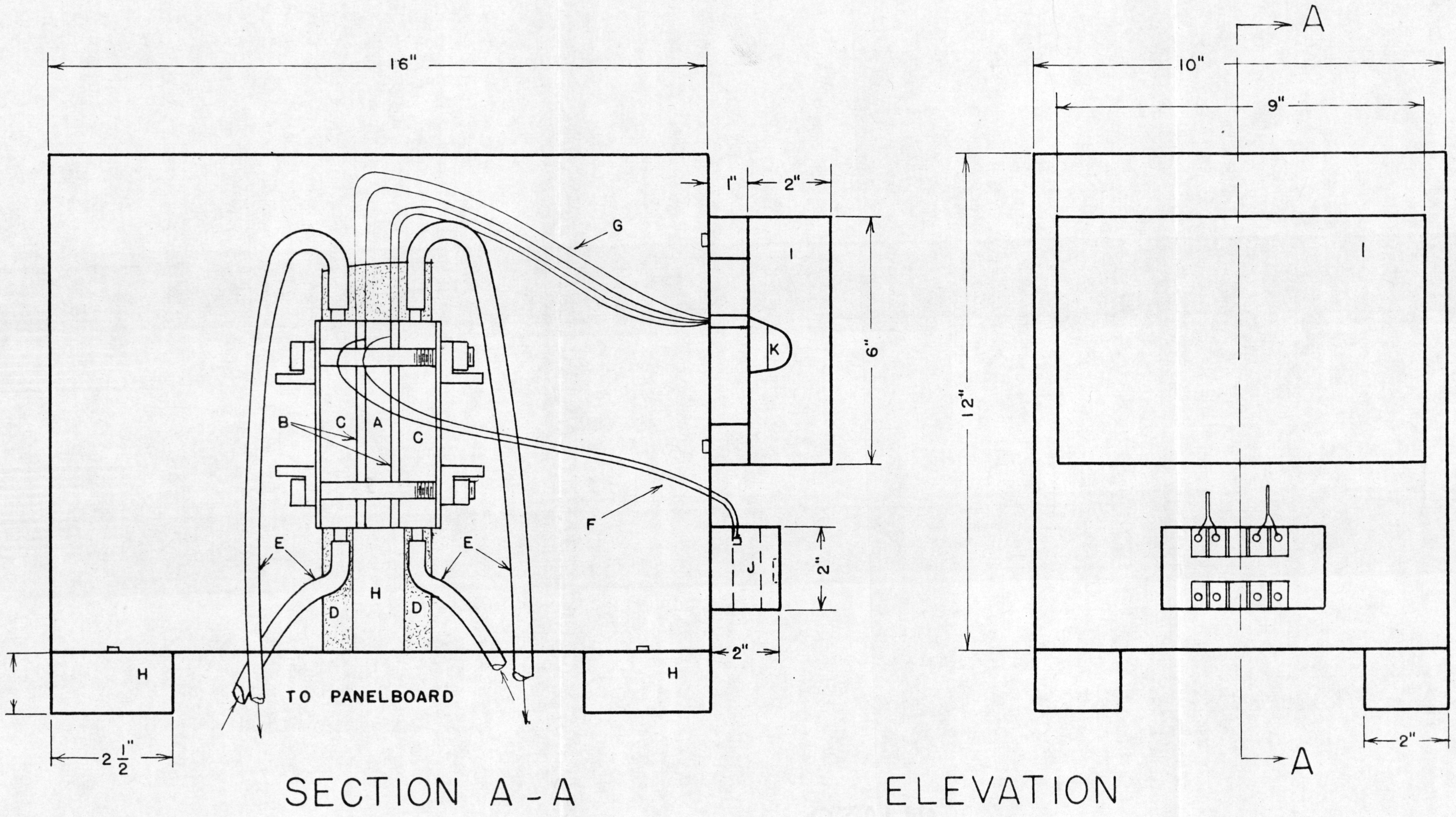
FIGURE 9
FILE NO. 53
CASE NO. 599



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 10
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Electric Heater. The heater was of the design called "Modified National Bureau of Standards Heater" which is described in a pamphlet published by the American Society for Testing Materials. 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 11, page 65.

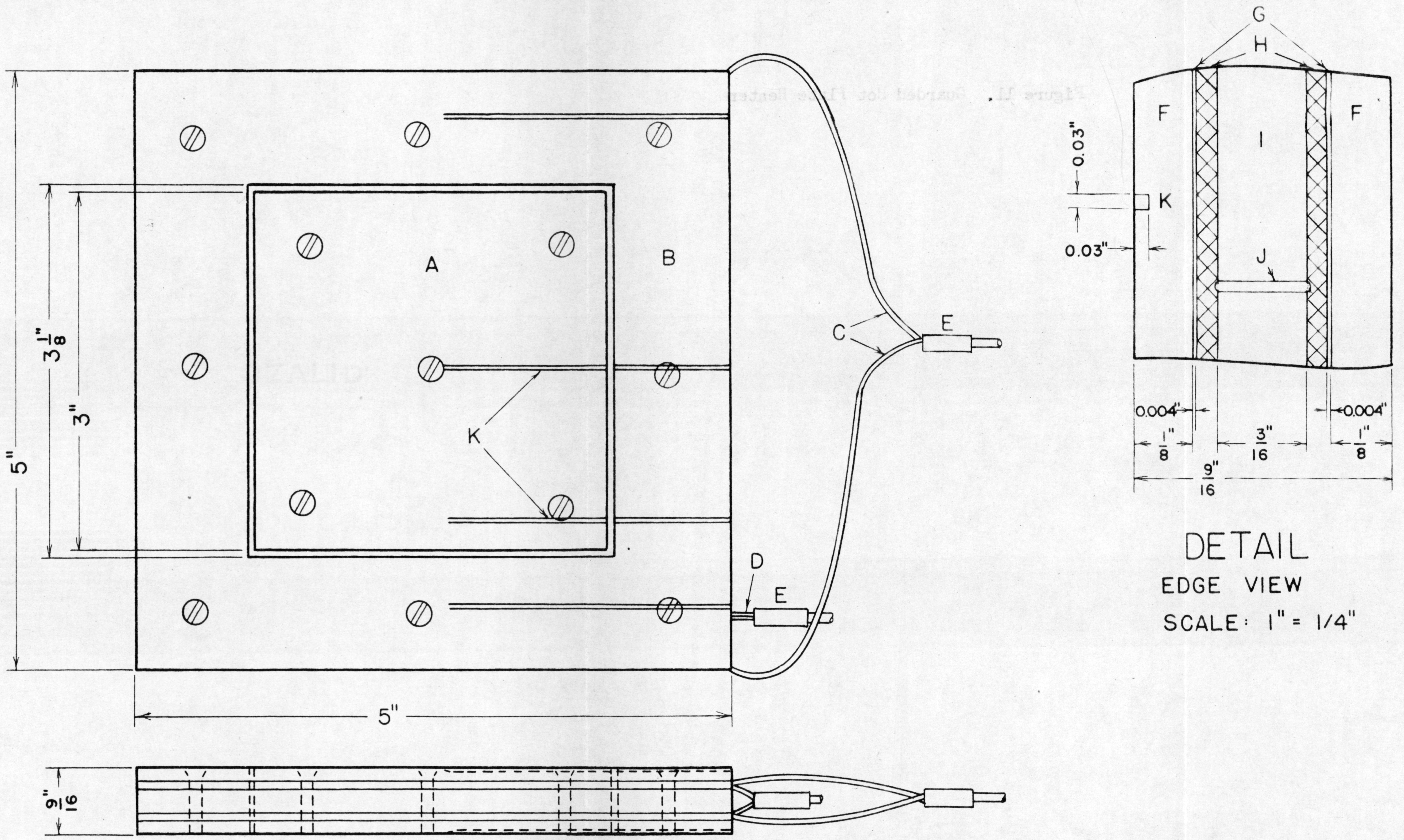
Heating Elements. The heating elements of the heater were formed by winding No 22 nichrome resistance wire on cores of asbestos shingles 1/4-inch thick in the arrangement shown in Figure 12, page 66.

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

Heater Assembly. The assembled heater consisted of two separate heaters in one unit, a center and guard heater, held in place by asbestos cloth and mica sheets.

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

Figure 11. 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 11
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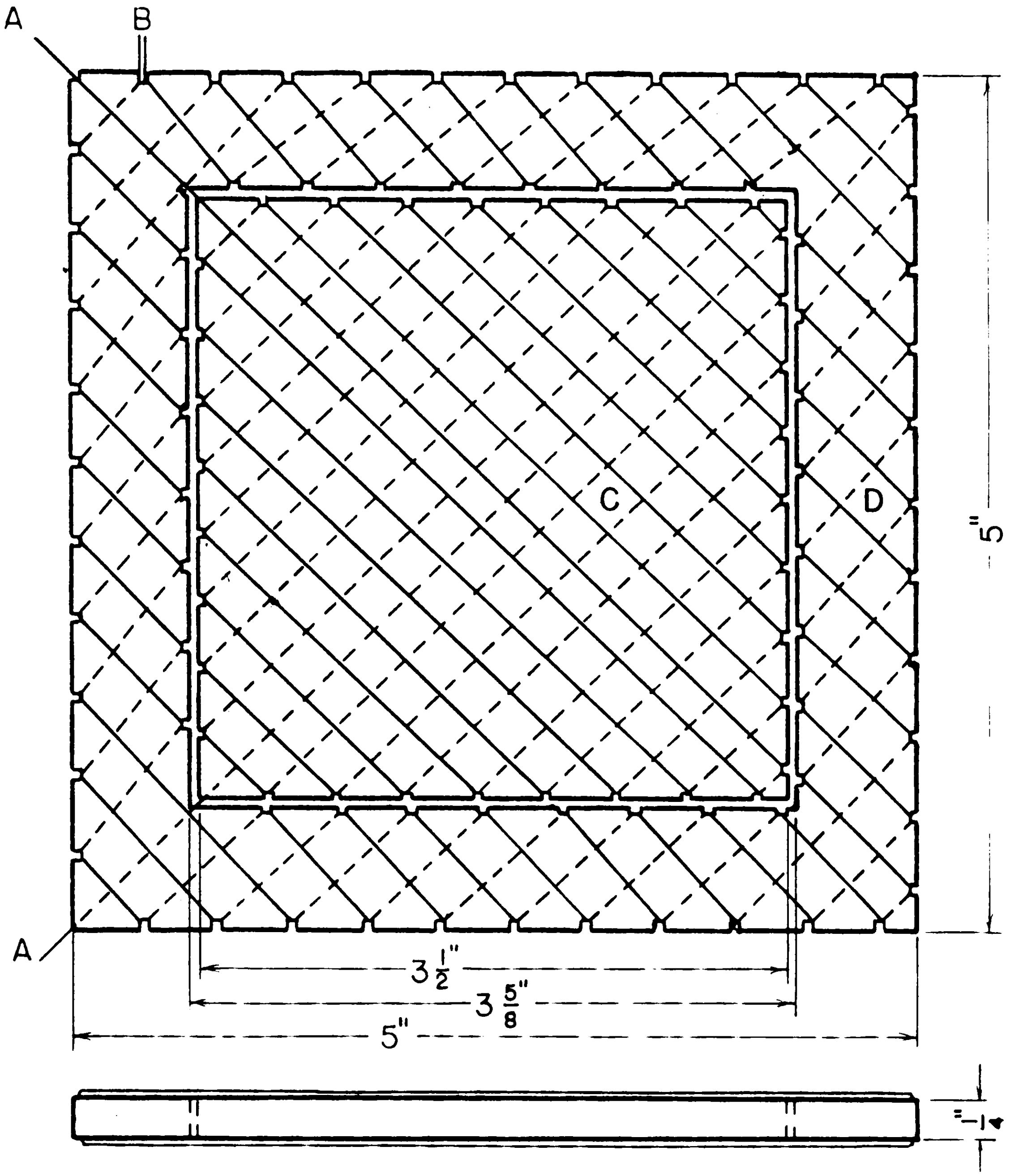

KEY

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 12
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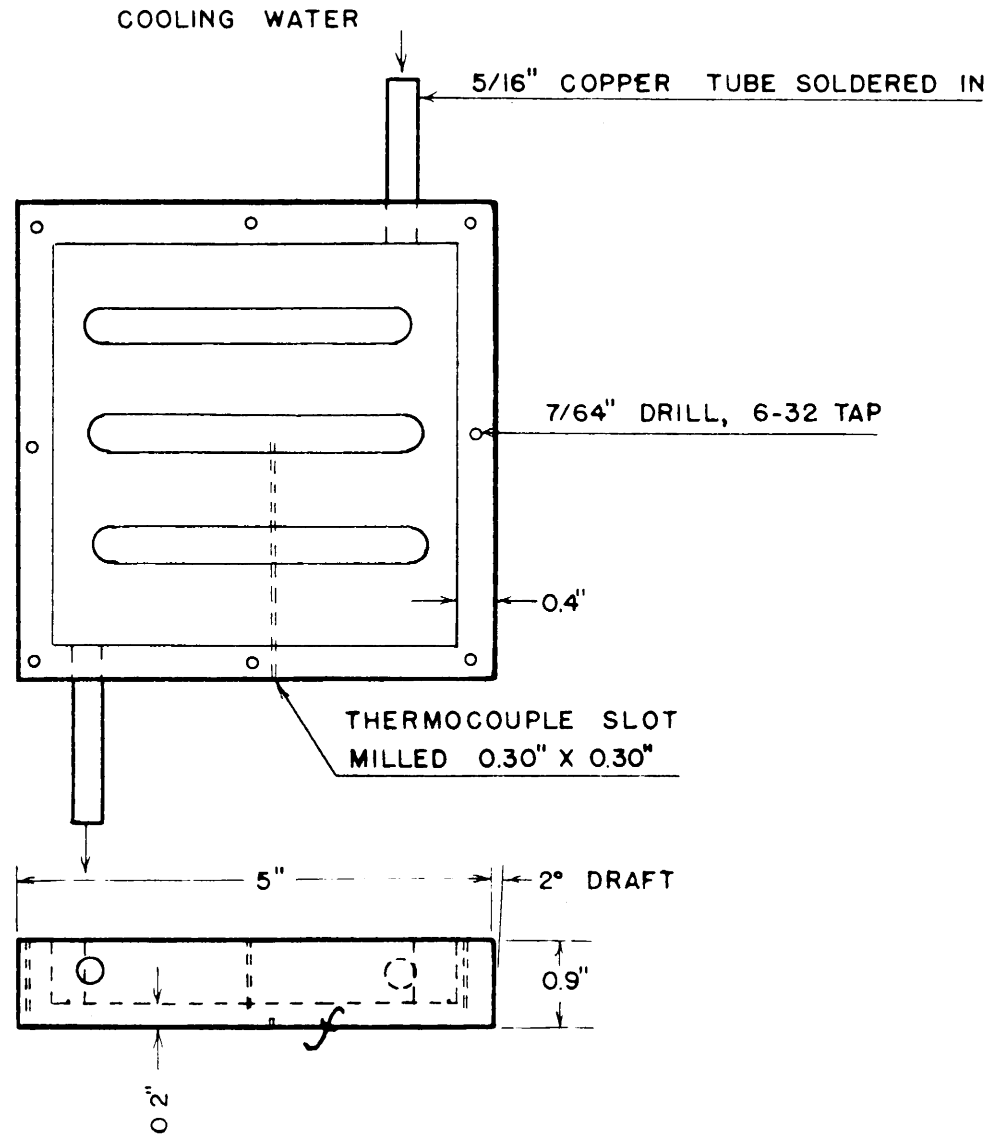
Cooling Blocks. The cooling blocks were cast of bronze by the Salem Foundry from a pattern made by Mr. Hale Sweeney of the Industrial Engineering Department, Virginia Polytechnic Institute. A cooling block is shown in Figure 13, page 68. The baffles in the hollow part of the blocks were provided to distribute the water flow. Nipples cut from 5/16-inch copper tubing were soldered into 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 manner as 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.

Two lengths of angle iron were welded to the cover of each cooling block. Four bolts were inserted through the holes in these to hold together the guarded hot plate with samples. These were the blocks used by Snow(64).

Thermocouples. Ten thermocouples were constructed by soldering together the ends of 18-inch sections of No 30 enamel-insulated constantan wire and No 30 enamel-insulated copper wire. The resulting thermocouples were placed in the slots on the faces of the heater. One thermocouple was also placed against the center of the cold side of each sample and insulated by means of two sheets of asbestos paper



MATERIAL OF
CONSTRUCTION:
CAST BRONZE

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COOLING BLOCK

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FIGURE 13
FILE NO. 53
CASE NO. 599

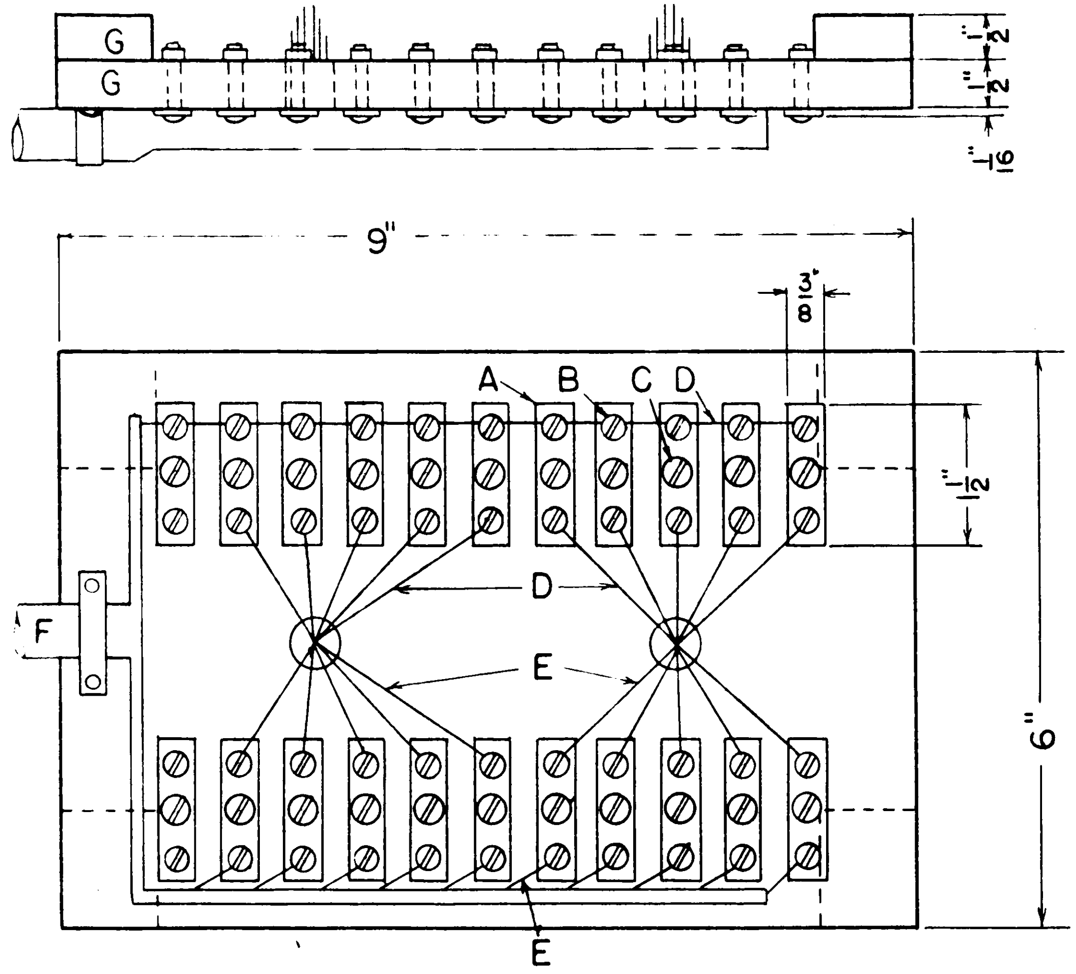
0.015 inches thick. (The ASTM method requires two such thermocouples on each surface, and this is the only deviation from the ASTM requirements in the guarded hot plate construction.)

In order to hold the thermocouples in place while the samples were being inserted into the guarded hot plate, the thermocouples were first wrapped with asbestos paper 0.002 inches thick and then wedged into each milled slot on the heater faces. This wrapping also provided insulation for the thermocouples and prevented short circuits in the lead wires.

Guarded Hot Plate Box. A steel box was obtained from the Chemical Engineering Stockroom to contain the guarded hot plate. It is shown in Figure 10, page 63, with the hot plate in position and with rubber hoses, thermocouples, and heater leads in place.

Zone Box. The zone box shown in Figure 14, page 70, was constructed to facilitate connecting the thermocouple wires to the lead wires, and to protect the connections from temperature differences due to air currents.

Thermocouple Cable. A lead-wire cable was constructed from thermocouple wire. It consisted of a common constantan wire and ten copper wires, connected to the binding posts in the zone box and leading to the thermocouple selector switches. Each wire in the cable was wrapped with aluminum foil after being wrapped with friction tape. This was done to shield the bundle of wires from stray magnetic fields, and the resulting cable was wrapped with friction tape. The aluminum



KEY

A - COPPER CONTACT PLATE
B - BINDING POST
C - MACHINE SCREW
D - CONSTANTAN THERMOCOUPLE WIRE
E - COPPER 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

SCALE: 1" = 2"	FIGURE 14
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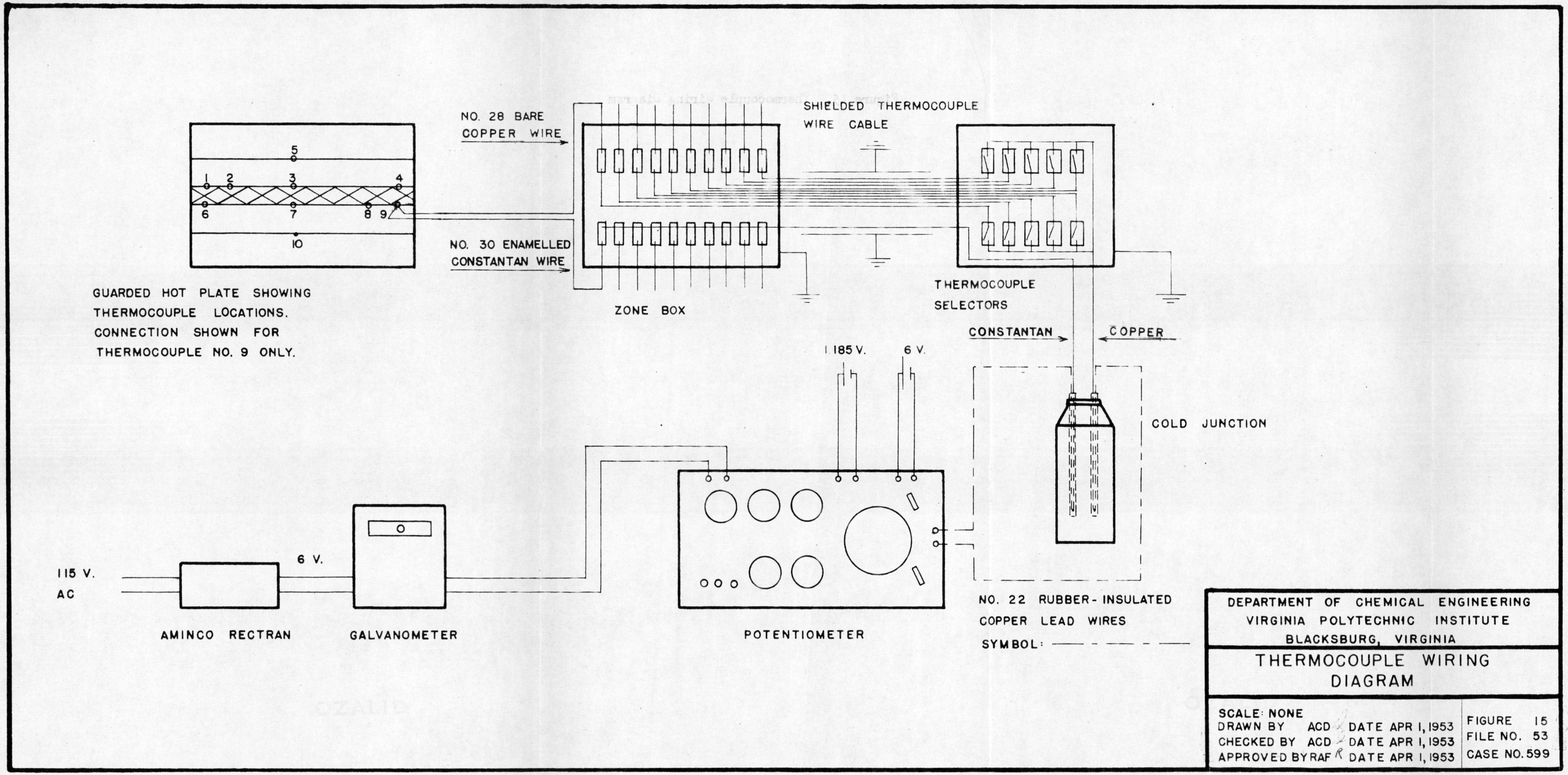
foil was grounded to the water pipe, as was the zone box cover, the guarded hot plate box, and the selector switch box. The cable passed behind the panelboard to the selector switch box.

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 steel cover was screwed to the back of the panelboard to protect the connections from drafts and magnetic fields.

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 15, page 72.

Hot Plate Heater Circuit. The hot plate heater circuit was assembled in the laboratory as shown in Figure 16, page 73. Alternating current at 115 volts from the constant-voltage transformer was supplied to a transformer which reduced the voltage to 38.3 volts. A Variac connected to the secondary of the transformer gave control of the voltage from zero to 38.3 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



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THERMOCOUPLE WIRING DIAGRAM

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FIGURE 15
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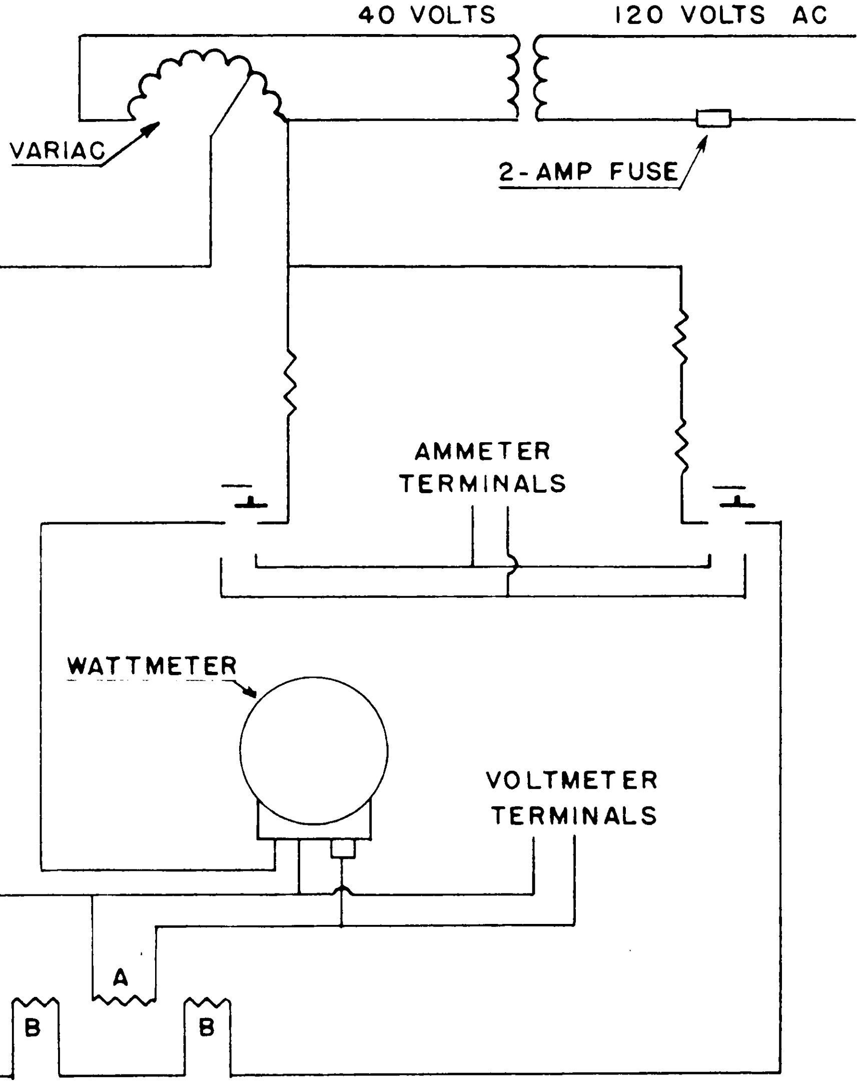
CASE NO. 599



KEY

A - CENTER HEATER

B - GUARD HEATER

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HOT PLATE HEATER CIRCUIT

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FIGURE 16
FILE NO. 53
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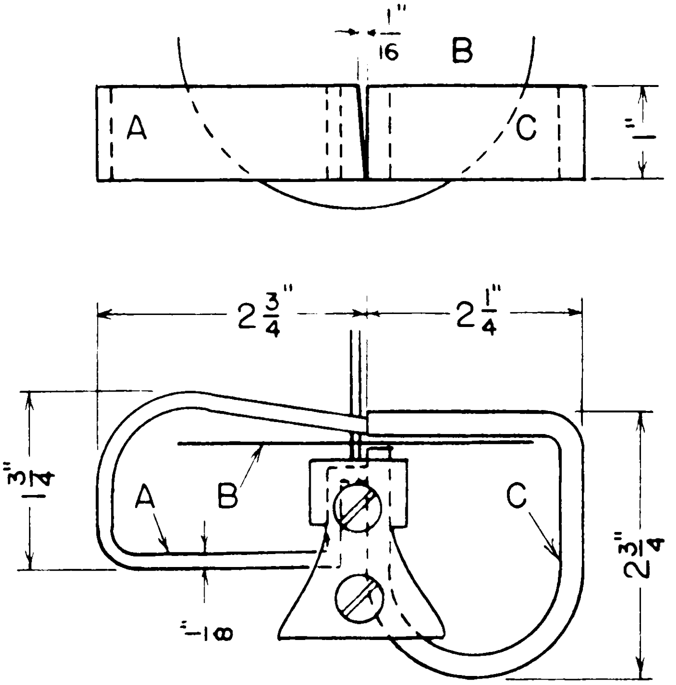
coarse adjustment of the heater temperatures. A voltmeter measured the potential across the center heater at the outlet on the panelboard.

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 17, page 75. The meter disk was marked so that the number of revolutions in a given time could be counted.

Circulating Water System. An arrangement was made to use cooling water direct from the water line. The incoming water was 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 rubber tubes to the sink.

Panelboard. A panelboard was constructed by Snow(65) in the laboratory and mounted on the bench. On it were mounted the control instruments. Figure 18, page 76, is a front elevation of the panelboard.

Thermocouple Calibration Equipment. Standard laboratory equipment was used to calibrate the thermocouples at the ice point, steam point, the temperature of condensing naphthalene vapors, and at the temperature of the room. Crushed ice in a glass beaker was used for the ice point. The thermocouples were held individually in the beaker and the crushed ice was packed around them. Enough distilled water was added to a



KEY

A- SOFT IRON SHUNT

B- WATTMETER DISK

C- PERMANENT MAGNET

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WATTMETER DETAIL
WITH MAGNETIC SHUNT

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FIGURE 17
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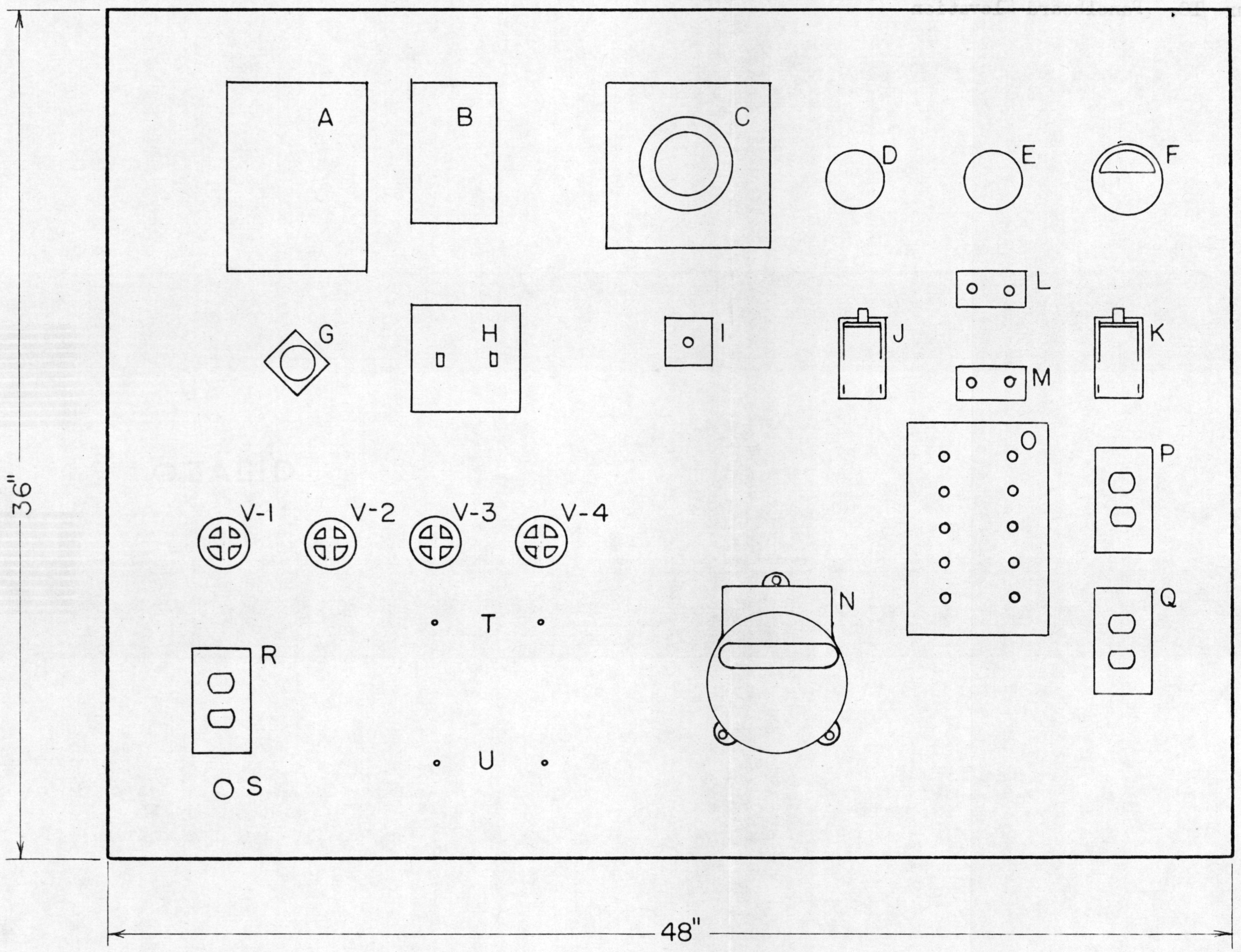
CASE NO. 599



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

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FIGURE 18
FILE NO. 53
CASE NO. 599

level where the ice would not float. A laboratory glass fractionating column and a distilling flask were used for determining the steam point and the naphthalene condensing point determination. The distilling flask and a rubber stopper fitted with a thermometer were used for the calibration at room temperature.

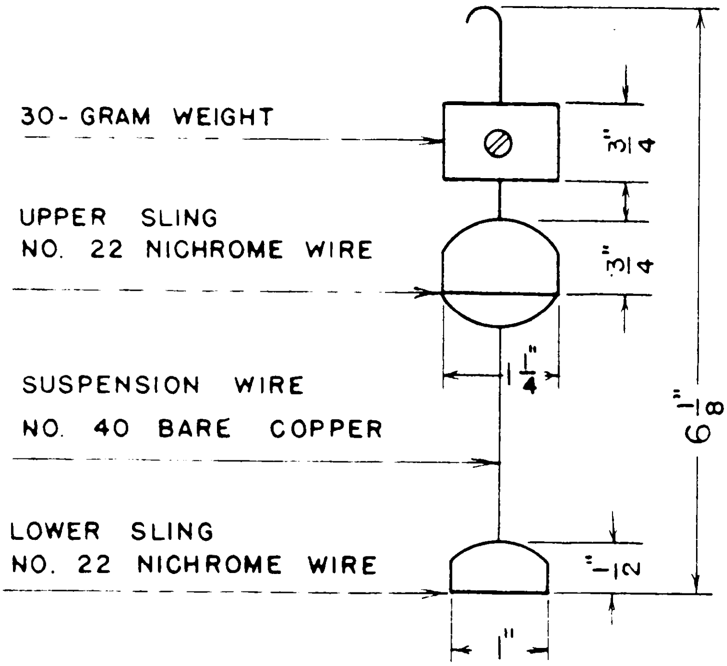
Sling for Density Measurements. To measure the density of samples of nylon, a wire sling, shown in Figure 19, page 78, was attached to the left-hand side of an analytical balance. The sling was constructed of No 22 nichrome wire, with copper weights attached to it. The lower sling, which dipped into a beaker filled with distilled 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. The nylon FM10001 rolled to one-half thickness was annealed in order to relieve internal stresses and strains and flatten the individual samples. The original samples were cast by the Polymer Corporation, Reading, Pa., using a special transfer molding process which was intended to produce a finished slab free from internal stresses and strains.

Samples tested were placed in the pan of the annealing apparatus and the cover screwed down. The pan was placed in the muffle furnace,



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BALANCE SLING

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FIGURE 19
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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 rheostat adjusted until the temperature reached 240 plus or minus ten °C. The furnace was maintained at that temperature for a period of two hours. The electric current was then shut off and the furnace allowed to cool. Then the gas stream was turned off.

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(43). This method assumes a linear relationship between degree of crystallization and density. The standard laboratory buoyancy procedure for density described by Bauer(17) 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 analytical balance and the sling shown in Figure 24. The tare weight was first determined. The weight of a sample weighing from one to five 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. The immersed sample was inspected for adhering air bubbles. Four samples were tested for each determination. The true densities of nylon unrolled and unannealed, annealed, and rolled and annealed were taken.

Rolling Nylon. The rolling of the nylon samples used in density determinations and in thermal conductivity determinations was done at Radford Arsenal, Radford, Va., under the supervision of Mr. R. C. Rhodes, using 16-inch diameter even-speed calendars heated with water at 170 °F. Twenty passes through the calendars were required to reduce the thickness from 0.260 to 0.121 inch.

Checking Degree of Crystallinity. X-ray diffraction patterns were made of two samples to check the results of the density determinations and degree of crystallinity. The work was carried out by Professor W. Richardson of the Physics Department. A sample of the original cast nylon and a sample both rolled and annealed at 240 °C was tested this way (see Figure 20, page 106). Copper Kα radiation was used from an x-ray tube using 35 kilovolts plate potential and 15 milliamperes plate current. 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. 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, with the plane of the sample sheet perpendicular to the x-ray beam. The exposure time was one-half hour. Contact prints were made from the resulting films on number five contrast paper. Qualitative deductions were made from the patterns concerning the effects of rolling and annealing on the degree of crystallinity and orientation of the molecules in the nylon.

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

For the calibration at the ice point, the thermocouples were held individually in a beaker and crushed ice was packed around them. Enough distilled water was added to a level where the ice would not float. After a period of five minutes had elapsed, 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 four microvolts.

For the calibrations at the steam point and at the naphthalene condensing point, the thermocouples were inserted into the side arm of the fractionating column through which the condensing vapors were passing. The side arm was covered with insulation to prevent errors due to radiation of heat.

For the calibrations at room temperature, each thermocouple was inserted individually into the distilling flask and a rubber stopper, fitted with the calorimetric thermometer, was used to seal the mouth. The flask was covered with insulation to prevent radiation errors and was allowed to stand for two hours before a measurement was made.

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. Seven determinations were made with a voltage applied to the load of 12 volts.

A piece of 0.0063-inch nichrome resistance wire three inches long was used as a heat generating resistance. The wire was soldered to the leads connecting the center heater outlet 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, page 76.

A plot was made of the temperature of the water in the calorimeter by reading the calorimetric thermometer at frequent intervals from five minutes before to five 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. Distilled water was used in the calorimeter, and the weight of water used was measured on a balance of 4.5 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 and one-half liters of distilled water the temperature of which was approximately that of the laboratory. The weight of the can and water was then taken. A constant-temperature bath fitted with a syphon and filled with distilled water adjusted to a temperature of 100 °F was placed on the bench so that it was at a higher level than the calorimeter. The calorimeter cover was put in place and the stirrer was started. For five minutes the temperature in the calorimeter was taken every 15 seconds and adjustments in the water bath were made to insure constancy of bath temperature. Then about a half-liter of water was run out of the constant temperature bath syphon to equalize the temperature of the syphon and the water, and one liter of the water from the bath was run into the calorimeter through a hole in the calorimeter cover. The temperature of the water in the calorimeter was then taken every 15 seconds for five minutes, and finally the filled calorimeter can was again weighed. This test was repeated seven times.

Preparation of Samples for Thermal Conductivity Measurement. The following procedure was used in preparing the various nylon 66 samples for thermal conductivity tests.

Unrolled Samples. The unrolled samples for use in conductivity measurement in a direction perpendicular to the plane and to the greatest length of the slab were cut from a cast slab of nylon 1/4 inch by 4-3/16 inches by 36 inches. Since the original slab used for this investigation was only 4-3/16 inches wide, and the guarded hot plate required the test samples to be five inches square, it was necessary to add on a smaller section of nylon 13/16 inch wide. The added piece was planed flat with a jack plane so that it fitted snugly against the main piece. The two pieces were then cemented together using approximately three cubic centimeters of 90 per cent formic acid.

In preparing unrolled samples for thermal conductivity measurement in directions other than perpendicular to the plane of the sheet, the slab was cut into strips approximately the same width as the thickness of the slab. The surface of the slab was marked beforehand with a scratch awl to identify the cut edges and then cut with a band saw. Cooling water flowed over the nylon while the cutting operation was performed. This work was done under the supervision of Mr. M. B. Smith of the Industrial Engineering Machine Shop Laboratory. The cut strips were then each rotated 90 degrees, fitted together again, and finally cemented together with 90 per cent formic acid to form a sample five inches by five inches. Approximately three cubic centimeters of the acid were used per strip. The surfaces of the resulting samples were then smoothed flat by mounting each piece in a jig and machining with a rotating cutting tool. Cooling water flowed over the sample during the operation to prevent overheating and possible warping. The individual samples for each thermal conductivity test were machined to the same thickness, with a tolerance of 0.004 inch.

<u>Rolled Samples</u>. The nylon samples which were rolled to one-half their original thickness and annealed two hours at 240 °C

were prepared for thermal conductivity tests by using the same method of procedure as previously described for preparing the unrolled nylon samples.

Determination of the Thermal Conductivity of Nylon. The thermal conductivity of nylon samples was determined using the guarded hot plate. Quadruplicate determinations of the conductivity of unrolled nylon samples and duplicate determinations of the rolled and annealed samples were made at a mean temperature of 80 °F.

To prepare for a conductivity test, 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 with a torque wrench. A torque of 20 foot-pounds was applied to each bolt.

The assembled guarded hot plate was next placed on blocks of wood in the steel box with the thermocouple and heater wires at the top (see Figure 10), 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 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.

The water inlet tubes were connected to the valve on the water main, and the outlet tubes were led to the sink. The water flow rate was roughly equalized in each cooling block.

The constant-voltage transformer was turned on, and the voltage across the center heater adjusted to 12 volts. 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 three hours.

Two beakers were filled with crushed ice and the two copper-constantan junctions were inserted into the ice for a depth of three inches. Water was poured into each beaker 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 °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 12 volts each time the resistors were adjusted. 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 0.005 millivolt, 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 the thermocouples on the two sides of the heaters were adjusted to within 0.01 millivolt. The system was considered to be in steady state when the heater thermocouple emf values agreed to within 0.005 millivolt and remained constant within 0.005 millivolt over a period of one hour. During this steady-state period the wattmeter was read ten times by observing the period of time required for the wattmeter disk to complete ten revolutions.

The thickness of the sample was measured before and after each test by applying a micrometer in twenty 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.

Data and Results

The following paragraphs describe the data and results obtained from the thermal conductivity studies of nylon 66.

Thermocouple System Calibration. The thermocouple system calibrations at fixed points are summarized in Table II. The average calibrations are included for use in computations, and the individual values to indicate precision of measurement.

Wattmeter Calibration. Table III is a summary of the intermediate quantities used to calculate the individual wattmeter calibration factors at a voltage of 12 volts. The average calibration is included for use in computations, while the individual values serve to indicate precision of measurement.

Nylon Density. Table IV shows the densities of nylon samples determined by the method of buoyancy in water, together with the weighings made to determine the densities.

The effect of physical treatment on the density and degree of crystallinity of nylon 66 is summarized in Table V. Quadruplicate determinations were made on samples of the original unrolled cast slab of nylon, unrolled samples which had been dried for one hour at 180 °C and ten hours at 130 °C, and samples which had been annealed two hours at 240 °C. Duplicate determinations were made on nylon samples which had been rolled from 0.260 inch to 0.121 inch and annealed two hours at 240 °C. Only the original cast nylon samples and the rolled-annealed

TABLE II

Thermocouple System Calibration at Fixed Points

Couple No	Emf in ice-water mixture, 32.0 °F	Emf against thermometer at 80.00 °F	Emf in condensing steam,[a] 209.16 °F	Emf in condensing naphthalene,[a] 419.54 °F
	millivolts	millivolts	millivolts	millivolts
1	-0.001	1.060	4.195	10.097
2	-0.001	1.060	4.198	10.097
3	-0.001	1.060	4.190	10.098
4	-0.001	1.060	4.190	10.096
5	-0.001	1.059	4.198	10.098
6	-0.001	1.060	4.195	10.097
7	-0.001	1.060	4.197	10.098
8	-0.001	1.061	4.199	10.098
9	-0.001	1.060	4.194	10.097
10	-0.001	1.060	4.195	10.097
Average	-0.001	1.060	4.195	10.097

[a] Fixed point temperatures calculated from equation in "Handbook of Physics and Chemistry," p. 1924. Chemical Rubber Publishing Co., N. Y., N. Y., 1950-51. 32 ed.

TABLE III

Wattmeter Calibrations

Applied Emf, volts	Weight of Water, lb	Wattmeter Disc Revolutions, No	Net Temperature Rise, °F	Heat Power, Btu/rev
12.0	5.602	50	2.06	0.2391
12.0	6.085	50	1.92	0.2407
12.0	5.941	50	1.95	0.2396
12.0	5.941	50	1.94	0.2395
12.0	6.121	50	1.89	0.2390
12.0	6.542	50	1.77	0.2389
12.0	6.474	50	1.79	0.2394
Average	-----	--	----	0.2395

TABLE IV

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

Sample No	Treatment	Wt in air, gm	Wt in water, gm	Temp, °C	Water density[a], referred to 4 °C	Density[b] of Sample at 25 °/4 °C
1	Untreated	5.0584	0.6571	27.8	0.99629	1.1450
2	Untreated	3.8561	0.4999	28.0	0.99623	1.1446
3	Untreated	3.2220	0.4173	26.5	0.99665	1.1449
4	Untreated	3.1871	0.4104	25.0	0.99704	1.1444
Average		------	------	----	-------	1.1447
5	Annealed 2 hours at 240 °C	5.0537	0.6669	25.0	0.99704	1.1486
6	Annealed 2 hours at 240 °C	3.8600	0.5056	25.0	0.99704	1.1473
7	Annealed 2 hours at 240 °C	3.1852	0.4183	25.0	0.99704	1.1478
8	Annealed 2 hours at 240 °C	3.2145	0.4256	25.0	0.99704	1.1492
Average		------	------	----	-------	1.1482
9	Heated 1 hour at 180 °C, 10 hours at 130 °C	4.4134	0.5361	25.0	0.99704	1.1349
10	Heated 1 hour at 180 °C, 10 hours at 130 °C	4.2755	0.5204	25.0	0.99704	1.1352
11	Heated 1 hour at 180 °C, 10 hours at 130 °C	3.2660	0.3971	25.8	0.99684	1.1348
12	Heated 1 hour at 180 °C, 10 hours at 130 °C	3.8002	0.4619	26.0	0.99678	1.1347
Average		------	------	----	-------	1.1349
13	Rolled to half thickness, annealed 2 hours at 240 °C	1.7869	0.2389	26.0	0.99678	1.1506
14	Rolled to half thickness, annealed 2 hours at 240 °C	1.5859	0.2122	25.7	0.99686	1.1509
Average		------	------	----	-------	1.1508

[a] Densities of water from "Handbook of Chemistry and Physics" (C. D. Hodgman, Editor), p.1788. Chemical Rubber Publishing Co., Cleveland, Ohio., 1950-1. 32 ed.

[b] Determined by the buoyancy method using water.

TABLE V

Effect of Physical Treatment on the Density and Degree of Crystallinity of Nylon 66

Treatment	Density at 25 °/4 °C	Degree of Crystallinity, %
None, original cast slab 0.260 inches thick	1.1454	---[a]
None, original cast slab 0.260 inches thick	1.1446	---[a]
None, original cast slab 0.260 inches thick	1.1449	---[a]
None, original cast slab 0.260 inches thick	1.1444	---[a]
Average	1.1447	---[a]
Heated 1 hour at 180 °C, 10 hours at 130 °C	1.1349	18.5
Heated 1 hour at 180 °C, 10 hours at 130 °C	1.1352	18.8
Heated 1 hour at 180 °C, 10 hours at 130 °C	1.1348	18.5
Heated 1 hour at 180 °C, 10 hours at 130 °C	1.1347	18.4
Average	1.1349	18.6
Annealed 2 hours at 240 °C	1.1486	29.2
Annealed 2 hours at 240 °C	1.1473	28.2
Annealed 2 hours at 240 °C	1.1478	28.5
Annealed 2 hours at 240 °C	1.1492	29.5
Average	1.1482	28.8
Rolled to 0.121 inches thick. annealed 2 hours at 240 °C	1.1506	30.7
Rolled to 0.121 inches thick, annealed 2 hours at 240 °C	1.1509	30.9
Average	1.1508	30.8

[a] Degree of crystallinity was indeterminate since the sample contained moisture.

samples were used for thermal conductivity tests. By drying, the density of nylon as received was reduced from 1.1447 to 1.1349 at 25 °/4 °C. This table also shows that annealing unrolled samples two hours at 240 °C increased the density and degree of crystallinity to 1.1482 at 25 °/4 °C and 28.8 per cent, and that annealing rolled samples increased the density and degree of crystallinity to 1.1508 at 25 °/4 °C and 30.8 per cent.

Nylon Thermal Conductivity Steady State Conditions. Tables VI to XI contain the nylon thermal conductivity test conditions of the guarded hot plate at steady state. These tables are 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 one 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 15. The average reciprocal wattmeter disk speed is included for each test.

Table VI contains data for the tests on unrolled nylon 66 samples with the heat flux in a direction perpendicular to the plane and to the greatest length of the slab. Thermal conductivity test data for unrolled nylon samples with heat flux in a direction perpendicular to the greatest length, but in the plane of the sheet are presented in Table VII, while test data for unrolled nylon with heat flux in the plane and

TABLE VI

Steady State Test Conditions for Thermal Conductivity of Unrolled Nylon with Heat Flow Perpendicular to the Plane and to the Greatest Length of the Sample

Test No	Elapsed Time, hr	Emf of Couple 1, v x 10^3	Emf of Couple 2, v x 10^3	Emf of Couple 3, v x 10^3	Emf of Couple 4, v x 10^3	Emf of Couple 5, v x 10^3	Emf of Couple 6, v x 10^3	Emf of Couple 7, v x 10^3	Emf of Couple 8, v x 10^3	Emf of Couple 9, v x 10^3	Emf of Couple 10, v x 10^3	Average Wattmeter Disk Speed^{-1}, sec/rev
1	0.0	1.541	1.550	1.550	1.541	0.672	1.541	1.550	1.550	1.541	0.673	-----
	0.5	1.549	1.560	1.560	1.549	0.672	1.549	1.560	1.561	1.549	0.673	-----
	1.0	1.563	1.563	1.563	1.563	0.670	1.563	1.561	1.563	1.563	0.673	-----
	1.5	1.557	1.557	1.557	1.557	0.673	1.557	1.557	1.558	1.557	0.677	-----
	2.0	1.557	1.557	1.557	1.557	0.673	1.557	1.557	1.558	1.557	0.677	-----
	2.5	1.557	1.557	1.557	1.557	0.673	1.557	1.557	1.558	1.557	0.677	15.69
2	0.0	1.515	1.533	1.533	1.515	0.671	1.515	1.533	1.534	1.515	0.671	-----
	0.5	1.541	1.551	1.551	1.541	0.680	1.541	1.551	1.553	1.541	0.680	-----
	1.0	1.566	1.566	1.566	1.566	0.683	1.566	1.566	1.566	1.566	0.674	-----
	1.5	1.566	1.566	1.566	1.566	0.676	1.566	1.566	1.566	1.566	0.680	-----
	2.0	1.566	1.566	1.566	1.566	0.675	1.566	1.566	1.566	1.566	0.680	15.75
3	0.0	1.546	1.553	1.553	1.546	0.656	1.546	1.553	1.554	1.547	0.686	-----
	0.5	1.593	1.581	1.581	1.593	0.653	1.593	1.581	1.583	1.591	0.693	-----
	1.0	1.569	1.568	1.568	1.569	0.663	1.569	1.569	1.571	1.568	0.684	-----
	1.5	1.568	1.568	1.568	1.568	0.678	1.568	1.568	1.571	1.568	0.680	-----
	2.0	1.562	1.563	1.563	1.562	0.675	1.562	1.564	1.570	1.567	0.680	-----
	2.5	1.562	1.563	1.563	1.562	0.670	1.562	1.564	1.570	1.568	0.680	15.72
4	0.0	1.560	1.569	1.570	1.560	0.689	1.560	1.569	1.571	1.560	0.673	-----
	0.5	1.592	1.581	1.580	1.593	0.644	1.592	1.581	1.576	1.572	0.675	-----
	1.0	1.557	1.562	1.562	1.555	0.673	1.557	1.562	1.559	1.559	0.676	-----
	1.5	1.566	1.562	1.566	1.566	0.676	1.566	1.566	1.567	1.566	0.673	-----
	2.0	1.559	1.562	1.559	1.559	0.676	1.559	1.559	1.558	1.559	0.673	-----
	2.5	1.555	1.559	1.555	1.555	0.676	1.555	1.555	1.561	1.555	0.670	15.73

TABLE VII

Steady State Test Conditions for Thermal Conductivity of Unrolled Nylon with Heat Flow in the Plane and Perpendicular to the Greatest Length of the Sample

Test No	Elapsed Time, hr	Emf of Couple 1, v x 10^3	Emf of Couple 2, v x 10^3	Emf of Couple 3, v x 10^3	Emf of Couple 4, v x 10^3	Emf of Couple 5, v x 10^3	Emf of Couple 6, v x 10^3	Emf of Couple 7, v x 10^3	Emf of Couple 8, v x 10^3	Emf of Couple 9, v x 10^3	Emf of Couple 10, v x 10^3	Average Wattmeter Disk Speed^{-1}, sec/rev
1	0.0	1.391	1.390	1.389	1.391	0.726	1.390	1.390	1.390	1.390	0.726	————
	0.5	1.405	1.402	1.403	1.405	0.724	1.405	1.402	1.402	1.405	0.724	————
	1.0	1.405	1.405	1.406	1.405	0.727	1.405	1.405	1.405	1.405	0.724	————
	1.5	1.406	1.406	1.406	1.406	0.727	1.404	1.406	1.406	1.404	0.724	————
	2.0	1.404	1.406	1.404	1.404	0.723	1.406	1.404	1.404	1.406	0.716	15.58
2	0.0	1.774	1.768	1.768	1.774	0.823	1.774	1.768	1.774	1.768	1.470	————
	0.5	1.420	1.417	1.417	1.434	0.774	1.434	1.417	1.420	1.417	0.755	————
	1.0	1.417	1.417	1.420	1.420	0.759	1.417	1.420	1.417	1.420	0.756	————
	1.5	1.411	1.411	1.420	1.417	0.759	1.420	1.420	1.411	1.417	0.754	————
	2.0	1.411	1.411	1.417	1.411	0.752	1.420	1.417	1.411	1.411	0.754	————
	2.5	1.411	1.411	1.417	1.411	0.752	1.420	1.411	1.411	1.411	0.750	15.82
3	0.0	1.392	1.392	1.392	1.392	0.739	1.392	1.392	1.392	1.392	0.751	————
	0.5	1.397	1.397	1.397	1.397	0.751	1.397	1.397	1.397	1.397	0.740	————
	1.0	1.396	1.396	1.396	1.396	0.737	1.396	1.396	1.396	1.396	0.741	————
	1.5	1.388	1.388	1.388	1.388	0.732	1.388	1.388	1.388	1.388	0.740	15.93
4	0.0	1.447	1.412	1.412	1.447	0.727	1.447	1.412	1.412	1.447	0.717	————
	0.5	1.404	1.386	1.386	1.404	0.710	1.404	1.386	1.386	1.404	0.729	————
	1.0	1.324	1.332	1.332	1.324	0.710	1.324	1.332	1.333	1.324	0.729	————
	1.5	1.352	1.352	1.353	1.353	0.707	1.352	1.353	1.353	1.352	0.707	————
	2.0	1.352	1.356	1.356	1.353	0.710	1.352	1.356	1.356	1.352	0.715	————
	2.5	1.367	1.367	1.367	1.367	0.715	1.367	1.367	1.367	1.368	0.715	————
	3.0	1.367	1.364	1.367	1.367	0.710	1.367	1.367	1.367	1.367	0.715	15.70

TABLE VIII

Steady State Test Conditions for Thermal Conductivity of Unrolled Nylon with Heat Flow in the Plane and Parallel to the Greatest Length of the Sample

Test No	Elapsed Time, hr	Emf of Couple 1, $v \times 10^3$	Emf of Couple 2, $v \times 10^3$	Emf of Couple 3, $v \times 10^3$	Emf of Couple 4, $v \times 10^3$	Emf of Couple 5, $v \times 10^3$	Emf of Couple 6, $v \times 10^3$	Emf of Couple 7, $v \times 10^3$	Emf of Couple 8, $v \times 10^3$	Emf of Couple 9, $v \times 10^3$	Emf of Couple 10, $v \times 10^3$	Average Wattmeter Disk Speed^{-1}, sec/rev
1	0.0	1.296	1.323	1.323	1.296	0.719	1.296	1.323	1.323	1.296	0.733	-----
	0.5	1.369	1.369	1.369	1.369	0.729	1.369	1.369	1.369	1.369	0.729	-----
	1.0	1.386	1.386	1.386	1.386	0.736	1.386	1.386	1.386	1.386	0.736	-----
	1.5	1.386	1.386	1.386	1.386	0.736	1.386	1.386	1.386	1.386	0.736	-----
	2.0	1.386	1.386	1.386	1.386	0.736	1.386	1.386	1.386	1.386	0.736	15.63
2	0.0	1.314	1.324	1.324	1.314	0.721	1.314	1.324	1.324	1.314	0.712	-----
	0.5	1.376	1.364	1.367	1.376	0.718	1.376	1.367	1.367	1.376	0.720	-----
	1.0	1.319	1.326	1.326	1.319	0.713	1.319	1.326	1.326	1.319	0.715	-----
	1.5	1.366	1.363	1.363	1.366	0.718	1.366	1.363	1.363	1.366	0.718	-----
	2.0	1.366	1.366	1.366	1.366	0.718	1.366	1.366	1.366	1.366	0.718	-----
	2.5	1.339	1.339	1.339	1.339	0.708	1.339	1.339	1.339	1.339	0.708	-----
	3.0	1.339	1.339	1.339	1.339	0.708	1.339	1.339	1.339	1.339	0.708	15.87
3	0.0	1.373	1.373	1.373	1.373	0.709	1.373	1.373	1.373	1.373	0.735	-----
	0.5	1.369	1.369	1.369	1.369	0.702	1.369	1.369	1.369	1.369	0.702	-----
	1.0	1.373	1.373	1.373	1.373	0.709	1.373	1.373	1.373	1.373	0.709	15.55
4	0.0	1.344	1.344	1.344	1.344	0.711	1.344	1.344	1.344	1.344	0.711	-----
	0.5	1.361	1.361	1.361	1.361	0.714	1.361	1.361	1.361	1.361	0.714	-----
	1.0	1.361	1.361	1.361	1.361	0.714	1.361	1.361	1.361	1.361	0.714	-----
	1.5	1.361	1.361	1.361	1.361	0.712	1.361	1.361	1.361	1.361	0.714	-----
	2.0	1.361	1.361	1.361	1.361	0.712	1.361	1.361	1.361	1.361	0.712	15.89

TABLE IX

Steady State Test Conditions for Thermal Conductivity of Rolled-Annealed Nylon with Heat Flow Perpendicular to the Plane and to the Direction of Rolling of the Sample

Test No	Elapsed Time, hr	Emf of Couple 1, v x 10^3	Emf of Couple 2, v x 10^3	Emf of Couple 3, v x 10^3	Emf of Couple 4, v x 10^3	Emf of Couple 5, v x 10^3	Emf of Couple 6, v x 10^3	Emf of Couple 7, v x 10^3	Emf of Couple 8, v x 10^3	Emf of Couple 9, v x 10^3	Emf of Couple 10, v x 10^3	Average Wattmeter Disk Speed^{-1}, sec/rev
1	0.0	1.437	1.399	1.399	1.437	0.695	1.437	1.405	1.399	1.437	0.695	-----
	0.5	1.389	1.376	1.376	1.389	0.692	1.389	1.376	1.376	1.389	0.692	-----
	1.0	1.414	1.389	1.389	1.414	0.698	1.414	1.389	1.389	1.414	0.698	-----
	1.5	1.384	1.376	1.376	1.384	0.696	1.384	1.387	1.376	1.384	0.696	-----
	2.0	1.384	1.380	1.380	1.384	0.699	1.384	1.387	1.380	1.384	0.702	-----
	2.5	1.384	1.380	1.380	1.384	0.699	1.384	1.387	1.380	1.384	0.702	15.70
2	0.0	1.342	1.336	1.336	1.342	0.689	1.342	1.339	1.338	1.342	0.689	-----
	0.5	1.346	1.341	1.341	1.346	0.692	1.346	1.343	1.340	1.346	0.697	-----
	1.0	1.366	1.361	1.361	1.366	0.697	1.366	1.361	1.361	1.366	0.697	-----
	1.5	1.366	1.362	1.361	1.366	0.697	1.366	1.363	1.361	1.366	0.692	15.81

TABLE X

Steady State Test Conditions for Thermal Conductivity of Rolled-Annealed Nylon with Heat Flow in the Plane and Perpendicular to the Direction of Rolling of the Sample

Test No	Elapsed Time, hr	Emf of Couple 1, $v \times 10^3$	Emf of Couple 2, $v \times 10^3$	Emf of Couple 3, $v \times 10^3$	Emf of Couple 4, $v \times 10^3$	Emf of Couple 5, $v \times 10^3$	Emf of Couple 6, $v \times 10^3$	Emf of Couple 7, $v \times 10^3$	Emf of Couple 8, $v \times 10^3$	Emf of Couple 9, $v \times 10^3$	Emf of Couple 10, $v \times 10^3$	Average Wattmeter Disk Speed^{-1}, sec/rev
1	0.0	1.264	1.294	1.294	1.264	0.779	1.264	1.294	1.294	1.264	0.774	-----
	0.5	1.289	1.298	1.298	1.289	0.779	1.289	1.298	1.298	1.289	0.774	-----
	1.0	1.308	1.309	1.309	1.308	0.784	1.308	1.309	1.309	1.308	0.773	-----
	1.5	1.308	1.309	1.309	1.308	0.784	1.308	1.309	1.309	1.308	0.785	-----
	2.0	1.308	1.311	1.311	1.308	0.784	1.308	1.311	1.311	1.308	0.784	-----
	2.5	1.309	1.310	1.310	1.309	0.783	1.309	1.310	1.310	1.309	0.785	15.67
2	0.0	1.184	1.236	1.236	1.180	0.758	1.179	1.236	1.237	1.184	0.753	-----
	0.5	1.332	1.337	1.337	1.332	0.828	-1.332	1.337	1.337	1.332	0.823	-----
	1.0	1.346	1.367	1.367	1.346	0.856	1.346	1.367	1.367	1.346	0.852	-----
	1.5	1.384	1.384	1.384	1.384	0.859	1.384	1.384	1.384	1.384	0.854	-----
	2.0	1.397	1.397	1.397	1.397	0.883	1.397	1.397	1.397	1.397	0.883	-----
	2.5	1.296	1.296	1.296	1.296	0.782	1.296	1.296	1.296	1.296	0.782	-----
	3.0	1.295	1.295	1.295	1.295	0.782	1.295	1.295	1.295	1.295	0.780	-----
	3.5	1.296	1.296	1.296	1.296	0.782	1.296	1.296	1.296	1.296	0.780	15.70

TABLE XI

Steady State Test Conditions for Thermal Conductivity of Rolled-Annealed Nylon with Heat Flow in the Plane and Parallel to the Direction of Rolling of the Sample

Test No	Elapsed Time, hr	Emf of Couple 1, $v \times 10^3$	Emf of Couple 2, $v \times 10^3$	Emf of Couple 3, $v \times 10^3$	Emf of Couple 4, $v \times 10^3$	Emf of Couple 5, $v \times 10^3$	Emf of Couple 6, $v \times 10^3$	Emf of Couple 7, $v \times 10^3$	Emf of Couple 8, $v \times 10^3$	Emf of Couple 9, $v \times 10^3$	Emf of Couple 10, $v \times 10^3$	Average Wattmeter Disk Speed^{-1}, sec/rev
1	0.0	1.229	1.229	1.229	1.229	0.841	1.229	1.241	1.229	1.229	0.810	——
	0.5	1.227	1.227	1.227	1.227	0.842	1.227	1.241	1.227	1.227	0.810	——
	1.0	1.231	1.231	1.231	1.231	0.842	1.231	1.246	1.231	1.231	0.818	——
	1.5	1.231	1.231	1.231	1.231	0.842	1.231	1.246	1.231	1.231	0.829	——
	2.0	1.236	1.236	1.236	1.236	0.842	1.236	1.245	1.236	1.236	0.829	——
	2.5	1.236	1.236	1.236	1.236	0.842	1.236	1.245	1.236	1.236	0.841	——
	3.0	1.235	1.235	1.235	1.235	0.842	1.235	1.245	1.236	1.235	0.841	15.79
2	0.0	1.242	1.222	1.222	1.242	0.743	1.242	1.249	1.222	1.242	0.704	——
	0.5	1.192	1.196	1.196	1.192	0.734	1.192	1.228	1.196	1.192	0.703	——
	1.0	1.196	1.196	1.196	1.196	0.731	1.196	1.232	1.196	1.196	0.719	——
	1.5	1.191	1.191	1.191	1.191	0.719	1.191	1.227	1.191	1.191	0.721	——
	2.0	1.178	1.178	1.178	1.178	0.707	1.178	1.219	1.178	1.178	0.711	——
	2.5	1.187	1.187	1.187	1.187	0.718	1.187	1.238	1.187	1.187	0.721	——
	3.0	1.139	1.139	1.139	1.139	0.718	1.139	1.234	1.139	1.139	0.727	——
	3.5	1.139	1.139	1.139	1.139	0.728	1.139	1.238	1.139	1.139	0.728	——
	4.0	1.139	1.139	1.139	1.139	0.728	1.139	1.232	1.139	1.139	0.728	15.42

in the direction of the greatest length of the slab are presented in Table VIII.

Table IX contains the steady-state thermal conductivity test data for nylon samples rolled to one-half their original thickness and annealed two hours at 240 °C. The heat flux was in a direction perpendicular to the plane and to the direction of rolling of the slab. Table X shows the steady-state conductivity data for the rolled-annealed nylon samples with the direction of heat flux in the plane, but perpendicular to the direction of rolling of the slab. Thermal conductivity test data for rolled-annealed nylon samples with heat flux in a direction in the plane and parallel to the direction of rolling of the slab are given in Table XI.

The average values of the thermal conductivity test conditions together with measured conductivities for the individual tests are presented in Table XII, so that the individual and average results may be compared for precision. The results of this table were calculated from the test data found in Tables VI to XI.

The relation between physical treatment, direction of heat flux, degree of crystallinity, and thermal conductivity of nylon 66 is summarized in Table XIII.

Table XIV presents the "direction average" thermal conductivities of the unrolled and rolled-annealed nylon 66 samples, showing the relationship of degree of crystallinity and thermal conductivity free from the anisotropic effects due to rolling and annealing. The values indicate that the thermal conductivity of nylon 66 decreased from

TABLE XII

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

Test No	q, Btu/hr	emf, millivolts	Δt, °F	k, Btu/hr-sq ft-°F/ft	Mean t, °F
1[a]	54.95	0.894	40.44	0.172	81
2[a]	54.74	0.889	40.22	0.180	83
3[a]	54.85	0.887	40.12	0.173	82
4[a]	54.81	0.882	39.90	0.174	82
			Average	0.175	82
5[b]	55.34	0.679	30.65	0.168	82
6[b]	54.50	0.662	29.89	0.170	81
7[b]	54.19	0.652	29.49	0.171	80
8[b]	54.91	0.653	29.55	0.173	79
			Average	0.171	81
9[c]	55.16	0.650	29.41	0.170	80
10[c]	54.32	0.631	28.55	0.173	78
11[c]	55.45	0.664	30.03	0.168	79
12[c]	54.25	0.649	29.35	0.168	79
			Average	0.170	79
13[d]	54.92	0.682	30.85	0.125	79
14[d]	54.50	0.668	30.15	0.127	79
			Average	0.126	79
15[e]	54.92	0.514	23.25	0.172	79
16[e]	55.02	0.525	23.75	0.169	79
			Average	0.171	79
17[f]	54.60	0.393	17.69	0.191	79
18[f]	55.91	0.411	18.59	0.188	75
			Average	0.189	77

[a] As received nylon with heat flow perpendicular to plane of slab, and perpendicular to greatest length of slab.

[b] As received nylon with neat flow perpendicular to plane of slab, but in plane of slab.

[c] As received nylon with heat flow parallel to greatest length of slab and plane of slab.

[d] Nylon sample rolled to half thickness, annealed two hours at 240 °F, and heat flow perpendicular to direction of rolling and perpendicular to plane of sample.

[e] Nylon sample rolled to half thickness, annealed two hours at 240 °F, and heat flow perpendicular to direction of rolling but in plane of sample.

[f] Nylon sample rolled to half thickness, annealed two hours at 240 °F, and heat flow in direction of rolling and plane of sample.

TABLE XIII

Relation Between Physical Treatment, Degree of Crystallinity, Direction of Heat Flux, and Thermal Conductivity of Nylon 66

Treatment	Direction of Heat Flow	Degree of Crystallinity	Thermal Conductivity	Mean Temperature
		%	Btu/hr-sq ft-°F/ft	°F
None[a]	Perpendicular to plane and to greatest length of sample	18.6	0.172	81
			0.180	83
			0.173	82
			0.174	82
		Average	0.175	82
None[a]	Perpendicular to greatest length but in plane of sample	18.6	0.168	82
			0.170	81
			0.171	80
			0.173	79
		Average	0.171	81
None[a]	Parallel to greatest length and in plane of sample	18.6	0.170	80
			0.173	78
			0.168	79
			0.168	79
		Average	0.170	79
Rolled to 0.121 inch, annealed two hours at 240 °C	Perpendicular to plane and to direction of rolling of sample	30.8	0.125	79
			0.127	79
		Average	0.126	79
Rolled to 0.121 inch, annealed two hours at 240 °C	Perpendicular to direction of rolling but in plane of sample	30.8	0.172	79
			0.169	79
		Average	0.171	79
Rolled to 0.121 inch, annealed two hours at 240 °C	Parallel to direction of rolling and in plane of sample	30.8	0.191	79
			0.188	75
		Average	0.189	77

---

[a] Original sample was a cast slab 0.260 inch thick.

TABLE XIV

Relation Between Physical Treatment, Degree of Crystallinity, and Thermal Conductivity of Nylon 66 Separate from the Anisotropic Effect

Physical Treatment,	Degree of Crystallinity, %	k, Btu/hr-sq ft-°F/ft
None[a]	18.6	0.172
Rolled to 0.121 inch, annealed two hours at 240 °C	30.8	0.157

[a] Sample as received, average thickness 0.260 inch.

0.172 to 0.157 Btu per hour - square foot - $^{o}F/ft$ when the degree of crystallinity of the samples was increased, by rolling and annealing, from 18.6 to 30.8 per cent.

Finally, the relationships of the direction of heat flux, average thermal conductivity, chemical bond strength, and unit cell dimensions of nylon 66 are indicated in Table XV. These relationships pertain to the samples which were rolled to one-half their original thickness and annealed two hours at 240 ^{o}C, and which exhibited a degree of crystallinity of 30.8 per cent. The original slab was 0.260 inch thick with variations in thickness of 0.004 inch.

Physical Changes Caused by Rolling and Annealing. One further test was made to determine the nature of the physical changes caused by rolling and annealing. A comparison of Figure 20a and 20b, page 106 , shows that for the unrolled nylon sample as received, the diffraction rings are complete circles. They are somewhat diffuse, indicating the sample contained a large percentage of amorphous material. The diffraction rings for the rolled-annealed nylon are arcs of circles, thicker at the top and bottom than on the sides. These observations were interpreted as an indication that the molecules in the rolled samples were considerably oriented in the direction of rolling, whereas the unrolled nylon apparently showed almost complete random orientation of its molecules.

TABLE XV

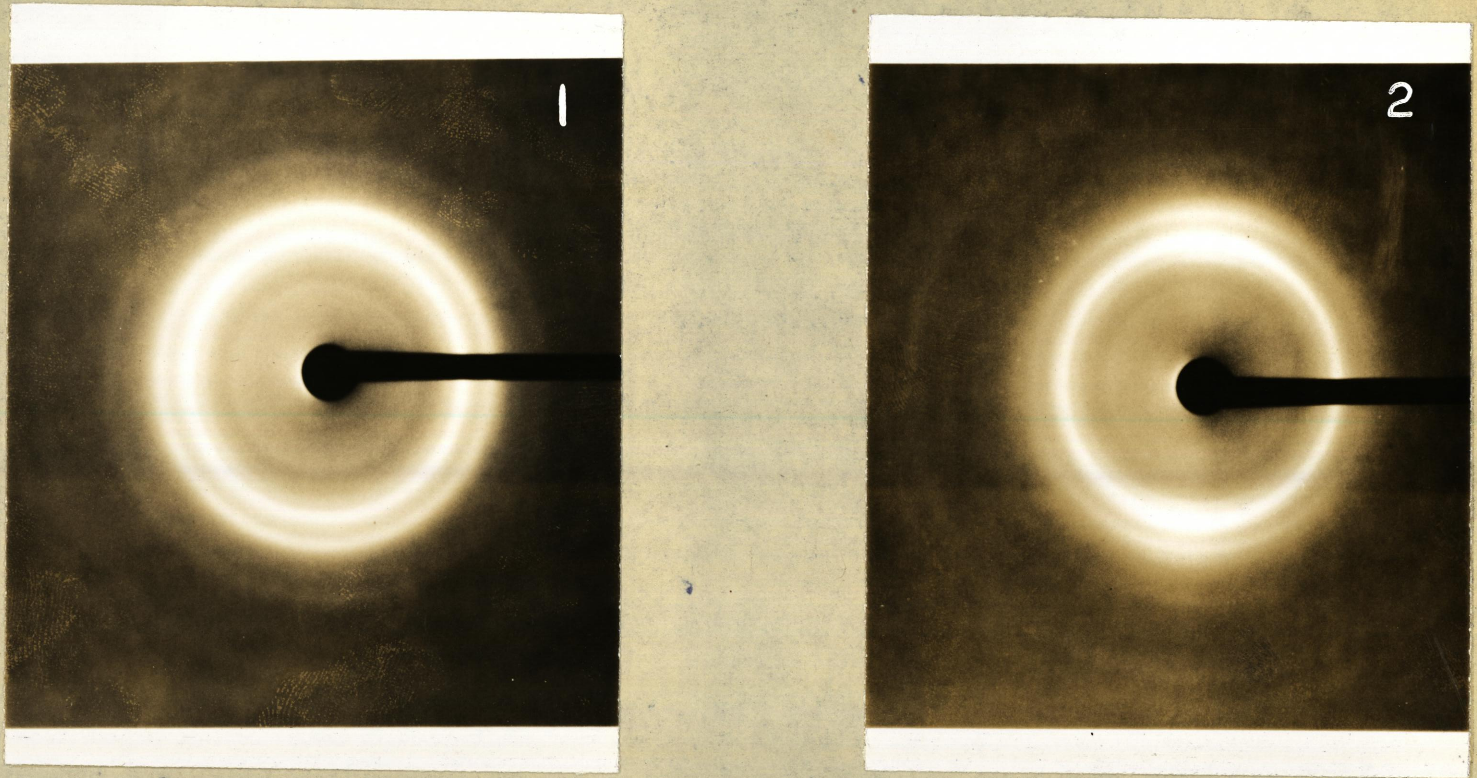
Relation Between Direction of Heat Flux, Average Thermal Conductivity, Relative Chemical Bond Strengths, and Unit Cell Dimensions of Rolled-Annealed Nylon 66 Having a Degree of Crystallinity of 30.8 Per Cent

Direction of Heat Flux	Thermal Conductivity Btu/hr-sq ft-°F/ft	Chemical Bond Strength[b] cal/gm-mol	Unit Cell Dimensions[c] Å
Perpendicular to direction of rolling and to plane of sample[a]	0.126	500- 5,000	5.4
Perpendicular to direction of rolling but in plane of sample[a]	0.171	5,000- 10,000	4.8
Parallel to direction of rolling and in plane of sample[a]	0.189	50,000-200,000	17.2

[a] Sample was rolled from 0.260 to 0.121 inches and annealed at 240 °C for two hours.

[b] Schmidt, A. T. and C. A. Marlies: "Principles of High-Polymer Theory and Practice," p. 34. Mc Graw-Hill Book Co., Inc., New York, N. Y. 1948. 1 ed.

[c] Bunn, C. W. and E. V. Garner: The Crystal Structures of Two Polyamides (Nylons), Proc. Roy. Soc. Lond., A189, 44(1949).



A. NYLON AS RECEIVED

B. NYLON ROLLED AND ANNEALED

FIGURE 20. X-RAY DIFFRACTION PATTERNS OF NYLON 66 AS RECEIVED AND ROLLED TO HALF THICKNESS AND ANNEALED TWO HOURS AT 240 °C.

Sample Calculations

The sample calculations illustrated in the following paragraphs were used to determine the results of the data obtained from the thermal conductivity studies of nylon 66.

Density of Nylon. The calculation of the density of nylon samples is illustrated for sample 5 from Table IV:

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

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(81) at the temperature of the test compared to the density of water at 4.0 °C.

$$d = 5.0537 \text{ gm} \times 0.99704 \,/\, (5.0537 - 0.6669) \text{ gm}$$
$$= 1.1486 \text{ at } 25\ {}^{\circ}/4\ {}^{\circ}\text{C}$$

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'(42) relation. Sample 5 of Table IV is 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(23) 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 du Pont Company(57) research laboratory, 1.111 at 25 °/4 °C.

$$D. C. = (1.1486 - 1.111) / (1.24 - 1.111) \times 100$$

$$= 29.2 \text{ per cent}$$

<u>Wattmeter Calibration</u>. The wattmeter calibration calculation is illustrated with the data from Table III, line one. The net 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 midtime of heating in order to correct for cooling losses. The calibration factor <u>R</u> was calculated from the following relation:

$$R = \frac{(C + W)\ (\Delta t)}{n}$$

where

R = calibration factor, Btu/wattmeter disk revolution

W = weight of water used in calorimeter, lb

C = water equivalent of calorimeter, 0.202 lb

Δt = net rise in temperature of calorimeter during heating, °F

n = number of revolutions of wattmeter disk during test.

$$R = (0.202 + 5.602)\text{lb} \times 2.06\ {}^{\circ}\text{F}\ /\ 50\ \text{rev}$$

$$= 0.2395\ \text{Btu/rev}$$

<u>Thermal Conductivity of Nylon</u>. 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 - °F/ft

q = heat flux, Btu/hr

L = thickness of sample, ft

A = heat transfer area, sq ft

Δt = temperature drop across sample, °F.

Data from Test 1, Table VI, are used in the following illustration.

<u>Heat Flux</u>. 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.

$$q = \frac{0.2395 \text{ Btu/rev} \times 3600 \text{ sec/hr}}{15.69 \text{ sec/rev}}$$

$$= 54.95 \text{ Btu/hr}$$

The thickness of the sample was measured with a micrometer, taking the average of twenty readings on each of the two samples before being placed in the guarded hot plate and after they were removed at the end of the test. The thickness was 0.0233 foot. The maximum variation in thickness of the samples was 0.0003 foot.

Temperature Drop. The temperature drop through the sample was calculated from the emf values of the thermocouples shown in Table VI. 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, °F

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

$\Delta E'$ = difference between average emf of thermocouples at 32.00 and 80.00 °F from Table II

$\Delta t'$ = temperature difference corresponding to $\Delta E'$, 80.00 - 32.00 °F.

$$\Delta t = 0.882 \text{ mv} \times 48.00 \ ^{\circ}\text{F} / 1.061 \text{ mv}$$

$$= 40.44 \ ^{\circ}\text{F}$$

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 foot, counting both sides.

Inserting these quantities into the equation for thermal conductivity we have:

$$k = \frac{54.95\ \text{Btu/hr} \times 0.0233\ \text{ft}}{0.1760\ \text{sq ft} \times 40.44\ ^{\circ}\text{F}}$$

$$= 0.172\ \text{Btu/hr - sq ft - }^{\circ}\text{F/ft}$$

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

"Direction-average" Thermal Conductivity. The "direction-average" thermal conductivity of the original unrolled samples and the samples rolled to half thickness and annealed two hours at 240 °C was calculated using the following relation:

$$k_{da} = \frac{3}{1/k_{\perp} + 1/k_{\perp\!\perp} + 1/k_{\parallel}}$$

where

k_{da} = "direction average" thermal conductivity of the sample, Btu/hr - sq ft - °F/ft

$k_{\perp}$ = arithmetic average thermal conductivity of the sample measured in a direction perpendicular to the plane and to the greatest length of the sheet, Btu/hr - sq ft - °F/ft

$k_{\perp\!\perp}$ = arithmetic average thermal conductivity of the sample measured in a direction perpendicular to the greatest length of the sample, but in the plane of the sheet, Btu/hr - sq ft - °F/ft

$k_{\parallel}$ = arithmetic average thermal conductivity of the sample measured in a direction parallel to the greatest length and in the plane of the sheet, Btu/hr - sq ft - °F/ft.

The average results for the unrolled samples, Table XIII, are used in the following illustration:

$$k_{da} = \frac{3}{1/0.175 + 1/0.171 + 1/0.170}$$

$$= 0.172 \text{ Btu/hr - sq ft - } {}^{\circ}\text{F/ft}$$

IV. DISCUSSION

A discussion of the results, technique of thermal conductivity measurement, actual and possible errors incurred, presentation of recommendations, and the limitations imposed upon the investigation are given in the accompanying sections.

Discussion of Results

The following discussion is presented as an attempt to clarify and interpret the experimental results of this investigation.

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 the 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 I.) In this investigation the density of nylon 66 was increased by cold-rolling and annealing from 1.1349 to 1.1508 at 25 °/4 °C. Snow(68) increased the density of nylon 66 by cold-rolling and annealing from 1.1387 to 1.1449 at 25 °/4 °C. Apparently the cast nylon used in this investigation was somewhat more crystalline than the undrawn filament. This would be expected since the larger sample would cool more slowly in the molding process and thus crystallize to a greater extent. The effect of drawing was more pronounced than cold-rolling.

This would be expected since the sample was smaller and minimized the internal stresses which would cause the larger slab to crack before advanced alignment of the molecules could take place.

Clark, Mueller, and Stott(25) showed that annealing without mechanical working increased the density of nylon slabs. Snow(68) obtained a density increase from 1.1387 to 1.1449 at 25 °/4 °C for nylon which had been annealed two days at 230 °C. The degree of crystallinity was increased from 21.2 to 26.2 per cent. A similar test was made for this investigation, in which nylon samples were annealed two hours at 240 °C. The density was increased from 1.1349 to 1.1482 at 25 °/4 °C with an accompanying increase in degree of crystallinity from 18.6 to 28.8 per cent.

Bunn and Garner(23) showed 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 indicate that cold-rolling and annealing nylon slabs increased the degree of crystallinity from 18.6 to 30.8 per cent. These values are in agreement with Snow(68), who treated nylon samples in the same manner as was done for this investigation. He found that the degree of crystallinity increased from 21.2 to 30.8 per cent.

Thermal Conductivity of Nylon 66. The values of thermal conductivity of nylon 66 determined in this investigation are in agreement with those obtained by Snow(72) for the same testing equipment. He reported a conductivity of 0.172 Btu per hour - square foot - °F per foot when measured in a direction perpendicular to the plane of the slab. The cast slab had a density of 1.1387 at 25 °/4 °C and a degree of crystallinity of 21.2 per cent. After having been cold-rolled from a thickness of 0.260 inch to 0.122 inch and annealed two hours at 240 °C, the conductivity was found to be 0.130 Btu per hour - square foot - °F per foot.

A unique phase of the present investigation was the measurement of thermal conductivity of nylon 66 not only in a direction perpendicular to the plane of the sample sheet, but also in a direction in which the heat flow was in the plane of the sheet, perpendicular to the greatest length of the sample sheet, and in the plane of the sample sheet, in the direction of the greatest length of the sample sheet. In this investigation the thermal conductivities of six samples of nylon 66 were determined. A slab of cast nylon having a density of 1.1349 at 25 °/4 °C and a degree of crystallinity of 18.6 per cent had a thermal conductivity of 0.175 Btu per hour - square foot - °F per foot when the direction of heat flux was perpendicular to the plane and to the greatest length of the slab. After cold-rolling from a thickness of 0.260 inch to 0.121 inch and subsequent annealing for two hours at 240 °C, the conductivity was found to be 0.126 Btu per hour - square foot - °F per foot. Values for the thermal conductivity of nylon with heat flux in other directions are discussed in subsequent paragraphs.

Effect of Variables on Thermal Conductivity of Nylon 66. Variables which were considered to affect the thermal conductivity of nylon in this investigation were the previous physical treatment, pressure on the samples in the guarded hot plate, the effect on the thermal conductivity of the 90 per cent formic acid used in cementing the nylon samples, and the moisture content.

Pressure on Samples. During the investigation, it was believed that the pressure on the samples in the guarded hot plate would have a decided effect on the calculation of thermal conductivity. Griffiths and Kaye(40) studied the effect of pressure on thermal conductivity and found that, for certain materials, the sample thickness changed under different pressures. Obviously this would affect the calculated result for the conductivity. They proposed that the thickness of samples be measured while under pressure in the apparatus and that the pressure be reported along with the conductivity. Although facilities were not available for accomplishing this during the present investigation, one particular precaution was taken to insure constancy of sample pressure from test to test. The four tightening bolts on the guarded hot plate were carefully tightened down gradually and then a torque of 20 foot-pounds was applied to each bolt with a torque wrench.

Thermal Conductivity of Formic Acid. During the investigation, 90 per cent formic acid solution was used to cement the cut strips of nylon used for preparing samples for conductivity measurement in directions other than in a direction perpendicular to the plane of the sample sheet. The formic acid had only a solvent action on the nylon. No chemical reaction takes place between formic acid and nylon 66. The effect on sample thermal conductivity of the cemented sides, where formic acid was used, could not be determined. However, a maximum of three cubic centimeters of the acid was used for each strip. Since the acid evaporated within 15 minutes after an application on a strip, it is believed that this effect was negligible. Evidence supporting this belief can be shown from the results in Table XIII. The unrolled nylon thermal conductivities in the three directions of measurement were essentially the same. It should be noted that the conductivities in the two directions other than perpendicular to the plane of the sheet differed by only 0.001 Btu per hour - square foot - °F per foot. The samples for conductivity measurement in these two directions were prepared by cementing cut strips of nylon, whereas the sample used for measurement perpendicular to the plane of the sheet was cut from the original cast slab of nylon. The conductivity perpendicular to the plane of the sheet was 0.175 Btu per hour - square foot - °F per foot, a difference of 0.004 to 0.005 Btu per hour - square foot - °F per foot higher than the other two values. If it is granted that the conductivities in the three directions were the same for the unrolled nylon, as is shown within experimental error by the results, this difference represents the apparent effect of formic acid on the thermal conductivity of the individual samples. Therefore, if the cemented sides were of importance, the value of the results would be still valid since the samples were each prepared in the same way, the only effect being to give relative values for the thermal conductivity and not absolute values.

Moisture Content. Vierweg and Gottwald(77) stated that moisture content may have an important effect on thermal conductivity of some non-metals. Moisture content determinations were not made on the nylon samples. Under exposure to air(30) at 50 per cent relative humidity, nylon will contain only 1.5 per cent moisture by weight. Since this amount is only a small portion of the total weight of any particular sample, the effect of moisture content in nylon on its thermal conductivity would probably be negligible.

Physical Treatment. The results of this investigation show that previous treatment has a significant effect on the thermal conductivity of nylon. This effect will be discussed in the next section dealing with the theory of thermal conduction in nylon 66.

Theory of Thermal Conduction in Nylon 66. The principal results of this investigation show that the thermal conductivity of nylon 66 in the three directions for which it was measured was essentially the same for the cast samples as received (See Table XIII.) Also the results show that the measured conductivities for the nylon samples which had been rolled to one-half thickness and annealed two hours at 240 °C were not the same in the three directions of measurement. It would be worthwhile to reconsider the theory of thermal conduction in order to understand and interpret these results.

The Debye Equation. The Debye equation(28) predicts that the thermal conductivity of substances is proportional to their density, other things being equal, but there is no experimental evidence to prove this prediction. Examination of Table V indicates that the density of the rolled-annealed nylon samples was higher than the density of the original cast samples. According to the Debye equation then, the thermal conductivity of the rolled-annealed nylon would have been increased. This was found to be true only for the measurement made when the heat flux was in the plane and in the direction of rolling of the sample. It seems then that the Debye equation can not be applied to the thermal conductivity of nylon 66 or any other material which exhibits anisotropy of thermal conductivity.

Degree of Crystallinity. According to Bragg(20), the more orderly the array of molecules the less interferences there should be between the thermal waves, and thus the conductivity should be greater for substances with higher crystallinity. Eucken(33) showed this to be true for silica. Apparently Bragg's idea does not apply to nylon 66 since the conductivity was different along the three major axes of the rolled-annealed samples. This was true even though the degree of crystallinity was increased from 18.6 to 30.8 per cent.

A method for relating degree of crystallinity and thermal conductivity of nylon 66 was tried in which the "direction-average" thermal conductivity of the nylon samples was calculated. This was done as an attempt to eliminate the anisotropic effect due to cold-rolling and annealing of the samples. As shown in Table XIV, the "direction-average" thermal conductivity was decreased from 0.172 Btu per hour - square foot - °F per foot for the cast nylon as received to 0.157 Btu per hour - square foot - °F per foot for the rolled-annealed samples. This change in conductivity accompanied a change in degree of crystallinity from 18.6 to 30.8 per cent. According to this correlation, the higher the degree of crystallinity in nylon 66, the lower should be the "direction-average" thermal conductivity. This result is not in accordance with the statements of Debye and Bragg, and raises a question of the validity of this type of correlation for predicting thermal conductivity of anisotropic materials.

Chemical Forces and Anisotropy of Thermal Conductivity. The results of Table XIII show that the rolled-annealed samples of nylon had different average thermal conductivities in the three directions of measurement, whereas the values for the unrolled nylon were nearly the same. The "direction-average" conductivity for the unrolled samples was 0.172 Btu per hour - square foot - °F per foot and the greatest deviation of the individual conductivities from this value was 0.003 Btu per hour - square foot - °F per foot, within experimental error. That the conductivities of the rolled-annealed nylon in the three directions of measurement were different exemplifies the fact that rolled-annealed nylon exhibits anisotropy of thermal 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 Figure 20a and 20b show that the rolled samples exhibit considerable preferential orientation of the crystallites, while the unrolled samples indicate a completely random orientation of the crystallites. The evidence for this fact is that the diffraction rings for the unrolled samples are complete circles. They are somewhat diffuse, indicating the sample contained a large percentage of amorphous material. The diffraction rings for the rolled-annealed nylon are arcs of circles, slightly less diffuse, and thicker at the top and bottom than on the sides, indicating preferential orientation of the crystallites in the direction of rolling of the samples. The two kinds of orientation that take place on rolling of nylon have been described by Bunn and Garner(23): 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.

It is of significance to note that the apparently constant values for the thermal conductivity of the unrolled nylon in the three directions of measurement would predict that the nylon crystallites were randomly oriented as indicated by the x-ray diffraction pattern and vice versa. Also the different values of conductivity for the rolled-annealed nylon, for the three directions of measurement, tend to verify the fact that the nylon crystallites were preferentially oriented.

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 that the crystals are so oriented. Baker(15) 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 valence forces between the paraffinic parts of the chains. During this investigation thermal conductivity of the samples was measured with respect to the orientation of these chemical bonds in the rolled-annealed samples. No quantitative measure of the degree of orientation was made however. Since the molecules in the unrolled nylon were not oriented, obviously measurement of thermal conductivity with respect to chemical bonds was not possible.

By measuring the thermal conductivity of the rolled-annealed nylon samples with heat flux perpendicular to the plane of the sheet, it was possible to determine the influence of the secondary valence forces between the paraffinic chains. Conductivity measurements with heat flux in the plane and perpendicular to the direction of rolling of the sheet determined the influence of the hydrogen bonds, while the conductivity through the primary valence bonds was measured when the samples were tested with heat flux in the plane and in the direction of rolling of the sheet. The results of this investigation indicate that chemical bond strength is related to the thermal conductivity of nylon 66.

Strength of Chemical Bonding and Thermal Conductivity. Austin(6) showed by a study of the thermal conductivity of inorganic compounds that those with the strongest bond forces have the highest conductivities. Schmidt and Marlies(59) 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. An attempted correlation between the thermal conductivity, in the three directions of measurement, and the strengths of such chemical bonds was made (See Table XV.) The results seem to indicate that the higher the chemical bond strength the higher the thermal conductivity. Bunn and Garner(23) showed by x-ray diffraction patterns that the strongest bonds (primary valenve 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(38) by infra-red absorption studies. Thus, to the extent that orientation occurs, only the weakest bonds (secondary valence bridges) remain in a direction perpendicular to the plane of the sheet. According to Austin(6) the thermal conductivity should be lowest in the direction in which the weakest bonds lie, through the sheet. The conductivity should be higher in the direction in which the hydrogen bonds lie, and the highest in the direction of the primary bonds, the direction of rolling. These facts are verified by the results of this investigation for the rolled-annealed nylon samples having a degree of crystallinity of 30.8 per cent. An explanation of these facts can be made partly from a general knowledge of the behavior of metallic and non-metallic crystals. In a typical metallic crystal there is a cloud of gas or highly mobile electrons. When heat passes through the metallic crystal a large part of it is reflected due to the presence of the cloud of electrons. Moreover, according to Debye(28), some of the heat is absorbed, distorted, and scattered. In polymeric crystals where the primary bonding is other than metallic, that it, covalent or coordinate, the electrons are far less mobile. Heat waves can not cause electron flow, but can cause transfer of energy only about mean equilibrium positions. For this reason, the thermal conductivity of polymers such as nylon 66 could be expected to be less than that of metals.

This argument is in agreement with Rehner(56), who postulated that the conductivity of polymers is mainly due to the primary bonds along the molecular chain. 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.

Relation Between Unit Cell Dimensions and Interatomic Distances. An attempt was made to correlate the unit cell dimensions of nylon 66(23) with respect to the observed conductivities along these dimensions (See Figure 5 and Table XV.) There was no particular relation between the two variables. The dimension in which the secondary valence forces were oriented was 5.4 Angstroms long and the thermal conductivity in this direction was 0.126 Btu per hour - square foot - °F per foot. The thermal conductivity in the direction in which the hydrogen bonds were oriented was 0.171 Btu per hour - square foot - °F per foot and corresponded to a length of the unit cell in this direction of 4.8 Angstroms. The conductivity was highest in the direction of the longest length, the direction in which the paraffinic chains were oriented, which was the direction of rolling.

Schmidt and Marlies(59) have stated the interatomic or intermolecular distances associated with the bond force values ordinarily encountered in high polymers. The values are:

	Bond Distance Å
Primary bonds	1 to 2
Hydrogen bonds	2 to 3
Secondary Valence bonds	3 to 5

When these values of the bond lengths are now compared with the respective observed thermal conductivities obtained in this investigation, it will be seen that there is an excellent correlation between the two (See Table XIII for conductivity values.) It will be noted that the conductivities are related inversely to the bond distances and related directly to the chemical bond strengths. Since the attractive forces are greater along the paraffinic chains, the bond distances would be expected to be less than those for the weaker hydrogen bonds and secondary bridges in nylon. It would seem then from the analysis that the relative proximity of the atoms or chains in the different directions in nylon is a governing factor in prediction of conductivity. Obviously, if the molecular chains or individual atoms are closer to each other, the chances for transfer of heat by conduction will be increased.

Summary. The thermal conductivity of cast nylon as received was the same for the three directions of measurement, indicating random orientation of the nylon molecules. This was verified by observation of an x-ray diffraction pattern of a sample of the unrolled nylon.

The thermal conductivity of rolled-annealed nylon 66 was anisotropic with the highest value in the direction of the primary valence forces; the next highest value was in the direction of the hydrogen bonds, and the lowest value was in the direction of the secondary valence forces. Because nylon 66 is anisotropic with respect to thermal conductivity, the Debye equation(28) can not be applied in predicting thermal conductivity of nylon 66.

The thermal conductivity of nylon 66 is directly related to the chemical bond strengths of and between its molecular chains. The conductivity is also related inversely to the interatomic bond distances between the atoms and chains. There is no apparent correlation between the unit crystal cell dimensions and anisotropy of thermal conductivity of nylon 66.

The "direction-average" thermal conductivity of nylon 66 apparently decreased with an increase in degree of crystallinity, but it is believed that the greatest changes in conductivity were brought about by a preferential orientation of the crystallites due to the rolling-annealing treatment. It has not been decided to what extent the degree of crystallinity affects the thermal conductivity in this respect. A way to determine more specifically the effect of degree of crystallinity would be to make tests on cast nylon (unrolled) samples which had been annealed at varied temperatures and for varied periods of time.

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 are measured in different directions and which have received different physical treatment. Although only one condition of rolling and annealing treatment was performed on the samples, all of the results indicate that further rolling and annealing treatment may cause even more variations in thermal conductivity. Also the results are an indication of the reliability of the published values of conductivity of polymers.

This investigation, in pointing out the importance of the primary bonds in determining thermal conductivity supports Rehner's 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 anisotropic.

Practical Observations Concerning Rolling and Annealing. While handling the rolled nylon samples, it was observed that they were not completely flat, but were concave in shape. The concavity was approximately 3/4-inch for a sheet five inches square. This concavity was attributed to a difference in the speed of the calendaring rolls during the rolling operation. After annealing the concavity was reduced considerably; however the sample was still not completely flattened.

Annealing also caused some shrinkage in the rolled samples. One particular sample which measured approximately five by five inches was annealed two hours at 240 °C, whereupon it measured approximately 4-3/4 by 4-5/8 inches. These changes were also accompanied by an increase in thickness from 0.121 to 0.148 inch. The direction of greatest shrinkage was in the direction of rolling.

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 method of procedure will be discussed.

Preliminary Remarks. A few preliminary remarks will be made concerning the thermal conductivity apparatus. It was of the guarded hot plate design recommended by the American Society for Testing Materials and constructed by Snow(63) for a previous investigation.

Panelboard. Most of the controlling apparatus was mounted on a panelboard which accomplished two purposes: It provided a compact unit for the measurement of thermal conductivity and allowed the measurements to be taken quickly and efficiently.

Electric Circuits. The particular electric circuits and controls were almost completely automatic once they had been adjusted.

This meant that while the apparatus was approaching steady state, the operator would not have to concentrate his efforts on any disrupting vagaries of the equipment.

Thermocouple Shield. The thermocouple lead wires were shielded by wrapping them with aluminum foil which was grounded to the water pipe. By doing this they were protected from stray magnetic fields arising from current fluctuations in the electrical circuits. If this were not done, the induced currents would have interfered with the measurement of 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 apparaus. The following assembly methods proved advantageous.

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 enough air bubbles in the water so that if they had remained in the cooling blocks they would have prevented maximum heat transfer between the water and the cooling blocks.

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 were facilitated. It was possible to tighten the bolts slowly, stopping occasionally to adjust the position of the samples and to make sure that the thermocouples were in the slots in the heater.

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 Thermocouples. The thermocouples 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 wrapping them with narrow strips of friction tape. The portions immediately next to the hot plate was insulated with porcelain spacers.

The portions of the thermocouple wires inside the hot plate were insulated by wrapping them with narrow lengths of asbestos paper and then wedged into the milled slots. This method proved satisfactory for the majority of the tests until constant usage of the hot plate caused the wires to pull out of the slots. The thermocouples on the cold side of the samples were insulated by inserting two pieces of asbestos paper 0.015 inch thick against the surfaces of the cooling blocks and the thermocouples squeezed between the paper and the nylon sample. The thermocouple sank mainly into the paper and very little into the sample. The two wires leading to each thermocouple bead were insulated from each other simply by keeping them separated.

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 eliminated by replacing the guard resistor with a 230-ohm variable resistor with more turns.

Center Voltage Adjustment too Rough. It was found that the voltmeter was too inaccurate for adjusting the voltage to the center heater. The wattmeter was calibrated at 12 volts for use in calculating the heat flow through the center heater. The scale on the voltmeter had a small range and did not allow as fine an adjustment to this voltage as would have been desired. The voltmeter should be replaced with one having finer graduations.

Actual and Possible Errors

Snow(82) has made a complete analysis of actual and possible errors associated with the use of the guarded hot plate apparatus used for this investigation. He recognized two classes of errors: accidental and systematic. These errors will be compared in magnitude with those estimated for this investigation.

Air Film Resistance. Nylon is elastic enough so that although the thickness of the samples varied by 0.003 inch, the sample conformed to the shape of the face plates. The relative resistance of an air film 0.0002 inch thick was estimated to contribute 1.5 per cent of the total sample resistance.

Uncertainty in Thickness of Sample. The rolled sample in Snow's investigation and the rolled and fabricated samples in this investigation varied in thickness by 0.003 inch. 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. According to Snow(82) the total uncertainty in the wattmeter calibration was 0.5 per cent, taking into account the deviations in the thermometer, uncertainty in weighing the water in the calorimeter, and the systematic error in determining the calorimeter constant. The same method of calibration of the wattmeter was used for this investigation and it is believed that the uncertainty in the calibration was about the same.

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 difference between the guard and center heater temperatures at steady state was too small to be measured so this error was neglected.

Thermocouple Calibration Error. The probable accidental 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 as sensitive. The probable error in the thermocouple calibrations, including these effects, was 0.3 °F maximum.

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

Area of Sample. The heat transfer linear dimensions were measured with a rule to within 0.05 inch. Since the center heater was not a perfect square, several measurements were taken and averaged. The resulting error in length of a side was 1.5 per cent.

Error in Thermal Conductivity Values. Snow(82) determined the effect of individual errors on the thermal conductivity by differentiating the definition of thermal conductivity and substituting the probable errors in the terms. The estimated actual error was 4.5 per cent, including systematic errors and assuming that errors did not cancel out. The average deviation of his values was 1.0 per cent. In this investigation the maximum deviation of the series of tests made was 2.9 per cent. The average deviation of all the tests was 1.4 per cent.

Nylon Density. The density of nylon was determined by weighing one to five-gram samples in air and in water. The weights for the balance 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.

The samples were inspected for cracks and bubbles, and none were found. The edges were trimmed with a knife to remove saw burrs. Precautions were taken in the method of procedure to insure that no air bubbles clung to the surface of the samples.

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.

Recommendations

The following recommendations are presented as suggestions for further investigations and improvements in the present work on thermal conductivity of nylon.

1. 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 further rolling and annealing operations. The thermal conductivity should be measured after each rolling and annealing operation, in three directions of heat flux, in order to obtain further data on anisotropy of thermal conductivity of nylon and its relation to bond strength.

2. It is recommended that tests be performed in order that it may be determined more specifically whether degree of crystallinity or molecular orientation is the factor which governs the thermal conductivity of nylon. This should be done by attempting to increase the degree of crystallinity of cast nylon (unrolled) in incremental amounts by successive annealing treatments under varied conditions of time and temperature of annealing. The conductivity should be measured in the three directions of heat flux.

3. 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(46). The density of the sample should then be measured and the density of amorphous nylon as defined by the following relation should be calculated:

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

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.

4. 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.

5. 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 molecular orientation, bond strength, and thermal conductivity.

6. It is recommended that a more sensitive ammeter and voltmeter be used to control the energy input to the center and guard heaters.

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

b. 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.

c. The thickness of the sample should be measured while being compressed at the pressure used in the guarded hot plate by the method described by Griffiths(40).

Limitations

The following limitations applied to the investigations of the thermal anisotropic property of nylon 66.

1. Nylon slabs of sufficient size to provide all the necessary samples for test from one slab were not obtainable. Test samples were cut from two slabs separately molded by the producer, with consequent opportunity for variation in properties.

2. Nylon slabs were limited to a width of 4-3/16 inches by the manufacturer's molding process.

3. The nylon slabs were rolled in the direction of their greatest length only.

4. The rolling operation on samples could not be personally supervised.

5. The rolled samples were tested for thermal conductivity only after subsequent annealing.

6. X-ray diffraction patterns taken were qualitative measures of orientation of the rolled-annealed nylon samples. No quantitative studies of orientation of nylon molecules were made.

7. One original and three check tests of the thermal conductivity were made on each sample of unrolled nylon 66.

8. One original and one check test of the thermal conductivity was made on each sample of rolled-annealed nylon 66.

9. The thermal conductivity of the samples was measured in three directions:

a. perpendicular to the plane of the sheet

b. in the plane of the sheet, but perpendicular to the greatest length of the slab

c. in the plane of the sheet and in the direction of the greatest length of the slab.

10. It was necessary to use cemented portions of samples for thermal conductivity tests made other than in the direction perpendicular to the plane of the sheet.

11. The thermal conductivity of the samples was measured at one mean temperature of 80 °F plus or minus three °F.

V. CONCLUSIONS

The following conclusions were reached from tests made on nylon slabs to determine the relationships among degree of crystallinity, molecular orientation, bond strength, and thermal anisotropy of conductivity, resulting from rolling-annealing treatment.

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 0.121 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 1.1349 to 1.1482 at 25 °/4 °C.

2. By annealing, the degree of crystallinity of nylon was increased from 18.6 to 28.8 per cent.

3. By rolling and annealing, the density of nylon was increased from 1.1349 to 1.1509 at 25 °/4 °C.

4. By rolling and annealing, the degree of crystallinity of nylon was increased from 18.6 to 30.8 per cent.

5. The nylon crystallites were preferentially oriented in the direction of rolling by the rolling operation.

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 0.121 inch thickness and annealed two hours at 240 °C were determined by using ASTM Method C177-45, the Guarded Hot Plate Method. Anisotropy of thermal conductivity was determined by measuring the conductivity in three directions of heat flow through the samples.

1. The thermal conductivity of nylon measured in a direction perpendicular to the plane of the sheet was decreased by rolling and annealing from 0.175 to 0.126 Btu per hour - square foot - °F per foot.

2. The thermal conductivity of nylon measured in a direction in the plane of the sheet and perpendicular to the direction of rolling was the same as the conductivity before rolling and annealing, the value being 0.171 Btu per hour - square foot - °F per foot.

3. The thermal conductivity of nylon measured in a direction in the plane of the sheet and in the direction of rolling was increased from 0.170 to 0.189 Btu per hour - square foot - °F per foot.

4. The thermal conductivity of the unrolled nylon was essentially the same when measured in the three different directions of heat flux.

5. The nylon crystallites were in a completely random state of orientation in the unrolled and unannealed state.

VI. SUMMARY

Massive nylon lends itself to many applications because of its outstanding toughness, abrasion-resistance, and chemical resistance. These properties make it a satisfactory bearing material, and in some applications it is superior to metallic bearings. However, the disadvantages of low melting point and low thermal conductivity prevent nylon from being used more extensively.

A previous investigation of the effect on thermal conductivity of change in crystallinity brough about by rolling and annealing nylon 66 indicated that it exhibits anisotropy of conductivity and that its thermal conductivity depends on primary physical factors related to its molecular structure.

The purpose of this investigation was to determine the relationships of anisotropy of thermal conductivity, bond strength, degree of crystallinity, molecular orientation, and the changes resulting from the rolling-annealing treatment of nylon 66.

A survey was made of the literature on the thermal conductivity of nylon in particular and non-metallic solids in general, of anisotropy of thermal conductivity, 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 experimental part of the work consisted of measuring the thermal conductivity of nylon along three directions of heat flux, and

the changes in internal structure and thermal conductivity in the three directions of heat flux resulting from rolling and annealing treatment.

The thermal conductivity of six samples of nylon 66 was determined. The first three samples were cut from a slab of cast nylon 1/4 inch thick. The conductivity was measured in a direction perpendicular to the plane of the sample and to the greatest length of the slab, in the plane of the sample, but perpendicular to the greatest length of the slab, and in the plane and in the direction of the greatest length of the slab. The other three samples were prepared from a 1/4-inch thick cast slab which had been cold-rolled to half the original thickness and then annealed for two hours at 240 °C.

To determine the effect of physical treatment on the internal structure and thermal conductivity, the density and degree of crystallinity were determined and x-ray diffraction patterns of the samples were made.

Standard laboratory procedures were used in all of 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 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 one to 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 and used by Snow for nylon.

The results of this investigation showed that when nylon slabs were rolled and annealed, the degree of crystallinity was increased, confirming the conclusions of previous investigators. The thermal conductivity was affected mainly by an orientation of the molecule produced by rolling rather than by the change in degree of crystallinity. Because of a preferential orientation of the molecules in the direction of rolling, the nylon thermal conductivity became anisotropic. These results support Rehner's hypothesis that the thermal conductivity of polymers is mainly dependent on the strength of the bonds in the molecular chain, and that thermal conduction in polymers is mainly molecular conduction, not lattice conduction.

The following conclusions were reached from tests made on the nylon slabs.

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 0.121 inch. 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.

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3. By rolling and annealing, the density of nylon was increased from 1.1349 to 1.1509 at 25 °/4 °C.

4. By rolling and annealing, the degree of crystallinity of nylon was increased from 18.6 to 30.8 per cent.

5. The nylon crystallites were preferentially oriented in the direction of rolling by the rolling operation.

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 0.121 inch thickness and annealed two hours at 240 °C were determined by using ASTM method C177-45, the Guarded Hot Plate Method. Anisotropy of thermal conductivity was determined by measuring the conductivity in three directions of heat flow through the samples.

1. The thermal conductivity of nylon measured in a direction perpendicular to the plane of the sheet and perpendicular to the

direction of rolling was decreased by rolling and annealing from 0.175 to 0.126 Btu per hour - square foot - °F per foot.

2. The thermal conductivity of nylon measured in a direction in the plane of the sheet and perpendicular to the direction of rolling was the same as the conductivity before rolling and annealing, the value being 0.171 Btu per hour - square foot - °F per foot.

3. The thermal conductivity of nylon measured in a direction in the plane of the sheet and in the direction of rolling was increased from 0.170 to 0.189 Btu per hour - square foot - °F per foot.

4. The thermal conductivity of the unrolled nylon was essentially the same when measured in the three different directions of heat flux.

5. The nylon crystallites were in a completely random state of orientation in the unrolled and unannealed state.

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