WOOD-POLYMER ALLOYS -- SOME FUNDAMENTAL CONSIDERATIONS

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by

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Engineering

McMaster University
October 1965

Master of Engineering (1965)
(Chemical Engineering)

McMaster University
Hamilton, Ontario.

Title : Wood-Polymer Alloys -- Some Fundamental Considerations

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Number of Pages : (x), 280

Scope and Contents:

An experimental investigation of graft copolymerization of styrene in wood was performed utilizing (1) Cobalt-60 radiation initiation, (2) impregnating solutions of styrene, methanol and water and (3) heat during the irradiation period. It was found that heating did not increase the grafting efficiency of the system. The grafting process was found to be dependent upon (1) the method of impregnation, (2) the density of the wood and (3) the amount of swelling agents in the impregnating solution.

Wood treated with styrene and swelling agents was weakened in all mechanical properties except the maximum crushing strength and properties associated with compression. In general, wood treated with pure styrene was strengthened. It is felt that the use of radiation in the formation of wood-plastic composites is commercially unjustified.

ACKNOWLEDGEMENTS

The author sincerely thanks the following persons:

-- Dr. J. W. Hodgins for the advice and guidance offered throughout this project

-- G. N. Werezak for his counsel and data, both of which were greatly appreciated

-- Dr. C. M. Crowe for his assistance in the statistical work performed

-- Dr. H. Robinson for his helpful suggestions in regard to the structural aspects of this work

-- Miss J. Sabo for her remarkable endurance in carrying out the task of typing this thesis

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INTRODUCTION

In 1964, according to the latest figures from the U. S. Dept. of Agriculture and the American Wood Preservers Association, some 228 million cubic feet of wood products were treated with preservatives and fire retardents. Some of this tremendous market holds promise for wood-plastic composites which consist of wood that has been soaked in a suitable monomer, then exposed to atomic radiation that causes in situ polymerization. Lockheed-Georgia Co. recently completed a plant (36,000 lbs/year) to demonstrate the efficiency of this process (94). It has been estimated by Arthur D. Little Inc. that the market for these composites can consume about 4.9 billion board feet of lumber annually (95, 96).

Surprizingly, very little work in this field has been carried out with the use of wood-swelling chemicals such as water and methanol; only with swelling agents will penetration into the cellulose structure and grafting occur; only by this type of infiltration will true dimensional stability occur. The preponderance of work done in the wood-plastic field at this university deals with grafting and the effect of same on the physical properties of wood.

The primary aim of this project started by Ramalingam in 1960 was to enhance the physical properties of wood, particularly the bending strength. It was assumed that the bending strength of wood would be improved by grafting polystyrene onto the cellulose in the wood by the efficient use of high-energy radiation for polymer initiation. The experimental procedure used by Ramalingam involved impregnating wood with a solution of styrene, methanol and water, irradiating with gamma rays from the McMaster Nuclear Reactor and then heating the product. The results of the work generated a great deal of excitement for it appeared that not only was the bending strength of wood increased by 50% by means of the <u>in situ</u> polymerization but also the treated wood has a much greater stability to dimensional change and water absorption than untreated wood. Also, it was believed that a further enhancement could be obtained; it was thought that many cellulose free radicals generated by the nuclear radiation were not being utilized in the grafting process. The reason for this belief was well founded: because the manganese in the wood was being rendered radioactive by absorption of thermal neutrons, the samples could be handled only after a time lapse of up to five hours after irradiation. The steep slope of the radical decay curve in this period made it reasonable to suspect that more grafting (and hence greater strength values) could be obtained if the heating step could be accomplished immediately after irradiation, to take advantage of the higher radical concentration. Thus, in the second phase of this work, careful assessment of free radical concentration was undertaken by Werezak and the time lapse between irradiation and heating was shortened to about twenty minutes by carrying out the irradiations in a cadmium casket, which effectively screened out the thermal neutrons. Werezak carried out an optimization study with respect to the bending strength of wood and found that the property enhancement obtained was not a significant improvement over that obtained by Ramalingam. Werezak measured the concentration of free radicals in the irradiated systems and the rate of decay under various atmospheric conditions. From the free-radical decay curves it was noted that there was still a great percentage of free radicals formed during irradiation that were not taking part in the grafting process. It was reasoned from Werezak's results that since an enhancement in bending strength of about 50% was realized with the use of only a small fraction of the generated free radicals, a much greater improvement would result if more radicals were utilized in the grafting reaction.

The present investigation partially concerns itself with the logical next step: heating the impregnated wood during the irradiation period. It was believed that this would increase the diffusion of monomer to the radical sites before they had a chance to decay by combination. As a result, the amount of grafting and the strength of the wood might increase. This would be the case if the increased mobility of the monomer is favoured over the higher rate of radical destruction at higher temperatures. In addition to the above objective, the present study includes a detailed analysis of the previous work, particularly the unpublished data of Werezak. This was done in order to gain more insight into the fundamental aspects of the kinetics of the wood-styrene reaction and to re-examine the property enhancement studies on a more rigorous basis.

Finally, this thesis has been divided into two sections. PART 1 involves an examination of some aspects of the kinetics of the radiation-induced polymerization of styrene in wood. PART 2 deals with the structural changes brought about by this in situ polymerization.

PART 1

KINETICS OF IN SITU POLYMERIZATION OF STYRENE IN WOOD

FUNDAMENTALS

1. High Energy Radiation (1, 2, 3, 5)

High energy or ionizing radiation refers to electromagnetic radiation of short wave-length such as gamma-rays and x-rays and to elementary particles moving with high velocity such as fast electrons, protons, neutrons and alpha particles. In radiation chemistry the term "high energy radiation" usually refers to quantum energies in the range $0.5x10^6$ - $2x10^6$ ev. Gamma rays are electromagnetic radiation emitted by the nuclei of natural or artificial radioactive isotopes. CO-60 has a half-life of 5.27 years and emits mainly two gamma rays having quantum energies of 1.17 and 1.33 Mev respectively.

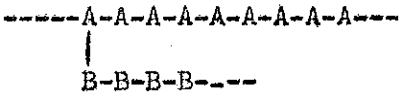
Gamma-rays interact with matter by means of three mechanisms: (1) photoelectric absorption (2) Compton scattering and (3) production of electron pairs. Photoelectric absorption consists of the transfer of all the energy of an incident photon to an electron of the irradiated substance. The photon disappears and is replaced by a fast electron which in turn dissipates most of its energy in the medium. This effect is usually important only for photons of energies less than 0.2 Mev. Compton scattering arises from the elastic collision between the incident photons and the orbital electrons of the medium. The incident photon transfers part of its energy to the electrons encountered and is itself reflected at a lower energy. For organic compounds and polymers most of the photons with quantum energies from 0.2 - 2 Mev dissipate their energies through Compton scattering. The recoil electrons (secondary electrons) cause most of the excitation and ionization of the irradiated molecules as the charged particles move through the medium. If the incident photons have energies above 1.2 Mev pair production occurs, an event producing a positron and an electron.

2. Graft Copolymers (1, 2, 3, 4, 5)

A copolymer is by definition a polymer consisting of two or more chemically different monomer units. In an ordinary or random copolymer, the monomer units are distributed at random along its chain. The structure can be represented as

-------A-A-B-A-B-B-B-A-A-B-B-A-A-A-B---- (1)

A graft copolymer is a polymer which contains two or more chemically different polymeric parts. It consists of a homopolymer substrate onto which side chains of a second polymer has been grafted by means of co-valent chemical bonds. The structure may be represented as



$$\begin{array}{l}\text{-----A-A-A-A-A-A-A-A-A---}\\ \quad\;\;|\\ \quad\;\;\text{B-B-B-B----}\end{array} \qquad (2)$$

If the two macromolecules A and B are linked together via one of the ends a block copolymer results:

----A-A-A-A-A-A-B-B-B-B-B--- (3)

Several methods are available for the preparation of graft copolymers. These involve chemical initiation (employing catalysts such as peroxides and ceric ion), thermal initiation or initiation by high energy radiation. The common feature of all the methods is that an active site is created in the pre-existing macromolecule. Of the various means of initiating, the latter method has the following advantages:

(a) it follows the principle of non-specificity. That is, the primary events in a given specimen occur at random. Thus active sites are produced homogeneously throughout the material.

(b) the resulting material will be free of chemical impurities.

(c) grafting can be produced at moderate temperatures.

3. Graft Copolymers Induced by High Energy Radiation

Radiation provides an efficient method for initiating chemical modifications in polymers by

(a) direct excitation which results eventually in the scission of the main chain.

(b) hydrogen extraction from the polymer molecule by free radicals formed in the radiolysis of a properly selected solvent.

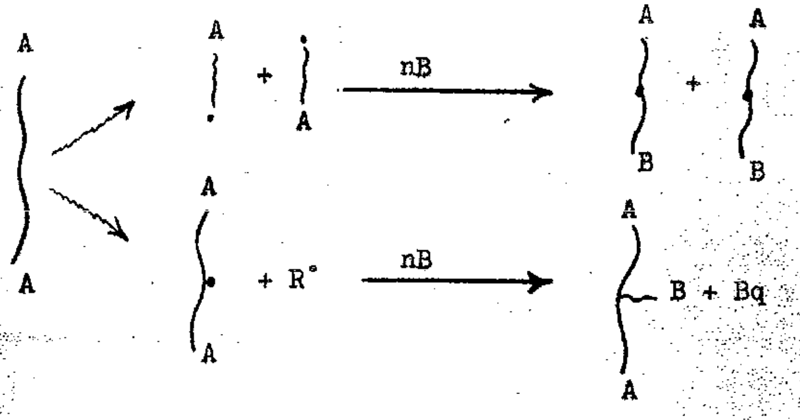
In both cases polymeric free radical sites are formed from which grafting may occur by three different methods:

(a) the direct radiation grafting of a vinyl monomer onto a polymer.

(b) grafting onto radiation-peroxidized polymers.

(c) grafting initiated by trapped radicals.

In direct or mutual radiation grafting, the polymer substrate and monomer are irradiated directly in the presence of each other. The reaction may be written



(4)

(5)

Here Bq represents the homopolymer of monomer B. $A\frown\cdot$, and $A\overset{\bullet}{\frown}A$ are polymeric free radicals derived from A_p, and $R^\cdot$ is a low molecular weight radical or a hydrogen atom. Reaction (4) is likely to occur if a polymer is of the degrading type. If A_p crosslinks under irradiation, reaction (5) is more likely to occur and this process leads to the formation of an equal number of graft copolymer and homopolymer molecules. In addition the monomer is also radiolysed in the process

$$B \rightsquigarrow R^\cdot \xrightarrow{nB} Bq \qquad (6)$$

Methods (b) and (c) usually occur by means of pre-irradiation (sometimes confusedly referred to as post-irradiation) techniques. The polymer substrate is irradiated first and then placed in contact with the monomer. If the irradiation takes place in oxygen or air the polymer is converted into labile peroxides which, upon thermal decomposition, react with the surrounding monomer. If the polymer is crystalline in nature (so that radical-radical collisions are minimized) grafting may occur via a free radical process. It can be seen that both peroxide and free radical reactions can take place simultaneously.

4. Aspects of Direct Radiation Grafting

(A) G-values* of polymer A_p and monomer B

Consider the following reactions

$$A_p \rightsquigarrow 2P^{\cdot} \quad (\text{or } P^{\cdot} + R^{\cdot}) \tag{7}$$

$$B \rightsquigarrow 2R^{\cdot} \tag{8}$$

Here $P^{\cdot}$ is a polymeric free radical and $R^{\cdot}$ a low molecular weight radical or an atom.

The rates of the above reactions may be written

$$R_{AP} = G_{AP}(A_p)I \tag{9}$$

and $$R_B = G_B(B)I \tag{10}$$

where G_{AP} and G_B are the G radical values (G_R) for the polymer A_p and monomer B respectively, (A_p) and (B) are the concentrations of the polymer A_p and monomer B and I is the exposure dose-rate.

It can be seen that grafting will be favoured with respect to hompolymerization if

(a) $G_{AP} \gg G_B$

(b) $(A_p) \gg (B)$

Thus, in theory, high yields of grafting can be obtained when the G_R value of the polymer substrate is high compared to that of the monomer and if the polymer A_p is present in excess of monomer B.

(B) Energy Transfer

If energy is transferred from the excited polymer to the

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* The G-value is defined as the absolute number of individual chemical events ocurring per 100 electron volts of absorbed energy. (1)

monomer a larger number of free radicals will be formed in the system than expected on the basis of the G_R values. As a result a greater amount of homopolymer will be formed. Similarly if the energy transfer occurs from the monomer toward the polymer the grafting yield will be higher than expected. A more comprehensive discussion of this subject is found in several of the standard texts (1 - 5).

(C) Total Radiation Dose and Dose-Rate

Total radiation dose determines the number of free radicals formed on the polymer substrate and thus the number of branches. Dose-rate affects the rate of initiation of graft copolymerization as shown in equation (9) and thus affects the kinetic chain length and consequently the length of the grafted branches. It should be noted that the length of the grafted branches is also a function of other parameters such as monomer concentration, the reaction temperature, the viscosity of the reacting medium, etc.

(D) The Gel-Effect and Diffusion Effects

In order to reduce the formation of homopolymer in graft copolymerization reactions, a limited amount of monomer is often used. Thus the reaction medium is extremely viscous and the diffusion of polymeric chains and to some extent that of the monomer may become the rate controlling steps. The reduction of the rate of chain termination (e.g., by bimolecular coupling, disproportionation or chain transfer) due to the limited mobility of the growing chains leads to the "gel-effect". The characteristics of the gel effect are

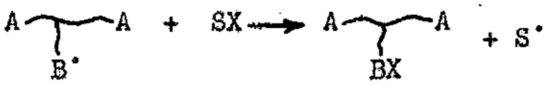
(1) acceleration in the overall rate of reaction

(2) increase in the molecular weight of the polymer
(3) local temperature rises
(4) marked "after effects"

Moreover the rate of diffusion affects the kinetics of grafting. If the rate of graft copolymerization is comparable to or exceeds the rate of diffusion of monomer, the reaction becomes monomer-diffusion controlled. Thus the overall rate of a grafting reaction may increase as the rate of initiation increases but reaches a maximum for some critical initiation rate, and remains constant or decreases upon a further increase.

(E) Chain Transfer

If the monomer or other added substance has a high transfer constant*, chain transfer from the polymer is expected according to the reaction



$$A\underset{B^{\cdot}}{\frown}A + SX \rightarrow A\underset{BX}{\frown}A + S^{\cdot} \qquad (11)$$

$$S^{\cdot} + nB \rightarrow SBn \qquad (12)$$

where SX is the monomer or added substance and X is the most labile atom of SX. This process reduces the grafting yield and increases homopolymerization. On the other hand, the situation may be reversed where transfer occurs pimarily toward the polymer. This process reduces the length of the grafted branches, increases the grafting efficiency and does not affect the grafting yield.

(F) Influence of Grafting Temperature

According to Chapiro (1) the influence of the reaction temperature

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* See Reference 69.

on the kinetics of graft copolymerization is extremely complex and no general rule can be formulated. The following can be said however:

(i) the onset of the gel effect is expected to be delayed with increasing temperature.

(ii) chain transfer is enhanced at elevated temperatures.

(iii) the same is true of the propogation step and consequently an increase in temperature may lead either to an increase or to a drop in the length of the grafted branches depending upon the controlling step.

(iv) the rate of diffusion of the monomer is increased with increasing temperature.

(G) Influence of Added Substances

1. Swelling Agents

In general a swelling agent for the polymer substrate will enhance the diffusion of the monomer into the polymer and hence increase the grafting yield.

2. Solvents

The simplest case of radiation polymerization in a solvent corresponds to a system in which the solvent does not interfere with any of the reaction steps involved and acts solely as an inert diluent for the monomer and polymer. Thus the rate of propagation and the kinetic chain length will be reduced according to equations (9) and (10). This effect is called the "Simple Dilution Effect". However in radiation polymerization no chemical substance is completely "inert" and thus any added substance is radiolysed leading to the production of additional free radicals which may contribute to chain initiation. Thus if the rate reaction for homopolymerization is

$$R_B = (G_s(s) + G_B(B))I \tag{13}$$

where G_s is the G-radical value for the solvent and (s) is the concentration of the solvent, it can be seen that the higher the value of G_s, the higher is the homopolymerization rate. Energy transfer processes in the solvent are also possible. Energy may be transferred from the excited solvent species to the monomer. This would necessarily lead to an increase in the rate of homopolymerization. On the other hand, energy may be transferred to the polymer and thus increase the rate of initiation for graft copolymerization.

If the graft copolymerization is carried out in a medium in which the resulting grafted polymer is not soluble, the growing polymer chains after having reached a critical length either precipitated from the solution to form a second phase or their formation leads to a marked increase in viscosity. This accelerative effect is ascribed to the fact that the growing polymer chains have become sufficiently immobilized (by means of curling up in the precipitating medium) to inhibit their rate of collision and hence of termination after grafting reaction. The overall effect is an increase in the rate of graft copolymerization. This effect has been called a "Trommsdorff-type effect" (6 - 11) and is in many ways similar to the "gel-effect".

5. Structure of Wood

A knowledge of the structure of wood is essential to the understanding of chemical reactions involving this complex material. This can be well appreciated when one realizes that the majority of grafting systems are heterogeneous; thus interface effects and diffusion play an important role in the reaction. A brief description of the microscopic and sub-microscopic structure of wood will be given here. A more detailed analysis of wood and cellulose may be found in several of the better known books in the field (11 - 18).

(A) Gross Structure of Softwoods

Wood is an aggregate of a great number of small cells. The cells of conifers or softwoods generally have their longest axis oriented longitudinally and are made up of long hollow tubular fibres tapered and sealed off at the ends. These fibres which serve for the conduction of sap are known as tracheids. Their length usually ranges from about 2.5 to 7 mm, averaging 3.5 mm. The coniferous tracheids are on the average one hundred times longer than their diameter. The fibre cross sections vary in shape between rectangular and circular. The outside diameter of the cells is on the average about 30 microns. The width of the fibre cavity (or lumen) varies greatly with the variation in specific gravity and is also a function of the period in the growth season during which the fibres were laid down (thicker walls are laid down in summer). As an order of magnitude, softwoods with a swollen specific gravity of 0.4 will have an average lumen width of 26 microns. The fibres or tracheids are arranged in uniform rows in the radial direction from the pith to the periphery but the arrangement is rather random in the tangential direction. Communication between fibres takes place through bordered pits. These pits are circular openings in adjacent cell walls. There are 50 to 300 pits per fibre. The pore diameter of these pits can vary greatly (.02 - 1.0 micron). Softwoods contain resin ducts which are continuous tubes extending in the fibre direction and are randomly located among the tracheid fibres. They are usually clogged with resin and hence are ineffective for the movement of liquids and gases over any appreciable distance. Although most of the units of woods are axially arranged, there are some tubular structures known as wood rays that are oriented radially. Their combined void volume usually ranges from a few per cent up to seven per cent of the total void volume. Communication between wood rays and the tracheids occurs through either half-bordered pits or simple pits. There are two important zones in a tree. The outer zone, known as sapwood, is active in the life process. The sapwood is usually lighter in colour than the inner non-active heartwood. This colour change is due largely to infiltration into the heartwood of various extractable extraneous materials. The deposition of these materials in the pits greatly decreases the permeability through the wood. The permeability through sapwood may be as high as one hundred times greater than through heartwood.

(B) Structure of Cell Walls

Each cell in a tissue is provided with a thin primary wall which surrounds a secondary wall which envelops a lumen or cell cavity (see Figure 1). The layer of intercellular substance between cells is called the "middle

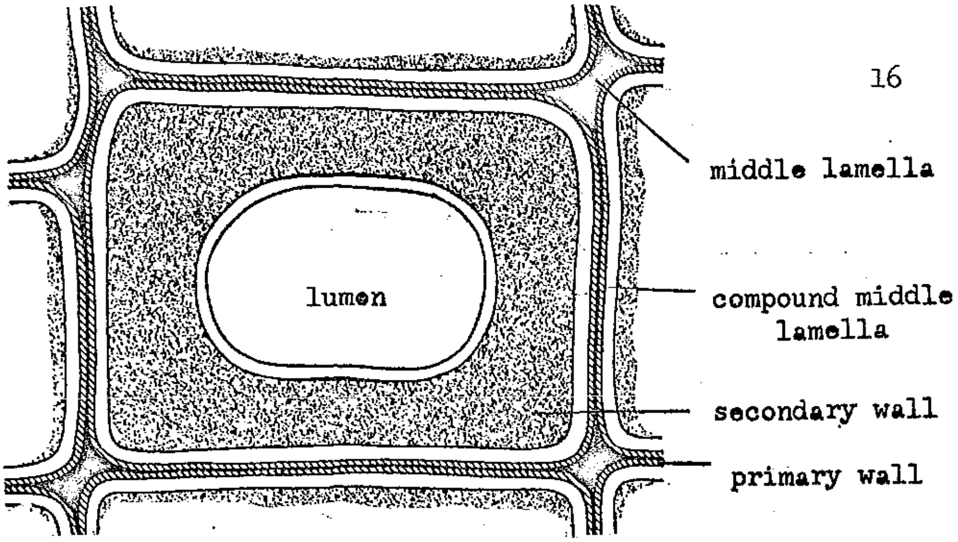

FIGURE 1 Wood Cell
(Textbook of Wood Technology)

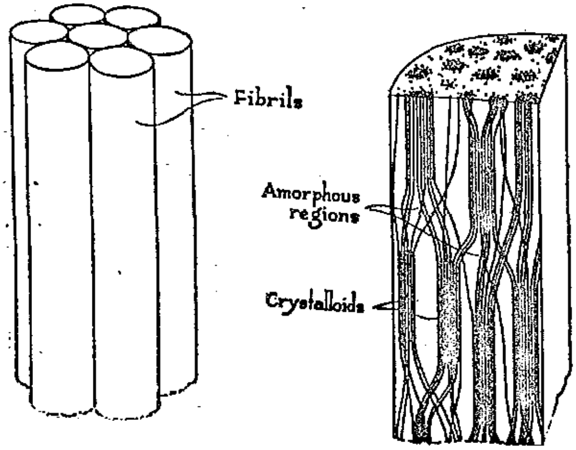

FIGURE 2 Alignment of Cellulose in Fibrils

(Textbook of Wood Technology)

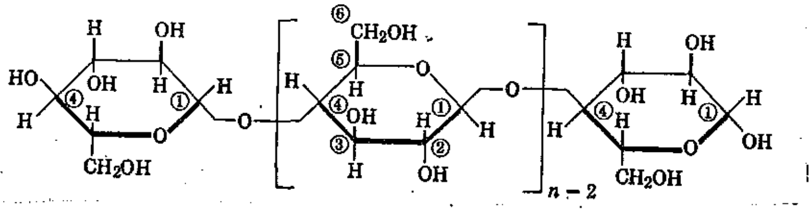

FIGURE 3 Cellulose Macromolecule

(Browning: The Chemistry of Wood)

lamella". It consists chiefly of lignin. The primary and secondary walls of the individual cells are also lignified. The primary wall is so heavily lignified that in reactions it behaves much like the middle lamella. It is for this reason that the primary wall along with the intercellular material is conventionally grouped together as the "compound middle lamella". The secondary wall consists largely of cellulose although some lignin is present. The cellulose lattice structure in this wall is believed to be made up of fine threadlike structures known as "fibrils". (See Figure 2.) These fibrils grade down in diameter from about one micron to beyond the range of visibility of the human eye.

From the ultramicroscopic viewpoint the fibrils of the cell wall are constructed of the polymer cellulose. Its chemical structure consists of a stereoregular chain of anhydroglucose monomer units joined together in the 1 - 4 configuration by primary valences (see Figure 3). The length of one pair of the monomer units is 10.3A°. The length of the entire chain is estimated to be from 4000 - 10,000A°. There may be one hundred or more of these long-chain molecules entering into the structure of a fibril. The pattern of the cellulose occuring in the fibrils is discontinuous (See Figure 2). This is the basis of the Fringe Micellar theory or the Micellar Network theory which states that the long chain molecules are parallel to each other lengthwise only at intervals (crystalline or non-accessible regions). The zones of parallelism (known as micelles or crystallites) alternate with less ordered regions (amorphous or accessible regions). The length of crystallites are in the range 400 - 600A° and the width, approximately 50A°. The width of the spaces between the crystallites vary from 10 - 100A°. There is no sharp distinction between zones of parallelism and amorphous regions. Also there is no connection between the length of the crystalline regions and the molecular chain length; therefore, it is believed that the chain ends do not correspond to the ends of crystallites but rather usually terminate within a crystalline zone. The parallel portions of chain molecules are believed to be held together by strong hydrogen bonds and somewhat weaker van der Waals forces. In the amorphous regions there is less or little linkage between the chain molecules. Thus the amorphous material is always attacked more rapidly than the crystalline material.

(C) Swelling of Wood

The term "swelling of wood" refers to the changes in its dimensions and in its volume resulting from changes in the amount of liquid contained in the cell walls. (It has been shown that the lumen volume stays essentially the same during the swelling process (12 - 14).) As swelling proceeds, liquids, which normally are incapable of entering the structure, can penetrate into the cellulose due to the destruction of the hydrogen bonding and the consequent loosening up of the cellulose structure. Sorption of a solvent on cellulose is dependent upon its ability to form hydrogen bonds and upon its molecular volume (14, 18). Except for extremely strong hydrogen-bonding agents (anhydrous ammonia) the swelling of the cellulose in the secondary wall is restricted to the intercrystalline amorphous regions. Water will produce a swelling of up to 10% depending upon the specific gravity of the wood. Methanol (which is less polar) has about 95% the swelling capacity of water (14). However, methanol can swell wood pulp to only about 60% the value reached by water. Non-polar liquids such as benzene only have negligible swelling power for cellulose. No data are available for styrene but it is assumed that its swelling behaviour is similar to that of benzene.

Specimens with a higher solid content, because they are capable of adsorbing more liquid, exhibit greater volumetric change than do those which are less dense. There appears to be a tendency for the following simple relationship to hold (14):

$$S = f.g. \qquad (14)$$

where S = total volumetric swelling from dry to green condition on a percentage basis

g = specific gravity based on oven-dry conditions

f = fibre-saturation-point on a percentage volume-per-weight basis

LITERATURE SURVEY

1. Effect of High Energy Radiation on Cellulose

A brief summary is given here. A more detailed survey is given in Appendix I.

(a) All types of native cellulose degrade on exposure to high energy radiation.

(b) Strength properties and intrinsic viscosity decrease with increasing dose but appear to be independent of atmospheric conditions or dose rate.

(c) An accelerated decrease in degree of polymerization occurs at dosages above 10^6 roentgens*.

(d) No decrease in crystallinity is noted.

(e) Presence of water appears to have no significant effect on the extent of degradation.

(f) Irradiated dry cellulose exhibits a strong post-irradiation degradation effect which is curtailed by the addition of water.

(g) Exposure of cellulose to irradiation in air produces carbonyl groups, carboxyl groups and chain cleavages in the ratio 19:0.5:1.

(h) Oxygen is consumed in the irradiation of cellulose.

(i) Hydrogen, carbon monoxide and carbon dioxide are evolved during the irradiation.

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* Roentgen: One roentgen corresponds to absorption of 83.8 ergs of energy per gram of air.

2. Graft Copolymerization of Styrene and Cellulose

In 1959 Pan et al (29) attempted to graft acrylonitrile, styrene, methyl methacrylate and 4-vinylpyridine onto cotton yarn by irradiation with high energy electrons. Small weight increases were obtained for acrylonitrile but no grafting was obtained with the other vinyl monomers.

Okamura and co-workers (30) in 1959 reported the radiation grafting of styrene onto rayon, cotton yarn and linen yarn. Dimethyl formamide was used as a swelling agent for cellulose by soaking the latter in a methanol-formamide solution and then centrifuging. The swollen cellulose was then irradiated with CO-60 gamma rays in a solution of styrene-methanol, styrene-acetone, and styrene-benzene. Solutions of styrene-benzene and styrene-acetone were found to retard the radiation-induced grafting whereas the presence of methanol accelerated it. For an irradiation dose of 0.219 Mr (1.4×10^4 r/hr),* maximum grafting occurred after a pretreatment by a 5% formamide solution and when the methanol-styrene solution was 75% styrene. Grafting of up to 1000% (gm. polymer/gm. rayon) was obtained for rayon, but was considerably lower for cotton and linen yarn. The percent grafting obtained for a given dose was found to decrease in the order: rayon $>$ cotton $>$ linen; which is in the order of increasing crystallinity of the three cellulosic materials. With higher radiation dose rates, the reaction appeared to be monomer-diffusion controlled. At lower dose rates, the gel effect of solution polymerization was observed.

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* rad: energy absorption of 100 ergs per gram of material.

Shinora (31) reported the successful grafting of styrene, methylmethacrylate, methyl acrylate, acrylonitrile and vinyl acetate onto cellulose in the form of rayon by the use of the pre-irradiation technique. Rayon was pre-irradiated in air with high energy electrons, then placed in the monomer solution containing water and methanol. The system was then evacuated. The grafting reaction was carried out at temperatures ranging from 30 - 80°C for several hours. For styrene maximum grafting occurred at 40 - 50°C and decreased at higher temperatures. Grafting did not occur when water was omitted from the monomer solution.

Kobayashi (32) in 1961 described the radiation grafting of styrene onto cellulose in the form of rayon using the pre-irradiation technique. The pre-irradiation step was carried out by immersing rayon in water containing hydrogen peroxide and then irradiating with CO-60 gamma rays. The rayon was then placed in a styrene (20%), methanol (72%), and water (8%) solution, evacuated and allowed to react at 50°C. A weight increase of c.a. 700%, half of which was occluded homopolymer, was found.

Demint et al (33) in 1962 published a significant paper discussing the radiation-induced interaction of styrene with cotton. A CO-60 source was used at an intensity of 0.45 M roentgens/hr. On irradiation of a solution of styrene (70%) and methanol (30%) in which cotton cellulose was immersed, the initial rate of polymerization (homopolymer + grafted polymer) was found to be about three times the rate in the absence of cellulose. It was postulated that the presence of radiation excited cellulose increased the rate of free radical formation of styrene and consequently the rate of polymerization of styrene. As the relative concentration of styrene to cotton was increased, the amount of styrene "interacting" with cotton cellulose increased to a weight ratio of about 3.5 to 1, styrene to cotton. Beyond this point the amount of styrene interacting with cotton increased only slightly with increasing concentration of styrene. Methanol was found to be slightly more effective at low concentrations than NN dimethylformamide. The moisture regain, when calculated on the basis of the cellulose contents of the final products, only ranged from 7.5 to 7.2%. This indicates that

(1) the polystyrene probably interacted with only a small fraction of the available hydroxyl groups.

(2) the changes in the chemical properties of the cellulose due to irradiation did not markedly affect the regain values.

(3) there was no marked alteration in the submicroscopic structure of cellulose.

The electron microscographs indicated that the polymer is located within the growth layers of the fibres and "is grafted to the cellulose".

Huang and Rapson (28, 34, 35) made use of the "inclusion solvent exchange" technique for grafting styrene and cellulosic materials. This method consisted of first swelling the cellulose in water and then gradually exchanging the water with methanol, benzene and finally styrene. No grafting was obtained by irradiation of simple cellulose-styrene mixtures without the use of the inclusion method. The amount of styrene grafted onto cotton cellulose was found to depend on the dose and irradiation atmosphere. At low doses, higher grafting was obtained in vacuum than in air. This was attributed to the fact that the oxygen in air acted as a free radical scavenger and inhibited the grafting reaction. At high doses above 2×10^{6} rads, the reverse was true and the presence of air appeared to enhance rather than inhibit the grafting. For cotton cloth, the percent grafting (gm. polymer per gm. cellulose x 100) increased with dose up to a certain point and then levelled off. The largest grafting results were obtained for a nitrogen atmosphere.

A pronounced post-irradiation grafting effect was observed on heat treatment (100°C for 48 hours), leading to a two-fold increase in grafting. This effect was believed to be caused by the residual trapped free radicals and peroxides. Grafting efficiencies (gm. grafted polymer per gm. total polymer x 100) were approximately the same for irradiations in air or in vacuum. Grafting efficiency decreased with increasing radiation dose (74% at 0.25 M rads and 50% at 4 Mrads), and percent grafting. This indicated that more ungrafted polystyrene was formed at high doses.

The structure of the cellulose-styrene graft copolymer was characterized by hydrolyzing the cellulose substrate, isolating the polystyrene chains and determining their molecular weights. The graft copolymer was found to consist of cellulose chains carrying a few very long polystyrene chains rather than many short polystyrene chains. It was estimated that only one in ten to twenty cellulose chains carried a grafted polystyrene chain; or, in other terms, one polystyrene side chain for every 4000 - 10,000 anhydroglucose monomer units. The average molecular weights of the grafted polystyrene side chains were approximately half a million. They were 2 - 3 times higher than the molecular weights of the extracted polystyrene and about twenty times higher than those of polystyrene formed by radiation polymerization of styrene in bulk.

It was found that the solubility properties of the cellulose-styrene graft copolymer were different than those of either cellulose or polystyrene. The graft copolymer was insoluble in solvents for either cellulose or polystyrene.

In 1963 the same authors, Huang and Rapson (36), reported their investigation of the direct radiation graft copolymerization of styrene and cellulosic materials and, in particular, the effect of swelling agents and solvents on the grafting process. Grafting of up to several hundred percent was obtained by controlling the reaction variables of cellulose preswelling, total radiation dose and styrene-solvent composition. The grafting was carried out in air at radiation doses in the range of 0 - 8 Mrads. Grafting occurred readily when the cellulose was first preswollen with a polar swelling agent such as water, formamide, formic acid or dimethyl sulfoxide, then placed in bulk styrene or a styrene-solvent solution and irradiated. The effect of water in the radiation grafting was investigated very thoroughly. In bulk styrene, for a given radiation dose, grafting was found to depend on the water content of the preswollen cellulose. For rayon, grafting increased sharply after 30% water content in rayon, passed through a maximum at 60 - 80% and then decreased again. For cotton cellulose, grafting occurred after 10% water content, increased up to approximately 20% and then remained constant. As in the case of the "inclusion method" experiments, efficiency of grafting was found to decrease with increasing percent grafting and radiation dose. Addition of small quantities of water to the styrene-solvent system was found to be necessary in grafting onto rayon but not onto cotton cellulose. The enhanced grafting obtained by preswelling the cellulose or by carrying out the grafting in solutions containing swelling agents was interpreted in terms of a "plasticizing" effect (37). The swelling agent is assumed to promote the diffusion of styrene monomer by breaking some of the hydrogen bonds and loosening the cellulose chains. Grafting was assumed to take place only in the amorphous (accessible) regions of cellulose.

V. Stannett has published an important series of papers regarding the radiation-induced graft copolymerization of cellulose and vinyl monomers. His research is really a lucid reflection of all the important and relevant work done in this field. In 1960, Stannett, with Chapiro (38), studied the direct radiation grafting of styrene and methyl methacrylate onto polyvinyl alcohol and cellulose.

They irradiated the polymer in a styrene-dioxane solution containing a small amount of water and found that the latter was necessary for grafting to occur. The effect of water was explained in terms of the enhanced diffusion of monomer due to the swelling of the hydrophilic polymer by the water. In radiation grafting onto various forms of cellulose with a total dose of 4.2×10^6 roentgens (dose-rate of 1.8×10^4 roentgens/hr) 210% grafting was obtained for cellophane, 15% for filter paper, 27% for cotton wool and 22% for glassine paper. The difference in grafting values was attributed to different crystallinity of the cellulose used.

In 1962 Stannett (39) investigated the styrene-cellulose acetate system. It was found that on exposure to high energy radiation and subsequent extraction with hot benzene some of the cellulose acetate became solubilized. A large amount of the polystyrene was insoluble in hot benzene. This portion was attributed to the grafted polymer. Fractional precipitation with dilute hydrochloric acid from a pyridine solution indicated that there is a gradual change in the composition of the precipitate from pure polystyrene to pure cellulose acetate. A large portion of the polystyrene formed was occluded.

In 1962 Stannett and Kesling (40) reported a detailed investigation of the pre-irradiation grafting of styrene onto cotton cellulose using gamma rays. The purified cotton was irradiated in vacuum or in air at a dose rate of 0.324 Mr/hr. and then immersed in a solution of styrene (32%), water (4.5%) and dioxane (63.5%). The treatment of the data dealt mainly with the total yield of polymer; viz., occluded and grafted polymer. Water which was added either to the cellulose or to the monomer solution increased the amount of polymerization. The greater polymer yield was presumably due to the greater accessibility of the moist samples to the monomer. The molecular weight of the polymer was similar regardless of the amount of water present. It was believed that, at lower temperatures, polymerization was mainly due to trapped radicals formed during the pre-irradiation. The yield of polymer as a function of time appeared to follow a second order rate process. The effect of temperature on the grafting reaction was studied and revealed that at temperatures above 35°C grafting curves increased upward with time as opposed to levelling off at lower temperatures. This indicated the possibility of a peroxide mechanism at higher temperatures. Iodimetric techniques showed that about six times as many molecules of peroxide as trapped radicals were present for irradiated cotton. The number of peroxide sites increased sharply when the irradiation was carried out in the presence of degassed water. This, along with the fact that the number of peroxide molecules formed was greater at 10^{-4} Torr than the amount of oxygen represented by the residual air, suggested to the authors that the bound water in the cellulose might provide the necessary oxygen. The cellulose-styrene graft copolymers were characterized by acid hydrolysis to remove the cellulose backbone and the molecular weights of the isolated polystyrene side chains were determined. The viscosity average molecular weights of the grafted side chains were found to be very high (ca. $2x10^6$) and remained fairly constant over a wide range of radiation doses.

It is interesting to note that in all of his papers up to 1962 (38 - 40), Stannett always qualified the use of the term "grafting". Up to this time, because of the difficulty of quantitative analysis, he had treated the data (as most investigators have) in terms of the total yield of polymer or the polymer remaining after a simple extraction. This latter technique of removing occluded homopolymer leads at best to only a maximum figure for the amount of grafting onto the substrate. Finally, in 1963, he and coworkers reported an extensive investigation dealing with the characterization of some cellulose graft copolymers (41). The following graft copolymers were prepared by the use of the ceric ion, ultraviolet light, mutual radiation (direct radiation) and pre-irradiation methods: (1) cellulose-acrylamide (2) cellulose acetate-styrene and (3) cellulose acetate-methyl methacrylate. In the radiation methods a CO-60 radiation source with a dose rate of 7,650 and 21,200 r/hr was used. The polymerization solution was made up of 90% distilled styrene monomer and 10% distilled dimethylformamide. The irradiations were carried out at room temperature or dry ice temperature and the polymerizations, in the case of the pre-irradiation method, were allowed to proceed at room temperature. The cellulose acetate-styrene grafts were analyzed by three different methods: (1) fractional extraction after the cellulose acetate was saponified to cellulose (2) fractional precipitation and (3) selective alternate extraction with solvents for the two homopolymers. The first method was used to determine whether grafting had indeed occurred. After saponification the precipitate was washed with methanol and then extracted three times with benzene. The benzene extracts were combined and the extracted polymer isolated by evaporation, weighed and the infrared spectra measured. By comparing physical mixtures of cellulose acetate and polystyrene with products prepared by the above-mentioned methods it was found that (a) complete separation of the mechanical mixture was achieved (b) a small amount of solubilization of the cellulose occurred (presumably by the grafted polystyrene side chains) (c) a considerable quantity of polystyrene was insoluble in benzene, (d) the gamma ray pre-irradiation products showed much more grafting than the ultraviolet products. It was concluded that actual grafting had occurred.

The method of fractional precipitation from solution showed that a clear separation of polystyrene was possible for a physical mixture but the grafted products showed continuous precipitation. The infrared examination of the various fractions showed the gradual change from pure polystyrene to pure cellulose acetate.

The method of selective extraction consisted of alternately extracting the grafted products with benzene and a mixture of 70% acetone, 20% 2-ethoxyethanol and 10% water which are solvents highly specific towards polystyrene and cellulose acetate respectively. This method made it possible to give maximum figures for the efficiency of the grafting process in terms of the percentage of each polymer actually combined in grafted form. With the pre-irradiation method nearly all (approximately 95%) of the polymerized styrene was attached to the cellulose acetate, whereas the mutual radiation and the ultraviolet methods lead to large proportions of occluded polymer (ca. 70% and ca. 60% respectively). These remarks apply to samples already washed free from accessible homopolystyrene. As far as the degree of grafting onto the cellulosic backbone is concerned, for all cases only a small percentage of the cellulose acetate had attached polystyrene side chains (from 1.9% to 13.6%). This was thought due to the lack of accessibility of the cellulose acetate to monomer under the heterogeneous conditions used. The pre-irradiation method gave increased yields when the irradiation was carried out at -78.5°C, presumably due to the prevention of migration and mutual termination of the radicals. Molecular weight measurements were carried out by the viscosity method and it was found that in all cases the grafts consisted of very long polystyrene side chains attached to comparatively short cellulose acetate backbone chains. The molecular weights of the polystyrene branches ranged from 4.37×10^5 to 1.2×10^6 and the number of polystyrene chains per cellulose acetate chain ranged from 0.41 to 3.44.

The method of separation and characterization of cellulose graft copolymers which were developed in the above study have been applied in some detail to the cellulose acetate-styrene grafting system by Stannett et al in 1964 (42). Both heterogeneous and solution grafting were carried out by the mutual radiation technique. The yields and molecular weights of the side chains have been shown to be mutually dependent and governed by the interplay of diffusion controlled growth and termination steps. It was shown that pyridine is a highly suitable solvent since it has a low radical yield on radiolysis compared with, (for example), dimethyl formamide. It also has reduced solvent power. Therefore, the effects on the grafting reaction (of pyridine vs. dimethylformamide) were compared. With thin films where diffusion control should be of less importance, dimethylformamide gave much greater yields of graft than pyridine in a 10% solution, but the situation was reversed with 20% solutions. Here the swelling was very high with dimethylformamide and the grafted side chains were only three times greater than the corresponding solution homopolymer. With thicker films the yield was increased by increasing the percent of either solvent. However, pyridine appeared to be more effective than dimethylformamide. In all cases there was a positive correlation between yields and molecular weights. Since there is virtually no change in radical production on changing from 10 to 30% pyridine, it is believed that the changes in yield were mainly due to molecular weight differences. In this paper Stannett gives an explanation why the participation of the cellulose acetate in the grafting process was so low in his previous investigation (41). One reason is that a low degree of swelling was realized; the other is that small total doses were used.

The Japanese researcher Sakurada and colleagues without question have been the most prolific investigators in the field of radiation-induced grafting reactions with cellulosic materials.

Fortunately their work in the form of six reports has been included in an AE.C. Translation Series (43 - 49).

Report #1

Sakurada and Kimura (43) studied the graft polymerization of styrene to cotton induced by pre-irradiation by electron beam. The average dose rate was ca. $1.5x10^4$ r/sec. Polymerization was mainly carried out under vacuum. The polymerization solution was a system of styrene, methanol and water in a ratio of 6.6:17:6.1. The influence of pre-irradiation dose and temperature of polymerization was investigated while the polymerization time (7 hours) was kept constant. When a dose of 10 Mr was used, the graft rate at 30, 50 and 80°C was 33.5, 224.8 and 108.5 respectively. It was found that when the polymerization time was varied, the graft rate was approximately proportional to the time. Pre-irradiated cotton was thermally treated after irradiation and then allowed to react with the solution at 50°C. The samples which were treated at 60 and 85°C did not show significant interfering effects after treatment of 60 and 15 minutes respectively. When the sample was treated at 180°C for five minutes, graft polymerization was completely absent.

Report #2

The same authors studied the influence of solvent on the grafting process (44). Grafting rates varied greatly with the solvent used: methanol (270%), ethanol (160%), n-propanol (131%), iso-propanol (41%), n-butanol (0%), iso-butanol (0%), sec-butanol (7%), tert-butanol

(8%), n-amylalcohol (0%), acetone (7.4%) and benzene (0%). Experiments were also carried out where samples were placed under vacuum immediately after irradiation, sealed off with polymerization solution and stored at 0°C. No polymerization occurred during storage. When the samples were heated to 50°C after fifty-five days of storage, graft polymerization proceeded in exactly the same fashion as in the case of samples heated immediately after irradiation.

Report #3

Sakurada, Okada and Hatayama (45) studied the effect of temperature and solution concentration in the graft polymerization of styrene onto different types of cellulose using the mutual irradiation technique. For ordinary rayon, when the irradiations were carried out in air, an initial induction period was observed and a tendency toward saturation of the graft rate was evident with high dose rates. The induction period was shorter, the greater the irradiation temperature. The results of the irradiations under a vacuum showed very little difference and no effects due to oxygen were seen. Graft polymerization was practically non-existent when only styrene was used and the graft rate increased with increasing concentration of methanol, approaching a maximum of ca. 50% methanol concentration. The grafting efficiency also approached a maximum at this level. When the temperature during the irradiation was confined between 30 - 80°C, the graft rate increased with increasing temperature approaching saturation near 80°C. The graft efficiency was also better at the higher temperature. A dose-rate effect was also noted and when the dose-rate was varied between $1.1\text{x}10^3$ - $8.1\text{x}10^4$ r/hr with a constant total dose, the graft rate was greater at the lower temperature. The effect of the addition of water to the polymerizing solution was checked with a 1:1 styrene-methanol system. A slight decrease was noted when water was added.

Work was also carried out on other types of cellulose. When ordinary rayon, super rayon, polynoschics and cotton were studied, an induction period was noted in each type and the rate decreased in the order polynoschics, cotton, ordinary rayon and super rayon. No grafting with styrene alone was observed with all the types. The reconstituted fibre showed a maximum graft rate at 50 - 60 percent methanol. The maximum graft rate with cotton came at 70 - 80 percent methanol. The graft rate increased with temperature with all types but the rates for polynoschics* and cotton decreased once the temperature exceeded 60°C. Super rayon showed a sharp increase in rate at 70 - 80°C and no decreasing tendency was seen.

Report #4

Sakurada and coworkers (46) continued their study of the effect of the fine structure of cellulose on grafting. The pre-irradiation method was used with electron beam from a Van de Graff machine. Again the four different types of cellulose were studied. It was found that

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* A highly crystalline form of rayon

there was an optimum temperature for polymerization with each type: 60°C for ordinary rayon; 55°C for super rayon; 50°C for polynoschic rayon and 45°C for cotton. As in the mutual irradiation experiments, water was added to styrene-methanol solutions. The effect of the addition on the grafting rate varied with the fibre type but generally an acceleration was noted. Work was also carried out with hydrogen peroxide solutions and ferrous ion catalysts.

Report #5

Sakurada et al (47) carried out graft polymerizations after pre-irradiation in different atmospheres in order to study the effect of oxygen and moisture on the graft reactions. The same four types of cellulose were studied. The material was irradiated with a 1.5 Mev 100 μa Van de Graff beta beam in air at room temperature and room humidity and the stability of the induced graft activity was checked. The polymerization solution was a styrene-methanol or a styrene-methanol-water mixture. The activity was gradually lost when the material was stored at 22°C in a 65 percent RH atmosphere, but storage in a vacuum at ambiant temperatures or in air at -78°C prolonged the activity considerably. Storage of the samples in a vacuum at elevated temperatures led to a decrease in stability. When PVA was irradiated in a vacuum, it rapidly lost its activity when immersed in water at room temperatures. However, when cellulose was immersed in water at room temperature, the loss in activity was only of the order seen with the storage in 65% RH atmosphere. The stability of the graft activity followed the order cotton > polynoschics > rayons (super and ordinary) and it is believed that the crystallinity and other fine structure properties are intimately related to the degree of stability. When the four types of cellulose were irradiated in air (room humidity), vacuum and dry air, the following results were obtained:

(1) The intensity of graft activity followed the order vacuum > dry air > air. Irradiations in any of the media resulted in graft polymerization.

(2) When cotton and polynoschic rayon were irradiated in any of the three atmospheres, the graft reactions readily took place in non-aqueous media. Higher grafting rates were seen with water-containing solutions.

(3) When ordinary or super rayon were irradiated in air, the graft reaction did not take place in a non-aqueous polymerizing solution; but the reaction was readily promoted in a water-containing solution (styrene-methanol-water in the ratio 20:72:8). On the other hand, when the irradiation was carried out under a vacuum or in dry air, the graft reaction proceeded even in a non-aqueous solution (styrene-methanol in the ratio 20:80). Similarly when these two rayons were irradiated in dry air and then stored at room temperature at 100 percent RH for three days, no grafting occurred.

Report #6

Sakurada, Okada and Hatakeyama (48) continued their study of the effect of solvents on the grafting of styrene onto the previously-mentioned four types of cellulose. They considered the solvents methanol, n-propanol, n-butanol, n-amyl alcohol, 1,4-dioxane, dimethylformamide, dimethylsulfoxide and formamide. Both simultaneous and pre-irradiation methods were used. Briefly, methanol was found to be effective for all types of cellulose while formamide and dimethylsulfoxide were fairly effective. Ethanol, n-propanol, acetic acid and dimethylformamide are effective only to a limited degree. Reactivity according to cellulose types followed the descending order of cotton, polynoschics, ordinary rayon and super strength rayon.

Hayashibe (49) reported an investigation of the graft polymerization of styrene to cellulose. Viscose rayon was pre-irradiated by gamma rays with a dose of 10^5 - 10^7r in air and experiments on graft polymerization in vacuum were carried out. At first, a solution consisting of equal volumes of styrene and one of the solvents methanol, ethanol and acetone with a 3.5 percent addition of water was used. Under fixed conditions the graft rate was greatest for methanol; second for ethanol and smallest for acetone. The above order is also the order of the degree of swelling of rayon in the three solvents.

Next a solution consisting of equal volumes of styrene and methanol with an addition of water from 0 to 5 percent was used for graft polymerization. Almost no graft polymerization was detected in the case of no water. A maximum graft rate was obtained with the addition of water between three and four percent. When the amount of water exceeded five percent, separation of the mixture started. Also the proportion of styrene to methanol was varied, but it was found that the one-to-one ratio gave the highest graft rate. At both polymerization temperatures, 50°C and 80°C, the graft rate was found to be linearly proportional to the dose of pre-irradiation up to a dose of 6×10^6r, after which saturation was reached. The highest attainable graft rate was obtained at 50°C.

Rayon, which was pre-irradiated in air, was stored in a refrigerator for 100 hours in the presence of air, water and methanol. Activation was almost completely preserved when the samples were left in water or methanol. The graft rate of samples left in air and styrene was reduced to one-half. When samples were heated in air for ten minutes at 80°C, grafting did not proceed at 50°C. Samples which were pre-irradiated in water or methanol gave higher graft rates than those pre-irradiated in air.

3. Electron Spin Resonance Studies on Cellulose

A very brief summary is given here. A more detailed survey of electron spin resonance work is given in Appendix II.

(a) Free radicals are formed on the irradiation of cellulose.

(b) The G-value for radical formation is calculated to be around 3, based on radical decay measurements.

(c) As a first approximation the number of radicals formed is proportional to the irradiation dose but independent of the dose-rate.

(d) An increase in dose does not alter the hyperfine structure of the electron spin resonance spectrum.

(e) There are probably two kinds of radicals present in gamma irradiated cellulose.

(f) The decay curves are made up of two regions, consisting of a precipitous fall in the radical concentration followed by a levelling-off region where the radicals are relatively stable, even over periods of several months.

(g) With elevated temperatures the decay of free radicals in dry cellulose requires several days at 70°C, many hours at 100 - 200°C and a few hours at 100 - 200°C.

(h) Fewer free radicals are present in moist cellulose.

(i) When the vacuum of a cellulose sample irradiated at 20°C is broken, a rapid decay of radicals occurs at room temperature until a constant level is reached. Irradiations in air yielded electron spin resonance spectrum very similar to the samples irradiated *in vacuo*.

(j) Free radicals formed in cellulose are unreactive toward SO_2 and this is thought to be due to inter- or intramolecular hydrogen bonding.

(k) The overall rate constant of radical decay is complicated by the fact that the radicals in the amorphous regions have a greater probability of combining than those in the crystalline regions.

(l) Differences in the crystallinity of cellulose have no obvious effect on the initial yield or nature of the radical electron spin resonance sprectrum.

4. Effect of High Energy Radiation on Wood

Saeman and Millett (20) in 1952 studied the degradation of wood pulp (96% cellulose) and spruce wood by the irradiation of a 800KV x-ray machine. The wood pulp degraded in a manner similar to cotton linters. The degree of polymerization for both the wood pulp and cotton linters decreased from about 1000 to 600 at 10^6 roentgens, 200 at 10^7 roentgens and 20 at 10^8 roentgens. The decomposition of carbohydrates for wood pulp and wood were studied by measuring the loss in potential sugar content. The wood pulp decomposed 5 and 17% at a dose of 10^7 and 10^8 roentgens respectively. The wood carbohydrates decomposed only 3 and 9% for the same doses. It was found that irradiation caused an increase in the rate of hydrolysis of the resistant portion, (i.e., the crystalline regions) of the cellulose in wood.

Smith and Mixer (58) in 1959 studied the protective effect of lignin on the holocellulose (cellulose + hemi-cellulose) in wood. It was found that gamma rays did not affect the gross analytical composition in redwood for a dose up to 20 Mrep. For doses of 7 and 20 Mrep, the degree of polymerization of the isolated holocellulose (free from lignin and extractives) decreased from 1377 to 405 and 254 respectively. However, for the holocellulose irradiated <u>in situ</u>, the degree of polymerization decreased to only 548 and 380. In terms of the average chain breaks produced by irradiation, the presence of lignin and extractives reduced the number of breaks from 2.4 to 1.5 (37% reduction) for a dose of 7 Mrep and from 4.4 to 2.9 (34% reduction) for 20 Mrep.

Hachihama and Takamuka (59) in 1960 reported their work on the effect of gamma irradiation on red pine wood meal and Brauns native lignin. The irradiation effects appeared at a dose of 4×10^6 rep. The degree of polymerization of holocellulose isolated from 10^8 rep irradiated wood meal was decreased from 748 to 156. (This represents $748/156 - 1 = 3.8$ average chain breaks.) Chemical, ultra-violet and infrared analysis of the isolated lignins showed that their chemical properties were not changed. The content of p-hydroxylbenzyl alcohol groups in wood was increased by irradiation. This was not observed for Brauns native lignin. Hence it was concluded that the lignin-change behaviour which appeared only in the case of irradiation of wood were caused mainly from the degradation of carbohydrates and the cleavage of the lignin-carbohydrate linkage.

5. Graft Copolymerization with Wood

There are a few published papers dealing with radiation-induced wood-monomer reactions. Most of these have been concerned primarily with the structural nature of the plasticized product (these will be discussed in Part 2). However, one paper by Stannett, Kenaga and Fennessay (60) is significant from a kinetic viewpoint. Ponderosa pine sapwood in the form of wafers (1/4" longitudinal direction, 2" in the tangential direction and 1 3/8" in the radial direction) was treated by the mutual irradiation technique using primarily a solution of dioxane-styrene-water in the volume ratio 75:25:5.75 respectively. Low vacuum (5 to 6 mm Hg) and high vacuum (10^{-4} to 10^{-5} mm Hg) techniques were used to degas the wood and monomer. A solvent displacement method was also used in which the water which had been soaked into the wood was displaced by an acetone-styrene solution. This was followed by acetone evaporation prior to irradiation. The total time of operation was more than six days. Experiments were carried out in which the dose rate was varied. It was found that there was a rapid drop in the efficiency of gamma radiation as an initiator for the styrene grafting-homopolymerization reaction as the dose rate was increased. This was attributed to the fact that the diffusion of monomer from the lumen into the cell wall was the controlling step. As the wafers were only 0.25 inches thick in the longitudinal direction, almost every cell lumen was open to the external solution; thus, diffusion into the cell cavity from the external solution should not retard the reaction. This expectation was experimentally confirmed by varying the wafer thickness from 0.06" to 0.25". Although the efficiency per unit of radiation decreased with dose rate, this decrease was not rapid enough to offset the effect of total dose delivered in unit time. Thus the result was a steady increase in the polymer retention per unit time as dose rate was increased. By leaching the irradiated impregnated wafer for twenty-four hours with dioxane, 20 - 30% of the polystyrene could be removed. A further 9 - 14% could be removed by chipping and grinding. It was found that there was little difference between the high and low vacuum methods with respect to retention of styrene at dose levels above 1.7 Mrads. At low dose levels the high vacuum technique gave higher retentions. It is believed that oxygen inhibits the reactions at low doses but, at high dose levels, the oxygen is depleted. Several solvent-styrene systems were tested to determine the effect of varying the solvent concentration. A solution of ethanol-water appeared to give the highest retention at a given dose rate. However, 82% of the polystyrene formed was homopolymer compared to 26% for the dioxane-styrene-water solution.

PREVIOUS WORK DONE ON THIS PROJECT

1. Hodgins and Ramalingam (61, 62)

In this study the researchers carried out preliminary work dealing with

(a) a study of conditions for the treatment of wood with styrene to obtain graft copolymerization and the assessment of the physical properties of the treated material.

(b) a study of the transient species responsible for graft copolymerization using the Electron Spin Resonance technique.

The structural aspects of this work will be discussed in PART 2 of this thesis.

The experimental method consisted of (1) evacuating a sample of wood (16" x 3/4" x 3/4") to the micron level for twelve hours (2) impregnating this sample with a styrene solution under a pressure of 35 psig by means of nitrogen gas for a period up to thirty-six hours (3) irradiating the sample in the McMaster swimming pool reactor at a dose rate of ca. 9×10^5 rads/hr (4) heating the sample for twenty-four hours at a temperature of 105°C (5) grinding the final dry treated sample to 40 Mesh in a Wiley mill (6) extracting the wood flour to constant weight in a Soxhlet extractor using benzene as a solvent.

Experiments were carried out with pure styrene, solutions of styrene, methanol and water, solutions of styrene and methanol, and solutions of styrene, methanol and water with a small amount of

TABLE 1

BENZENE EXTRACTION OF POLYMER (after Ramalingam)

Solution (wt %)	Irradiation (Mr)	Polymer Extracted*	Solution	Irradiation (Mr)	Polymer Extracted*
Pure Styrene	nil	94.0	52% Styrene 43.5% Methanol 4.5% Water	9.0	21.4
	4.5	90.5		14.4	23.0
	9.0	85.4		18.9	19.1
	14.4	72.6	30% Styrene 61% Methanol 9% Water	4.5	4.8
	18.9	52.0		9.0	5.7
76% Styrene 22.5% Methanol 1.5% Water	4.5	19.1	76% Styrene 22.5% Methanol 1.5% Water	nil	62.8
	9.0	20.1		nil	63.0
52% Styrene 43.5% Methanol 4.5% Water	1.35	24.8	76% Styrene 22.5% Methanol 1.5% Water + 0.2% Benzoyl Peroxide	nil	81.2
	2.70	20.3		nil	81.8
	4.5	19.0	54% Styrene 46% Methanol	9.0	26.8
77.5% Styrene 27.5% Methanol	9.0	26.4	33.5% Styrene 66.5% Methanol	9.0	14.8

Thermal treatment in all cases: 105°C for 24 Hours

* Weight of polymer extracted per 100 grams of polystyrene formed, per 100 grams of dry wood

chemical initiator, benzoyl peroxide, added. The dose was varied from nil to 18.9 Mrads. The results are summarized in Table 1. The following conclusions were drawn from the results.

(1) For the case of pure styrene, little grafting had occurred. This suggests that the styrene was not penetrating into the cellulose in wood. (The correlation between dose and polymer extracted, as shown in Table 1, will be discussed later.)

(2) For the case of a styrene-methanol-water solution, there was a considerable decrease in the amount extracted compared to the pure styrene-treatment. Thus it was concluded that grafting of polystyrene with cellulose took place when the styrene was able to diffuse to cellulose in wood.

(3) Thermal polymerization without radiation initiation resulted predominantly in homopolymerization.

(4) Runs that were carried out in the absence of water (styrene and methanol only) showed that the amount of extractable polymer was approximately 50 to 100% greater than for the case where 1.5 - 4.9% water was used.

The Electron Spin Resonance results indicated that free radicals were formed in the irradiated wood. Quantitative measurements indicated that the number of free radicals present one hour after an irradiation of approximately 10 Mr was around 10^{18} per gram. Continual radical measurements after irradiating the wood sample in air showed that the concentration dropped off rapidly in the first three hours and then decreased more slowly for several days. It was also observed that by heating the irradiated wood at 105°C a more rapid decrease in radical concentration occurred.

2. Hodgins and Werezak (54, 62)

In this research work, the following study was carried out:

(a) Using bending strength as the dependent variable, a two-factorial experimental design was set up with the following six variables: time of evacuation, composition of impregnant, uptake of impregnant, total gamma dosage, duration of the heating treatment and temperature of the heating treatment. (This work will be discussed in detail in PART 2 of this thesis.)

(b) A qualitative and quantitative analysis of free radicals using Electron Spin Resonance Spectrometry was carried out with the following materials:

(i) wood irradiated in air
(ii) air dried cellulose, Spruce-Periodate lignin, Dioxane lignin and Braun's Native lignin irradiated in air
(iii) impregnated wood and α-cellulose irradiated *in vacuo*
(iv) wood irradiated *in vacuo*

The results of the Electron Spin Resonance study are summarized below.

1. Air dried wood, Spruce Periodate lignin and Dioxane lignin gave similar Electron Spin Resonance spectra on irradiation.

2. Similar to the work of Abraham and Wiffen (50), wood

maintained a symmetrical double spectrum throughout the time interval measured.

3. Wood irradiated with a smaller dose yielded fewer free radicals but a similar radical spectrum.

4. Irradiation of air-dry α-cellulose gave a persistent spectrum indicative of a 3 peaked absorption.

5. Irradiation of Braun's lignin yielded a broad complex spectrum with decay characteristics suggesting the production of more than one type of free radical.

6. For wood impregnated with acrylonitrile, styrene or a ternary solution of styrene-methanol-water, the first derivative of the absorption curves was similar to those observed for wood-in-air. The same results were found for α-cellulose.

7. No difference in Electron Spin Resonance spectrum was obtained for samples of wood irradiated in vacuo (10^{-6} mm Hg) and that irradiated in air indicating that the decaying radicals are not peroxides.

8. The decay curve for wood in air appeared more rapid than either the α-cellulose or the lignins.

9. Wood irradiated in air appeared to have two and possibly three distinct decay regions. The first region involved the decay of more than half of all radicals formed. This region, which appeared to terminate about three hours after irradiation, was followed by a more gradual decay which persisted for approximately

120 hours. From this point the radicals appeared to be almost stable.

10. Per gram of sample, α-cellulose irradiated in air gave slightly fewer radicals immediately after irradiation than did wood. However, its slower decay rate resulted in a higher radical count 3 to 22 hours after irradiation.

11. For the lignins, the number of radicals produced on irradiation was lower by a factor of eight or more, than for a comparable amount of wood.

12. In general, the decay rate of radicals present in wood irradiated with styrene or acrylonitrile <u>in situ</u> was similar to the decay rate when wood was untreated.

13. With the ternary solution as impregnant, the initial rapid decay was not observed and the initial radical concentration was reduced by as much as a factor of eight.

14. All experiments with wood appeared to yield similar radical counts after approximately 100 hours.

15. The irradiation of α-cellulose in the presence of an impregnant gave radical decay curves very similar to those for α-cellulose in air.

16. The irradiation of wood <u>in vacuo</u> gave a decay system which maintained a high radical concentration over a long interval. When air was admitted to the wood the radical decay was greatly accelerated after an induction period of approximately an hour. This indicates that the radicals being measured are not due to

thermally decomposing peroxides.

3. Analysis of Unpublished Work by Werezak

(A) Introduction

As mentioned previously, PART 1 of Werezak's research program consisted of carrying out an optimization of the bending strength of wood with respect to six variables. It will be shown in PART 2 of this thesis that the factorial design was erroneously interpreted. Despite this, many important kinetic aspects of the graft copolymerization of wood and polystyrene can be extracted from the unpublished data of this worker. The experimental procedure used was essentially that used by Ramalingam (see Page 45) except that

(1) The dose rate used was 1 Mrad/hr.

(2) Three different impregnating solutions were used. The ratios of styrene to methanol to water for these were 76:22.5:1.5, 65:32:3 and 54:42:4.

(3) Evacuation time for the wood prior to impregnation was varied from 10 to 24 hours.

(4) The time of impregnation was varied from 8 minutes to 65 minutes, and the pressure of impregnation was varied from atmospheric to 35 psig.

(5) The total gamma dose was varied from 3.5 to 5 Mrads.

(6) The temperature of the heating treatment was varied from 75 to 105°C.

(7) The duration of the heating step was varied from 9 to 24 hours.

The results are summarized in Tables 2 - 20.

(B) Definitions

1. Specific Gravity

This term is the specific gravity of the wood samples before treatment. It is based on the oven-dried wood (wood dried to a constant weight at a constant temperature of 105°C). Unfortunately, the weight at room conditions and not the oven-dry weight was measured by Werezak. However, based on the average moisture content of red pine wood at room temperature (calculated as 6.15% for 50 samples), the oven-dry weight can be estimated.

2. Monomer Uptake (gms styrene/cc of wood)

This quantity is the weight of styrene taken up by the wood divided by the volume of the wood. For example, if 100 cc of wood took up 100 gms of the solution 76:22.5:1.5 (styrene, methanol, water ratio), this term would be 0.76.

3. Polymer Retention (gms polymer/cc of wood)

This term represents the weight of the polymer remaining in the wood after the treatment divided by the original volume of wood. The weight of polymer was deduced from the difference of the weight of the final treated sample and the original weight of the oven-dried wood (estimated).

4. Retention Efficiency

This term is the ratio of the ultimate weight of polymer divided by the weight of styrene originally taken up by the wood sample. Hence it is a measure of the efficiency of polymerization (grafted + homopolymer) or retention.

5. Percent Retention (gms of polymer/gms of wood)

The percent retention is the weight of ultimate polymer divided by the weight of the wood substrate. This term has very little fundamental significance when one is dealing with a heterogeneous material like wood. However, it has been included for its usefulness in comparison with a similar term found throughout the literature, often called percent grafting.

6. Associating Efficiency

This term represents the amount of polymer remaining in a treated sample of wood after extraction with hot benzene divided by the amount of polymer before extraction. If the extraction with benzene were able to remove all homopolymer (polymer not chemically bound to the wood substrate), this term would be a measure of the grafting efficiency of the treatment. However, in conformity with the superb work carried out by Stannett (38 - 42), we shall assume that the unextractable polymer is made up of grafted polystyrene and polystyrene chains entangled within the cellulose network. This unextractable polymer can conveniently be called "associated polymer". It should be noted that this term is different from that used by Werezak (54).

(C) Results

1. Dose, Temperature and Time of Heating

The three independent variables, dose, temperature of the

TABLE 2

Experiment 2

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene, Methanol, Water

EVACUATION LEVEL: 1.5 Microns

DOSE: 4.5 Mr

TIME OF EVACUATION: 12 Hours

TEMPERATURE: 105°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 24 Hours

TIME OF IMPREGNATION: 36 Hours

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.389	.570	.431	1.125	.758	111.0	.756
.372	.546	.410	1.02	.750	110.0	.676
.438	.509	.356	1.145	.700	81.2	----
.419	.520	.420	1.13	.807	100.0	----
.433	.486	.380	1.13	.782	87.6	----
.439	.501	.388	1.13	.774	88.4	----
.435	.472	.341	1.11	.722	78.3	----
.440	.492	.379	1.11	.772	85.6	----
Average Values						
.421	.511	.388	1.12	.758	92.7	----

TABLE 3

Experiment 3

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene, Methanol, Water

EVACUATION LEVEL: 2 Microns

DOSE: 4.5 Mr

TIME OF EVACUATION: 12 Hours

TEMPERATURE: 105°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 24 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.388	.555	.433	1.22	.780	111.5	----
.400	.539	.375	1.13	.696	92.6	----
.358	.545	.425	1.20	.780	119.0	----
.358	.540	.431	1.18	.800	120.0	----
.370	.527	.416	1.20	.785	105.7	----
.360	.520	.411	1.17	.789	105.0	----
Average Values						
.372	.537	.415	1.18	.772	109.0	----

TABLE 4

Experiment 4

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene, Methanol, Water

EVACUATION LEVEL: 1 Micron

DOSE: 4.5 Mr

TIME OF EVACUATION: 12 Hours

TEMPERATURE: 105°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 24 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.528	.454	.394	1.08	.869	74.5	.632
.541	.455	.397	1.06	.872	72.1	.667
.560	.460	.411	1.06	.894	75.0	.660
.545	.489	.390	1.06	.798	71.5	.646
.514	.481	.421	1.065	.875	85.0	.674
.488	.498	.431	1.09	.865	91.3	.629
Average Values						
.529	.472	.407	1.07	.862	78.0	.651

TABLE 5

Experiment 5

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene, Methanol, Water

DOSE: 3.5 Mr

TEMPERATURE: 85°C

TIME OF HEATING: 24 Hours

EVACUATION LEVEL: 1 Micron

TIME OF EVACUATION: 12 Hours

PRESSURE OF IMPREGNATION: 35 psig

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.508	.486	.484	1.11	.995	95.0	.654
.489	.497	.447	1.04	.900	95.0	.732
.468	.511	.500	1.08	.977	107.5	.705
.463	.510	.508	1.15	.996	109.5	.650
.446	.525	.545	1.13	1.04	122.0	.714
.469	.539	.526	1.17	.978	116.5	.716
Average Values						
.474	.511	.501	1.11	.981	107.6	.695

TABLE 6

Experiment 6

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene, Methanol, Water

EVACUATION LEVEL: 30 Microns

DOSE: 3.5 Mr

TIME OF EVACUATION: 12 Hours

TEMPERATURE: 85°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 24 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.392	.448	.430	1.13	.960	109.0	.843
.394	.452	.475	1.19	1.05	120.0	.814
.410	.454	.460	1.20	1.01	112.0	.847
.411	.450	.500	1.19	1.11	122.0	.794
.419	.450	.487	1.19	1.07	116.5	.780
.405	.445	.488	1.15	1.09	121.0	.761
Average Values						
.405	.450	.473	1.175	1.05	116.0	.807

TABLE 7

Experiment 7

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene,
Methanol, Water

EVACUATION LEVEL: 9 Microns

DOSE: 3.5 Mr

TIME OF EVACUATION: 10 Hours

TEMPERATURE: 85°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 12 Hours

TIME OF IMPREGNATION: 10 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.370	.460	.455	1.19	.988	123.0	.862
.398	.444	.444	1.14	.998	111.5	.455*
.405	.425	.425	1.13	1.00	105.0	.771
.378	.450	.386	1.13	.855	102.0	.720
.408	.432	.448	1.12	1.04	110.0	.805
.404	.418	.444	1.14	1.06	110.0	.785
Average Values						
.394	.435	.434	1.14	.998	110.2	.789

* Reject

TABLE 8

Experiment 8

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene,
Methanol, Water

EVACUATION LEVEL: 8 Microns

DOSE: 4.5 Mr

TIME OF EVACUATION: 12 Hours

TEMPERATURE: 105°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 12 Hours

TIME OF IMPREGNATION: 8 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.426	.439	.464	1.19	1.06	108.5	.778
.412	.431	.454	1.24	1.07	110.0	.740
.444	.406	.395	1.19	.970	89.0	.239*
.444	.413	.387	1.19	.939	87.0	.716
.443	.422	.416	1.215	.985	96.0	.742
.424	.421	.415	1.19	.990	98.0	.743
Average Values						
.432	.422	.422	1.20	1.00	98.1	.744

* Reject

TABLE 9

Experiment 9

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene, Methanol, Water

EVACUATION LEVEL: 9 Microns

DOSE: 4.5 Mr

TIME OF EVACUATION: 10 Hours

TEMPERATURE: 105°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 24 Hours

TIME OF IMPREGNATION: 67 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.387	.459	.475	1.19	1.04	123.0	.822
.390	.459	.465	1.19	1.01	119.0	.791
.392	.464	.438	1.23	.947	112.0	.768
.403	.451	.445	1.19	.985	110.0	.772
.396	.467	.455	1.19	.970	115.0	.788
Average Values						
.394	.460	.456	1.20	.990	116.8	.788

TABLE 10

Experiment 10

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene, Methanol, Water

EVACUATION LEVEL: 5 Microns

DOSE: 5 Mrads

TIME OF EVACUATION: 11.5 Hours

TEMPERATURE: 75°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 9 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.411	----	.415	1.17	----	100.5	.649
.411	----	.418	1.19	----	101.5	.654
.405	----	.425	1.14	----	105.0	.655
.399	----	.394	1.16	----	94.5	.648
.410	----	.357	1.15	----	87.0	.573
.339	----	.490	1.17	----	144.0	.639
Average Values						
.396	----	.417	1.16	----	105.4	.636

TABLE 11

Experiment 11

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene, Methanol, Water

EVACUATION LEVEL: 4 Microns

DOSE: 5 Mr

TIME OF EVACUATION: 13.5 Hours

TEMPERATURE: 75°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 21 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.448	----	.522	1.125	----	116.5	.688
.453	----	.571	1.10	----	125.5	.745
.448	----	.508	1.15	----	113.0	.683
.448	----	.485	1.125	----	108.0	.693
.445	----	.489	1.125	----	109.5	.707
.416	----	.509	1.15	----	122.0	.686
Average Values						
.443	----	.510	1.13	----	115.8	0.700

TABLE 12

Experiment 12

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene, Methanol, Water

EVACUATION LEVEL: 4 Microns

DOSE: 4 Mr

TIME OF EVACUATION: 13.5 Hours

TEMPERATURE: 95°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 9 Hours

TIME OF IMPREGNATION: 60 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.435	----	.341	1.17	----	78.2	.332*
.415	----	.356	1.12	----	85.6	.616
.436	----	.304	1.14	----	69.9	.579
.439	----	.294	1.10	----	67.0	.589
.420	----	.245	1.10	----	58.4	.541
.363	----	.523	1.21	----	144.0	.708
Average Values						
.418	----	.344	1.14	----	83.9	.607

* Reject

TABLE 13

Experiment 13

GRAFTING VARIABLES

SOLUTION: 65:32:3 Styrene, Methanol, Water

EVACUATION LEVEL: 2 Microns

DOSE: 4 Mr

TIME OF EVACUATION: 11.5 Hours

TEMPERATURE: 95°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 21 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.469	----	.475	1.21	----	101.0	.695
.465	----	.529	1.37	----	114.0	.725
.454	----	.441	1.17	----	97.3	.702
.471	----	.505	1.20	----	107.0	.705
.466	----	.464	1.21	----	99.7	.680
.460	----	.427	1.24	----	92.7	.707
Average Values						
.464	----	.474	1.23	----	102.0	.702

TABLE 14

Experiment 14

GRAFTING VARIABLES

SOLUTION: 54:42:4 Styrene, Methanol, Water

EVACUATION LEVEL: 1 Micron

DOSE: 4 Mr

TIME OF EVACUATION: 11.5 Hours

TEMPERATURE: 75°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 9 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.400	----	.565	1.19	----	141.0	.767
.430	----	.508	1.19	----	119.0	.742
.415	----	.587	1.19	----	141.0	.768
.430	----	.574	1.24	----	133.5	.805
.419	----	.560	1.16	----	133.5	.758
.434	----	.588	1.21	----	136.0	.764
Average Values						
.423	----	.563	1.20	----	134.0	.767

TABLE 15

Experiment 15

GRAFTING VARIABLES

SOLUTION: 54:42:4 Styrene, Methanol, Water

EVACUATION LEVEL: 8 Microns

DOSE: 4 Mr

TIME OF EVACUATION: 13.5 Hours

TEMPERATURE: 75°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 21 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.376	----	.628	1.17	----	166.5	.803
.428	----	.487	1.17	----	116.0	.728
.430	----	.343	1.14	----	79.8	.680
.439	----	.334	1.12	----	76.1	.674
.452	----	.262	1.14	----	58.0	.632
.437	----	.337	1.12	----	77.3	.656
Average Values						
.427	----	.399	1.14	----	95.6	.696

TABLE 16

Experiment 16

GRAFTING VARIABLES

SOLUTION: 54:42:4 Styrene, Methanol, Water

EVACUATION LEVEL: 1 Micron

DOSE: 5 Mr

TIME OF EVACUATION: 13.5 Hours

TEMPERATURE: 95°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 9 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.469	----	.399	1.125	----	85.1	.673
.476	----	.406	1.14	----	85.4	.705
.475	----	.411	1.125	----	86.8	.675
.474	----	.460	1.19	----	97.1	.686
.479	----	.468	1.19	----	98.1	.701
.484	----	.450	1.17	----	92.8	.709
Average Values						
.476	----	.432	1.16	----	90.9	.692

TABLE 17

Experiment 17

GRAFTING VARIABLES

SOLUTION: 54:42:4 Styrene, Methanol, Water

EVACUATION LEVEL: 1 Micron

DOSE: 5 Mr

TIME OF EVACUATION: 11.5 Hours

TEMPERATURE: 95°C

PRESSURE OF IMPREGNATION: 35 psig

TIME OF HEATING: 21 Hours

TIME OF IMPREGNATION: 65 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.376	----	.381	1.17	----	99.5	.687
.358	----	.377	1.10	----	105.0	.691
.372	----	.383	1.14	----	103.0	.704
.376	----	.366	1.10	----	96.5	.683
.396	----	.358	1.06	----	89.9	.688
.414	----	.367	1.06	----	88.2	.655
Average Values						
.382	----	.382	1.12	----	97.0	.685

TABLE 18

Experiment 18

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene,
Methanol, Water

DOSE: 3.5 Mr

TEMPERATURE: 105°C

TIME OF HEATING: 12 Hours

EVACUATION LEVEL: 0.4 mm

TIME OF EVACUATION: 12 Hours

PRESSURE OF IMPREGNATION: Atmospheric

TIME OF IMPREGNATION: 10 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.510	.258	.239	1.07	.927	46.9	.560
.518	.362	.287	1.12	.794	55.5	.594
.477	.164	.151	1.06	.921	31.7	.340
.429	.178	.187	1.085	1.05	42.5	.423
.419	.438	.398	1.21	.909	96.1	.698
.402	.506	.479	1.24	.945	119.0	.660

TABLE 19

Experiment 19

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene, Methanol, Water

DOSE: 3.5 Mr

TEMPERATURE: 105°C

TIME OF HEATING: 12 Hours

EVACUATION LEVEL: 10 Microns

TIME OF EVACUATION: 10 Hours

PRESSURE OF IMPREGNATION: Atmospheric

TIME OF IMPREGNATION: 35 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.421	.239	.216	1.08	.905	51.4	.449
.428	.186	.176	1.085	.947	41.1	.474
.432	.223	.198	1.06	.889	46.0	.569
.440	.257	.224	1.08	.873	51.1	.631
.450	.236	.228	1.08	.967	50.7	.564
.417	.359	.340	1.165	.947	81.5	.650

TABLE 20

Experiment 20

GRAFTING VARIABLES

SOLUTION: 76:22.5:1.5 Styrene, Methanol, Water

EVACUATION LEVEL: 3 mm

DOSE: 3.5 Mr

TIME OF EVACUATION: 10 Hours

TEMPERATURE: 85°C

PRESSURE OF IMPREGNATION: Atmospheric

TIME OF HEATING: 24 Hours

TIME OF IMPREGNATION: 10 Minutes

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Ultimate Volumetric Change	Retention Efficiency	Percent Retention	Associating Efficiency
.414	.306	.360	1.11	1.18	87.4	.625
.454	.153	.176	1.08	1.15	38.8	.351
.421	.431	.496	1.22	1.15	117.5	.698
.404	.438	.471	1.195	1.08	117.0	.673
.406	.421	.440	1.15	1.04	108.5	.667
.404	.448	.536	1.19	1.19	132.5	.673

TABLE 21

EFFECT OF SOLUTION

SOLUTION: styrene:methanol:water ratio	76:22.5:1.5	65:32:3	54:42:4
Reference	Tables 2-5	Tables 6-13	Tables 14-17
Number of Samples	26	47	24
Average Specific Gravity	0.440	0.418	0.427
Average Void Volume of Dry Wood: cc's void per cc of wood	0.702	0.722	0.715
Density of Solution gm/cc	0.875	0.866	0.855
Total Solution Uptake Gms of solution/cc of wood	.665	.690	.821
Estimated Volume of Solution in Wood $\frac{\text{cc of solution}}{\text{cc of wood}}$	.761	.797	.961
$\frac{\text{Estimated Volume of Solution in Wood}}{\text{Average Void Volume of Dry Wood}}$	1.08	1.10	1.34
Monomer Uptake gm styrene/cc of wood	0.505	0.448**	"0.444"
Polymer Retention gm polymer/cc of wood	0.425	0.441	0.444
Retention Efficiency	0.836	0.984	"1.00"
% Retention gm polymer/gm of wood	96.6	110.3	104.4
Ultimate Volumetric Change cc's of final sample per cc of original wood	1.13	1.17	1.16
Associating Efficiency	.679*	.721	.710
Estimated Variance of Associating Efficiency: S^2	.00159	.00577	.00183

* based on 14 samples

** based on 23 samples

heating treatment and the duration of the heating treatment, undoubtedly affect the dependent variables; (e.g., % retention, retention efficiency, etc.). However, a close analysis of the results, as summarized in Tables 2 - 20, will reveal that the range of these variables is such that the effect of the upper and lower limits is essentially equivalent. That is, the doses 3.5 Mrads and 5.0 Mrads affect the dependent variables in the same manner. Similarly, the same is true of the temperatures in the range 75 - 105°C and the time of heating in the range 9 - 24 hours. It is believed that the total doses are such that enough free radicals are generated at the 3.5 Mr level to have complete polymerization. Heating in the range 75 - 105°C for any period of time from 9 - 24 hours will almost entirely gelate the system.

2. Effect of Solution

The effect of varying the ratio of styrene, methanol and water on the various dependent variables is shown in Table 21, which is a synopsis of Tables 2 - 17.

The average void volume was calculated on the basis of a wood-substance density of 1.50 gm/cc. (The density of cell-wall substance is fairly constant in all kinds of wood.)

The ratio of the volume of the solution taken up to the void volume of the dry wood was included in Table 21 for the following reason: when wood absorbs a non-polar compound like benzene, the maximum volume of liquid that could be taken up is the void volume of the wood. On the other hand, when wood is placed in a humid environment, the cell walls are saturated first (fibre saturation point), after which time the cell cavities begin to fill. This indicates that if wood absorbs a greater volume than the void volume, sorption into the cellulose itself has taken place. For example, if the ratio of volumes is 1.05 we know that sorption into the walls has occurred. However, it should be noted that the cell cavities need not necessarily be totally filled in order to obtain this ratio, for the walls may be completely saturated and the cavities only partially filled.

Unfortunately the weights of samples for the experiments using the 54% styrene solution (Tables 14 - 17) were not taken immediately after impregnation and therefore for these runs the retention efficiency could not be calculated. However, based on this author's work, it is assumed that 100% of the monomer taken up was polymerized.

(A) Solution and Monomer Uptake

As mentioned previously, there are two distinct regions in which solution uptake can take place -- the cell cavities and the cell walls. Due to the prevalence of hydrogen bonding, the cell walls can be penetrated only by polar compounds and hence the penetration of styrene into the cell wall is dependent upon the amount of water and methanol present in the solution. It is seen from Table 21 that the volume of solution uptake is increased as the proportion of methanol and water is increased. For the experiments using the 76:22.5:1.5 styrene, methanol and water solution (hereafter referred to as the

76% treatment), the wood takes up 8% more solution than the cell cavities theoretically can accommodate. Similarly for the 65% and 54% treatments, this value is 10% and 34% respectively. Hence, one, two, or all of the three components of the solution have diffused at least partially into the cell wall. It is also probable that the more methanol and water in a solution, the greater is the sorption into the wall (but not necessarily in the ratio 8:10:34 for the three solutions because the cell cavities may not be filled to the same extent). It is also evident that although the solution uptake is greater for the 65% and 54% treatments than for the 76% treatment, the monomer uptake is less.

(B) Retention Efficiency and % Retention

It appears that for the 76% treatment, about 16% of the monomer taken up by the wood has not been converted to either homo- or grafted polymer whereas for the other treatments, 100% conversion has been realized. This can be explained by the effect of methanol. Methyl alcohol has a G_R value of ca. 10 (1) as compared to 0.69 for styrene. Thus, an increase in polymerization will be caused by the radiolysis of methanol into free radicals which are capable of initiating homopolymerization. This sensitization effect of methanol has been found by several workers (1, 6 - 11, 28, 33, 44, 45, 48, 49). The effect of water, per se, has been found to have no effect on the polymerization of styrene (28, 40). In comparing the three treatments, it is seen that more monomer is taken up by the wood in the 76% treatment but less is converted into polymer. This cancellation of effects results in approximately the same amount of polymer retained in all samples; i.e., .422, .441 and .444 gm/cc for the 76, 65 and 54% treatments respectively.

The % retention is a function of the retained polymer and the original weight of the wood. Since the retained polymer and the specific gravity are both based on the volume of the original wood, the % retention is simply the ratio of the former to the latter. The results show that approximately 50% of the final treated sample is polymer and 50% is wood.

(C) Ultimate Volumetric Change

Red pine wood, when saturated with water will swell about 11.6%. (This value was calculated from the experimental work carried out by Werezak in which 67 oven-dry wood samples were soaked in water for one month.) It is thus surprising that the ultimate volumetric change of the wood swollen with polymer is larger than this value. The change ranges from 13% for the 76% treatment to 17% for the 65% treatment. It appears that the larger styrene molecules which have penetrated into the walls with the aid of the swelling agents (methanol and water) are capable of swelling wood to a greater extent than water. This phenomenon has also been observed by Kenaga et al (60). They found that water-saturated solutions of styrene in dioxane and acetone swelled similar ponderosa pine wafers in the tangential direction 113.6 percent and 105.9 percent in the radial direction (based on a water-swell of 100%). These workers believed that the large increase in total swell is due to an opening of the more ordered areas of the micelles during treatment. Now, it can be shown that there is no significant difference between the volumetric changes for the 65% and 54% treatment at the 95% confidence level, but that there is a difference between these and the change for the 76% treatment*. It seems reasonable to assume that the more polystyrene that is present in the cell wall, the greater is the swelling of the wood. Thus more polystyrene is probably present in the cell walls of the wood treated with the 65 and 54% solutions than for that treated with the 76% solution. This argument is given more weight by an analysis of the associating efficiency.

(D) Associating Efficiency

It would be helpful to review briefly how the associating efficiency was obtained. After an impregnated sample was irradiated, it was heated in an oven. This heating drove out any unreacted monomer and the solvents methanol and water. The sample was then ground to a fine mesh and then extracted with hot benzene for six days. Since benzene is a non-polar compound it is unlikely that very much extraction of the polymer imbedded in the cellulose network occurred. However, the complete extraction of the homopolymer in the cell cavities is probable. Thus the associating efficiency (A. E.)

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* The estimate of the population standard deviation is equal to 0.0489, 0.0373 and 0.0332 for the volumetric changes 1.13, 1.17 and 1.16 respectively.

seems to be a good measure of the percentage of the polymer in the final treated sample which is in intimate contact with the cellulose in the secondary wall. Now it can be shown that, based on a "t" test at 95% confidence limits, there is no significant difference between the A. E. of the 65% and 54% treatments (.721 and .710 respectively); but there is a difference between the A. E. of the 76% treatment (.679) and either of the other two. This confirms the ultimate-volumetric-change-results.

The equivalence of the associating efficiences for the 65% and 54% was unexpected. If it be assumed that the swelling of the wood is due to the homogeneous penetration of the solution into the cell wall, then the 54% treatment would yield a much higher proportion of associated polymer than the 65% treatment because of the much greater solution volumetric uptake beyond the cell cavity volume (34% vs. 10%). Hence a higher associating efficiency would be obtained. In order to explain the results it is therefore necessary to reject the assumption that there is a "homogeneous" sorption of solution into the cell wall. A possible explanation for the results is as follows: when an evacuated sample is immersed in a solution of styrene, methanol and water, the cell cavities take up the bulk of the solution as in the case of a pure non-polar liquid like benzene or styrene. Now it is known that the cellulose in the secondary wall has a great affinity for water and to a less extent for methanol. On the other hand, the bulky non-polar styrene molecule is not able to penetrate the cellulose network at all unless the latter is already swollen. Thus it seems likely that the wall preferentially "extracts" water and methanol from the solution leaving most of the sytrene in the cell lumen. This process can be thought of as analogous to dialysis separation. After the secondary wall is sufficiently swollen, styrene will diffuse slowly into the cellulose displacing methanol and water. The literature indicates that this replacement of one liquid by another is indeed slow. It has been shown that water in fully swollen cross sections of wood can be replaced by methyl alcohol almost completely by repeatedly transferring the specimens to fresh methyl alcohol about once a day for about two weeks (14). Huang (28) found that by using the "inclusion technique", the total time of operation took as long as 24 hours, even with the use of five or six fresh displacement liquids. Similarly, Kenaga, Fennessey and Stannett (60), on using the solvent displacement method with water, acetone and styrene, allowed six days for the operation, even though they used wood wafers 1/4" in the longitudinal direction. Thus, considering the fact that

(1) the samples were impregnated for only 8 - 65 minutes
(2) the samples were 16 inches long, a length which would create diffusion problems,

it is probable that diffusion of styrene into the cell wall from the lumen was still occurring during the irradiation step. Also, according to Kenaga et al (60), it is possible that there is an interaction between the cellulose and the solution, leading to an opening of the more ordered areas of the cellulose. This would also contribute to the diffusion of styrene from the lumen into the wall during the irradiation step. This assumption is corroborated by the observation that the volumetric change of the wood samples directly after impregnation was, in almost all cases, less than the final volumetric change after irradiation and heating, notwithstanding the fact that polystyrene has a specific volume of 0.952 and styrene, 1.11.

Now it is evident that two important competing processes are occurring during irradiation:

(1) the diffusion of styrene into the secondary wall

(2) the homopolymerization of styrene in the cell cavities

Methanol increases both effects: the first, by opening (along with water) the tightly hydrogen-bonded cellulose structure to allow styrene diffusion; the second, by forming free radicals on radiolysis which are capable of initiating homopolymerization in the cell lumen. Hence it is seen from Table 21 that, although increasing the solvent content of the styrene-methanol-water solution will increase the swelling of the secondary wall, it will also increase the homopolymerization of the styrene in the cell cavities. The net result is very little difference among the associating efficiencies of the three treatments. As will be shown later, it is believed that water plays a very important positive role in the grafting (or associating) process; however, the swelling-homopolymerization effect of methanol probably overrides the difference in grafting caused by the change from 3% to 4% for the 65 and 54% treatments respectively.

It is noted that the estimated variance, S^2, for the 65% treatment is more than three times that of the other two treatments (.00577 vs. .00159 and .00183). Experiments 6 - 9 (shown in Tables 6 - 9) were carried out months before experiments 10 - 13. The former have associating efficiencies about 15% higher than the latter. This cannot be explained. However, this difference in A.E. values resulted in an estimated variance which is significantly higher* than that of the other two treatments.

Based on this author's work, in which two soxhlet extractions were carried out per sample (for thirteen samples), the estimated variance of the A. E. was calculated to be 3.28×10^{-4}. This can be used as a measure of the precision of the actual technique of measuring the A. E. Since the variance of a final measurement is equal to the sum of the individual factors causing deviations and since the estimated variances for the experiments (.00159, .00577 and .00183) are significantly higher than 3.28×10^{-4} it is assumed that factors other than "solution" do affect the associating efficiency.

3. Effect of Solution or Monomer Uptake

The results (Tables 2 - 20) definitely indicate that under the experimental conditions used (within a given solution) the monomer uptake is the predominant factor influencing polymer retention, percent

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* Based on F test at the 0.05 probability level

retention and associating efficiency. It is obvious that the percent retention is dependent upon the monomer uptake, for in most cases the retention efficiency is about 100%. It should be noted that the percent retention and polymer retention can be deliberately restricted by limiting the quantity of solution absorbed by the wood. Most researchers in this field have irradiated the cellulose or wood substrate in an excess of solution.

The positive correlation between monomer uptake and associating efficiency is more difficult to explain. If it is assumed that constant weight was not reached during the extraction stage, then the samples with a greater initial polymer concentration would obviously yield a higher A. E. However, Ramalingam and Werezak studied this aspect of the extraction process and concluded that constant weight was reached well before the six days of actual extracting. Also, Huang (28) found that constant weight was reached after about 50 hours of extracting. Looking at the problem superficially, one would expect that the higher the ratio of wood to monomer (i.e., less uptake), the higher would be the associating efficiency because there would appear to be more wood available for "associating" per gram of monomer. Since this is not the case, a more detailed examination is necessary.

The main factors (aside from the type of solution) affecting monomer uptake are:

(1) degree of vacuum

(2) time of evacuation

(3) pressure gradient during impregnation
(4) time of impregnation
(5) specific gravity of wood
(6) type of wood (sapwood or heartwood)

(A) Method of Impregnation

Pumping to a lower ultimate pressure will permit more solution to be taken up by the wood for a given time and pressure of impregnation. The pressure of impregnation would increase the solution uptake because it would force the solution into regions inaccessible by atmospheric treatment. In all runs carried out by Werezak except those shown in Tables 18 - 20, the degree of evacuation varied from less than one micron to thirty microns for periods of 10 - 13.5 hours. The pressure of impregnation for these same experiments was 35 psig and the time of impregnation varied from 8 to 65 minutes (except for Experiment 1, shown in Table 1). It is difficult to determine the effect of the evacuation and impregnation on the solution uptake for these experiments because of the similarity of treatment. Fortunately, in Experiments 18 - 20, Werezak attempted to reduce the uptake by decreasing the evacuation, reducing the pressure to atmospheric and decreasing the time of impregnation. In the treatment, some samples floated above the impregnating solution for varying times and then sank, and others sank immediately. As is shown in the results, the monomer uptake varied considerably; viz., from 0.153 to 0.506 gm styrene/cc of wood. (The cell cavities can theoretically accommodate an average of (1 - 0.435/1.50) x 0.875x0.76 = 0.473 gm/cc based on the average specific gravity of 0.435.) Now if the difference in monomer uptake is thought to be caused simply by the difference in the number of cells that are filled in a given manner, then the associating efficiency will be essentially the same in all cases; i.e., the associating efficiency is independent of the number of tracheids that contain polystyrene. However, a plot of associating efficiency versus monomer uptake (Figure 4) shows that there is a significant positive correlation (at 99.9 confidence level)*. The result indicates that the increase in monomer uptake is brought about primarily by the increase in monomer content in the secondary wall. This increase of penetration is brought about by the combination of higher vacuum, higher pressure of impregnation and a longer period of impregnation (and one other factor discussed on Page 100).

Because of the relatively large range of monomer uptake values for Experiments 18 - 20 (Tables 18 - 20), it would be interesting to determine whether there is truly a relationship between the ultimate volumetric change and the monomer uptake. Figure 5 shows that there is a relatively good positive correlation between the two. A similar plot is shown in Figure 6. Here the ultimate volumetric change is plotted versus the associated polymer (associating efficiency x polymer retention). The good correlation verifies the assumption that the

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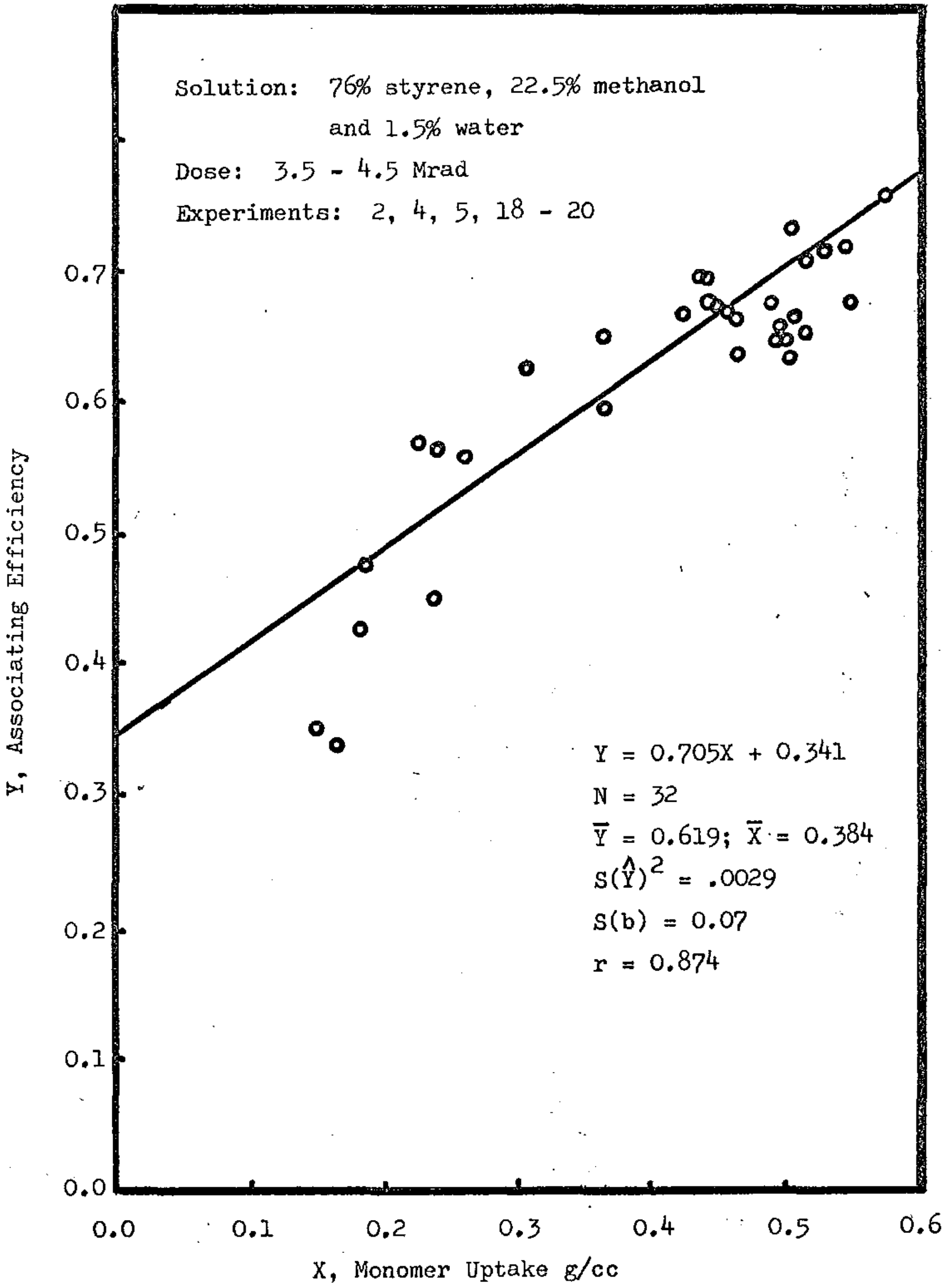
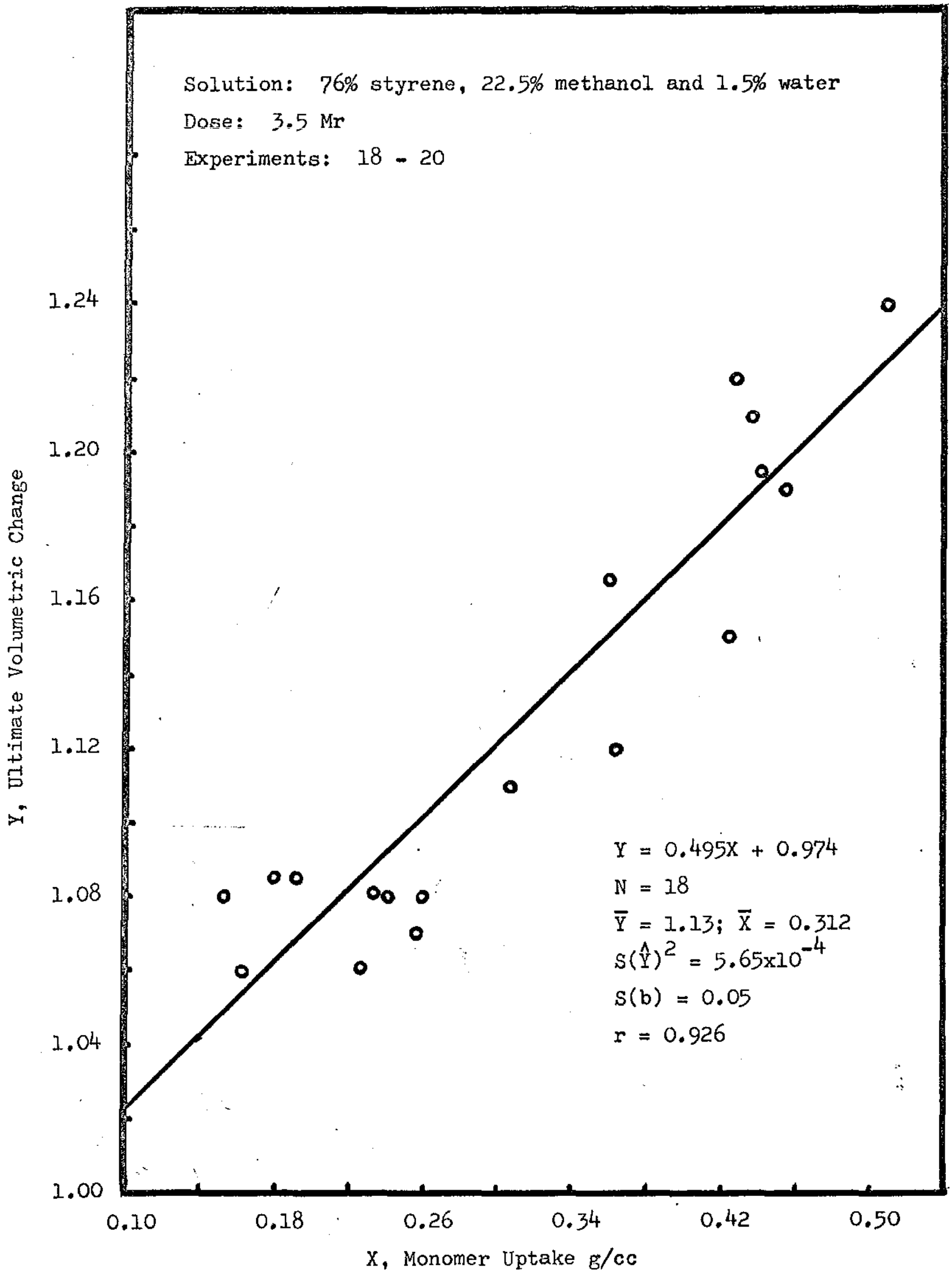
* (Included in this graph are Experiments 2, 4 and 5 in which higher evacuation and pressure were used)

FIGURE 4



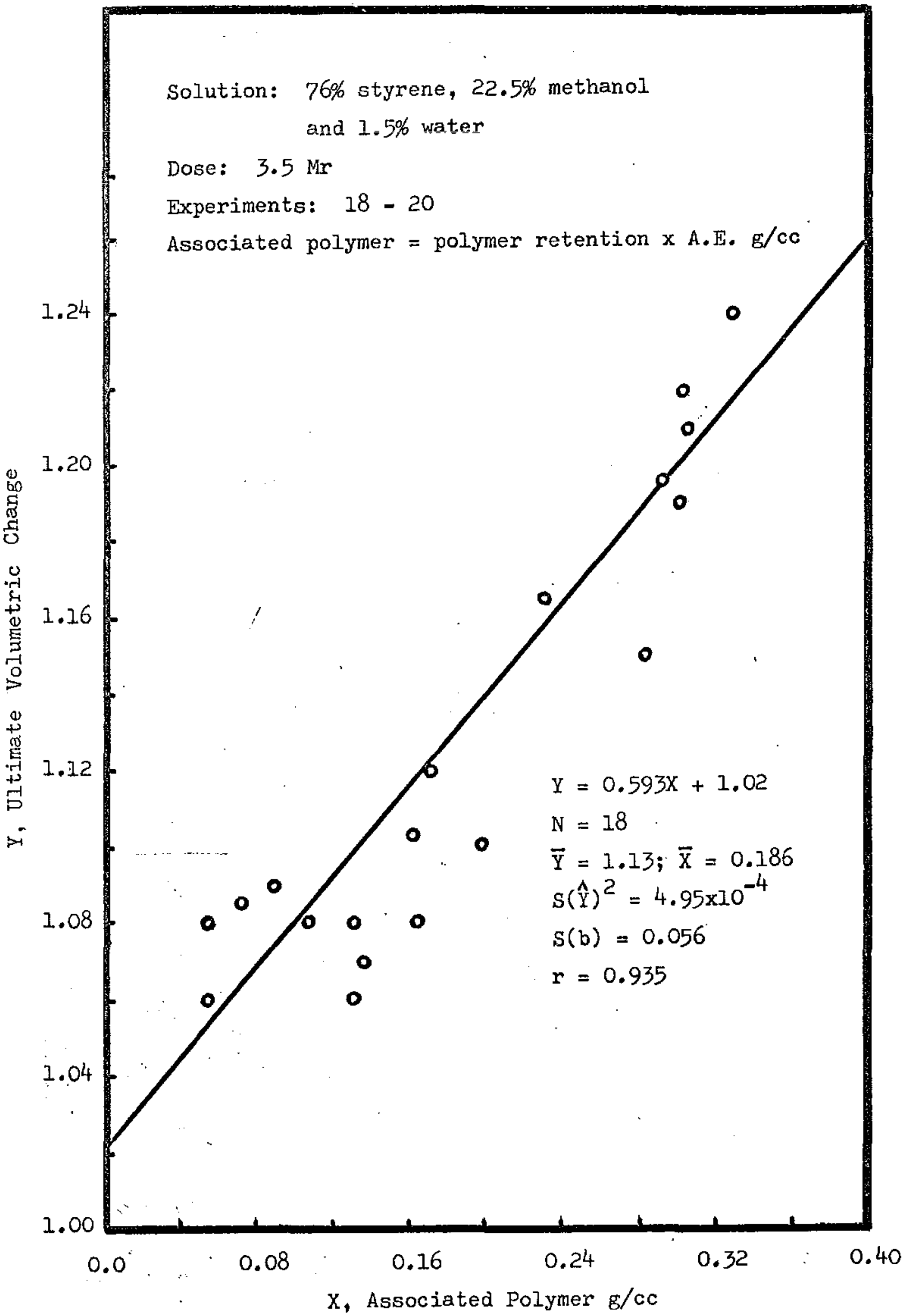
EFFECT OF MONOMER UPTAKE ON ASSOCIATING EFFICIENCY
(after Werezak)

FIGURE 5



EFFECT OF MONOMER UPTAKE ON THE ULTIMATE VOLUMETRIC CHANGE
(after Werezak)

FIGURE 6



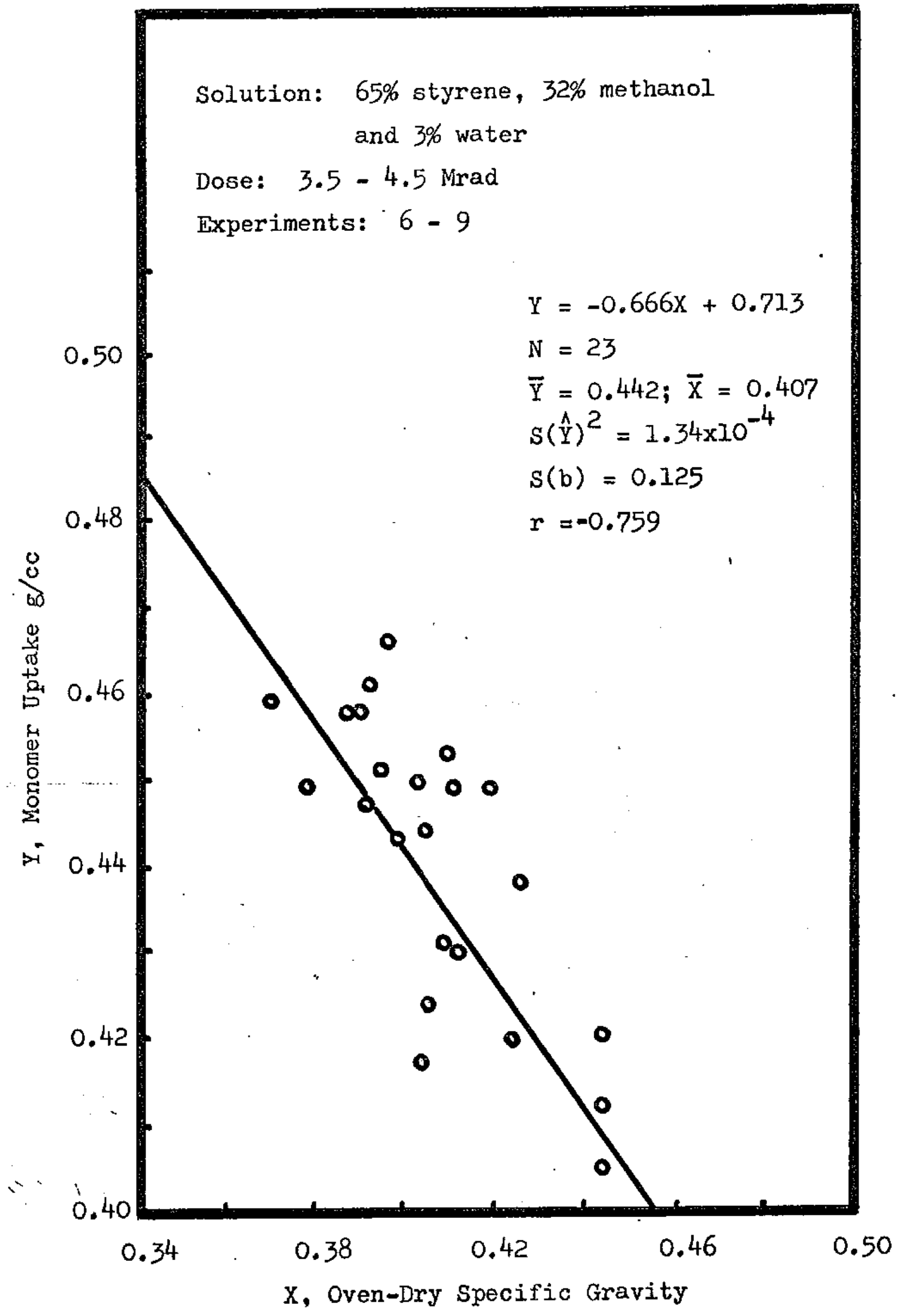
RELATIONSHIP BETWEEN ULTIMATE VOLUMETRIC CHANGE AND ASSOCIATED POLYMER (after Werezak) associated polymer is primarily in the walls.

In Tables 18 - 20 it is noted that the average retention efficiency is significantly larger than the values in Tables 2 - 5 in which the same solution was used as impregnant. One possible explanation is that since there is a higher wood-to-monomer ratio and since wood is believed to increase polymerization by an energy or chain transfer process (discussed later), the retention efficiency will increase.

(B) Effect of Specific Gravity

The specific gravity or density of wood is strongly dependent upon the thickness of the secondary wall of the wood cells. Thus a less dense sample of wood should theoretically be capable of absorbing more of a non-polar liquid like benzene than a more dense sample because of the greater voidage or lumen volume. For polar liquid, such as water, the same is true (for wood whose specific gravity lies in the range 0.35 - 0.55) because the walls will adsorb only 25 - 30% by weight whereas the cell cavities will absorb up to 200% (based on weight of wood). Thus there should be a relationship between monomer uptake (or solution uptake) and specific gravity. Figures 7 and 8 show that there is indeed a valid correlation between these two factors for the 65% and 76% styrene solutions. For the experiments using the 54% styrene solution (Tables 14 - 17), (assuming monomer uptake = polymer retention), the correlation is less evident. However, if one disregards Table 17 (perhaps these samples are heartwood; see

FIGURE 7



Solution: 65% styrene, 32% methanol and 3% water

Dose: 3.5 - 4.5 Mrad

Experiments: 6 - 9

$Y = -0.666X + 0.713$

$N = 23$

$\overline{Y} = 0.442$; $\overline{X} = 0.407$

$S(\hat{Y})^2 = 1.34 \times 10^{-4}$

$S(b) = 0.125$

$r = -0.759$

EFFECT OF SPECIFIC GRAVITY ON MONOMER UPTAKE

(after Werezak)

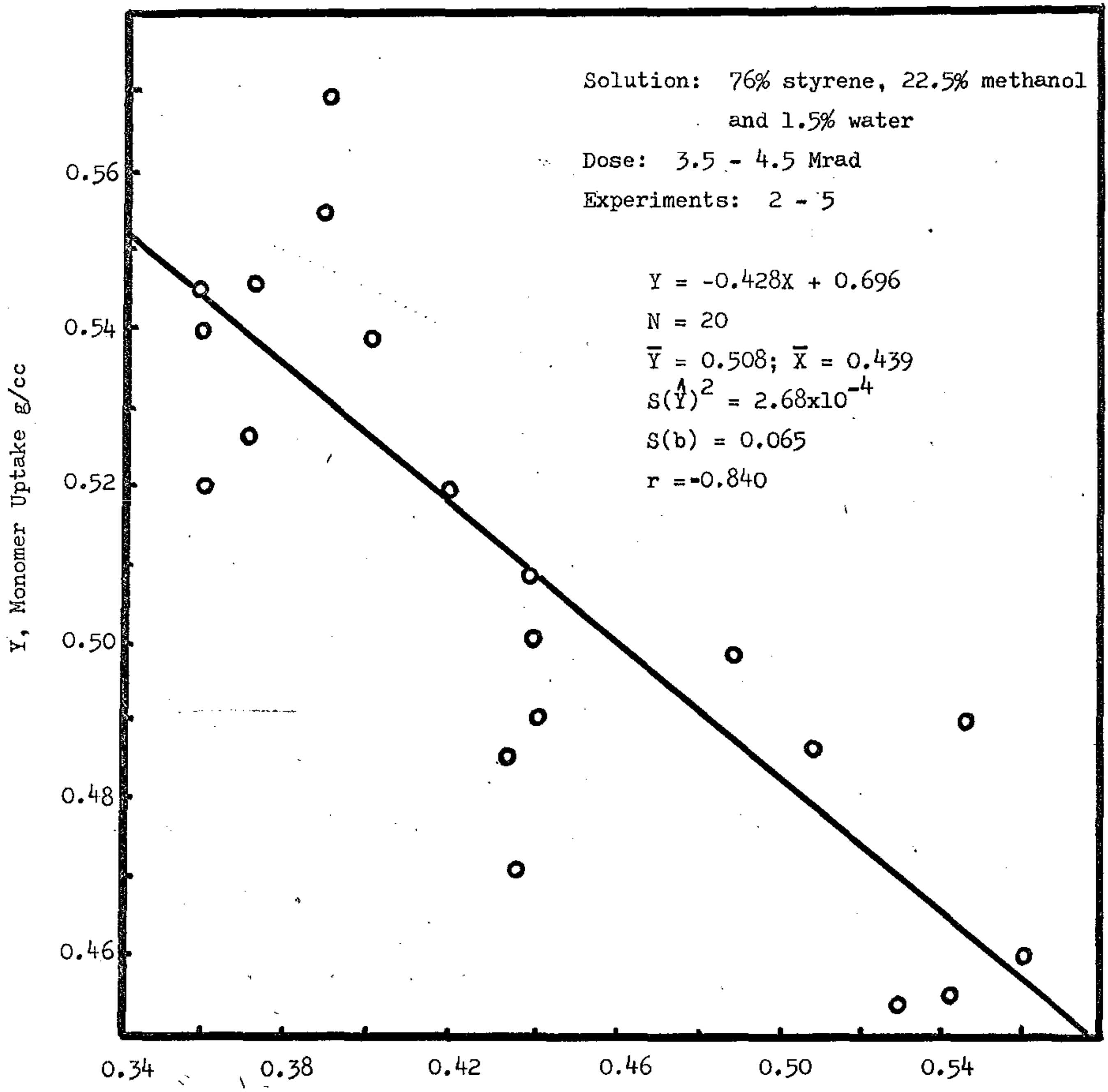


FIGURE 8

EFFECT OF SPECIFIC GRAVITY ON MONOMER UPTAKE

(after Werezak)

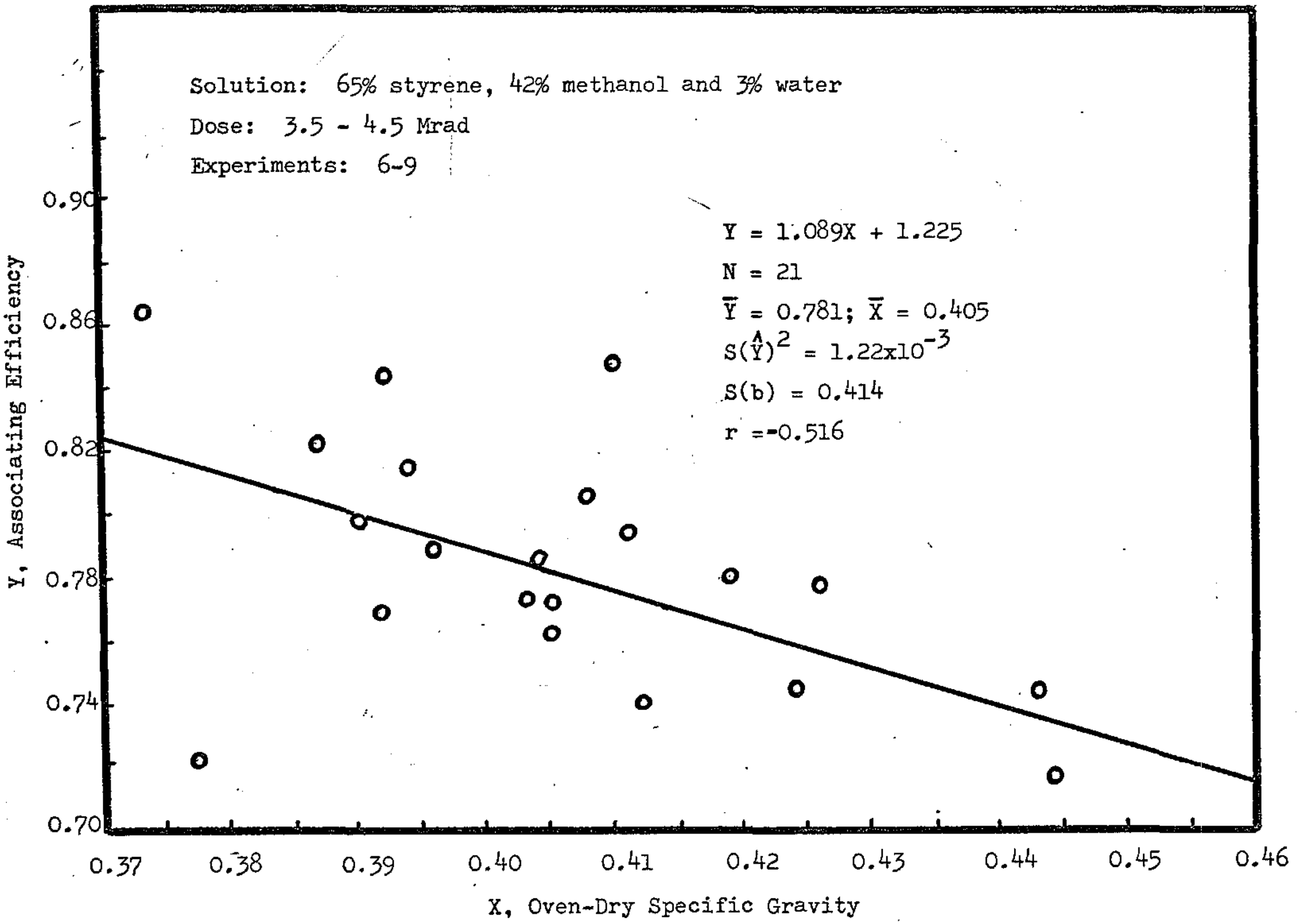
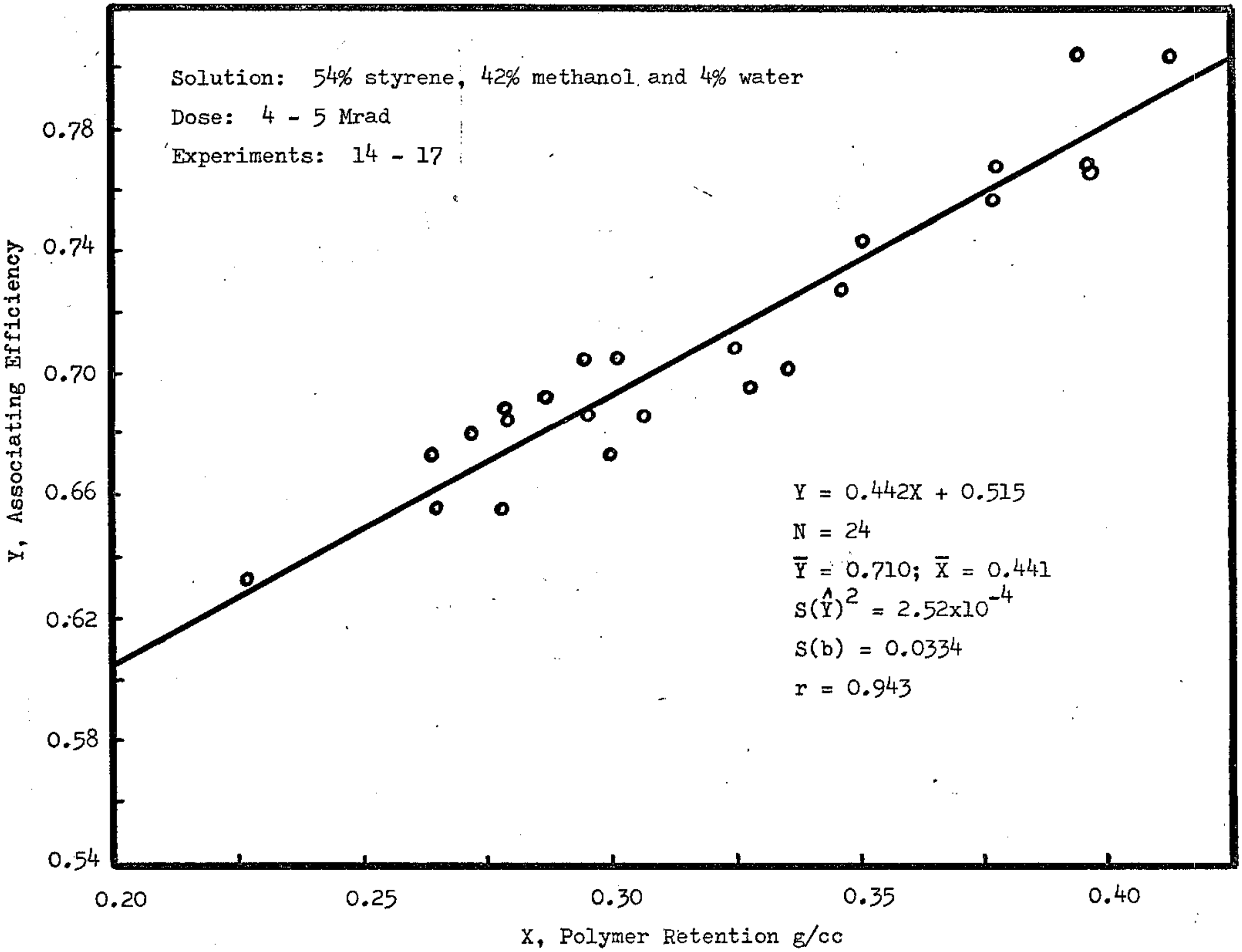


FIGURE 9

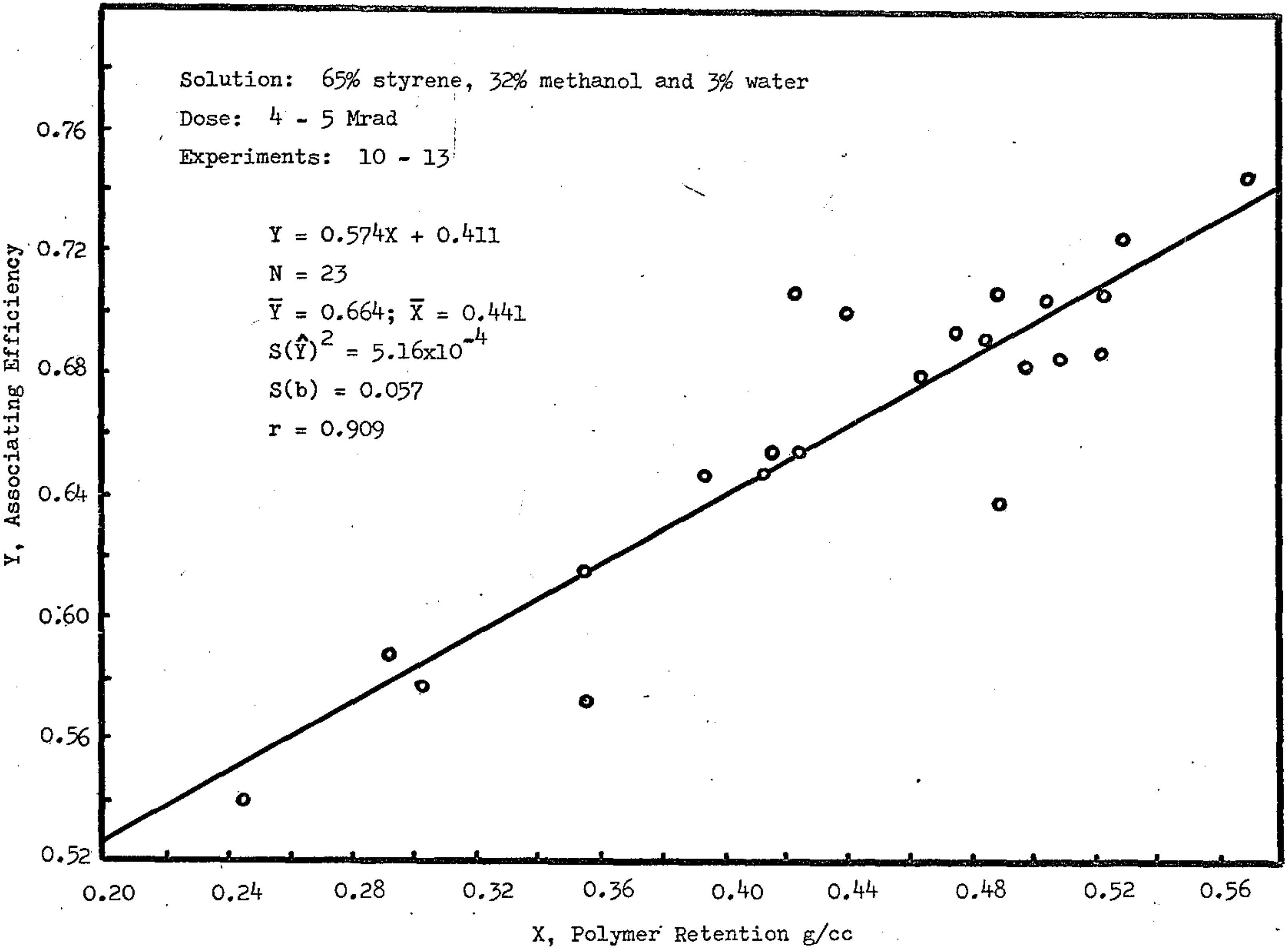
EFFECT OF SPECIFIC GRAVITY ON ASSOCIATING EFFICIENCY (after Werezak)

FIGURE 10



RELATIONSHIP BETWEEN ASSOCIATING EFFICIENCY AND POLYMER RETENTION (after Werezak)

FIGURE 11



RELATIONSHIP BETWEEN ASSOCIATING EFFICIENCY AND POLYMER RETENTION (after Werezak)

Page 100), a relationship between specific gravity and polymer retention is definitely noted.

In these experiments in which the monomer uptake is related to the specific gravity of the wood, the associating efficiency, in turn, seems to be dependent upon the monomer uptake, as in the case of the experiments shown in Tables 18 - 20. In Figure 9, the associating efficiency is plotted against the specific gravity for the experiments using 65% styrene solution (Tables 6 - 9) and a significant correlation is obtained. In Figures 10 and 11, the associating efficiency is plotted versus the polymer retention and significant positive correlations are obtained. The surprising results aid in determining where the polystyrene is located within the wood structure. There are several possibilities:

(1) exclusively on the lumen surface
(2) throughout the secondary wall
(3) partially within the secondary wall

(1) <u>On the Lumen Surface</u>

There are several reasons why grafting cannot be limited to the inner surface of the secondary wall (as would be the case for pure styrene). Firstly, the treatment causes the wood to swell. Since the lumen volume does not change as the secondary wall swells (12 - 14), this indicates that penetration into the walls has occurred. Secondly, there are far too few radicals available for the reported grafting of the polystyrene onto the lumen surface alone (see Appendix

III). Thirdly, it can be shown that if we assume that grafting or associating is a function of the percentage of polymer in intimate contact with cellulose, the associating efficiency theoretically increases (and not decreases as shown in Figure 9) with increasing density of the original wood or decreases (and not increases as shown in Figures 10 and 11) with increasing polymer retention. For example, consider Figure 7. The equation is

$$M = 0.713 - 0.666\, S_d \text{ ------} \qquad (1)$$

where M is the monomer uptake in gm/cc and S_d is the specific gravity of the original wood. Now the specific gravity can be expressed in terms of the average lumen diameter, d, and the tracheid diameter, D.

$$1.50.L.n\left[\left(\frac{\pi D^2}{4}\right) - \left(\frac{\pi d^2}{4}\right)\right] = S_d.L.n\left(\frac{\pi D^2}{4}\right)$$

where n is the number of cells per c.c. of wood and L is the average length of these cells. The final equation is

$$S_d = 1.50\left(1 - \frac{d^2}{D^2}\right) \qquad (2)$$

Combining (1) and (2),

$$M = d^2/D^2 - 0.287 \qquad (3)$$

Now the associating efficiency can be expressed as a function of the lumen circumference (circumference x length of tracheid = surface area for grafting) over the monomer uptake:

$$\text{Associating Efficiency} = f\left(\frac{n\pi d.L}{\frac{d^2}{D^2} - 0.287}\right) \qquad (4)$$

It is seen that the value of the associating efficiency increases with decreasing d (i.e., increasing specific gravity) if the grafting is a surface phenomenon. This is contrary to the results as shown in Figure 9. Thus the grafting cannot be exclusively a surface phenomenon.

(2) Throughout the Secondary Wall

If styrene monomer (and subsequently, polystyrene) were located throughout the secondary wall, a greater percentage of grafting (or associating) would occur in the situation where the ratio of initiating species (cellulose) to the monomer was the highest (i.e., for the case of the denser wood). The opposite, in fact, is true. Also, it would be expected that if polymer were located throughout the secondary wall, a greater dimensional change would occur for wood with the highest specific gravity (see Page 19). No correlation in fact was found between specific gravity and the ultimate volumetric change. Thus, for these two reasons, it is unlikely that the grafted or associated polymer is located throughout the cell walls.

(3) Partially Within the Secondary Walls

Having rejected the possibility that the associated polymer is located exclusively on the lumen surface or throughout the cell walls, it remains that the polymer is located partially within the walls. An equation similar to Equation (4) can be derived for this model.

$$\text{Associating Efficiency} = f\left(\frac{n.L.\pi.t(d+t)}{\frac{d^2}{D^2} - 0.287}\right) \tag{5}$$

where t is the depth of penetration of the associated polymer.

If we assume a homogeneous diffusion of solution into the cell wall, it can be shown that the styrene-concentration gradient in the wall is essentially the same for all tracheids regardless of wall thickness (63). For equal values of t, it can be shown that Equation (5) yields a higher associating efficiency for samples of wood with a higher specific gravity or lower "d". Again this is contrary to the experimental evidence.

The results can be explained, as in a previous discussion, on the basis of "preferrential extraction" from the solution by the cellulose in the walls. A sample of wood will absorb the solution into the cell cavities. The methyl alcohol and water will be sorbed relatively quickly into the cell walls, enabling the subsequent diffusion of the styrene molecules. A less dense sample will absorb more solution and consequently will have more methanol and water available for opening up the cellulose network per unit weight of cellulose. As an example, consider Table 15. The sample with a specific gravity of 0.376 will absorb 0.628x42/54 = 0.489 grams of methanol and 0.628x4/54 = 0.0465 grams of water per 0.376 gm. of wood or 1.30 gm. of methanol and 0.124 grams of water per gram of wood. The sample with a specific gravity of 0.452 will similarly absorb 0.447 gm. of methanol and 0.043 gm. of water per gram of wood. Thus the less dense sample will have more than twice the amount of methanol and three times the amount of water available for loosening-up the cellulose structure and opening the path for subsequent grafting

(0.803 vs. 0.632 for the examples cited). The "t" of Equation (5) can be thought of as being larger for the less dense samples.

If the samples of wood, (as in some instances), regardless of specific gravity, absorb more methanol than the cell walls can accommodate (fibre saturation point), the methanol-to-wood ratio would have little effect on the associating efficiency because the amount of methanol beyond the fibre saturation point will remain in the lumen. However, the literature seems to indicate that water has a much greater effect on the grafting process than methanol. The presence of traces of water has been shown to increase greatly the swelling of wood in liquids (14). Huang (28) found that mixtures of styrene and 99.5% methanol gave substantial grafting onto rayon (7 - 8% moisture content) but when the methanol and rayon were dried over P_2O_5, very little grafting (ca. 5%) occurred. Ramalingam (61) found that an increase in water content (1.5 to 9%) in a styrene-methanol-water solution decreased the polymer extracted (i.e., increased the associating efficiency) by 20 - 100%. Similar results have been found by other workers (31, 36, 38, 40, 46, 47, 49). Thus, since the amount of water absorbed by the wood samples is much smaller than the amount needed to saturate the walls, the wood with a specific gravity of 0.376 will sorb into the walls almost three times as much water as the 0.452 specific gravity sample and therefore yield a higher associating efficiency.

(C) Type of Wood

Permeability, as measured as the rate of flow of water through water-saturated wood under a fixed pressure, has been found to be more than 100 times as great through sapwood as through heartwood (14). Erickson and Balatinecz (64) found similar results when they forced catalyzed monomeric styrene into wood and polymerized the liquid to a solid condition. Microscope slides showed that sapwood contained a far greater percentage of penetrated cells than did heartwood. It is possible that the samples used by Werezak in Experiment 17 (Table 17) were heartwood because of the low monomer uptake. Similarly, the lack of correlation between specific gravity and monomer uptake for Experiments 10 - 13 might have been caused by the presence of heartwood samples. It should be noted, however, that there is still a correlation between associating efficiency and polymer retention (see Figure 11). This can be explained by an argument similar to the one used in the last section; i.e., the samples which take up more solution have more methanol and particularly more water available for swelling per weight of wood.

Similarly, the increase in monomer penetration for the experiments shown in Tables 18 - 20 can be explained on the same basis.

SCOPE OF PRESENT INVESTIGATIONS

This thesis is the third in a series of research programs carried out with the particular aim of improving the structural properties of wood by means of the radiation-induced graft copolymerization of this material with styrene. At the outset of this study, analysis of previous work led one to believe that

(1) there was a direct correlation between the grafting and the bending strength of wood.

(2) there were many free radical sites not being utilized in the grafting process.

(3) the diffusion of monomer toward these sites could be enhanced by means of increasing the temperature of the reaction.

Because the earlier irradiations had all been carried out in the McMaster swimming pool reactor, previous workers had not been able to heat the system at a time when the radical concentration was highest; namely, during the irradiation period. Hence, for this work, an apparatus was constructed in which a sample of wood large enough for a standard bending strength test could be irradiated at elevated temperatures. The experimental method used was essentially the same as that used by Ramalingam (61) and Werezak (54) except for the irradiation step. The experimental conditions optimized with respect to the bending strength by Werezak (62) were used.

This work can be divided conveniently into two sections:

(1) a study of the effect of wood on the polymerization of

styrene.

(2) a study of the effect of homo- and grafted polystyrene on the wood.

The second investigation concerns itself with the structural changes brought about by the treatment and will be discussed in PART 2 of this thesis. The first study consists of a brief look at some kinetic aspects of the polymerization of styrene within the wood structure. This investigation was necessarily subordinate to the structural analysis because all the materials and procedures used in this thesis program were selected with respect to the latter. Hence, the following section is restrictive in scope and qualitative in nature. It has been divided into three main sections:

(A) the effect of temperature on the radiation-induced polymerization of pure styrene and styrene in solution.

(B) the effect of temperature on the radiation-induced polymerization of styrene in wood.

(C) the effect of irradiation dose and post-irradiation treatment on the radiation-induced polymerization of styrene in wood.

EXPERIMENTAL DETAILS

A. Materials

(1) Wood

Red pine sapwood was used for this work. A description of this wood is found in the "Textbook of Wood Technology", Vol. 1, Page 458 (12).

(2) Styrene

Styrene monomer (Eastman Organic Chemicals, Highest Purity) was purified by removing the inhibitor (tert. butyl pyrocatechol) with a 10% sodium hydroxide solution, washing with distilled water and then drying over anhydrous calcium sulphate. Before using, the styrene was always checked for indications of polymerization by adding a small amount to an excess of methanol.

(3) Methanol

Reagent grade methanol (Fisher A.C.S. Reagent Grade) was used. This solvent contains 0.5 - 1.0% water.

(4) Water

Distilled water was used.

(5) Benzene

Pure benzene (Fisher A.C.S. Reagent Grade) was used both for the Soxhlet extraction and the molecular weight determinations.

B. Experimental Procedure

The experimental procedure used in this work was in general similar to the procedure used by Ramalingam (61) and Werezak (54).

In the previous work, control samples were used because of the intrinsic chemical and physical variability of wood. Samples were examined in groups of three. One piece (16" x 3/4" x 3/4") from a given longitudinal strip was impregnated and irradiated; one was irradiated without impregnation and the other retained as a control.

In this work, this method was not used for the following reasons:

(1) the gamma-irradiating facility was such that only one sample could be irradiated at a time.

(2) the variability of wood is such that in general the assumption of equal properties for the control and the treated sample was unjustified considering the relatively large dimensions of the samples.

(3) a preliminary study showed that most of the variable factors in wood (e.g., specific gravity) could be taken into account.

Before Evacuation

Clear knot-free samples of red pine sapwood were chosen at random from an assortment of over two hundred pieces. These were planed to a dimension of approximately .675" x .625" x 16", and measured to 5/1000 of an inch by a caliper. The average ring count was measured. The weight of the sample was taken at room conditions and after heating in an oven at 100° - 105°C to constant weight.

Evacuation

After drying, the samples were evacuated in the apparatus described in detail by Ramalingam (61) and in the literature (62).

Briefly, the samples were placed in a glass tube which is suspended in a thick-walled glass cylinder fitted at either end with brass plates. There are three ports in the top plate connected to a vacuum line, a reservoir of impregnating solution and a nitrogen cylinder. The evacuation of the wood was carried out using a Duo-Seal high capacity oil pump placed at the end of a vacuum line containing two liquid air traps and a McLeod Gauge. Evacuation was carried out for twelve hours at a level of 1 - 20 microns.

Impregnation

After evacuation, the vacuum line was closed and the impregnant was added to the wood. The liquid was added until the wood samples had been completely immersed after which a pressure of 35 psig of nitrogen was applied to the liquid surface. The samples were left in this condition for 65 minutes, after which they were directly irradiated or wrapped in aluminum foil and sealed in polyethylene thin-walled lay-flat tubing. The wrapped samples were placed in a refrigerator and left for no more than four days.

The monomer solutions employed in this study were:

1. pure styrene
2. 54% styrene, 42% methanol and 4% water by weight.

Irradiation

The irradiation facility used in this work is described in the literature (65) and supplementary information is given in Appendix IV. Briefly, the one sample of wood was sealed in a square aluminum canister and placed in the apparatus which consisted of a "railway" containing a gamma source which swept the sample with a uniform gamma flux. On February 25, 1964, the dose-rate was calculated to be 0.299 Mr/hr (based on Cobalt glass dosimeters). On January 25, 1965, due to the natural decay of CO-60, the dose-rate was 0.262 Mr/hr. Temperature could be controlled to ±0.2°C over the range 39°C to 105°C. The samples were irradiated for doses of 1 - 5 Mr at room temperature, and at controlled temperatures from 39°C to 80°C.

After Irradiation

After irradiation, the samples were either dried in an oven at 100 - 105°C or allowed to dry at room temperature. When these latter samples had reached constant weight, they were dried in an oven at 100 - 105°C for twelve hours. The dimensions of all the samples were measured to the nearest 5/1000 of an inch, and then put through a series of structural tests. (See PART 2 of the thesis.)

Extraction of Treated Wood

A portion of the treated wood was ground in a Wiley Mill through a 40/60 mesh (0.25 - 0.44 mm) and then extracted with hot benzene for six days in a Soxhlet extractor. The associating efficiency could be obtained by the following formula:

$$\text{A. E.} = 1 - \left(\frac{(\text{S.W.})_i - (\text{S.W.})_f}{(\text{S.W.})_i\ (\text{P.S. Fraction})}\right)$$

where

$(\text{S.W.})_i$ and $(\text{S.W.})_f$ are the oven-dried sample weights before and after extraction and P.S. Fraction is the fraction of the oven-dried sample weight $(S.W.)_i$ which is polystyrene.

Molecular Weight Determinations

Because it was believed that temperature would affect the molecular weight of the polystyrene branches, it was necessary to carry out molecular weight measurements in order to estimate how the polymer was distributed on the cellulose backbone. For example, a treated sample containing a grafted polymer of a certain molecular weight attached at a certain number of sites on the cellulose would yield the same amount of grafted polymer (or yield the same grafting efficiency for a given polymer retention) as a sample whose grafted polymer had twice the molecular weight but was attached at only half the number of sites.

Unfortunately, molecular weights of only the homopolymer were obtained but it is believed that there is a relationship between the homo- and grafted polymer. The molecular weight of polystyrene was determined by viscometry in benzene at 30°C in a Cannon-Ubbelohde dilution-type viscometer, Size 50. Specific viscosities were determined at 4 or 5 concentrations between 0.3 - 1.0 g/100 ml. The intrinsic viscosity, (η), was obtained by extrapolating the straight line through the experimental points on a reduced viscosity vs. concentration plot, to zero concentration. The number average molecular weight, $\overline{M}n$, was calculated from the intrinsic viscosity by using the equation $\overline{M}n = 16700\ (\eta)^{1.37}$ of Mayo et al for unfractionated polystyrene in benzene at 30°C (66).

RESULTS OF EXPERIMENTATION

A. Effect of Temperature on the Radiation-Induced Polymerization of Styrene

Before studying the effect of temperature on the radiation-induced grafting onto cellulose in wood, an examination of the temperature effect on pure styrene and a styrene solution seemed necessary in view of the fact that little work has been carried out in this area. Twenty-five ml. samples were irradiated with a dose of 4.5 Mr (dose rate = 0.265 Mr/hr.) at 5 temperatures.

The effect of temperature on the radiation-induced polymerization of pure styrene is shown in Figure 12, which is a composite plot of molecular weight and percent polymerization vs. temperature. The results indicate that, in contrast to thermal polymerization, the percent polymerization and the molecular weight of polystyrene increase with increasing temperature. The samples became increasingly viscous as the percent polymerization increased until complete solidification occurred after (or during) the 80°C treatment. Two experiments were carried out at room temperature with no temperature control. The temperature of the sample increased from 27°C to 35°C in 5 hours and then levelled off at 30°C. The average molecular weight of the polystyrene under these circumstances was 69500, which is higher than the M. W. of the polystyrene resulting from irradiation at a controlled temperature of 40°C (55600). The higher molecular weight is probably caused by the local temperature rises due to the heat evolved by the

EFFECT OF TEMPERATURE ON MOLECULAR WEIGHT AND
PERCENT POLYMERIZATION FOR PURE STYRENE

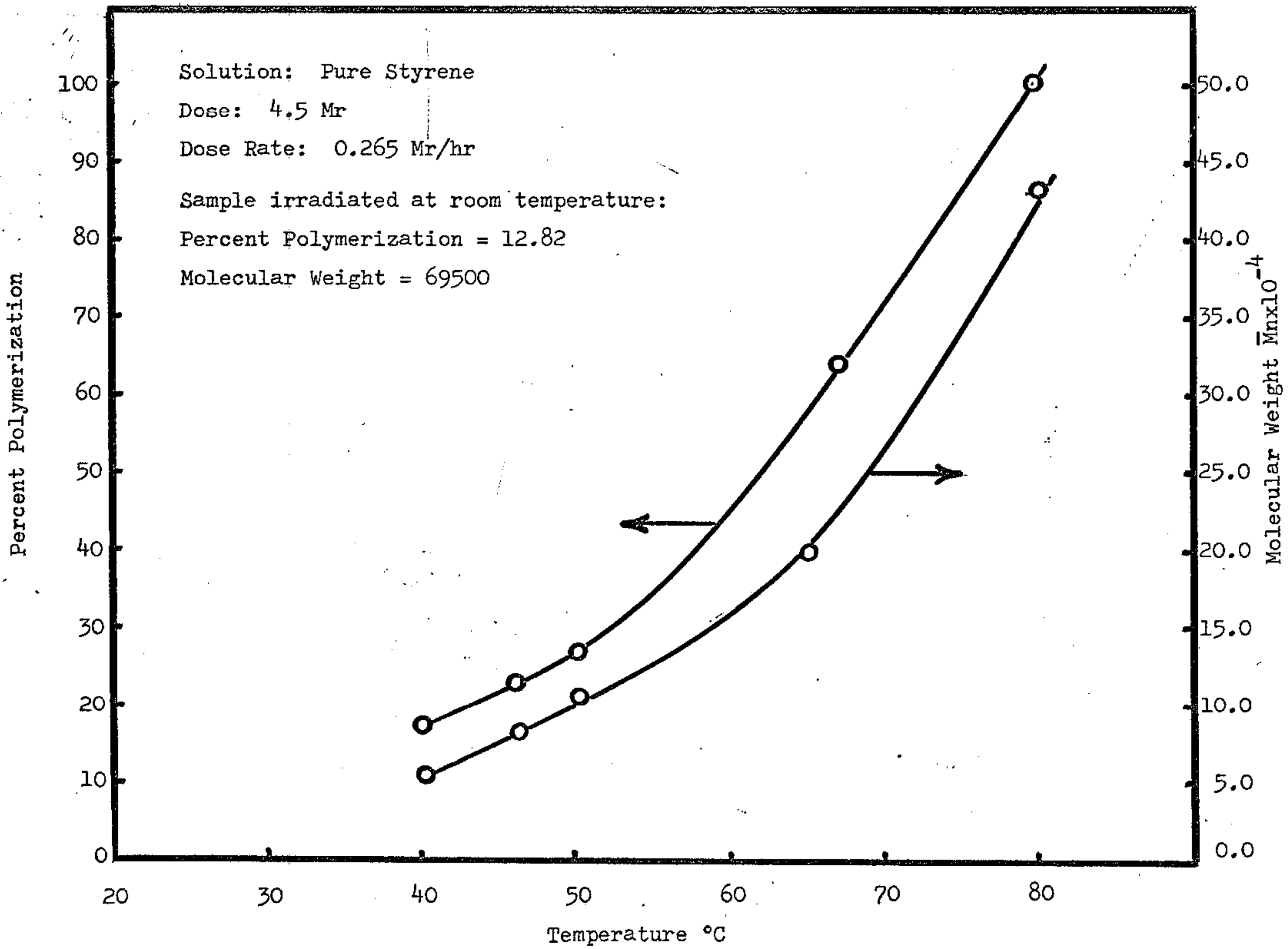


FIGURE 12

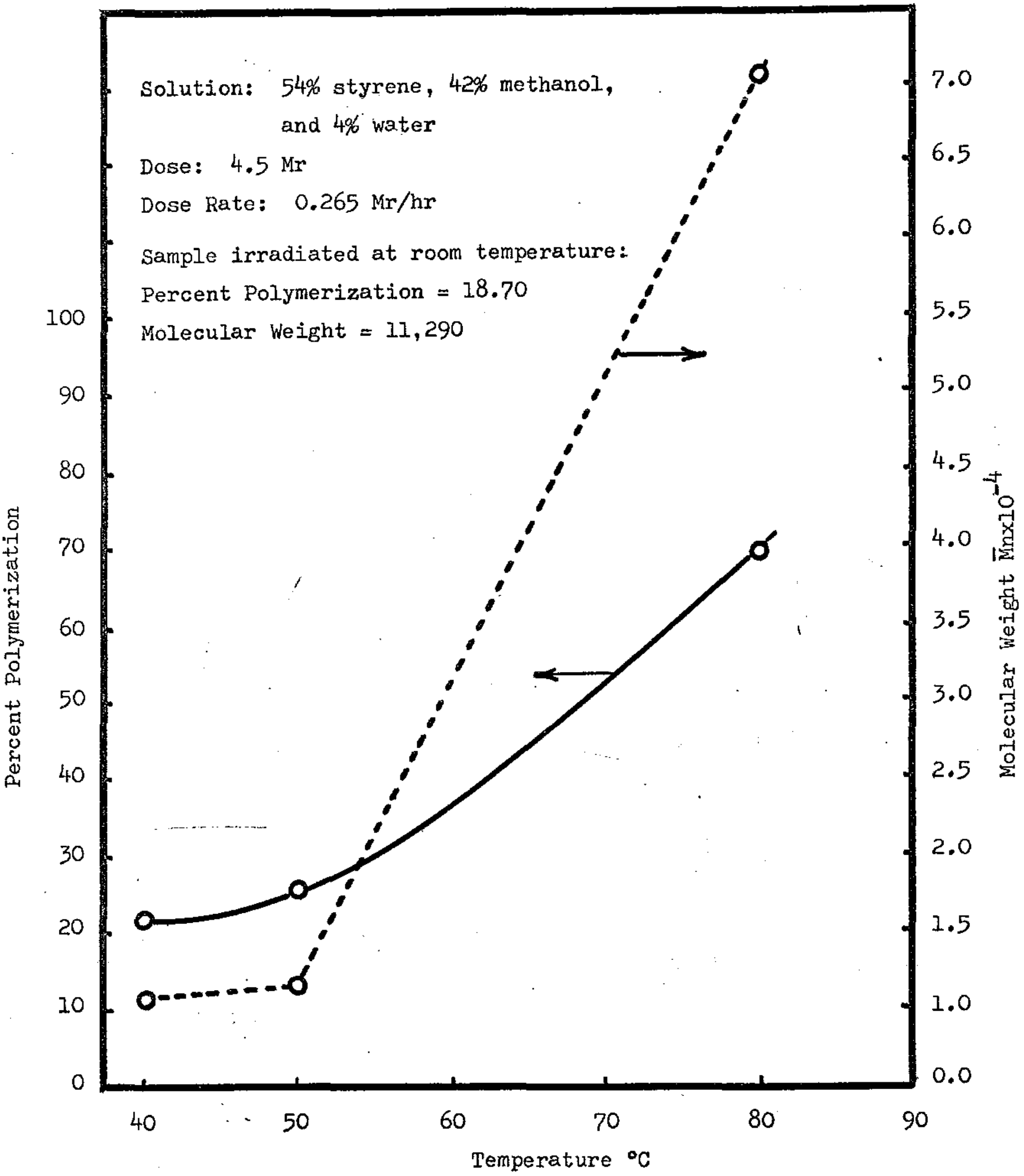


FIGURE 13

EFFECT OF TEMPERATURE ON MOLECULAR WEIGHT
AND PERCENT POLYMERIZATION
FOR A 54% STYRENE SOLUTION

polymerization (ca. 17 Kcal/mole). It is difficult to say why the percent polymerization of the sample irradiated at room temperature is lower while its molecular weight is higher than the sample irradiated at 40°C. A study of the molecular weight distribution may help explain this apparent contradictory result.

The results, however, compare favourably with those of Ballantine et al (68) who studied the gamma-ray-initiated polymerization of styrene at -18°C, 25°C and 72°C using dose-rates (0.173 Mr/hr. to 0.242 Mr/hr.) similar to those employed in this work. At 25°C and 72°C they found percent polymerizations of 10.3% and 59.5% and corresponding molecular weights of 70,000 and 280,000 respectively.

A solution of 54% styrene, 42% methanol and 4% water was irradiated at room temperature and at three controlled temperatures. The results are shown in Figure 13 using a plot similar to Figure 12. The results indicate that temperature has a slight positive effect on the polymerization of styrene up to a temperature of 50°C, after which there appears to be an accelerative rise in both the molecular weight and the percent polymerization. Similar to the pure styrene samples, a rise in temperature was noted for the styrene-solution samples irradiated at room temperature and a higher molecular weight but a lower percent polymerization resulted compared to samples irradiated at a controlled temperature of 40°C. At lower temperatures, the percent polymerization of the styrene in solution is almost 50% higher than that of pure styrene (18.70 vs. 12.82) indicating that the radiolysis of methanol is contributing free radicals which augment the polymerization of styrene. At higher temperatures, however, the percent polymerization is lower than that of pure styrene. This indicates that the gel-effect was taking place much sooner for the pure styrene than for styrene in solution. This is probably due to the greater viscosity of the pure styrene-polystyrene solution, a factor which would inhibit chain termination and hence increase polymerization. For the case of the styrene solution, the low molecular weights (ca. 11,000) up to 50°C compared to pure styrene is due to the "Simple Dilution Effect". The slight change in the molecular weight up to 50°C indicates that the gel-effect was not significant. However, above this temperature, the accelerative increase in molecular weight and percent polymerization indicates that a Trommsdorff-type effect or gel-effect may be occurring.

B. Effect of Temperature on the Radiation-Induced Polymerization of Styrene in Wood

(1) Pure Styrene

The results of the radiation-induced polymerization of styrene in wood are shown in Table 24. The results represent the average of three or four replications for each temperature treatment. The samples of wood were treated in the conventional manner and after treatment were left standing at room conditions until constant weight had been reached. It can be shown that on the average about 90% of the cell cavities were filled. Some cells appear to be impermeable to liquid styrene, as has been shown by other workers (64). Also, no

TABLE 24

THE RADIATION-INDUCED POLYMERIZATION OF STYRENE IN WOOD AT DIFFERENT TEMPERATURES

Dose = 4.5 Mr   Dose Rate = 0.280 Mr/hr

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Retention * Efficiency	Associating Efficiency	Molecular Weight $\overline{M}n$	Temperature C°
0.392	0.563	0.361	.640	-0.072	181,000	room
0.440	0.581	0.320	0.550	0.063	104,000	39.0
.393	0.590	0.433	0.737	0.045	229,500	52.0
0.424	0.575	0.499	0.870	0.031	137,000	77.5

* Retention Efficiency = Percent Polymerization/100

styrene enterred the walls because there was no dimensional change during the entire operation.

Temperature changes and the presence of wood could conceivably affect all four elementary types of reaction -- initiation, propagation, transfer, and termination -- that are involved in the addition polymerization of styrene. The complexity of factors makes the results very difficult to interpret. However, several effects are noted:

(a) A negligible amount of polystyrene is grafted to the cellulose. The associating efficiency values range from -0.072 to 0.100. This result is expected because the number of free radicals available for grafting on the inner surface of the secondary wall is insignificant (see Appendix III). Ramalingam (61) obtained a smooth relationship between dose and "polymer extracted" (see Table 1) and thus assumed that surface grafting was taking place. However, it is far more probable that the unextractable polymer was actually crosslinked polystyrene. This assumption seems to be valid considering that the critical gel dose of 10 Megarep for polystyrene (1) falls within the dose range (0 - 18.9 Mrad) used by Ramalingam.

(b) The retention efficiency (which is equivalent to the percent polymerization/100) and the molecular weight for the samples irradiated at room temperature (with no temperature control) are higher than those irradiated at a controlled temperature of 39°C. The temperature of the samples increased from about 27°C to 35°C during the irradiation period.

(c) As the temperature increases, the percent polymerization or retention efficiency increases.

(d) The molecular weights of the extractable polystyrene for the 39°C and 52°C treatments are higher than the corresponding values for pure styrene in the absence of wood (see Figure 12). The same is true of the percent polymerization values. For either temperature, since the molecular weight increases along with the percent polymerization, the apparent increase in the polymerization rate may be due to the onset of the gel-effect rather than chain or energy transfer from the cellulose. However, it seems improbable that the gel-effect can entirely account for the increase because the lumen diameter is very large with respect to the polymer chain lengths formed; (e.g., about 300,000A° vs. 2000A° for a M.W. of 100,000). A contributing factor causing the apparent higher polymerization rate of the styrene in wood could be the after-effect. Immediately after the pure styrene was irradiated, the polymerization was inactivated by pouring the entire styrene-polystyrene solution into an excess of methanol, thus causing the precipitation of polystyrene. For the styrene-in-wood experiments the samples were left at room conditions from three weeks to two months, after which the constant-weight samples were put in an oven at 100 - 105°C for periods up to 24 hours. Now during the irradiation it is likely that many of the bordered pits became blocked with polymer and hence the diffusion of monomer styrene out of the wood was greatly hindered. Thus it is possible that the constant-weight samples contained a relatively high trapped-styrene content which polymerized during the oven treatment.* Even after the oven treatment there appeared to be trapped monomer, for during the grinding operation a distinct odour of styrene vapours was detected.

(e) The molecular weights of the polymer extracted from the samples treated at 77.5°C are lower than those treated at 52°C and also are lower than similarly treated pure styrene samples. Chain or energy transfer processes may have been occurring from the cellulose. This transfer process would increase the rate of polymerization as well as decrease the molecular weight of the polystyrene.

(2) Styrene Solution

The results of the experiments involving the irradiation of wood impregnated with a solution of 54% styrene, 42% methanol and 4% water by weight at different temperatures are shown in Table 25. The results represent the averages of 4 to 6 replications for each temperature treatment. After irradiation, the samples were left at room conditions until constant weight was reached.

(a) Monomer Uptake

The average monomer uptake for these experiments was

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* It is unlikely that polymerization occurred at room temperature for the initial rate of thermal polymerization at 60°C is 0.089%/hr. The same rate at 100°C is 2.15%/hr. with an average molecular weight of 420,000 (70).

TABLE 25

THE RADIATION-INDUCED POLYMERIZATION OF STYRENE (IN SOLUTION) IN WOOD AT DIFFERENT TEMPERATURES

Dose = 4.5 Mr   Dose Rate = 0.280 Mr/hr   Solution: 54:42:4 styrene, methanol, water

Specific Gravity	Monomer Uptake gm/cc	Polymer Retention gm/cc	Retention * Efficiency	Associating Efficiency	Molecular Weight $\overline{M}n$	Temperature C°
0.398	0.380	.365	0.961	0.749	43,200	room
0.439	0.355	0.330	0.931	0.711	39,900	39.0
0.460	0.363	0.327	0.902	0.727	42,100	52.5
0.448	0.332	0.310	0.935	0.766	50,400	60.0
0.423	0.368	0.341	0.927	0.739	61,200	77.5

* Retention Efficiency = Percent Polymerization/100

0.360 grams of styrene per cc. of wood. The average uptake for the experiments carried out by Werezak using the same solution was 0.444 gm/cc (see Table 23). The same experimental technique was used except for one modification; viz., the dimensions of the samples used in this work were about 16 inches in the longitudinal direction, 0.625 inches in the tangential direction and 0.675 inches in the radial direction, whereas in the previous work these dimensions were 16", 0.75" and 0.75" respectively. It has been shown that the bulk of liquid flow occurs in the fibre direction from tracheid to tracheid through their bordered pits (14, 64). Since the transfer area in the fibre direction was decreased by about 25% in this work, it is possible that the time of impregnation (65 minutes) was not sufficiently long for a higher sorption to occur.

(b) <u>Retention Efficiency</u>

The retention efficiencies for these experiments are greater than 0.90. It appears that 6 - 10% of the monomer had not been converted to polymer. However, most of the monomer weight loss (about 3 - 5 gms) occurred by volatization during the transfer of the sample to the aluminum canister and during the irradiation period when small amounts of monomer escaped from the wood and polymerized on the inside surface of the aluminum container. Hence it is seen that 4.5 Mr was sufficient radiation to entirely polymerize the styrene monomer.* Unfortunately, because of this, the effect of

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* Hence the assumption of 100% polymerization on Page 75 is valid.

temperature on the percent polymerization cannot be studied since complete conversion occurred throughout the range of temperatures studied. The percent polymerization in these experiments compared with the same styrene solution in the absence of wood (Figure 13) shows that the wood appears to greatly increase the rate of polymerization. It will be shown later that this increase is probably due to (1) the gel-effect and (2) energy and/or chain transfer occurring in the secondary wall.

(c) Molecular Weights

The relationship between molecular weight of the extractable polystyrene and the temperature during irradiation is shown in Figure 14. As previously discussed, it is assumed that this polymer is that which is located predominantly in the cell cavities. In contrast to the molecular weights found for the same solution in the absence of wood, there is a steady linear increase in molecular weight as a function of temperature. The effect of temperature is such that possibly the onset of the gel-effect is delayed with increasing temperature and the rate of propogation is increased, consequently yielding a higher molecular weight.

On comparing Figures 13 and 14 it is evident that the molecular weights of the polystyrene extracted from the cell cavities is substantially higher than the molecular weights of the polystyrene formed in solution in the absence of wood. This could be due to a gel-effect caused by the presence of wood. A more plausible explanation

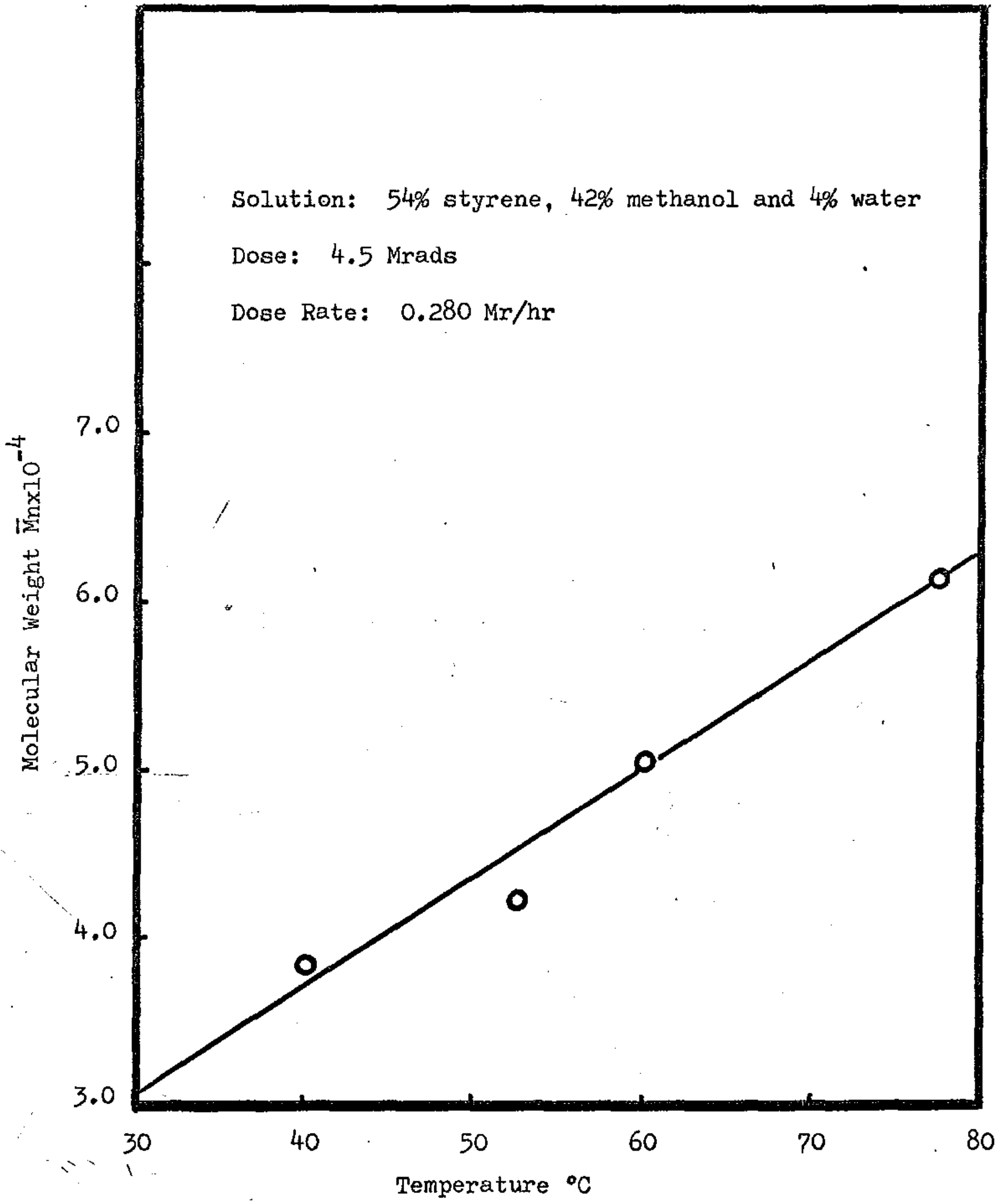

FIGURE 14

EFFECT OF TEMPERATURE ON THE MOLECULAR WEIGHT OF EXTRACTABLE POLYSTYRENE is the following: the process of "preferrential extraction" is probably occurring in the wood structure (see previous discussions on this subject). Consequently, the solution in the cell cavities contains much less methanol than the 42% in the original solution. Therefore, the concentration of styrene has increased and as a result the molecular weight of homopolymer is higher (see equation (10), p. 9).

The molecular weight of the associated polymer was not measured. However, the work carried out by Huang (28, 34) indicates that the molecular weight of the polymer extracted with cold and hot benzene is substantially lower than that of the grafted polystyrene obtained by hydrolysis. Also, his unpublished results (28) suggest that there is a correlation between the molecular weight of the homopolymer and that of the grafted polymer. For example, two experiments carried out with an irradiation dose of 4 Mr yield:

Polymer Extracted with Cold Benzene	Polymer Extracted with Benzene in Soxhlet	Grafted Polystyrene side chains obtained by hydrolysis
209,500	272,600	576,400
128,000	180,000	399,400

Hence it is possible that the molecular weight of the associated polymer in the present work is similarly related to that of the extracted polymer; i.e., an increase in temperature increases the molecular weights of both the homo- and associated polymer. The high molecular weights for the grafted polymer is probably due to the gel-effect caused by the presence of cellulose in the walls in intimate contact with the styrene and polystyrene. The cellulose undoubtedly inhibits the mobility of the polystyrene chains and reduces their rate of termination. This effect would explain the large differences in the percent polymerization values between the styrene (in solution) without and in the presence of wood. Chain and/or energy transfer from the cellulose is also possible. This effect would increase the rate of polymerization as well.

(d) Associating Efficiency

The values for the associating efficiency vary from 0.711 to 0.766 over the temperature range of ambient to 77.5°C. It can be shown that there is no significant difference between the average values.* Also there is no significant difference between these values and the average value, 0.710, obtained by Werezak using the same solution (see Table 23). There are two possible explanations for the results:

(1) If it is assumed that the associating efficiency is truly a measure of the actual grafting (i.e., the Soxhlet benzene extraction has removed all ungrafted polymer both in the cavities and in the walls) then it appears that the increase in temperature has

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* At the 95% confidence level: the reason for this is the high variance between replications at each temperature level; e.g., for the 77.5°C experiments the A.E. values varied from 0.682 to 0.785.

not promoted a higher utilization of free radicals. The results suggest that the increase in temperature (a) destroys radicals (by radical-radical combination) in the cellulose at a faster rate than it enhances the diffusion of monomer toward them and (b) increases the kinetic chain length of the grafted polymer chains. The superimposed effect would be that at higher temperatures longer grafted polymer chains are attached to fewer sites as compared to lower temperatures where shorter chains are attached to more sites. It seems improbable that these two effects would act in such a manner as to yield equal associating (or grafting) efficiencies for all temperature treatments.

(2) A more plausible explanation is the following: under the experimental conditions, the Soxhlet extraction removes primarily only the homopolymer in the cell cavities; the occluded ungrafted polymer in the walls is essentially inaccessible to the benzene. This assumption is borne out in the literature.

(a) Using the mutual irradiation technique, Stannett (41) found that the amount of unextractable polystyrene that was actually grafted to cellulose was as low as 30.5%.

(b) Ramalingam (61) found that the thermal and catalytic induced polymerization of a styrene solution in wood yielded about 20 - 40% unextractable polystyrene.

Thus a given treatment would yield a higher associating efficiency only if it induced relatively more styrene to diffuse from the lumen into the secondary wall. The results indicate that the diffusion of styrene into the walls is more dependent upon the amount of solvent (water and methanol) available for swelling the cellulose than upon the temperature. From the above argument, it is evident that although temperature changes may greatly affect the molecular weight of the grafted polymer and the reaction with free radicals in the cellulose, it will not significantly affect the associating efficiency. This result is contrary to the hope which prompted this particular set of experiments.

C. Effect of Dose and Post-Irradiation Treatment on the Radiation-Induced Polymerization of Styrene (in solution) in Wood

Experiments were carried out with the 54% styrene, 42% methanol and 4% water solution at a temperature of 39.0°C in the dose range of 1 - 5 Mr. After the irradiation, the samples were either left at room conditions or put in an oven at 100 - 105°C until constant weight was reached. The results are shown in Table 26. No replications were performed.

(a) Molecular Weights

Except for the 1 Mrad oven treated result (which may be spurious) it appears that the molecular weight increases with increasing dose up to about 3 Mr after which the values level off. It is difficult to explain the results, for the irradiation dose, per se, should theoretically affect only the number of polystyrene chains and not the kinetic chain length. However, a combination of parameters

TABLE 26

EFFECT OF DOSE AND POST-IRRADIATION TREATMENT ON THE RADIATION-INDUCED POLYMERIZATION OF STYRENE (IN SOLUTION) IN WOOD

Solution: 54% styrene, 42% methanol, 4% water

Temperature during irradiation: 39.0°C

Post Irradiation Heat Treatment	Dose Mrads	Retention Efficiency	Molecular Weight of Extracted Polymer $\overline{M}n$	Associating Efficiency
room conditions	1	.258	26,200	.729
	2	.715	37,200	.766
	3	.926	46,100	.707
	4	.895	48,500	.669
	5	.903	46,700	.657
oven at 100 - 105°C	1	.427	42,400	.702
	2	.887	33,800	.836
	3	.778	48,800	.705
	4	.800	52,800	.712
	5	.895	45,600	.756

(such as the concentration of trapped free radicals, the viscosity of the reaction medium, transfer mechanisms, etc.) may actually increase the molecular weight with increasing dose; on the other hand, since no replications were carried out, it is also possible that there is, in fact, no correlation between molecular weight and dose under the given experimental conditions.

(b) Retention Efficiency

The effect of dose on the retention efficiency is evident. For the samples which were left at room conditions after irradiation, the percent polymerization increases with increasing dose until a maximum is reached at about 3 Mrad. Above this dose the value naturally stays constant. For the samples that were put in the oven, no obvious trend is noted. Now the temperature of the post-irradiation heat treatment can affect both the rate of polymerization (homo- and graft) and of volatization of the unreacted styrene monomer. At low doses (1 - 2 Mr) it appears that the high temperature treatment causes relatively more polymerization than the lower temperature treatment, whereas at higher doses (3 - 5 Mr) the opposite seems to be true.

(c) Associating Efficiency

The average associating efficiency for the samples left at room conditions after irradiation is 0.706. Omitting the value at the dose of 1 Mr, it is seen that a decrease of associating efficiency (from 0.766 to .657) occurs as the dose is increased. Huang found the same effect (28). He found that for a range of 0.25 to 4 Mr, the grafting efficiency decreased from 74.0 to 49.8.

The samples which were put in the oven after irradiation yielded an average associating efficiency of 0.742. There seems to be no correlation between the associating efficiency and dose.

PART 2

MECHANICAL PROPERTIES OF WOOD-POLYSTYRENE COMBINATIONS

INTRODUCTION

Wood's most troublesome property from a structural viewpoint is its tendency to swell and shrink. The stabilization of wood to dimensional change caused by moisture has been investigated for many years. All present methods for attaining improved dimensional stability of wood fall into one or more of five different types (14):

1. Laminating of thin sheets as in plywood.
2. Applying water-resistant surface and internal coating.
3. Reducing the hydroscopicity of the cellulose.
4. Bulking the fibre.
5. Cross-linking the cellulose chains of the component fibres.

Unfortunately there is generally a decrease in the strength properties of the wood treated by the above methods. It is therefore desirable to find a method of improving the dimensional stability and strength of wood or at worst enhancing the former without depreciating the latter.

The technique in this present work as well as that used by Werezak previously, in which a solution of styrene, methanol and water was used as an impregnant, results in the deposition of polystyrene in the less ordered regions of the cellulose in the cell walls. This bulking improves the stability of wood simply by preventing water from entering into these regions. How the presence of this grafted foreign material affects some mechanical properties of the wood will be discussed in this section of the thesis.

In addition, although bulking the cell cavities with a plastic material will not reduce the ultimate dimensional change attained by wood in a moist environment, it will decrease the rate of moisture absorption. Thus this technique has been also employed in this work and the mechanical properties of the resulting product have been studied.

(a) Effect of Ionizing Radiation on the Strength of Cellulose

The effect of high energy electrons on cellulose results in degradation (83). When native cellulose was irradiated, its ordered regions were broken down at about the same rate as its loss in strength (84).

Cotton yarn was irradiated in a vacuum of 1 micron or less with CO-60, neutrons and β-rays (85). The loss in tenacity varied from 30 to 40%. The presence of water vapour and atmospheric oxygen during irradiation had little or no effect on the strength of the cotton yarn. Cotton cellulose irradiated in air and in vacuum showed similar decreases in tensile strength and elongation (86). At 10^7 r.e.p. the decrease in tensile strength for cellulose in air and vacuum was 30.3% and 31.9% respectively.

Cotton, rayon and acetate yarns were irradiated with CO-60 gamma rays and nuclear radiation (87). It was found that

(1) tenacity, elongation, elastic modulus and stiffness of the fibres decreased with increasing dose,

(2) the degradation produced in cellulosic materials by nuclear radiation is a function of total dose and does not depend on dose-rate,

(3) the effect of nuclear radiation is equivalent to that of

gamma rays, and

(4) the relative order of stability toward nuclear radiation of the fibres considered was acetate > rayon > cotton.

The physical properties of cotton, sliver lap, yarn and fabric irradiated with high energy electron and gamma rays were investigated (29). Tensile strength, elongation and toughness decreased with radiation dose but little change occurred below a dose of 10^6 roentgens. Tensile strength measurements showed a maximum in the 0.05 - 0.1 Mrep region. This was attributed to a release of points of residual internal strain permitting a better distribution of stress within each fibre. Tensile strength decreased appreciably above 1 Mrep.

(b) Physical Properties of Cellulose Graft Copolymers

Ionizing radiation was used to initiate "internal" polymerization of acrylonitrile onto filter paper (88). Polymerization was performed with the filter paper (1) immersed in the monomer or a monomer solution and then irradiated, (2) saturated with monomer or a monomer solution and irradiated in air or under nitrogen, (3) irradiated in air or in nitrogen and subsequently immersed in monomer or monomer solution. The following results were observed:

(1) A maximum increase in both retention of wet strength (55%) and dry tensile strength (106%) were observed (strength measured in lbs. per inch of width of filter paper) when the paper was saturated with pure monomer and then irradiated in air.

(2) Use of an aqueous solution of acrylonitrile decreased

the dry tensile strength below that of untreated paper but resulted in a 3 - 22% increase in the wet tensile strength.

Styrene, methyl methacrylate, methyl acrylate, ethyl acrylate, acrylonitrile and vinyl acetate were grafted onto cellulose in the form of rayon by the use of the pre-irradiation method (31). Investigation of the tensile properties showed that the modulus of rigidity of the rayon grafts increased when the grafted polymer had a high transition temperature such as polystyrene, poly-methyl methacrylate and poly-acrylonitrile, but decreased when it had a low transition temperature such as poly-methyl acrylate and poly-ethyl acrylate. The breaking strength of the rayon-methyl acrylate graft was comparable to that of the original rayon and showed an increase for the rayon-methyl methacrylate graft copolymer. The tenacity or breaking strength in grams/denier which takes into account the weight increase, decreased for both cases. Similar behaviour was observed for rayon-styrene and rayon-acrylonitrile graft copolymers. In order to avoid excessive loss in tensile properties the author recommends that radiation doses be kept below 1 Mrad.

Acrylonitrile was grafted onto cotton using CO-60 gamma rays (89). The monomer was added as an aqueous solution of zinc chloride. When compared to the original unirradiated control, the grafted yarn (26% acrylonitrile) decreased 15% in breaking strength, 45% in breaking stress and 65% in average stiffness. The elongation-at-break increased 70%.

Huang (28, 36) carried out physical testing on styrene-grafted rayon at various levels of grafting. The results are summarized below:

(1) Denier (weight in grams per 900 metres) increased with percent grafting, though not quite proportionately to the amount of grafted styrene.

(2) Tenacities (g/denier) decreased considerably due to the increase in denier. Breaking load or tenacity x denier remained more or less constant.

(3) Breaking elongation increased considerably above 65% grafting. For example, the breaking elongation at 105% grafting is three times that of the original rayon.

(4) Conditioned modulus (Young's) did not improve sufficiently to compensate for the large increase in denier and consequently decreased considerably.

(5) Secondary swelling decreased considerably with increased grafting, indicating that the treated rayon became more hydrophobic as the percent grafting increased.

(6) Moisture regain decreased with increasing percent grafting of polystyrene.

(c) Physical Properties of Wood-Plastic Combinations

Karpov et al (90) described the modification of wood with styrene, methyl acrylate, methyl methacrylate and acrylonitrile. It was found that it was possible to increase the chemical resistance, fire resistance, strength and dimensional stability of wood and decrease the water absorption. For pine wood impregnated with 120% (by weight) of styrene and irradiated at 0.8 Mr/hr. an increase in static bending of 65.7% and an increase in compressive strength of 185.8% when irradiated for a total dose of 15.5 Mr were noted. The resistance to static bending for unimpregnated irradiated wood showed a steady decrease as the total dosage was increased.

Kenaga, Fennessay and Stannett (60) irradiated ponderosa pine sapwood pre-impregnated with a dioxane-styrene-water solution. The experimental details have been described earlier in this thesis. The results can be summarized as follows:

(1) Effect of Retention on Stabilization

The amount of styrene required for a given order of stabilization was relatively high compared to such methods as acetylation. It was determined that the homopolymerization within the cell lumen was not the dominating cause of this inefficiency; the main reason was the opening up of the more ordered cellulose areas by means of the impregnation and irradiation. In this manner water enters and swells regions which under ordinary circumstances are inaccessible.

The displacement or "inclusion technique" was used in order to eliminate the nonproductive use of polystyrene in the cell cavities. This method gave an increase in the antishrink efficiency* because there was a reduction of material deposited in the lumen and there was less opening up or swelling of the cellulose structure.

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* For definition see Page 152

(2) Tensile Strength (Parallel to the Grain)

Three impregnating solutions were used in this part of the work: (A) 25% styrene, 75% dioxane and 5.75% water (B) 2.5% styrene, 12.5% ethyl acrylate, 75% dioxane and 5.75% water and (C) 25% toluene, 75% dioxane and 5.75% water; all by volume. The results are tabulated below:

TABLE 27

TENSILE STRENGTH OF STABILIZED WOOD (AFTER KENAGA ET AL)

Solution	Dose Mrad	Percent Retention	Modulus of Elasticity (1000 psi)	Moisture Content, %	Maximum Load psi
A	0.75	11.22	1207	7.01	12470
	1.20	27.56	1407	6.07	11340
	1.65	39.33	1347	5.37	10320
B	0.75	16.22	1307	6.93	12460
	1.20	27.60	1440	6.38	11360
	1.65	42.39	1292	5.59	10020
C	0.75	3.15	1302	6.68	12730
	1.20	2.49	1148	7.01	11170
	1.65	2.94	1150	7.46	11000
un-irradiated control	0		1309	10.04	11430

An analysis of variance of the above data showed that

(a) the modulus of elasticity is affected only by the treatment (significant to the 5% level).

(b) the maximum load is affected by dose which is significant to the 1% level.

respectively. The largest value (21.1) was obtained for wood impregnated with triethylene glycol dimethylacrylate.

(d) Previous Work on this Project

1. Ramalingam and Hodgins

Ramalingam and Hodgins (61) carried out experiments where wood samples were irradiated in a swimming-pool reactor up to doses of 32.4 Mr/hr. The bending strength (in pounds of load) decreased as the total irradiation received by the sample increased, as shown in Figure 15. Wood samples were treated with different styrene solutions and polymerization was initiated by radiation, thermally or catalytically (see Table 1). All wood was humidified prior to testing. The percent change in bending strength (in pounds) varied from -5.5 to 56.8%. The results seem to indicate that the bending strength of the samples is strongly dependent upon the polystyrene in the sample and not the method of initiation. For example, consider the results shown in Table 28. It is evident that the bending strength, measured in pounds of load, of the treated samples is substantially higher than that of the controls. For the samples treated with pure styrene, it may be assumed that the modulus of rupture (which takes into account the stressed area of the specimen) exhibits exactly the same increase because this treatment does not swell the wood. Therefore, for the wood impregnated with pure styrene, irradiated with a dose of 4.5 Mr, humidified at 76% R. H. and stressed in bending, the increase in modulus of rupture would be 56.8% as compared to the humidified untreated control. A different situation

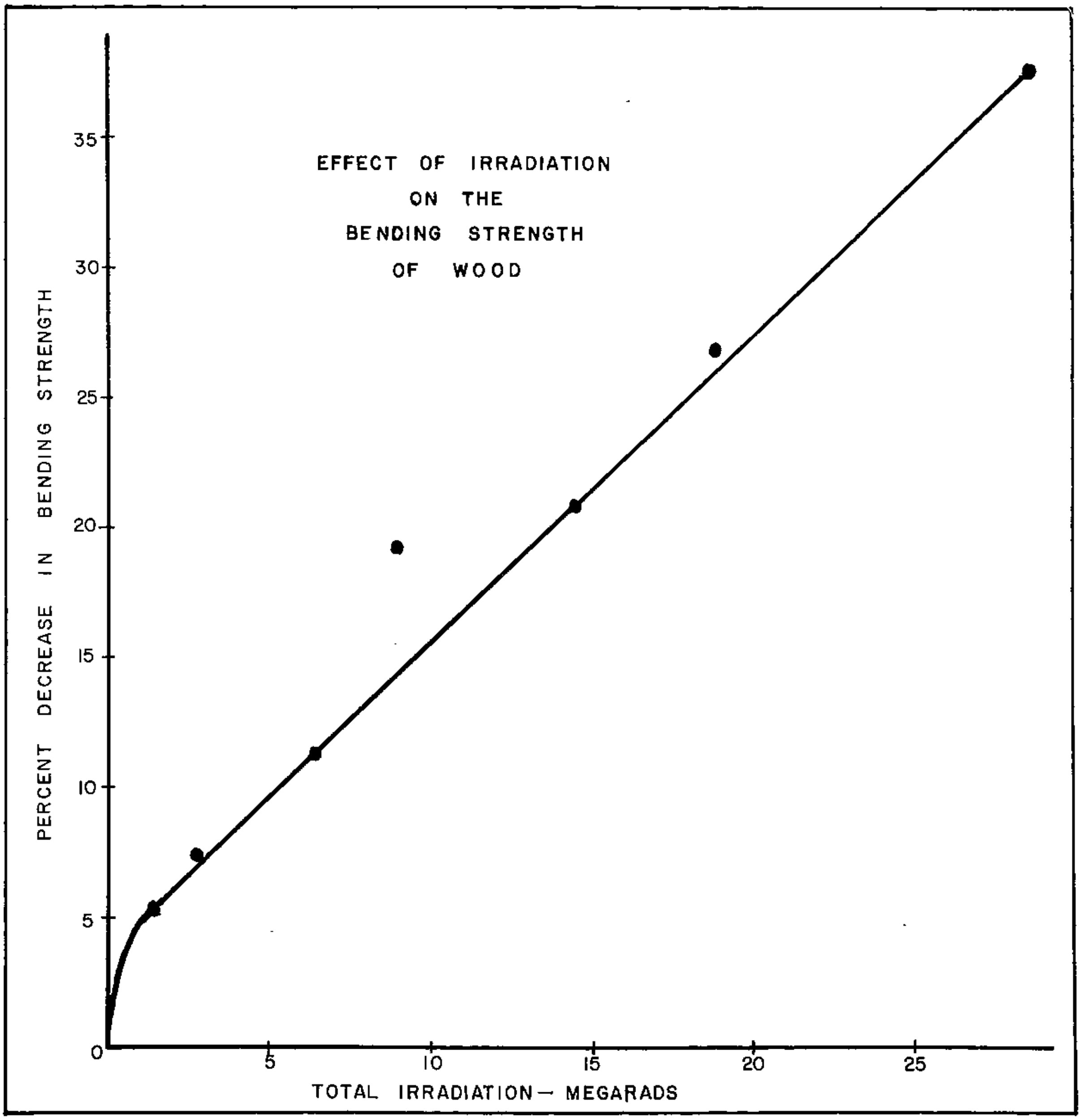

FIGURE 15

(after Ramalingam and Werezak)

TABLE 28

EFFECT OF POLYSTYRENE ON THE BENDING STRENGTH OF WOOD

(after Ramalingam)

Impregnant	Initiation	$\frac{\text{Wt. of Polystyrene in sample}}{\text{Wt. of wood prior to treatment}} \times 100$	$\frac{\text{B.S. of treated wood (lbs.)}}{\text{B.S. of control (lbs.)}} \times 100$
pure styrene	thermally at 105°	100	156.0
pure styrene	4.5 Mr	100	156.8
76% styrene 22.5% methanol 1.5% water	4.5 Mr	90	146.5
76% styrene 22.5% methanol 1.5% water	thermally at 105°	42	127.4
76% styrene 22.5% methanol 1.5% water	thermally at 105°	80	141.3
76% styrene 22.5% methanol 1.5% water	0.2% by vol. benzoyl peroxide	46	127.0
76% styrene 22.5% methanol 1.5% water	0.2% by vol. benzoyl peroxide	74	141.7

exists for the solution-treated samples. Since the treatment with water and methanol leads to swelling of the wood, the area stressed in bending is larger than that of the control. Hence the percent increase in modulus of rupture will not be as high as the values for the percent increase in bending load. This will be discussed in detail later with Werezak's results.

The percent decrease in moisture absorption (measured by placing the samples in a 76% R. H. environment) also appears to be a strong function of the amount of polymer in the wood and independent of the type of initiation. For samples impregnated with pure styrene and irradiated with a dose varying from 0 to 18.9 Mrad, the percent decrease in moisture absorption was relatively constant at 65%. Most other treatments yielded about the same value. Because this term is based on the weight of the oven-dry treated sample, it is somewhat misleading. For example, a given treatment may increase the weight of the sample 100% and not decrease the absolute amount of water enterring the cell walls; yet the "moisture absorption" will have been halved. In any event the treatments undoubtedly decrease the amount of moisture absorbed in the wood, on any basis.

Some treatments yielded no grafted polymer (e.g., pure styrene) and others gave a high amount of grafted polymer. In view of the fact that the uptake of water vapour occurs primarily by capillary action through the cell walls, (i.e., it by-passes the cell cavities), the wood treated with pure styrene should theoretically take up much more water vapour than the grafted samples where polymer is located within the walls. Since this was not the case (even on the basis of the weight of wood prior to treatment) it is likely that the absorption was diffusion controlled. Kent et al (92) obtained results similar to these before they reduced their samples to wafer-size in order to eliminate the diffusion problem.

The decrease in water absorption (measured by immersing the samples in distilled water) for the treated samples varied from 43 to 85%. Again the results indicate that the water absorption is a strong function of the amount of polymer in the sample. This result is expected since the polystyrene (grafted and homo-) is occupying volume which the incoming water would normally fill.

Generally, the dimensional stability of the wood was improved by the treatment. For the "optimum" treatment of 76% styrene, 22.5% methanol and 1.5% water at a dose of 4.5 Mrad, the volumetric shrinkage was reduced by about 80 percent. Also the swelling of wood was reduced by about 85 percent.

2. Werezak and Hodgins

Werezak, in continuing Ramalingam's work, carried out a two-factorial experimental design using bending strength as the indicator with the following six variables: time of evacuation, composition of impregnant, uptake of impregnant, total gamma dose, duration of heating treatment and temperature of heating treatment (see Tables 2 - 21). A gradient search of the results appeared to establish trends. An equation for the relationship of variables was set up as

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 \ldots\ldots b_nx_n$$

where Y = the product yield (e.g., bending strength increase)

b_0, b_1 ... b_n = constant coefficients

x_1, x_2 ... x_n = the value of each dependent variable such as time of evacuation, total gamma dose, etc.

The coefficients or slopes represent the change in Y per unit change in x. If the coefficients for a given factorial design are known, a second design can be set up from the trend indicated by the slopes. Unfortunately, Werezak calculated these slopes without calculating their standard deviation. It can be shown that for his Factorial Design No. 1 the values of b vary from -4.1 to 6.8 with a standard deviation of $\pm$ 10.09 and for the second design these values range from -5.5 to -2.8 with a standard deviation of $\pm$7.37 (80). In other words, these coefficients are not significantly different from zero. This does not necessarily indicate that the variables, per se, do not affect the percent change in bending strength; but it does show that either

(1) the range of the variables is so narrow that no correlation between them and the "percent change in bending strength" may be obtained. For example, it is improbable that an evacuation time of 11 hours would lead to a significantly different bending strength than a time of 13.5 hours.

and/or (2) some highly influential variable was omitted from the design. This exclusion might have obscured the effect of the other variables.

It is probable that both of the above factors are important. It has been shown earlier in this thesis that three of the variables selected (total gamma dose, duration of heating treatment, and temperature of heating treatment) had ranges so small that their effect on the kinetics of the system was not discernible. This should also be true for the mechanical behaviour of the wood.

In addition, it is known that the strength properties of wood are strongly dependent upon the specific gravity or density of the specimen. The large variation of bending strength (due to the variation in density) could have clouded the effect of the other important variables such as impregnant uptake.

The choice of indicator, (Y), was also not suitable. This term was the bending strength increase based on the loads, in pounds, required to fracture the samples. The wood samples that were treated swelled on the average 13 - 17%, depending on the impregnating solution (see Table 21). This indicator, unlike the modulus of rupture, does not take the increase in volume into consideration.

In general, Werezak obtained results very similar to those of Ramalingam in regards to strength properties of the treated sample and dimensional stability improvements. In addition, one other physical characteristic was examined: resistance to microbiological attack. The weight loss by decay (using a culture of Lenzites Trabea) averaged about 14%, compared to a mean loss of 71% by the untreated controls.

SCOPE OF PRESENT INVESTIGATION

The conclusions drawn by Ramalingam and Werezak about the enhancement of the bending strength of wood by in situ polymerization of styrene have been found to be inexact.

First, the true measure of a specimen's bending strength is the modulus of rupture which is simply the fracture load divided by the stressed area.* It is quite evident that the fracture load itself is not a meaningful index of strength unless the dimensions of the treated and control specimens are identical. Since the ultimate volume of the treated sample was significantly larger than that of the control, the stress and not the load must be measured and used as a gauge of strength.

Second, the previous researchers found that the water vapour uptake for the treated wood was substantially lower than for the untreated controls. Since the standard A.S.T.M. tests that were used require the specimens to be humidified at a humidity of 76% R. H., it is seen that the treated samples contained much less water in the cells than the controls during testing. Since it is known that water has a degradative effect on the strength of wood, one cannot say with certainty whether the treated wood is inherently "stronger" than the control or whether the "improvement" in strength is due to the different water content for both types of wood.

Third, the specific gravity or the density of wood was not considered in the studies of the previous workers. It is known that the strength of wood is very strongly dependent on the density of the wood.

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* more precisely: stress = Moment/Section Modulus

In dealing with wood of wafer-size, it is convenient to use a "control" system because it is possible to obtain specimens which are closely identical in physical and chemical properties; however, for the large sample size considered in this work, this is not practicable. The assumption of equal properties for the control and the treated sample prior to treatment leads to, at best, approximate results.

In addition, an unsatisfactory aspect of this work from a theoretical viewpoint is the use of bending strength as an indicator of strength. Although modulus of rupture is an accepted criterion of strength, this term does not help one gain a clear insight into the rudimentary effect of grafted and homo-polystyrene on the mechanical properties of wood. This is so because the process of bending involves two primary stresses -- compression and tension; an increase in one and decrease in the other might lead to no change in bending strength and to the subsequently false impression that the polystyrene has not affected the wood in any manner. Tension and compression tests are necessary for an elucidation of the fundamental effect of the treatment on the strength of wood.

With the above considerations in mind, the following work was carried out.

From the load-deflection curves obtained by Werezak for the impregnated and irradiated, irradiated and control wood, the modulus of rupture, stress at the proportional limit, modulus of elasticity, work to the proportional limit and work to the maximum load were calculated. The data were regressed with respect to specific gravity. The altered wood was compared to the untreated, unirradiated wood at common specific gravity values.

It was desirable to compare the treated and untreated wood on the basis of equal moisture contents. The most convenient moisture level to work with was zero. Thus all the free moisture in the wood was driven out of the samples by oven-drying. The treated wood was compared to the untreated wood on the oven-dried basis in a manner similar to that described above for Werezak's data. The effect of moisture on the strength of wood is also studied.

It was realized in the early stages of this work that the solution treatment (styrene, water and methanol) did not actually improve the bending strength of wood when moisture, specific gravity and stressed area were considered as parameters. For this reason, work was also carried out with pure styrene in the absence of swelling agents.

Compression and tension tests were carried out with oven-dried samples. The ultimate stresses were regressed with respect to the specific gravity and compared at common values of the latter.

EXPERIMENTAL DETAILS

The selection and treatment of samples are discussed in the experimental section of PART 1 of this thesis. In addition to the two impregnating liquids mentioned (pure styrene and a solution of 54% styrene, 42% methanol and 4% water by weight) a solution of 27% styrene, 65% methanol and 8% water was used.

Before the bending tests were performed, all samples, either treated or untreated, were put in an oven at 100 - 105°C and left until constant weight was reached. They were then immediately weighed and their dimensions were measured with a vernier caliper.

Static Bending

Before testing the samples, they were allowed to come to room temperature as the strength properties of wood undergo reduction at higher temperatures (13). Using a Tinius Olsen Universal Tester, the bending of wood was carried out in accordance with the A.S.T.M. procedure (77) except that the cross-sectional dimensions of the samples were not 3/4" x 3/4". For the treated samples these dimensions were about 0.7" x 0.7". Although an "effect of depth" exists on the modulus of rupture (76) the effect can be considered negligible for a reduction in depth from 3/4" to 0.7". In all cases the bearing block was applied to the tangential face of the test sample. The load was applied continuously at a rate of 0.1"/min. Load deflection curves were determined by using a deflectometer which is auxiliary to the tester. An example of deflection as a function of applied load is given in Figure 32 for untreated and treated wood. From these curves, the modulus of rupture, stress at the proportional limit, modulus of elasticity, work to the proportional limit and work to maximum load were calculated. A brief description of the meaning of these mechanical terms and the formulae by which they were calculated is given below. The span of the specimens in all cases was 16 inches and the beams were stressed by centre loading.

Modulus of Rupture, R

This property is a measure of the ability of a beam to support a slowly applied load for a short time. It is an accepted criterion of strength.

$$R = \frac{1.5\ PL}{bh^2}$$

Stress at the Proportional Limit, P.L.

This property is the computed stress in the wood specimen at which the strain (or deflection) becomes no longer proportional to the stress (or load).

$$P.L. = \frac{1.5P_1L}{bh^2}$$

Modulus of Elasticity, E

This property is a measure of the stiffness or rigidity.

$$E = \frac{P_1L^3}{4Dbh^3}$$

Work in Bending to the Proportional Limit, S

This expression is a measure of the energy absorbed by a beam when it is stressed to the proportional limit.

$$S = \frac{P_1 D}{2V}$$

Work in Bending to the Maximum Load, W

This property is a measure of the combined strength and toughness of wood under bending stresses. It can most easily be evaluated from the total area under the load-deflection curve from zero deflection to the deflection at maximum load.

Legend:

b, h, L = breadth, height and span of specimens, inches

D = total deflection at elastic limit, inches

P = maximum load; pounds

P_1 = load at elastic limit, pounds

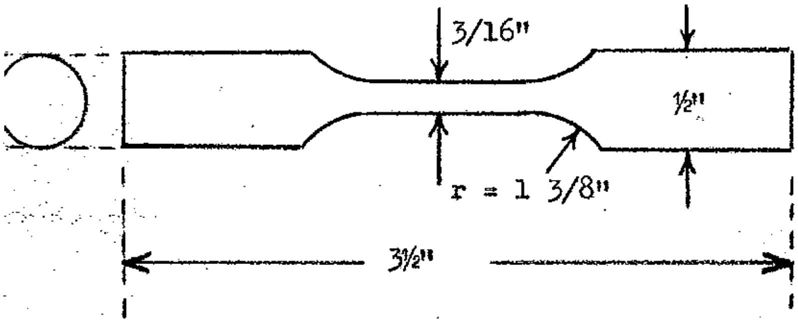
V = volume of beam between supports, cubic inches

Compression Parallel to the Grain

Compression tests were carried out with samples cut from the ends of the small beams used in the bending tests. These were 3/4" - 1 1/2" in the longitudinal direction and had cross-sectional dimensions of about 0.7" x 0.7". Some of the control samples used by Werezak were found and, on clear sections of these, compression and tension tests were performed. These samples were equilibrated in a humidifier at an R. H. of 69% and a temperature of 25°C before testing. All other samples were oven-dried to constant weight and placed in a desiccator and allowed to reach room temperature before testing. The same procedure was used for the tensile samples discussed below. The Tinius-Olsen tester was used for the crushing. No load-deflection curves were obtained and hence only the maximum crushing load was recorded. The load was applied continuously throughout the test at a rate of 0.01 in. per minute.

Tension Parallel to the Grain

The measurement of the tensile strength of wood parallel to the grain is rarely carried out because of the difficulty of attaching the wood specimens; when an external collar-type clamp is used the stress is usually concentrated around the periphery. This sets up shear stresses in the wood. In an effort to minimize the effect of shear it is customary to taper a sample at the centre (60, 72, 74, 76). In this work, several methods of preparing the specimen and two methods of testing were attempted. The samples were cut from the ends of the beams that were fractured in the bending tests and were, in consequence, restricted in dimension. Exploratory tests revealed that the most satisfactory type of test piece had the following description: the specimen was cylindrical in shape with an overall length varying from 3 - 6 inches and a diameter of 1/2". The central portion was waisted by means of a lathe to a cross-sectional diameter of from 0.135 to 0.260" over a length of at least 3/4". The curved portion was of a radius of 1 3/8". A typical specimen is drawn below.



Initial tests were performed on an Instron Tensile Testing Machine (Model No. TTCL); however, since the total time involved per sample was close to one hour, and since it was difficult to "book time" on the machine (over 100 samples were involved), it was decided that the less sophisticated but more convenient Hounsfield Tensometer Type W could be used. In this machine the specimen is stressed manually by means of a wheel and the load is measured by a capillary mercury gauge. Special clamps to fit the wood specimens were made in the Chemical Engineering Machine Shop. To prevent crushing in the clamps, the ends of the sample were soaked with epoxy-resin which was allowed to cure at room conditions. The polymer-wood samples did not need this treatment because of their inherent hardness and resistance to compression. All samples in which failure did not occur in the central waisted portion of the test piece were rejected.

RESULTS

A. General

As mentioned previously, "control" samples were not employed in this work. Rather an attempt was made to organize the data in such a way as to express most mechanical properties for untreated and the treated samples as a function of the oven-dry specific gravity of the wood or the oven-dry specific gravity of the samples prior to treatment. In this manner, regression curves for the treated and untreated wood could be compared. Once in this form, the data could then be used to relate strength properties at any specific gravity within the range of this work. Regression analyses were carried out on an I.B.M. 7040 digital computer. A simple program was developed to evaluate the statistics of the data, such as the least-squares line (Appendix VI). Multiple regressions were carried out using a versatile computer program developed by Petryschuk and Hill at this university (78). The results have been generally kept free of the details of the statistical analysis; these are found in the appendices. All correlations shown in graph form are significant at the 95% confidence level. All average values presented in table form (or otherwise) are presented with their 95% confidence limits. These limits have not been "rounded off" so that the exact standard deviations may be extracted from them and, if so desired, used in "t" and "F" comparison tests. Any mention of "significance" refers to the 95% level unless stated otherwise. The symbols shown on the graphs are defined as follows (79):

(a) $Y = bX + a$: the least-squares line

(b) N: the number of data points

(c) $\bar{Y}$ and $\bar{X}$: average values of Y and X

(d) $S(\hat{Y})^2$: variance of estimate from the correlation line

(e) S(b): standard deviation of the slope, b

(f) r: correlation coefficient

With the above data, the confidence limits of the correlation can be obtained. (An example is given in Appendix VI.)

B. Dimensional Stability

A term that is used quite extensively in measuring the effectiveness of a given dimensional stabilization treatment is the "Antishrink Efficiency" (14). It can be calculated by the following formulae (60):

$$\% \text{ swell} = 100 \times \frac{S-OD}{OD}$$

where S is the volume of the water-soaked, treated sample; and OD is the volume of the same sample in the oven-dried state

and

$$\% \text{ Antishrink Efficiency} = 100 \times \frac{SCW-STW}{SCW}$$

where SCW is the percent of swell in the control wafer; and STW is the percent swell in the treated wafer.

Werezak carried out dimensional stability studies on all the samples he treated. The most suitable experiments for demonstrating the effect of polymer retention on the stabilization of wood are

Experiments 18 - 20 (see Tables 18 - 20 in PART 1 of this thesis). This is so because of the wide distribution of polymer retention values; viz., 0.151 to 0.496 gm/cc. As recalled, in these experiments the impregnation solution was composed of 76% styrene, 22.5% methanol and 1.5% water by weight. The pressure of impregnation was atmospheric; the time of impregnation was 10 - 35 minutes; the dose was 3.5 Mrad; the heating temperature was 85 - 105°C and the time of heating was 12 - 24 hours.

The volumetric swelling experiments were carried out by Werezak in the following manner: oven-dried treated and control samples of known volumes were placed in distilled water at room temperature and atmospheric pressure for 28 days. The dimensions of the samples before and after soaking were measured and % volumetric swelling was determined.

Figure 16 is a plot of Antishrink Efficiency versus % retention (defined in PART 1). These results compare favourably with those of Kenaga et al (60) for values of % retention in the range of this present work (greater than 30%).* The data of Kenaga are based on wood samples which had been treated with a solution of 25% styrene, 75% dioxane and

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* All the data of Kenaga et al above 30% retention fall within the 66% confidence region of the data; i.e., ± S(Y) from the correlation line.

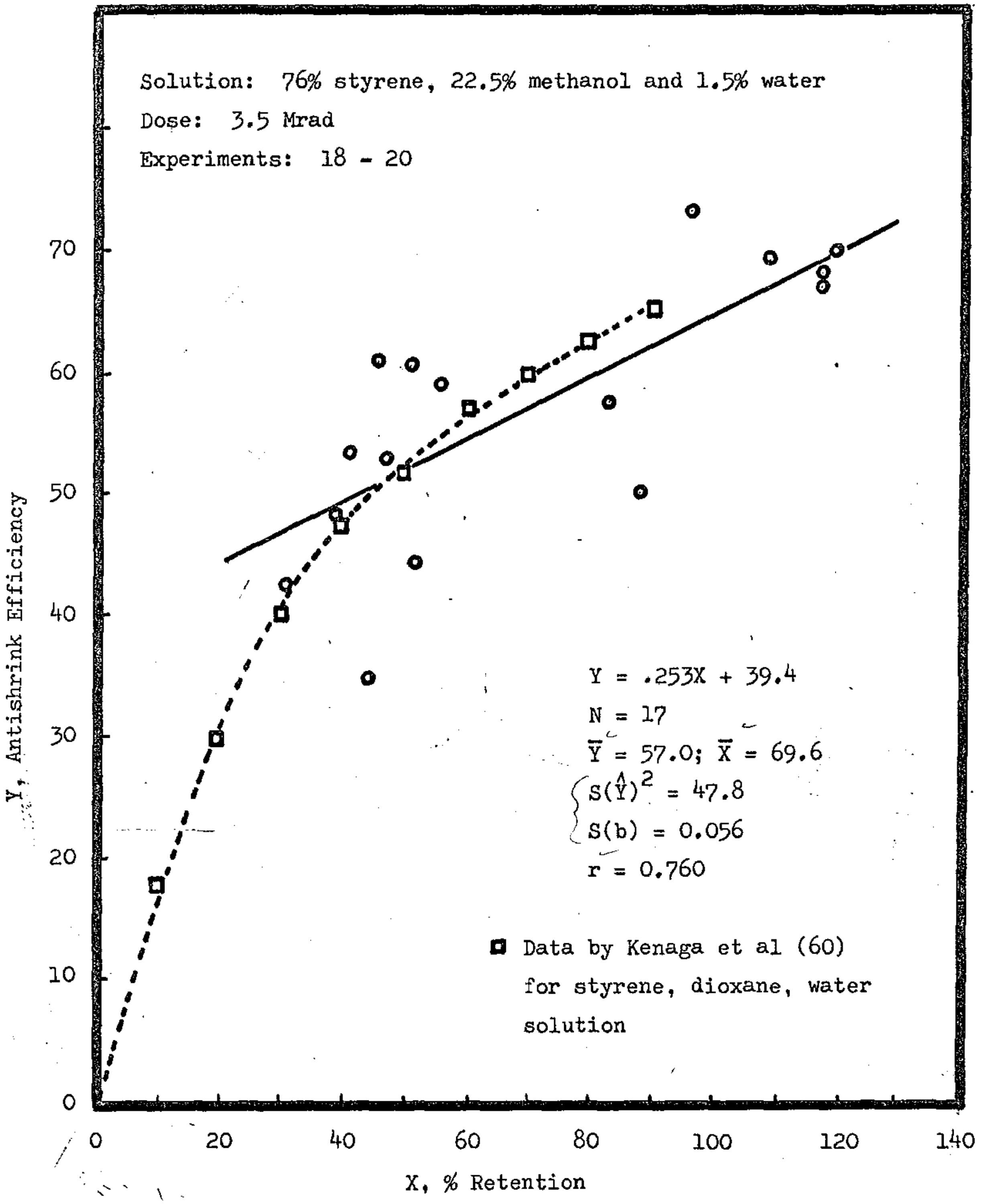


FIGURE 16

RELATIONSHIP BETWEEN ANTISHRINK EFFICIENCY
AND PERCENT RETENTION
(after Werezak)

5.75% water. The amount of polystyrene that was removed by chipping, grinding and leaching the final samples was 29 - 44% of the total polymer retained. In the present work the corresponding amount of extractable polymer for the samples used in experiments 18 - 20 was 30 - 66%. Unfortunately, no experiments were carried out for % retentions below 30% but in theory the values should slope toward the origin, as shown by Kenaga's data.

The amount of material required for a given order of stability is high as compared to other methods. Taking an Antishrink value of 60%, the % retentions for this treatment, the acetylation treatment and the phenol formaldehyde treatment are 80, 20 and 23% respectively. The reason for this inefficiency has been explained by Kenaga. There are two main factors: (1) the non-productive use of polystyrene resulting from its deposition in the cell lumen and (2) the opening up of the more ordered areas of the cellulose to permit greater swelling. This last point is discussed in detail in Appendix V.

C. Strength Properties of Untreated Wood

It is well established that aside from actual strength tests, the density of a specimen of wood is the most satisfactory criterion of its clear-wood strength (12 - 14, 72 - 74). In fact, within a given species for which the average density and strength values are already known, it may be even more satisfactory than the actual testing (72). All mechanical properties measured in this work display this dependence on specific gravity.

In all the following graphs the abcissa is the oven-dry specific gravity. That is, it is the specific gravity of the sample based on the weight obtained after heating to constant weight at 100 - 105°C. For the samples tested by Werezak this value was estimated.

1. Static Bending

(a) General

Werezak carried out bending strength measurements by two methods. In one case the load-deflection curves were determined by recording the deflection at various load increments; in the other, these curves were obtained automatically by a recording device (deflectometer) auxiliary to the universal tester. It will be shown later that these two methods yielded significantly different rupture values for the wood. Thus care is taken in this work to separate the results into: (1) the samples analyzed with the deflectometer and (2) the samples analyzed without the deflectometer.

A summary of the following results is given in Tables 34 and 35. In Table 34, the strength properties of untreated and treated wood are compared at an average specific gravity or "specific gravity prior to treatment" of 0.431. For the treated wood, in some instances, no correlation existed between the considered strength characteristic and the specific gravity. In these cases the comparisons were made on the basis of the average "specific gravity prior to treatment" for the treated samples.

(b) Effect of Irradiation on Modulus of Rupture

In Figure 15 it is shown that irradiation decreases the bending strength of wood. (This curve is based on data by Ramalingam (61).) Also, Werezak found that the average bending strength decrease (based on the strength value of the controls) was 8.2% for 3.5 Mrad and 9.5% for 4.5 Mrad. These values are based on the load in pounds and are valid only on the assumption that the control and irradiated samples have equal physical properties. More accurate results can be obtained when (1) the strength data are normalized with respect to the stressed area and (2) average values of the control and irradiated samples are compared at equal specific gravities.

Figure 17 is a plot of Modulus of Rupture versus the oven-dry specific gravity of the samples stressed (without the deflectometer). These samples were equilibrated to constant weight in an atmosphere of 68% relative humidity and 25°C. Figures 18 and 19 are similar plots for samples irradiated with 3.5 and 4.5 Mrad respectively. It can be shown that there is a significant difference between the correlation of either of the irradiated samples and that of the controls (Appendix VI, Section C). Figure 24 is a superposition of the correlation lines of Figures 17 - 19, showing the effect of the irradiation (and specific gravity) on the modulus of rupture. At an oven-dry specific gravity of 0.431 the modulus of rupture is decreased by 3.7 ± 2.9% for an irradiation dose of 3.5 Mrad and 9.9 ± 3.7% for 4.5 Mrad.

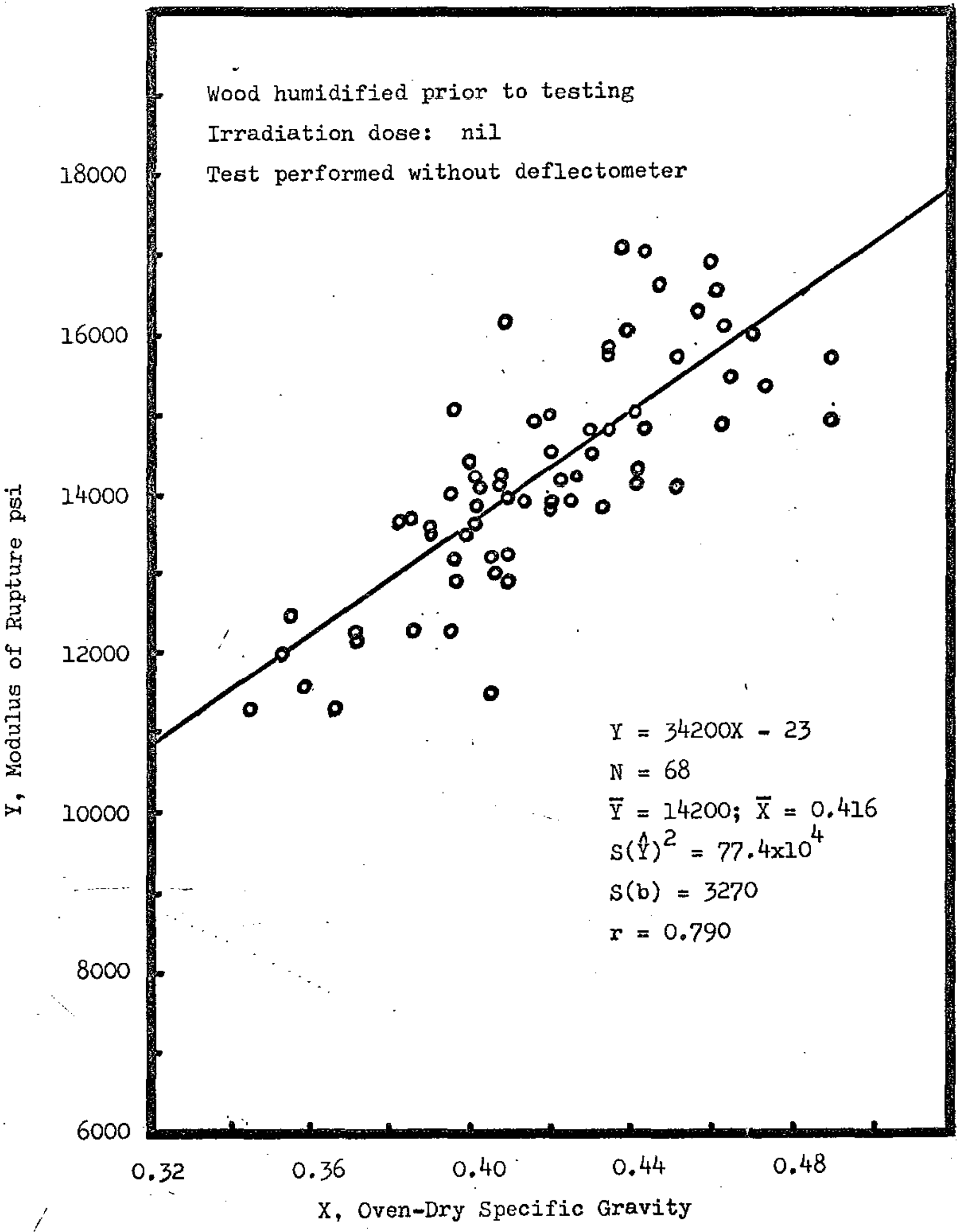


FIGURE 17

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND SPECIFIC GRAVITY
FOR HUMIDIFIED WOOD
(after Werezak)

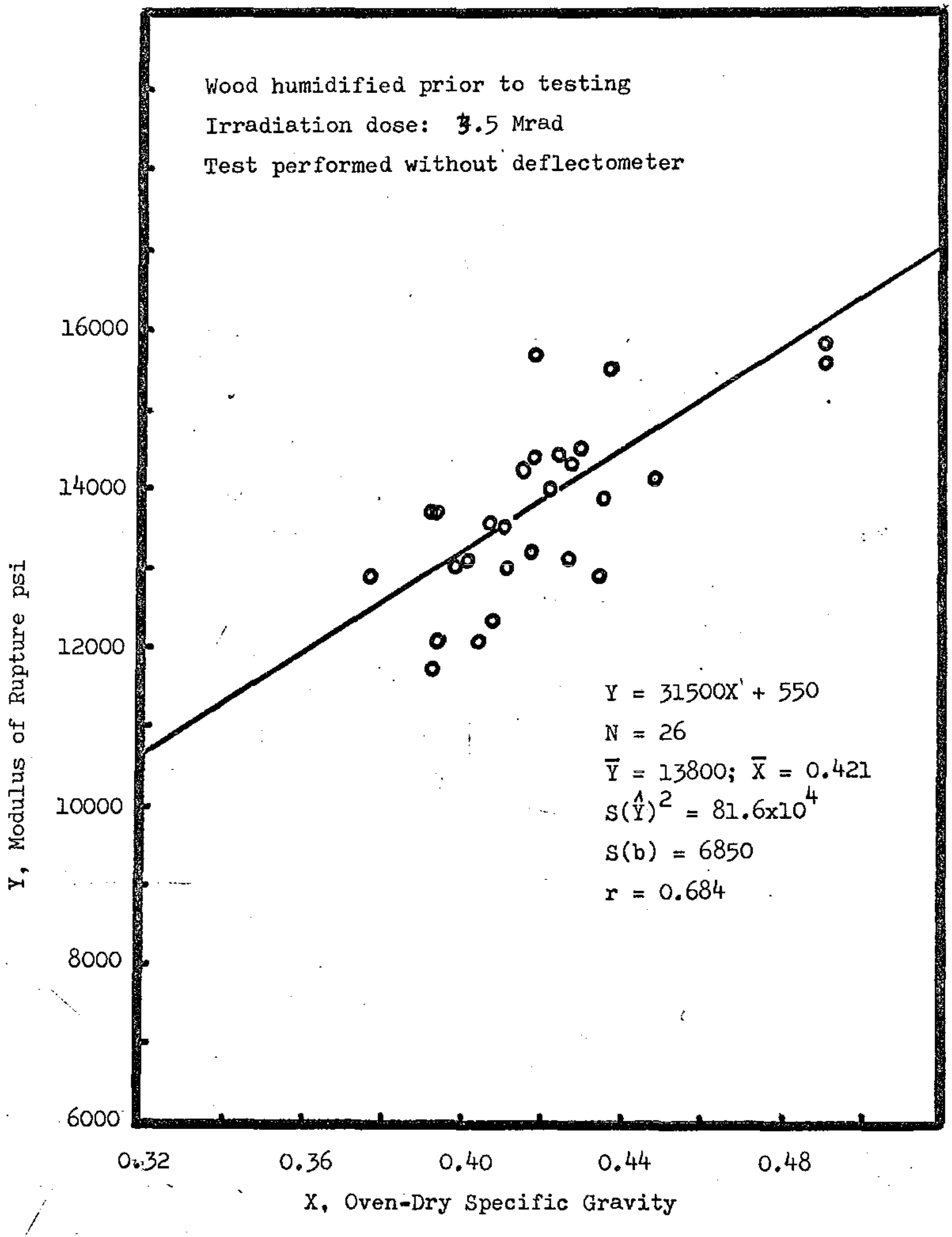


FIGURE 18

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND SPECIFIC GRAVITY FOR WOOD IRRADIATED WITH 3.5 Mrad
(after Werezak)

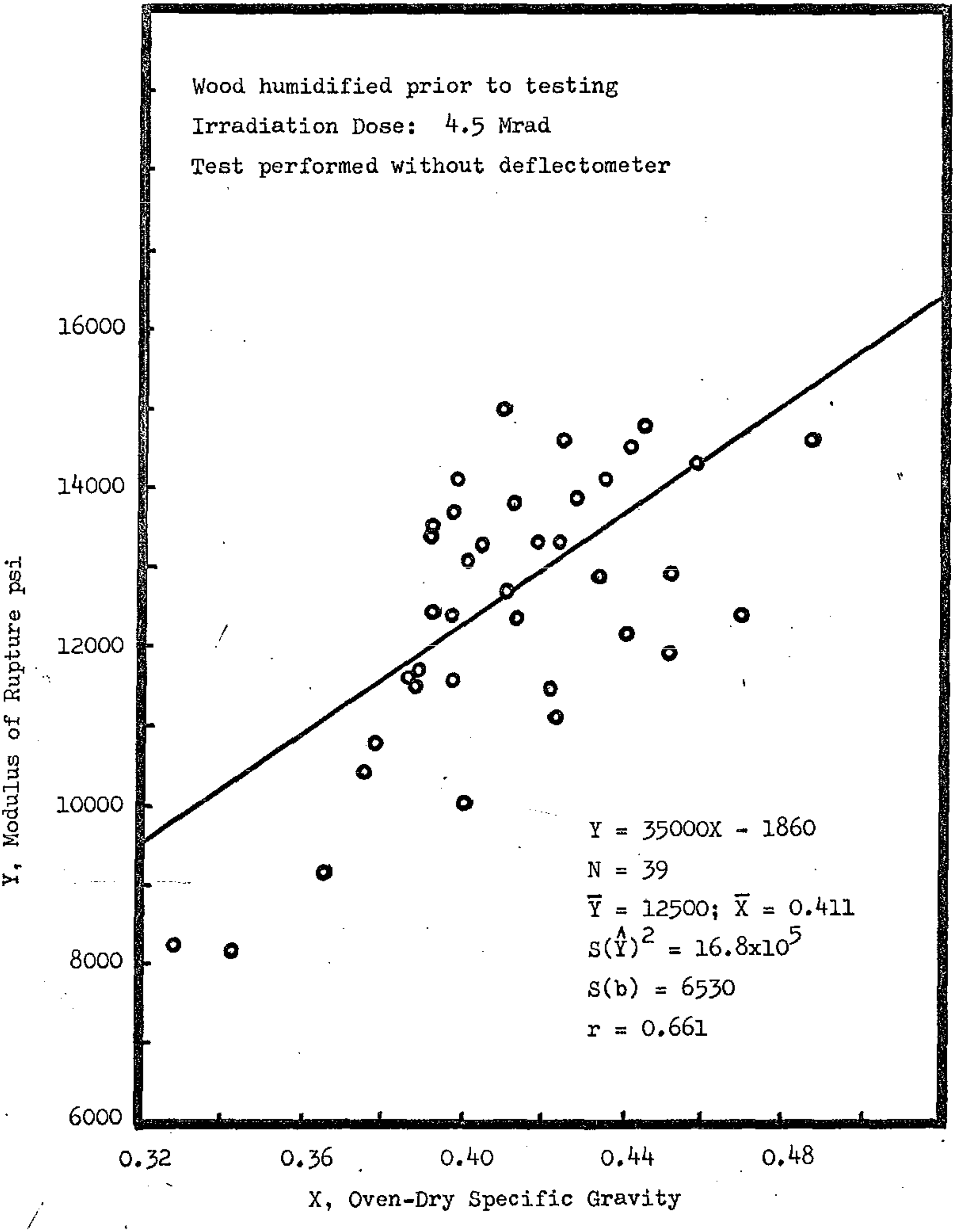


FIGURE 19

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND SPECIFIC GRAVITY FOR WOOD IRRADIATED WITH 4.5 Mrad
(after Werezak)

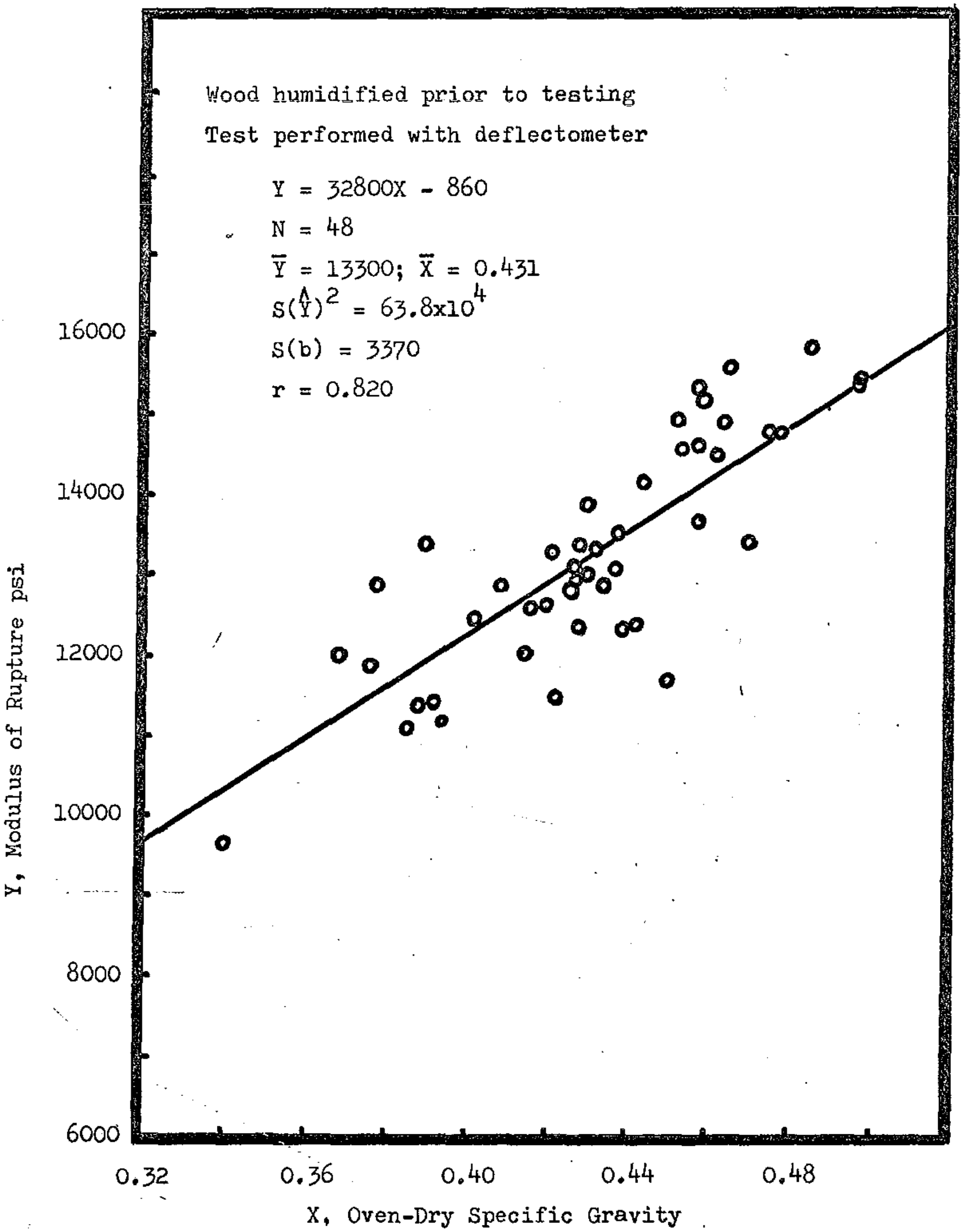


FIGURE 20

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND SPECIFIC GRAVITY
FOR HUMIDIFIED WOOD
(after Werezak)

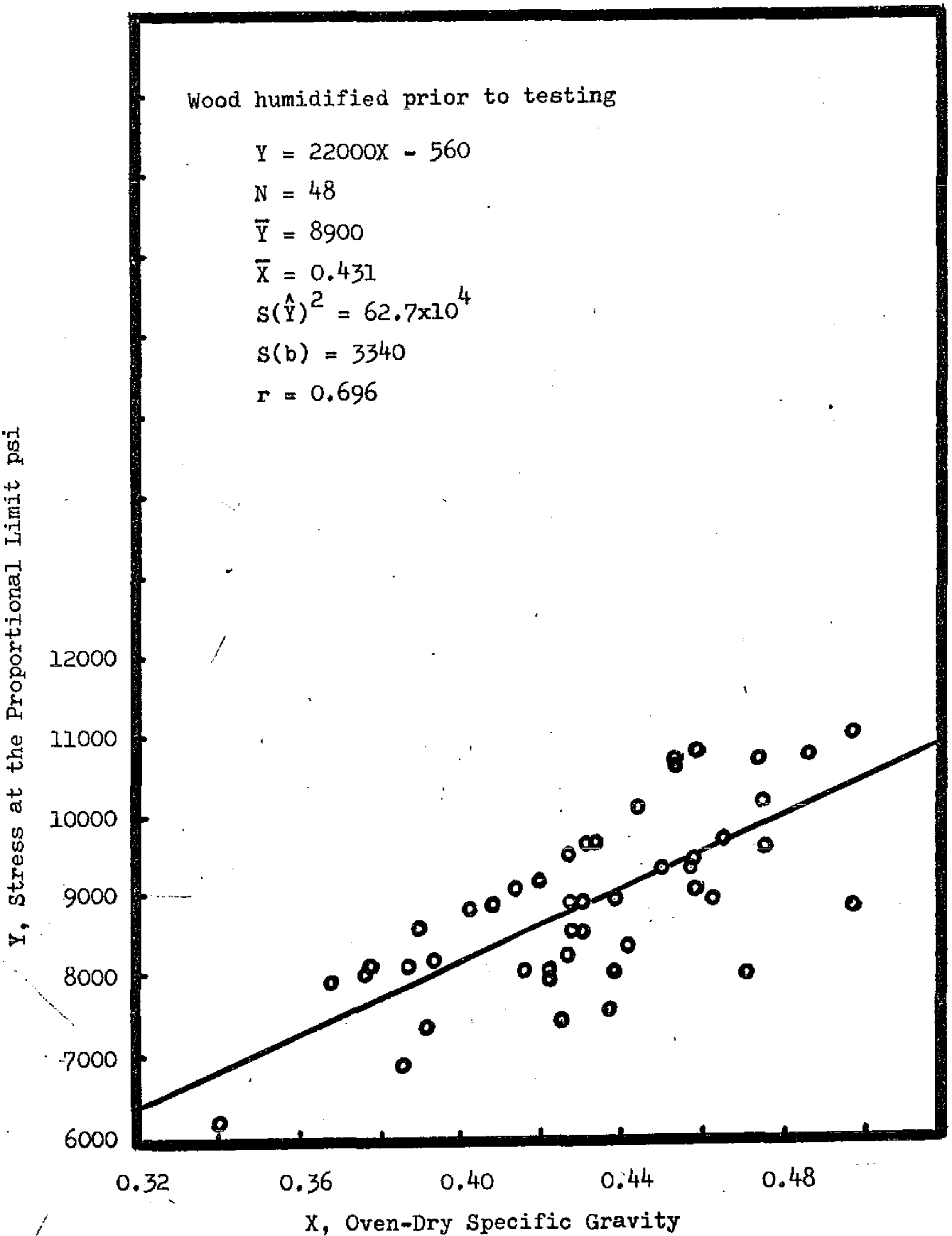


FIGURE 21

RELATIONSHIP BETWEEN STRESS AT THE PROPORTIONAL LIMIT
AND SPECIFIC GRAVITY
FOR HUMIDIFIED WOOD
(after Werezak)

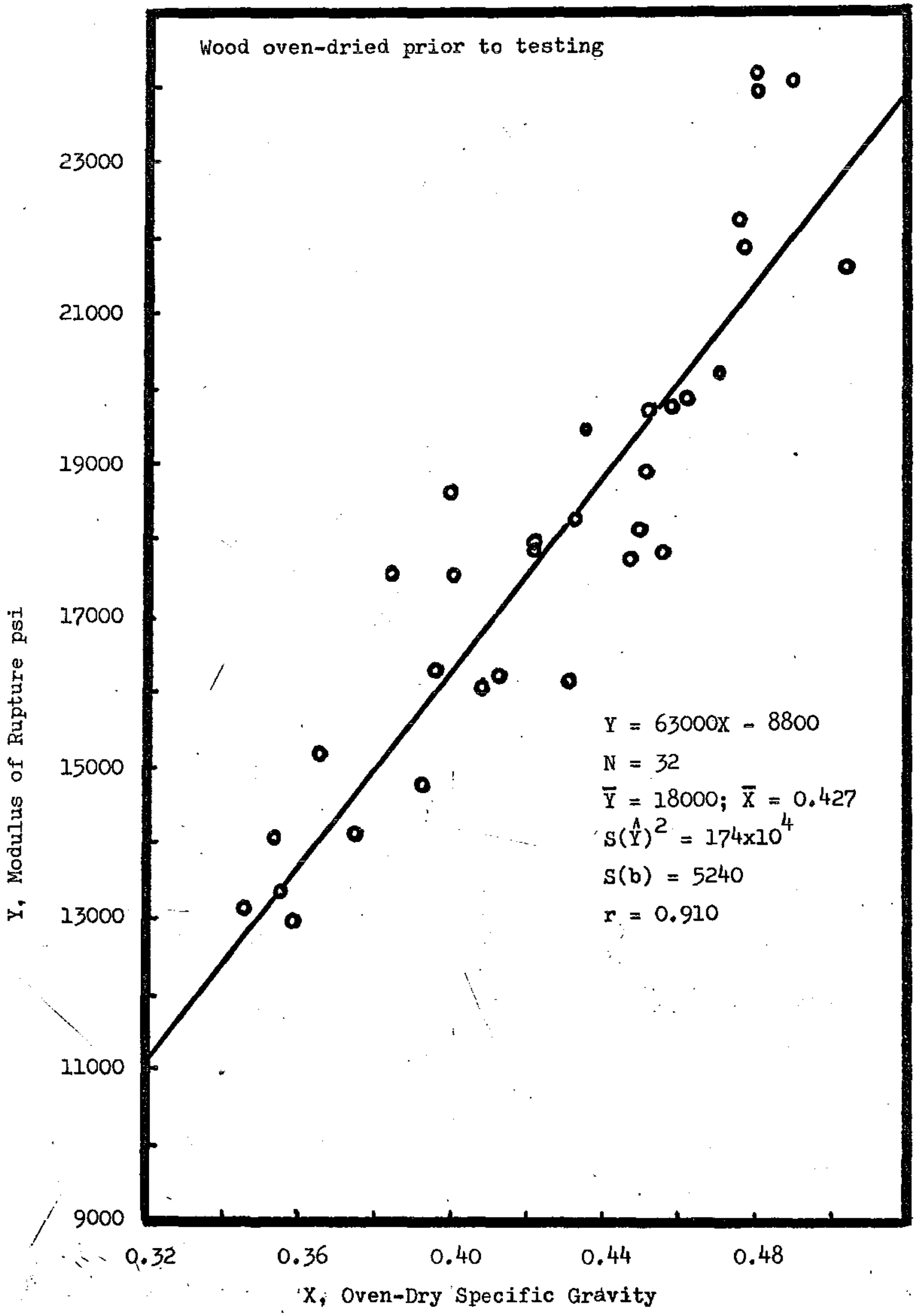
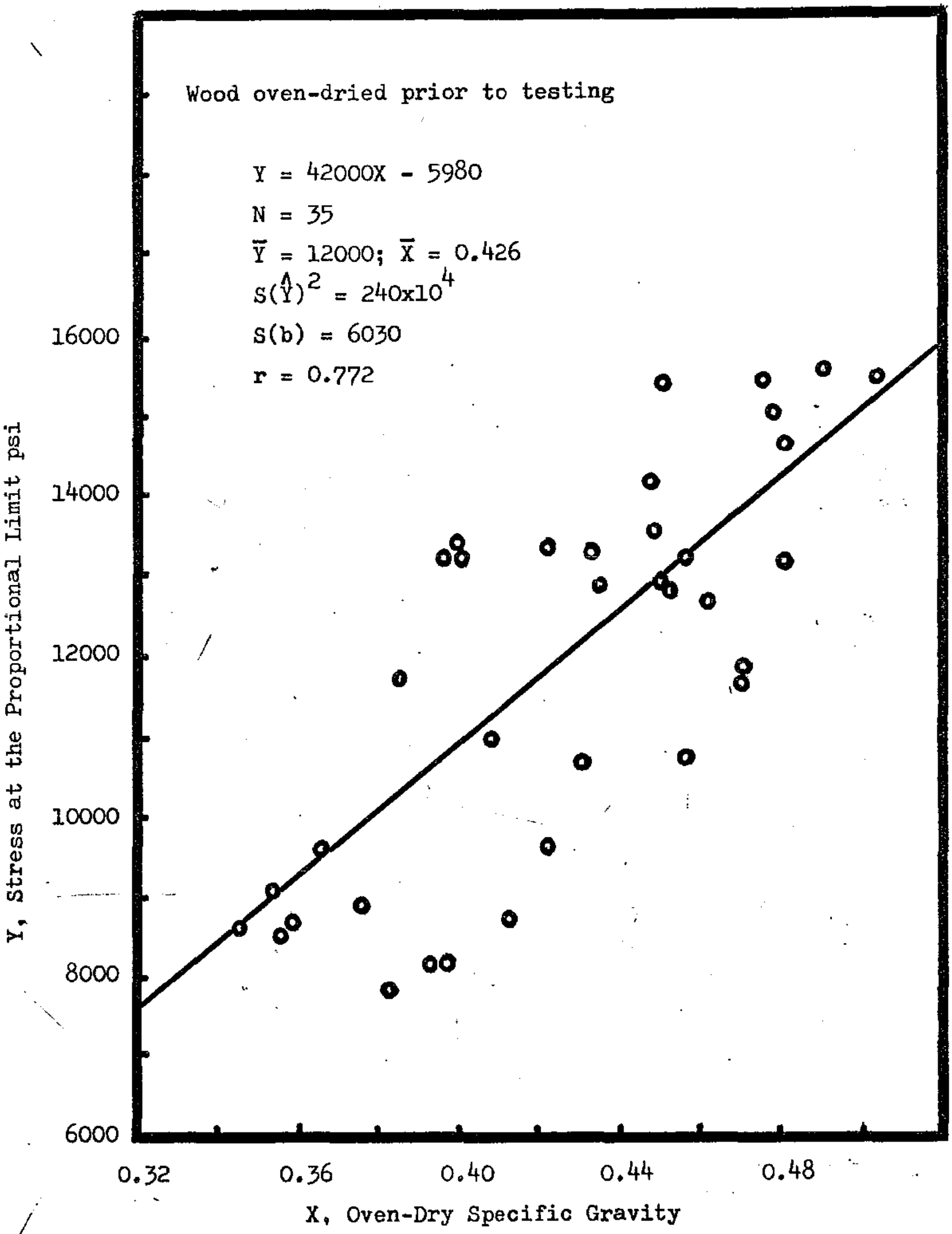


FIGURE 22

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND SPECIFIC GRAVITY
FOR OVEN-DRIED WOOD

FIGURE 23



RELATIONSHIP BETWEEN STRESS AT THE PROPORTIONAL LIMIT
AND SPECIFIC GRAVITY
FOR OVEN-DRIED WOOD

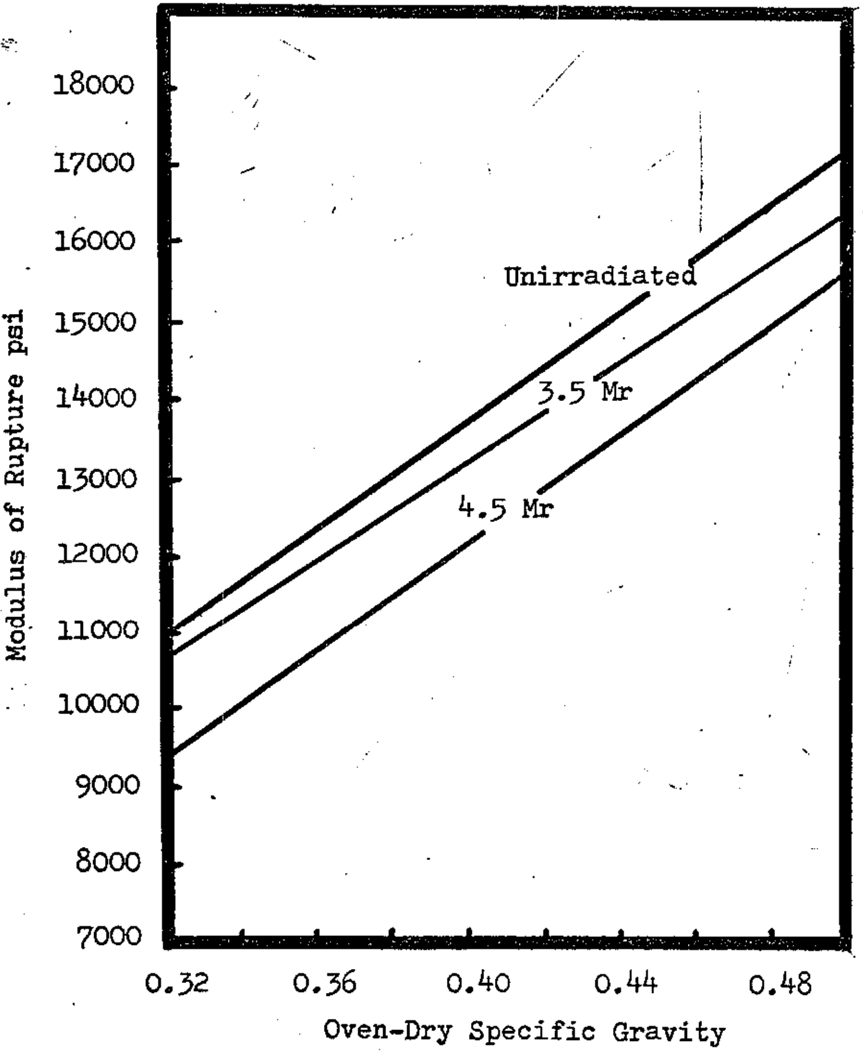


FIGURE 24

EFFECT OF IRRADIATION AND SPECIFIC GRAVITY ON MODULUS OF RUPTURE

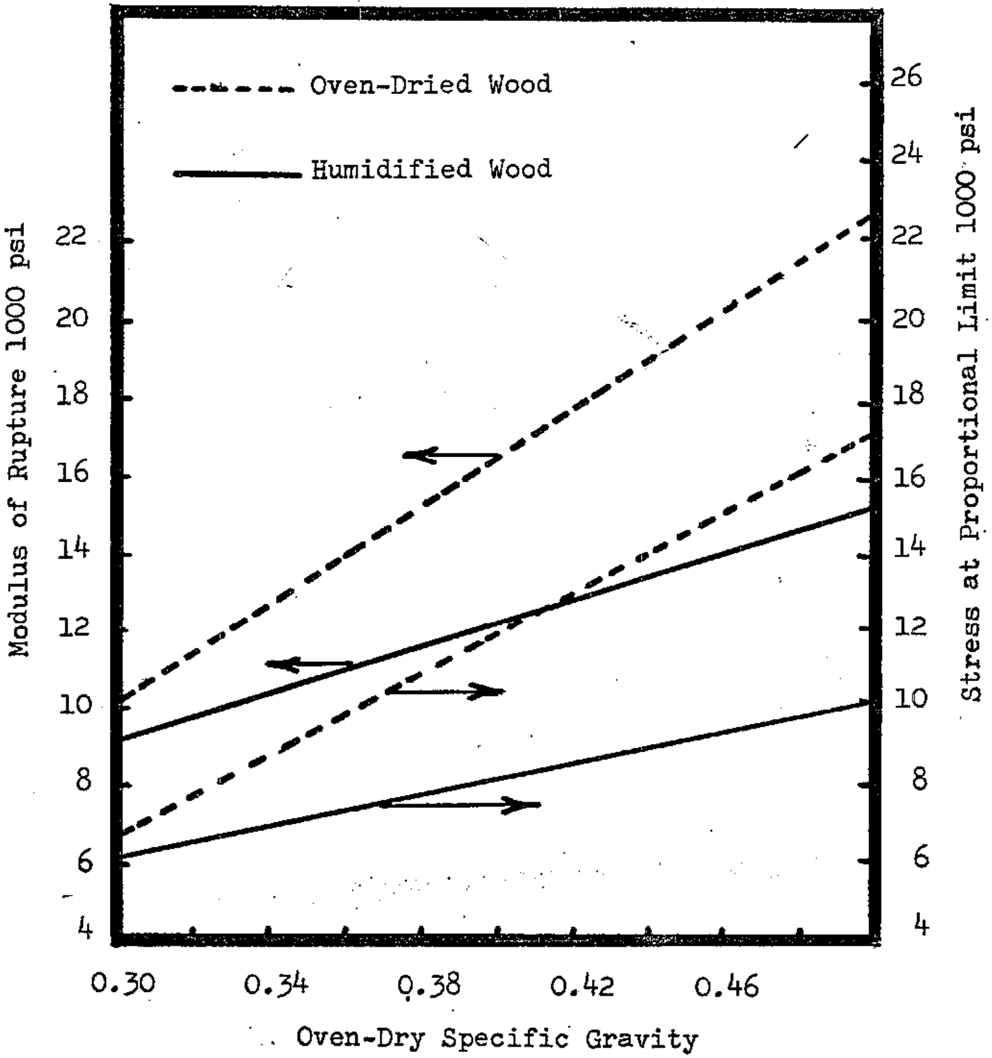


FIGURE 25

EFFECT OF MOISTURE AND SPECIFIC GRAVITY ON MODULUS OF RUPTURE AND PROPORTIONAL LIMIT

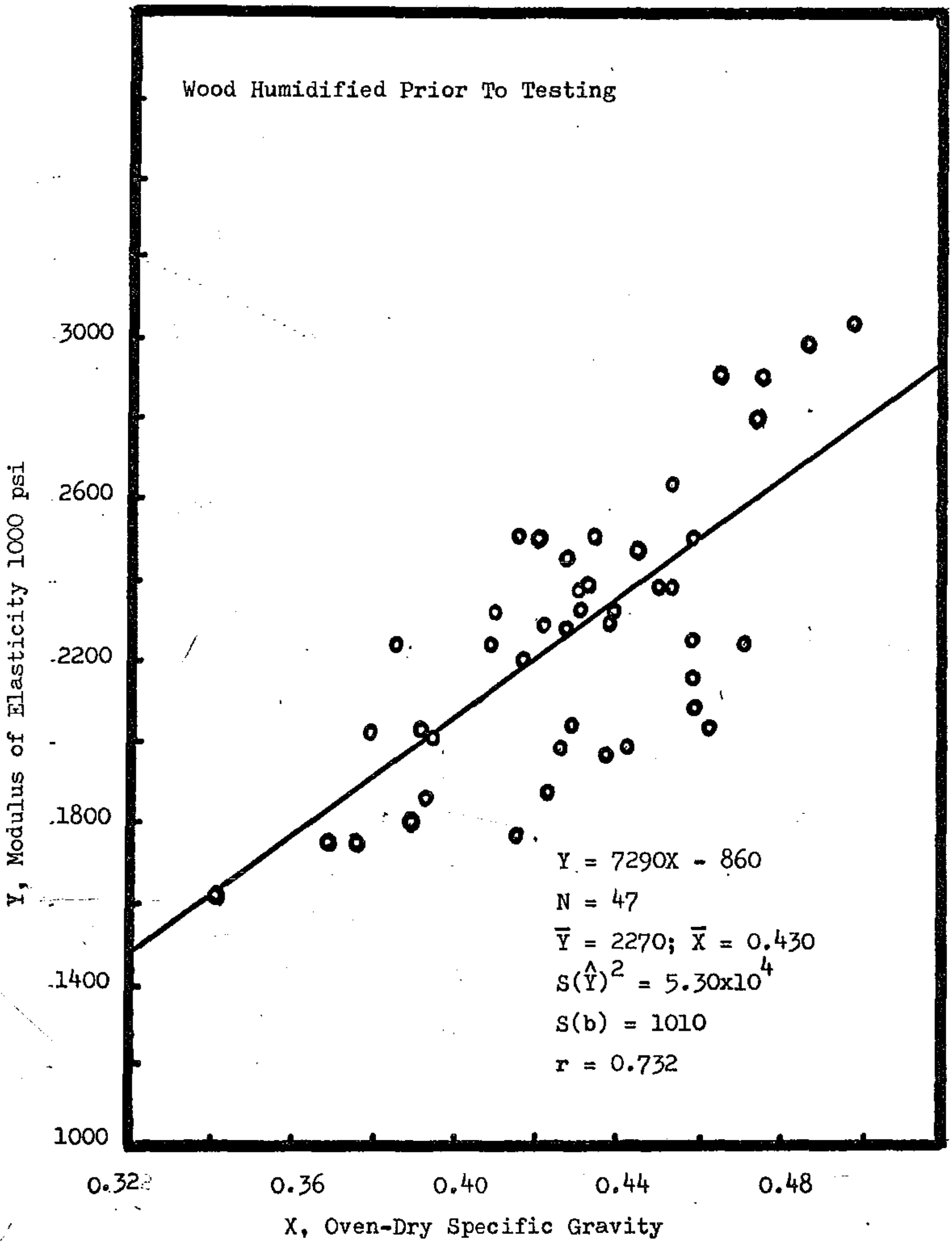


FIGURE 26

RELATIONSHIP BETWEEN MODULUS OF ELASTICITY AND SPECIFIC GRAVITY FOR HUMIDIFIED WOOD

(after Werezak)

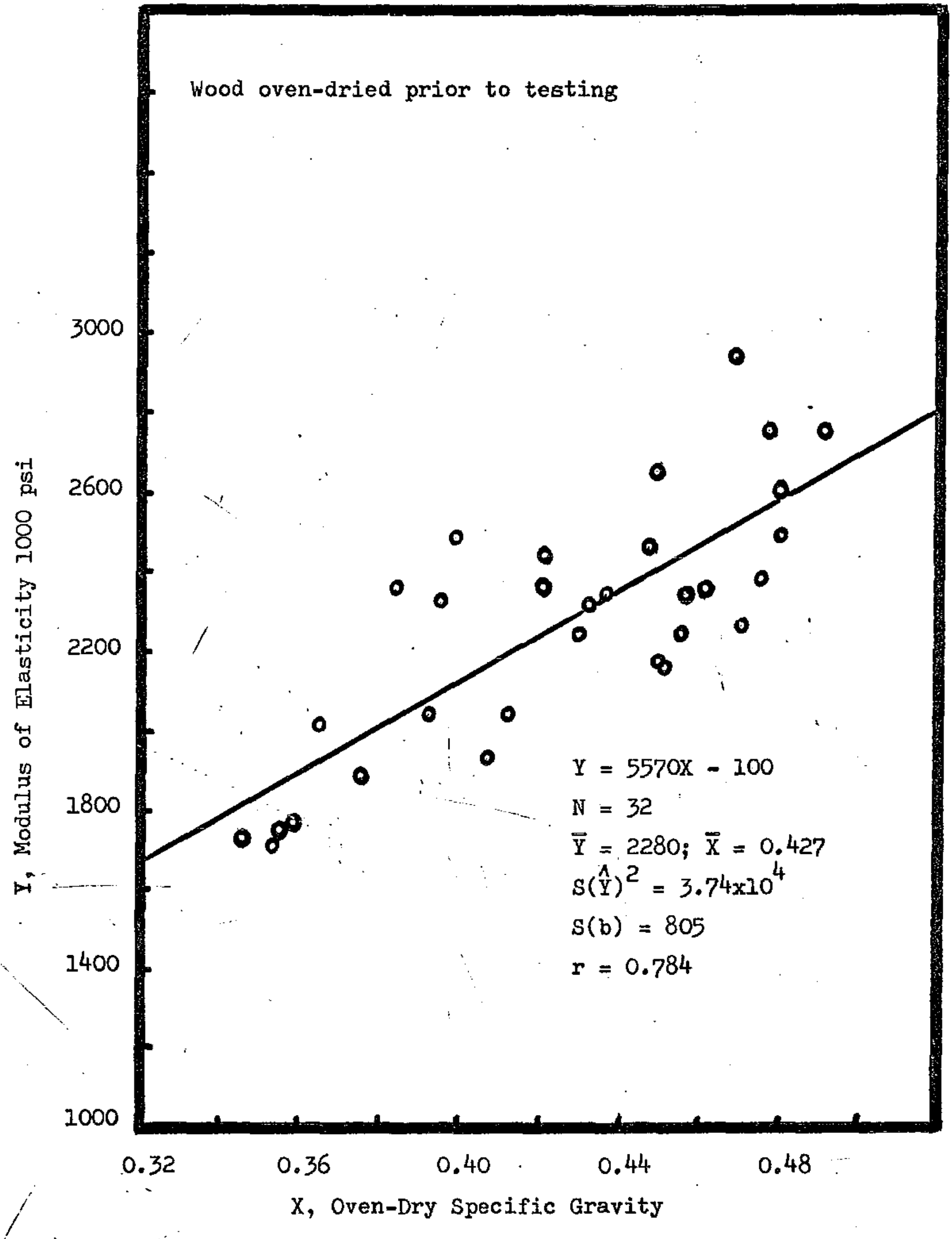


FIGURE 27

RELATIONSHIP BETWEEN MODULUS OF ELASTICITY
AND SPECIFIC GRAVITY FOR OVEN-DRIED WOOD

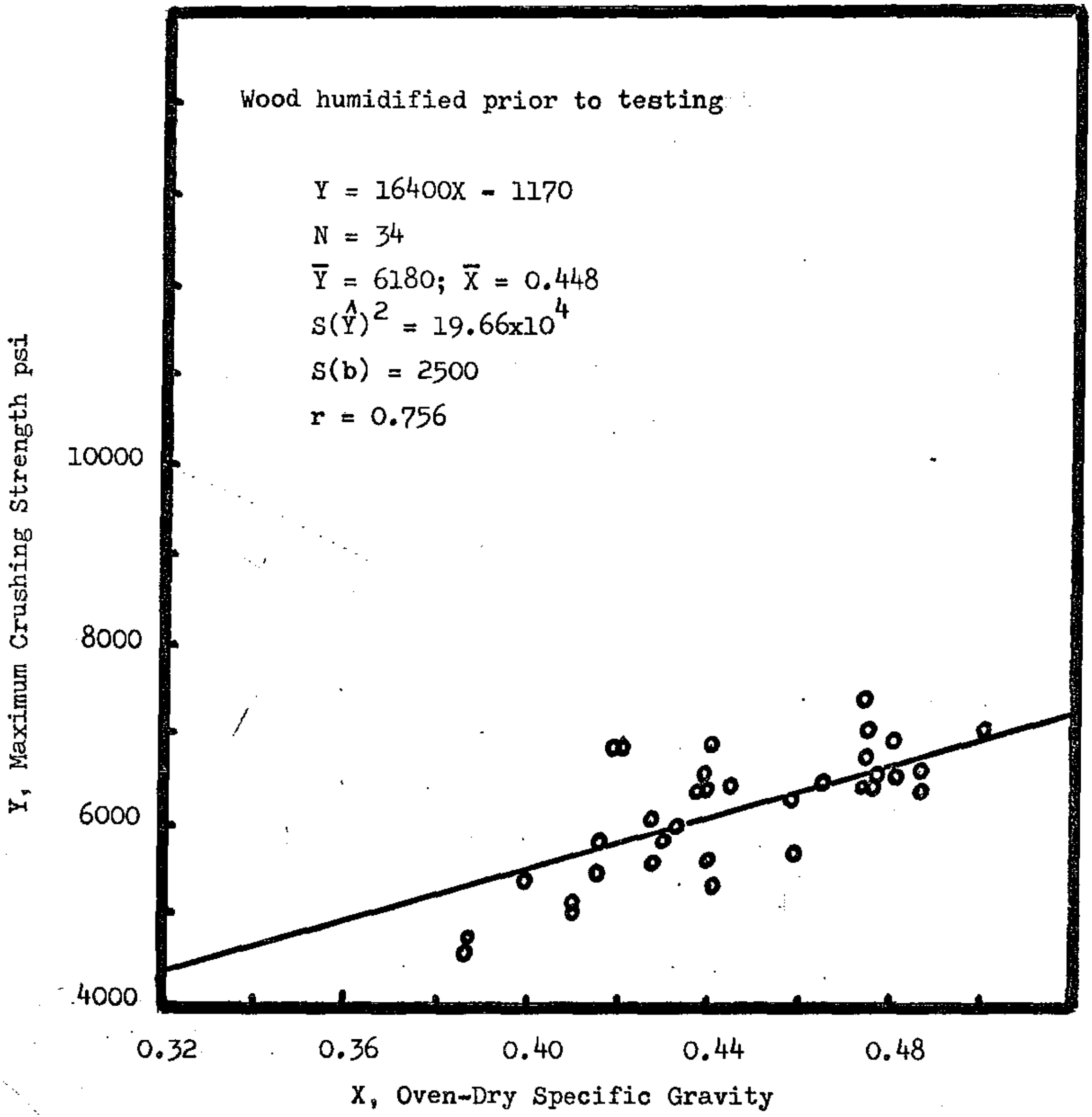


FIGURE 28

RELATIONSHIP BETWEEN MAXIMUM CRUSHING STRENGTH
AND SPECIFIC GRAVITY
FOR HUMIDIFIED WOOD

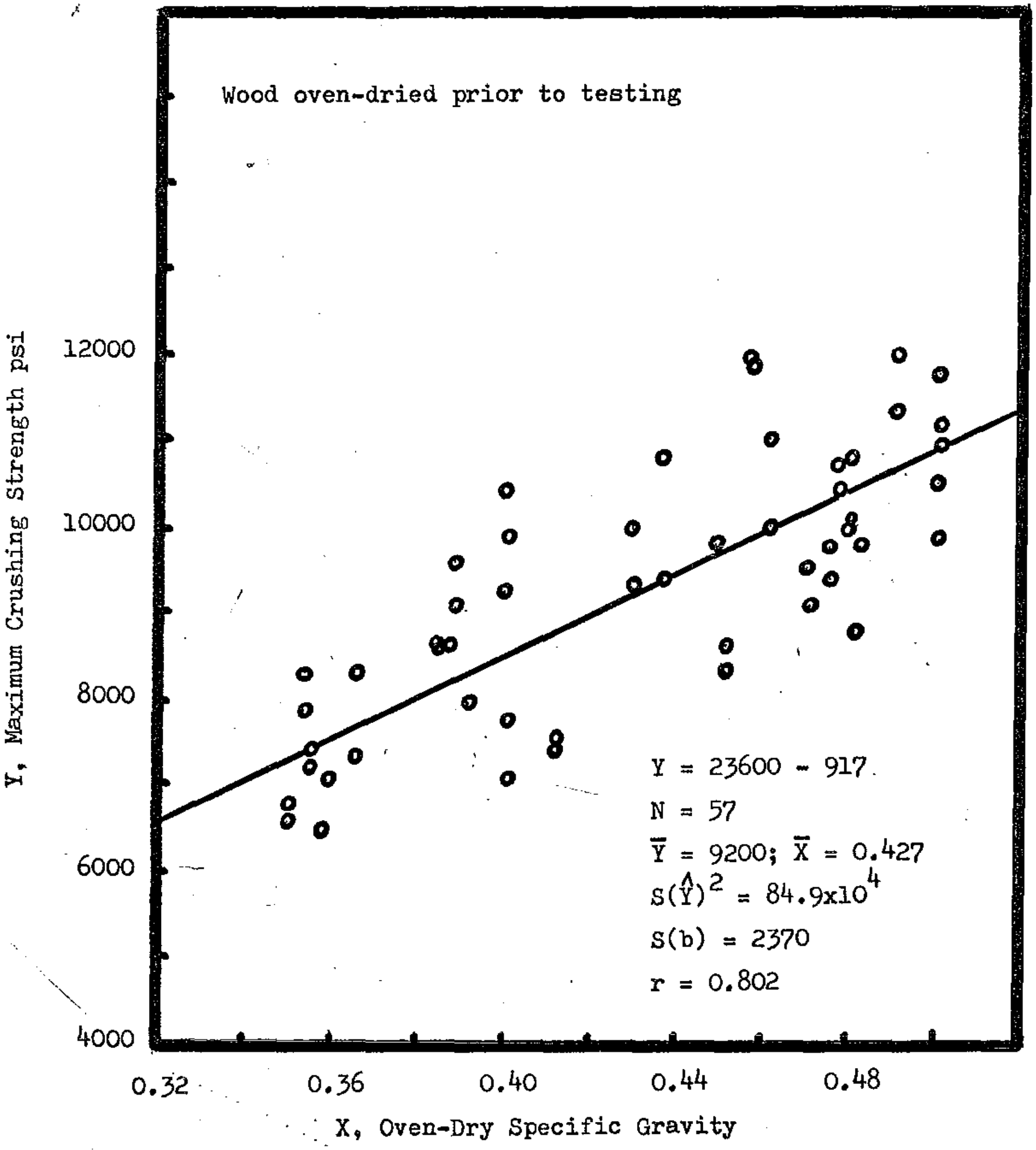


FIGURE 29

RELATIONSHIP BETWEEN MAXIMUM CRUSHING STRENGTH
AND SPECIFIC GRAVITY
FOR OVEN-DRIED WOOD

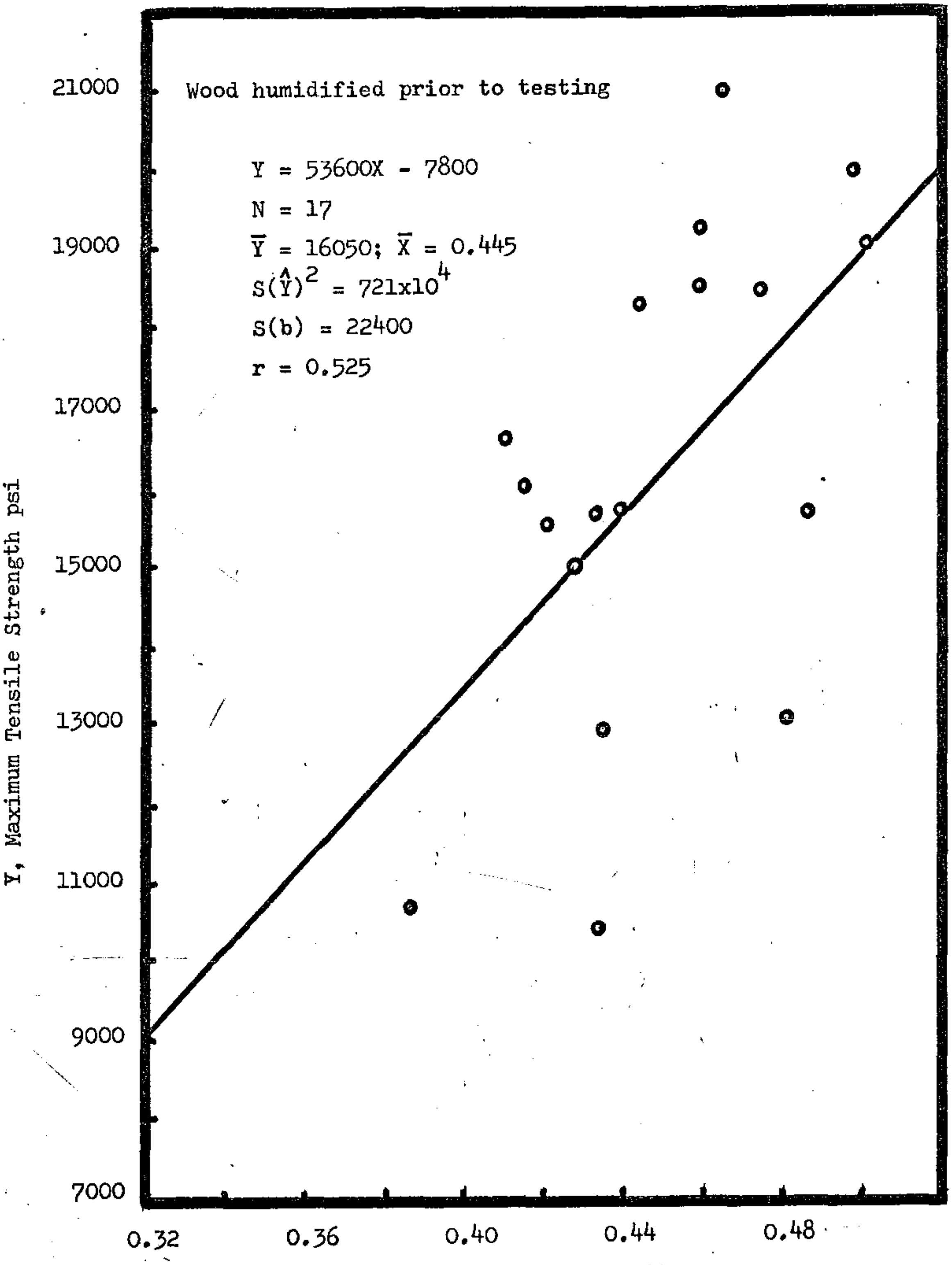


FIGURE 30

RELATIONSHIP BETWEEN MAXIMUM TENSILE STRENGTH
AND SPECIFIC GRAVITY
FOR HUMIDIFIED WOOD

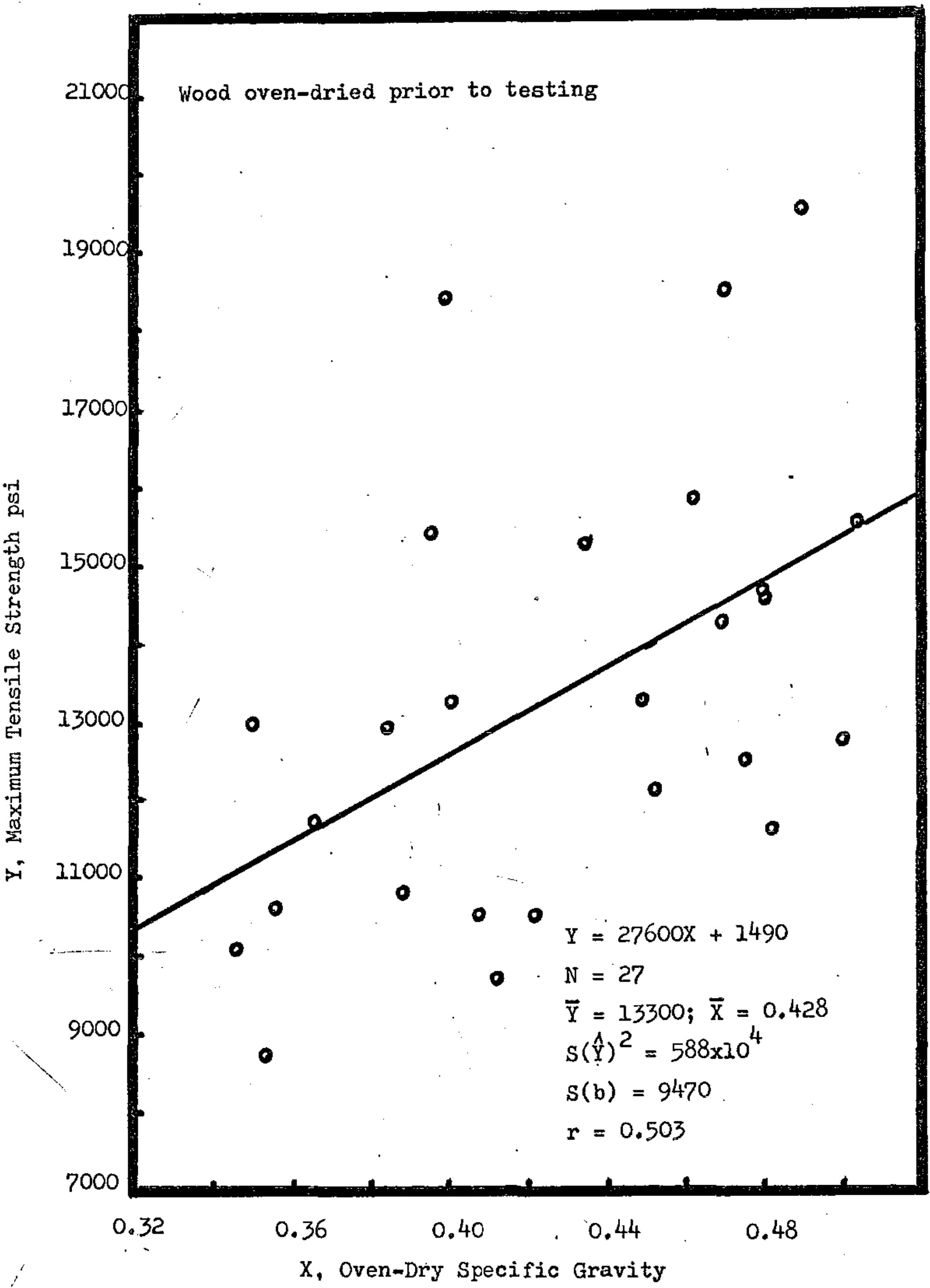


FIGURE 31

RELATIONSHIP BETWEEN MAXIMUM TENSILE STRENGTH
AND SPECIFIC GRAVITY
FOR OVEN-DRIED WOOD

(c) Effect of Moisture on Modulus of Rupture and Stress at the Proportional Limit

Figure 20 is a plot of modulus of rupture versus oven-dry specific gravity for the samples tested by Werezak with the aid of the deflectometer. Figure 21 is the corresponding plot for the stress at the proportional limit. These samples were humidified at 68% RH and 25°C before testing. At these conditions the average moisture content of the wood was 9.7%. Figures 22 and 23 are similar plots for the oven-dried wood. The testing procedure for these samples was the same as that used by Werezak except that the samples were dried in an oven at 100°C until constant weight was attained, allowed to come to room temperature and then tested. The moisture adsorbed just before and during testing was estimated to be 1/2 - 1% of the total weight of the wood.

It can be shown that the correlation based on the samples tested without the deflectometer (Figure 17) is significantly lower than that based on the samples tested with the deflectometer (Figure 20). This result cannot be explained.

(Figure 25 shows the superposition of the correlations of Figures 20 - 23.) It is quite evident that the oven-dried samples have strengths higher than the humidified samples. At a common oven-dry specific gravity of 0.431 the increase in modulus of rupture is 38.4 ± 3.9% and the increase in the stress at the proportional limit is 35.9 ± 6.2% based on the strength of the humidified wood. It is noted that the variability (as measured by the variance) is significantly higher for the oven-dried samples than for the humidified ones. Similar results have been obtained by Robinson (75).

(d) Modulus of Elasticity

The modulus of elasticity as a function of oven-dry specific gravity is shown in Figures 26 and 27 for the humidified and oven-dried samples respectively. At a specific gravity of 0.431 the average strength values are $2280 \pm 69 \times 10^3$ psi and $2300 \pm 71 \times 10^3$ psi. There is no significant difference between these average values or the correlations shown in the figures. This indicates that the 9.7% moisture in the humidified samples does not affect the modulus of elasticity of the wood. In the Wood Handbook (73) the average increase in the modulus of elasticity for a 1 percent decrease in moisture content is given as 2%. This value was calculated in the moisture-content range of 12 - 25% moisture and may not be valid for drier conditions.

(e) Work to Proportional Limit and to Maximum Load*

Average values for work done in static bending for the humidified and oven-dried wood are given in Table 29. The results show that work in bending is a very sensitive function of the moisture content of the wood. The work to the proportional limit is increased 77.8 ± 10.9%

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* For a discussion of the data-presentation for this section see Appendix VI - D.

TABLE 29

WORK IN BENDING TO PROPORTIONAL LIMIT AND TO MAXIMUM LOAD FOR HUMIDIFIED AND OVEN-DRIED WOOD*

	Work to Proportional Limit** in-lb. per cu. in.	Work to Maximum Load** in-lb. per cu. in.
Humidified Wood	1.98 ± 0.10	7.65 ± 0.85
Oven-dried Wood	3.51 ± 0.35	10.50 ± 1.16

* Average oven-dry specific gravity = 0.427.

** The data are presented in the form $\bar{\bar{Y}} \pm ts$ where s = standard deviation of the mean and t = student "t" value at 95% confidence level.

and the work to the maximum load is increased 37.3 ± 18.7% when the moisture level of the samples is decreased from 9.7% to the dried state.

2. Compression Parallel to the Grain

Figures 28 and 29 are plots of the maximum crushing strength versus oven-dry specific gravity for the humidified and oven-dried samples respectively. At a specific gravity of 0.431 the oven-dried samples have an average maximum crushing strength which is 57.4 ± 3.4% higher than that for the humidified wood.

3. Tension Parallel to the Grain

Figures 30 and 31 are plots of the maximum tensile strength versus oven-dry specific gravity for the humidified and oven-dried samples respectively. Although the expanded scale on the graphs makes the correlations appear trivial, these are significant at the 95% confidence level -- the correlation removes about $(r = 0.5)^2 = 25\%$ of the variance in the data. However, there is a large variance in the data and this is due to the following facts: (1) the Hounsfield Tensometer has an estimated reproductibility of ± 2 - 3% (2) the error in determining the stress area for the small samples is estimated to be ± 3% (3) the error in assuming that the specific gravity of the small samples was the same as that of larger beam from which it was cut is estimated to be ± 2.3%. It can be seen that if these errors are added to the natural variability of wood, the resulting variance will be relatively large. In addition it is also possible that the large variability in strength with respect to specific gravity after the regression is due to the fact that, in actuality, the tensile strength is not a strong function of specific gravity. Very few data are available in the literature to substantiate this possibility. Comben (76), using Douglas Fir wood samples with dimensions of 11½" x 2 cm. x ¼" waisted at the centre to give a minimum cross-section of 1/8" x 1/4" over a 2" length, carried out tension tests. His results are shown below.

TABLE 30

MAXIMUM TENSILE STRENGTH FOR DOUGLAS FIR (AFTER COMBEN)

Specific Gravity (ca. 11% moisture)	Maximum Tensile Strength psi
0.497	17460
0.458	17670
0.462	13520
0.502	17300
0.511	19910
0.536	16050
0.494	16990

There is no significant correlation between the above two variables.*

Also the few articles in the literature indicate that the ultimate tensile strength of wood is affected only slightly by the amount of moisture in the wood (72, 74, 76). It can be shown that the two correlations shown in Figures 30 and 31 are not significantly

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* $r = 0.324$

different and that one overall fit can represent the data as well as the two separate fits (see Appendix VI - C). The statistics for this overall correlation are given below in Table 31.

TABLE 31

STATISTICS FOR OVERALL FIT OF HUMIDIFIED AND OVEN-DRIED WOOD: MAXIMUM TENSILE STRENGTH vs. OVEN-DRY SPECIFIC GRAVITY

$Y = 36900X - 1690$

$N = 44$

$\bar{Y} = 14350; \bar{X} = 0.435$

$S(\hat{Y})^2 = 7.43\text{x}10^6$

$S(b) = 9460$

$r = 0.516$

D. Strength Properties of Treated Wood

1. Static Bending

Figure 32 (after Werezak) shows a typical load-deflection curve for an untreated (control) and a solution-treated sample of wood. It is seen that for a given deflection, the load for the treated sample is greater; also the ultimate breaking load is greater for the treated sample than for the untreated one. Since the former has on the average 16% more volume than the latter, it is evident that the ultimate strength of the treated samples, expressed in terms of stress (lbs/area), may not necessarily be greater and indeed may be less.

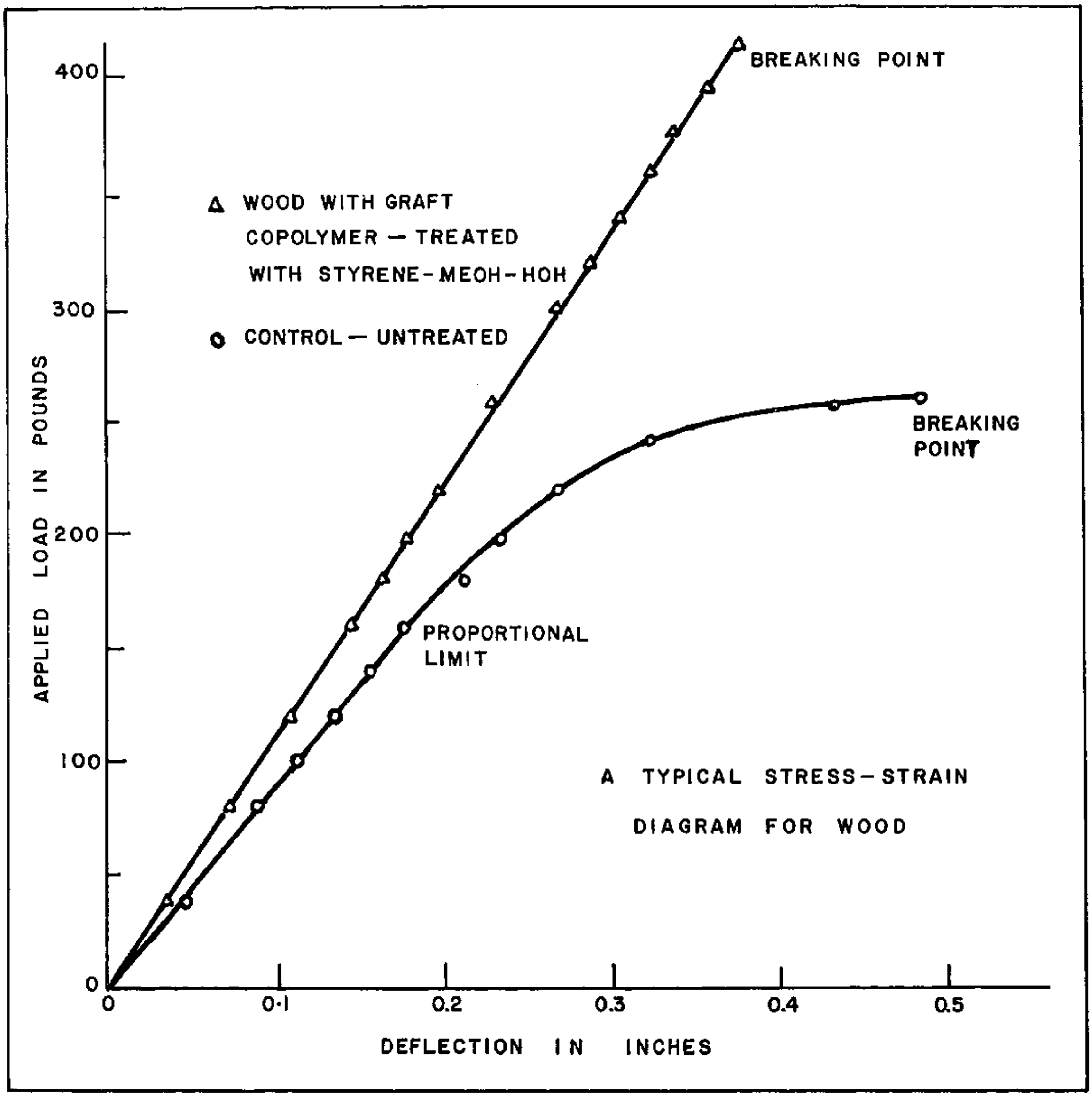

FIGURE 32

(after Werezak)

(a) Modulus of Rupture

(i) Wood Treated and Tested by Werezak

The samples of wood treated by Werezak can be conveniently divided into two sections; viz., those that were tested in bending with the aid of the deflectometer and those which were tested without this accommodation. The treatment of the former has been described in detail in PART 1 of this thesis (Tables 14 - 17). The following solutions were used: 54:42:4 and 65:32:3 weight ratio of styrene, methanol and water. The dose used was 4 or 5 Mrad. Before testing, the treated samples were humidified to constant weight in an atmosphere of 68% R.H. and 25°C. The samples contained about 4% by weight moisture based on the weight of the oven-dried treated sample or about 8% by weight when based on the weight of wood in the treated sample.

When the maximum bending loads for these treated samples were normalized with respect to the stressed areas, the modulus of rupture values were obtained. Attempts were made to correlate the rupture values with respect to several parameters. No significant correlations could be obtained for the modulus of rupture and any expression relating to the presence of polymer in the treated sample (e.g., fraction polymer in the treated sample, associated polymer in gms/cc or polymer retention). In fact, this statement holds true for all solution-treated samples (but not those treated with pure styrene) and for all strength properties associated with these samples. However, most strength properties could be correlated with respect to

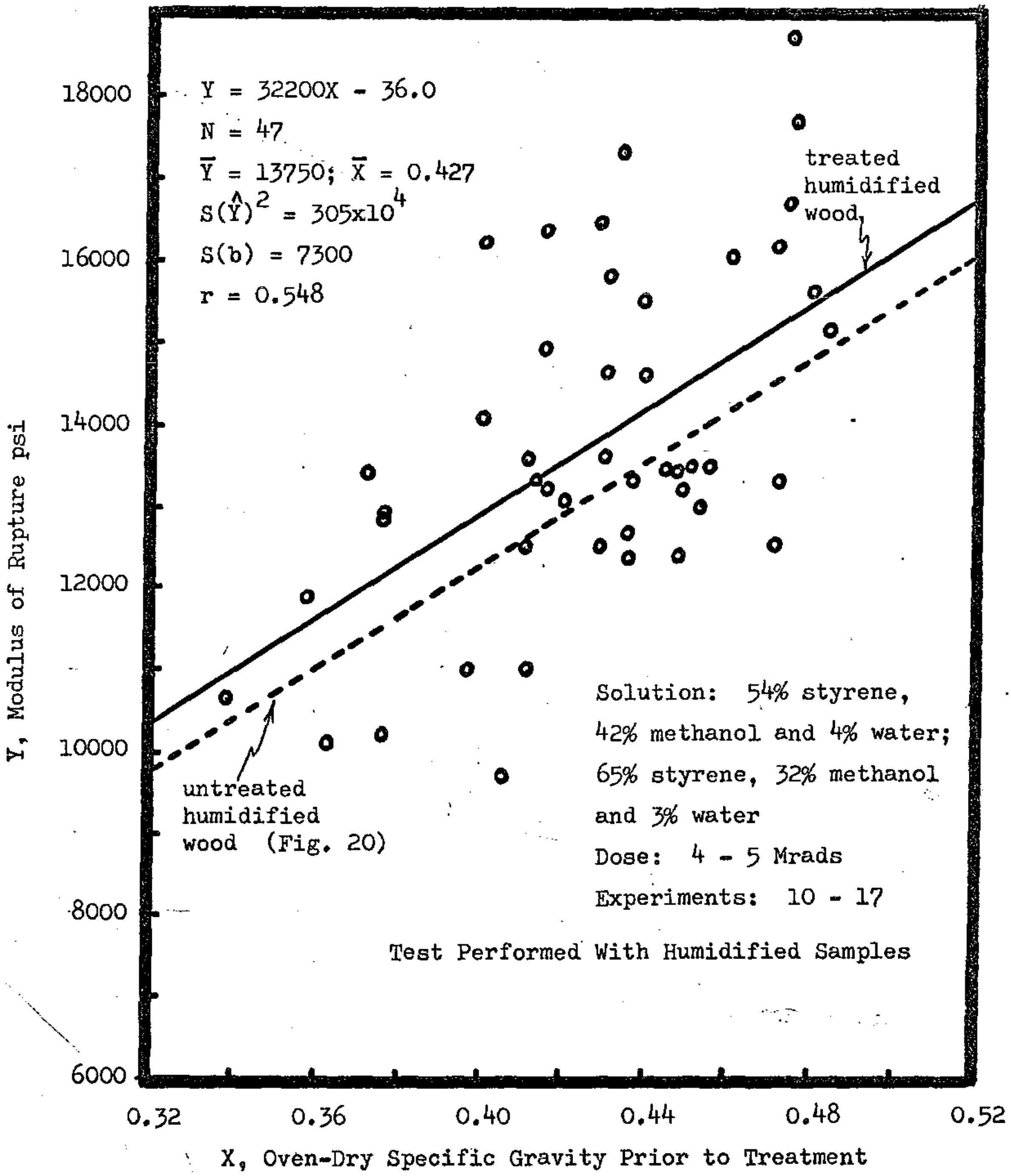

FIGURE 33

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND "ORIGINAL" SPECIFIC GRAVITY
FOR WOOD TREATED WITH 54% AND 65% STYRENE SOLUTIONS
(after Werezak)

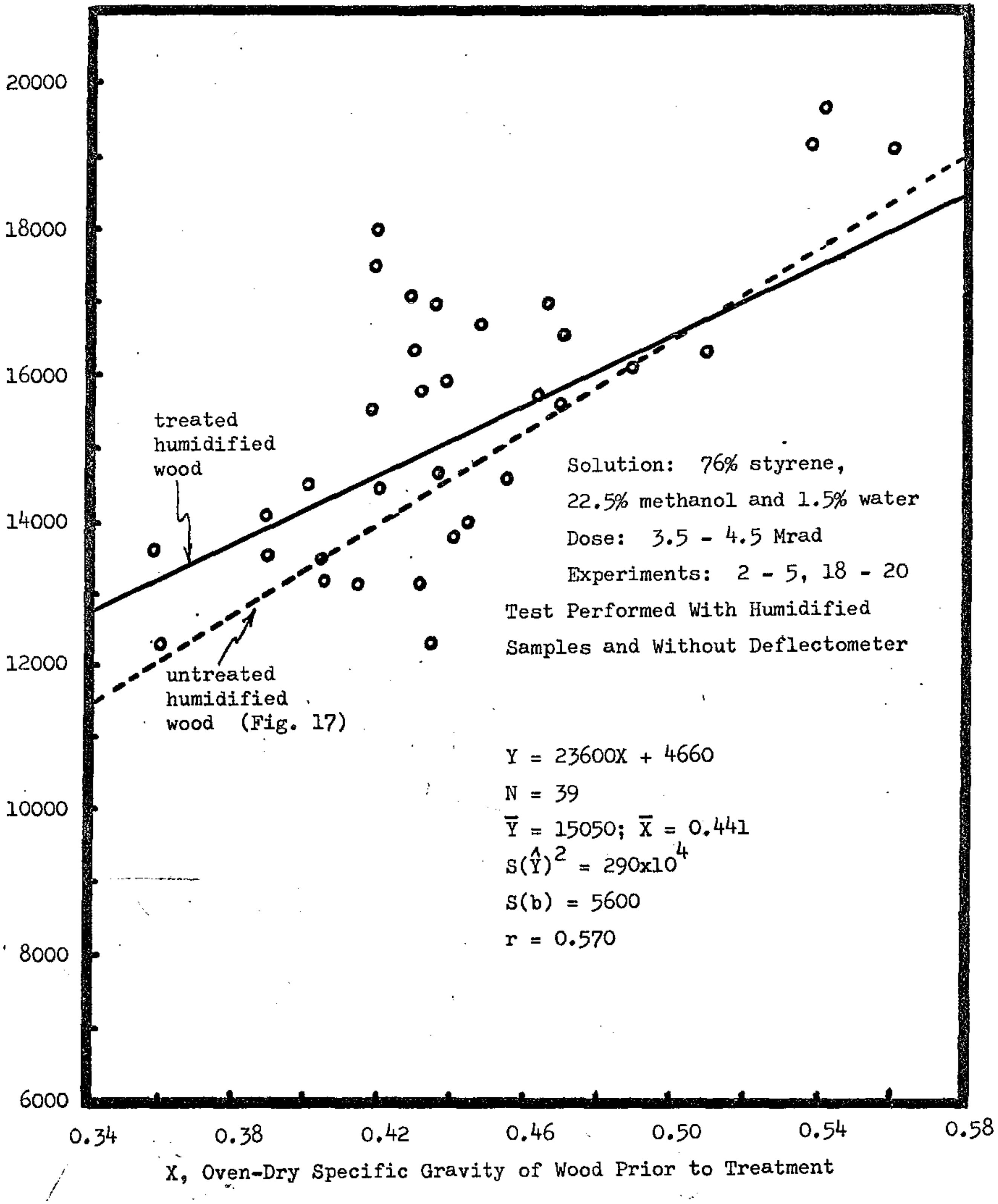

FIGURE 34

RELATIONSHIP BETWEEN MODULUS OF RUPTURE
AND "ORIGINAL" SPECIFIC GRAVITY
FOR WOOD TREATED WITH 76% STYRENE SOLUTION

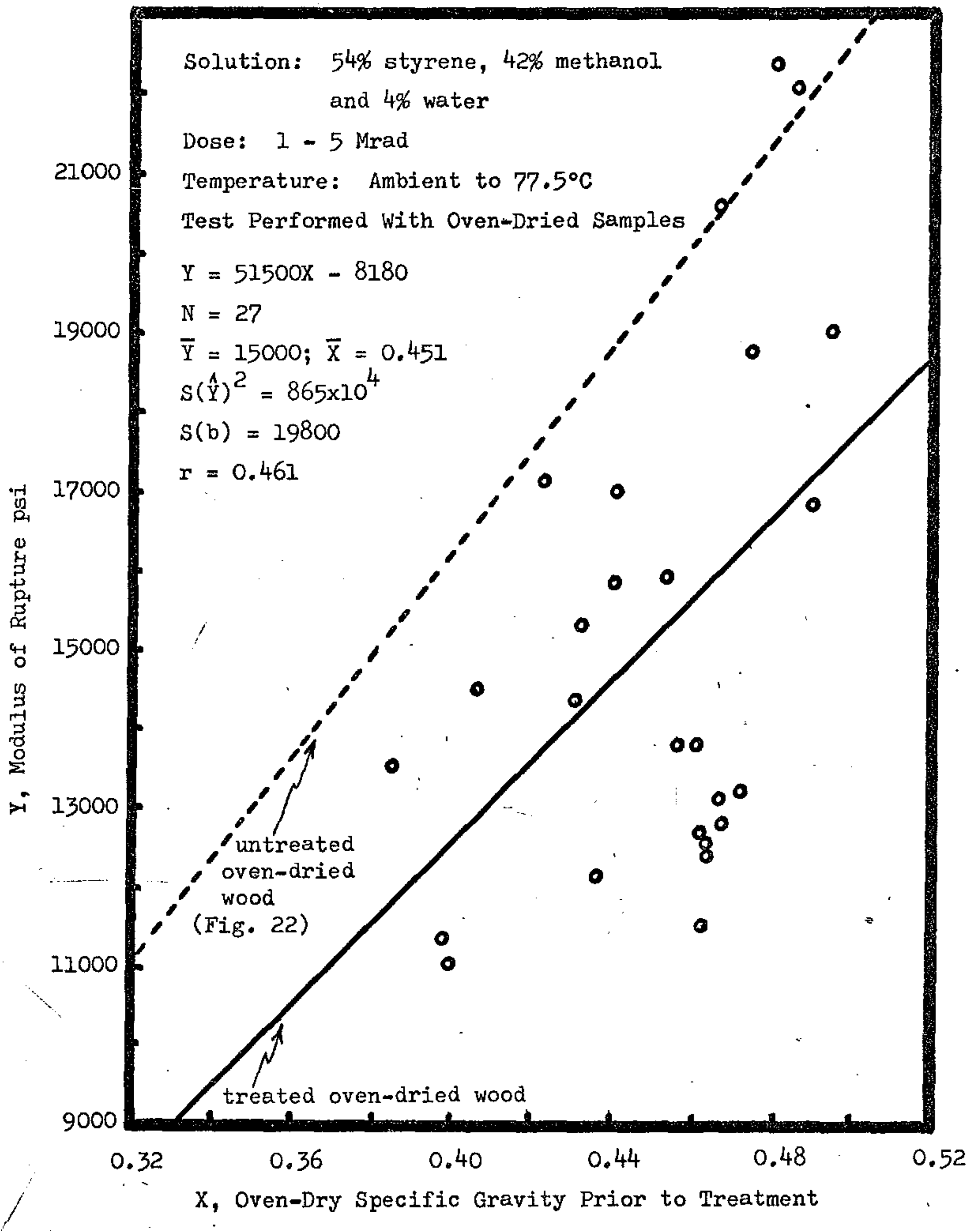

FIGURE 35

RELATIONSHIP BETWEEN MODULUS OF ELASTICITY AND "ORIGINAL" SPECIFIC GRAVITY FOR WOOD TREATED WITH 54% STYRENE SOLUTION

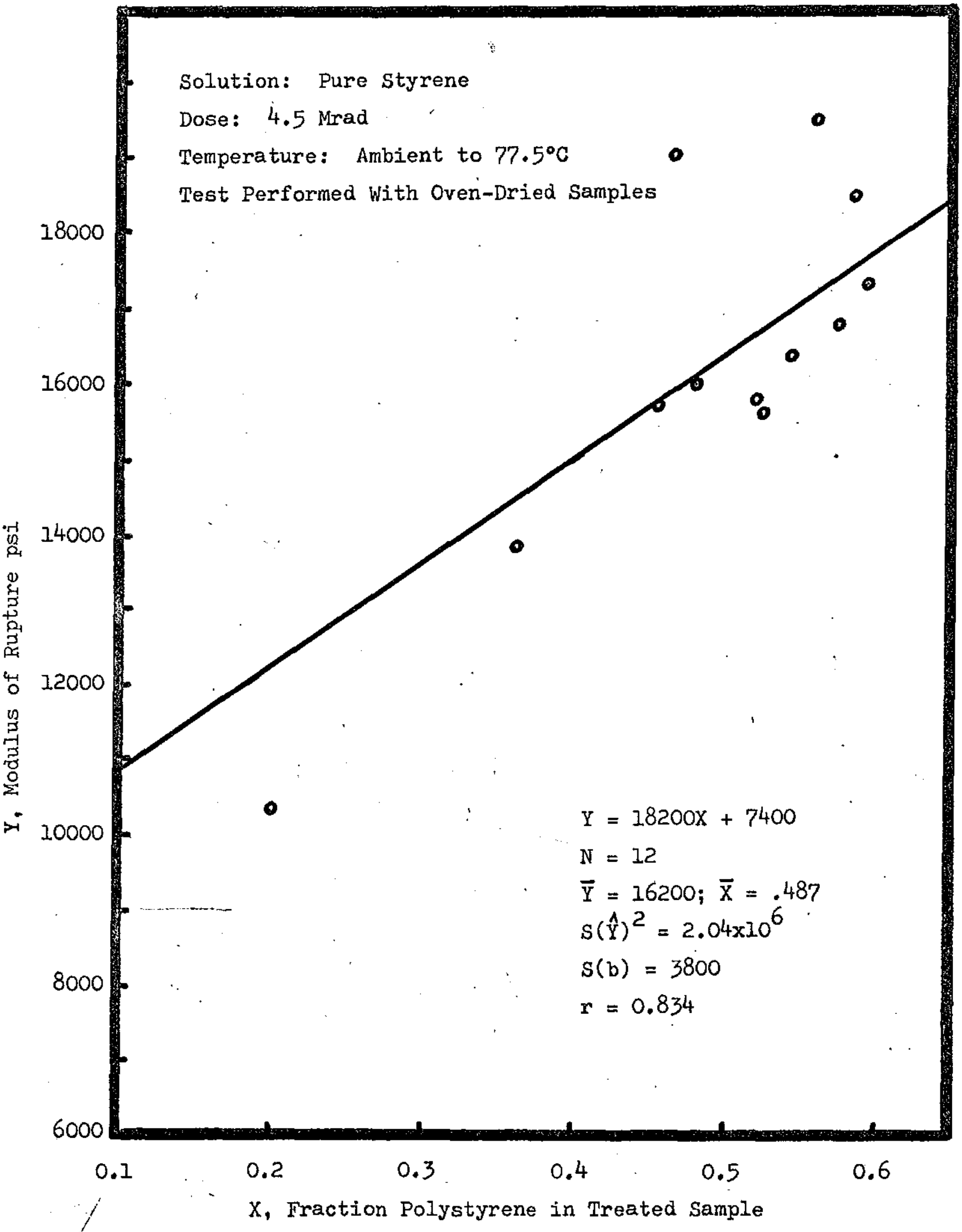

FIGURE 36

RELATIONSHIP BETWEEN MODULUS OF RUPTURE AND F.P.S.
FOR WOOD TREATED WITH PURE STYRENE

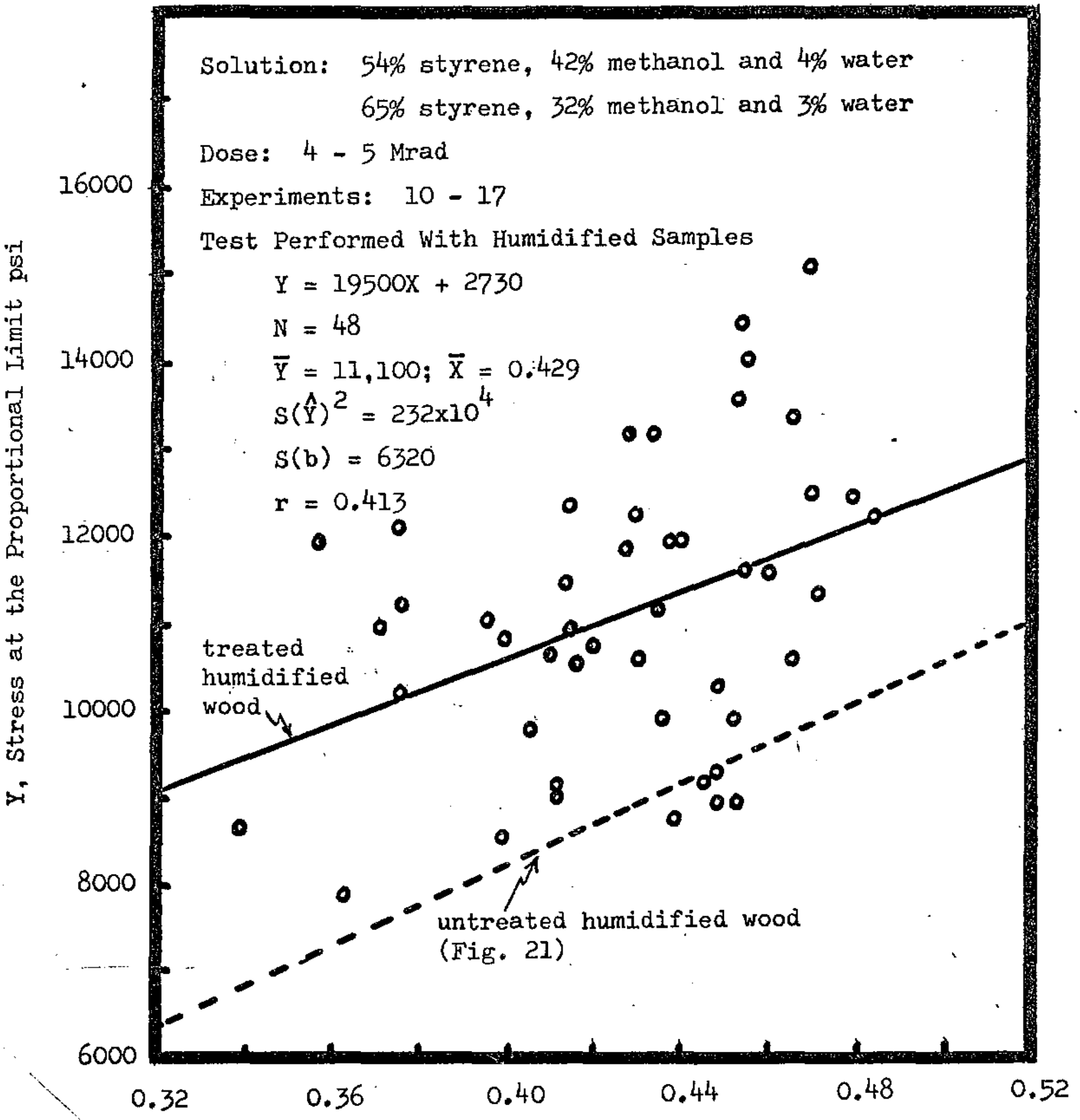

FIGURE 37

RELATIONSHIP BETWEEN STRESS AT PROPORTIONAL LIMIT
AND "ORIGINAL" SPECIFIC GRAVITY
FOR WOOD TREATED WITH 54% AND 65% STYRENE SOLUTIONS
(after Werezak)

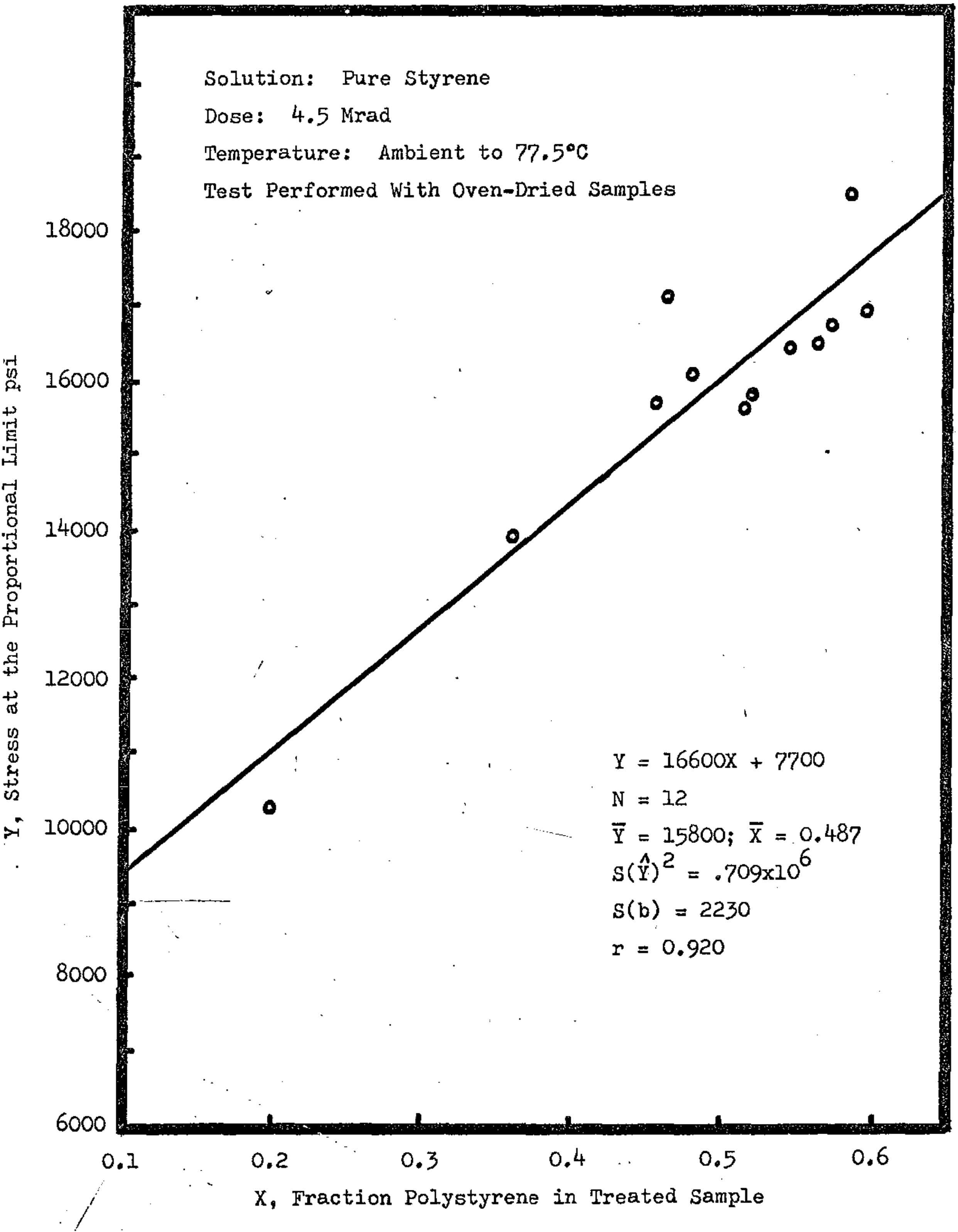

FIGURE 38

RELATIONSHIP BETWEEN STRESS AT PROPORTIONAL LIMIT AND F.P.S.
FOR WOOD TREATED WITH PURE STYRENE

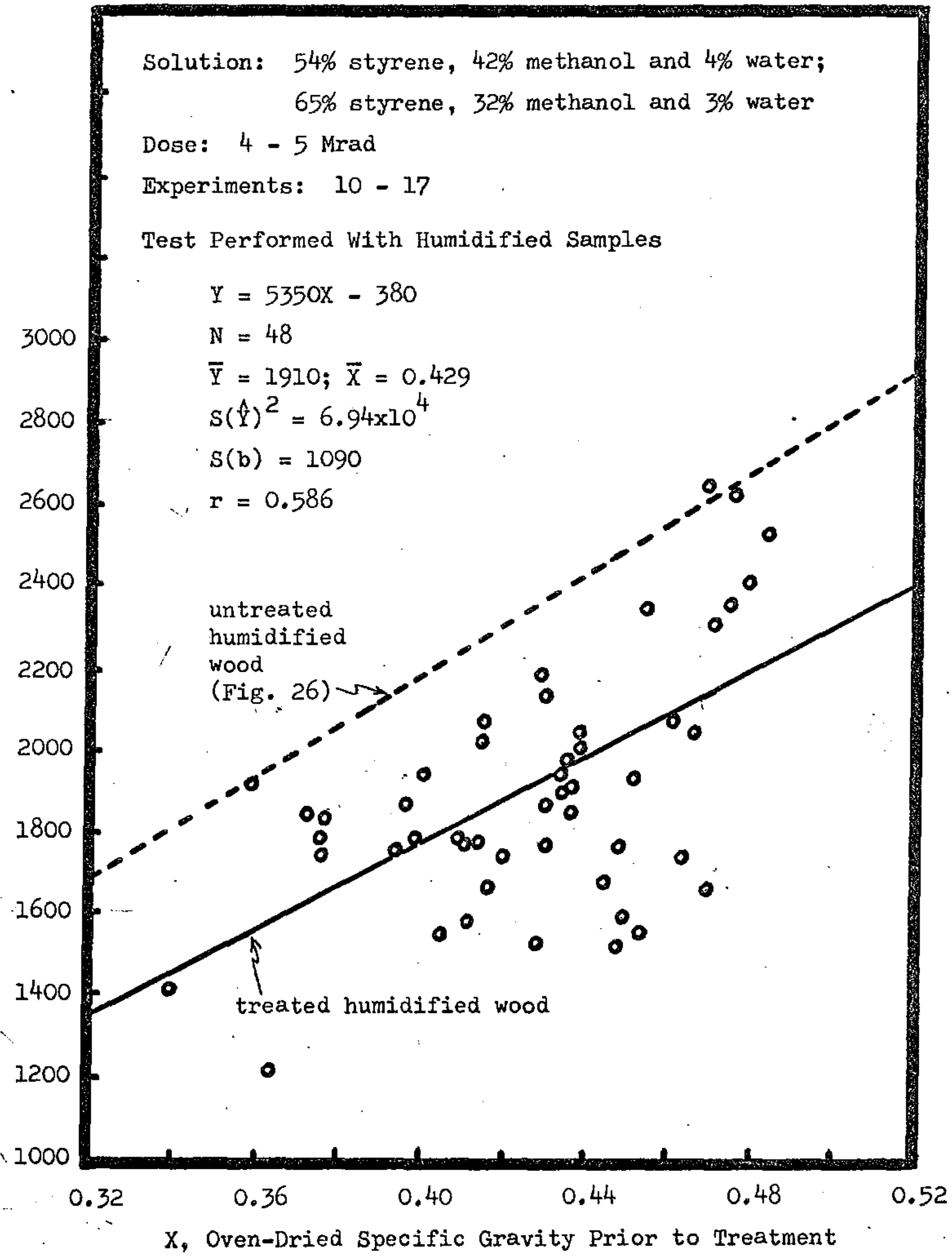

FIGURE 39

RELATIONSHIP BETWEEN MODULUS OF ELASTICITY
AND "ORIGINAL" SPECIFIC GRAVITY
FOR WOOD TREATED WITH 54% AND 65% STYRENE SOLUTIONS
(after Werezak)

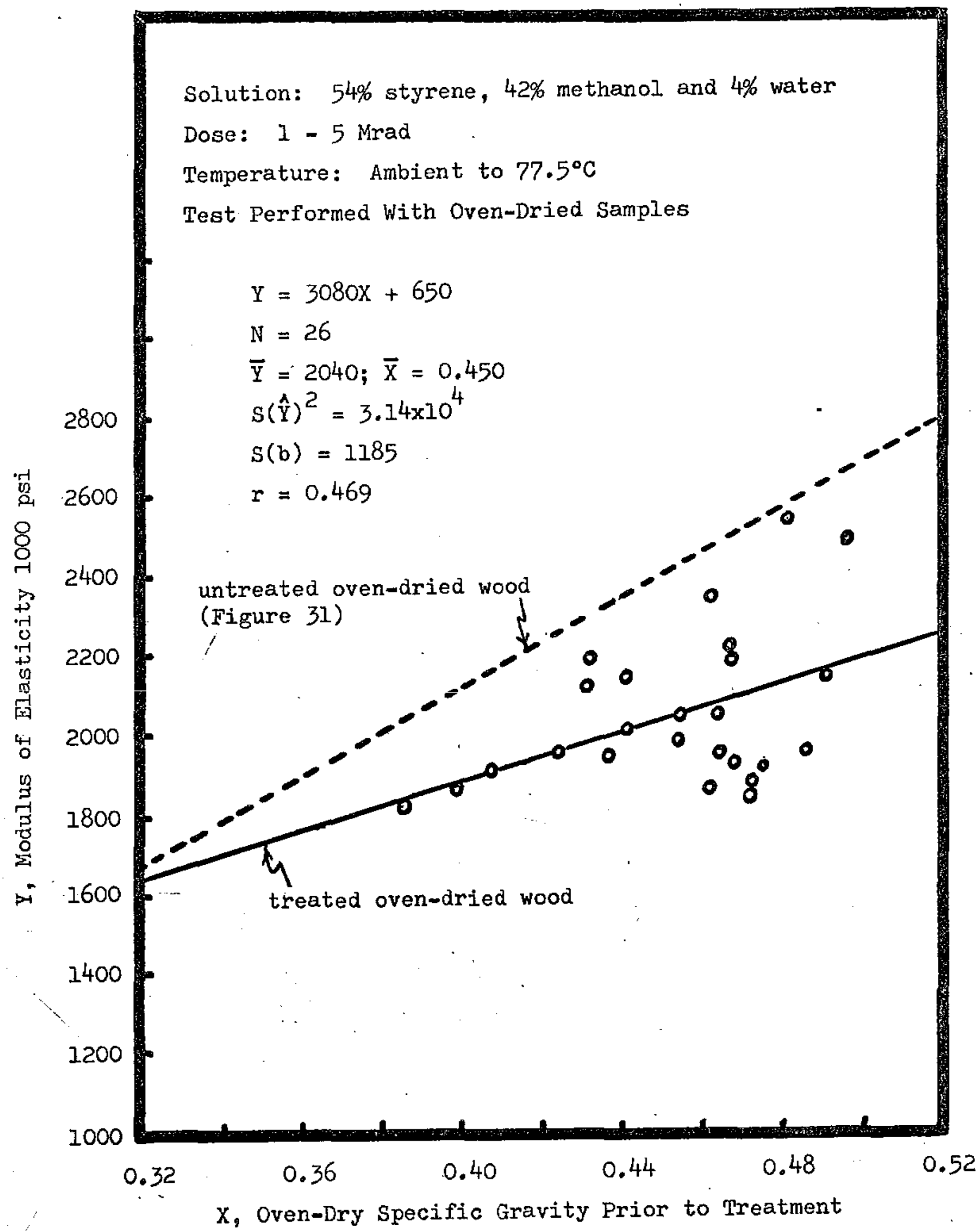

FIGURE 40

RELATIONSHIP BETWEEN MODULUS OF ELASTICITY
AND "ORIGINAL" SPECIFIC GRAVITY
FOR WOOD TREATED WITH 54% STYRENE SOLUTION

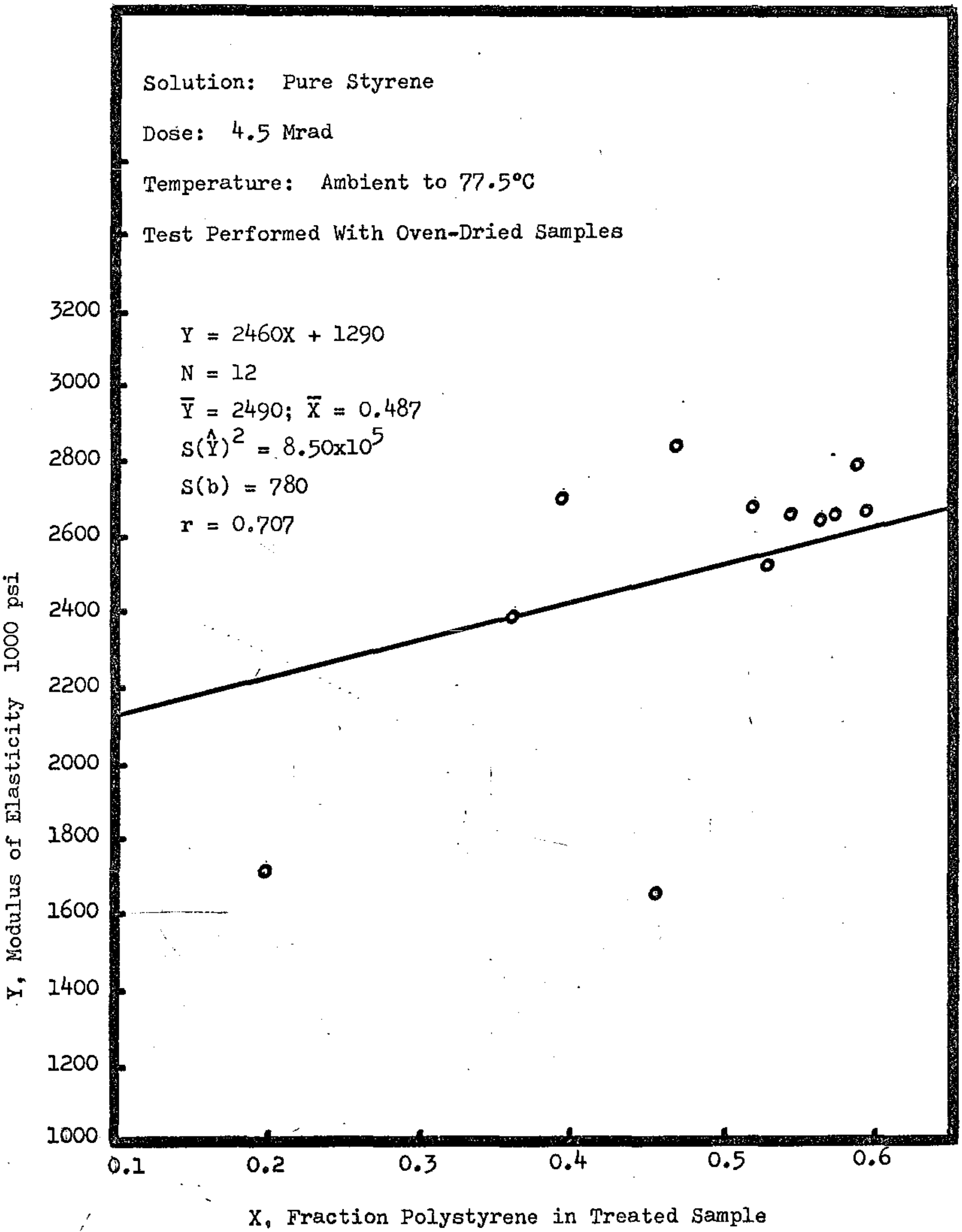

FIGURE 41

RELATIONSHIP BETWEEN MODULUS OF ELASTICITY AND F.P.S. FOR WOOD TREATED WITH PURE STYRENE

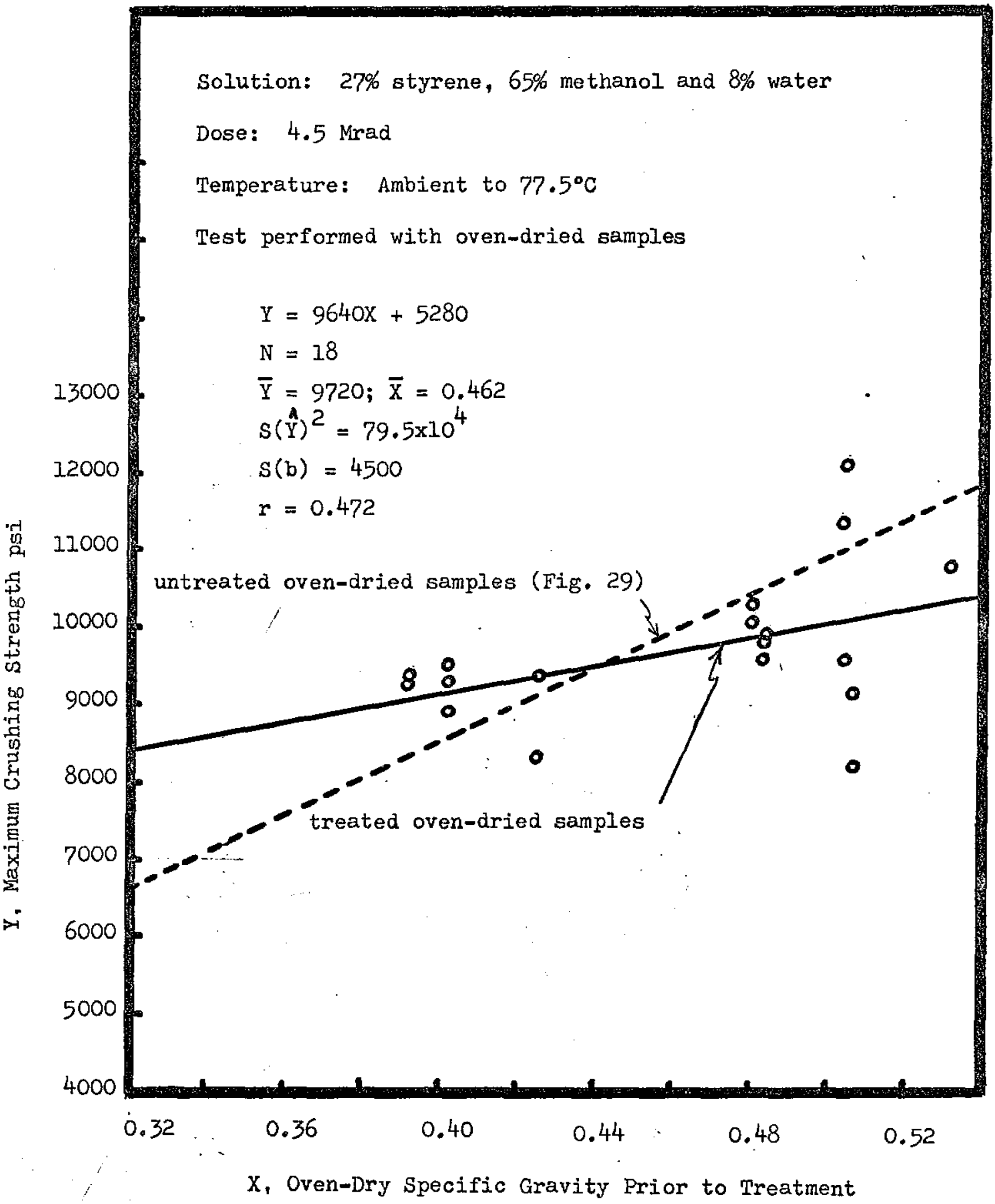

FIGURE 42

RELATIONSHIP BETWEEN MAXIMUM CRUSHING STRENGTH
AND "ORIGINAL" SPECIFIC GRAVITY
FOR WOOD TREATED WITH 27% STYRENE SOLUTION

the oven-dry specific gravity of the treated samples prior to the treatment. This was convenient in that it allowed the strength properties of the treated wood to be compared graphically to the untreated data since the same co-ordinate system was used in both cases.

Figure 33 is such a plot of the treated data. The solid line in the graph is the least-squares fit for the data. The dashed line is the least-squares line for the data of the untreated humidified samples described in a previous graph (Figure 20). It should be emphasized that although the data is greatly scattered, the correlation line is a significant improvement over a horizontal line through the data (i.e., no correlation). In fact, the regression line remove $(0.528)^2 = 30\%$ of the variance that exists about a horizontal line through the average value of the data. Now it can be shown that the correlation line for the treated wood is not significantly different (except for the variance) than that for the untreated humidified wood (Appendix VI - C).

Similar results are found for the samples which were treated with a 76% styrene, 22.5% methanol and 1.5% water solution (Tables 2 - 5 and Tables 18 - 20 in PART 1). These treated samples were humidified and tested without the deflectometer and hence the rupture values are compared to the correlation line obtained in Figure 17. It can be shown that except for the variance there is no significant difference between the correlations of the treated and untreated data.

(ii) Treated Wood Tested in the Dried Condition

It would be desirable to compare strength characteristics of treated and untreated wood on the basis of equal moisture content, as moisture is known to weaken wood. Since the humidified-treated samples described above contain less moisture per weight of sample or even per weight of wood-substance in the sample the effect of the treatment per se on the strength properties is difficult to discern. It is for this reason that in this present work all strength tests were performed on oven-dried treated and untreated wood.

Figure 35 is a plot of modulus of rupture versus oven-dry specific gravity of the treated wood prior to treatment (hereafter referred to as "original" specific gravity). The treatment of these samples has been described in detail in PART 1 of this thesis (Tables 25 and 26). The impregnating solution was made up of 54% styrene, 42% methanol and 4% water by weight. The dose used was 1 - 5 Mrad and the temperature during irradiation varied from ambient to 77.5°C. An evident aspect of the correlation shown in Figure 35 is the significantly higher residual variance as compared to the correlation for similarly treated samples which were humidified before testing (Figure 33). This observation is the same as the one noted for the untreated samples where the variance was higher for the oven-dried wood as compared to the humidified wood. It can be shown that except for significant difference in variance, the correlation of Figure 35 is not significantly different from that of Figure 33; i.e., the oven-dried solution-treated samples of this work have modulus of rupture values which are not different than those of the samples treated by Werezak. From Figure 35 it is also seen that the modulus of rupture for the treated oven-dried samples is substantially lower than the untreated oven-dried wood. At a specific gravity of 0.431 the average value is 14020 ± 1420 psi which is 23.8 ± 8.1% lower than the strength of the untreated wood. Therefore on the basis of moisture-free wood the treated samples are weaker in ultimate bending strength than the untreated wood.

The treatment with a solution of 27% styrene, 65% methanol and 8% water leads to a similar weakening of wood. No correlation could be found for the modulus of rupture with respect to any parameter. The average rupture value is 13600 ± 3900 psi. The average "original" specific gravity is 0.464 and the average fraction-polystyrene in the treated sample is 0.158. The 95% confidence limits of the mean value are high because the latter is based on only nine samples. At a specific gravity of 0.464 the strength of the oven-dried untreated samples is 21000 ± 625 psi. This is 35.2 ± 18.8% higher than that of the treated samples based on the former.

In contrast to the samples treated with a solution of styrene, methanol and water, wood treated with styrene alone has no polystyrene present in the walls of the cells. Figure 36 is a plot of modulus of rupture versus fraction polystyrene which is in the treated sample (designated as F.P.S.). The treatment of these samples is given in PART 1 of this thesis and the relating physical data is is given in Table 24. Briefly, wood was treated with pure styrene at a dose of 4.5 Mrad at temperatures varying from ambient to 77.5°C. There was no correlation between the modulus of rupture and the "original" specific gravity of the treated samples; it appears that the effect of polystyrene in the sample is so strong that it obscures the contribution of the woody-substance on this strength property. The average rupture value for these samples at an F.P.S. of 0.487 is 16200 ± 921 psi. The average "original" specific gravity is 0.414. The average modulus of rupture value of the untreated oven-dried wood at this specific gravity is

$$Y = 63000\ (0.414) - 8800 \qquad \text{(Figure 22)}$$
$$= 17300 \pm 494 \text{ psi}$$

Hence the average strength for the treated samples at an F.P.S. value of 0.487 is 6.4 ± 6.2% lower than that of the untreated wood at a common specific gravity value of 0.414.

It is noted that the average rupture values of the samples treated with styrene alone (16200 psi) is higher than that of the samples treated with the 54% styrene solution (see Figure 35). Since the average fraction-polystyrene in the treated sample (F.P.S.) = 0.487 for the former and 0.382 for the latter, it would be interesting to determine whether a significant difference in strength exists when both sets of treated data are compared at common "original" specific gravity and F.P.S. values. If we let these values be 0.414 and 0.382 respectively, the average rupture values for the samples treated with the 54% solution (Figure 35) and that for the samples treated with styrene alone (Figure 36) become 13120 ± 1910 psi and 14350 ± 1280 psi respectively. Unfortunately the standard deviation of the mean is so large that the 9.4% difference between values must be considered statistically insignificant.

(b) Stress at the Proportional Limit

(i) Wood Treated and Tested by Werezak

Figure 37 is a plot of the stress at the proportional limit versus the oven-dry specific gravity of the treated samples prior to treatment ("original" specific gravity) for the same samples used for Figure 33. It can be shown that the least-squares correlation line is significantly higher than that for the untreated humidified samples shown in Figure 21. At a specific gravity of 0.431 the values are 11130 ± 445 psi and 8900 ± 230 psi respectively (a difference of 25.1 ± 6.2%). As shown in Figure 37, although the correlation is significant at the 95% confidence level, it is not particularly good; i.e., only $(0.413)^2 = 17\%$ of the variance is removed by the regression line.

(ii) Treated Wood Tested in the Dried Condition

In contrast to the modulus of rupture data shown in Figure 35, no correlation existed between the stress at the proportional limit and any parameter for the samples treated with the 54% styrene solution. The average stress at the proportional limit for these 27 samples is 14200 ± 1160 psi at an "original" specific gravity of 0.451. In order to compare the proportional limit values of the oven-dried treated and untreated wood the latter is calculated from Figure 23 as

$$Y = 42000\ (0.451) - 5980$$
$$= 12970 \pm 622 \text{ psi}$$

There is no significant difference between the two strength values. Also it can be shown that there is a significant difference between the average stress value for these treated samples (14200 ± 1160 psi) and those treated by Werezak (11530 ± 523 psi - see Figure 37) compared at a common specific gravity of 0.451. The difference is 23.2 ± 10.6% based on the latter.

The samples which had been treated with the 27% styrene solution, when stressed in static bending yielded linear load-deflection curves until ultimate failure occurred. Therefore the stress at the proportional limit was equivalent to the modulus of rupture which is 13600 ± 3900 psi. The stress at the proportional limit for the untreated oven-dried samples at an average specific gravity of 0.464 (i.e., the average "original" specific gravity of these treated samples) is 13520 ± 705 psi. Thus the average strength values are equivalent except for the much higher variance for the treated samples.

For the samples treated with pure styrene, the load-deflection curves deviated only slightly from a linear relationship. Thus the correlation between the stress at the proportional limit and the F.P.S. is very similar to the correlation for the modulus of rupture data shown in Figure 36. The stress at an average F.P.S. value of 0.487

and an "original" specific gravity value of 0.414 is 15800 ± 541 psi. The stress at the proportional limit for the untreated oven-dried samples at a specific gravity = 0.414 is 11420 ± 551 psi which is 38.3 ± 6.3% lower than treated average stress.

(c) Modulus of Elasticity

(i) Wood Treated and Tested by Werezak

A plot of the modulus of elasticity versus the "original" specific gravity of the samples treated and tested by Werezak is shown in Figure 39. It is evident that the correlation for the treated samples is significantly lower than that for the untreated humidified samples. At an average specific gravity of 0.431 the modulus of elasticity values for the humidified treated and untreated samples are 1910 ± 77 x 10^3 psi and 2280 ± 69 x 10^3 psi respectively.

(ii) Treated Wood Tested in the Dried Condition

Figure 40 is a plot of modulus of elasticity versus the "original" specific gravity of the samples treated with the 54% styrene solution. It can be shown that there is a significant difference between the correlation for these treated samples and that for the oven-dried untreated samples. At an average specific gravity of 0.431 the modulus of elasticity values are 1980 ± 89 x 10^3 psi and 2300 ± 71 x 10^3 psi respectively. In addition, there is no significant difference between the correlation for these treated samples and that for the samples treated by Werezak with solutions of 54% and 65% styrene (Figure 39).

The average modulus of elasticity for the wood treated with the 27% styrene solution, based on nine samples is 1810 ± 674 x 10^3 psi at an average "original" specific gravity of 0.463. The modulus of elasticity for the untreated oven-dried wood at a specific gravity of 0.463 is 2480 ± 93 x 10^3 psi. More than nine samples are required in order to say with 95% confidence that there is a difference between these values.

Similar to the modulus of rupture and the stress at the proportional limit, the modulus of elasticity for the samples treated with pure styrene is not correlatable with the "original" specific gravity but has a correlation with the "fraction-polystyrene in the treated sample". This is shown in Figure 41. The average modulus of elasticity value for an average F.P.S. of 0.487 and "original" specific gravity of 0.414 is 2490 ± 188 x 10^3 psi. The modulus of elasticity for the oven-dried untreated wood at a specific gravity of 0.414 is 2200 ± 80 x 10^3 psi which is not significantly lower than the average treated value.

(d) Work to Proportional Limit and to Maximum Load

No correlation was obtained between either work expressions and the "original" specific gravity for any of the treatments. The results are summarized on Tables 34 and 35.

2. Compression Parallel to the Grain

Maximum Crushing Strength

All the treated samples were oven-dried prior to testing.

No correlation was obtained between maximum crushing strength and the "original" specific gravity or the F.P.S. in the treated sample for the samples treated with the solution 54% styrene, 42% methanol and 4% water. The average strength at an average "original" specific gravity of 0.449 and average F.P.S. of 0.374 based on 49 samples is 11350 ± 558 psi. The maximum crushing strength of the untreated oven-dried samples at a specific gravity of 0.449 is 9680 ± 264 psi. The treated samples, on the average, are 17.3 ± 5.3% stronger in compression than the untreated wood.

For the samples treated with the 27% styrene solution, a correlation between the crushing strength and the "original" specific gravity existed and is shown in Figure 42. It can be shown that the correlation for these samples is significantly different than that for the untreated oven-dried samples (Figure 27) at the 0.05 probability level*. It is noted that at a specific gravity of 0.443 both correlations for treated and untreated samples yield a strength of 9540 psi. Below this specific gravity, the treated samples appear to be stronger in compression whereas above this value, they appear to be weaker. In any case, it is seen that the difference is slight.

For the wood treated with pure styrene, it was found that there was a significant multiple correlation for the maximum crushing strength as a function of the "original" specific gravity and of the

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* but not at the 0.01 level

F.P.S. in the treated sample. The statistics of the correlation are given below.

TABLE 32

MAXIMUM CRUSHING STRENGTH AS A FUNCTION OF "ORIGINAL" SPECIFIC GRAVITY AND "FRACTION POLYSTYRENE IN TREATED SAMPLE" FOR WOOD TREATED WITH PURE STYRENE

M.C.S. = 33700 (S.G.) + 16800 (F.P.S.) - 8700

N = 40

$\overline{MCS}$ = 13000; $\overline{SG}$ = 0.407; $\overline{FPS}$ = 0.468

$S^2(MCS) = 5.33\text{x}10^6$

$S(b_{SG}) = 12200$ $S(b_{FPS}) = 2990$

R* = 0.738

For a specific gravity of 0.431 and F.P.S. of 0.468, the maximum crushing strength equals

33700 (0.431) + 16800 (.468) - 8700

= 13650 ± 944 psi

This value is 47.1 ± 10.3% higher than the strength of the untreated wood -- 9280 ± 251 psi.

Again it would be interesting to compare the strength of the wood treated with the 54% styrene solution and that of the wood

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* Multiple correlation coefficient; defined in Appendix VI - E

treated with styrene alone. The "original" specific gravity and F.P.S. for the former are 0.449 and 0.374 respectively.

Thus $\quad$ M.C.S. = 33700 (.449) + 16800 (.374) - 8700

$\quad\quad\quad$ = 12580 ± 1310* psi

This value is not significantly different from 11350 ± 558 psi which is the average crushing strength for the 54% styrene solution-treated samples.

3. Tension Parallel to the Grain

Maximum Tensile Strength

No correlation was obtained between the maximum tensile strength and the "original" specific gravity or the F.P.S. for the samples treated with the 54% styrene solution. The average strength is 10350 ± 685 psi at an average original specific gravity of 0.452 and an average F.P.S. of 0.381 based on 20 samples. The maximum tensile strength for the untreated wood at specific gravity of 0.452 is 15000 ± 894 psi which is 31.0 ± 7.3% higher than that of the treated samples.

As in the previous case no correlations were obtained for wood treated with the 27% styrene solution. The average maximum tensile strength is 11300 ± 1910 psi for an average "original" specific gravity of 0.464 and F.P.S. of 0.146 based on 8 samples. The strength for the untreated wood at a specific gravity of 0.464 is 15410 ± 1010 psi which

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* The 95% confidence limits of this average value, 12580 psi, are worked out in Appendix VI - E.

is 26.7 ± 14.4% higher than that of the treated samples.

There is a significant multiple correlation between the maximum tensile strength and the "original" specific gravity and F.P.S. for the wood treated with pure styrene. The statistics are given below.

TABLE 33

MAXIMUM TENSILE STRENGTH AS A FUNCTION OF "ORIGINAL" SPECIFIC GRAVITY AND "FRACTION POLYSTYRENE IN TREATED SAMPLE" FOR WOOD TREATED WITH PURE STYRENE

$\text{M.T.S.} = 87400\,(\text{SG}) + 36500\,(\text{F.P.S.}) - 41900$

$N = 13$

$\overline{\text{MTS}} = 12700$; $\overline{\text{SG}} = .407$; $\overline{\text{FPS}} = 0.521$

$s^2(\text{MTS}) = 2.39\text{x}10^6$

$s(b_{SG}) = 19500$; $s(b_{FPS}) = 8700$

$R = 0.836$

At a specific gravity of 0.431 and F.P.S. of 0.521 the maximum tensile strength equals 14750 ± 1140 psi. This is not significantly higher than the strength of the untreated wood at the same specific gravity; viz., 14200 ± 835 psi. On comparing the average maximum tensile strength for these samples with the one for the samples treated with the 54% styrene solution, the average specific gravity and F.P.S. values for the latter are used.

Thus $\quad \text{MTS} = 87400\,(.452) + 36500\,(.381) - 41900$

$\quad = 11500 \pm 3900$ psi

TABLE 34

STRENGTH PROPERTIES**

STATIC BENDING WITHOUT DEFLECTOMETER

STRENGTH PROPERTY	Untreated Humidified	Irradiated with 3.5 Mrad	Irradiated with 4.5 Mrad	Treated with 76% styrene, 22.5% methanol, and 1.5% water : Irradiated and humidified.
Modulus of Rupture: psi	14700 ± 234	14150 ± 392	13250 ± 503	14860 ± 564
Oven-Dry Specific Gravity	0.431	0.431	0.431	0.431

STATIC BENDING WITH DEFLECTOMETER

Modulus of Rupture psi						
Oven-Dry Specific Gravity	Untreated Humidified	Untreated Oven-Dried	Treated with 54% and 65% styrene solutions; irradiated; humidified	Treated with 54% styrene solution; irradiated; oven-dried	Treated with pure styrene; irradiated; oven-dried*	Treated with 27% styrene solution; irradiated; oven-dried
0.414		17300 ± 494			16200 ± 921	
0.431	13300 ± 231		13900 ± 515			
0.431		18400 ± 482		14020 ± 1420		
0.464		21000 ± 625				13600 ± 3900
Stress at the Proportional Limit psi						
0.414		11420 ± 551			15800 ± 541	
0.431	8900 ± 230		11130 ± 445			
0.451		12970 ± 622		14200 ± 1140		
0.464		13520 ± 705				13600 ± 3900

.... cont'd.

TABLE 34 (cont'd.)

Modulus of Elasticity 1000 psi						
Oven-Dry Specific Gravity	Untreated Humidified	Untreated Oven-Dried	Treated with 54% and 65% styrene solutions; irradiated; humidified	Treated with 54% styrene solution; irradiated; oven-dried	Treated with pure styrene; irradiated; oven-dried*	Treated with 27% styrene solution; irradiated; oven-dried
0.414		2200 ± 79			2490 ± 188	
0.431	2280 ± 69		1910 ± 77			
0.431		2300 ± 71		1980 ± 89		
0.463		2490 ± 93				1810 ± 674
Work to Proportional Limit in.-lb. per cu. in.						
	1.98 ± 0.10	3.51 ± 0.35	3.52 ± 0.21	5.88 ± 1.09	5.75 ± 0.75	5.55 ± 1.59
Work to Maximum Load in.-lb. per cu. in.						
	7.65 ± 0.85	10.50 ± 1.16	6.28 ± 0.87	6.98 ± 1.24	6.09 ± 0.96	5.55 ± 1.59

COMPRESSION PARALLEL TO THE GRAIN: Maximum Crushing Strength psi

Oven-Dry Specific Gravity	Untreated Humidified	Untreated Oven-Dried	Treated with 54% styrene solution; irradiated; oven-dried	Treated with pure styrene; irradiated; oven-dried*	Treated with 27% styrene solution; irradiated; oven-dried
0.431	5900 ± 180				
0.431		9280 ± 251		13650 ± 944	
0.431		9280 ± 251			9430 ± 534
0.449		9680 ± 264	11350 ± 558		

.... cont'd.

TABLE 34 (cont'd.)

TENSION PARALLEL TO THE GRAIN: Maximum Tensile Strength psi				
Oven-Dry Specific Gravity	Untreated; Combined Humidified and Oven-dried	Treated with 54% styrene solution; oven-dried	Treated with pure styrene; oven-dried*	Treated with 27% styrene solution; oven-dried
0.431	14200 ± 835		14750 ± 1140	
0.452	15000 ± 894	10350 ± 685		
0.464	15410 ± 1010			11300 ± 1910

** data presented as $Yi \pm ts(\hat{Y}i)$ where Yi = average strength value at xi

t = student "t" value at 95% confidence limit

$S(\hat{Y})$ = standard deviation of Yi at xi

based on $$S^2(\hat{Y}i) = S^2(\hat{Y})^2\left[\frac{1}{N} + \frac{(\bar{x} - xi)^2}{\Sigma^1 x^2}\right]$$ .... Page 237 (79)

for simple correlations.

* selected at the average F.P.S. value

TABLE 35

COMPARISON OF STRENGTH PROPERTY DATA*

STRENGTH PROPERTY	ALTERED WOOD	BASIS	PERCENT INCREASE IN PROPERTY
Modulus of Rupture	Oven-dried	Humidified Wood	38.4 ± 3.9
	Irradiated with 3.5 Mrad and humidified		- 3.7 ± 2.9
	Irradiated with 4.5 Mrad and humidified		- 9.9 ± 3.7
	Treated with 54% and 65% styrene solutions, irradiated and humidified		nil
	Treated with 76% styrene solution; irradiated and humidified		nil
	Treated with 54% styrene solution; irradiated and oven-dried	Oven-dried Wood	-23.8 ± 8.1
	Treated with 27% styrene solution; irradiated and oven-dried		-35.2 ± 18.8
	Treated with pure styrene; irradiated and oven-dried		- 6.4 ± 6.2

.... cont'd.

TABLE 35 (cont'd.)

STRENGTH PROPERTY	ALTERED WOOD	BASIS	PERCENT INCREASE IN PROPERTY
Stress at the Proportional Limit	Oven-dried	Humidified Wood	35.9 ± 6.2
	Treated with 54% and 65% styrene solutions; irradiated and humidified		25.1 ± 6.2
	Treated with 54% styrene solution; irradiated and oven-dried	Oven-dried Wood	nil
	Treated with 27% styrene solution; irradiated and oven-dried		nil
	Treated with pure styrene; irradiated and oven-dried		38.3 ± 6.3
Modulus of Elasticity	Oven-dried	Humidified Wood	nil
	Treated with 54% and 65% styrene solution; irradiated and humidified		-16.3 ± 4.5
	Treated with 54% styrene solution; irradiated and oven-dried	Oven-dried Wood	-13.9 ± 4.7
	Treated with 27% styrene solution; irradiated and oven-dried		nil
	Treated with pure styrene; irradiated and oven-dried		nil

.... cont'd.

TABLE 35 (cont'd.)

STRENGTH PROPERTY	ALTERED WOOD	BASIS	PERCENT INCREASE IN PROPERTY
Work to Proportional Limit	Oven-dried	Humidified Wood	77.8 ± 10.9
	Treated with 54% and 65% styrene solutions; irradiated and humidified		78.2 ± 12.2
	Treated with 54% styrene solution; irradiated and oven-dried	Oven-dried Wood	70.4 ± 34.2
	Treated with 27% styrene solution; irradiated and oven-dried		58.1 ± 45.1
	Treated with pure styrene; irradiated and oven-dried		63.8 ± 24.9
Work to Maximum Load	Oven-dried	Humidified Wood	37.3 ± 18.7
	Treated with 54% and 65% styrene solution; irradiated and humidified		-17.9 ± 15.5
	Treated with 54% styrene solution; irradiated and oven-dried	Oven-dried Wood	-33.2 ± 16.2
	Treated with 27% styrene solution; irradiated and oven-dried		-47.1 ± 17.6
	Treated with pure styrene; irradiated and oven-dried		-42.0 ± 14.4

.... cont'd.

TABLE 35 (cont'd.)

STRENGTH PROPERTY	ALTERED WOOD	BASIS	PERCENT INCREASE IN PROPERTY
Maximum Crushing Strength	Oven-dried	Humidified Wood	57.4 ± 3.4
	Treated with 54% styrene solution; irradiated and oven-dried	Oven-dried Wood	17.3 ± 5.3
	Treated with 27% styrene solution; irradiated and oven-dried		nil
	Treated with pure styrene; irradiated and oven-dried		47.1 ± 10.3
Maximum Tensile Strength	Treated with 54% styrene solution; irradiated and oven-dried	Combined Humidified and Oven-dried Wood	-31.0 ± 7.3
	Treated with 27% styrene solution; irradiated and oven-dried		-26.7 ± 14.4
	Treated with pure styrene; irradiated and oven-dried		nil

* Data presented with 95% confidence limits; see Appendix VI - E for details.

There is no significant difference between this value and the average for the solution treated wood -- 10350 ± 685 psi.

DISCUSSION OF RESULTS

Compression Parallel to the Grain

The oven-dried untreated wood is 57.4 ± 3.4% stronger in compression than the humidified untreated wood. A compressive force tends to cause the fibre wall of a wood to buckle. Of course, the chain molecules also buckle and in consequence lateral restraining forces are introduced that increase as the moisture content of the wood decreases (13). Therefore resistance of wood to compression increases as water is lost from cell walls because the walls attain greater stiffness.

The results show that the samples that were treated with the 54% styrene solution (average F.P.S. = 0.374) are on the average 17.3 ± 5.3% stronger than the oven-dried untreated wood. Undoubtedly the action of the polystyrene in the cell wall is similar to that of water; i.e., a destruction of hydrogen bonds has occurred. However, the bulking properties of the plastic, both in the cell wall and in the lumen, have compensated for the loss of strength associated with the separation of the cellulose chains. For the samples treated with 27% styrene solution there is no significant difference between the maximum crushing strength as compared to the oven-dried samples. This indicates that the bulking action of the polystyrene (F.P.S. = 0.154) is just enough to nullify the strength loss caused by breaking of the hydrogen bonds.

The samples treated with pure styrene at an average F.P.S. of

0.468 are 47.1 ± 10.3% stronger than the untreated oven-dried samples. Also the multiple correlation shows that the compressive strength is a function of the polymer content. For example, a 25% increase in F.P.S. (0.4 to 0.5) will increase the strength 14.5% (11710 to 13400 psi). This is reasonable in view of the fact that polystyrene is relatively strong in compression; viz., 11000 - 16000 psi.

The average crushing strength of the samples treated with pure styrene when compared to that of the samples treated with the 54% styrene solution at a common "original" specific gravity and F.P.S. yielded values of 12580 ± 1310 and 11350 ± 558 psi respectively. It can be shown that there is no significant difference between these values at the 95% confidence limits*; i.e., the variance of the mean at an original specific gravity of 0.449 and an F.P.S. value of 0.374 is so large that a difference of $\frac{12580 - 11350}{12580} = 10\%$ must be considered insignificant at this confidence level. At any rate, the results show that the compressive strength of the wood treated with pure styrene is not 10% higher than that of the wood treated with the 54% styrene solution at common F.P.S. and specific gravity values.

Tension Parallel to the Grain

The ultimate tensile strength for the solution-treated samples is substantially lower than that of the untreated samples. For those treated with the 54% styrene solution (average F.P.S. = 0.381) the

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* However, there is a significant difference at the 90% level.

decrease was 31.0 ± 7.3%. For the samples treated with the 27% styrene solution (average F.P.S. = 0.146) the decrease was 26.7 ± 14.4%. This reduction in strength could be due to two factors:

(1) the penetration of styrene into the walls has led to a loss in molecular cohesion accompanying the swelling or the separation of the cellulose chains.

(2) the radiation dose has degraded the wood and caused a decrease in the average D. P. of the cellulose in the walls.

The samples treated with pure styrene yield an average tensile strength which is insignificantly different from the untreated samples based on a common specific gravity of 0.431 and an average F.P.S. of 0.521 for the treated samples. If we equate the average strength values of the treated and untreated samples we get

$$14200 = 87000\,(.431) + 36500\,(\text{F.P.S.})$$

whence $\text{F.P.S.} = 0.506.$

Thus at Fraction Polystyrene values above 0.506 the treated samples are stronger than the untreated; below this value they are weaker. It is possible that two simultaneous effects are causing this behaviour: (1) the degradation and weakening of the wood by radiation and (2) the strengthening of the wood as a result of the bulking and cementing due to the presence of polystyrene in the zones of weakness in the tracheids; namely, the bordered pits (13). At around F.P.S. = 0.506 these effects cancel each other. It is noted that since no polystyrene is present in the walls for these samples, no separation of the cellulose fibres occurs.

It was felt that a comparison between the samples treated with pure styrene and those treated with the 54% styrene solution (average F.P.S. = .381) would be unjustified because it would involve a gross extrapolation of the multiple correlation; i.e., only 1 value out of 13 had an F.P.S. value less than 0.453. In addition, the sample size was relatively small and the variance high. Consequently the variance of the mean was large and strength values differing from the mean have associated with them very broad confidence limits. For example, at an "original" specific gravity of 0.452 and F.P.S. of 0.381, the average strength value of the samples treated with pure styrene is 11500 ± 3900 psi. Therefore strength values differing by less than about 30% must be considered statistically equal. This inability to firmly establish the significance of small differences is inherent in all the data in this work where a large variance and a small sample size are involved.

Static Bending

When beams are tested under static bending the convex surface is stressed in tension and the concave surface in compression. The initial failure of wood during bending occurs by compression. (The deviation from linearity on the load-deflection curve is a result of a compression failure.) However, the ultimate breaking of wood in bending is a failure in tension.

Modulus of Rupture

In general, for untreated wood, the maximum tensile strength is slightly greater than the corresponding bending strength value (13, 14). This is not the case for the treated samples; however, the maximum bending strength may still be considered strongly dependent on the ultimate tensile strength of the sample.

The results show that irradiation and moisture have a deleterious effect on the maximum bending strength of wood. For an irradiation dose of 3.5 Mrad a decrease in strength of 3.5 ± 2.9% is noted; for 4.5 Mrad the modulus of rupture decreases 9.9 ± 3.7%. Irradiation is known to decrease the D.P. and the tensile strength of cellulose (20, 29, 83 - 87). Being dependent upon the tensile strength, the maximum bending strength also decreases.

The average modulus of rupture for the oven-dried wood was 38.4 ± 3.9% stronger than that for the humidified wood which contained about 9.7% moisture by weight. The increase in strength as the cell walls lose water is caused by progressive hydrogen bonding of the hydroxyl groups of the cellulose chains as water is removed. The samples treated with solutions of (1) 54% styrene, 42% methanol and 4% water, (2) 65% styrene, 32% methanol and 3% water and (3) 76% styrene, 22.5% methanol and 1.5% water by weight, when humidified and tested under static loading yielded modulus of rupture values which were not significantly different from the untreated humidified samples. It is believed that the equivalence of the breaking strengths for treated and untreated humidified wood is fortuitous. The treated wood has a lower tensile but higher compressive strength than the untreated wood; these two effects probably nullify each other.

Wood treated with a solution of 54% styrene, 42% methanol and 4% water, when oven-dried and stressed in bending, showed a 23.8 ± 8.1% decrease in maximum bending strength relative to the oven-dried untreated wood. Therefore, the treated wood has an intrinsically lower maximum bending strength than the untreated wood. The effect of humidifying both treated and untreated wood is now evident. The treated wood, although inherently weaker than the untreated wood, undergoes less of a strength decrease on humidification because of a lower moisture adsorption (about 30% less based on the weight of woody material in the sample).

In addition it can be shown that the oven-dried wood treated with 54% styrene solution yielded modulus of rupture values equivalent to the humidified wood treated with 54% and 65% styrene solutions. Two conclusions can be drawn from this result:

(1) the moisture in the humidified treated wood does not appear to change significantly the maximum bending strength of wood.

(2) the treatment used in this work; viz., heating the impregnated samples during irradiation, is not an improvement, insofar as strength is concerned, over the treatment used by Werezak and Ramalingam.

The wood treated with the 27% styrene, 65% methanol and 4% water solution led to similar results. These samples had a maximum bending strength which was 35.2 ± 18.8% lower than the oven-dried untreated wood. This large decrease is accounted for by the 27.2 ± 12.0% decrease in tensile strength and the negligible improvement in compressive strength.

The samples which were treated with pure styrene showed only a 6.4 ± 6.2% decrease in bending strength when compared to the oven-dried untreated wood at an F.P.S. of 0.487 and an "original" specific gravity of 0.414. The fact that the modulus of rupture is a very strong function of the maximum tensile strength of wood and not very dependent on the ultimate crushing strength is demonstrated here. Compared to the untreated wood, the maximum bending strength changed very little as did the tensile strength, even though the maximum crushing strength improved 47%.

Comparing the samples treated with pure styrene with those treated with the 54% styrene solution leads to very large variances of the mean. The strength of the above treated samples at an original specific gravity of 0.414 and F.P.S. of 0.382 are 14350 ± 1280 and 13120 ± 1910 respectively. Because of the large confidence limits it cannot be said that the $\frac{14350 - 13120}{13120} \times 100 = 9.4\%$ difference in values is significant.

Stress at the Proportional Limit

Because initial failure in bending is usually compressive in nature, it follows that stress at the proportional limit in compression parallel to the grain, not stress in tension along the grain, controls the proportional limit of wood when it is used as a beam. Unfortunately, the stress at the proportional limit in compression was not determined in this work; however, it is believed that the stress at the proportional limit in static bending for the treated samples, as for the untreated ones, is a strong function of the ultimate crushing strength of the wood.

As in the case of the other strength properties, the stress at the proportional limit is highly dependent upon the moisture content of the wood. The oven-dried wood is, on the average, 35.9 ± 6.2% stronger than the humidified wood. The corresponding increase in the compressive strength is 57.4 ± 3.4%.

The samples treated by Werezak with the 54 and 65% styrene solutions and then humidified, are, on the average, 25.1 ± 6.2% stronger in the stress at the proportional limit than the untreated humidified samples. On the other hand, the oven-dried samples which had been treated in the present work with the 54% solution, display no improvement in this strength property when compared to the oven-dried untreated wood at a common "original" specific gravity.* Now it can be shown that in contrast to the modulus of rupture results, the oven-dried

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* There is a significant difference at the 90% confidence level. This value is 9.5 ± 8.3%.

treated samples are 23.2 ± 10.6% stronger in the proportional-limit stress than the corresponding humidified treated samples. It seems reasonable to assume that the difference in compressive strengths would be similar to this value. With this assumption, it is easily shown that the humidified treated wood would be 40 - 50% stronger in compression than the humidified untreated wood (average value = 5900 psi).

The wood treated with the 27% styrene solution shows no significant improvement over the untreated oven-dried samples for the stress at the proportional limit. This result is expected since no improvement in the compressive strength was obtained. In fact, it is believed that the initial and only failure in these samples was tensile in nature since the load-deflection curves displayed no deviation from linearity.

For the wood treated with pure styrene the increase in the proportional-limit stress as compared to the oven-dried untreated wood was 38.3 ± 6.3%. The corresponding increase in compressive strength was 47.1 ± 10.3%. Thus, it is seen that the stress at the proportional limit is related to the maximum crushing strength. This relationship is more readily discerned by the following table, comparing the average values of both strength properties.

	Stress at Proportional Limit psi	Maximum Crushing Strength psi
untreated humidified wood	8900	5900
untreated oven-dried wood	12100	9280
wood treated with 27% styrene solution	13600	9430
wood treated with 54% styrene solution	14200	11350
wood treated with pure styrene	15800	13650

In summary:

(1) for treated and untreated wood alike the stress at the proportional limit is a function of the compressive strength.

(2) the solution treated wood when humidified displays an increase in the stress at the proportional limit as compared to untreated humidified wood.

(3) the solution treated samples when oven-dried showed no increase in this strength property when compared to oven-dried untreated wood.

(4) wood, when treated with pure styrene, showed a marked increase in the stress at the proportional limit.

Modulus of Elasticity

The modulus of elasticity E is a measure of the stiffness or rigidity of a material. Consider the following relationship.

$$E = \frac{\sigma}{\varepsilon} = \frac{P/A}{S/\ell} = \frac{P\ell}{AS}$$

where P = load

A = stressed area

σ = stress

S = total deformation

ℓ = length of member

ε = strain

It is seen for a given stressed area and length of beam, a material will have a higher modulus of elasticity if it deforms less for a given load. In other words, for a beam, the modulus of elasticity is a gauge of its resistance to deflection.

The results indicate that the treatment of wood with styrene has not improved this material's stiffness. On the contrary, the rigidity has decreased for some of the treatments.

The samples treated with the 54% and 65% styrene solution and humidified before testing have an average Modulus of Elasticity 16.3 ± 4.5% lower than the humidified untreated sample. Similarly, the samples treated with the 54% styrene solution and oven-dried before testing display a 13.9 ± 4.7% decrease in this strength property when compared to oven-dried untreated wood.

The samples treated with the 27% solution have an average Modulus of Elasticity of $1810 \pm 674 \times 10^3$ psi based on nine samples. The untreated oven-dried samples have an average value of $2480 \pm 93 \times 10^3$ psi at a specific gravity of .464. It cannot be said with 95% confidence that these values are significantly different. More samples need to be tested in order to say that there is, in fact, a significant difference..

The modulus of elasticity for the samples treated with pure styrene is not significantly greater than the untreated oven-dried wood.

The reason for the lack of improvement in the modulus of elasticity for the solution treatments is

(1) the resulting separation of cellulose fibres due to the infiltration of polystyrene in the wall has attenuated the chain-to-chain forces.

(2) polystyrene is a relatively flexible material which has a Modulus of Elasticity ($E = 4.0 - 5.0 \times 10^5$ psi) substantially lower than that of wood.

Work to Proportional Limit and to Maximum Load

The work in bending to the proportional limit is a measure of the elastic potential energy which is stored in the beam as a result of the load. It indicates the ability of the wood to absorb shock without permanent damage; i.e., it sets a value on the resilience of the beam. The work to the maximum load in static bending represents the ability of the wood to absorb shock with some permanent deformation. It is a measure of the combined strength and toughness of wood.

The presence of moisture greatly affects the work expressions. The oven-dried samples have an average value of work to the proportional limit 77.8 ± 10.9% higher than that of the humidified samples. The corresponding increase for the work to the maximum load is 37.3 ± 18.7%.

All humidified treated samples have work to proportional limit values which are on the average 78.2 ± 12.2% higher than those of the untreated humidified wood. Similarly, the values of the average work to proportional limit for oven-dried treated samples are from 58.1 ± 45.1% to 70.4 ± 34.3% higher than those of the untreated oven-dried wood. This indicates that the resilience of all the treated samples is substantially higher than that of wood alone.

On the other hand, the work to the maximum load associated with the treated samples is much lower than the value of the untreated wood. The humidified solution-treated wood has an average work to maximum load which is 17.9 ± 15.5% lower than the humidified untreated wood. Similarly, the decrease in work for the oven-dried treated samples varies from 33.2 ± 16.2% to 47.1 ± 17.6%. Thus the treated wood is less tough than the untreated wood.

EPILOGUE

The initial aim of this investigation was to enhance the bending strength of wood by means of the radiation-initiated, in situ graft copolymerization of styrene in wood. It was believed that heating solution-impregnated wood during the irradiation step would increase the diffusion of styrene monomer to the free radical sites which, in the previous work, had not been utilized in the grafting process; more grafting would necessarily occur and, as a result, an increase in bending strength would (hopefully) be obtained. Therefore, the objective of this work (as well as that of Ramalingam and Werezak) is based on the premise that (1) heating increases the amount of grafting and (2) grafting and bending strength are positively related. From PART 1 of this thesis, particularly the analysis of Werezak's unpublished data, an attempt was made to show that heating was not an important step in the grafting or associating process. It was determined that grafting or associating (measured by the amount of polystyrene that was unextractable) is a function of the transfer of monomer from the cell lumen into the cell wall where actual grafting (initiated by cellulose free radicals) and entangling or cross-linking occur. This transfer is dependent upon such factors as the method of impregnation, the specific gravity of the wood and moreover the amount of swelling agents, particularly water, that is present in the impregnating solution. It was theorized that the mechanism whereby styrene entered the cell wall was "preferential extraction". This process consists of an initial selective adsorption of water from the solution by the cellulose in the walls followed by a slow diffusion of styrene into the sufficiently swollen structure. However, the transfer of monomer into the walls was found to be independent of the temperature during irradiation; i.e., an increase in temperature did not increase the diffusion of styrene into the cell wall. It is thought that this transfer can only be accomplished by swelling the wall beforehand. Hence the assumption that heating the wood-styrene system increases the amount of grafting (or associating) must be rejected.

The belief that grafting per se would increase the bending strength of wood is still not confirmed. This is due to the fact that the grafting technique introduces other effects which weaken the wood. Two such effects are permanent swelling of the wood and degradation of cellulose by irradiation. It is unfortunate that the previous researchers used bending load rather than modulus of rupture as the index of strength because the increase in swell was not taken into account. As a result, increases in bending strength of 50% were reported. In fact, as shown in this work, the bending strength (as measured by the modulus of rupture) of the wood treated by Werezak shows no significant improvement when compared to the humidified untreated wood. Indeed, when moisture and density are taken into consideration, it is found that the solution-treated wood is about 24% weaker in bending. In addition, the modulus of elasticity, the work to the maximum load and the ultimate tensile strength are weaker for the treated wood. The very fact of having to use swelling agents (water and methanol) to accomplish grafting has attenuated the hydrogen bonding between cellulose macromolecules and the result is a lower strength uncompensated by the grafted polystyrene. Although no work was carried out to determine the frequency of grafting, it is assumed to be very low. Whether a greater frequency would lead to an increase in strength is still open to question. On the other hand, the maximum crushing strength and the strength properties associated with compression such as the stress at the proportional limit and the work to the proportional limit are equal or higher for the treated wood than for the untreated. This is believed to be due to bulking. Therefore, it can be seen that wood treated with a solution of styrene, methanol and water, although being weaker in some properties, displays improvements in others. However, the enhancement, in contrast to that reported by the previous workers, is not striking. In fact, from an industrial viewpoint, the use of swelling agents in the radiation-initiated in situ polymerization of styrene in wood looks far from promising.

This is not necessarily the situation for the wood treated with pure styrene. From Ramalingam's results it was shown that this wood, when humidified, is about 50% stronger in modulus of rupture than the untreated humidified wood. When compared on a moisture-free basis, the treated wood is only about 6% weaker. On the same basis, this wood is as strong as or stronger than the untreated wood for all other measured properties except the work to the maximum load. Now it is noted from Ramalingam's results that wood in which pure styrene was allowed to polymerize thermally with a catalyst yields modulus of rupture values which are identical with the radiation-initiated treated wood. It is assumed that the other physical properties behave similarly. This is important from an industrial consideration. The commercial enterprises sponsored by the U.S. Atomic Energy Commission have used exclusively nuclear radiation for the initiation of <u>in situ</u> polymerization. Is this justified? The point is this:

(a) gamma radiation is useful because it uniquely produces graft-copolymerization.

(b) swelling agents must be employed if grafting is to be achieved.

(c) the weakening effect of the swelling agents outweighs the strength contribution (if any) of the graft copolymer.

(d) thermal polymerization is at least as effective as radiation polymerization in conferring enhanced strength properties and dimensional stability to wood.

Therefore the use of radiation polymerization in the preparation of wood-plastic composites appears unjustified.

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APPENDICES

APPENDIX I

Effect of High Energy Radiation on Cellulose

Schoepffle and Connell (19) in 1929 observed that paper, on exposure to cathode rays, gave off hydrogen, carbon dioxide and carbon monoxide. It became brittle and crumbly on prolonged exposure.

In 1952, Saeman, Millett and Lawton (20) irradiated wood, wood pulp, cotton linters and glucose with high energy electrons. The main effect was found to be the degradation of cellulose -- i.e., scission of the main cellulose chain -- accompanied by the decomposition of the monomer glucose unit. A sharp decrease in the degree of polymerization occurred at dosages exceeding 10^6 equivalent roentgens. Cellulose was converted to water soluble products after a radiation dose of 5×10^8 roentgens. In contrast to conventional chemical reactions of cellulose, it was observed that radiation-induced changes occurred randomly; that is, no distinction was made between the effects in amorphous and crystalline regions.

In 1957, Glegg and Kertesz (22) reported their investigation of the degradative effect of gamma rays from a CO-60 source on cotton linters and wood pulp containing different amounts of water. The irradiations were carried out in air. The presence of water (3.3 - 5.6%) had no significant effect on the extent of radiation-induced degradation. The intrinsic viscosity (η) for the cellulose decreased linearly as a function of the log of the irradiation dose. Irradiated dry cellulose samples exhibited a strong post-irradiation degradation effect which continued for 60 - 70 days after irradiation. Subsequent work on the decrease of the intrinsic viscosity (23) showed that this after-effect could be curtailed by the addition of water or water vapour. The addition of oxygen during or after irradiation was found to contribute to a further decrease in (η).

In the period from 1958 to 1962, Arthur and colleagues published a series of excellent papers dealing with the effects of high energy radiation on cotton cellulose. In 1958, Blouin and Arthur (24) irradiated purified cotton linters in oxygen and nitrogen atmospheres and determined the chemical and physical effects by standard methods of cellulose chemistry. The main effects were the formation of carbonyl and carboxyl groups on the cellulose and chain cleavage. The ratio of these effects was approximately 20:1:1 respectively. The effect of gamma radiation on cellulose was found to be slightly less in a nitrogen atmosphere than in oxygen. By infrared spectrum analysis it was postulated that there was no change in the crystalline structure of the cellulose.

In another paper, Arthur (25) proposed a mechanism to explain the effect of high energy radiation on some molecular properties of cotton cellulose. These properties could be related by the equation

$$\ell nP = k\ell n\,Nn+K$$

where Nn is the radiation dose, P is the molecular property such as degree of polymerization, carbonyl or carboxyl group formation, and k and K are constants. By making a log-log plot of the experimental data, straight lines were obtained, confirming the form of the equation for a dose range of 10^5 - 10^8 roentgens.

In 1960, Blouin and Arthur (26) made a detailed investigation of the specific nature of groups formed on cotton cellulose irradiated in air, oxygen and nitrogen atmospheres to a dose of 10^8 roentgens. The ratio of carbonyl:carboxyl groups:chain cleavages formed was accurately determined to be 19:0.5:1. The irradiated cellulose was fractionated and the acid and reducing group content of each fraction was compared to the total content before fractionation. The number of acidic groups increased as the molecular weight of the fractions decreased. This observation strongly indicated that the acidic groups were at the ends of the chains. The carbonyl groups appeared to be evenly distributed along the chain since the carbonyl content did not change with the fractions. Analysis of the water soluble and water insoluble fractions gave negative results indicating the absence of peroxide groups within the accuracy of the method*. The following mechanism of the interaction of ionizing radiation with cellulose was proposed: the two carbon atoms involved in the glucosidic linkage are the C1 and C4 positions; therefore, activation of these two positions could most likely lead to chain cleavage. The ratio of

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* It takes a very small amount of peroxide (ca. 0.01 - 0.02%) to account for all of the free radicals required for graft polymerization.

19:0.5:1 for carbonyl:carboxyl group:chain cleavage, show that for every two chain cleavages, an acidic group is formed. This indicates that the formation of acidic groups occurs at the chain ends. When the C1 position is activated, chain cleavage occurs, forming 2-ketogluconic acid on the reducing end. Activation of the C4 position results in chain cleavage, liberating the reducing end of the chain as an unaltered glucose unit and producing a ketone group in the C4 position on the non-reducing end of the other chain. Activation of the C2, C3, C5 and C6 positions caused carbonyl group formation with the evolution of hydrogen without chain cleavage. The predominant reaction on irradiation of cellulose was dehydrogenation with the production of reducing groups, either ketones or aldehydes. The gases produced during irradiation were isolated and analysed by mass spectrometry. Carbon monoxide, carbon dioxide and hydrogen were found. When available, large amounts of oxygen were consumed during the irradiation. This could have been due to reaction with the liberated hydrogen to form water or to formation of acidic groups or of carbon dioxide. The carbon dioxide and carbon monoxide were considered to be secondary degradation products formed by decomposition of the carbonyl groups for carbon monoxide and by decarboxylation of carboxyl groups in the case of carbon dioxide.

A subsequent paper by Arthur et al (27) reported that oxygen was reacting with the ionized cellulose at a faster rate than gases were being evolved. By mass spectrometry, the ratio of the principal gases evolved, hydrogen, carbon dioxide and carbon monoxide was found to be:

For nitrogen atmosphere	(1×10^8 roentgens)	1:1.1:1.8
For oxygen atmosphere	(0.9×10^8 roentgens)	1:4.2:11
For air atmosphere	(0.8×10^8 roentgens)	1:2.2:4.6

Huang (28) in 1963 studied the degradation of cotton cellulose by gamma ray irradiation in air. The dose rate of his source was $1.3 - 1.4\times10^6$ r/hr. The degree of polymerization of the cellulose decreased steadily with increasing dose:

Dose (10^6 rads)	Degree of Polymerization
0	1676
0.1	1252
1.0	557
10	116
100	18

The results show good agreement with Saeman et al (20) and with Arthur (25). This suggests that, since dose rates varied considerably among the three investigations, the depolymerization of cellulose is a function of total radiation dose and is independent of intensity.

APPENDIX II

Electron Spin Resonance Studies

Glegg and Kertesz (22) in 1957 obversed the presence of free radicals in -cellulose irradiated in air. A small resonance was noted after five days for the cellulose samples containing 0.32% and 4% moisture. After thirty days, a weak signal was obtained from the former sample and essentially none from the latter. The post-irradiation decrease in intrinsic viscosity was postulated to be due to free radicals.

Abraham and Whiffen (50) in 1958 investigated the electron spin resonance of cellulose irradiated in vacuo. A narrow electron spin resonance spectrum with marked assymetry was obtained.

Florin (51) in 1960 reported his studies on the investigation of the electron spin resonance of gamma ray irradiated cellulose. It was established that there are two kinds of radicals present, one of which has considerable electron density on oxygen and the other is a carbon-ended radical. He suggested that because of cage effects C-H and O-H breaks are somewhat more likely than C-C and C-O breaks. The free radicals formed in dry cellulose were relatively stable, even over a period of several months at room temperature. With elevated temperatures the decay of radicals in dry cellulose required several days at 70°C, many hours at 100 - 120°C and a few hours at 100 - 200°C. The G-value of radical production was estimated to be around 2.6.

Kavage (52) in 1960 studied the electron spin resonance spectra of radicals produced in cellulose irradiated in vacuum and in dry air. Cellulose samples irradiated under vacuum at 75°C and then heated at 100°C yielded initial electron spin resonance spectra consisting of the overlapping of the spectra of several species. In the final stages of heat treatment only radicals showing doublet or triplet spectra (two or three absorption peaks) were thought to remain. When the vacuum of a sample irradiated at 20°C was broken, a rapid decay of radicals occurred at room temperature until a constant level was reached after which the spectra changed very little. When the cellulose was irradiated at room temperature and in air there were not great differences in the spectra immediately following irradiation compared to the same spectra for vacuum irradiation. The time change in air at 20°C was the same as the change that resulted when the material irradiated in vacuum was unsealed. The decay rate was found to be very rapid.

Kuri and Ueda (53) in 1961 studied the electron spin resonance spectra of the free radicals produced in gamma irradiated cellulose. The cellulose was (1) irradiated in vacuo (2) irradiated in sulphur dioxide (3) irradiated in vacuo and followed by the introduction of sulphur dioxide. Identical spectra were obtained for the three methods. Other hydrophilic polymers such as starch, carboxymethylcellulose, sodium alginate and polyvinyl alcohol produced similar results. In contrast, polyethylene yielded three different electron spin resonance spectra under the same experimental conditions; this indicates a reaction with sulphur dioxide. It was concluded that the free radicals formed in hydrophilic polymers were unreactive toward SO_2 and this effect was thought due to inter- or intramolecular hydrogen bonding.

Werezak (54) summarized further work carried out by Ueda and Kuri (55). Various sugars and high polymers such as cellulose, cellubiose and sucrose were irradiated in vacuum at a dosage of 10^7 r. Mono- and polysaccharides were found to give radicals which did not react with O_2, NO or H_2S. It appeared that in the solid state these radicals were entirely unreactive at room temperatures. Irradiated samples were treated thermally for eleven minutes and their electron spin resonance absorption intensity compared with the intensity at 20°C. It was found that for temperatures up to ca. 80°C very little change of intensity occurred. However, for higher temperatures, a very sharp decrease was noted. From these and other results it was concluded that the radicals produced in compounds with OH groups are stabilized by hydrogen bonding. The unreactivity of these radicals in the solid state with gases may be ascribed to the hydrogen bonding network which prevents the gas entry. While there was a gradual disappearing of radicals even at relatively low temperatures, at higher temperatures there were still portions with small molecular chain motion. This was explained on the basis of heterogeneous distribution of crystal states in high polymers. Although glucose, cellubiose, maltose, cellulose and starch have the same constituents, the radicals produced have different decay rates presumably due to different crystalline states. The radicals in cellulose disappeared more rapidly than those in cellubiose presumably due to the more crystalline state of the latter. An explanation for the change in the shape of the electron spin resonance curve by thermal treatment is that the crystal state (or the state of hydrogen bonding) is disturbed. Another possible reason given is that when the radicals disappear, dehydration takes place and the resulting water has some effect of the spectrum.

Kesting and Stannett (40) in 1962 investigated the formation and decay of free radicals in cotton cellulose using electron spin resonance spectrometry. CO-60 gamma rays were used at a dose rate of 0.324 Mr/hr. Moist and dry samples were irradiated in air and in vacuum. Electron spin resonance measurements showed that fewer trapped radicals were present in moist cellulose. It is suggested that some of the cellulose trapped radicals combined with the more mobile radicals produced by the radiolysis of water. For dry cellulose the free radical build-up in air at 25°C was about 10% lower than that in vacuum at the same temperature. The concentration of radicals increased continually with dose. Direct radical decay measurements showed a second order rate process ($K = 1.3 \times 10^{-3}$ litres moles^{-1} sec^{-1}). The authors believe that the kinetics of decay is complicated by the heterogeneous nature of the cellulose; i.e., radicals formed in the amorphous regions have a greater probability of combining than those in the crystalline regions. Thus the overall rate constant is likely to be a superposition of many decay rate constants.

It was found that the ratio between the increase in the number of polymer chains and the decrease in the number of radicals remained nearly constant. This strongly indicates that the polymerization was initiated by the trapped free radicals which propogate in the normal manner and terminate by mutual destruction. Also, electron spin resonance curves and grafting yields were similar for pre-irradiation in vacuum and for pre-irradiation in air at room temperature. This would not be expected had grafting been initiated by peroxides. However, it is believed that peroxide grafting may be significant at higher temperatures.

Florin and Wall (56) in 1963 published their work on the electron spin resonance of irradiated cellulose. Purified cellulose samples (cotton, hydrocellulose, filter paper) were irradiated up to 64 hours at a dose rate of 0.5×10^6 r/hr in a CO-60 gamma facility at 20°C and -196°C. The electron spin resonance spectra obtained resemble closely those of Abraham and Whiffen (50). It was found that differences in crystallinity had no obvious effect on the yield or nature of the radical electron spin resonance spectrum. The changes in spectral shape upon heating as well as the general asymmetry indicated several different types of radical species. Thermal decay was found to be imperfectly second-order, fairly rapid above 120°C. Generally speaking, the decay curves were made up of two regions, consisting of a precipitous fall in radical concentration followed by a levelling-off. Thus it appears that radicals were being destroyed during irradiation at rates exceeding by several orders of magnitude the simple thermal decay rates. Formation of radicals at -196°C was found to be about 30% lower than at 20°C. This is thought to be due to cage effects. Addition of water to samples irradiated at room temperature modified the hyperfine structure of the electron spin resonance spectra and seemed to cause an immediate disappearance of some radicals after which time the remainder disappeared only somewhat faster than the decay of radicals in the untreated dry samples. The radicals formed in a wet sample were just as long-lived as those formed in dry material but their number was smaller. Exposure of irradiated samples to air accelerated the rate of decay ten-fold without any large initial decay. The G-value for radical formation was calculated to be 2.8 radicals/100 ev abosrbed. Because the authors' G_R value is much less than the G-value calculated by Charlesby (G = 10) on the basis of chemical changes, it is suggested that many energetically "hot" or chemically unstable radicals exist during irradiation and these react as formed with each other and with stable radicals. The levelling off of the decay curves to an apparently unreactive remainder is thought due to radicals which are isolated rather than existing in close pairs or clusters and which recombine, primarily by diffusion with several energies depending on site and type of radical. Water is believed to serve as a reactant when present during irradiation but its principal role if added later is to facilitate diffusion into noncrystalline regions and to open up the crystalline regions for diffusion. Nevertheless, it is believed that a few sites were completely immune to this action of water in view of the levelling off of the decay curves and the long life of radicals formed with water present.

Bernard, Gagnaire and Servoz-Gavin (57) in 1963 reported a very interesting study of the radicals found before, during and after the radiation-initiated copolymerization of styrene onto cellulose using the electron spin resonance technique of detection. Cotton linters were irradiated with CO-60 gamma rays with a dose of 2.4 Mrads ($8x10^5$ r/hr) at room temperature. The initial hyperfine structure of the cotton irradiated in a 10^{-4} mm Hg vacuum was essentially the same as that from samples irradiated in air. The asymmetrical curves were similar to those found by previous workers (56). As a first approximation the number of radicals formed was proportional to the irradiation dose. An increase in dose did not affect the shape of the hyperfine structure. The initial spectrum was modified by soaking the samples in water, then drying under vacuum. The samples treated in this manner yielded an electron spin resonance spectrum which was essentially symmetrical with 5 lines extending over 75 gauss (generally speaking, one species of radicals will give a symmetrical hyperfine structure). The spectrum representing the structure of the radicals destroyed by the water was obtained by subtracting the resulting curve from the initial one. A spectrum which is practically symmetrical on 4 lines was obtained. By a double integration of the curves, the authors estimated that the percentage of radicals destroyed by water was 56%. The initial spectrum was then explained by the superposition of the spectrum of two classes of radicals differing by their reactivity with water:

(1) radical type A; a stable radical; 5 lines over 75 gauss, the relative intensity of the order 1-3-6-3-1.

(2) radicals of type B; less stable radicals; 4 lines over 75 gauss with relative intensities of 1-10-10-1.

The authors also studied the effect of different styrene solutions on the radicals formed in cellulose. Pure styrene added to the irradiated cellulose led to a negligible amount of graft. The electron spin resonance spectrum thus obtained showed the disappearance of radicals of type B and a very small decrease of radicals of type A. Styrene added to an irradiated cellulose sample in a mixture of methanol and water (20% styrene, 72% methanol and 8% water) led to a very high amount of graft, 90% by weight. There was a disappearance of radicals of type B and a noticeable decrease of radicals of type A. The mutual radiation of cellulose soaked in styrene carried out in an evacuated sealed tube yielded no graft. Radicals identical to those found in the pre-irradiation with pure styrene were found. On using the inclusion method, a 130% grafted product was obtained along with a complete disappearance of both types of radicals. In all cases styrene radicals were not observed at any time. It is postulated that water and styrene react (or destroy) radicals of type B and that graft copolymerization with styrene is initiated by radicals of type A whose sites are made accessible by means of swelling by water (which does not react with these radicals). The authors suggest that radicals of type B may be those formed by a hydrogen abstraction from carbon 6 of the anhydroglucose unit and those of type A may be due to hydrogen abstraction from carbons 2 and 3.

APPENDIX III

Free Radicals Available for Grafting

(a) In the Secondary Wall

The G-value for main chain scission (number of scissions formed per 100 ev absorbed) in cellulose has been estimated by Charlesby (21) to be 11. Florin and Wall (56) obtained a G-value for radical production of 2.8. This was based on electron spin resonance measurements; the low value, as compared to that obtained by Charlesby was believed due to the inability to detect many unstable free radicals which cause degradation during irradiation. Imamura et al (71) found a G-rupture value of 9 and Demint et al (33) calculated a value of about 7. Blouin and Arthur (26) found that the ratio of carbonyl:carboxyl groups:chain cleavages formed was 19:0.5:1. From this it seems reasonable to assume that there are free radicals formed in cellulose that do not lead to main chain fracture. However, let us choose a conservative value of 10 for G_R.

Considering a dose of 3.5 Mr, the energy absorbed per gram of cellulose is

$$3.5 \text{ Mr} \times \frac{10^6 \text{rad}}{1 \text{ Mr}} \times \frac{6.25\text{x}10^{13} \text{ev}}{\text{gm}} \times \frac{1}{\text{rad}}$$

$$= 2.18\text{x}10^{20} \text{ e.v.}$$

Now wood contains about 25% lignin (12); also about 50% of the total cellulose content is inaccessible to both water and styrene (18). Therefore the number of free radicals that might take part in the grafting process is

$$0.50 \times 0.75 \times 2.18 \times 10^{19} = 8.2\text{x}10^{18} \text{ radicals/gm-wood}$$

Now each gram of wood takes up about one gram of styrene (see Tables 2 - 21). For an average molecular weight of 100,000 for the grafted polystyrene the number of polystyrene chains in 1 gram of wood would be

$$\frac{6.02\times10^{23}}{100,000} = 6.02\times10^{18}$$

Therefore 6.02×10^{18} radicals (assuming 1 radical/chain) would be required in order completely to graft 1 gram of polystyrene onto cellulose. Since 3.5 Mr will form 8.2×10^{18} radicals, complete grafting is theoretically possible.

(b) On the Lumen Surface

The following data was taken from Stamm, Chapter 11, "Internal Surface and Accessibility", Pages 187 - 200 (14).

Wood with a dry-volume specific gravity of 0.4 will have a lumen surface of 2.0×10^{13} cm^2/g. The internal area of contact (within the secondary wall) with swelling agents is ca. 250 m^2/g for water and 212 m^2/g for methyl alcohol. Taking the lowest value, we get 212/0.2 = 1060 times as much surface area in the secondary wall as on the lumen surface. The distribution of free radicals formed during irradiation is likely to have the same ratio, which indicates that there are $8.2\times10^{18}/1060 = 7.75\times10^{15}$ free radicals formed on the lumen surface for one gram of wood. Since the number of free radicals necessary for complete polymerization in the cell cavities is about 6.02×10^{18}, it can be seen that there are 1000 times too few radicals available on the lumen surface for total conversion of styrene to grafted co-polymer. Thus other factors (such as cross-linking of the polystyrene) must be the cause of the high content of unextractable polystyrene.

APPENDIX IV

Radiation Facility

The apparatus used for the irradiation of the samples is described in the accompanying reprint of a brief article appearing in the literature (65). Two views of the apparatus are given in Figure 43 and Figure 44. Three factors warrant a more detailed discussion.

(1) There were very small leaks in the loop which were difficult to remove. Hence, it was found that it would be more practical to use air as the heat-carrier gas rather than nitrogen as originally planned. In order to prevent the diffusion of oxygen into the impregnated sample and also to prevent the volatization of the impregnant, a leak-free, thin-walled aluminum canister was constructed to contain the samples. Material balances on the sample, before and after irradiation, showed that up to temperatures of 80°C no impregnant was lost.

(2) The temperatures of the system were measured by means of copper-constantan thermocouples which were calibrated in boiling water. Two thermocouples were located in the gas stream. Three thermocouples were imbedded into the surface of the aluminum canister. The sample was placed in the loop after temperature equilibrium was reached (30 - 60 minutes, depending upon the temperature). It took about ten minutes to reach steady-state temperatures after the introduction of the sample. The temperature difference between the ends of the sample (16" long) was 0 C° for 39°C and 0.25 C° for temperatures from 39 - 80°C. In order to determine whether there was a substantial

A Versatile Radiation Source for Studying Gamma-Initiated Reactions

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Reprinted in Canada from
THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING
43: 117-119: June 1965
A Publication of The Chemical Institute of Canada
48 Rideau Street, Ottawa 2, Ontario.

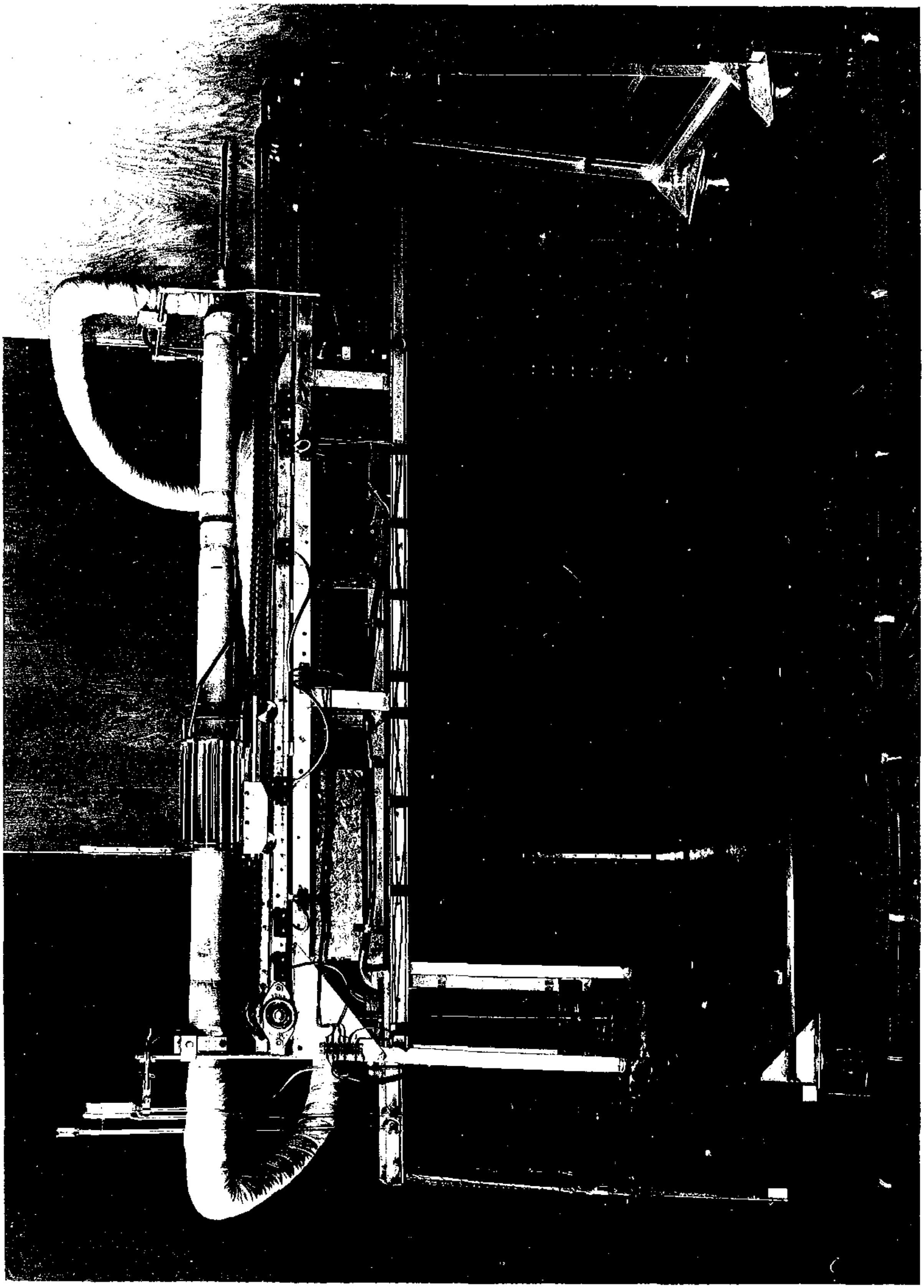


FIGURE 43

PHOTOGRAPH OF SWEEP APPARATUS: FRONT VIEW

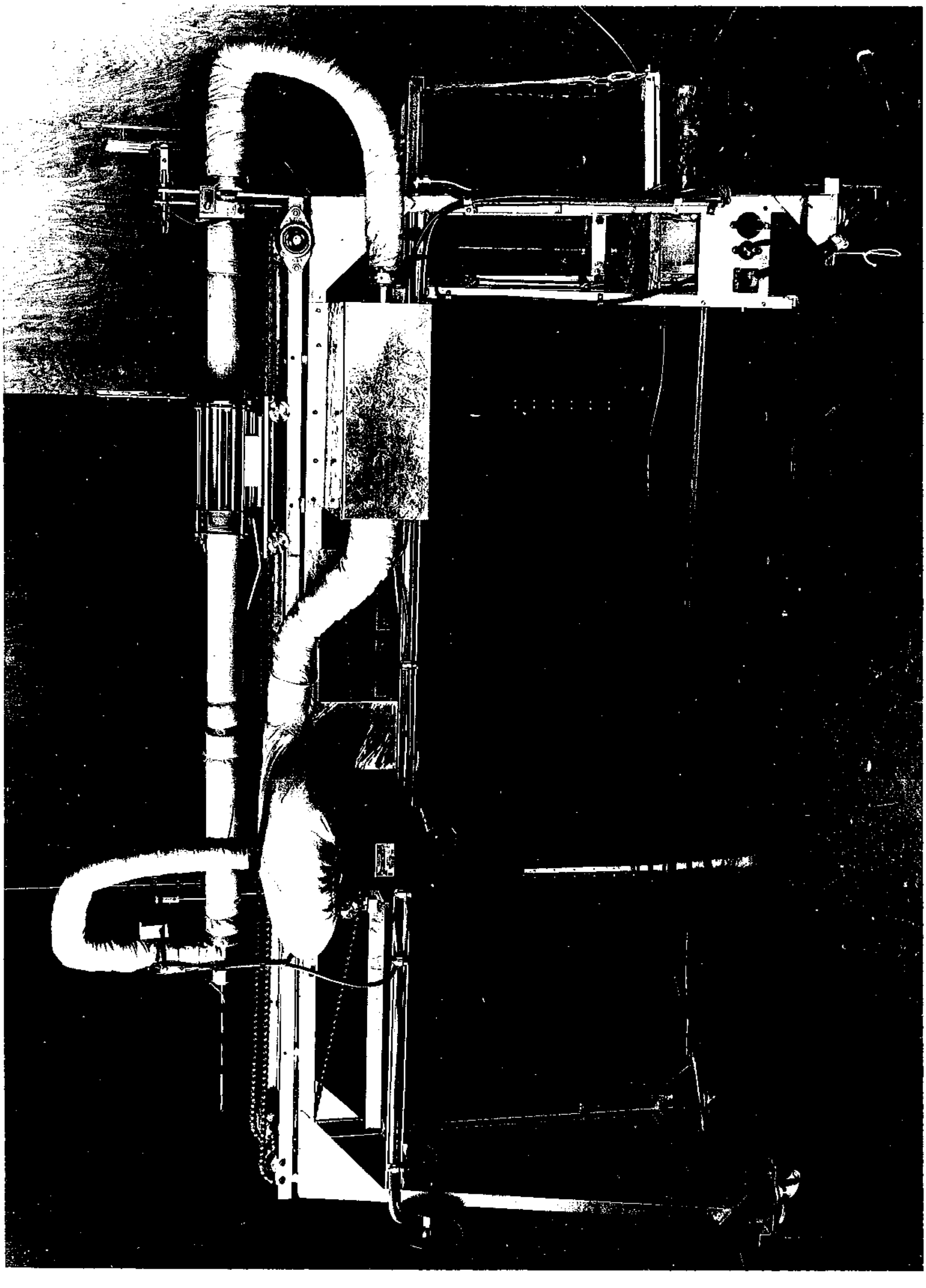


FIGURE 44

PHOTOGRAPH OF SWEEP APPARATUS: REAR VIEW gradient within the wood sample, two runs were performed in which three thermocouples were imbedded, at different depths, into the wood and their recorded temperatures compared with the temperatures on the aluminum canister. After steady state was reached, a temperature difference of less than 1 C° was noted at low temperatures (39°C) and a difference of less than 2 C° for higher temperatures (ca. 75°C).

(3) The dosimetry was carried out using the colour change of cobalt glass on exposure to ionizing radiation. This change in optical density was then used to determine the dose received by the glass. Previous work (67) had related the optical change of cobalt glass to ferrous ions oxidized to ferric in a Fricke dosimeter on exposure to radiation. Optical density measurements were performed with a Beckman DK-1 spectrophotometer. A wavelength of 4000A° was used for all measurements.

Each point on Figure 5 of the accompanying reprint represents the average of experiments in which four cobalt glass samples were attached to a 20" piece of wood. It was found that

(1) there was no significant difference between the optical density changes of the four samples for a given radiation period. Hence, the wood samples received a uniform gamma flux.

(2) the cobalt glass samples received negligible radiation during the loading and unloading stages.

(3) the dose received by the glass was independent of the speed of the truck carrying the CO-60 source.

(4) there was a linear relationship between total dose and radiation period (see Figure 5, reprint).

APPENDIX V

Swelling in Wood

In PART 1 of this thesis it was shown that the radiation-induced polymerization of styrene (in solution with methanol and water) causes a greater swelling in wood than that caused by water. Consider experiments 18 - 20 where the impregnating solution was 76% styrene, 22.5% methanol and 1.5% water. The percent swell (based on the volume of the oven-dry untreated wood) as a function of the polymer retention (gms polystyrene/cc of wood) is shown in Figure 45. It can be seen that the percent swell increases rapidly with increasing polymer retention. At zero retention the percent swell should obviously be zero. This is shown by the dashed line on the graph. Werezak immersed these dry treated samples in distilled water at room temperature and atmospheric pressure for 28 days. Figure 46 shown the percent swell (based on the oven-dry untreated wood) caused by the water uptake as a function of polymer retention. There is a slight decrease in swelling as the retention of polymer increases. At zero retention the percent swell should be 11.6% which is the average swell for the untreated wood. The reason for the increase in swell due to the treatment and decrease in swell due to water infiltration for increasing polymer retention is as follows: as more solution is taken up by the wood, the associating efficiency increases (see Figure 4) for reasons explained in PART 1. Thus there is relatively more polymer in the cell walls. This inevitably leads to greater swelling of the wood due to the treatment and less swelling of the wood in water. Figure 47 shows that the total swell of the treated wood based on the volume of the oven-dry untreated wood is largely due to the large amount of dimensional change caused by the treatment.

FIGURE 45

RELATIONSHIP BETWEEN % VOLUMETRIC SWELL DUE TO TREATMENT AND POLYMER RETENTION

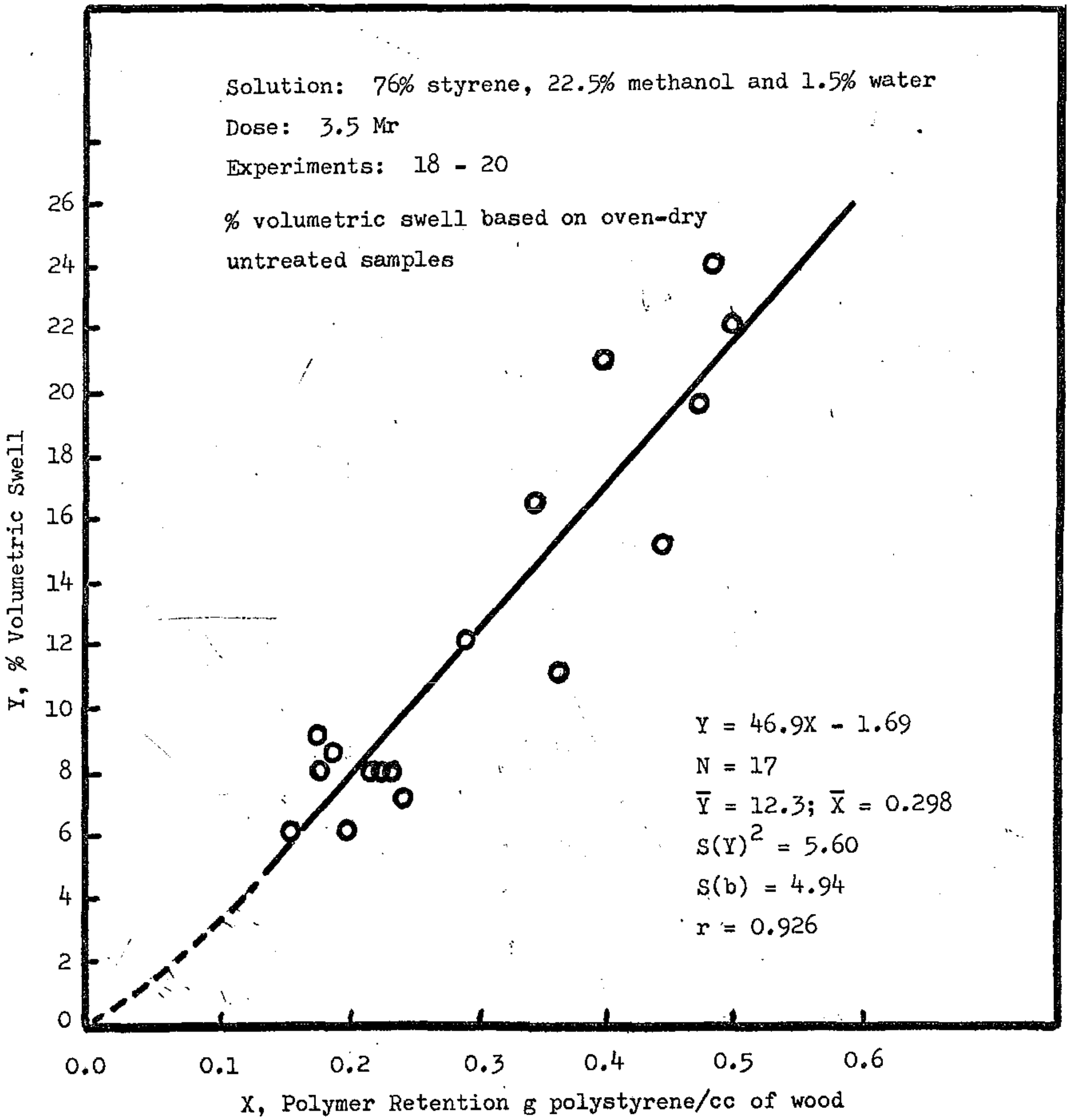
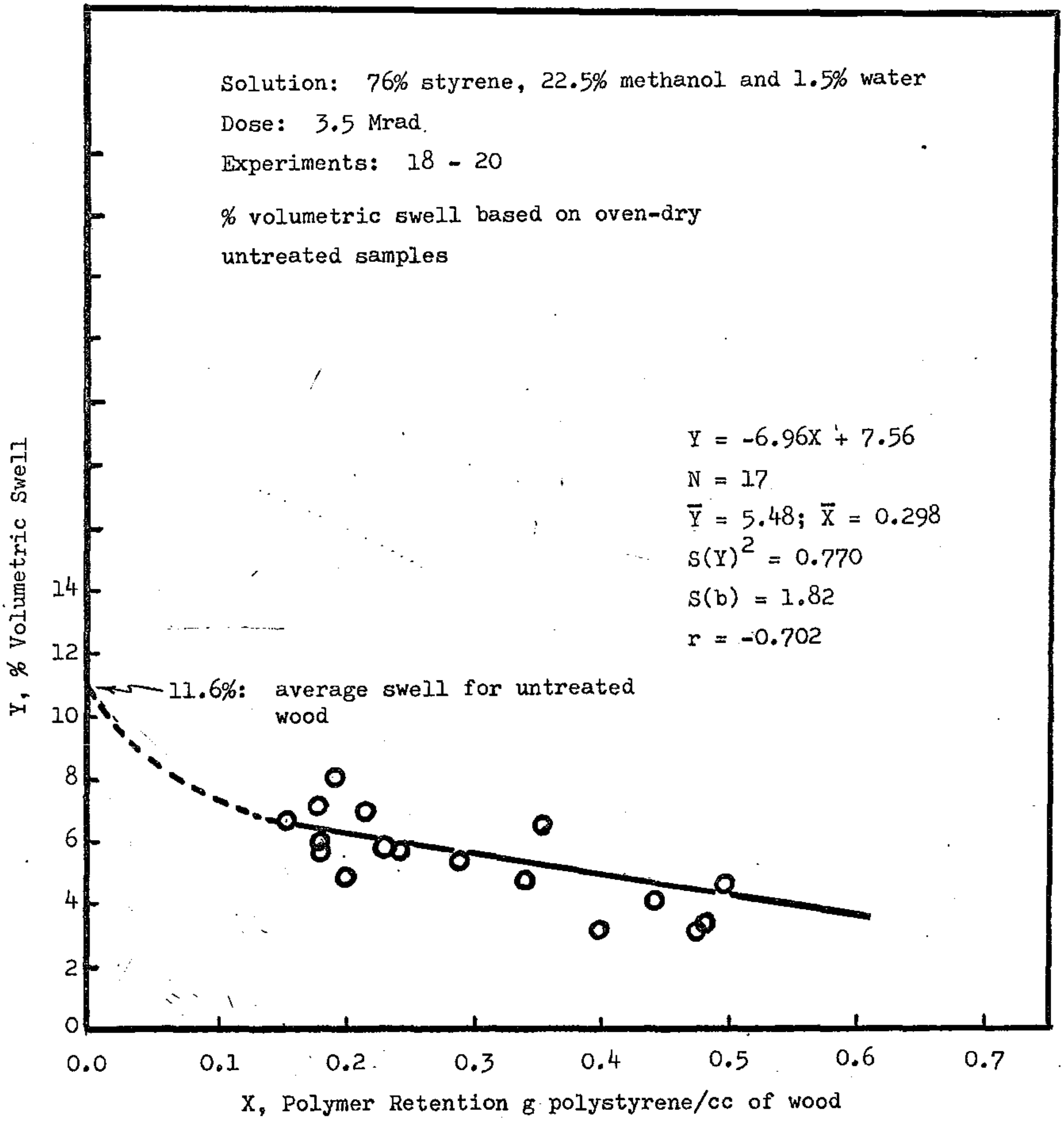


FIGURE 46

RELATIONSHIP BETWEEN % VOLUMETRIC SWELL IN WATER AFTER TREATMENT AND POLYMER RETENTION



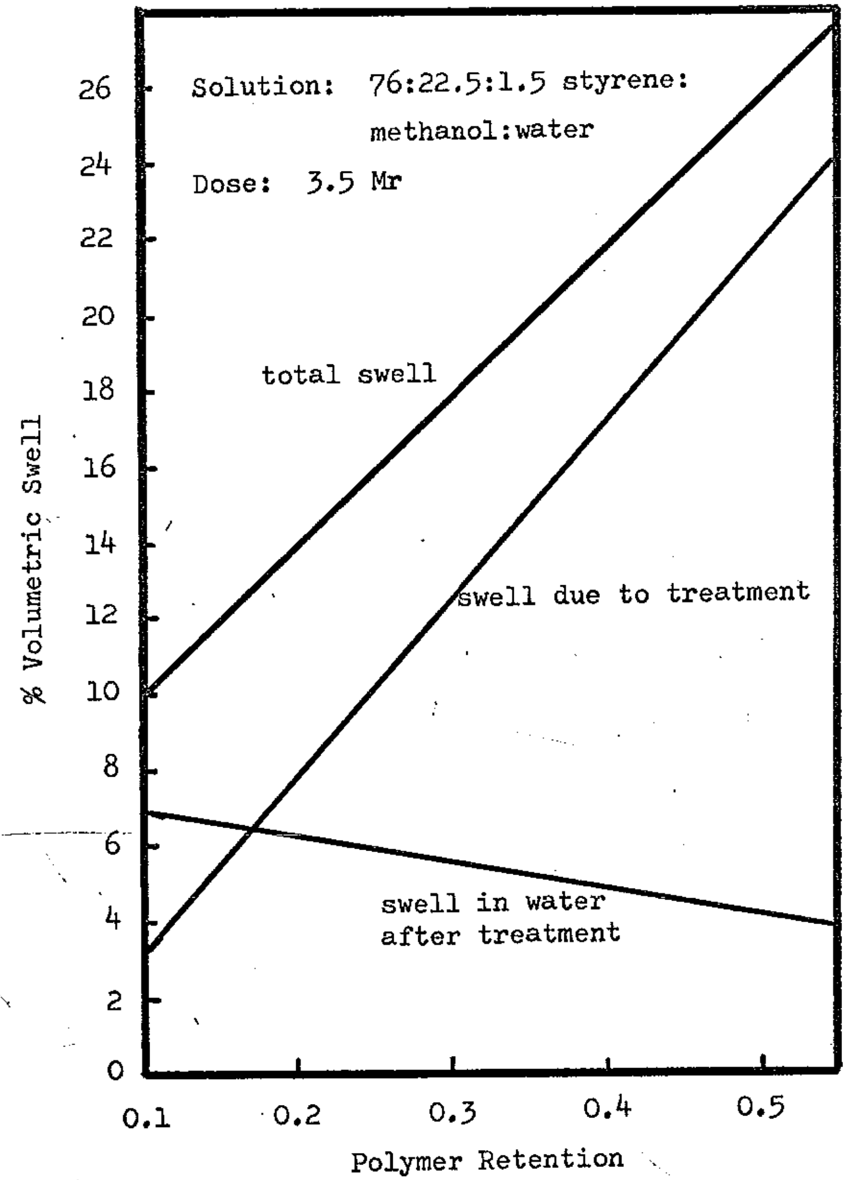


FIGURE 47

TOTAL PERCENT VOLUMETRIC SWELL
= SWELL DUE TO TREATMENT
+ SWELL IN WATER

APPENDIX VI

Statistical Analysis of Data

A. General Definitions

The method of analysis is similar to that suggested by Volk in "Applied Statistics for Engineers" (79). Other references are given (80 – 82). The "correlation coefficient" program is shown on the following page.

(1) Linear Correlation of Two Variables

For least square line

$$\hat{Y} = a + bx \tag{1}$$

$$a = \bar{y} - b\bar{x} \tag{2}$$

and $$b = \left[\Sigma xy - \frac{\Sigma x \Sigma y}{N}\right] \div \left[\Sigma x^2 - \frac{(\Sigma x^2)}{N}\right] \tag{3}$$

where N = number of data points

$\bar{X}$ and $\bar{Y}$ are the mean values.

(2) Significance of Linear Correlation

The significance of a linear correlation can be measured by the "correlation coefficient". This term ranges from 0 to ± 1.0 and indicates the goodness of a fit; zero for no correlation and ± 1.0 for a perfect correlation. The value is equal to

$$r = \frac{\Sigma xy - \frac{\Sigma x \Sigma y}{N}}{\left[\left(\Sigma x^2 - \frac{\Sigma x^2}{N}\right)\left(\Sigma y^2 - \frac{\Sigma y^2}{N}\right)\right]^{1/2}} \tag{4}$$

On Page 231 of Volk's book, the values of r corresponding to various

TABLE 38

COMPUTER PROGRAM FOR STATISTICS

```
      READ10,M
     DO 100 I=1,M
      SUM YY=0.0
      SUM X=0.0
      SUM Y=0.0
      SUM XY=0.0
      SUM XX=0.0
      READ 10,N
      DO 50 J=1,N
      READ 11,X,Y
      SUM X=SUM X + X
      SUM Y=SUM Y + Y
      SUM XY=SUM XY + X*Y
      SUM XX = SUM XX + X*X
 50   SUM YY = SUM YY + Y*Y
      SIZE = N
      SUM1YY=SUM YY-SUM Y*SUM Y/SIZE
      SUM1XX=SUM XX-SUM X*SUM X/SIZE
      SUM1XY=SUM XY-SUM Y*SUM X/SIZE
      R=SUM1XY/(SQRT(SUM1XX*SUM1YY))
      PRINT 112,N
      PRINT 200
      PRINT 113,SUM X,SUM Y,SUM XY,SUM XX,SUM YY,SUM1YY,SUM1XX,SUM1XY
      PRINT 14, R
      SY=(1.0-R*R)*SUM1YY/(SIZE-2.0)
      SB=SQRT(SY/SUM1XX)
      BETA = (SUM X*SUM Y-SIZE*SUM XY)/(SUM X*SUM X-SIZE*SUM XX)
      ALPHA = (SUM Y-BETA*SUM X)/SIZE
      PRINT 13, SB
100   PRINT 12, ALPHA, BETA
 10   FORMAT (20I4)
 11   FORMAT (2X,10E13.5)
200   FORMAT (2X,100H      SUMX            SUMY            SUMXY           SUMXX
    1  SUMYY           SUM1YY          SUM1XX          SUM1XY    //)
113   FORMAT (2X,8E13.5//)
 38  FORMAT(5X,F10.5,4X,F10.7,F10.4,F10.5,F10.1,F10.5)
112   FORMAT (15H  NUMBER DATA, I10//)
 12   FORMAT (2X, 24HALPHA AND BETA IN ORDER=,2E13.5//)
 13   FORMAT (4H SB=,F20.5//)
 14   FORMAT (3H R=, F20.5//)
      STOP
      END
```

probability levels (0.001 to 0.1) and degrees of freedom based on the null hypothesis that there is no correlation between the two variables involved.

(3) Variance Test of Correlation

It is possible to test the estimated variance removed by the linear correlation against the estimated variance remaining after the correlation by using

(a) the F ratio test for 1 and N-2 degrees of freedom on the ratio $S^2(C)/S^2(\hat{Y})$

where $S^2(C) = r^2\Sigma(y-\bar{y})^2/1$ = the variance estimate or the sum of squares of deviation attributable to the correlation divided by the degree of freedom of 1

and $S^2(\hat{Y}) = (1 - r^2)\Sigma(y - \bar{y})^2/N - 2$ = the sum of squares of deviation from the least square line divided by the degrees of freedom N - 2.

(b) a "t" test using the ratio

$$t = r\sqrt{N - 2}\,/\sqrt{1 - r^2}$$

(c) the "r" test described above.

(4) Confidence limits of Slope and Least-Squares Line

The following formulae give the estimated variances of the various quantities involved in a linear correlation.

Variance of estimate, $S^2(\hat{Y}) = \dfrac{\Sigma(y - \hat{y})^2}{N - 2}$ (5)

Variance of $\bar{y}$, $S^2(\bar{y}) = \dfrac{S^2(\hat{Y})}{N}$ (6)

Variance of slope $S^2(b) = \dfrac{S^2(\hat{y})}{\Sigma x^2 - \dfrac{\Sigma x^2}{N}}$ (7)

Variance of any average estimated value $\hat{Y}i$

$$S^2(\hat{y}i) = S^2(\hat{Y}) \left[\frac{1}{N} + \frac{(\bar{x} - xi)^2}{(\Sigma x^2 - \dfrac{\Sigma x^2}{N})} \right] \tag{8}$$

Variance of any single estimated value Yi

$$S^2(\hat{Y}i) = S^2(\hat{Y}) \left[1 + \frac{1}{N} + \frac{(\bar{x} - xi)^2}{\Sigma x^2 - \dfrac{\Sigma x^2}{N}} \right] \tag{9}$$

B. Example: 12% moisture Modulus of Rupture vs. specific gravity

Consider as an example Werezak's data for the Modulus of Rupture for humidified samples (Figure 20).

Y = Modulus of Rupture in psi

X = oven-dry specific gravity

$N = 48$

$\Sigma X = 20.68 \quad \bar{X} = 20.68/48 = 0.431$

$\Sigma Y = 636750 \quad \bar{Y} = 636750/48 = 13300$

$\Sigma x^2 = 8.967 \quad \Sigma x^2 - \Sigma x^2/N = 0.0563$

$\Sigma Y^2 = 8.537 \times 10^8 \quad \Sigma Y^2 - \Sigma Y^2/N = 0.899 \times 10^8$

$\Sigma XY = 0.276 \times 10^6 \quad \Sigma XY - \Sigma XY/N = 0.1847 \times 10^4$

$$b = \frac{\Sigma^1 XY}{\Sigma^1 X^2} = 32800 \tag{3}$$

$$a = \bar{Y} - b\bar{X} = -864 \tag{2}$$

$\hat{Y} = -864 + 32800X$

$$r = \frac{\Sigma^1 XY}{(\Sigma^1 X^2 \Sigma^1 y^2)} = 0.821 \qquad (4)$$

$$S^2(\hat{Y}) = \frac{(1 - r^2)\Sigma^1 Y^2}{N - 2} = 63.8 \times 10^4$$

$$S^2(b) = \frac{S^2(Y)}{\Sigma^1 X^2} = 1.13 \times 10^7$$

$$S(b) = 3370$$

$$S^2(\bar{Y}) = \frac{S^2(\hat{Y})}{N} = 1.33 \times 10^4 \qquad S(\bar{Y}) = 115$$

$t_{0.05,\ N-2} = 2.02$ (Table 6.1, (79))

95% confidence range of $\bar{Y} = 13300 \pm (2.02)(115) = 13070$ to 13530

95% confidence range of $b = 32800 \pm (2.02)(3370) = 26000$ to 39600

The r value of 0.821 for 48 − 2 = 46 degrees of freedom is larger than the 0.001 value of 0.465 on Table 81 in "Volk". Hence there is less than one chance in 1000 of being in error in concluding that there is a correlation between these variables.

C. Comparing Two Correlations

It is sometimes very difficult to determine whether two correlations are significantly different merely by visually comparing the correlation curves or the points of both sets of data. This is particularly true for data which have a great deal of scatter.

Stating that two correlations are statistically equivalent is tantamount to saying that both sets of data can be represented by one fit or correlation without any significant gain in variance. We proceed by making the null hypothesis that both sets of data can be represented by one overall fit. Now it is obvious that the two separate correlations will have less residual error than that of the single fit of the combined data; i.e., some of the residual error associated with the overall fit is removed by using two separate fits. If the error or variance removed from the overall fit by the two individual fits is significantly larger than the residual error remaining after the data have been regressed by these same two fits, then we must reject the hypothesis that both sets of data can be represented by one overall fit; i.e., the individual correlations are significantly different. In addition, one other necessary criteria for determining whether two sets of data can be represented by one correlation curve is that there must be a significant correlation for the overall fit. This can be determined by the correlation coefficient. As an example, consider the following problem. We wish to know whether there is any significant difference between the correlation of the modulus of rupture as a function of the oven-dry specific gravity for the case where no deflectometer was used (Figure 17), as compared to the case where the deflectometer was employed (Figure 20).

The data was combined and the least-squares line was found. The correlation coefficient of the combined fit was found to be 0.676 with 114 degrees of freedom. Thus this correlation is highly significant; i.e., there is less than one chance in 1000 of being wrong if one said a correlation existed (see Table 8.2 (79)).

Now the error in fit 1 (with deflectometer, Figure 20)

$= A = S(\hat{Y}_1)^2(N_1 - 2) = \Sigma(y_1 - \hat{y}_1)^2$ with $N_1 - 2$ degrees of freedom.

The error in fit 2 (without deflectometer, Figure 17)

$= B = S(\hat{Y}_2)^2 \times (N_2 - 2) = \Sigma(y_2 - \hat{y}_2)^2$ with $N_2 - 2$ degrees of freedom.

The total variance or residual error of the two separate fits

$= (A + B)/(N_1 + N_2 - 4)$

Similarly the error in the combined fit

$= C = S(Y_c)^2 \times (N_1 + N_2 - 2) = \Sigma(y_c - \hat{y}_c)^2$

Ho: error removed by using two fits rather than one equals the residual error in the two separate fits.

Error removed by two fits $= \left[C - (A+B)\right]$

with $N_1 + N_2 - 2 - (N_1 - 2 + N_2 - 2) = 2$ degrees of freedom

Error remaining in the two fits $= (A+B)$ with $N_1 + N_2 - 4$ degrees of freedom.

Therefore Ratio of Variances $= \dfrac{\left[C - (A+B)\right]/2}{(A+B)/N_1 + N_2 - 4}$

Now $C = 1.36\text{x}10^8$

$A = 0.294\text{x}10^8 \qquad N_1 = 48,\ N_2 = 68$

$B = 0.510\text{x}10^8$

Therefore Ratio $= \dfrac{1.36 - 0.804) \times 112}{0.804 \times 2} = 39.0$

$F(0.05), 2, 112 = 3.07$

Reject Ho.

Therefore, the two correlations are significantly different.

It is interesting to note that the variances for each correlation are not significantly different.

Ho: $S(\hat{Y}_1)^2 = S(\hat{Y}_2)^2$

$$\frac{S(\hat{Y}_2)^2}{S(\hat{Y}_1)^2} = \frac{77.4}{63.8} = 1.21$$

$F(0.05), 66, 46 = 1.60$

Accept Ho.

Thus whatever caused the difference in values between the two methods did not affect the precision of the measurements.

In a similar manner, the various correlations in this present work have been compared. They are presented in Table 37. If the ratio of variances is greater than the F value at the .05 level we say that the correlations are significantly different.

Throughout this thesis all statistical work has been based on the 95% confidence level. The exception is the analysis of the tensile data for the untreated wood. As noted in Table 37, the ratio of variances has a value of 4.46.

Now $F(0.05), 2, 40 = 3.23$ and $F(0.01), 2, 40 = 5.18$

Thus we can combine the two sets of data and fit the total to an overall fit based on the 0.01 probability level but not at the 0.05 level. That is, if we reject the hypothesis that the error removed by using the two separate fits rather than one overall fit is the same as the combined residual error in the two fits we have less than 5 but more than 1 percent

TABLE 37

ANALYSIS OF VARIANCE: COMPARISON OF TWO CORRELATIONS

Comparing	Reference	Overall Correlation Coefficient	Sum of Squares $\Sigma(yi - \hat{y})^2$	Sum of Squares for overall fit	N total	Ratio of Variances	F(0.05), 2, N-4
Modulus of Rupture; untreated wood; with deflectometer	Fig. 20	0.676	0.294x10^{8}	1.36x10^{8}	116	39.0	3.07
untreated wood without deflectometer	Fig. 17		0.510x10^{8}				
Modulus of Rupture untreated wood; without deflectometer	Fig. 17	0.750	0.510x10^{8}	.770x10^{8}	94	4.15	3.10
untreated wood irradiated with 3.5 Mr	Fig. 18		0.195x10^{8}				
Modulus of Rupture untreated wood; without deflectometer	Fig. 17	0.685	0.510x10^{8}	1.68x10^{8}	107	34.6	3.08
untreated wood; irradiated with 4.5 Mr	Fig. 19		0.620x10^{8}				

.... cont'd.

TABLE 37 (cont'd.)

Comparing	Reference	Overall Correlation Coefficient	Sum of Squares $\Sigma(yi - \hat{y})^2$	Sum of Squares for overall fit	N total	Ratio of Variances	F(0.05), 2, N-4
Tensile Strength untreated wood; humidified	Fig. 30	0.516	1.08×10^8	3.12×10^8	44	4.46	3.23*
untreated wood; oven-dried	Fig. 31		1.47×10^8				
Modulus of Rupture 54% and 65% styrene; humidified	Fig. 33	0.633	1.37×10^8	1.745×10^8	95	2.04	3.10
untreated wood; with deflectometer	Fig. 20		0.294×10^8				
Modulus of Rupture 54% and 65% styrene; humidified	Fig. 33	0.525	1.37×10^8	3.59×10^8	74	0.595	3.13
wood treated with 54% styrene solution; oven-dried	Fig. 35		2.16×10^8				

.... cont'd.

TABLE 37 (cont'd.)

Comparing	Reference	Overall Correlation Coefficient	Sum of Squares $\Sigma(yi - \hat{y})^2$	Sum of Squares for overall fit	N total	Ratio of Variance	F(0.05), 2, N-4
Modulus of Rupture 76% styrene; humidified	Fig. 34	0.692	1.07×10^8	1.635×10^8	107	1.80	3.08
untreated wood; without deflectometer	Fig. 17		0.510×10^8				
Stress at P.L.; 65% styrene, humidified	Fig. 37	0.386	1.065×10^8	2.55×10^8	96	40.9	3.10
untreated wood; humidified	Fig. 21		0.288×10^8				
Modulus of Elasticity 54% and 65% styrene; humidified	Fig. 39	0.556	3.19×10^6	9.05×10^6	95	28.4	3.10
untreated wood; humidified	Fig. 26		2.38×10^6				
Modulus of Elasticity 54% styrene; oven-dried	Fig. 40	0.475	$.755\times10^6$	3.61×10^6	58	24.8	3.17
untreated wood; humidified	Fig. 27		1.12×10^6				

.... cont'd.

TABLE 37 (cont'd.)

Comparing	Reference	Overall Correlation Coefficient	Sum of Squares $\Sigma(yi - \hat{y})^2$	Sum of Squares for overall fit	N total	Ratio of Variance	F0.05, 2, N-4
Maximum Crushing Strength 27% styrene; oven-dried	Fig. 42	0.751	$.466\text{x}10^8$	$.656\text{x}10^8$	75	3.78	3.13
unheated oven-dried wood	Fig. 29		$.127\text{x}10^8$				

* F0.01, 2, 40 = 5.18

chance of being in error. Hence since

(1) it seems unlikely that the tensile strength of the oven-dried samples is, in fact, lower than that of the humidified samples

(2) the tensile strength is known not to be a strong function of the moisture content and

(3) the combination of data is justified at the F(0.01) probability level,

the tensile strength data for both the oven-dried and humidified samples have been combined into one overall fit.

D. Work in Bending to Proportional Limit and to Maximum Load

The "work expressions" for the untreated wood were regressed with respect to the oven-dry specific gravity. The following correlation coefficients were obtained.

	Work to Proportional Limit			Work to Maximum Load		
	r	N	Average S.G.	r	N	Average S.G.
Humidified Wood	0.378	48	0.431	0.180	24	0.426
Oven-Dried Wood	0.706	35	0.426	0.515	35	0.426

Except for the work to maximum load for the humidified samples all correlations are significant at the 95% confidence level. However, the data was not represented in two-variable plots in the main body of the thesis because all treated samples yielded work values independent of "original" specific gravity; thus, average work values independent of specific gravity are compared. This is not a rigorous analysis of the data because the comparisons should be made on the basis of a common specific gravity. However, the trend of higher work to proportional limit and lower work to modulus of rupture values for the treated samples as compared to the untreated wood is evident.

E. Comparison of Average Values

To test whether the means of two different samples could have come from the same population or from populations with the same means is usually a simple matter. A "t" test is conventionally used with a pooled estimate of the standard deviation. A difficulty arises when the variances of the two sets of data cannot be assumed to be equal. In this work, the treated samples generally have significantly higher variances associated with their mean strength values than the untreated wood. When this is the case, a conventional "t" cannot be applied. An approximate solution (81) is to calculate the standard error from:

$$\text{S.E. } (\bar{x}_1 - \bar{x}_2) = \left(\frac{S_1^2}{N_1} + \frac{S_2^2}{N_2}\right)^{1/2}$$

where S_1^2 and S_2^2 are the variances of the two sets of data. The approximate confidence limits are

$$(\bar{x}_1 - \bar{x}_2) \pm t_a \left[\text{S.E. } (\bar{x}_1 - \bar{x}_2)\right]$$

where t_a is the student "t" value. This value is not calculated from the usual degrees of freedom but rather from

$$\frac{1}{\varphi} = \frac{1}{\varphi_1}\left(\frac{S_1^2/N_1}{S_1^2/N_1 + S_2^2/N_2}\right) + \frac{1}{\varphi_2}\left(\frac{S_2^2/N_2}{S_1^2/N_1 + S_2^2/N_2}\right)$$

where φ = degrees of freedom used to calculate t_a

φ_1 and φ_2 are the degrees of freedom for the two sets of data.

As an example, consider the comparison of the modulus of rupture for the samples treated with the 54% styrene solution (Figure 35) with that for oven-dried untreated wood (Figure 22). We wish to make the comparison at a specific gravity of 0.431. For the treated samples the strength at S.G. = 0.431 is

$$Y_1 = 51500\ (.431) - 8180$$

$$= 14020 \text{ psi}$$

The 95% confidence limits of this value are larger than those at the mean of the data; viz., $\bar{Y} = 15000$ and $\bar{X} = 0.451$. The variance estimate of the mean at S.G. = 0.431 can be calculated from

$$S^2(\hat{Y}_i)^2 = S^2(\hat{Y})^2\left[\frac{1}{N} + \frac{(\bar{x} - x_i)^2}{\Sigma^1 x^2}\right] \qquad \text{..... Page 237 (79)}$$

$$S_1^{\,2}(\hat{Y})^2 = 865 \text{ x } 10^4$$

$$N = 27$$

$$\bar{X} = 0.451$$

$$x_i = 0.431$$

$$\Sigma^1 x^2 = \Sigma x^2 - \frac{(\Sigma x)^2}{N} = 0.022$$

whence $S_1^{\,2}(\hat{Y}i = 0.431) = 47.6 \text{ x } 10^4$

Similarly for the untreated wood

$$Y_2 = 18400 \text{ at S.G.} = 0.431$$

and $S_2(\hat{Y}_i = 0.431) = 5.44 \text{ x } 10^4$

Now $\varphi_1 = 27 - 2 = 25$

and $\varphi_2 = 32 - 2 = 30$

Therefore $\frac{1}{\varphi} = \frac{1}{25} \quad \frac{47.6\text{x}10^4}{47.6\text{x}10^4 + 5.44\text{x}10^4} \quad + \frac{1}{30} \quad \frac{5.44\text{x}10^4}{47.6\text{x}10^4 + 5.44\text{x}10^4}$

whence $\varphi = 30.4$

from a "t" table at a .05 probability level with 30.4 degrees of freedom, $t = 2.04$

Also $\quad S.E. \ (\bar{x}_1 - \bar{x}_2) = (47.6\text{x}10^4 + 5.44\text{x}10^4)^{½}$

$$= 7.28\text{x}10^2 = 728$$

Thus the difference in strengths at S.G. = 0.431

$$= 18400 - 14020 = 4380 \pm 2.04 \text{ x } 728$$

$$= 4380 \pm 1490 \text{ psi}$$

Now we wish to express this difference as a percentage change based on the untreated oven-dried wood. For a "division" operation, $\frac{Y_1 \pm t\,S_1}{Y_2 \pm t\,S_2}$ the variance of the quotient can be obtained from (Page 143 (79))

$$s^2(\frac{Y_1}{Y_2}) = (\frac{Y_1}{Y_2})^2 \left[\frac{S_1^{\ 2}}{Y_1^{\ 2}} + \frac{S_2^{\ 2}}{Y_2^{\ 2}} \right]$$

Thus

$$s^2(\frac{Y_1}{Y_2}) = \left[\frac{4380}{18400}\right]^2 \cdot \left[\frac{53.0\text{x}10^4}{(4380)^2} + \frac{5.44\text{x}10^4}{(18400)^2} \right]$$

$$s^2(Y_1/Y_2) = .00157$$

whence $\quad s(Y_1/Y_2) = .0396$

the % decrease in strength is

$$\left[\frac{4380}{18400} \pm 2.04 \text{ x } .0396 \right] \text{ x } 100$$

$$= 23.8 \pm 8.1\%$$

E. Multiple Correlations

It was found that the maximum crushing strength and the maximum tensile strength for the samples treated with styrene alone could be correlated with respect to the "original" specific gravity and the F.P.S. The statistics for the multiple correlation are similar to those for simple correlations.

As an example consider the compression data. The correlation coefficient R was calculated by means of the formula given in Volk, Page 275.

$$R = \left(r_{yi} b_1 \left(\frac{\Sigma^2 x_1^{\;2}}{\Sigma^1 y^2}\right)^{1/2} + r_{y2} b_2 \left(\frac{\Sigma^1 x_2^{\;2}}{\Sigma^2 y^2}\right)^{1/2} \right)$$

where b_1 = the coefficient associated with the "original" specific gravity

b_2 = the coefficient associated with the F.P.S.

r_{y1} = the simple correlation coefficient between the crushing strength and the specific gravity

r_{y2} = the simple correlation coefficient between the crushing strength and F.P.S.

$$R = \left[0.383 \times 33700 \left(\frac{0.0365}{.43\times10^9}\right)^{1/2} + 0.672 \times 16800 \left(\frac{.610}{.43\times10^9}\right)^{1/2} \right]^{1/2}$$

$$R = 0.738$$

The "F" test for the multiple correlation is (79)

$$F = \frac{R^2(N - K - 1)}{(1 - R^2)K}$$

where K is the number of independent variables

$$F = \frac{0.545 \times 37}{.455 \times 2} = 22.2$$

$F(0.05), 2, 37 = 4.10$

Therefore this correlation is highly significant.

In addition it can be shown statistically that the multiple correlation is a better fit than any simple correlation.

The same analysis was carried out for the correlation with the maximum tensile strength and similar results were obtained.

The variance of an average estimated value for these multiple correlations is calculated from the formula (Page 278, (79))

$$S^2(\hat{Y}_i) = S^2(\hat{Y}) \left[\frac{1}{N} + C_{11}(x_1 - \bar{x})^2 + C_{22}(x_2 - \bar{x}_2)^2 + 2C_{12}(x_1 - \bar{x}_1)\ (x_2 - \bar{x}_2)\right]$$

where C_{11}, C_{22} and C_{12} are the Gaussian multipliers

For an "original" specific gravity of .449 and an F.P.S. value of .374 we get

$$S^2(\hat{Y}_i) = 5.33\text{x}10^6 \left[\frac{1}{40} + 26.9 \times (.449-.407)^2 + 1.61\ (.374-.468)^2 + 2\text{x}.88\ (.449 - .407)\ (.374 - ,468)\right]$$

$$= 42.1 \times 10^4$$

Therefore $S(\hat{Y}_i) = 649$ $t = 2.02$

$\pm\ ts(Y_i) = \pm\ 1310$ psi

```
 APPENDIX  VII   STRENGTH PROPERTY DATA

 O.D. S.G.=OVEN-DRY SPECIFIC GRAVITY
 F.P.S.=FRACTION POLYSTYRENE IN TREATED SAMPLE
 UNITS ARE SAME AS THOSE ON GRAPHS

MODULUS OF RUPTURE
 UNTREATED ,UNIRRADIATED,HARD MAPLE WOOD

O.D. S.G.     STRENGTH

.410          12450.0
.432          13300.0
.427          12950.0
.434          12850.0
.394          11400.
.422          11450.
.426          12650.
.420          12600.0
.415          12050.
.386          11075.0
.428          12300.
.439          12300.
.444          14150.
.436          14600.
.438          13650.
.340          9675.0
.388          11425.0
.430          13000.0
.428          13350.
.408          12900.
.438          13350.
.442          12375.
.437          13050.
.462          14500.
.421          13275.
.430          13900.
.427          13100.
.438          13500.
.416          12605.
.392          11400.
.430          11700.
.453          14950.
.453          14950.
.459          15150.
.470          13450.
.497          15350.
.480          15650.
.477          15450.
.474          14900.
.465          15600.
.475          14800.
.476          14800.
.390          13450.
.378          12900.
.368          12000.
.376          11500.
.389          12875.
.415          12700.
```

```
         MODULUS OF RUPTURE
UNTREATED WOOD. NO DEFLECTOMETER

         O.D. S.G.     STRENGTH

         0.370         12200.
         0.407         14200.
         0.344         11300.
         0.354         12500.
         0.348         11000.
         0.352         12000.
         0.471         15500.
         0.461         14900.
         0.469         16000.
         0.440         14100.
         0.462         16100.
         0.488         14900.
         0.489         15700.
         0.456         17100.
         0.457         16000.
         0.433         15700.
         0.404         13200.
         0.395         13200.
         0.421         14200.
         0.434         14600.
         0.434         15800.
         0.445         16600.
         0.428         14800.
         0.395         12900.
         0.394         12300.
         0.393         14000.
         0.409         12950.
         0.419         13950.
         0.405         13000.
         0.412         13900.
         0.407         16150.
         0.401         14100.
         0.407         13950.
         0.398         13300.
         0.419         15000.
         0.389         15500.
         0.415         14950.
         0.400         15850.
         0.399         14200.
         0.374         12850.
         0.400         13000.
         0.440         15000.
         0.425         14200.
         0.408         13250.
         0.419         14500.
         0.429         14300.
         0.424         13300.
         0.384         15700.
         0.394         15050.
         0.382         15700.
         0.389         15350.
         0.398         14400.
         0.406         14100.
         0.460         16500.
```

```
        MODULUS OF RUPTURE(CONT.)
UNTREATED WOOD, NO DEFLECTOMETER

        O.D. S.G.     STRENGTH

        0.459         16900.
        0.450         14100.
        0.463         15450.
        0.441         14600.
        0.385         12550.
        0.406         11500.
        0.370         12300.
        0.365         11300.
        0.431         15600.
        0.415         13700.
        0.441         17000.
        0.441         14200.
        0.450         15700.
        0.455         16250.

MODULUS OF RUPTURE
 UNTREATED ,UNIRRADIATED,OVEN-DRIED WOOD

O.D. S.G.    STRENGTH

.421          17750.
.407          16000.
.430          13050.
.455          17800.
.356          12900.
.480          24100.
.480          25900.
.475          21200.
.452          18400.
.449          18100.
.384          17500.
.451          19700.
.345          15070.
.400          17500.
.395          18200.
.450          18850.
.353          14000.
.461          19800.
.470          20150.
.421          17900.
.399          18550.
.477          21800.
.490          24000.
.447          17700.
.375          14100.
.412          16200.
.392          14700.
.355          15300.
.365          15100.
.469          19750.
.503          21800.
.455          19400.
```

MODULUS OF RUPTURE
WOOD IRR. WITH 5.5 MRAD

O.D. S.G.	STRENGTH
0.434	12900.
0.448	14200.
0.490	15800.
0.490	15600.
0.438	16500.
0.418	15700.
0.427	14500.
0.396	15050.
0.437	13900.
0.410	13500.
0.421	14000.
0.424	14450.
0.426	13150.
0.411	13000.
0.392	11750.
0.406	13600.
0.418	14400.
0.417	13200.
0.415	14300.
0.429	14500.
0.407	12300.
0.404	12100.
0.394	12050.
0.391	15700.
0.377	12900.
0.400	15100.

MODULUS OF RUPTURE
WOOD IRR. WITH 4.5 MRAD

O.D. S.G.	STRENGTH
0.396	12400.
0.423	13350.
0.344	8160.
0.328	8250.
0.440	12150.
0.458	14300.
0.428	15900.
0.442	14500.
0.451	11800.
0.397	11600.
0.400	10200.
0.386	11000.
0.378	10300.
0.366	11500.
0.389	11750.
0.391	12450.
0.391	13450.
0.375	10400.
0.365	9150.
0.423	11100.

```
          MODULUS OF RUPTURE(CONT.)
    WOOD TRT. WITH 4.5 MRAD

              O.D. S.G.    STRENGTH

              0.421          11500.
              0.409          13000.
              0.412          12550.
              0.432          12950.
              0.434          12900.
              0.486          14550.
              0.489          12450.
              0.444          14800.
              0.455          11100.
              0.412          15800.
              0.418          13550.
              0.410          12700.
              0.425          14600.
              0.398          13700.
              0.405          13100.
              0.391          13500.
              0.400          13200.
              0.404          13300.
              0.398          14100.


          MODULUS OF RUPTURE
     WOOD TREATED WITH PURE STYRENE

              O.D. S.G        F.P.G.        STRENGTH

              0.399          0.465          17050.
              0.392          0.479          18100.
              0.366          0.198          16300.
              0.400          0.593          17300.
              0.381          0.561          19500.
              0.405          0.504          18500.
              0.395          0.542          16400.
              0.485          0.526          15600.
              0.388          0.375          16800.
              0.442          0.320          13800.
              0.447          0.359          13900.
              0.476          0.453          15700.


    STRESS AT PROPORTIONAL LIMIT AND MODULUS OF RUPTURE
     WOOD TREATED WITH 27 PERCENT STYRENE SOLUTION

              O.D. S.G.       F.P.G.        STRENGTH

              0.506          0.067          15000.
              0.331          0.151          15200.
              0.467          0.081          15900.
              0.480          0.198          11800.
              0.592          0.112          16000.
              0.460          0.257          15400.
              0.483          0.200          17600.
              0.402          0.272          11000.
              0.432          0.091          16200.
```

MODULUS OF RUPTURE
WOOD TREATED WITH 54 + 65 STYRENE SOLUTION,HUMIDIFIED

O.D. S.G	F.P.S.	STRENGTH
0.400	0.583	16200.
0.430	0.505	15800.
0.415	0.555	16350.
0.430	0.540	14600.
0.429	0.536	16450.
0.434	0.544	17450.
0.376	0.500	12000.
0.428	0.504	12500.
0.430	0.403	15800.
0.439	0.392	15300.
0.432	0.522	15500.
0.437	0.590	15300.
0.411	0.463	15550.
0.411	0.466	11000.
0.405	0.476	9680.
0.399	0.449	14050.
0.410	0.426	12550.
0.339	0.560	10650.
0.448	0.505	12400.
0.455	0.523	13000.
0.448	0.496	13200.
0.448	0.463	13400.
0.445	0.486	13450.
0.416	0.517	13200.
0.435	0.398	12650.
0.415	0.422	14900.
0.436	0.370	12500.
0.439	0.358	14600.
0.420	0.322	13050.
0.363	0.486	11100.
0.469	0.467	12400.
0.465	0.500	12450.
0.454	0.456	13500.
0.471	0.483	16150.
0.468	0.464	15500.
0.460	0.442	16000.
0.476	0.420	17700.
0.475	0.424	16700.
0.474	0.455	16700.
0.479	0.458	15600.
0.434	0.443	15150.
0.376	0.466	12900.
0.358	0.476	11900.
0.372	0.472	15400.
0.376	0.454	12300.
0.396	0.455	11000.
0.414	0.450	15500.

```
      MODULUS OF RUPTURE
WOOD TREATED WITH 54 PERCENT STYRENE SOLUTION,OVEN-DRIED

      O.D. S.G        F.P.S.       STRENGTH

      0.490          0.366        16800.
      0.425          0.439        17100.
      0.452          0.492        15300.
      0.486          0.465        22000.
      0.457          0.446        15800.
      0.454          0.390        15900.
      0.472          0.345        15600.
      0.464          0.425        12500.
      0.463          0.205        11500.
      0.461          0.440        13800.
      0.460          0.430        12800.
      0.464          0.364        12500.
      0.431          0.164        14300.
      0.467          0.240        13100.
      0.456          0.327        12600.
      0.335          0.407        13500.
      0.398          0.481        11250.
      0.462          0.248        12650.
      0.406          0.439        14300.
      0.495          0.425        19000.
      0.475          0.447        18800.
      0.437          0.270        12100.
      0.399          0.475        11000.
      0.441          0.400        17000.
      0.441          0.377        15800.
      0.461          0.343        22400.
      0.467          0.421        20700.


      MODULUS OF RUPTURE
WOOD TREATED WITH 76 PERCENT STYRENE SOLUTION

      O.D. S.G.    STRENGTH

      0.369        13500.
      0.438        15750.
      0.419        16000.
      0.433        12350.
      0.439        14900.
      0.455        17000.
      0.444        14000.
      0.388        14050.
      0.400        14500.
      0.356        12500.
      0.358        13600.
      0.370        12700.
      0.360        12350.
      0.541        19650.
      0.560        19100.
      0.408        16100.
      0.508        16300.
      0.469        11700.
      0.408        15600.
      0.463        15700.
```

MODULUS OF RUPTURE(CONT.)
WOOD TREATED WITH 76 PERCENT STYRENE SOLUTION

O.D. S.G.	STRENGTH
0.446	16700.
0.469	16350.
0.529	15800.
0.535	15200.
0.477	15400.
0.429	16350.
0.419	17500.
0.436	14550.
0.428	17100.
0.432	15750.
0.440	15750.
0.465	17000.
0.417	15500.
0.414	13100.
0.434	14500.
0.431	15100.
0.404	13500.
0.420	14450.
0.404	15150.

STRESS AT PROPORTIONAL LIMIT
WOOD TREATED WITH 54 PERCENT STYRENE SOLUTION,OVEN-DRIED

O.D. S.G.	STRENGTH
0.406	14500.
0.495	18000.
0.475	17500.
0.457	12100.
0.399	11000.
0.441	15800.
0.441	15800.
0.481	21400.
0.467	19300.
0.490	12200.
0.423	17100.
0.432	15300.
0.486	17700.
0.457	13100.
0.454	15900.
0.472	13200.
0.464	10400.
0.465	11500.
0.461	15500.
0.468	11600.
0.464	12500.
0.431	14300.
0.467	11500.
0.456	12600.
0.385	13000.
0.398	9910.
0.462	12610.

STRESS AT PROPORTIONAL LIMIT
UNTREATED ,UNIRRADIATED,[illegible] WOOD

O.D. S.G.	STRENGTH
.410	8640.
.432	9340.
.427	9520.
.434	9840.
.420	9200.
.415	9100.
.366	6650.
.428	8360.
.439	8960.
.444	10100.
.438	10800.
.438	9560.
.340	6160.
.388	8120.
.430	8960.
.428	8960.
.408	8780.
.394	8195.
.422	8025.
.426	7450.
.458	9120.
.442	8400.
.437	7550.
.462	8950.
.421	7920.
.430	8500.
.427	8290.
.438	8025.
.416	8025.
.392	7380.
.450	9560.
.453	10600.
.453	10700.
.459	9580.
.470	8000.
.497	8900.
.486	10750.
.497	11000.
.474	10700.
.465	9710.
.475	10150.
.476	9830.
.390	6670.
.378	8150.
.368	7880.
.376	8040.
.369	8040.
.415	10180.

STRESS AT PROPORTIONAL LIMIT
 UNTREATED ,UNIRRADIATED,OVEN-DRIED WOOD

O.D. S.G.	STRENGTH
.421	13300.
.399	15400.
.477	15000.
.490	15500.
.447	14150.
.375	8900.
.412	8700.
.392	8160.
.355	6480.
.365	9980.
.469	11600.
.503	15400.
.435	12850.
.384	11700.
.451	12800.
.345	8650.
.456	13200.
.400	13250.
.395	13200.
.450	15580.
.355	9110.
.461	12700.
.470	11650.
.421	9580.
.407	10950.
.449	12900.
.450	10650.
.455	10700.
.358	8650.
.460	14650.
.480	13080.
.362	7825.
.475	15400.
.432	13350.
.449	13500.

STRESS AT PROPORTIONAL LIMIT
 WOOD TREATED WITH PURE STYRENE

O.D. S.G	F.P.S.	STRENGTH
0.399	0.465	17100.
0.392	0.479	16100.
0.366	0.198	10500.
0.400	0.595	10900.
0.381	0.561	13500.
0.405	0.584	10500.
0.395	0.542	10400.
0.485	0.526	15600.
0.500	0.570	15800.
0.442	0.520	15800.
0.447	0.559	15900.
0.470	0.455	15700.

STRESS AT PROPORTIONAL LIMIT
WOOD TREATED WITH 54 % CC STYRENE SOLUTION,[illegible]

O.D. S.G.	F.M.C.	STRENGTH
0.414	0.430	11100.
0.396	0.435	11300.
0.376	0.454	11200.
0.372	0.472	10350.
0.358	0.476	11900.
0.376	0.466	12050.
0.464	0.445	12100.
0.479	0.458	12300.
0.474	0.455	11300.
0.475	0.424	14400.
0.470	0.420	13950.
0.469	0.421	13000.
0.460	0.441	11500.
0.466	0.464	11300.
0.471	0.465	11250.
0.454	0.456	13500.
0.465	0.500	10300.
0.469	0.467	12400.
0.363	0.436	7860.
0.420	0.322	10700.
0.459	0.356	11900.
0.436	0.370	9830.
0.415	0.422	10900.
0.435	0.390	11100.
0.416	0.517	10300.
0.445	0.456	9040.
0.448	0.455	9210.
0.448	0.496	8390.
0.453	0.325	6840.
0.448	0.505	10230.
0.359	0.560	8640.
0.410	0.420	10600.
0.399	0.440	8420.
0.405	0.478	7680.
0.411	0.466	5970.
0.411	0.466	7150.
0.437	0.350	8620.
0.452	0.322	9830.
0.439	0.392	11900.
0.430	0.400	10500.
0.428	0.504	11750.
0.376	0.598	10200.
0.454	0.544	13050.
0.429	0.558	10150.
0.430	0.540	12200.
0.415	0.515	12300.
0.430	0.505	12300.
0.400	0.555	10800.

```
MODULUS OF ELASTICITY
UNTREATED ,UNIRRADIATED,HUMIDIFIED WOOD

        O.D. S.G.    STRENGTH X1000

        0.410           2320.
        0.432           2380.
        0.427           2450.
        0.434           2500.
        0.420           2500.
        0.415           2500.
        0.386           2240.
        0.428           2040.
        0.439           2320.
        0.444           2460.
        0.458           2500.
        0.458           2240.
        0.340           1620.
        0.388           2230.
        0.430           2320.
        0.428           2320.
        0.408           2240.
        0.394           2010.
        0.422           1870.
        0.426           1960.
        0.458           2080.
        0.442           1990.
        0.437           1960.
        0.462           2030.
        0.421           2240.
        0.436           2380.
        0.427           2280.
        0.438           2290.
        0.416           2200.
        0.392           1860.
        0.450           2380.
        0.453           2380.
        0.453           2670.
        0.459           2160.
        0.470           2240.
        0.486           2980.
        0.497           3030.
        0.474           2790.
        0.465           2900.
        0.475           2800.
        0.470           2790.
        0.390           2030.
        0.378           2020.
        0.368           1775.
        0.376           1750.
        0.389           1800.
        0.415           1780.
```

```
MODULUS OF ELASTICITY
UNTREATED ,UNIMPREGNATED,OVEN-DRIED WOOD

        O.D. S.G.    STRENGTH X1000

        0.421          2360.
        0.407          1950.
        0.449          2650.
        0.450          2240.
        0.455          2240.
        0.358          1770.
        0.480          2800.
        0.480          2400.
        0.475          2560.
        0.432          2510.
        0.449          2170.
        0.421          2440.
        0.399          2480.
        0.477          2750.
        0.490          2780.
        0.447          2460.
        0.375          1850.
        0.412          2040.
        0.392          2190.
        0.355          1750.
        0.365          2050.
        0.409          2940.
        0.435          2340.
        0.364          2530.
        0.451          2160.
        0.345          1755.
        0.456          2340.
        0.395          2520.
        0.450          2270.
        0.355          1710.
        0.401          2580.
        0.470          2280.


MODULUS OF ELASTICITY
WOOD TREATED WITH 27 PERCENT STYRENE SOLUTION

        O.D. S.G.    STRENGTH X1000

        0.508          1800.
        0.351          1260.
        0.487          2040.
        0.400          2030.
        0.392          2020.
        0.480          1950.
        0.485          2040.
        0.402          1840.
        0.452          1700.
```

```
MODULUS OF ELASTICITY
WOOD TREATED WITH 34 + 65 STYRENE SOLUTION,[illegible]

         O.D. S.G         [illegible]        STRENGTHX1000

         0.414            0.400              1700.
         0.396            0.435              1830.
         0.376            0.454              1780.
         0.372            0.472              1690.
         0.300            0.476              1910.
         0.376            0.403              1810.
         0.484            0.443              1510.
         0.479            0.458              1710.
         0.474            0.455              2350.
         0.475            0.424              2620.
         0.476            0.420              2820.
         0.469            0.421              2640.
         0.460            0.442              2170.
         0.466            0.404              2040.
         0.471            0.463              2370.
         0.454            0.456              2240.
         0.465            0.500              1740.
         0.469            0.467              1660.
         0.503            0.466              1210.
         0.420            0.322              1740.
         0.439            0.316              2040.
         0.436            0.370              1840.
         0.415            0.422              2020.
         0.435            0.356              1970.
         0.416            0.317              1660.
         0.445            0.486              1680.
         0.448            0.433              1730.
         0.446            0.455              1590.
         0.453            0.525              1550.
         0.448            0.505              1520.
         0.359            0.560              1410.
         0.410            0.426              1700.
         0.399            0.449              1750.
         0.405            0.476              1550.
         0.411            0.466              1390.
         0.411            0.466              1780.
         0.437            0.398              1910.
         0.452            0.322              1930.
         0.459            0.392              2000.
         0.450            0.400              1800.
         0.428            0.504              1520.
         0.376            0.398              1730.
         0.434            0.344              1940.
         0.429            0.338              2190.
         0.430            0.540              1750.
         0.415            0.555              2070.
         0.450            0.545              2150.
         0.400            0.595              1940.
```

MODULUS OF ELASTICITY
WOOD TREATED WITH 54 PERCENT STYRENE SOLUTION.OVEN-DRIED

O.D. S.G.	STRENGTH X1000
0.490	2140.
0.467	2180.
0.423	1950.
0.432	2180.
0.486	1940.
0.454	2040.
0.472	1880.
0.464	1940.
0.463	2040.
0.461	1860.
0.468	1920.
0.431	2110.
0.467	2220.
0.456	1980.
0.385	1820.
0.398	1820.
0.462	2340.
0.472	1840.
0.406	1910.
0.495	2490.
0.475	1910.
0.437	1940.
0.399	1850.
0.441	2020.
0.441	2140.
0.481	2340.

MODULUS OF ELASTICITY
WOOD TREATED WITH PURE STYRENE

O.D. S.G	F.P.S.	STRENGTHX1000
0.399	0.463	2830.
0.392	0.479	2700.
0.366	0.193	1710.
0.400	0.593	2660.
0.381	0.561	2640.
0.405	0.584	2790.
0.399	0.542	266 .
0.433	0.526	2520.
0.386	0.573	2660.
0.442	0.520	2680.
0.447	0.359	2390.
0.476	0.453	1630.

```
WORK TO PROPORTIONAL LIMIT
UNTREATED ,UNIRRADIATED,HUMIDIFIED 100%

    O.D. S.G.    STRENGTH

    0.415         3.090
    0.309         2.050
    0.376         2.140
    0.366         2.020
    0.378          1.92
    0.350         1.970
    0.476         1.940
    0.475         2.090
    0.465         1.880
    0.474         2.210
    0.497         2.130
    0.466         2.250
    0.497         2.000
    0.470         1.580
    0.459         2.380
    0.433         2.390
    0.455         2.590
    0.450         2.090
    0.392         1.330
    0.416         1.600
    0.438         1.730
    0.427         1.680
    0.430         1.720
    0.421         1.600
    0.462         2.120
    0.437         1.610
    0.442         1.960
    0.458         2.290
    0.426         1.750
    0.422         1.920
    0.394         1.950
    0.408         2.010
    0.428         1.880
    0.430         1.910
    0.386         1.770
    0.340         1.330
    0.438         2.130
    0.438         2.330
    0.444         2.250
    0.439         1.900
    0.428         1.940
    0.386         1.250
    0.415         1.770
    0.420         1.920
    0.434         2.060
    0.427         1.690
    0.432         2.160
    0.416         1.000
```

```
WORK TO PROPORTIONAL LIMIT
UNTREATED ,UNIRRADIATED,OVEN-DRIED WOOD

          O.D. S.G.     STRENGTH

          0.470           3.460
          0.481           3.870
          0.533           2.720
          0.450           5.610
          0.375           3.990
          0.400           3.500
          0.456           4.250
          0.345           2.460
          0.451           4.200
          0.384           3.500
          0.435           3.770
          0.503           4.010
          0.469           3.480
          0.365           2.680
          0.355           2.280
          0.392           1.790
          0.412           2.100
          0.375           2.330
          0.447           4.410
          0.490           4.720
          0.477           4.500
          0.399           4.000
          0.421           3.250
          0.449           4.250
          0.432           4.240
          0.475           3.810
          0.362           1.550
          0.480            3.530
           .480           4.600
           .353           1.330
          0.455           3.000
          0.430           2.900
          0.449           3.640
          0.407           3.400
          0.421           2.120
```

WORK TO PROPORTIONAL LIMIT
WOOD TREATED WITH 54 % [illegible]

O.D. S.G.	STRAIN
0.414	4.000
0.378	3.020
0.370	3.900
0.372	3.700
0.398	3.440
0.376	4.300
0.484	2.570
0.479	3.640
0.474	3.160
0.475	4.500
0.470	4.110
0.469	4.740
0.460	3.700
0.466	4.800
0.471	2.920
0.454	4.390
0.465	3.420
0.469	4.950
0.363	2.440
0.420	3.260
0.439	3.940
0.436	3.000
0.415	3.200
0.435	3.250
0.445	2.760
0.448	2.670
0.448	3.270
0.455	2.940
0.448	3.840
0.416	3.740
0.359	0.000
0.410	3.440
0.397	2.540
0.411	2.730
0.411	2.730
0.437	2.120
0.452	2.800
0.439	3.750
0.430	3.380
0.428	2.600
0.376	2.000
0.434	4.700
0.429	4.360
0.430	4.270
0.415	4.070
0.430	3.940
0.400	3.240

WORK TO PROPORTIONAL LIMIT
WOOD TREATED WITH 54 PERCENT STYRENE SOLUTION,OVEN-DRIED

O.D. S.G.	STRENGTH
0.481	9.720
0.441	6.140
0.441	6.200
0.462	3.830
0.398	2.990
0.385	5.050
0.456	4.460
0.467	3.460
0.431	5.220
0.464	11.57
.468	3.93
.461	4.65
.463	3.890
.464	2.95
0.472	5.02
0.454	6.81
0.457	6.26
0.486	8.55
0.432	7.02
0.423	7.96
0.490	3.88
0.467	9.63

WORK TO PROPORTIONAL LIMIT
WOOD TREATED WITH PURE STYRENE

O.D. S.G.	STRENGTH
1.05	5.26
.876	7.940
.719	4.370
.920	5.670
0.860	4.110
0.922	5.770
0.870	5.480
0.972	7.020
0.858	5.750
0.987	6.540
0.454	3.500
0.606	6.280
0.764	5.470
0.726	7.350

```
WORK TO MAXIMUM LOAD
UNTREATED ,UNIRRADIATED,HUMIDIFIED WOOD

        O.D. S.G.    STRENGTH

        0.388          7.040
        0.378          9.320
        0.390          9.180
        0.474          10.99
        0.497          6.920
        0.486          8.100
        0.453          8.900
        0.453          6.460
        0.450          3.370
        0.427          8.040
        0.430          7.070
        0.421          7.320
        0.458          9.730
        0.426          7.450
        0.422          5.100
        0.430          5.830
        0.388          4.080
        0.340          4.770
        0.439          10.00
        0.428          10.20
        0.386          6.400
        0.427          7.260
        0.432          9.180
        0.410          9.340


WORK TO MAXIMUM LOAD
WOOD TREATED WITH 54 PERCENT STYRENE SOLUTION,OVEN-DRIED

        O.D. S.G.    STRENGTH

        0.461          10.70
        0.441          5.140
        0.441          7.700
        0.462          3.850
        0.398          4.510
        0.385          7.950
        0.456          4.450
        0.467          4.610
        0.451          5.220
        0.484          11.57
         .466          5.530
         .461          5.100
         .465          5.890
         .464          4.77
         .472          5.711
         .454            6.6
         .457           7.20
        0.486          13.00
        0.432           7.02
        0.423           7.96
        0.450           6.42
        0.467          11.10
```

```
WORK TO MAXIMUM LOAD
UNTREATED ,UNIMPREGNATED,CON[illegible]

        O.D. S.G.    STRENGTH

        0.470         15.40
        0.461         12.00
        0.355         5.800
        0.450         8.500
        0.355         11.01
        0.400         11.60
        0.456         5.670
        0.545         6.910
        0.451         13.00
        0.384         12.32
        0.405         11.70
        0.503         14.50
        0.465         10.10
        0.365         11.10
        0.355         7.390
        0.372         7.750
        0.412         14.00
        0.375         8.110
        0.447         7.250
        0.490         14.30
        0.477         11.00
        0.359         11.80
        0.421         7.430
        0.449         8.100
        0.452         11.70
        0.475         13.81
        0.382         8.040
        0.460         15.70
         .460         18.60
         .556         5.950
         .455         11.30
        0.450         7.190
        0.445         5.500
        0.407         8.500
        0.421          5.35

WORK TO MAXIMUM LOAD AND TO PROPORTIONAL LIMIT
WOOD TREATED WITH 27 PERCENT STYRENE SOLUTION

        O.D. S.G.    STRENGTH

        0.506          8.50
        0.331         4.550
        0.487         5.550
        0.480         5.450
        0.392         8.050
        0.460         4.550
        0.483         8.010
        0.402         4.450
        0.452         5.600
```

```
WORK TO MAXIMUM LOAD
WOOD TREATED WITH 54 + 05 STYRENE SOLUTION,UNMODIFIED

          O.D. S.G.    STRENGTH

          0.372         5.700
          0.350         5.440
          0.376         5.450
          0.475         6.700
          0.476         7.630
          0.469         9.580
          0.454         4.350
          0.465         5.220
          0.469         4.930
          0.436         5.240
          0.415         7.520
          0.435         5.230
          0.455         8.210
          0.448         6.450
          0.416         7.120
          0.410         5.900
          0.411         4.740
          0.411         7.940
          0.456         7.140
          0.428         3.470
          0.376         2.560
          0.415         8.300
          0.436         7.590
          0.400         9.540


WORK TO MAXIMUM LOAD
WOOD TREATED WITH PURE STYRENE

          O.D. S.G.    STRENGTH

         1.03         5.20
            .676        7.940
            .719        4.370
            .920        5.670
            .660        4.110
          0.922         5.770
          0.676         5.460
          0.972         7.020
          0.858         8.840
          0.567         6.540
          0.454         2.500
          0.606         7.920
          0.764         2.470
          0.726         7.550
```

MAXIMUM CRUSHING STRENGTH
UNTREATED ,UNIRRADIATED, [illegible]

O.D. S.G.	STRENGTH
0.436	[illegible]
0.436	6360.
0.415	5450.
0.415	5810.
0.438	[illegible]
0.438	[illegible]
0.486	6410.
0.486	6610.
0.427	5540.
0.427	6620.
0.432	5610.
0.432	5970.
0.420	6830.
0.420	6840.
0.480	6950.
0.480	6910.
0.476	6425.
0.476	6550.
0.410	5510.
0.410	5100.
0.444	6275.
0.444	6350.
0.497	6450.
0.497	6650.
0.459	6550.
0.459	6420.
0.386	4660.
0.386	4640.
0.474	7410.
0.474	7620.
0.475	6770.
0.475	6400.
0.465	6450.
0.426	5700.

MAXIMUM CRUSHING STRENGTH
UNTREATED (UNIRRADIATED) [illegible]

O.D. S.G.	STRENGTH
0.490	11350.
0.490	11950.
0.505	11750.
0.505	11150.
0.451	8520.
0.451	8550.
0.358	6454.
0.358	7060.
0.469	10100.
0.469	9530.
0.480	10050.
0.480	10050.
0.353	7850.
0.353	8300.
0.480	10800.
0.480	9930.
0.345	8740.
0.345	8000.
0.365	7330.
0.365	8300.
0.452	10000.
0.452	9300.
0.384	8580.
0.384	8550.
0.461	10200.
0.461	11100.
0.477	10450.
0.477	10700.
0.475	9750.
0.475	9400.
0.412	7530.
0.412	7370.
0.456	12000.
0.456	11900.
0.449	9720.
0.449	9740.
0.399	10400.
0.399	9860.
0.355	7340.
0.355	7220.
0.435	10800.
0.435	9400.
0.470	9050.
0.350	8780.
0.350	8610.
0.366	8625.
0.366	9030.
0.366	9970.
0.400	9250.
0.400	7740.
0.400	7000.
0.500	10550.

MAXIMUM CRUSHING STRENGTH(CONT.)
UNTREATED ,UNIRRADIATED,OVEN-DRIED WOOD

O.D. S.G.	STRENGTH
0.500	9870.
0.500	10950.
0.481	9750.
0.481	8750.
0.392	7950.

MAXIMUM CRUSHING STRENGTH
WOOD TREATED WITH PURE STYRENE

O.D. S.G	F.P.S.	STRENG ..
0.399	0.463	11700.
0.399	0.463	15900.
0.399	0.463	13200.
0.392	0.479	10600.
0.392	0.479	10100.
0.416	0.322	10350.
0.416	0.322	10000.
0.416	0.322	13100.
0.416	0.322	12500.
0.366	0.198	6720.
0.366	0.198	7300.
0.366	0.198	7000.
0.366	0.198	6680.
0.400	0.593	19500.
0.400	0.593	16700.
0.381	0.561	11350.
0.381	0.561	10300.
0.381	0.561	10250.
0.405	0.584	14600.
0.405	0.584	16800.
0.405	0.584	18500.
0.399	0.542	12400.
0.399	0.542	13900.
0.399	0.542	12500.
0.485	0.526	14900.
0.485	0.526	12300.
0.386	0.573	16000.
0.386	0.573	17400.
0.362	0.550	10000.
0.362	0.550	11000.
0.442	0.520	13200.
0.442	0.520	17250.
0.442	0.520	18250.
0.406	0.545	12150.
0.406	0.545	13150.
0.447	0.339	12150.
0.447	0.339	13250.
0.476	0.450	13850.
.416	.522	12000.
.366	.573	10000.

MAXIMUM CRUSHING STRENGTH
WOOD TREATED WITH 30 PERCENT STYRENE [illegible]

[illegible]	[illegible]	STRENGTH
0.420	0.566	[illegible]
0.420	0.530	[illegible]
0.423	0.451	11530.
0.423	[illegible]	[illegible]
0.432	0.452	[illegible]
0.432	0.452	[illegible]
0.437	0.470	9740.
0.437	0.448	[illegible]
0.454	0.550	14500.
0.454	0.570	[illegible]
0.454	0.550	[illegible]
0.454	0.590	[illegible]
0.472	0.542	[illegible]
0.472	0.543	10300.
0.461	0.423	[illegible]
0.464	0.423	9800.
0.463	0.233	7420.
0.465	0.285	8450.
0.465	0.285	8170.
0.463	[illegible]	[illegible]
0.461	[illegible]	[illegible]
0.460	0.430	[illegible]
0.460	0.430	[illegible]
0.472	[illegible]	[illegible]
0.434	0.304	11700.
0.421	0.164	9490.
0.421	0.154	7550.
0.467	0.246	12500.
0.467	[illegible]	[illegible]
0.450	0.327	[illegible]
0.585	[illegible]	[illegible]
0.505	0.407	[illegible]
0.585	0.407	[illegible]
0.590	0.401	[illegible]
0.598	0.481	14350.
0.457	0.270	10500.
0.457	0.270	[illegible]
0.472	[illegible]	[illegible]
0.472	0.230	[illegible]
0.472	0.361	[illegible]
0.472	0.168	12000.
0.461	0.342	[illegible]
0.461	0.345	[illegible]
0.461	0.345	[illegible]
0.555	[illegible]	[illegible]
0.555	[illegible]	[illegible]
0.500	0.345	[illegible]
0.457	0.446	10000.
0.457	0.446	[illegible]

MAXIMUM CRUSHING STRENGTH
WOOD TREATED WITH 27 PERCENT STYRENE SOLUTION

O.D. S.G.	P.V.C.	STRENGTH
0.506	0.087	9170.
0.506	0.087	9150.
0.531	0.131	10800.
0.504	0.061	12100.
0.504	0.061	11400.
0.504	0.061	9600.
0.480	0.198	10300.
0.480	0.198	10100.
0.392	0.112	[illegible]
0.392	0.112	[illegible]
0.483	0.200	9890.
0.483	0.200	7650.
0.483	0.200	7780.
0.402	0.272	9500.
0.402	0.272	[illegible]
0.402	0.272	9300.
0.425	0.091	9710.
0.425	0.091	8200.

MAXIMUM TENSILE STENGTH
UNTREATED ,UNIRRADIATED,NONMODIFIED WOOD

O.D. S.G.	STRENGTH
0.465	21000.
0.439	15700.
0.444	18300.
0.506	10700.
0.476	16500.
0.456	17250.
0.420	15900.
0.427	14900.
0.456	15700.
0.454	12950.
0.497	20000.
0.415	13000.
0.456	16500.
0.480	13000.
0.432	15000.
0.410	16000.
0.434	10400.

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MAXIMUM TENSILE STENGTH
UNTREATED ,UNIRRADIATED,OVEN-DRIED WOOD

        O.D. S.G.   STRENGTH

        0.345        10100.
        0.469        14250.
        0.399        16400.
        0.432        13300.
        0.480        14600.
        0.461        15800.
        0.365        11700.
        0.451        12100.
        0.421        10500.
        0.503        15500.
        0.490        19500.
        0.449        13300.
        0.480        14550.
        0.353         8660.
        0.481        11600.
        0.350        13000.
        0.470        18500.
        0.508        10000.
        0.412         9680.
        0.435        15250.
        0.395        15400.
        0.384        12900.
        0.475        12500.
        0.555        16600.
        0.407        10500.
        0.500        12700.
        0.400        13250.


MAXIMUM TENSILE STENGTH
WOOD TREATED WITH PURE STYRENE

        O.D. S.G         P.P.S.         STRENGTH

        0.399           0.463          11500.
        0.392           0.479          11650.
        0.400           0.593          14000.
        0.381           0.561          12300.
        0.405           0.584          16800.
        0.399           0.542          10000.
        0.386           0.573          11000.
        0.382           0.550          11500.
        0.442           0.520          18100.
        0.403           0.545          11900.
        0.476           0.433          15200.
        0.381           0.561          12250.
        0.447           0.359           9680.
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MAXIMUM TENSILE STENGTH
WOOD TREATED WITH 34 PERCENT STYRENE SOLUTION,OVEN-DRIED

      O.D. S.G.        P.P.S.      STRENGTH

      0.490            0.308       10500.
      0.423            0.409        7020.
      0.432            0.433        9970.
      0.457            0.446       13200.
      0.455            0.390       10350.
      0.464            0.424       12800.
      0.465            0.285       10700.
      0.461            0.440        6120.
      0.468            0.450        8430.
      0.431            0.104       10300.
      0.456            0.327        8280.
      0.365            0.407       10000.
      0.398            0.401       11950.
      0.472            0.368       12200.
      0.495            0.423        9780.
      0.441            0.400        9510.
      0.441            0.377        8670.
      0.441            0.377        9870.
      0.500            0.346       10850.
      0.467            0.240       12030.

MAXIMUM TENSILE STENGTH
WOOD TREATED WITH 27 PERCENT STYRENE SOLUTION

      O.D. S.G.        P.P.S.      STRENGTH

      0.508            0.087       10500.
      0.531            0.131       10050.
      0.487            0.081       10400.
      0.480            0.190        7710.
      0.392            0.112       12870.
      0.465            0.203       15100.
      0.462            0.272        9500.
      0.432            0.091       11750.
```