CURING OF DRYING OIL IN WOOD FIBRE WEBS

BY GAMMA-IRRADIATION

by

LASZLO PASZNER

B.S.F. (Sopron Division) University of British Columbia 1959

M.F. University of British Columbia 1963

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department of Forestry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March, 1966
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FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

OF

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B.S.F., The University of British Columbia
(Sopron Division), 1958
M.F., The University of British Columbia, 1963

TUESDAY, MARCH 29, 1966 at 10:30 A.M.
IN ROOM 239, FORESTRY AND GEOLOGY BUILDING

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CURING OF DRYING OIL IN FIBRE WEBS
BY GAMMA-IRRADIATION

ABSTRACT

Means are described for improving mechanical properties of wood fibre webs made from high yield acid sulfite, kraft and groundwood pulps, as well as blends of both chemical pulps with groundwood. The procedure includes saturation of dried fibre webs with hydrocarbon drying oil and subsequent polymerization of the oil by prolonged high temperature curing or by use of $^{60}$Co gamma-ray irradiation as energy source. The treatment was shown to strengthen interfibre bonding. No effects on intrinsic fibre strength were noted.

Tensile strength parameters (maximum stress, ultimate strain, elastic modulus and tensile energy absorption) were used for sorting treatment effects on paper handsheets prepared from the various materials. Wood fibres arising from the dissimilar pulping processes were shown to behave in the same manner observed previously as thermal "oil tempering" of highly lignified mechanical pulps. Mathematical models were used to describe mechanical property adjustments as related to treatments. Briefly, thermal polymerization raised maximum tensile strength by 50-80% for the high yield chemical pulps and 120% for groundwood. Gamma-irradiation induced curing provided up to 70% of values had by thermal treatment. Thermal after-treatment of irradiated samples provided maximum values, suggesting similar mechanism for the two methods.

Maximum efficiency of gamma-irradiation induced curing occurred between $10^2$-$10^5$ rad integral dosage. This is below the critical level causing serious degradation of wood fibre carbohydrates. The technique provides some advantages over thermal curing, such as more rapid polymerization rate, lower elastic moduli and much less discoloration with highly lignified pulps.
Residual lignin in pulp fibres appears to be an important variable controlling extra strength development by oil polymerization treatments. Evidence was sought for distinguishing between homopolymer and oil-lignin graft copolymer formation through assessment of basic mechanical strength parameters and fibre fracture patterns and by use of organic solvent techniques. In addition to the main materials of the study, highly purified pulps and glass fibre were examined in this regard. The presence of an oil-lignin graft copolymer was not shown conclusively.

GRADUATE STUDIES

Fields of Study: Wood Technology (Forestry) and Chemistry

Research in Wood Properties
Research in Wood Anatomy
Physical and Chemical Properties of Wood
General Forestry Seminar
Modern Analytical Methods in Chemistry
Advanced Organic Chemistry
Digital Computer Programming

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ABSTRACT

A technique is described for improving wood fibre web strength by copolymerization of a hydrocarbon drying oil (CTLA Polymer) within hand-sheets made from pure and admixed forms of high yield chemical (sulfite and sulfate) and groundwood fibres. Oil polymerization can be initiated successfully by prolonged thermal treatment at 145°C, as well as by the novel method of low dosage gamma-ray irradiation. The treatment strengthens inter-fibre bonding.

Evidence for copolymerization was sought through assessment of tensile and related strength data on variously treated standard handsheets. Effectiveness of the polymerization on pulp types investigated as initiated by heat and low dosage irradiation is strongly related to surface colloidal and basic physical and mechanical properties of the fibres. Maximum strength parameters were obtained with oil saturated sulfite and groundwood handsheets following polymerization by thermal treatment. Copolymerization efficiency by irradiation, on the other hand, is estimated as 73 % for sulfite, 65 % for groundwood and 50 % for kraft handsheets. Effectiveness of oil polymerization by irradiation was found to be proportional to dosages up to $10^5$ rad. As anticipated, limit of strength improvement was not set entirely by intrinsic fibre strength, but was also influenced by surface colloidal properties of the fibres. Blends made from chemical-groundwood fibre mixtures behaved more or less proportional to individual pulp strengths and extent of blending. Copolymerized sulfite-groundwood blends at equal proportions approximated the tensile strength of similar kraft papers suggesting better economy with kraft fibres when papers of limited strength are produced.
All other strength parameters (elastic modulus, tensile strain and tensile energy absorption) followed similar trends, or if different were of aid in explaining certain phenomena characteristic to treated fibre webs.

The presence of graft copolymer could not be conclusively proven, since both the copolymer and oil homopolymer are insoluble in the usual organic solvents. A dual character of the oil polymer was demonstrated with glass filterpaper and highly purified commercial cellulose fibres. Effectiveness of oil polymerization in highly lignified mechanical pulps was greatly depressed by mild sodium chlorite treatment, although the strength and bonding capacity of such fibres increased considerably. This was taken as direct evidence for the possibility of a lignin-CTLA Polymer copolymer system. Site of chemical reaction has not been described, although means for assessment of such information are suggested.

The study proves the usefulness of gamma-irradiation as energy source for the copolymerization of drying oils in handsheets as replacement for the prolonged thermal treatment hitherto used by the hardboard industry. Added advantages of irradiation processed copolymerized papers are less discoloration, especially with high lignin content pulps, and lower elastic modulus, a factor clearly objectionable for some paper uses.
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The author acknowledges with gratitude his appreciation to Dr. J. W. Wilson, Professor, Faculty of Forestry, for his valuable professional assistance in planning and experimental phases and preparing the thesis, as well as for his conscientious and understanding guidance over the past four years at this University; to Dr. R.W. Wellwood, Professor, Faculty of Forestry and Dr. L.D. Hayward, Associate Professor, Department of Chemistry, for helpful suggestions and criticism; to Dr. A. Kozak, Assistant Professor, Faculty of Forestry, for the statistical analysis and computer programming; to Dr. J.A.F. Gardner, Dean, and Dr. J.H.G. Smith, Professor, Faculty of Forestry, for their advisory help; and to Dr. B. Leopold, Director, Empire State Paper Research Institute, State College of Forestry, Syracuse University, for serving as External Examiner of the thesis; to MacMillan, Bloedel and Powell River, Limited, for the experimental pulp material and providing facilities for handsheet preparation; to Mr. A.G. Davies of Atomic Energy of Canada, Limited, for the gamma-ray irradiation treatments; to Mr. H. Green, Pulp and Paper Research Institute of Canada, for preparation of the scanning electron photomicrographs; to Miss J. Ethridge and Mr. U. Rumma, Technician, Faculty of Forestry, for their help in preparing the handsheets; to the National Research Council of Canada, for repeated financial support during the three-year academic programme; to the Pulp and Paper Research Institute of Canada for assistance; and last, but not least to Mrs. M. Paszner for her patience, devotion and kind understanding throughout these memorable years.
INTRODUCTION

During the past decade intense competition has developed between cellulosic materials and various synthetic polymers. Some traditional cellulose markets have partly or entirely given way to man-made fibres and films. The effect has been to promote new research efforts directed at improvement of wood and wood product properties by modifying both their physical and chemical structure. Part of the answer is being found by blending native wood properties with those of quite dissimilar materials. This has led in recent years to development of methods for grafting and copolymerization of various polymers onto wood base constituents namely, cellulose and lignin. An attractive energy source for forming such composites has been found in the form of gamma-rays.

Early observations of irradiation effects on various synthetics has stirred great hopes regarding adjustment of polymer properties. Exposure of natural rubber to ionizing radiation is known to decrease its viscosity, iodine number, molecular weight, and softening point. Short, intense bursts of electrical discharge cause rubber vulcanization. Either chain scission or cross-linking results from ionization of a variety of natural and synthetic polymers (9, 29, 47, 125, 177, 222).

With wood the major effect of irradiation is degradation. Below \(10^5\) rad integral dosage degradation is small (86) and hardly detectable on mechanical strength (21, 39). However, irradiation dosages in excess of \(10^5\)
rad result in depolymerization of cellulose (26, 48, 70, 76, 86, 179, 200). Depolymerization is thought to be a random process affecting both cellulose crystalline and amorphous regions equally, so that acid hydrolysis and enzyme activity is greatly enhanced (123, 180). At higher irradiation dosages, such as at 10 to 15 Mrad, cellulose degradation is advanced (86), while treatment with $3 \times 10^8$ rad dosage gives a water-soluble cellulose.

Greater resistance of lignin to irradiation effects in comparison to polysaccharides has been suggested by Smith and Mixer (204), Freidin and co-workers (70, 70/b) and Rollins et al. (184) and has been explained on the basis of its aromatic character. It is further suggested that lignin in intimate chemical admixture with wood carbohydrates may exert a protective effect as shown by decreased amounts of water-soluble carbohydrate products, carboxyl content and per cent of decomposed carbohydrates (70). It is noted in this regard that condensed lignin preparations, isolated with strong acids, are more stable to irradiation than preparations isolated by neutral solvents, suggesting that lignin history is an important factor with regard to its degree of polymerization and consequently its state of chemical reactivity.

The great interest and enthusiasm aroused in the field of wood irradiation is mainly due to discoveries that strength, heat resistance and dimensional stability may be improved by suitable monomer saturation followed by irradiation. Application of various known catalyst-heat grafting techniques can now be extended to irradiation copolymerization as a faster and better controlled energy source. Attempts to improve wood strength and hygroscopicity by grafting of vinyl type monomers in wood are reported with
various levels of success, and information in this field is growing rapidly. Concentration of radioactive wastes in large quantities has led to numerous practical applications of irradiation processes in other fields.

There has been very limited extension of wood and cellulose radiation technology to treatment of wood fibre webs. The low strength of mechanical wood pulps has always been one serious limitation to their application as furnish for many paper grades, and much interest has continued in search for means to improve this property. With continually rising wood costs, the advantage of high yield had with mechanical pulps has become a strong incentive to finding methods for increasing allowable proportions of mechanical pulps for various types of papers. The improvement of certain properties of cellulosic materials used in ordnance packaging is considered highly desirable. For similar reasons high yield chemical pulps are receiving new attention.

For most paper uses it is desirable to have capacity for absorbing large amounts of energy before failure. The objective can be accomplished in two ways, by maximizing the surface area resisting the stresses or by maximizing the stress resisting bond strength. The former procedure is chiefly controlled by structural considerations while the latter is influenced by the chemistry of the system. It is the latter avenue that is pursued in this study with systems new to the paper industry, but known in part for some time for improvement of flexural properties of paperboards possessing high amounts of residual lignin (178).

Although the evidence collected so far does not allow for clear description of the oil tempering mechanism, since it is still considered as
extremely qualitative, beneficial effects accompanying oil polymerization within wood fibre products has sufficient significance and practical meaning to warrant further investigation.

The present study is concerned with the curing of drying oil in wood fibre webs and has been designed around four main objectives.

First, to determine if wood fibres arising from quite dissimilar processes behave in the same manner as observed with chemical pulps. Since earlier results with Asplund fibre (179) and newsprint (178) suggest lignin quality as the most important single variable controlling extra strength development in oil polymerization treatments, emphasis is placed on new materials demonstrating qualitative and quantitative differences in lignin content. Thereby, western hemlock groundwood, high yield acid sulfite and unbleached kraft pulps are included in the comparison, as is the entire range of blends between groundwood and the two chemical pulps. As a further feature, highly purified sulfite and sulfate commercial pulps and glass fibre webs are used to represent the lower end of the lignin scale. The materials contain at least three types of lignin in amounts from 0 to 28.9 % and show other major differences in fibre strength, fibre geometry and fibre conformity.

Second, to explore the prospect of using gamma-irradiation as energy source for curing drying oil in wood fibre webs. This new technique could show some advantages over the established practice of thermal curing used with some wood fibre products.

Third, to describe the range of physical properties that can be had by thermal and irradiation polymerization of drying oil in wood fibre webs. Analyses of tensile stress-strain curves are especially suited for
evaluating these effects.

Fourth, to further develop understanding of the polymerization mechanism(s) with wood: fibre webs. Through assessment of basic mechanical strength parameters, observation of fibre fracture systems and by use of organic solvent techniques evidence is sought for partition of oil homopolymer and oil-lignin graft copolymer effects. In this regard, evidence for graft copolymer was provided recently for isolated hydrochloric acid lignin and methyl methacrylate (116, 117).
I. RESIDUAL LIGNIN IN WOOD PULPS

The great diversity of paper properties obtained with pulps made from the same wood source by various processes reflects the broad spectrum of changes taking place in the preparation of wood fibre. The changes may be physical, chemical or physico-chemical in nature (23, 36, 115, 194, 197, 220). Although the differences in wood characteristics may well explain some of the variation in final paper properties, they are not sufficiently large to account for major differences found between sulfite, kraft and high yield Asplund pulps. Explanations of such differences, though often sought, have not been easily found. At least one variable, the amount, distribution and state of residual lignin within the fibre walls appears to influence intrinsic fibre strength and interfibre bonding of various papers and reconstituted wood fibre products (25, 36, 94, 95, 96, 104, 106, 115, 132, 179, 189, 194).

Since lignin is essentially hydrophobic in nature, its presence may be expected to decrease the degree of interfibre bonding in paper. Thus, it was suggested by Jayme and von Koeppen (94) that the lower acidity of kraft pulps and, thereby, the lower ion bonding capacity is cause of the lower strength of kraft pulps as compared to sulfite pulps of the same lignin content. The presence of larger amounts of residual lignin in a pulp may
restrict swelling and decrease adhesion between fibres due to its hydrophobic nature and predominant location at the fibre surface (108, 115).

Further, it was shown (59, 66) that lignin through its stiffening effect acts as inhibitor to fibre conformity, i.e., fibre conformity is inversely proportional to lignin content. In some treatments, however, high yield pulps such as Asplund and Masonite are reconstituted into high density structural boards by application of heat and pressure in the presence of moisture. Lignin plasticization and recondensation has been credited with formation of strong interfibre bonds in these materials (192).

1. **Pulps from Mechanical and Semi-chemical Processing**

Since groundwood pulp represents almost the entire wood substance delivered to the grinder, its chemical composition is at least as complex as that of wood. Whether, or to what extent chemical changes occur during the grinding process has not been well established. At any rate, the net mechanical effects of grinding and subsequent refining are realized in a tremendously increased surface area of exposed fibre walls for chemical reactions, as compared to areas realized with chemical pulps. This mechanical fragmentation is due to abrasion, fibrillation and cutting of the fibres (32). Observations on groundwood pulps show that much of the extra area exposed is fibre lumen, quite different from external fibre surface exposed by chemical digestion (32, 66).

The decrease of wood interfibre bond strength with increase of temperature may be utilized in groundwood processing. Actual temperatures at the wood-stone interface are difficult to measure, but may at the moment of fiberizing reach the softening range of lignin (140). Such high
temperatures (170 to 180°C) in the presence of water could lead to extensive thermal cross-linking or polymerization of lignin. Experiments (109, 110) show that, with temperatures above the softening point of lignin, hot water-soluble carbohydrates are removed from association with lignin, and this is the primary factor in reduction of the lignin interfacial area by causing lignin coalescence at the vacated sites. The reduction in lignin interface has been followed by SO$_2$ and phenol sorption on prehydrolysis of the wood (109, 110, 111). The difficulty in chemical pulping of Asplund fibre and even in lignin determination of the material also suggests a change of lignin constitution due to high temperature treatment in the presence of water. Further evidence of lignin condensation within wood, thermally treated in the presence of water, was shown by Leopold (129, 130, 131) as reduction in the yield of aromatic aldehydes (vanillin and syringic aldehyde) obtained by alkaline nitrobenzene oxidation. It seems that lignin condensation reactions occurred whether or not there was initial chemical linkage between the carbohydrates (mainly hemicellulose) and lignin (109). Interestingly, the extent of lignin coalescence was less pronounced when supersaturated steam was substituted for hot water (109), suggesting that Kleinert (109) is correct in his observation on effect of free space caused by "leaching" of hemicelluloses.

Literature descriptions of residual lignin in groundwood pulps are scarce. Most of these deal with some specific problem related to improvement of pulp quality (frequently bonding and brightness) and thereby rarely treat the basic phenomena. The high lignin content of groundwood has been considered as the primary source of color in these pulps (229).
Brightening is brought about by oxidation of chromophoric groups, preferably without additional yield loss (189, 229). The mechanism of these oxidation reactions is largely unknown. It has been suggested (7) that peroxide oxidation of mechanical pulps is selective for such chromophores, and involves the total pulp lignin. The primary sites of attack are believed to be carbonyl groups and possibly phenolic hydroxyls in the lignin structure (98). Rapson and co-workers (229) showed that the permanganate number and chlorine demand of peracetic acid bleached groundwood are very little affected. It would seem that sites on the lignin molecule which are susceptible to attack by chlorine are not affected by this bleaching reaction. Furthermore, the relatively small decrease in permanganate number by peracetic acid bleaching suggests that the actual amount of oxidation must be very small.

Reeves and Pearl (189) sorted relationships between various lignin functional groups and effectiveness of alkaline peroxide bleaching of lignin-related model compounds and came to the conclusion that only those compounds reacted which possessed carbonyl (formyl) groups on the aliphatic side-chain. Since compounds without this carbonyl group (ferulic acid) did not react, it was suggested that the initial point of attack is probably at an oxygen-containing functional group. Although presence of the carbonyl was mandatory for the oxidation reaction, it was not the only requirement. In addition to the carbonyl, a free phenolic hydroxyl seemed to be necessary, as has been suggested by Jones (98). However, an independent carbonyl reaction was shown with the model compound (3,4-dimethoxy phenyl)-2 propanone. The isolated reaction product indicated enolization and subsequent cleavage of the double bond. In alkaline nitrobenzene oxidation of lignin, Wacek and
Kratzl (224) found that the presence of a free phenolic hydroxyl group in para position to the side-chain favoured oxidation of the side-chain. On the other hand, Koshijima and Muraki (117) have reported a marked effect of free phenolic hydroxyl on the degree of methyl methacrylate grafting onto hydrochloric acid lignin.

In a recent investigation by Paszner and Wilson (179) the reactivity of various Asplund pulp components toward condensation reactions involved in oil-tempering of hardboard with CTIA Polymer was reduced by mild oxidative delignification of the fibre with sodium chlorite. It was also shown that precondensation with catechin tannin lowered fibre reactivity on heat treatment. In degradation studies of lignin-methyl methacrylate graft copolymers, reported by Koshijima and Muraki (116), the polymethyl methacrylate became soluble from the copolymer upon mild oxidation with sodium chlorite. Thereby, it is evident that whatever lignin site is involved in the polymerization process, it is preferentially deactivated or destroyed by the oxidizing action of sodium chlorite or may be otherwise complexed (179). This also suggests that two mechanisms, i.e., polymerization by thermal treatment or ionizing irradiation, involve the same reaction sites on the lignin molecule and may very well be the same. The difference in speed between polymerizations could be due to differences in the applied energy, as well as to the efficiency of free radical formation by the two processes.

In summary, it is safe to conjecture that lignin accessibility may be increased by investment of mechanical energy in a mechanical pulp. According to the available evidence, reactions with lignin appear to depend
on the side-chain structure and are enhanced by the presence of free phenolic hydroxyls. Native lignin in situ probably has less accessible or exposed molecular structure and thereby reacts less readily.

2. Pulps from Chemical Processing

Many of the questions raised more than a decade ago by Bland and Stamp (158) on the constitution and character of residual lignin in chemical pulps are still unanswered. For example, does the residual lignin in pulp differ from that found in original wood; has it been altered during the pulping process, or was it different originally? These are questions of major importance, with answers that would serve as good basis for attempting problems of pulp and paper improvements involving lignin reactions.

Numerous investigators have concerned themselves with quantitative estimations of residual lignins in various pulps and attempted explanation of pulp behavior by the amount of residual lignin therein. It is generally accepted that sulfite pulps bleach much more readily than kraft pulps from the same wood origin and at the same residual lignin level (23, 36, 115, 232). Other major evidence on sulfite - sulfate lignin difference occurs from commercial chlorination. Sulfite chlorolignins are mostly (but not entirely) water soluble. Sulfate chlorolignins require alkali treatment. Thus Giertz (75) found that bleachability depends not only on the amount but also on the state of the lignin present.

Chemical pulping processes are found to affect the chemical and physical nature of ligno-cellulosic materials in different ways, thereby providing pulps with different reactivity and strength. Although not much
difference is shown by conventional cellulose parameters in indicating fibre damage by either process (94), the definite effects on swelling and surface colloidal properties must relate to overall qualitative differences of some residual fibre constituents, such as the hemicellulose and lignin (23, 94, 96, 115, 197). Knowledge of these differences is very limited, indeed.

a. Residual lignin in acid sulfite pulps

In acid sulfite pulping the delignification is believed to start at the middle lamella (16), whereas in the case of alkaline pulping a more selective delignification is said to operate (24). This was demonstrated by Jayme and von Koeppen (94) who obtained a structureless, amorphous lignin powder from kraft pulp by strong acid hydrolysis of fibre carbohydrates, whereas sulfite fibres given the same treatment retained their original shape as a lignin skeleton. It is believed (92) that difference in residual lignins within sulfite and kraft chemical pulps is due to different reaction mechanisms during pulping. In the sulfite process the chemical attack on wood lignin has been found to proceed topochemically (92, 156) starting from the radial middle lamellae (the attack may be aided by the numerous boardered pits on this surface), whereas tangential walls are initially relatively unchanged.

Solution of lignin proceeds simultaneously in both inter- and intrafibre zones although the deeper parts of the fibre walls are relatively untouched (92). Thus, microfibrils within the secondary layer can remain more or less "coated" with protective substances, such as hemicellulose and lignin. In addition, the relatively high lignin content on the sulfite fibre
surface gives some degree of rigidity to the fibres. Accepting that some of the partially sulfonated lignin is still retained within and on the fibre, Giertz (74) explained the better hydration capacity of sulfite fibres by the improved hygroscopicity of lignin. In his opinion, lignosulphonic acids, as strong acids, swell more readily in water and thereby allow a higher degree of hydration than do kraft residual lignins. The prominent role of hemicellulose swelling, however, is not mentioned.

Reactivity of sulfite pulp residual lignin can be estimated from the rather facile bleaching characteristics of such pulps. This has been attributed to the lower degree of condensed lignin within the sulfite fibre wall (194). The ready chlorination and water solubility of chlorolignins involved high-molecular weight lignosulfonic acid fragments (partial sulfonation of residual lignin was determined as 0.2 to 0.3 S/OCH₃) whereby approximately 80% of the residual lignin was found accessible to the bleaching agents. The rather ready reactions of sulfite pulps towards acetylation (23, 151) and methylation (151) in contrast to kraft pulps, is also an indication of higher reactivity and less condensed nature of sulfite pulp residual lignin. It has been shown (141) that methylation with diazomethane or methanol-hydrochloric acid decolorized both native and pulp lignins by elimination of almost all groups capable of reduction (carbonyls). This result suggests reaction of 1,2-dicarbonyl groups, such as o-quinones, as well as 1,4-configurations of the quinone methide type. Acetylation was shown to produce similar results, possibly for the same reasons, although this treatment is accompanied by a reduction in pulp strength due to reduced hydrogen bonding of the cellulose (151).
According to Adler (3) some carbonyl groups in the lignin molecule are protected by the formation of loosely bound bisulfite ions as alpha-hydroxyl sulphonates, but since such ions were shown to disappear towards the end of long cooks, darkening of pulp color is possibly due to condensation of carbonyl groups in the lignin. The rather light color of sulfite pulps is attributed to the above protective effect. The reddening of unbleached sulfite pulps to a stable brown color has been related to presence of quinone and quinone methide groups by Adler and Haggroth (4). These reactions are thought to operate through air oxidation, involving the free phenolic hydroxyl in para position to the side-chain. Such oxidation is usually catalyzed by the presence of metal ions, mainly iron and copper. Similar effects were shown to be due to the formation of pyrocatechol-type structures in lignin as a result of demethylation during the cooking process (112). Another similar effect occurs when mill process water containing appreciable amounts of chlorine is used for dilution or washing sulfite raw stock, particularly western hemlock. The condensed systems involving alpha-carbonyl groups usually contain free phenolic hydroxyls which strongly resemble the carbinol bases of triphenyl methane dyestuffs. Such systems are condensation products of alpha-carbon atoms on one molecule with the $C_5$-atom of the next. The presence of dihydroxy-benzyl alcohol (and thus quinone methide) structures have been shown following acid hydrolysis (194).
b. **Residual lignin in sulfate (kraft) pulps**

As mentioned earlier, delignification during the sulfate cook proceeds at a more uniform rate throughout the fibre wall and at greater speed of reaction in alkaline media (17, 23, 53, 59, 107, 232). Through swelling caused by the alkali greater lignin accessibility is obtained and thereby a more homogeneous delignification is guaranteed. According to Kleinert (108) lignin and cellulose both suffer fragmentation by forming free radicals during alkaline pulping of wood. It is easily imagined that these free radicals combine in a series of secondary reactions in which lignin macromolecules might become grafted by covalent bonding onto the cellulose pulp. A similar view was expressed by Bland and Stamp (25). Such grafting (which was distinguished from redeposition) was shown to depend on the presence of free phenolic hydroxyls, as well as on the presence of reduceable groups such as aldehydes. The presence of condensed lignin is also shown in highly bleached sulfite pulp following strong alkali treatment above 140°C by the presence of microscopic dark spots.

Distribution of residual lignin in kraft pulp was shown by Jayme and von Koeppen (94, 115) to be almost uniform across the fibre wall. It was also demonstrated that residual lignin concentration within the fibre wall is never high enough to retain the original fibre skeleton after careful hydrolysis of the carbohydrate portion. Such lignins are always recovered as a powder, not a facsimile of the fibre.

In spite of increased accessibility and more uniform lignin distribution within fibre walls, kraft pulps are decidedly more difficult to bleach than sulfite pulps containing the same amount of lignin (23, 194).
One likely explanation for this phenomenon is the higher degree of lignin condensation occurring during the high-temperature (160-170°C) kraft cook (23, 53, 72). In addition, condensation in alkaline cooking is favoured by the formation of additional phenolic groups in splitting of alkyl-aryl ether linkages (72, 194) with elimination of methoxyl groups (52, 194). A condensation product is usually formed between benzyl alcohol groups, activated by free phenolic hydroxyls, and an unoccupied C₅ position or by formation of dibenzyl methane structures upon elimination of one of the side-chains. Condensations of the above type are usually counteracted by the formation of lower molecular weight condensation products with formaldehyde on elimination (cleavage) from the side-chain (194).

Discoloration of the pulp occurs at an early stage in the kraft process (10). This discoloration is taken as the first sign of lignin condensation, resulting from initial splitting of alkyl-aryl ether linkages (alpha-aryl, beta-aryl ethers) by the alkali with subsequent formation of quinone methide type intermediates (72). The accompanying reaction is alkaline hydrolysis as indicated by the comparatively low molecular weight of the solubilized lignin, as well as the loss of methoxyl groups from the molecule. As a result of these competing reactions only few of the initial carbonyl, benzyl alcohol or alkyl ether groups are found in the residual pulp lignin (160). As consequence of extensive splitting of alkyl-aryl ether groups the number of free phenolic hydroxyls is increased to almost 1.0 per monomer in the residual lignin (62), as compared to 0.3 in milled-wood lignin and 0.29 in borohydride treated lignin following two hours cooking in 2N NaOH at 170°C, as determined by Gierer et al. (72). As with acid
condensation, the C5 position of the aromatic nucleus is the most reactive site of condensation (43, 190) and the formation of free phenolic hydroxyl groups during the cook is likely to increase its reactivity.

Probably the higher proportion of condensed lignin is also the cause of relatively low kraft pulp reactivity in acetylation (23, 151) and methylation (3) treatments. The lower methoxyl content of kraft pulps, as compared to sulfite pulps of the same apparent Klason lignin content, has been demonstrated by Kleinert and Roberge (112), although a possible relationship between cooking degree (lignin content) and bromine consumption was not significant. Stability of methoxyl groups to periodate oxidation was investigated by Gierer et al. (72), who found the aromatic methoxyls were more stable than benzyl methyl ethers. Methylation of milled-wood lignin phenolic hydroxyls with diazomethane prevented cleavage of the alkyl-aryl ether, whereas methylation of alcoholic hydroxyls in alpha position with methanol-hydrochloric acid methylating agent prevented epoxide formation and subsequent cleavage of the beta-aryl ether linkage, even when free phenolic hydroxyls were present.

Alkaline nitrobenzene oxidation products from kraft residual lignin degradation suggested that the essential framework of this lignin is similar to that found in wood, although the aldehyde yield was greatly reduced (158). The fact that acetoguaiac-acone was isolated to a greater extent from the wood pulp than from wood lignin indicated the presence of a modified phenylpropane group. The general pattern of ultraviolet absorption spectra from kraft residual lignin was practically the same as that obtained for wood lignin. The fact that methods for determining wood lignin are more or
less applicable to pulp lignin determinations supports these statements.

3. Differences in Residual Lignin as Result of Processing

In summary, there are obvious differences between the three types of fibres and their residual lignins. These differences are mainly qualitative and quantitative with regard to respective position within the cell wall. While residual lignin in groundwood fibres is thought to be only slightly modified due to coalescence, its distribution within the fibre wall should not be much different than that of normal wood. On the other hand, effects of chemical cooking seem to alter not only types of lignin residues, but also the amounts and relative distribution within various layers of the fibre wall. These changes in lignin chemical composition and position are reflected in altered functional groups, as well as physical considerations of lignin accessibility. This must have bearing on reactivity toward further modifications such as bleaching, sizing, chemical derivative formation and modifications relating to copolymerization with suitable monomers.

It is known that better interfibre bonding of pulps is obtained by increasing the degree of delignification (10, 105, 179). Obviously, differences in residual sulfite and kraft pulp lignins are of more importance with lignin-rich pulps. Thus it is accepted (10, 95, 96) that all pulping processes display an optimal lignin content below which no further improvement in fibre bonding is experienced without modification subsequent to delignification. The absolute level of this optimum lignin content is in the order of 5 to 10% based on the original wood weight depending on type of
wood and process characteristics. This level of residual lignification is estimated as only slightly below the point of fibre liberation from whole wood (194). The fact that such relatively high lignin contents are tolerated within pulp fibres without serious detriment to physical and mechanical properties of resultant papers has economic importance, as well as offering opportunity for further processing involving improvements by lignin copolymer systems.
II. THERMAL TREATMENT OF WOOD AND WOOD FIBRE PRODUCTS

Water is held within the cell wall of cellulosic materials in three distinct ways -- namely, water of constitution, surface bound water and capillary condensed water (234). In normal air drying of wood it is the relatively loosely bound capillary condensed water that is removed first. This process of water removal is reversible and is not accompanied by appreciable change within the structural network of wood. Evaporation of capillary condensed water is followed by loss of surface bound water through diffusion and re-condensation mechanisms until an equilibrium is set up between the wood substance and the relative humidity of the surrounding environment. Removal of surface bound water is accompanied by major dimensional changes in the form of shrinkage (207). On accelerated drying of wood through removal of the surface bound water, diffusion of moisture from inside the wood is much slower than evaporation from the surface. Due to differential shrinkage rates the smaller shell can no longer accommodate the large interior, leading to drying stresses often great enough to cause rupture of the fibre network. The dimensional changes, if water removal is not carried to extreme, are more or less reversible on moisture reabsorption and swelling.

It is removal of the final small amount of water, the water of constitution, usually by high-temperature heating (above the boiling point of water) that brings about drastic and irreversible changes within wood products.
1. **High-Temperature Treatment of Wood**

The effect of prolonged heat treatment of wood at temperatures below those required to initiate combustion and pyrolysis, i.e., 228°C (207), produces slow degradative changes, a loss of strength (195) and decreased hygroscopicity (213). The rate of change has been found to be a function of temperature and time, allowing calculation of wood durability at ordinary temperatures (210). When wood is exposed to various levels of thermal treatment for longer periods of time the logarithm of residual wood weight varies directly with time (207). The initial weight loss is usually due to loss of the various forms of water. As drying conditions become more severe carbon dioxide and carbon monoxide, together with large amounts of volatile organic compounds, are lost as distillate and flue gases. Among these are acetic and formic acids, esters and aldehydes, methyl alcohol and various phenolic compounds. These are ascribed to degradation of various wood components (58). As demonstrated by Stamm (207) wood hemicellulose is degraded by far the most rapidly, followed by the cellulose and lastly by the lignin.

In heating wood to the extent where loss in oven-dry weight occurs, a significant change in hygroscopicity is observed with resultant reduction in the extent to which it will swell and shrink. The degree of such dimensional stabilization was shown to be significantly greater per unit weight loss when heating was performed in the absence of air (166). Unfortunately, large gains in dimensional stability are accompanied by extensive loss in strength properties, mainly toughness and tensile strength.
Much more effective methods have been found recently for increasing dimensional stability by impregnating wood with bulking agents (sugar, wax, resin, polyethylene glycol (207)), by chemical modification of wood through acetylation (214), formaldehyde cross-linking (60, 209) and by numerous grafting techniques with the cellulose fraction with or without catalysts in addition to thermal treatments (63, 147, 161). The advantages are in most cases quite considerable as far as dimensional stability is concerned, although adverse effects on mechanical strength properties may accompany the treatments (209).

2. Thermal Treatment of Wood-Fibre Products

This group of cellulosic materials includes wood fibre boards, pulps and various paper products. Thereby, two basic subdivisions may be made based on residual lignin content in the starting material. It is expected that presence of lignin influences effectiveness of heat treatment with these two types of wood products.

a. Heat treatment of wood fibre boards

Heat treatment has become common practice for increasing dimensional stability and to some extent improving flexural properties of hardboards (78, 101, 221). The chemical composition of hardboards made from coarse wood fibres is changed somewhat by removing the water of constitution, which results in higher strength and dimensional stability. Recently, Klinga and Back (113) introduced the concept of cross-linking stresses in hardboards which counterbalance the permanent drying stresses already existing in wet-
process hardboards. The cross-links are believed to be of the hemi-acetal type and are formed between the cellulose and hemicellulose at very low humidity conditions. Cross-linking is claimed to produce permanent shrinkage in the plane and thickness of the sheet. A strength increase of 50% followed heating at 160°C for 3 hr, while dimensional stability increased 80% by heating at 160°C for 8 hr. Interestingly, the times required for maximum development of strength and dimensional stability do not coincide, since considerable strength loss was reported following an 8 hr treatment at the same temperature.

Further consideration should be given to the effect of lignin in hardboards. The opposing theories of lignin recondensation and complete dehydration of hemicellulose are currently debated in the literature. The strength increase of hardboards on heat treatment can hardly be due to increase of intrinsic fibre strength, but must result from improved fibre bonding in which hemicellulose and lignin may both have some share. The fact that lignin plasticization can occur at high temperatures and with prolonged heating (77) should not be without effect. However, the effect of heat treatment on interfibre bonding cannot be fully realized as increased strength since the individual fibre strength is already utilized up to 70 to 80%, as evidenced by the nature of mechanical test failures. The limit of proportionality is increased practically to the point of failure, indicating less relaxation and a higher degree of order within the board. McKnight and Mason (145) attribute the improved hygroscopic properties of these materials to lower water sorption of the heat treated lignin.

Further improvement in hardboard flexural and dimensional
properties is obtained by copolymerizing unsaturated drying oils on heat treatment with high quality hardboards (122, 179). Investigation of the underlying mechanism (179) showed that Douglas fir Asplund pulp lignin quality was more important than lignin quantity, and that the condensation reaction depended mostly on reactive sites within the lignin molecule. The fibre material could be inactivated by mild sodium chlorite treatment, possibly by oxidizing lignin aldehyde groups or by tannin condensation. Lignin was thought to be responsible for 80% of the strength increase (110%) that was obtained by oil tempering over that obtained by heat treatment only. Since the detailed structure of the lignin macromolecule is still unknown, the site of copolymerization could be only surmised.

In lignin condensations with formaldehyde in acid solution (60) several reactions occur whereby soluble formaldehyde lignins are obtained. In the proposed lignin molecule, ether linkages are assigned between phenylpropane units at arbitrary positions. Further, cross-linking markedly lowers lignin solubility. Such linkages are apparently not numerous enough to prevent swelling. In condensation reactions, even with self condensation and cross-linking, loss of water probably occurs. Perhaps the alpha position in the side-chain and the C6-position in the aromatic nuclei are involved in such condensations, because the former is easily sulphonated when lignin is heated in aqueous sodium bisulfite and the latter can be chlorinated. Acid solubility of formaldehyde lignin suggests that the formaldehyde has condensed at activated lignin centers which normally cross-link with each other to form insoluble Klason lignin (60).

Only moderate strength increase (7 to 10%) was reported recently.
by Klinga and Tarkow (114) on vapour phase acetylation of hardboard. On the other hand, dimensional stability increased by 30%.

b. Heat treatment of paper

It is well recognized that the heating of cellulosic fibres and fibre webs at elevated temperature, but below the ignition point, has pronounced degrading effect upon their physical and mechanical properties (35, 208). Ott and Spurlin (175) reported lower strength data following several hours heat treatment of cotton tire cord. Murphy (162) studied the thermal decomposition of natural cellulose in vacuo and found that water, carbon dioxide and carbon monoxide were the main degradation products. The amount of decomposition products was related to the state of degradation. Above a certain temperature the swelling capacity of the cellulose fibre is irreversibly reduced.

Experiments with Whatman No. 1. filterpaper by Britt and Yiannisos (35) showed that the zero span tensile strength, tear resistance and folding endurance, after an initial slight increase, decreased significantly after prolonged heat treatment, whereas stiffness was considerably increased. This was explained by depolymerization of the cellulose and embrittlement of the fibre structure. Interestingly, even very low temperature and initial pulpwood drying is reported to have a very detrimental effect on resulting paper properties. In this regard, Jayme (90) showed that the water retention value (WRV) of pulps is considerably lowered and that the original state of swelling can never be restored even by very prolonged soaking. The strength of paper prepared from pre-dried wood or pulps was shown to be inferior to
that produced from never-dried materials by Giertz (73), Jayme (90), Teder (218) and Teder and Stockman (216). The alkali solubility decreased and viscosity of the pulps increased if the air temperature exceeded 120°C during the pulp drying. The fact that some strength properties are only slightly reduced is due to the predominant role that interfibre bonding plays in normal tensile strength development of paper. Only after considerable loss in individual fibre strength is normal tensile strength appreciably affected. In highly bonded paper sheets, therefore, a loss in fibre strength would be reflected to a greater degree. Oddly enough, bleached kraft pulp strength is more influenced by heat treatment than that of bleached sulfite pulps (216). Deterioration in bleached kraft pulp was so extensive that the concept of constant tear factor at constant breaking length of fibre mats did not hold (216). Dried pulps, however, showed less degradation under similar conditions, indicating the effect of moisture on the degradation of bleached pulps during high-temperature treatment. The unbleached pulp strength was only moderately influenced by comparable heat treatment (216.)

It seems that stretching introduced by the "dried-in" stresses with restrained pulp sheets increases the apparent crystallinity of the structure (similar to some synthetic high-polymers) involving formation of highly bonded areas, and thereby restricting free mobility of the macromolecules (73). Papers dried without shrinkage by freeze drying and solvent exchange methods were found to be without wet strength (216). Rehydration of "denatured" (90) pulps can be aided by breaking the critical bonds with stronger swelling agents that water (alkali) or by mechanical action (beating or ultrasonic treatment).
Most remarkable, is the effect of heat treatment on the wet-strength of both sulfite and sulfate papers (18, 19, 51) with effects approaching those had with addition of 5 to 10% wet-strength resin to the furnish. According to Back and Klinga (19), who stress the formation of internal cross-links as a result of heat treatment, this improved wet-strength can be taken as evidence for presence of cross-links in paper as introduced by heat treatment. It appears that the intensity of heat treatment should be related to basis weight of the paper product to avoid significant dry-strength losses on prolonged heating.

The overall chemical reactions induced by heat treatment are described as cross-linking (18, 19) or formation of hydrophobic furfural type residues from hemicellulose degradation products (207). The addition of aldehydes has been shown to promote cross-linking, whereas borohydride addition delayed it (19). The fact that kraft lignin exists in a more degraded and condensed state within the fibre (23, 53) makes unbleached kraft pulps more heat resistant. The lower proportion of hemicellulosic is also shown to be a contributing factor (91).

Formaldehyde has been found in the volatile degradation products of hardboards (113). This would be expected to arise also from residual lignin of other high yield pulps, but to a lesser extent. It might contribute to cross-linking as also might furfuraldehyde as formed by the thermal degradation of hemicellulose (19).

On extensive heating, a hydrolytic degradation of cellulose and hemicellulose occurs as usually indicated by the titratable acidic material and increase in water soluble fraction (19). The process is evidently an
oxidative bond cleavage. It is important to point out that the hydrolytic degradation reactions are endothermic, while reactions leading to cross-linking are exothermic. Therefore, it is expected that with increase in curing temperature the equilibrium between bond formation and cleavage in the cellulose material would shift toward increased bond cleavage.

Internal cross-linking reactions may be catalysed by polyvalent metal salts, acids and hydrogen ions (51, 208). The net effect of inclusion of such salts or acids is the reduction of temperature level for obtaining a certain degree of dimensional stability, however, the dry-strength of these materials is adversely affected. Consequently, it was suggested by Stamm (208) that better results are obtained without inclusion of such catalysts in the process.

Dimensional stabilization of paper has been attempted with various systems of chemical bulking reactions involving cyanoethylation with acrylonitrile (142, 212) acetylation with acetic anhydride (211, 212) and by cross-linking with formaldehyde (208, 212). The numerous methods for grafting monomers onto cellulose by chain transfer, redox systems, heat treatment and irradiation and addition polymerization techniques using acrylonitrile, styrene, methyl methacrylate and acrylamide are summarized by Schwab, Stannett and Hermans (199). The works of Lynch (142), Paszner (178, 179) and others, have shown that results of catalysed (167) and non-catalysed polymerization reactions give improvements in properties comparable to those obtained by irradiation, but considerably higher than obtainable with thermal treatment alone.

No mention has been found in the literature, other than possible
condensation of lignin with formaldehyde (113) and that of copolymerization of drying oils in hardboard (179), of cases where the reactivity of residual pulp lignin was used for the purpose of graft copolymer formation with monomeric impregnants, nor has the possibility been mentioned that some vinyl monomer impregnants might have condensed with available reactive centers of residual lignins in pulps.

3. **Summary of Thermal Effects**

Prolonged heat treatment at high temperature has been shown to cause degradation of both wood (210) and wood pulps (73, 90, 216, 218) prepared therefrom. Degradative effects are manifested in loss of dry-weight and change of hygroscopic and mechanical properties. Large gains in dimensional stability are paralleled by considerable loss of mechanical properties, mainly toughness and tensile strength (207).

Heat treatment of wood fibre products, such as hardboard and paper (113) results in increased dimensional stability and to some extent improved mechanical properties. The effect is ascribed to formation of cross-links between the cellulose and hemicellulose at very low humidity conditions. Chemical changes involve furfural type resin formation from hemicellulose and cross-linking within the lignin molecule (207).

Substantially larger property gains are reported by newer techniques involving grafting of vinyl type monomers onto cellulose (199). Gamma irradiation has been successfully applied as energy source in these copolymerization processes.
III. **GAMMA RADIATION AS ENERGY SOURCE IN CHEMICAL REACTIONS**

1. **General Description of Gamma-Rays**

Although about fifty years have passed since ionizing radiations were first observed, systematic investigation in the field has taken place only within the last decade. This recent advance results mainly from the large range of radiation sources that have become available. Features associated with use of high-energy irradiation for initiation of chemical reactions are: 1. the enormous surfeit of energy in the photon; 2. the non-specific character of radiolysis; and 3. the complexity of changes, both physical and chemical, that occur.

Nearly all known elements exist in several isotopic forms which either occur naturally or are formed artificially in nuclear reactors (64). Many of these isotopes are unstable as characterized by their constantly disintegrating nuclei ejecting energized particles and/or by emission of electromagnetic radiation in the form of gamma-rays (46, 64).

Gamma-rays having no mass at rest are undeflected by electric and magnetic fields and possess extremely high penetrating power. The energy quantum, or energy per photon, of gamma-rays is inversely proportional to the wavelength (46). The penetrating power of gamma-rays increases with decreasing wavelength. The gamma-ray wavelength spectrum is defined as that between $3 \times 10^{-9}$ to $3 \times 10^{-11}$ cm, or 40 kev to 4 Mev (46).

The isotope which has received greatest attention, as a source
of radiation energy, is undoubtedly Cobalt – 60 ($^{60}\text{Co}$). It is prepared from $^{59}\text{Co}$ by neutron capture via two capture reactions that produce isotopes having half-life times of 10 min and 5.27 yr. The 10 min isotope decays by an isomeric transition to the 5.27 yr isotope. The preferred use of $^{60}\text{Co}$ is due to its ready availability, relatively uniform high-energy radiation (1.173 to 1.33 Mev) and the long half-life (5.27 year). Gamma-rays are also preferred for industrial applications because they leave no residual radioactivity in treated materials.

2. Mechanism of Radiation Ionization

In the process of irradiation by gamma-rays energy deposition occurs along the ray trajectory in the material due to elastic and inelastic collisions. In spite of numerous studies, the basic phenomenon of energy deposition is not really understood for compressed and condensed systems (149). It is known that the energy content of gamma-rays is much greater than that required to excite molecules or to break chemical bonds (20). Apparently, only a minor fraction of the total energy deposition is involved in such processes. Most of the energy, in this view, goes into collective excitation (40). Gamma-rays tend to lose their energy through a single interaction, whereby a portion is absorbed and the other part is transmitted with full initial energy. It is thought that collisions result in ionization by a transfer of energy between the high-energy quanta and atoms of the medium through which they pass. The chemical changes following such collisions are mainly due to the ejection of high-speed electrons. Displacement of electrons in chemical bonds comes about by energy transfer from the
charged particle and if the displacement is sufficient for stripping an electron from the parent molecule, ionization occurs. At low levels of displacement only molecular excitations occur. In cases where an electron is ejected from its orbit with sufficient kinetic energy it, too, can cause excitation and ionization. Such an effect is called secondary excitation or secondary ionization. Consequently, at each point of initial ionization groups of ion-pairs are formed (161, 182, 226). The density of water ionizations by $^{60}\text{Co}$ rays on the average is one per 1000Å, as estimated by Phillips (182). The number of free radicals formed was found to be one per $10^4$ to $10^5$ glucose units in cellulose (177).

In ionized and excited molecules a variety of secondary processes may occur before the final chemical change takes place. In the course of excitation and ionization the affected molecule may break into fragments by rupturing weak bonds (226). Rupture may occur in carbon-hydrogen bonds, forming hydrogen atoms and alkyl radicals;

$$R - H \rightarrow R' + H.$$ 

or in carbon-carbon bonds in a polymer chain, forming two polymeric radicals with unpaired electrons;

$$R_1 - R_2 \rightarrow R_1' + R_2'.$$

The extent to which these reactions occur, other things being equal, will depend upon activation energies. Thus, a large number of the molecular fragments become free to react with each other and with reactive molecules in the surrounding environment.

The presence and number of free-radicals was actually determined
through study of electron paramagnetic resonance spectra (ESR)\(^1\) by Abraham and Whiffen (2), Glegg and Kertesz (76), Park (177) and by Rapson and co-workers (84) in cellulose and by Ramalingam, Werezak and Hodgins (186) in cellulose, cellulose pulp impregnates, wood pulp impregnates and lignin. A quantitative estimation of free radicals in the foregoing materials is presented in Fig. 1 (186). For the procedure diphenylpicrylhydrazyl was used as primary standard (0.1 mg of the standard represented \(1.5 \times 10^{16}\) spins). The absorption curves were obtained by graphical integration of the derivative curves and the radical concentrations were calculated from comparisons of integrated areas.

The effect of heating on free radical concentration is shown in Fig. 2 (186). Such changes \textit{in vacuo} are believed due to secondary chemical mechanisms, such as cross-linking.

The decay of free radical concentration was also followed by Arthur and co-workers (14, 26) who found that free radicals of irradiated cellulose interacted with the free oxygen of the air, whereby further chain scissions were produced. The existence of such long-lived free radicals was shown to originate from the cellulose in cellulose-monomer-solvent mixtures (186) and was followed over a period of 20 days (85, 186). These post-irradiation effects resulted in continuous decrease in cellulose viscosity (26, 85) and an increase in graft yield (85) with time from date of

---

\(^1\) Electron paramagnetic resonance spectrometry is based on resonance absorption of electro-magnetic energy by unpaired electrons in substances exposed to an external magnetic field. Since free radicals are characterized by the presence of one or more unpaired electrons they are expected to exhibit electron paramagnetic resonance absorption (76, 186).
irradiation. Similar observations were made by Majumdar and Rapson (150). The rapid decay of free radicals observed on admitting air to the irradiated sample is due to oxygen which acts as a radical scavenger (186).

Figure 1. Free radical concentrations in irradiated wood and wood products. Decay at 25°C. Radiation dosage ca. 10 Mrad (186).
The chemical reactions and rearrangements which take place after initial ionization and excitation are dependent on the physical structure of the irradiated material (26). With polymeric materials, irradiated in the solid state, the radicals and excited molecules are relatively immobilized and cannot readily interact with other activated species by simple collision as in gaseous and liquid states. Equilibrium is attained by interaction with other activated species that have close enough proximity through intramolecular rearrangement, energy transfer interactions with more mobile molecules or by activated species initially present or produced by irradiation (150).

The understanding of energy transfer in polymeric systems still poses some problems. Mechanisms that have been proposed are similar to those observed in gaseous and liquid systems (29, 149). These mechanisms describe energy transfer primarily as an electronic excitation (149) of photons
originating from recombination of ejected electrons with ions in the system (22, 29, 47). The main evidence pointing towards an excitation transfer of energy is scintillation of fluorescent solutes in non-fluorescing solvents under radiation (120).

Intermolecular transfer of radiation-induced ionization energy has also been observed in condensed systems (120, 235). Some organic and organo-metallic compounds are capable of exerting a protective effect, as well as a retarding effect on degradation sensitive compounds. Thus aromatic compounds have been shown to be much more stable than cyclic hydrocarbons (such as cyclohexane) towards radiolysis effects (31, 41, 120, 235). The aromatic ring was observed to absorb without chemical change not only the energy it received directly, but also that which was intermolecularly transferred to it. Aromatic rings tend to stabilize the molecule with a resulting low efficiency of radical production (41). In such compounds most of the energy is transferred into the benzene ring as a whole without residence at any one bond long enough to break it (41). This direct intermolecular energy transfer should be at least followed by an equally powerful intramolecular effect and thereby effectively protect more susceptible molecules from degradation. Thus, aromatic rings attached to polymer chains may increase the resistance to radiation damage by serving as "energy sinks", i.e., they draw energy away from more radiosensitive bonds and dissipate it non-destructively. The protective effects of some benzene-ring compounds as compared to some simple hydrocarbons and their halogen derivatives are demonstrated in Table I (29).
The striking effect of electronegative halogen substituents is also evident. Such protective aromatic compounds were found to exert effects similar to anti-oxidants (8).

Table I. Production of free radicals by gamma irradiation of organic liquids (29).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Free radicals produced per 100 ev.</th>
<th>Energy Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>1.6</td>
<td>2.8</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>6.3</td>
<td>11.0</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>9.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>17.3</td>
<td>26.0</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>9.9</td>
<td>17.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>14.3</td>
<td>24.5</td>
</tr>
<tr>
<td>Dioxane</td>
<td>20.0</td>
<td>34.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>24.0</td>
<td>41.5</td>
</tr>
<tr>
<td>Propanol</td>
<td>30.0</td>
<td>51.5</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>33.0</td>
<td>57.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>50.0</td>
<td>87.0</td>
</tr>
<tr>
<td>Ethyl bromide</td>
<td>28.0</td>
<td>39.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>59.5</td>
<td>88.4</td>
</tr>
</tbody>
</table>

In the copolymer system of butadiene and styrene (235) the styrene not only absorbed the radiation energy that it received directly, but
was able to absorb and dissipate non-destructively the energy transferred to it from neighboring butadiene units. In physical mixtures, the styrene was found to dissipate harmlessly the energy it received, but since no energy transfer was possible butadiene degradation and cross-linking was evident. The styrene units in physical mixtures can protect butadiene only by decreasing the gross amount of incident radiation energy. This implies that a protective agent must be an integral part of, or possibly in homogeneous solution with, the polymer chains to exert protective effects (8, 235). Such a situation may or may not exist or may exist only to a limited extent in ligno-cellulosics.

3. Degradation versus Cross-Linking of Polymers

The effects of radiation on a single polymeric system are usually realized in two types of reactions:

1. scission of the molecular chain resulting in degradation, i.e., decreased average molecular weight, and increased solubility in solvents; and

2. cross-linking of polymer chains to form an insoluble network.

Both processes have been found to occur simultaneously in such a system; the initial effect being ionic and covalent bond breaking. The resulting radicals can react then in a number of ways. Reactions of degradation (depolymerization) and cross-linking are characteristic of particular polymers. It has been shown, for instance, that while polyethylene mainly undergoes cross-linking (186), pure cellulose is severely depolymerized (84, 182). Vinyl polymers bearing alpha substituents (such as CH₃, Cl, etc.)
instead of alpha hydrogens undergo scission on irradiation. This effect is believed to be due to steric strains which weaken the carbon-carbon bond of the main chain. Wall (225) also related low heats of polymerization of certain compounds to predominant scission reactions. However, present explanations of these phenomena are not satisfactory. Mechanisms such as rearrangement in the presence of alpha-methyl groups to double bonds and factors involving relative tendency of radicals to produce chain scission are described in the literature (225). It has been shown, however, that the presence of oxygen tends to encourage scission (26, 150) and certain polymers may show predominant scission or cross-linking depending on whether oxygen is present or absent (29, 103, 186, 222).

The possibility of cross-linking between long-chain polymers by chemical means offers many interesting possibilities. In the first place, it provides means for producing materials with any required degree of cross-linking. This can be accomplished in many cases without heat treatment, which might affect other properties of the materials (such as strength and color), and without the introduction of foreign atoms (139). Since the mechanism of cross-linking is quite different from that realised in conventional chemistry (49) a wide range of new plastics can be cross-linked. The method also allows mechanical and physical properties to be studied as functions of the degree of cross-linking.

Occurrence of cross-linking is usually attributed to the formation of polymer radicals on adjacent sites of neighboring chains (22, 29, 49). If the radicals are produced at random sites, close radical pairs do not occur often enough to account for any observable cross-linking. Reactions
accompanying cross-linking and also of chain scission are mainly the splitting off of hydrogen, methane, ethane, carbon monoxide and carbon dioxide, in increasing order. Consequently, cross-linkages apparently form between neighboring chains with elimination in homopolymerization (47). The amount of elimination products formed are not always indicative of the number of cross-linkages formed but may arise also from double bond formation, a less common result of irradiation (139).

4. Fundamentals of Radiation Grafting

In recent years considerable attention has been given to modification of synthetic and natural high-polymers by combining polymeric side-chains with the main polymer under various conditions to form graft copolymers. Grafting is a special reaction of cross-link formation between an already existing polymeric structure and specially positioned reactive monomer (34, 153).

Irradiation grafting of polymers may be divided into two broad classifications (153):

A. Simultaneous irradiation or mutual technique, in which the substrate to be grafted upon is impregnated with the monomer followed by irradiation. The chemical reaction is said to rely on chain transfer mechanisms (202). Success of such radiation polymerization is dependent on the number of strong chain transferring active groups which in turn are activated by free radicals (230). In addition to complete compatibility of such systems, sufficient polar interaction between the free radicals and monomer active centers is required. Further, negligible chain transfer
resulting in the formation of a homopolymer must be assumed (230).

B. Pre-irradiation of the substrate, whereby free radical type centers are planted on the existing polymeric system and the monomer is impregnated after pre-activation (202, 226, 230).

Normal copolymers of two or more monomers can be linear or branched (153) and the original chemical entities may be combined in either regular or irregular fashion. In the latter case, the components are intimately mixed in the copolymer molecule without a particular systematic order. The resulting polymer properties, therefore, are weighted averages of the properties of the polymeric components (49, 119, 153). In systems where uniform chemical components exist in larger stretches or segments, block copolymers are obtained. Alternate positions of polymeric components with only a secondary degree of lateral bonding result in linear copolymers.

It was observed (230) that with polymers which predominantly cross-link on irradiation, a monomer (usually of the vinyl type) adds to active centers before they can combine to form cross-links. In polymers that mainly undergo degradation, the monomer may add to broken chain ends and thereby form block copolymers. Alternatively, radicals formed by elimination reactions of atoms or side-groups may add monomers and form graft copolymers. Disruption of side-chain radicals, in the absence of monomer, is possible. This provides chain scissions.

Most early studies of grafting induced by high-energy radiation included determination of weight gains after thorough homopolymer extraction (13, 85, 103, 150, 230), as well as measurement of mechanical strength increase (38, 69, 79, 103, 148, 185, 202, 238). These have been used as
measures of apparent grafting rate, leaving open the question of relative amount of true covalent grafting and caged homopolymer. In other cases (13, 38, 84, 185, 230, 238), changed solubility characteristics of the basic polymer have been accepted as evidence for extent of graft copolymerization. Most often, however, solubility differences between graft copolymers and homopolymers are not large enough to allow adequate separation. Therefore, exact amounts and composition of such copolymers are infrequently known. This is a serious limitation, since many graft polymers are produced by heterogeneous reactions and reactions such as chain transfer, where considerable homopolymer formation can be anticipated (238). This is particularly true of methods where the degree of grafting is obtained from the increase in weight after homopolymer extraction. In particular, the proportion of original polymeric substrate possessing grafted side-chains is not known at all. Furthermore, difficulty in removing the occluded homopolymer leads at best to only a maximum figure for the amount of grafting. Such lack of knowledge has prevented the establishment of any accurate picture on kinetics and mechanism of grafting.

Most grafting methods yield products that are mixtures of graft and homopolymer (84, 85, 103, 119, 150, 226, 238). In many cases the number average graft yields are low because only a limited number of often relatively long side-chains is attached to the backbone of the pre-existing polymer (13, 84, 119, 153, 215, 230, 238). Molecular weight of the side-chain is always many times larger than that of the homopolymer concurrently produced in the monomer solution (215). Such is the case with heterogeneous systems (84, 215, 230, 238) as explained by gel effects.
The yield of graft copolymer increases steadily with radiation dosage, but decreases at higher dose rates. Due to the diffusion controlled growth mechanism, grafting rates at high dose rates are never as high as those with lower dosages (215). This latter effect is probably due to decreased availability of monomer molecules in the immediate neighborhood of active sites of growing chains. If the dose rate is high, sufficient monomer cannot diffuse into the interior of the polymer and termination of active radicals occurs without copolymerization. However, by increased swelling of the parent polymer and with appropriate solvents at fixed parent polymer thicknesses, penetration becomes less of a problem, and, thereby, grafting rate can be increased with simultaneous reduction in graft molecular weight (215). At low dose rates, on the other hand, no thickness effects should be observed. However, the presence of wetting agents still remains a prerequisite for successful grafting (84, 103, 186, 238). Long and Thompson (136) observed that the rate of organic vapour diffusion into plasticized hydrophilic films was faster than into non-plasticized films. This effect is believed to be caused by the breaking of hydrogen bonds with water, or any good swelling agent for that matter, thus providing greater segment mobility of the polymer molecules and facilitating improved diffusion of monomers. Enhancement of diffusion by swelling occurs even in systems where the penetrant molecules are not miscible with the swelling agent (85). Huang and Rapson (85) attribute the indirect effects of solvents on radiochemical graft yields to the interaction of solvent with both the monomer and parent polymer to increase the accessibility of activated sites to the monomer.

Per cent homopolymerization in heterogeneous systems was found
to increase almost linearly with irradiation dosage, irrespective of whether or not simultaneous or post-irradiation grafting techniques were used in the presence or absence of a suitable swelling agent (150). Homopolymerization also increased with increasing graft yield, possibly due to the fact that free radicals are produced in pairs; one fixed and one mobile. Each of these two free radicals may initiate polymerization. The fixed free radical initiates grafting (or chain scission in the absence of monomer), whereas the mobile one causes homopolymerization.

In case of short-lived free radicals incapable of polymerization, Dalton et al. (54) reported marked increase in polymerization by addition of some solids capable of trapping electrons. A study of the mechanism suggests that in the absence of additive no polymerization could occur. Apparently, the surface area of such catalysts is of great importance (29).

From the foregoing sections it should be understood, that all three major effects of irradiation, namely chain scission, cross-linking and grafting accompanied by homopolymerization, are simultaneous radiochemical reactions. Predominance of any one, or their combination, is mainly dependent on conditions of irradiation and is thereby subject to some control.
IV. EFFECT OF IONIZING RADIATION ON THE PHYSICAL AND CHEMICAL PROPERTIES OF WOOD AND WOOD HIGH POLYMERS

Much work has been reported on use of high speed electron and gamma-radiation from $^{60}$Co sources as polymerization initiator for cross-linking (38, 47, 124, 125, 127, 184, 235), grafting reactions (13, 76, 84, 85, 103, 119, 153, 186, 202, 203, 223, 226, 230, 238) and as means of random depolymerization for cellulosic wood materials (86, 165). In this early stage of investigation, most published works have been concerned with changes in mechanical and physical properties as measured at room temperature. A wide variety of miscellaneous wood-polymer combinations have been also investigated on a semiquantitative basis with little attempt to study the chemical processes that take place. Due to large difficulties still existing in lignin chemistry, most chemistry studies on irradiated wood deal with the carbohydrate fraction, whereas works on lignin are scarce and highly speculative in nature. Similarly, much has been done with wood and cellulose behavior in graft copolymerization, but little is known about reaction with the lignin constituent alone.

1. Effects with Wood

Investigations on wood exposed to the action of ionizing radiation show collectively degradation with little cross-linking, especially following high dosage irradiation (21, 39, 70, 70/b, 123, 124, 183, 200). At
high dosage levels (above $10^6$ rad) the radiation induced degradation seems to be independent of dosage rate. Garnett and Merewether (71) reported chemical changes in irradiated wood following $10^7$ rad treatment which showed an increase in phenolic hydroxyls and degraded carbohydrate bonds. A strength decrease in wood compression and impact bending for pine, spruce and beech wood was reported by Becker and Burmester (21) when the wood was exposed to $10^7$ rad dosage. Tensile and compression strength tests of irradiated woods gave similar results, as demonstrated by Ifju (86) and Burmester (39), respectively. A marked reduction in toughness was reported by Loos (138) above $10^6$ rad dosage. Kenaga and Cowling (102) reported only slightly increased hygroscopicity following $4 \times 10^7$ rad dosage, although the total amount of absorbed water was practically the same as had with non-irradiated wood. Further to changes in physical and mechanical properties a slight darkening of wood and embrittlement accompanied by characteristic odor may be observed after irradiation to $10^7$ rad dosage (183). Such embrittlement becomes more obvious when irradiation is followed by swelling (69), mechanical disintegration or ultrasonic beating (183). Similarly, the decay resistance of wood was found to be decreased only by irradiation dosages larger than $3.2 \times 10^5$ rad as reported by Scheffer (196). Finally, wood exposed to high dosage irradiation was more susceptible to acid hydrolysis as evidenced by higher sugar yield on fermentation of irradiated sawdust (165).

Low dosage irradiation, on the other hand, has been found to be beneficial to some mechanical and physical wood properties. Though strength increases were not always statistically significant (21) they were characteristic. A slight initial strength increase was found for impact bending,
compression, tensile strength parallel and perpendicular to grain and
toughness as reported by Becker and Burmester (21) and Burmester (39) for
pine, spruce and beech and by Kenaga and Cowling (102) for ponderosa pine.
With increase of irradiation dosage tensile strength showed the first sign
of deterioration, whereas compression strength was relatively unaffected
(39). Hygroscopicity and swelling characteristics of wood varied only
slightly (102). Such effects may be eventually explained by different
radiosusceptibility of the various wood constituents controlling these wood
properties.

2. Effects with Isolated Wood Carbohydrate Fractions

The earlier investigations of Lawton and co-workers (123, 124,
200) on irradiated wood and cellulose showed that the net effect of
irradiation is degradation of the wood substance (11,201), especially the hemi-
cellulose and cellulose. Extent of degradation was almost directly
proportional to the irradiation dosage for the cellulose portion, increasing
substantially above $10^6$ rad dosage (27, 48, 76, 86, 100, 180, 183, 200).

Since resistance of wood to dilute acid hydrolysis is consider-
ably diminished by radiolytic disturbance of the cellulose macro-
molecule, the solubility of wood polysaccharides increases with increasing
dose rates. Apparently hemicellulose is more affected than cellulose
(70/b, 165). With dosages above 1 Mrad severe degradation of hemicellulose
and cellulose occurs and at $2 \times 10^8$ rad dosage water soluble cellulose is
obtained. Such degradation mainly affects 1,4-beta-glucosyl bonds (139).
The soluble portion is made up of mono-, di-, and oligosaccharides in addition to acids. Large quantities of gases (hydrogen, carbon monoxide and carbon dioxide) are also evolved during treatment. Freidin and co-workers (70, 70/b) studied the degradation products of wood cellulose, lignin-free hemicellulose, dioxane lignin and lignin preparations. An irradiation dosage from zero to 500 Mrad (with an average dose rate of 0.7-0.9 Mrad per hour) increased iodine number of inverted hemicelluloses from 10.6 to 78.0%, cellulose solubility in NaOH from 4.1 to 36.2% and that of cotton cellulose from 0.0 to 50.8%. All components of the lignin-carbohydrate complex were found to be subject to changes on radiolysis, but greatest change occurred in the hemicellulose. Lignin elemental composition was changed (C=62.3, H= 5.95, OCH$_3$=14.26% vs. C=61.05, H- 5.83, OCH$_3$=13.35%) by 200 Mrad dosage. Dioxane lignin showed slight loss in methoxyl (OCH$_3$=12.7% vs. 11.5% at 500 Mrad). The largest volume of gas was collected from the cotton cellulose sample (2.42 ml/100 g), followed by the lignin-free hemicellulose (1.2 ml/100 g) and wood (0.99 ml/100 g). Thereby, it could be shown that degrading effects of equivalent irradiation dosages were somewhat lower for the wood cellulose than for pure cotton cellulose. Glegg and Kertesz (76) have reported that moisture content has no significant effect on cellulose degradation at comparable irradiation dosages. At 0.3% moisture content cellulose was shown at least as susceptible to degradation as at higher moisture content. Cotton samples with excess water gave the same degree of degradation as the sample with only 3.5% moisture content. This is in line with expectations regarding aqueous solutions and the large ability of water to capture electrons, as shown by Magee (149). Thereby, it was concluded
that water did not accentuate cellulose degradation by irradiation.

Lawton and co-workers (200) carried out tests to determine the effect of high-energy, high-intensity radiation (0.14 Mrad/sec) on pure cellulose. They found little degradation below $10^5$ rad, but a considerable effect above $10^6$ rad and complete degradation to water soluble materials at $2 \times 10^8$ rad irradiation dosage. Irradiation of dry methyl cellulose by Arthur and co-workers (28) produced a decrease in its specific viscosity. In aqueous solutions of methyl cellulose insoluble gels were obtained with concommittant loss of methoxyl content. The gel formation in aqueous solution was said to be due to cross-linking in the irradiated material.

Cotton and wood cellulose is a unique polymeric species. It consists of long linear chains which pass through highly crystalline and amorphous regions (157). The crystalline regions of cellulose are almost impermeable to liquids and even to gases (36). Temperature elevation usually does not improve chain mobility. These properties of cellulose are a result of linear closely packed chains, a steric requirement of the basic building units and especially of strong hydrogen bonding between hydroxyl groups of neighboring chains that are in perfect alignment (36, 86, 234). Due to reduced accessibility imparted by such high molecular order, chemical attack on the bulk of the cellulosic material is restricted to the surface of crystallites and the more accessible amorphous regions (85, 165). The chemical reactivity of cellulose can be greatly enhanced by extensive modification of its crystalline fine structure through some chemical or physical pre-treatment (84, 127, 165, 182).

The penetrating power of high-energy radiation is not influenced
by the crystalline-amorphous nature of the cellulose (26). Each anhydroglucose unit has an equal probability of being ionized. Indeed, free radical activity was shown in both grafted and non-grafted cellulose long after irradiation by comparative ESR spectra as evidence of ionization and trapped free radicals (76, 186). The nature of changes that take place in cellulose after high-energy irradiation are dependent upon the particular carbon atom ionized, or the particular carbon atom to which the ionized atom is bound; the chemical nature or position of the carbon atom in the basic unit with regard to its substituents (primary or secondary hydroxyls, potential aldehyde group); or the atmosphere during irradiation (26). Description of mechanisms in cellulose irradiation chemistry requires consideration of both chemical and physical properties of the cellulose material, as well as features of the irradiation treatment itself.

Free radicals form in both amorphous and crystalline cellulose areas (76, 186). Exposure to oxygen produces free radical dissipation in the more accessible regions. Interaction of free radicals with oxygen results in chain cleavage (26, 28, 84, 182). Irradiation in a nitrogen atmosphere slightly reduced the extent of degradation at low dosage levels (182), indicating that oxygen is involved only in a secondary process. Free radical concentrations as estimated from post-irradiation changes in cellulose viscosity (84, 186) and ESR spectra were shown to decrease rapidly within the first 4 to 5 hr but were considerable even after 20 days. Such post-irradiation changes in viscosity were not accompanied by strength loss (26), indicating that even though post-irradiation cleavage of cellulose does take place on exposure to air, no product deterioration would be
expected following radiation dosage levels studied.

No post-irradiation changes in viscosity were observed with pure cotton (12, 26) or methyl celluloses (28) as compared to those found with wood cellulose itself. Long-lived free radicals were also detected in the above two cellulose species (186). These results suggest that energy dissipation occurred via another mechanism in these systems. Indeed, a loss in yield of acid and carbonyl groups was observed with irradiated methyl cellulose.

Cellulose and its derivatives are polymers which are degraded by direct irradiation and cross-linked under suitable conditions (126). Degradation proceeds at a well defined rate by a series of dehydration mechanisms (165). The process results in a random degradation and affects both the crystalline and amorphous regions (26, 69, 85, 177, 182). An almost linear relationship was obtained when cellulose degree of polymerization (DP) was plotted against irradiation dosage, as reported by Huang and Rapson (84), and shown in Table II and Fig. 3.

Such data support the work of Blouin and Arthur (23) showing that cellulose degradation is a function of total radiation dosage, but is independent of the source intensity (84). At high intensity a larger proportion of primary radicals is formed (84) which favour cross-termination rather than polymerization or degradation. Such cross-termination results in cross-linkages, a closer coherence of the fragmented cellulose chains. Due to close packing within ordered regions of the cellulose it is suggested (177) that cross-linking occurs only in the amorphous cellulose. Thereby, dissolution on hydrolysis or solvolysis will occur primarily in regions
Table II. Degradation of cellulose by gamma-irradiation (84).

<table>
<thead>
<tr>
<th>Total radiation dose, x 10^{-6} r</th>
<th>Intrinsic viscosity (CED), ([\eta]), 100 ml/g</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.10</td>
<td>1676</td>
</tr>
<tr>
<td>0.1</td>
<td>8.45</td>
<td>1252</td>
</tr>
<tr>
<td>0.5</td>
<td>5.78</td>
<td>823</td>
</tr>
<tr>
<td>1.0</td>
<td>4.06</td>
<td>557</td>
</tr>
<tr>
<td>2.0</td>
<td>2.92</td>
<td>387</td>
</tr>
<tr>
<td>5.0</td>
<td>1.82</td>
<td>202</td>
</tr>
<tr>
<td>10.0</td>
<td>0.98</td>
<td>116</td>
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<tr>
<td>50.0</td>
<td>0.33</td>
<td>35</td>
</tr>
<tr>
<td>100.0</td>
<td>0.18</td>
<td>18</td>
</tr>
</tbody>
</table>

Figure 3. Degradation of cellulose by gamma-irradiation (\(60^{th}\)Co source central intensity 1.3 x 10^6 r/hr) (84).
free of cross-linkages and if these are the crystalline regions (183) an amorphous cellulose should result. Indeed, it has been shown by x-ray diffraction patterns (177) that mainly the crystalline portions are rendered soluble after irradiation cross-linking of regenerated cellulose as evidenced by absence of diffraction arcs. It was shown (177), however, that the stable radicals formed in cellulose by high-energy radiation are located in the highly ordered or crystalline portion of the material. Extraction with cuprammonium hydroxide removed all free radicals. This demonstrates the selective removal of ordered regions of cellulose following irradiation. Such preferential attack on ordered regions is a different effect than obtained by other means such as hydrolytic and enzymatic reagents.

High energy irradiation of cellulose has been reported as producing an effect similar to oxidative degradation (28). The result is extensive depolymerization at high irradiation dosage levels with introduction of carboxyl and carbonyl groups (26, 28, 84). Initiation or ionization occurs either at or on C₁ and C₄ positions in the anhydroglucose unit (28, 139) resulting in chain cleavage when the C₁ position is affected. On cleavage, 2-keto-gluconic acid is formed on the reducing end by utilizing one mole of oxygen. An unaltered glucose unit is left on the other end of the chain. Interaction at C₄ results in chain cleavage and liberation of the reducing end of the chain as an unaltered glucose unit by producing a ketone group in the C₄ position on the non-reducing end of the molecule. Thereby, only one-half mole of oxygen is consumed. Activation of other carbon atoms than C₁ and C₄ (C₂, C₃, C₅ and C₆) of the anhydroglucose unit yields hydrogen and new reducing groups, either ketones or aldehydes (28).
The actual loss of molecular weight has been found to be less than the apparent degradation as indicated by end-group analysis methods. By comparison it was shown that $2 \times 10^{18}$ radicals are formed per gram of cellulose substance (186) which is approximately 1 to 2 free radicals per cellulose molecular unit (assuming a DP of 1500 to 3000). This suggests that the unpaired electron location is at the end of the molecule. Indeed, with up to $6 \times 10^7$ rep dosage there are on the average 2.1 end groups formed per ion pair. Thus the end result of each ionization, wherever it occurs in the molecule, is production of two end-groups (182). In dextrin, with further degradation during irradiation an increase in branching was observed. For a twenty fold decrease in molecular weight the branching per molecule dropped only by a factor of two, suggesting that all the branch points are probably tetra-functional (182). Out of the five ion pairs produced by irradiation, one provides a tetrafunctional branch, 1.1 provide a break in the chain and the rest lead to rupture in the D-glucose ring without occurrence of either degradation or eventual branching.

3. Effects with Wood Aromatic Compounds and Radio-protection of Polymeric Carbohydrates

Findings of Alexander and Charlesby (204), Arthur and Mares (15), Freidin, et al. (70/b), Lueck and Dell (139), Manion and Burton (152) and Smith and Mixer (204) show that there is evidence for radio-protection of carbohydrates in mixtures with aromatic ring containing compounds. Aromatic groups are reported to exert a protective effect by intermolecular energy transfer mechanisms, and by acting as energy dissipators or "energy sinks".

In the radiation chemistry of solid matter, energy transfer
effects depend on the mechanism of energy loss to molecules by incident radiation, the initial random non-localized energy deposition within the molecule and finally on the rapid rate of energy localization within the molecule (15). Energy localization within the molecule results in chemical changes such as dehydrogenation (165), activation by long-lived exited sites (186), degradation of the molecule or depolymerization (84). Time required for this presumed localization process was estimated as not exceeding $10^{-13}$ sec (40). Furthermore, it has been suggested by Burton (40) that the effects of non-localized high-energy depositions can extend over distances ranging to 100 Å.

Inter- and intramolecular transfers of energy in the localization process with carbohydrates has been shown to depend on physical structure, complex formation with other molecules and chemical substitution of molecules (181, 182). Arthur and Mares (15) investigated the protective effects by benzoylation of cotton cellulose to various levels of substitution. Effective radio-protection was observed even at very low substitution levels and low irradiation dosages. However, at the higher dosage level ($1.3 \times 10^{21}$ e.v./g) the radio-protection was negligible. At an intermediate degree of substitution (D.S.1.1) much greater radio-protection was obtained. Further evidence for radio-protection was obtained by comparing ESR spectra of substituted and non-substituted irradiated samples. With increasing degree of substitution of benzoyl groups, the relative signal strength of spectra from irradiated samples decreased. On enlarged attenuation of the resonance spectra of highly substituted (D.S. 1.5) samples it was found that the spectrum structure was similar to that had with irradiated purified cellulose. This similarity of spectra suggests that although benzoyl groups radio-protect
cellulose to a considerable extent, the localization of non-dissipated radiation induced resonance in the cellulose molecule is not substantially altered on substitution. It is demonstrated, that the relative free radical concentration of irradiated benzoylated cellulose diminishes rapidly at even low degree of substitution and reaches a constant value at D.S. 1.0 to 1.1. Thereby, the loss of free radicals in benzoylated cellulose is responsible for the higher strength retention following irradiation.

By assuming that benzoyl groups are randomly distributed on the cellulose backbone and each hydroxyl group is equally accessible for reaction, the minimum distance between benzoyl groups along the cellulose molecule can be calculated as a function of degree of substitution. Such calculations by Arthur and Mares (15) are presented in Table III.

The effect of gamma irradiation on the calculated distance between molecular cleavages or viscosity of benzoylated cellulose as a function of degree of substitution is presented in Fig. 4 (15).

Molecular weight values were obtained from changes in breaking strength on the assumption that the breaking strength of purified cotton cellulose decreases linearly with increasing number of molecular cleavages. At a dosage of $1.3 \times 10^{21}$ e.v./g cellulose the retention of breaking strength of irradiated substituted cellulose (D.S. 1.1 to 1.50) was as high as 60%. The corresponding calculated spacing of benzoylated groups was 10 to 20 Å. At the same irradiation dosage the average estimated distance between molecular cleavages was increased from about 50 cellobiose units or $515\text{Å}$ (one cellobiose unit in cotton is about $10.3\text{Å}$ in length (76)) for unsubstituted cellulose to about 300 cellobiose units ($3400\text{Å}$) for benzoylated...
cellulose (D.S. 2.0). Apparently, the intramolecular energy transfer can be affected by the presence of benzoyl groups at least several cellobiose units away from the place of initial energy deposition.

Table III. Calculated maximum distance between benzoyl groups as a function of degree of substitution\(^a\) (15).

<table>
<thead>
<tr>
<th>Degree of substitution (^b)</th>
<th>Maximum number of cellobiose units per benzoyl group</th>
<th>Maximum distance between benzoyl groups, Å(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>0.2</td>
<td>7-8</td>
<td>72-82</td>
</tr>
<tr>
<td>0.5</td>
<td>3-4</td>
<td>31-41</td>
</tr>
<tr>
<td>1.1</td>
<td>1-2</td>
<td>10-21</td>
</tr>
<tr>
<td>1.5</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2.0</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^a\) Calculated as a binomial distribution of benzoyl groups with a probability of reaction \(\geq 0.95\).

\(^b\) Assuming that benzoyl groups are randomly substituted on the cellulose molecule and that each hydroxyl group is equally accessible for reaction.

\(^c\) In an experimental case for the same level of probability of reaction the maximum distance between benzoyl groups will be greater than that assumed in case b.
Indications for radio-protection were also found for wood cellulose, although the extent is not exactly known. Freidin and co-workers (70/b) reported a protective effect of lignin over cellulose when wood cellulose and cotton cellulose solubilities were compared following severe degradation. While sodium hydroxyde solubility of wood cellulose increased from 4.1 to 36.2% after exposure to dosages of zero to 500 Mrad, the same dosage increased the solubility of purified cellulose from zero to 50.8%. This represents nearly 16% difference in solubility of cotton cellulose. Similar effects of lignin protecting of cellulose were observed by Smith and Mixer (204) and Seifert (201).

Comparable strength values and appropriate DP values were presented by Ifju (86) and are summarized in Table IV.
It is rather interesting to note that although DP retention was the same for both wood zones, latewood strength retention was higher (86). This is in a way contradictory to some earlier discussions on mechanism of cellulose degradation and radio-protection by lignin. By accepting the findings of Wu (236) that earlywood contains on a weight basis more lignin than latewood (2-3%) a reversed effect would be expected. It is not known, however, whether integral radiation dosages were calculated on the basis of apparent wood weight of growth zone samples or by some conventional dosimetry. Therefore, based on actual rad/g wood substance basis (or available cellulose substance basis) the earlywood sections may have received much larger radiation dosages than indicated. A factor of 2.5 to 3 (ratio of latewood-earlywood specific gravity) could be easily applied. In light of such considerations an improvement in earlywood DP and strength retention could be expected, but it is not known at this time whether or not any precautions were made during irradiation to compensate for the higher specific gravity of latewood. In view of this fact no valid conclusions could be drawn from the data presented above. On the other hand, Butler (42) showed that specific gravity had a marked effect on tensile
strength loss of wood after irradiation. High specific gravity sections were more severely degraded.

Rollins and co-workers (184) reported on an interesting phenomena which is directly related to resistance of lignin against radiolytic degradation and possibly radio-protection on cellulose. Upon exposure of thin wood cross-sections to high irradiation dosage (1.5x10^8 rad) and rinsing the irradiated wood sections with water on a microscope slide, the secondary walls were found to dissolve completely, although the primary wall remained intact. This apparent resistance of the primary wall was attributed to the high concentration of non-cellulosic materials, such as lignin, which were not converted to water-soluble products on irradiation.
V. INFLUENCE OF RADIATION ON ORGANIC HYDROCARBON POLYMERS

Irradiation of organic hydrocarbons has been extensively studied by researchers of the petroleum and food processing industries. Their findings are mainly available in the patent literature through descriptions of the effects noted which rarely treat the basic phenomena.

Irradiation of polyethylene predominantly causes cross-linking as found by Charlesby (50), Lawton et al. (124) and Little (135). Such products show rubber-like elasticity when heated, and reduction of weight due to hydrogen loss.

Cross-linking in n-paraffins was investigated by Charlesby (49). He found that the critical dosage varied inversely with increase in molecular weight. On irradiation of hydrocarbons the composition of gases evolved was shown to be approximately 98% hydrogen with the remaining 2% made up of methane, ethane, propane and butane (49). These volatiles are not taken as evidence of direct chain scission, but rather as originating from scission of chain ends and branch ends. This has little effect on mechanical properties or solubility of the resultant polymers (29).

Unsaturation in certain hydrocarbons has been found to disappear at about 15 to 20 Mrad dosage. Measurements made on saturation rates indicate rapid and preferential reaction at the unsaturated centers (133, 163).

Poly-isobutylene (used as source for polymers and copolymers) has a marked tendency to undergo thermal degradation by "unzipping" to the monomer level (29). This is due to the steric strain within the molecule as
reflected by the low heat of polymerization (10 to 13 Kcal/mole of monomer). Because of such low main chain bond strength, poly-isobutylene mainly undergoes scission when subjected to ionizing radiation (124).

Polystyrene, predominantly a straight chain polymer, is preferentially cross-linked by gamma-radiation in absence of oxygen (8, 103, 119, 153). The efficiency of cross-linking is low because of the protective effect exerted by the aromatic ring (8, 31, 41).

The effect of radiation on natural rubber and synthetic diolefins (diene polymers and copolymers) has been subject to much study. It is clear that the effect is predominantly cross-linking unless the proportion of olefin is very low (222, 237).

Heisig (81, 82) found that irradiation of aliphatic, alicyclic and olefinic hydrocarbons with double bonds produced good yields of polymeric products. Polymer yields in reactions initiated by gamma-irradiation were found to depend largely on pressure applied for duration of the irradiation treatment (133). Gas yields were considerably lower than from polyethylene, probably due to enhanced reactivity at double bonds combined with a general protection of all other possible sites for cross-linking reactions. The sites of cross-linking have not been determined as yet.

According to Kuzminsky and co-workers as cited by Turner (222), unsaturated compounds undergo marked changes on irradiation. Natural rubber was reported to have lost 50% of its unsaturation following an irradiation dose of 240 Mrad. Other workers have found this effect relatively small (29).

Protective effects of aromatic compounds in liquid hydrocarbon mixtures were shown by Alexander and Charlesby (8), Manian and Burton (152) and Witt (235).
VI. RADIATION GRAFTING ONTO WOOD AND WOOD CONSTITUENTS

1. Grafting onto Wood

Studies of various mechanical and physical properties of irradiated wood indicate behavior similar to and quite consistent with that of synthetic high polymers, although there appears to be a wide range of dosages where these effects may have been observed. The rather modest improvements in wood properties on irradiation have been shown to be greatly enhanced by forming composites of wood with various vinyl monomers (103). By continued research on wood and polymer composites there are good indications that wood and wood products can be tailored to give desired properties by selecting the type of monomer, degree of impregnation and total exposure to radiation. Wood properties such as dimensional stability (79, 103, 186, 202, 203), water absorption (79, 148), strength (38, 79, 150, 186, 226) and hardness (79, 100) can be improved with high polymer loading and treatment at relatively low irradiation dosages.

As an example, working with whole wood Kenaga et al. (102, 103) impregnated ponderosa pine cross-sections with water-saturated dioxane solutions of styrene and exposed these to $^{60}$Co irradiation. They found that polymer retention increased with dose rate, showing the importance of monomer diffusion to free radical sites in determining rate of graft copolymerization. Thereby, it has been shown that means of proper monomer positioning is very critical in grafting processes.
2. **Grafting onto Cellulose**

One intriguing possibility presented by irradiation grafting is preparation of polymers combining cellulosic properties as base structure with hydrophobic properties of selected vinyl monomers grafted onto the cellulose trunk. A difficult feature in carrying out graft copolymerization of cellulose with monomers is the relative unreactivity of the cellulose chain and difficulty of graft initiation (223). Since modification of the cellulose structure is difficult to characterize, basic structure of many cellulose graft copolymers is largely unknown.

The results of cellulosic high-polymer polymerizations with various vinyl and related monomers by gamma-irradiation has been extensively investigated. Among the graft copolymers which have received detailed attention are those of pure cellulose with styrene (13, 84, 85, 103, 186, 202, 203, 206, 215, 230, 238), methyl methacrylate (103, 127, 185, 186, 226), acrylonitrile (14) and other monomers (2, 42, 178, 226).

When dry cellulose is irradiated in the presence of pure styrene no grafting is observed and only homopolymer has been isolated (84, 150, 202, 203, 206, 215). Chapiro and Stannett (45) reported on polymerizing vinyl monomers with films of polyvinyl alcohol, cellophane and cotton. Irradiation in the dry state led only to surface grafting, whereas considerable grafting depth was achieved only in the presence of water. Huang et al. (14, 84) grafted styrene onto cellulose by using a solvent exchange technique to introduce styrene onto cotton cellulose prior to irradiation.

Huang and Rapson (85) studied the effect of various swelling agents on radiation grafting of styrene onto cellulose. Increased swelling
led to increased diffusion of monomers to reaction sites and resulted in increased amounts of isolated graft yields. Anhydrous swelling agents were also used with success, showing that water is not absolutely necessary. Magee (149) considers the presence of water only from the standpoint of an electron capture medium, whereby secondary effects accompanying irradiation such as degradation are greatly reduced.

Blouin and Arthur (12) reported that radio-chemical yield of styrene graft was zero when pure monomer was used, but was high with a mixture of 98% styrene and 2% methanol. Ternary solutions of styrene, methanol and water were also used with good success (29, 186). Grafting rate determinations of Sobne et al. (206) showed a decrease of graft with increasing amount of methanol and reduced amounts of styrene. Below 60% styrene the polystyrene separated as a precipitate and the cellulose acetate films turned opaque. Number average degree of polymerization was the same for both the grafted copolystyrene and homopolystyrene. The high DP value of polystyrene indicated a reduction in termination rate arising from lowered mobility of propagating polymer radicals in the films. Good graft yields were obtained in the range of 25 to 50% styrene concentration, which may be due to reduction in homopolymerization. According to Blouin and Arthur (12) the indirect effect of solvents in the mutual irradiation technique are probably due to interaction of solvents with both the monomer and activated cellulose to increase accessibility of activated sites to the monomer.

Usmanov and co-workers (223) found that grafting of acrylonitrile with cellulose can be observed only if the solvent for acrylonitrile is a
polar compound. With pure acrylonitrile, formation of a graft copolymer was insignificant although large amounts of homopolyacrylonitrile were formed. In the presence of benzene as solvent no graft polymer was isolated. This is due to the fact, that wettability of cellulose by benzene is small, and thereby benzene evidently does not further penetration of acrylonitrile into the intermolecular spaces of cellulose. It was concluded that graft copolymer formation only takes place in cases where the cellulose is wetted by the acrylonitrile and where the solvent is sorbed by the cellulose.

Some solvents such as methanol and N,N-dimethylformamide were found to increase the efficiency of activation between cotton cellulose and styrene (12, 14).

Direct radiation grafting of styrene onto cellulose is thought to be a heterogeneous reaction (85, 165, 215) in which penetration of the monomer into the fibre is necessary for grafting to occur. The participation of cellulose and its derivatives in grafting is mainly due to low degree of accessibility even on swelling. Normally, it is extremely difficult to follow the changes in cellulose constitution during the radiation grafting process due to complexities introduced by simultaneous homopolymerization. The graft copolymer can be separated from the homopolymer by simple extraction procedures (85, 222, 225, 226). Furthermore, there is an additional solubility difference between the cellulose trunk and graft polymer (230, 238), thus the cellulosic backbone can be hydrolysed away whereby molecular weight and molecular weight distribution curves of the graft copolymer can be obtained (84, 230, 238). This method, however, provides little information about the cellulose trunk itself as it has to be destroyed usually by acid.
hydrolysis, during isolation of the graft side-chain.

It was found that even when most of the polymerization arises by grafting mechanism only a small fraction of the cellulose substrate participates in the grafting process. The reason for this is mainly the inaccessibility of cellulose to the monomer under heterogeneous reaction conditions (84, 230). Many disappointing performances with physical characteristics of graft copolymers are evidently due to gross heterogeneity and to far greater length of the grafted side-chain.

The proof for graft formation has rested upon the fact that the polymer cannot be extracted quantitatively and is usually insoluble in organic solvents (84, 85, 150, 185, 238). One additive feature of graft polymers is that the average molecular weight distribution curve, obtained by fractional precipitation, differs from similar curves determined for physical mixtures (185).

By extracting the graft polymer of acrylonitrile from highly purified paper (Whatman No. 2 filter paper) Putnam (185) observed loss of strength reinforcement obtained on grafting. Since the polymer was extractable, rupture of primary valence forces was assumed. The IR spectra of the graft polyacrylonitrile and homopolyacrylonitrile were identical suggesting that the major portion of the polyacrylonitrile "add-on" was not grafted to the cellulose trunk. Thus, other explanations had to be found for substantial strength reinforcement of the treated paper. The possibility of simple mechanical reinforcement by the intervening polymer resulting from secondary valence forces forming additional hydrogen bonds should be also considered.

The non-linear elasticity of paper in load elongation curves
has been explained as extensible hydrogen bonds by Nissan (169, 170, 171). Non-linearity of the load elongation curve is due to variation of force application with stretching of hydrogen bonds, whereby elastic deformation is then a result of stretching, breaking and reforming of hydrogen bonds.

Runce (187), on the other hand, considers the non-linear nature of the paper elasticity curve as due to progressive strain concentration within the stressed material rather than to non-linear elasticity of the secondary bonds. Therefore, elongation of paper is visualized as the straightening of bent and curved fibres firmly fixed at points of interfibre bonding. Only at conclusion of the straightening process can tensile elongation of the fibre begin. The effect is terminated by rupture of hydrogen bonds linking the fibres to one another.

Simple deposition of a polymer within fibre networks should give linear, non-elastic deformation as viewed by Nissan's fibre model. A similar deposition into Runce's network might cause a small increase in elasticity due to the bending force of the polymer molecules at low loads. But since "frictional" forces must be less than the energy content of available hydrogen bonds, the major contribution would be due to slippage and thereby would be inelastic in character.

Putnam (185) found that grafted and untreated paper deformation was identical and thereby the strength contribution could not be due to slippage. Based on some experimental evidence (log of paper density vs. log of modulus of elasticity giving a straight line) the strength increase was attributed to hydrogen bonding within the paper network.

If polymerization of acrylonitrile in non-swelling solvents
(50 % mixture with ethyl alcohol, acetone and benzene treated at $10^6$ rad dosage) in the presence of cellulose results in secondary bond formation between the polymer and fibre exterior it is difficult to understand reasons for primary bond formation or graft copolymerization within the fibre network. Usmanov et al. (223) showed that degree of cellulose swelling is related to the amount of non-extractable polymer remaining in the cellulose. Intercrystalline swelling of cellulose was shown by Huang and Rapson (85) to take place within the more accessible amorphous regions. Graft polymer formation with acrylonitrile occurs only in those cases where the cellulose is well wetted by the solvent and where the solvent is sorbed by the cellulose.

The amount of styrene graft under proper conditions was found to increase with increasing dose rate (13, 85) even over several days following irradiation. The effect was attributed to slow diffusion of nonpolymerized monomer towards trapped long-lived free radicals (84, 150, 186). At high radiation dosage rates the presence of air appeared to enhance rather than inhibit grafting (14) whereby, in addition to radiation induced free radicals, decomposition of peroxide intermediates may have aided further grafting. It was shown by Huang et al. (84) that despite the large weight ratio of polystyrene grafted to cellulose only one in every 20 cellulose chains had a grafted styrene side-chain, or only one grafted polystyrene side-chain existed per 4,000 to 10,000 anhydroglucose units. Molecular weight of branched chains was approximately 26,000 (84). From the viewpoint of physical properties it may be desirable to produce cellulose graft copolymers having a larger number of grafted branches of lower molecular weight.
Good results could be expected with the pre-irradiation techniques if a polar monomer could be found that is also a good swelling agent for wood (202).

3. Grafting onto Lignin

Little is known about graft polymerization onto lignin either in wood or in isolated form. There is no reason why such systems could not occur. Based on consideration that the lignin macromolecule contains numerous functional groups and potential sites for ionization, shows a three-dimensional random structure (31) and is accessible to various solvent systems (both organic and inorganic) makes it especially suitable for graft copolymerization. It is possibly the great complexity and diversity of reactions that both natural and isolated lignins exhibit that has made chemists retreat from this vast source of natural high-polymer. Lignin is the second largest constituent in wood, and is mostly considered as a contaminant of cellulose requiring separation and disposal.

Attempts to demonstrate the usefulness of lignin in polymerization have been only partially successful. Through mild oxidative treatment with sodium chlorite Paszner and Wilson (179) were able to markedly lower strength reinforcement in oil-tempering of hardboards made from Douglas fir Asplund pulp. Suggestion in this is that lignin quality was most affected and that this factor was responsible for at least 80% of the extra strength through condensation-polymerization with the unsaturated hydrocarbon oil used. In an extended study (178) the curing reaction was induced by gamma-irradiation. This study included high lignin content groundwood paper as a second material
for examination of effects of relatively unmodified lignin on the polymerization mechanism. It was shown that gamma irradiation induced property changes in both types of fibres only to one-half the extent had with thermal polymerization. Description of the mechanism has not been attempted.

Recently Butler (42) attempted in situ graft copolymerization of lignin with CTLA oil polymer as initiated by gamma irradiation. Microtome tangential sections from several species, representing a large specific gravity range (0.2 to 0.7 g/cm³), were saturated with the polymeric oil and irradiated to various dosage levels in anticipation of strength increase. However, no changes occurred in microtensile strength or related work functions -- following either gamma-irradiation or conventional thermal treatment. No explanation for the failure was offered.

Results on separated hydrochloric acid lignin polymerizations by gamma-irradiation with methyl methacrylate, styrene and vinyl acetate were published by Koshijima and Muraki (116, 117). They showed through step by step substitution of the lignin hydroxyl groups that the rate of methyl methacrylate graft polymerization was greatly enhanced when substitution was made on the phenolic hydroxyl group. Benzene, dimethyl sulfoxide and chloroform were used as solvents.

It was found (117) that the yield of graft polymer on lignin was 131% at 10⁵ rad dosage for the lignin sample on which only the phenolic hydroxyl was substituted. A general substitution of all potential hydroxyls reduced the graft to 38%. The lignin-methyl methacrylate copolymer was found to be insoluble in organic solvents. A true graft polymer with lignin was found only with methyl methacrylate at 10⁴ to 10⁵ rad dosage, whereas
vinyl acetate and styrene formed only surface gels and were found unsuitable for grafting with lignin.

On oxidation of lignin methyl methacrylate copolymer with sodium chlorite (116), the graft polymer was isolated without degradation. The average molecular weight of the side-chain was larger than that of the homopolymer. Based on the assumption that molecular weight of hydrochloric acid lignin is approximately the same as that of sulphonic acid lignin (i.e., 10,000 to 120,000) the graft polymer molecular weight was at least 10 to 100 time that of the trunk polymer. Through degradation of the branch polymer it was shown that the polymethyl methacrylate was a true graft polymer to lignin.

4. Summary Section

Recognition of potential in graft copolymerization procedures has resulted in two major contracts originating from the U.S. Atomic Energy Commission to make radiation processed composites of wood and plastics (1). Difficulties experienced with efficiency of irradiation induced grafting to cellulose and lignin prompts further research for clarification of basic reaction mechanisms. The need for such studies is well demonstrated by the fact that explanations of most failures cannot be demonstrated experimentally and, thereby, remain only ad hoc assumptions without real value to further studies.
The fact that free radicals have been shown to exist in irradiated wood and isolated wood constituents is encouraging. A next step in successful application of radiation treatments is to find ways for maximizing use of these available reactive sites.

It is interesting to note that potential with the lignin component of wood has been little studied, although the presence of lignin free radicals has been shown by Ramalingam et al. (186) through careful examination of ESR spectra from irradiated wood, as well as periodate, dioxane and Brauns' native lignins. Lignin has been observed to yield a free radical spectrum on irradiation which has not been specifically identified.
MATERIALS AND METHODS

It was desirable to include both a wide quantitative range of lignin, as well as nominally different (modified) lignins in the fibre materials under study, with the common feature of origin from an important single wood species. The choice was restricted to three major pulp types namely, mechanical and chemical fibres in the form of groundwood, sulfate and acid sulfite pulps. Asplund pulp was found to be unsuitable for making good quality handsheets and therefore was not included in this study. This imposed no limitation on the study, since effects of gamma-irradiation with thin (0.03 cm nominal thickness) experimental hardboards made from Douglas fir Asplund fibre had been investigated in a preliminary study (178). Thus, three pulp samples were selected so as to satisfy the two basic requirements.

Originally, it was intended to include and partly repeat the study of irradiation grafting with thin, green Douglas fir microtome wood sections (42) with the objective of treating a lignin species which had not been exposed to conditioning treatments other than normal air drying. Preliminary investigation of this approach showed that replication of the above investigation would result in continued limited success, since treatment effects are completely overshadowed by inherent structural limitations of thin wood sections. Explanations of failure with the process applied to whole wood is offered in a later section.
I. MATERIALS

1. Pulp Types

The pulp materials were obtained from MacMillan, Bloedel and Powell River, Ltd. as commercial stock furnish. These closely complied with the requirements as stated. Thus, commercial groundwood represented a high lignin content mechanical pulp, while commercial high yield sulfate (hereafter called kraft for better distinction from the similarly sounding, but different acid sulfite) and acid sulfite pulps represented two lignin species having characteristic modifications induced by processing. The pulps were obtained as wet stock that had never been dried. In addition, an unbeaten, bleached hemlock kraft, a TAPPI Standard pulp, high alpha-cellulose "viscose" pulps and glass filterpaper were included as representatives of various types of lignin-free materials. Origin of major pulps with regards to wood composition is described in Table V. The pulps were stored in polyethylene bags at 5°C until further processed.

Table V. Wood species composition of pulps.

<table>
<thead>
<tr>
<th>Pulp Types</th>
<th>Wood Species, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood</td>
<td>W. hemlock: 50%, Spruce: 20%, Mixed true fir: 20%, Other: 1% (Douglas fir, pine).</td>
</tr>
<tr>
<td>Acid sulfite</td>
<td>W. hemlock: 73%, Mixed true firs: 27%</td>
</tr>
<tr>
<td>Kraft</td>
<td>W. hemlock: 100%</td>
</tr>
</tbody>
</table>
a. **Groundwood pulp**

Unbleached groundwood pulps are used extensively as partial furnish in manufacture of newsprint, book, magazine, writing, absorbent towel and other inexpensive papers. In 1962 9,200,000 tons, representing 23% of world pulp production, were produced on this continent (229). For newsprint, groundwood is mixed with 20 to 35% of its weight with unbleached sulfite pulp, or 15 to 30% semi-bleached kraft pulp. There is good prospect that the introduction of higher strength groundwood will increase demand and that factors then limiting the amount of chemical pulp which can be replaced by groundwood in papers where brightness is of lesser importance, will be the strength that can be attained over the regular blended pulp strength.

Groundwood pulps represent almost the total wood fraction delivered to the grinders and are obtained in 97% or better yield in conventional operations (33, 66). Mechanical pulps are rigid due to their high lignin content, whereby they do not collapse on drying and do not conform well in dried paper webs. They are made up of a wide range of fragmented wood including a large proportion of fines and fibre bundles, but only a small fraction of intact individual fibres. Strength of groundwood papers has been shown to depend largely on the ratio of fines to coarse fractions as shown by Brecht and Erfurt (32), Forgacs (66, 68), and Marton and Alexander (155). Shape of the larger particles is symptomatic of wholewood pulps, whereby they exhibit little fibrillation without any preferred plane of rupture during fibre separation (66). Rigidity of groundwood fibres, together with their irregular shapes is important because the specific bonded area or combined close fibre contact between any two such fibres in a paper
network is small, giving high bulk to the resultant papers. The low bonding potential of the long fibre in mechanical pulps (including Asplund pulps) is reflected in low tensile strength of handsheets made from such fractions. It was shown recently by Forgacs (66) that certain disk-refined groundwood pulps develop higher sheet strength due to formation of ribbon like structures as a continuation of longitudinal cracks observed on "intact" stone-ground fibres. Such ribbon-like particles were shown to originate from unraveling of the cracked fibre surface during the refining process. These are extremely scarce in commercial groundwood pulps.

The increased paper strength had by addition of long chemical pulp fibres to groundwood is due to better conformity of the ribbon-like chemical fibres (32, 66, 155). In such mixtures Forgacs and Attack (68) found 1.4 times more groundwood on the wire side and showed that uniform fibre distribution was very difficult to maintain due to difference in bulk characteristics of the fibres.

Strength of paper made from groundwood was shown to increase considerably following stock delignification. Thus, Jahn and Holmberg (89) and Watson (227) reported that a general increase in strength properties accompanied progressive delignification of groundwood by acidic sodium chlorite. However, yield losses were relatively high following such treatments since substantial gains in strength were obtained only after 50 to 75% of the lignin had been removed (227).

The groundwood used for this investigation was commercially refined and screened and had Canadian Standard Freeness (TAPPI T 227-m58 method) at 109 CSF. Moisture content of the pulp was 239% (29.5% b.d. solids)
as received. The fibre length distribution was not determined. Replicate samples of Klason lignin (TAPPI T222-m54 method) gave 29.6 and 28.3% lignin content (28.9% average) as corrected for alcohol-benzene solubles (TAPPI T 6-m59 method). The methoxyl content of an air-dry sample was found to be 5.32% on extractive-free, oven-dry pulp basis.

b. Acid sulfite pulp

There is voluminous literature on differences between fibre characteristics of sulfite and kraft pulps, often with slightly conflicting observations. Besides individual contributions (23, 36, 37, 56, 59, 73, 88, 95, 96, 115, 144, 158, 194, 197, 219, 227), two extensive summaries have been published by Jayme (91) and Dinwoodie (57) on physical and chemical differences and effects of various factors on the strength properties of resultant papers. These summaries present a comprehensive review of what is known about paper properties, as well as factors and processing methods influencing them.

The localized attack of acids across the entire wood cell wall has been long suspected as cause of low strength with acid sulfite fibres (194). It may be accepted that fibres weakened by acid hydrolysis cannot be beaten for further strength development to the same extent as nonhydro- lized fibres before fibre damage occurs. The extent of acid hydrolysis across the fibre wall has been measured by Jayme and von Koeppen (94) through DP comparisons. However, quantitative data relating the degree of acid hydrolysis and the strength of individual paper-making wood fibres do not appear in the literature. The higher strength of papers made from
unbeaten or slightly beaten sulfite pulps, as compared to unbeaten kraft pulps, is in contradiction to the acid damage theory, as pointed out by McKenzie and Higgins (144).

Jayme and von Koeppen (94) have shown that the lower flexibility of sulfite fibres is mainly due to the relatively high lignin concentration in the outer layers of the sulfite fibre wall. Papers made of high yield sulfite pulp had the appearance of an open network with relatively un-collapsed fibres (37), but had lower bulk than kraft papers at the same lignin content. Since paper sheet bulk is controlled by such factors as fibre length, fibre flexibility, the filling of voids by fine fibres and degree of bonding (154), it is expected that the lower bulk of sulfite papers results from slightly shorter, better conforming fibres (194) and a larger proportion of fines. Although sheet strength has been shown to increase with fibre length (59, 83, 88, 219), tensile strength was shown to increase to a maximum with addition of up to 40% fines to the separated long fraction of sulfite pulp (154). Bonding strength due to better swelling capacity has been shown to be higher for sulfite pulps (73, 74, 91) as evidenced by the larger portion of broken fibres on close examination of tensile failures (37, 83, 88, 219). Possible cause for such increase in fibre failure was attributed by Forgacs (67) to weak spots (nodes) on the fibres.

The high yield sulfite pulp used in this investigation was measured at 638 CSF and contained 252% water (28.4% b.d. solids). It had a 40 ml permanganate number (K No.) according to TAPPI T 236-m60, of 38.4, corresponding to 18.98% Klason lignin. The methoxyl content of the air-dry
pulp was found to be 3.77% on extractive-free, oven-dry pulp basis.

c. Kraft pulp

Kraft pulps differ from sulfite pulps in both quantitative and qualitative distribution of fibre chemical constituents which is thought to control physical properties (115). It has been reported earlier that coalescence of lignin, during the high-temperature kraft digestion, leads to lower reactivity and stronger hydrophobic properties within the cell wall. High solubility of hemicellulose in the alkali cooking medium is said to result in lower hemicellulose retention (159), whereby swelling capacity of the fibres is further reduced. Uniform overall lignin distribution across the fibre wall was shown to impart better fibre flexibility to the cell structure than with sulfite fibres of the same lignin content (94), although equal bond strength with kraft pulps cannot be developed without considerable beating (57, 94, 115, 194) at the expense of increased energy input (5, 83).

Unbeaten kraft pulp was shown to have an open structure with poorly conforming fibres which have not collapsed on removal of water from the sheet, as well as virtual absence of fibrillation (37). Thereby, kraft papers appear bulky and highly opaque. Kraft fibres also show weak spots (nodes) similar to sulfite fibres (67). Failure of paper made from unbeaten kraft fibres is mainly due to fibre pull-out over a deep fracture zone (37). Close observation of the bond area after fracture reveals no or little material transfer, an indication of low interfibre bond strength in such papers. However, the larger tear resistance of kraft papers was related by
van den Akker and co-workers (6) to the fact that with long fibred kraft paper only a small percentage of fibres break in shear as compared to predominant fibre failure in tear testing of sulfite papers. This was taken as evidence for lower energy requirement in breaking fibres in shear than rupturing interfibre bonds in tension. Numerous fibre crossings over the length of a long fibre may be the reason why kraft papers show higher tear as compared to sulfite papers having the same breaking length (115).

Theoretically, the maximum mean pulled out fibre length when breaking paper along a line should be \( L/4 \), where \( L \) is the mean fibre length. In practice, however, 10 to 15\% higher values are obtained, which is obviously due to the wide fracture zone found for unbeaten pulps as demonstrated by Helle (83). Thereby, Helle (83) concluded that the width of the fracture zone for chemical handsheets is an indication of the degree of bonding.

The high yield kraft pulp used in this study had 739 CSF freeness and was received at 263\% moisture content (27.5\% b.d. solids). It contained 9.60\% Klason lignin and gave a K No. of 32.6 (40 ml). The methoxyl content, based on extractive-free, oven-dry pulp was found to be 1.62\%.

A summary of pertinent pulp properties and their method of determination is presented in Table VI.

<table>
<thead>
<tr>
<th>Table VI. Summary of pertinent data on pulps.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pulp Types</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Groundwood</td>
</tr>
<tr>
<td>Acid Sulfite</td>
</tr>
<tr>
<td>Kraft</td>
</tr>
</tbody>
</table>
d. Other fibre materials

Earlier investigations (178, 179) suggested that oil polymerization with hardboards and newsprint was mostly specific for lignin. Only one-fifth of the extra strength development was attributed to fibre constituents other than lignin, possibly a secondary reaction with some carbohydrate fraction, and mechanical adhesion at the fibre-oil polymer interface.

To further examine these phenomena various purified pulps and a chemically inert web (glass fibre filterpaper) were included in the present study. Unfortunately, no specific data are available for the three pulp types which were an unbeaten, bleached western hemlock kraft pulp, a TAPPI Standard pulp (30) and a sulfite viscose dissolving pulp containing 50% western hemlock as wood furnish.

2. Wood Microtome Sections

One-hundred-fifty-micron thick tangential microtome sections were cut from a wood block taken from the sapwood of a freshly felled, straight grained Douglas fir grown at the south side of the University Endowment Lands, Vancouver, B.C. The sections were stored in the sequence taken between strips of wet blotting paper and kept wet in a polyethylene bag at 3°C until further processed.
3. Drying Oil

Fresh commercial drying oil (CTLA Polymer) was obtained from Van Waters and Rogers of Canada, Ltd., a distributor of the raw oil manufactured by Imperial Oil, Ltd. Information as to ingredients and special additives (linseed oil and 1% maleic anhydride) was obtained from The Chemical Products Department, Imperial Oil, Ltd., Toronto, Canada (55, 61).

The drying oil, is a pre-polymer of a cracked naphtha gas-oil fraction which contains straight, branched and cyclic mono- and di-olefines, naphthanes, as well as normal and iso-paraffins. It is heat reactive and is prepared by partial polymerization of the fraction over hot clay. The polymer, being highly unsaturated, dries both by oxidation and polymerization. A characteristic property of the polymer is its tendency for depolymerization or rearrangement on extensive heating. This has been observed as an inherent characteristic of dicyclopentadienes with an endo-methylene bridge in the molecule. To reduce heat requirement for oil polymerization, a 1% maleic anhydride addition is made. This provides a new polymer, which is claimed to give greater strength and better flexibility than can be had with the initial polymer alone. The reduced heat requirement also lessens danger of self-ignition in the hardboard tempering process. The tendency for depolymerization on prolonged heating is further reduced by addition of certain amounts of linseed oil.

The drying oil is soluble in aromatic, paraffinic and chlorinated hydrocarbons, acetates, ketones and alcohols above butyl alcohol. It is compatible with various other drying-oils, both raw and bodied, such as
linseed, tung, soyabean, castor and fish oils. Furthermore, it is also compatible with rosin, rosin esters, coumars, modified alkyds, modified phenolics, natural and synthetic rubbers and nitrocellulose.

Besides application to hardboard processing, CTLA Polymer is used extensively in other industries, such as core oil testing where it replaces natural drying-oils.

Specifications and some typical properties of CTLA Polymer are given in Table VII.

<table>
<thead>
<tr>
<th>Test</th>
<th>Value</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, API</td>
<td>6 - 14</td>
<td>ASTM D 278 - 55</td>
</tr>
<tr>
<td>Viscosity, SSU at 210°F</td>
<td>100 - 250</td>
<td>ASTM D 88 - 53</td>
</tr>
<tr>
<td>Nonvolatile matter, Wt. % Min.</td>
<td>80</td>
<td>ASTM D 154 - 53</td>
</tr>
<tr>
<td>Iodine No., cg./g., Min.</td>
<td>240</td>
<td>ASTM D 555 - 54</td>
</tr>
<tr>
<td>Water Vol., % Max.</td>
<td>0.8</td>
<td>ASTM D 95 - 46</td>
</tr>
<tr>
<td>Flash, COC °F., Min.</td>
<td>210</td>
<td>ASTM D 92 - 52</td>
</tr>
</tbody>
</table>
II. METHODS

The general plan of the investigation required preparation of handsheets from two series of pulp blends made from sulfite-groundwood and kraft-groundwood at various levels of mixture followed by the various treatments. Thereby, groundwood became an internal standard. The two series, included 11 and 10 sets of pulp handsheets in which the groundwood content ranged from 0 to 100% at 10% intervals. Such close examination of radiation effects with blends was expected to extend the useful information obtained, notwithstanding the basic physical characteristics of such blends. Blending of the various fibres was considered to have substantial practical meaning, since it includes the entire range of stock mixtures used by various industries.

1. Preparation of Handsheets

Following pre-weighing, dilution and mixing of appropriate proportions of the various pulps (to give handsheets of a nominal basis weight of 60 g/m²), 30 handsheets of each blend were prepared on a British Sheet Machine according to TAPPI Standard T 205-m58. After formation of sheets, they were couched with two blotters, a sheet metal plate and a roll, in the standard manner. The handsheets were interleaved between dry blotters and a press-plate, and were wet-pressed at 60 psi for 3.5 min. Following the above pressing cycle the handsheets were transferred with their respective
press-plates to dry blotters and re-pressed for 2.5 min. Conditioning of the handsheets was done between drying rings at controlled humidity conditions (75°F and 50 % R.H.) until air-dry (3 to 5 hr). The air-dry handsheets were then oven-dried between polished ferro plates at 145°C for 10 min without pressure, after which they were sealed in polyethylene bags until further treatment.

Basis weight of the various prepared handsheets is given in Table VIII.

Table VIII. Basis weight of handsheets made from various blends of sulfite-groundwood (SG) and kraft-groundwood (KG) pulps.

<table>
<thead>
<tr>
<th>Groundwood %</th>
<th>Sulfite Series</th>
<th>Weight, g per Handsheet</th>
<th>Basis Weight, g/m²</th>
<th>Kraft Series</th>
<th>Weight, g per Handsheet</th>
<th>Basis Weight, g/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>S*</td>
<td>1.20</td>
<td>60.0</td>
<td>K**</td>
<td>1.20</td>
<td>60.0</td>
</tr>
<tr>
<td>10</td>
<td>S10G</td>
<td>1.18</td>
<td>59.0</td>
<td>K10G</td>
<td>1.20</td>
<td>60.0</td>
</tr>
<tr>
<td>20</td>
<td>S20G</td>
<td>1.21</td>
<td>60.5</td>
<td>K20G</td>
<td>1.21</td>
<td>60.5</td>
</tr>
<tr>
<td>30</td>
<td>S30G</td>
<td>1.25</td>
<td>62.5</td>
<td>K30G</td>
<td>1.20</td>
<td>60.0</td>
</tr>
<tr>
<td>40</td>
<td>S40G</td>
<td>1.29</td>
<td>64.5</td>
<td>K40G</td>
<td>1.20</td>
<td>60.0</td>
</tr>
<tr>
<td>50</td>
<td>S50G</td>
<td>1.25</td>
<td>62.5</td>
<td>K50G</td>
<td>1.20</td>
<td>60.0</td>
</tr>
<tr>
<td>60</td>
<td>S60G</td>
<td>1.23</td>
<td>61.5</td>
<td>K60G</td>
<td>1.15</td>
<td>57.5</td>
</tr>
<tr>
<td>70</td>
<td>S70G</td>
<td>1.20</td>
<td>60.0</td>
<td>K70G</td>
<td>1.16</td>
<td>58.0</td>
</tr>
<tr>
<td>80</td>
<td>S80G</td>
<td>1.15</td>
<td>57.5</td>
<td>K80G</td>
<td>1.14</td>
<td>67.0</td>
</tr>
<tr>
<td>90</td>
<td>S90G</td>
<td>1.13</td>
<td>56.5</td>
<td>K90G</td>
<td>1.18</td>
<td>59.0</td>
</tr>
<tr>
<td>100</td>
<td>G***</td>
<td>1.15</td>
<td>57.5</td>
<td>G</td>
<td>1.15</td>
<td>57.5</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>--</td>
<td>--</td>
<td>BK****</td>
<td>1.18</td>
<td>59.0</td>
</tr>
</tbody>
</table>

*S : Acid sulfite; **K : Kraft; ***G : Groundwood; ****BK : Bleached kraft
2. **Paper Treatments**

For purpose of clarity the various treatments used are listed as follows:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Untreated (control)</td>
<td>S, G, K, SC, KG, BK</td>
</tr>
<tr>
<td>B. Heat treated only</td>
<td>SH, GH, KH, SGH, KGH</td>
</tr>
<tr>
<td>C. Irradiated only</td>
<td>SR, GR, KR, SGR, KGR</td>
</tr>
<tr>
<td>D. Oil dipped</td>
<td>SD, GD, KD, SGD, KGD, BKD</td>
</tr>
<tr>
<td>E. Thermally polymerized</td>
<td>SO, GO, KO, SGO, KGO, BKO</td>
</tr>
<tr>
<td>F. Radiation polymerized</td>
<td>SRT, GRT, KRT, SGRT, KGR</td>
</tr>
<tr>
<td>G. Radiation plus thermally polymerized</td>
<td>SRTH, GRTH, KRTH, SGRTH, KGRTH</td>
</tr>
</tbody>
</table>

A. **Untreated controls**

The number of tensile specimens necessary for proper replication was determined experimentally for each basic pulp type (groundwood, sulfite and kraft) from preliminary tests on standard tensile specimens. These specimens were prepared with a \( \frac{1}{2} \)-ton Arbor press, equipped with a cutting die of 1.5 cm width and 15.0 cm length. This device for sample preparation has been described earlier by Ifju (86) and Wellwood (231) for microtome wood sections and by Paszner (178) for paper. Pertinent data from which the necessary number of replicates were calculated are presented in Table IX.
Table IX. Necessary number of tensile strength replicates for groundwood, sulfite and kraft handsheets.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Number of Tests</th>
<th>Ave. Max. Tens. Strength, psi</th>
<th>SD, psi</th>
<th>N at t&lt;sub&gt;0.05&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood</td>
<td>10</td>
<td>1184</td>
<td>63.5</td>
<td>9.37</td>
</tr>
<tr>
<td>Sulfite</td>
<td>10</td>
<td>4620</td>
<td>78.0</td>
<td>1.01</td>
</tr>
<tr>
<td>Kraft</td>
<td>10</td>
<td>2213</td>
<td>72.0</td>
<td>2.66</td>
</tr>
</tbody>
</table>

From these calculations it was decided to use 10 specimens for replication with groundwood and 5 specimens per treatment for sulfite and kraft pulps, as well as all blends containing them. Five tensile specimens can be obtained easily from each handsheet, but to minimize effects of between handsheet variation test specimens for all treatments without oil dipping (Treatments A, B, C) were punched out at the same time, and the necessary number of specimens was allotted to the treatments in a random fashion. Thereby, a double randomization was achieved within each blend series. Furthermore, each set of handsheets was divided into lots of 7 and 10 sheets (the latter to provide extra sheets for various levels of irradiation treatments) and individual specimens were further randomized and allotted to sheet treatments.

Each tensile specimen was properly labelled and sealed in a thin polyethylene bag, specially made for this purpose, to protect the specimens from moisture re-absorption. Specimens related by single treatments were sealed into larger bags.

Control specimens (Treatment A) were oven-dried for 20 min at 145°C before bagging to ensure complete moisture-free conditions.
B. **Heat treated controls**

The cut tensile specimens, prepared and selected in the manner described, were exposed to heat treatment in a forced air circulating laboratory oven at 145°C (+/− 2°C) for 1.5 hr. The temperature and time combination was determined as optima for maximum strength development with these materials by methods to be described. Such heat treatment is designed to account for the effect of heating various types of papers without oil additive and thereby allows calculation of strength increase resulting from interaction of additive and thermal treatment without the confounding effect of heat alone. Following this treatment the tensile specimens were quickly transferred into small polyethylene bags. The bags were partially heat sealed and, following complete evacuation and replacement of vacuum by dry nitrogen gas, completely sealed with the aid of a soldering gun.

C. **Irradiated controls**

The specimens designed as controls for the irradiation treatment were prepared in much the same way as samples for Treatment A. According to the plan, 5 specimens were allotted for each of the 5 irradiation dosage levels namely, 10, 10², 10³, 10⁵ and 2x10⁷ rad.

Irradiation of the samples was done by Atomic Energy of Canada, Ltd., Chemical Products Division, Ottawa, Canada. Samples with low dosage levels of 10 and 10² rad were ⁶⁰Co irradiated in a therapy unit at 60 rad/hr, whereas the higher dosages were applied in a "Gamma Cell 200" at 0.60 Mrad/hr dosage. Further description of these facilities has been presented by Ifju (86), and Paszner and Wilson (179).
Chemical changes at the various irradiation levels were followed by determination of methoxyl contents of the wood pulps. At least replicate determinations were run for each of the three pulp species for each of the radiation dosage levels. Two numbers were accepted as true replicates only if their percentages agreed within ± 0.05 % about their mean. The effect of radiation on average methoxyl content of the different pulps is presented in Fig. 5.

D. Oil dipped controls

Handsheets reserved for oil treatment were first re-dried at 145°C for 10 min, followed by 15 min cooling in a polyethylene bag, before dipping into the drying oil. For good penetration and swelling of the lignin the drying oil was diluted with benzene in the ratio of 1:3. Benzene has been shown to possess at least intermediate swelling power for lignin (198) (swelling parameter d=9.15 (cal/cc), whereas solvents with swelling parameters around 11 are good lignin solvents) and was found to be fully compatible with the drying oil. As shown by McLaughlin (146), the use of fugitive coalescing agents (solvents), especially those which are capable of swelling polymer networks, permits a much better saturant penetration.

Excess oil was removed from the handsheet surface by brief stacking between blotting paper. During subsequent preparation of test specimens the handsheets could not be protected from air moisture. However, it is expected that little, if any, moisture absorption took place during this phase due to continued evaporation of excess benzene.
Figure 5. Change of pulp methoxyl content as a function of irradiation dosage.
Solvent was removed from the specimens, following specimen cutting and bagging, by applying vacuum (100 to 200 μHg) in a large desiccator at room temperature. Since the samples were stored over phosphorus pentoxide in the desiccator under vacuum for three days, it is expected that these precautions reestablished the oven-dry condition. Thereby, variable moisture in the samples did not influence the strength tests. The vacuum was replaced by dry nitrogen and the specimens were sealed in their respective bags. These precautions were necessary in view of findings of van den Akker and co-workers (233), Brecht and Erfurt (32), Cohen, Stamm and Fahey (51), Rieman and Kurath (191) and Thode and Ingmanson (219) who showed that tensile strength increases almost asymptotically to a maximum with a decrease in moisture content from 5 to 0%. Apparently, elongation is much less sensitive to such small changes in moisture content (51).

E. Thermally Polymerized

Test specimens of one set of the above oil-dipped samples were removed once more from their bags and were suspended in an oven for thermal treatment at 145°C over a period of 1.5 hr.

Optima of time and temperature of thermal treatment were determined in a preliminary study involving the three basic pulps. Thereby, it was found that the strength of tensile specimens was practically unchanged (except for some normal variation not exceeding the standard deviation values given in Table IX) within 140 to 155°C range applied over a period of 1 to 2 hr. Lower strength values were obtained outside these ranges due to incomplete oil polymerization at the lower temperatures and shorter times.
and possibly thermal degradation on prolonged high-temperature heating. The conditions chosen as result of this experiment were somewhat arbitrary in the sense that any number of justifiable combinations occur within the above-mentioned range. The fact that the specimens were severely discolored at higher temperatures and prolonged times suggests advantage by use of lower temperature and shorter time.

The treated samples were cooled, replaced in their respective bags with a minimum of contact with the atmosphere, and stored in vacuum over phosphorus pentoxide before the final seal was applied.

F. **Radiation polymerized**

Eight sets of oil dipped samples were irradiated. Conditions and dosages during irradiation were the same as those described for Treatment C.

G. **Radiation plus thermally polymerized**

Three sets of samples were allotted to this treatment. The treatment was designed to reveal certain differences in polymerization mechanism between the two major methods under examination. It was expected that strength recovery on thermal treatment following irradiation should indicate possible blocking or destruction of reactive sites available for grafting on thermal treatment and thereby give some indication of efficiency and possible sites of grafting.

Only three irradiation levels were used, namely $10^2$, $10^2$ and $2 \times 10^7$ rad dosages. Maximum efficiency in similar systems was shown
to occur earlier with about $10^2$ rad dosage (134), whereas the effect of intrinsic strength loss due to gamma-ray degradation was expected to occur as result of $2 \times 10^7$ rad irradiation dosage (86).

All treatment procedures including oil dipping, irradiation and the subsequent thermal treatment were carried out in exactly the same manner as described for Treatments D, E, and F.

Re-extraction of oil polymer from oil dipped samples of the three basic pulps (groundwood, sulfite and kraft) was attempted by Soxhlet extraction with a benzene:chloroform mixture (9:1). Results of these extractions together with initial oil absorption values are given in Table X.

<table>
<thead>
<tr>
<th>Pulp Sheet</th>
<th>Oil Abs, %</th>
<th>Weight Loss on Extraction following treatment, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A D E C</td>
<td>10 $10^5$ $2 \times 10^7$</td>
</tr>
<tr>
<td>Groundwood</td>
<td>83 .64 67 7.5</td>
<td>0.0 0.0 0.5</td>
</tr>
<tr>
<td>Sulfite</td>
<td>42 .10 26 13.5</td>
<td>.50 .70 0.0</td>
</tr>
<tr>
<td>Kraft</td>
<td>61 .60 44 5.6</td>
<td>.10 .50 1.1</td>
</tr>
</tbody>
</table>

3. Tension Test Methods

Tensile strength of paper sheets is considered to result from resistance of hydrogen bond chains to stresses by means that will be discussed in a subsequent section. The chains are quite independent and under tensile strain fail independently, each requiring a certain energy to
produce failure. The sum of the energies is equated to the rupture energy of paper.

In this study tensile properties of the experimental papers were determined by use of a table model Instron Tensile Tester. The external stress was applied with continuous motion of the moving cross-head causing a constant rate of elongation at 0.05 in./min in all types of papers. The initial distance between the grips was set at 10 cm. Stressing the specimens under these conditions caused 0.0127 in./min nominal rate of strain. Load-elongation curves were recorded automatically with the chart moving at constant speed of 1 in./min. Following rupture of specimens the test diagram was evaluated for ultimate tensile load, load to unit strain within the proportional limit and ultimate elongation. Appropriate strength values (ultimate tensile strength, modulus of elasticity and ultimate strain) were calculated by relating test data to the load resisting cross-section of paper strips. The total area under the load elongation curve was measured, using a planimeter, from which maximum tensile energy absorption (TEA) was calculated. As mentioned above, individual specimens were tested in oven-dry condition, sealed in polyethylene bags. A total of 1600 specimens were tested in tension for the study.

4. Statistical Analyses

The large amount of data available required reduction to simple arithmetic means for treatment replications. These average values were tabulated (Table 12-19, Appendix) and plotted for the two independent variables ($X_1 = \%$ blend, $X_2 = \log.$ irradiation dosage, rad) to evaluate the necessary
degree of the polynomial that best described the various sets of data in these two dimensions.

a. Curve fitting

Multiple curvilinear regression (134) was used to find equations of response surfaces for evaluating the main treatment effects. Degree of polynomial for initial equations was defined by graphical methods. Plotting the various dependent variables over independent variables indicated that a common third degree polynomial would be sufficient for describing effects of the independent variables. \((X_1 = \text{blending in } \%, X_2 = \log. \text{irradiation dosage, rad})\). The initial equation employed for all response surfaces had the following general form:

\[
Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_1^2 + b_4 X_2^2 + b_5 X_1 X_2 + b_6 X_1^3 + b_7 X_2^3 + \\
+ b_8 X_1^2 X_2 + b_9 X_2 X_1^2 + b_{10} X_1 X_2^2 + b_{11} X_1^3 X_2 + b_{12} X_1^2 X_2^2 + \\
+ b_{13} X_2^3 X_1 + b_{14} X_2^2 X_1^2 + b_{15} X_1^3 X_2^2.
\]

This equation was evaluated by a new regression programme provided by Kozak and Smith (118). The program eliminates contribution of nonsignificant independent variables from the initial model using the so-called, "Miller's t-prime" procedure (164). At each step of elimination a test of significance can be carried out to estimate significance of contributions of the remaining variable components to the multiple regression. Thereby, an equation can be obtained in which all residual independent variables are significant.
b. Analysis of variance

A single analysis of variance was designed to test significance for differences between behavior observed on the two types of chemical fibres with groundwood. The effect of additional treatments was evaluated by testing the interaction between basic pulp response and treatments for both types of pulp blends. The basic model for analysis of variance is presented in Table XI.

Table XI. Analysis of variance for tensile strength of handsheets made from sulfite- and kraft-groundwood pulp blends.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum SQ</th>
<th>Mean SQ</th>
<th>F</th>
<th>F.05</th>
<th>F.01</th>
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<td>0.13463E 08</td>
<td>210.15**</td>
<td>4.03</td>
<td>7.17</td>
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<tr>
<td>TREAT</td>
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<td>0.66060E 08</td>
<td>0.13212E 08</td>
<td>206.24**</td>
<td>2.40</td>
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<tr>
<td>PER.</td>
<td>10</td>
<td>0.74524E 08</td>
<td>0.74524E 07</td>
<td>116.33**</td>
<td>2.02</td>
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<tr>
<td>SXT</td>
<td>5</td>
<td>0.34908E 07</td>
<td>0.69815E 06</td>
<td>10.90**</td>
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<td>SXP</td>
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<tr>
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</table>

Symbols:  
S : Sulfite  
K : Kraft  
Per.: X_ (blending in per cent)  
Treat: Treatment A, B, D, E, F and G.

c. Relationship between dependent variables

Relationships between dependent variables (strength parameters) were first examined by visual inspection of plots produced by the computer. Following inspection of respective plots it was found that the data grouped naturally into three parts according to the three major types of treatments.
Simple linear regressions were calculated for ultimate tensile strength ($Y_1$) versus modulus of elasticity ($Y_2$), ultimate tensile strain ($Y_3$) and tensile energy absorption ($Y_4$). $Y_2$ vs. $Y_3$ and $Y_4$ vs. $Y_3$. Calculated points were derived from significant equations of respective correlations.
RESULTS

Change in pulp methoxyl content for the three basic pulp types as a function of irradiation dosage is presented in Fig. 5. Pertinent data relating to differences in oil absorption and re-extractable oil fractions before and after oil dipping and polymerization are tabulated in Table X.

Results of analysis of variance on pulp type, extent of blending ($X_1$, Treatment A) and paper treatments (heat treatment (B), oil dipping (D), grafting by gamma-irradiation (F), thermal (E) and combined irradiation and thermal (G) treatments) and their interaction on tensile strength are presented in the usual tabular form in Table XI.

Tensile fractures with pertinent strength and other data for treated and non-treated wood microtome sections are presented in Fig. 6 (a to f). Scanning electron photomicrographs together with characteristic strength values are shown for pure groundwood in Fig. 7 (Fig. 7, g to i), for sulfite (Fig. 7, j to l) and kraft (Fig. 7, m to o). In addition a deep tensile fracture characteristic of kraft paper is presented as Fig. 8.

Mean values of measured and calculated strength parameters for all pulp blends are summarized in Table XII through XV and in Fig. 9 through 12 for sulfite and in Table XVI through IXX and Fig. 13 through 16 for kraft papers. Equations for the calculated response surfaces are presented in Table XX.

Effect of thermal and irradiation polymerization of drying oil on strength properties of handsheets made from the three basic pulps is summarized in Table XXI. Values for absolute strength parameter increases are
plotted in Fig. 17. Fig. 18 shows the effect of extractable monomer residues and soluble homopolymer fractions on tensile strength. Tensile strength variation of pulp handsheets, calculated from the significant interaction between pulp type and level of blending is demonstrated in Fig. 19.

Table XXII presents per cent strength increase values obtained on purified cellulose pulps before and after sodium chlorite treatment and oil polymerization by thermal treatment.

Relationships between dependent variables (Y-s) are plotted in Fig. 20 through 24 for which the appropriate equations can be found in Table XXIII.

Based on recommendations made for further investigation of oil copolymerization with lignin (and possibly cellulose) a scheme for selective lignin methylation is described in Fig. 25.

Comparison between thermal and irradiation treated samples is demonstrated by actual specimens presented as Fig. 26.
DISCUSSION

During the past few years a great deal of effort has been expended on investigation of graft copolymers. Mostly, these studies have dealt with development of new techniques and provide limited understanding of reaction mechanisms and actual graft copolymer structures. Most reactions involving graft copolymerization suffer from the disadvantage of concomitant homopolymerization of the saturant within the copolymer network. Few, if any, pure graft copolymers have been conclusively proven so far. With wood and wood components the situation is even more complex. Information on sites and specificity of grafts is limited indeed, due to the nature of parent wood polymers such as cellulose and lignin.

In the present study polymerization phenomena between a commercial unsaturated drying oil (CTIA Polymer) and three wood pulp types was investigated. Polymerization reactions were initiated by gamma-irradiation from a $^{60}$Co source and by prolonged high-temperature heat treatment. In all instances considerable gains were made in paper sheet strength properties. The treatment may be of importance where interfibre bond strength is the limiting factor on fibre web strength. For example, it could be applied to a wide variety of specialty papers designed for uses where strength improvement of low cost, high yield fibre furnish is desired.

Following the treatments, evidence was sought to distinguish between homopolymerization and graft copolymerization through assessment of basic mechanical strength parameters and by use of usual organic solvent
techniques.

I. THERMAL POLYMERIZATION WITH THIN WOOD SECTIONS

Earlier attempts by Butler (42) to modify wood elasticity and work functions by soaking a variety of wood sections in CTLA Polymer followed by application of thermal and irradiation energy to induce copolymerization gave no conclusive results. Due to the limited scope of the study no evidence was sought for this failure. It was suggested, however, that cause of failure to show polymerization effects might be due to relatively low reactivity of natural lignin in situ, and that possibly high-temperature treatment in the presence of moisture is required to activate lignin in preparation for copolymerization reactions. Since there was no difference in strength, between control and oil dipped wood sections, following irradiation treatments the discussion was limited mainly to evaluation of irradiation effects as a function of wood density, the main independent variable of the study.

Such explanation may not adequately describe effects with natural lignin. Through further experimentation strength data on matched specimens were obtained for both earlywood and latewood microtome sections with and without thermal polymerization treatment. Surprisingly, again strength increase of the oil treated sections never exceeded 15\%. The increase was found to be lower, but more reproducible, for earlywood sections than for latewood. Neither thermal pretreatment (boiling in water or heat treatment between moist paper towels at 170\°C), nor methylation of the wood sections in alkaline dimethyl sulfate at room temperature improved results. Therefore,
it was concluded that failure to obtain strength increases proportional to difference in lignin content of earlywood and latewood tissues was not due to insufficient lignin reactivity toward copolymerization. The answer is contained in part in tensile failure patterns as presented in Fig. 6.

Observations on wood micro-tensile failures were made by Ifju and Kennedy (87). It was shown that earlywood specimens always fail in tension across fibre walls, whereas latewood sections fail between fibres by shear of the middle lamella. Following thermal polymerization with the drying oil both earlywood and latewood sections failed in tension as evidenced on the scanning electron photomicrographs shown in Fig. 6. There is practically no change in earlywood fracture pattern (Fig. 6, a, b and c) as one progresses from untreated wood sections to highly irradiated (10\(^7\) rad) or thermally treated oil soaked sections. Strength appears to be limited by intrinsic fibre strength in earlywood sections. On the other hand, a successive change in fracture pattern can be observed on inspection of latewood photomicrographs (Fig. 6, d, e and f). In Fig. 6, d, a typical shear failure between the middle lamellae of adjacent fibres is shown. This indicates high intrinsic fibre strength. Following high-dosage irradiation (Fig. 6, e) strength of the latewood specimens was reduced to 43% of the original, possibly due to cellulose depolymerization and thereby loss of intrinsic fibre strength. In this instance the fracture changed from pure shear to a combination of shear and tensile failure, an indication of unchanged interfibre bonding but decreased intrinsic fibre strength. Thermal polymerization with the drying oil works in the opposite direction as demonstrated by Fig. 6, f. By only 14.1% increase in tensile strength the fracture pattern changed from pure shear to
pure tensile failure indicating that improvement in inter-fibre bonding did take place. An ultimate limit to strength improvement seems to be set by intrinsic fibre strength, similar to the case with earlywood tissue.

The above observations suggest that wood fibre strength is utilized close to its maximum tensile capacity in both growth zones. This also implies that substantial change in wood strength cannot be effected without raising both limiting factors, i.e., interfibre bonding and intrinsic fibre strength. Indeed, there is experimental evidence (1) showing that strength properties of monomer saturated wood were higher when a mixture of styrene and methyl methacrylate were used, than by either one of the monomers used alone. This observation is consistent with work of Koshijima and Muraki (117), who found that lignin preferentially polymerized with methyl-methacrylate on irradiation, whereas styrene gave very low graft yields. Similarly, Rapson and Kvasnicka (187/b) observed a strong synergistic effect with styrene and acrylonitrile when simultaneously grafted onto cellulose by gamma irradiation. The effect showed not only a higher strength increase, but permitted an extremely large reduction in irradiation dosage for a given weight of polymer addition to cellulose.

II. THERMAL AND IRRADIATION INDUCED POLYMERIZATION WITH PULP HANDSHEETS

Since mechanical evidence is much used in this study for sorting thermal and irradiation treatment effects, it is appropriate to review factors influencing basic rheological behavior of wood fibre webs.

Theoretically, such mechanical comparisons are permissible since
bonding in paper has been accepted as mainly dependent on secondary valence forces between fibre contacts (168, 176), as well as on surface colloidal properties of fibres (91, 227). Since the stress-strain curve obtained by tensile testing of paper webs reflects the nature and organization of the sheet components, it is well suited for evaluating effects of fibre and paper sheet treatments.

1. Mechanism of Bonding in Paper

The resistance of wood fibre webs to rupture as assessed by a conventional procedure such as tensile testing, is believed to depend on several factors. Since the fibres form a three-dimensional, attached network in the paper sheet the strength of the structure is in part due to the strength of sheet forming elements (fibres) and in part to the joints or bonds between them (5, 83, 109, 174, 197, 219). The latter is dependent upon the total area of such contacts, as well as on the quality of the bond area or the strength of bonds. Considering that paper strength is measured as rupture strength its value also depends on energy distribution within the fibre network and, thereby, on the relative density of bonded areas along any particular cross-section of the sheet being stressed.

The strength of paper is generally attributed to hydrogen bonding between fibres (5, 44, 83, 158, 168, 169, 170, 171, 172, 174, 176, 187, 205), suggesting that bond strength should be uniform for all cellulosic paper products (173). As the bond strength is calculated per unit of bonded area in various papers it is found that the number of bonds per unit area differs for pulps of various qualities. Factors affecting the bond strength
were examined by Giertz (74), Jayme and Lockmueller-Kerler (95, 96) and Nordman (174), by investigating the effects of wood constituents and by Leopold (128, 132) and Schniewind et al. (197) by studying effects of strength and bonding characteristics of earlywood and latewood fibres. Further, Einspahr (59), Helle (83), Ingmanson and Thode (88), McIntosh (143), Marton (154) and Mayhood, Kallmes and Cauley (158) studied the contribution of intrinsic fibre strength and shear strength of individual fibre-to-fibre contacts to strength of papers.

The strength of a bond between adjacent fibres is the product of bond area and strength of the material with respect to its bonding capacity. The area of the bond is largely determined by the flexibility of fibres (132, 197, 219), the geometry of fibre surfaces (59, 83, 88, 154), the externally applied pressure used in sheet formation (154, 174, 205, 219) and internal tension processes during dewatering and drying phases (Campbell effect) (44). Paper formation, from a dilute fibre suspension to the finished sheet, represents a complex physico-chemical process in which water-to-water hydrogen bonds are superseded by cellulose-to-water hydrogen bonds, and finally as surface tension forces draw the fibres into intimate contact, by cellulose-to-cellulose hydrogen bonds (168). Therefore, the bond strength per unit area of fibre may be assumed to be a function of fibre surface chemistry which is definitely influenced by botanical origin and subsequent chemical processing. The rheological behavior of paper depends to a large extent on the hydrogen bond system which has been imposed upon the fibre assemblage and the response of that system to the test environment.

Numerous theories have been advanced wherein bonding within a
sheet of paper is explained in terms of molecular structure (5, 44, 168, 169, 170, 171, 172, 176, 187, 205). The only point on which all these theories agree is the importance of hydrogen bonds as a primary source of paper strength. In fact, numerical calculations have been advanced by Nissan (168), based on a number of arbitrary assumptions as pointed out by Page (176), to account for hydrogen bond strength as measured by absorption of strain energy. Nissan (168) assumes the strain in paper under stress is derived from the extension of hydrogen bonds which are, if accepted, ubiquitous to cellulosic materials. Difficulties in observing strain distribution in cellulose webs is mainly due to the fact that cellulose amorphous regions are not accessible to direct viewing by X-ray. It is postulated (168), however, that the absorbed strain energy is taken up entirely by the amorphous region, whereas the crystalline portion of cellulose only transmits energy. On the other hand, Page (176) believes that calculation of cellulose elastic moduli (191) must be based on a more detailed assumption, whereby the chain molecules can be considered individually, and that deformation arises from both stretching and angular deformation of covalent linkages.

Discrepancies in Nissan's theory (168) arise from the fact that strain within a fibre held in a sheet can vary considerably from one locality to another due to nonuniform shear and bending of the randomly arranged network. The molecular approach does not allow prediction of such anomalies for paper (176).

Paper has been recognized by Kallmes and Bernier (99) as consisting of a randomly arranged, approximately two-dimensional array of fibres bonded at fibre crossings. On this basis strength was defined as arising
from the bending, stretching and shearing of fibre segments between bond sites. The theory, however, fails to describe the strength and number of bonds on a truly quantitative basis, since it neglects deformation of the fibres themselves at bond sites. However, the principle of complex sheet deformation, including fibre bending, stretching and shearing is acceptable.

2. **Stress-Strain Properties of Paper Webs**

The stress-strain curve of a strip of paper tested in tension is an extremely sensitive index of the nature and organization of sheet components (59, 88, 128, 158, 174, 191), effect of fibre treatments (88, 90, 137, 146, 176, 211, 219), sheet formation (174, 228) and previous stress history of the paper both during and after drying (18, 51, 73, 216).

At present there are sufficient data available to demonstrate that both molecular and interfibre macroscopic effects play an important role in determining paper resistance to stresses. Fibre components within a sheet are not free to twist and change shape or slide over each other during deformation. As pointed out by Jayme (97), the response of pulp fibres to stresses is primarily, but not entirely, elastic. Deformation of real solids is always accompanied by dissipation of a part of the applied energy (121, 217). The irreversible processes responsible for energy dissipation generally show a relaxation spectrum with time which is characteristic of the solid under investigation. A small portion of the energy absorbed during straining is lost due to creation of new surface free energy with carbohydrates at their air interfaces on rupture (217). A second portion is lost in various motions during bond breaking, ultimately appearing as heat and sound but a large
portion is consumed for plastic deformation of the fibres (176). It is the
total energy input which results in direct bond breaking that is of interest,
because it reflects the mechanical properties of the various papers. Thus,
the observed non-linearity of stress-strain curves (5, 171, 173, 174, 176,
191, 217) is derived in an appreciable way from the non-linearity of internal
energy of the system. The departure from linearity is associated with break­
age of bonds within the paper sheet, as well as energy dissipation and onset
of creep (176, 193).

Bonds start to fail at very low strain values (158, 173, 187,
217) (elastic region) which accounts for non-linearity of the initial portion
of the stress-strain curve. Bond failure becomes of much greater amplitude
as the "plastic" region of the curve is reached. It is this region where
measureable energy is consumed in the process of irreversible fibre separa­
tion (158). As the strain is increased, bond failures occur randomly through­
out the sheet until a weak spot has developed (217). Further stresses are
concentrated within this area until the sheet fails completely. Since it is
mainly contact failures that differentiate irreversible from elastic regions
of the curve, extension of the theory to regions beyond the straight line is
contingent upon insight into the strength of individual fibres and fibre
contacts.

The strain resistance of paper is dependent on the quality of
three physical factors: 1. stress-strain properties of individual fibres
(59, 132, 154); 2. shear resistance of optical contact areas between fibres
(158, 197); and 3. degree of interfibre bonding (37, 88, 172, 174, 205).
a. **Fibre strength**

The fibre strength usually depends on the internal fibre structure (115, 128, 154, 197) and the extent of mechanical damage (.83, 154) imposed upon the fibres during the process of fibre separation, preparation and formation of the sheet. The extent of fibre breakage at failure of the sheet (a measure of fibre strength in paper) is closely correlated with bond strength. It has been found that the number of fibre pull-outs decreases with increasing breaking length (83). In order to compare fibre strength in sulfite and kraft papers the extent of fibre bonding would have to be the same. Tensile strength of individual loblolly pine fibres from both early- and latewood origin was tested by Leopold (128) and McIntosh (143) who found that these two fibre types contribute differently to paper strength due to differences in intrinsic fibre strength, bonding capacity and fibre geometry.

b. **Bond strength**

Shear resistance of optical contact areas between fibres, on the other hand, is governed by the bonding potential (143, 197) and surface area (83, 168, 173, 174, 219) of the fibres as related to their flexibility and plasticity, as well as geometric arrangements within the paper sheet (219). On theoretical grounds, Nissan (168) estimated bond strength within paper as being equal to $2 \times 10^{10}$ dynes/cm$^2$ which represents only 1% of the available hydrogen bonds.
c. Degree of fibre bonding

Bonded area has been defined by Nordman and Gustafson (174) as the difference in surface area of the pulp (cm$^2$/g) and the free surface area of the sheets made therefrom. Since strength properties of paper are considered to be intimately related with magnitude of the bonded area, numerous methods have been devised for its determination. The optical method based on Kubelka-Munk theory has been developed by Ratliff (188) and expanded to gas absorption by Haselton (80). Recently, a new method was developed by Smith (205) involving direct current electrical conductivity measurements on paper. The method takes advantage of the difference in dissociation energy between metallic cations and hydrogen ions, along the cellulose molecules, in chemical bonding with oxygen atoms of potential hydroxyls as ion generating sites. On applying an external potential to cellulose the metallic cations stream towards the cathode along absorbed (hydrogen bonded) water bridges or successive ion generating sites. The process is terminated by the absence of water molecules from the cellulose chains.

Due to relative simplicity, determination of optical bonded area is the most widely used measurement for this property (88). However, Jayme and Hunger (93) have shown that operative factors are not the surfaces that come into contact as shown by the light microscope, but rather microfibrils as proven by electron microscopy. On the shear surfaces the microfibrils were torn from each other and partly torn themselves combined with the breaking of primary valence forces. Furthermore, it was possible to present a series of photomicrographs with magnifications of $10$, $10^2$, $10^3$, $10^4$ and $10^5$ times showing essentially the same patterns recurring on the cellulosic
fibres, fibrils, and microfibrils. By enlarging the optically "intact" area with a light microscope to an electronically observed area of 100x magnification the real area was only 10 to 20%. Thereby, the "law of invariance of cellulosic fibrillar pattern with magnification" is invoked and it appears that the optically intact area is in fact only $(0.1)^3$ to $(0.2)^3$ while the rest is void.

It has been shown by Ingmanson and Thode (88, 219) that at a given total bonded area the strength of paper is independent of the degree of fibrillation or the amount of fines. Fibrillation and fines are considered to provide only greater surface tension forces during drying. The total dry fibre area available for bonding is the original unbeaten fibre surface, irrespective of the degree of refining.

The ratio of breaking length to bonded area in paper is high with kraft papers (174). With sulfite papers, on the other hand, a considerable degree of fibre breakage occurs at the expense of increased work at high breaking loads. With kraft paper approaching sulfite paper strength nearly all fibres pull away. This happens even in admixtures of the two types of fibres, suggesting that for a unit bonded area higher strength values are obtained with kraft than sulfite (174). Thereby, it seems possible that the whole bonded area of the sheet does not contribute equally to the strength of paper.

As pointed out by Helle (83), Leopold and McIntosh (132) and Norman and Gustafson (174) optimum sheet strength is obtained by a critical balance of intrinsic fibre strength, fibre-to-fibre bonding and bond density. Usually, the type of failure gives some answer to the relationship of these
parameters and paper quality. Rupture with excessive fibre pull-out at high strength can indicate a low degree of interfibre bonding and strong fibres, whereas tensile fibre fracture suggests weaker fibres and strong interfibre bonding.

3. **Polymerization with Groundwood Handsheets**

Earlier observations on low strength of groundwood handsheets in comparison to papers made from chemical pulps are well founded and can be further supported with results of this experiment.

Tensile strength of groundwood control specimens is approximately one-fourth to one-fifth of that had with chemical pulps. This low strength is believed to be due in part to the large proportion of fines (66), but mostly to poor conforming capacity of the high-lignin content fibre fragments. As a result, bonding capacity in such fibre webs is low. Treatments improving bonding or conformity of groundwood fibres should yield simultaneous increase in tensile properties. Substantial strength improvements, however, do not necessarily require increase in intrinsic fibre strength (as is the case with solid wood sections), since interfibre bond strength in groundwood is far below the level required for failing fibres by tensile stressing.

Substantial strength increases have been reported earlier by delignification of mechanical pulps, such as Asplund (179) and groundwood (98, 151). In this study a 15 % weight loss following 1 hr treatment with acidic sodium chlorite (corresponding to approximately 52 % lignin loss) increased the tensile strength from 1230 to 7314 psi or by 495 %. Such strength gain is not approached by the oil polymerization technique under study.
This effect clearly points toward lignin removal as a most important means for improving paper strength.

a. **Thermal treatment**

Somewhat more moderate but still substantial strength improvements can be obtained by CTLA polymer saturation and subsequent thermal induced polymerization. The strength increase is 110 to 120 % by prolonged heat treatment or about one-fourth to one-fifth that of delignified fibre strength.

Further effects of oil polymerization with groundwood handsheets is evident from Table XXI and XXII. Oil dipping of handsheets followed by thermal treatment raised tensile strength to a level closely approaching that of handsheets made from unbeaten high yield kraft pulp. It is interesting to note that oil dipping alone decreased tensile strength by 21 % and tensile energy absorption by 74 %. In comparison, strength reduction by oil dipping was even higher for the highly purified pulps (Table XXII). Consequently, strength reductions seem to be inversely related to the residual lignin content of parent pulps. By comparison with chemical pulps the strength reduction with groundwood handsheets is 30 to 40 % higher than that found on sulfite and kraft pulps although the absolute level of strength reduction was twice as high in the chemical pulps. Such an effect is evidently due to a swelling of fibres by either the solvent (benzene) or some other oil ingredient, a process which would be expected to lower hydrogen bonding capacity of groundwood fibres. Thermal polymerization of the oil polymer within handsheets made of sodium chlorite delignified groundwood pulp resulted in 8930 psi tensile strength which was only 22 % higher than the strength of handsheets
made from the same type of fibre without oil saturation. This finding is exactly the same as reported previously for delignified Asplund pulps (179). It seems that sodium chlorite treatment only affects residual pulp lignin, thereby imparting an inhibiting effect on high lignin content fibres. Such behavior is not evident, however, with high purity cellulose fibres, although the sodium chlorite treatment reduced sheet strength for all types of pulps investigated. These effects are shown in Table XXII.

The strength of interfibre bonding was raised to such an extent by thermal polymerization of drying oil within the paper network that clear evidence of exclusive fibre tensile failure was obtained. Depth of the tensile fracture zone was thereby greatly reduced (compare Fig. 7.g to i). The process is always accompanied by an increase in stiffness (in this case the increase was 67%), an effect clearly objectionable for many paper uses requiring high tear resistance and folding endurance. Furthermore, such treated papers are highly discolored due to thermal oxidation of color chromophores such as lignin within the wood pulp (Fig. 26).

b. Gamma-ray irradiation treatments

Using gamma-irradiation as energy source for oil polymerization within the paper web gave a 76% strength increase. This strength increase was produced by applying up to $10^5$ rad irradiation dosage for the particular groundwood samples studied, although maximum strength values were obtained at lower irradiation dosages for other pulp samples and in other experiments (178).

These results show the rather poor reproducibility of
polymerization by irradiation of supposedly similar materials as also reported by Rapson and co-workers (84). Where extra strength results from graft copolymerization such inconsistency is mainly a result of reaction heterogenity due to problems encountered in penetration and wetting of the parent polymer by the saturant. It seems that penetration problems are much more severe with cellulosic materials having high residual lignin content, possibly due to the hydrophobic nature of lignin. It is also possible that a lignin-oil copolymer, induced by either thermal or irradiation energy, disrupts continuity of the oil polymer within bond contact areas without really contributing to bond strength. Such copolymer sites may, therefore, act as weak links in the bond increasing process. Indeed, such speculation is supported by the fact that tensile strain of thermally polymerized samples increased by 20% which is about the same amount found for irradiated oil saturated samples. The increase in strain could be a result of non-uniform energy distribution, i.e., stress concentrations at fibre to fibre contacts.

All strength values evaluated show an increase with increasing irradiation dosage between 10 to $10^5$ rad as evidenced in Table XII, XIII, XIV and XV and Fig. 9, 11, 13 and 15. At $2\times10^7$ rad integral dosage, however, strength losses are evident. It can be noted, on the other hand, that strength losses following high dosage irradiation are never as drastic with groundwood samples as had with chemical pulps treated to the same level. As discussed earlier, strength losses following such irradiation dosage may be due to loss of intrinsic fibre strength (86), as regulated by the protective effect of aromatic compounds such as lignin on the carbohydrates (70, 70/b, 123, 204).
As found with wood (42, 86), modulus of elasticity was affected only by substantial increase in irradiation dosage. Irradiation of oil saturated handsheets, on the other hand, resulted in a 46\% stiffness increase at $10^5$ rad integral dosage. Explanations of this effect must be sought in basic structural considerations of papermaking wood fibres and handsheets made therefrom. A change in modulus of elasticity can only take place if the relative proportion of amorphous to crystalline area is changed within the basic cellulose network or if the total number of secondary valence forces connecting the cellulose molecules and holding the fibres together in a sheet of paper is changed. Since the relative proportion of crystalline to amorphous cellulose is believed to remain unchanged (200) no adjustment in overall deformation would be expected. Therefore, if it is accepted that bonding in oil saturated handsheets is increased by covalent linkages either to cellulose or lignin fractions, it may be projected that paper sheets made of such reinforced fibres will have much greater loadbearing capacity and be capable of much greater deformation without rupture. This could be due to increased number of bonds and more uniform energy distribution within the paper webs.

Non-linearity of the stress-strain diagram is the result of energy loss and failure of individual fibre to fibre contacts under stress concentrations due to non-uniform stress distribution and formation of weak spots in paper (83, 176). As a consequence, increase in paper elasticity should be reflected as improved linearity of the stress-strain curve, since modulus of elasticity is calculated as the slope of the initial part of the stress-strain curve. Equal resistance of all bonds within a sheet of paper
up to relatively high external stresses should result in a longer and better
defined straight portion in the stress-strain curve. The slope of the initial
straight portion is still defined by the load bearing capacity of the bonds
and uniformity of strength distribution within the fibre network.

Indeed, it has been found that the initial straight portion of the
stress-strain curves was greatly increased by irradiation as oil polymeriza­
tion initiating treatment. Further, this was extended almost to the point of
failure following further thermal treatment. The combined treatment effects
of low dosage irradiation followed by thermal after treatment gave practically
the same results as had with thermal treatment alone.

Lower resultant strength values by irradiation compared to
thermal treatment are believed to be due to incomplete polymerization by
irradiation. This was demonstrated by: 1. relationship between non-extract­
able oil following gamma-irradiation and tensile strength as shown in Fig. 18; and
2. the additive effect of polymerization by irradiation followed by thermal
treatment. The lower bond strength of irradiation treated handsheets is
demonstrated by a larger proportion of fibre pull-outs as compared to other
fracture patterns (Fig. 7, h vs. i).

From the foregoing it is clear that groundwood sheet strength
can be considerably improved by oil saturation followed by either irradiation
or thermal polymerization of the saturant within the paper sheet. With
irradiation treatment as energy source for oil polymerization a dosage level
between \(10^2\) to \(10^5\) rad is required. In such case the strength increase is
more or less an exponential function of logarithm of irradiation dosage up
to \(10^5\) rad integral dosage.
Limits of improvement are apparently set by the lower efficiency of irradiation within the useful irradiation dosage range, as compared to polymerization by heat treatment, and by chemical, physical and structural considerations of the papermaking fibres. Bleaching of groundwood by conventional methods followed by an oil treatment as proposed would lead to groundwood papers of very high strength and stiffness possibly coupled with improved moisture resistance. At least 75% of the maximum strength may be developed by continuous processing of such papers with irradiation sources of high intensity, since cellulose degradation depends only on the amount of absorbed energy absorbed, but is independent of source intensity (84). This suggests means for continuous processing.

Such irradiation cured oil saturated groundwood papers have a pleasing light brown color as compared to the lifeless, dark brown color of samples cured by prolonged heat treatment (Fig. 26).

4. Polymerization with Sulfite Handsheets

The high yield sulfite pulp used for this investigation contained 18.98% Klason lignin. As such it was considered to be representative of high yield acid sulfite pulp. When formed into standard handsheets of 60 g/m\(^2\) nominal basis weight it gave a tensile strength of 4185 psi (Table XII and Fig. 9), a relatively high modulus of elasticity at 460 x 10\(^3\) psi (Table XIII and Fig. 11) and a high tensile energy absorption of 144.2 in.1b/cm in. (Table XV and Fig. 15). All strength values, except tensile strain (Table XIV and Fig. 13), are three times higher than had with groundwood handsheets suggesting better interfibre bonding. The untreated sheets showed some
evidence of fibre tensile failures, although fibre pull-out was still pre-
dominant within the fracture zone (Fig. 7 j). Due to the longer fibres the 
fracture zone is considerably deepened as compared to fractures observed with 
groundwood paper. Furthermore, good conformity of fibres is also evident as 
in Fig. 7, j and l, thereby providing maximum fibre surface for interfibre 
bonding. In spite of the unusually high Klason lignin content of this pulp 
it showed higher strength than the high yield kraft pulp, a feature contra-
dictory to some earlier reports.

a. Thermal treatment

Oil dipping of oven-dry handsheets resulted in a 15 % drop in 
tensile strength, as well as 23 % reduction in tensile energy absorption. 
Oil dipping followed by heat treatment resulted in a 52% strength increase 
on an absolute strength basis, the increase being 2200 psi, almost as much 
as initial strength of the kraft paper and twice that of the groundwood paper 
used in the study. The thermal polymerization treatment increased the 
strength of interfibre bonding to such an extent, that only tensile fibre 
failures occurred within the fracture zone. The fracture zone was reduced to 
almost a single plane across the test specimen cross-section. A typical 
fracture zone following thermal polymerization and tensile testing is pre-
sented in Fig. 7 l. The discoloration due to oxidation and oil polymerization 
of fibre surfaces is especially evident on this photomicrograph as a non-
lustrous appearance. The effect is only partially evident in Fig. 7 k, where 
polymerization is only partially completed.

It is considered that ultimate tensile strength is also proportional
to maximum tensile strength of the fibres incorporated into these papers. The high tensile strength and correspondingly high modulus of elasticity is indicative of the high bond strength following oil polymerization within sulfite fibre webs. There is no treatment known which increases fibre bonding without seriously affecting intrinsic fibre strength. Without this, maximum tensile strength of sulfite fibres in paper webs cannot be measured.

b. **Gamma-ray irradiation treatment**

By using gamma-irradiation as energy source for initiating oil polymerization with sulfite papers a 38 % maximum strength increase was observed. This is approximately 73 % of that obtained by thermal polymerization (Table XXI). The accompanying increase in modulus of elasticity was 29 % or 88 % of that had with thermal polymerization. In spite of lower strength values achieved by irradiation polymerization, the tensile energy absorption remained at the same level as found for higher strength thermally polymerized paper. It is believed that this is due to a slight swelling effect of unpolymerized oil fractions which provides increase in strain.

Although strength reached only 73 % of the thermal maximum there is evidence of major fibre pull-out in failure zones of irradiated specimens (Fig. 7 k). The failure in this case closely resembles that found by other workers for kraft papers, i.e., fibre tips are broken off, while the rest of the fibre is pulled away in tensile rupture. This may be explained by considering that fibre collapse may not be uniform along the length of individual fibres. The somewhat thicker fibre ends therefore take up a larger proportion of the pressure on sheet drying operations and may develop better bonding
with neighboring fibres. On further increase of interfibre bond strength the fibre tips become anchored so strongly in the paper network that they are capable of larger deformations and distribution of stresses, whereas stress concentrations at such bonding surfaces will break the fibres due to the tapered cross-section. It takes less energy to break the fibres in tension than shear all bonded areas along the total fibre length (6). It is expected that in a process where few fibres fail in tension, but many fail by shear of fibre contacts, the amount of tensile energy absorbed should be high.

On the other hand, the increase of stiffness may be ascribed to decreased mobility of structural defects. Any hindrance to the motion of structural elements or defects will result in less dampening relaxation under stresses and thereby in greater stiffness. Such change may be looked upon as an increase in the level of internal stresses. The modulus of elasticity, therefore, will reach a maximum with maximum internal stresses, i.e., obtains highest value under conditions where the number of bonds broken is especially high.

Thermal treatment following irradiation did not yield additional strength with sulfite papers, possibly due to the higher demand of intrinsic fibre strength in sulfite papers following thermal polymerization. Although no measurements were conducted, it is expected that cellulose degradation may proceed at a faster rate with delignified or partially delignified tissues than with whole wood. The fact that lignin content is minimum in the secondary wall of sulfite fibres may have a direct bearing on carbohydrate degradation by gamma-irradiation even at relatively low irradiation dosage.
levels. It is further possible that the greater ion generating efficiency of irradiation may have caused grafting of the oil polymer to either cellulose or lignin, a process that was suggested earlier as detrimental to lignin bonding efficiency with the oil polymer.

At the present state of knowledge regarding mechanism of extra strength development by oil polymerization within paper sheets, it is difficult to point out any factor or fibre constituent that definitely influences the process. From the foregoing discussion it is clear, however, that strength gain of oil saturated paper sheets treated by irradiation is related to surface colloidal properties of the fibres and is limited by intrinsic fibre strength. Efficiency of oil polymerization by gamma-irradiation seems to be highest on the sulfite pulps which may be due to higher reactivity and better mechanical stress distribution by the longer, better conforming sulfite fibres.

c. Other materials

On comparing the efficiency of oil polymerization in various paper webs at various levels of cellulose purity, there seems to be a relationship between initial strength of the paper and that following the oil saturation and polymerization treatment (Table XXII).

In this series relating to sulfite pulps studies with high alpha viscose pulp should be mentioned. Strength of the untreated paper made from this pulp was only 565 psi. Upon oil saturation followed by thermal polymerization a 713% increase in tensile strength was observed (Table XXII). Treatment of the initial pulp by acidic sodium chlorite reduced the untreated
paper strength by 68 %, but increased effectiveness of oil polymerization within the handsheets to 860 %. Similar observations were made on a TAPPI Standard pulp, results of which are presented in Table XXII.

In another experiment, chemically inert glass fibre filterpaper gave low initial tensile strength (6.5 psi), but greatly improved properties following the oil polymerization treatment. These results suggest that tensile strength of these particular glass fibres is 52 % lower than that of the weakest, high purity cellulose fibres, disregarding sheet density. Since glass paper failures occurred mainly across fibres the absolute shear strength of the polymer bond could not be estimated. Similar failures have been observed for all paper specimens. Thereby, it is not possible to tell whether the higher strength values of chemical pulps are due only to improved adhesion of the fibres or partly to a cellulose or lignin graft copolymer with the oil.

5. **Polymerization with Kraft Handsheets**

The behavior of kraft pulp in the oil saturation and curing treatment was of particular interest in this study. The results may be of interest to the packaging industry, mainly for containers where high strength, rigidity and moisture resistance are of primary concern. Surface colloidal properties of kraft fibres have been shown to differ markedly from those of sulfite fibres, whereby behavior of kraft fibres in paper sheets has been found to depend on the amount of residual lignin and more resistant hemicelluloses. With increase in residual lignin the bonding capacity of fibres usually decreases, possibly because of the lower conformity of high lignin content fibres.
On the other hand, retention of hemicelluloses has been shown to raise swelling capacity of kraft fibres and consequently provide larger drawing forces and closer fibre bonding following sheet drying. For condensation reactions (grafting) specific to lignin there seems to be good possibility for increasing both intrinsic fibre strength and bond strength due to rather uniform residual lignin distribution over the entire fibre wall. Such treatment could provide papers with improved strength, stiffness and dimensional stability.

a. Thermal treatment

It was found that handsheet strength with unbeaten kraft pulp containing 9.60% residual Klason lignin could be increased as much as 84% on saturation with CTLA Polymer followed by prolonged heat treatment. This did not take full advantage of intrinsic fibre strength as shown in Fig. 7o. The fact that failure for the oil treated kraft paper was a combination of fibre breakage and interfibre bond shear explains the high tensile energy absorption values found by analysis of stress-elongation curves and recorded in Table XIX and XXI. It is concluded that the treatment did not maximize kraft paper strength, possibly due to some surface inhibition preventing the oil from providing maximum reinforcement of interfibre bond areas. From the failure pattern, however, there is suggestion that further strength development might be obtained, to a point where all failure would occur across the fibres, similar to that observed with papers made from acid sulfite pulp.

Strength data were obtained with paper made from bleached kraft fibres (Table XXII). This has a different source than used for the unbeached kraft paper sheets. Removal of most of the residual lignin by conventional
bleaching techniques may have increased tensile strength by 10-20%. Oil polymerization with such papers by prolonged heat treatment gave a 138% strength increase which brought absolute strength to a level nearly 20% higher than that had with the unbleached sulfite paper (Table XX). Microscopic examination of fracture zones showed that the failure pattern was similar to that shown in Fig. 7 o. This indicates that both fibre and bond strength in kraft papers is inversely affected by presence of alkali lignin and that this is detrimental to extra strength development on oil polymerization. Although further treatment of the bleached kraft pulp by sodium chlorite lowered initial sheet strength by as much as 77%, the strength loss was recovered on oil polymerization through proportionally higher strength gains.

b. Gamma-ray irradiation treatment

While strength increase by gamma-irradiation of oil treated sheets was 73% for sulfite and 69% with groundwood compared to polymerization by prolonged heat treatment, it was only 50% for kraft handsheets. This is in line with observations on thermal polymerization. The lower efficiency, however, seems to be specific to kraft pulps as evidenced in Fig. 18.

It is customary to examine suspected graft copolymers by solubility in various organic solvents for proof of copolymerization. Since the amount of graft copolymer found is usually proportional to irradiation dosage (or amount of energy applied), the former is also frequently proportional to increase in the physical property being measured. Since the oil homopolymer obtained on glass fibres was mostly insoluble in organic solvents the reciprocal of grafting (or degree of polymerization) was determined by extraction
as expressed in per cent weight loss of the saturated paper samples. The efficiency of polymerization treatment became obvious by relating weight losses on extraction of various treated papers to tensile strength before extraction. At the same degree of polymer formation as had with sulfite papers the strength developed with treated kraft papers was considerably lower and did not show a straight line relationship (Fig. 18) as found for both groundwood and sulfite. It is interesting to note, that while the absorbed, but uncured, oil could be quantitatively recovered from the glass filterpaper, under the experimental conditions used an irreversible absorption was observed for all types of pulp fibres as evidenced in Table X. Such irreversible absorption could not be due to a simple caging effect within the parent polymer although the amounts retained were practically the same for both chemical pulps, but somewhat lower for groundwood.

The rather low interfibre bond strength had with treated kraft papers is evident from the extended fracture zone as shown in Fig. 8. In spite of the 42% increase in strength following oil polymerization by irradiation no change in fracture pattern was observed (Fig. 7 n). The full extent of one half of a deep fracture zone is presented in Fig. 8. From the photomicrograph it is evident that the zone extends far into the paper web, appearing longer than the average fibre length. Such a process of failure would be expected to involve shearing of a large number of fibre crossings, thereby contributing to the relatively high tensile energy absorption had in combination with lower ultimate tensile strength of such papers.

Increase in modulus of elasticity on oil polymerization suggests a reduction in the normal high folding endurance of kraft papers. However,
it was still observed, that oil treated and cured papers retained a fair amount of pliability even following the prolonged heat treatment. While failure of tensile specimens was abrupt for groundwood and sulfite papers following treatment, the kraft specimens showed more gradual failure possibly due to the slow release of interfibre bonds. Stress-elongation curves obtained with treated kraft papers showed only a short portion of direct proportionality, as well as a rugged, jittery curve immediately before specimen failure. The latter portion is evidently due to fibre pull-out throughout the fracture zone.

From the foregoing it is evident that extra strength development by treatment of specimens prepared from groundwood, sulfite and kraft pulps can be obtained with up to 70% efficiency when gamma-irradiation is substituted for prolonged high temperature treatment as energy source for oil polymerization. The efficiency seems to be related to both basic paper strength and state of residual lignin in that relatively higher strength increases were realized with papers of lower untreated strength in increasing order of groundwood, kraft and sulfite. On the other hand, availability of larger amounts of lignin on the fibre surface seemed to aid strength development following polymerization by gamma-irradiation. Reasons for lower polymerization efficiency by the irradiation technique are unknown. At any rate, degree of polymerization (strength increase) has been shown to be proportional to the irradiation dosage (Fig. 10, 18, Table XVI) and is strongly related to basic paper strength. Among other strength parameters, modulus of elasticity (Fig. 12, Table XVII) and tensile energy absorption (Fig. 16, Table XIX) following polymerization increased in a manner similar to that with thermal treatment. Since these parameters are more sensitive indices of energy distribution within
stressed papers they suggest close similarity of sites involved in the re-
inforcing process as induced by the two types of treatments. It is interest-
ing to note, that total additivity of polymerization effects by combined
treatments was achieved only with the high lignin-content groundwood paper,
whereas chemical pulps showed lower strength values following the combined
treatment. The relatively lower strength values may be due to more cellulose
degradation by irradiation as indicated from reduced strain and tensile
energy absorption for samples designated $G_{\text{max}}$. These results seem to indicate
a lower degree of carbohydrate protection by residual lignins in the chemical
pulps.

Based on projections regarding CTLA oil polymerization within
paper webs made from high yield pulps, the relatively high strength increases
had with high purity cellulose papers and inert sheets such as glass filterpaper
cannot be satisfactorily explained. Apparently, the oil is capable of homo-
polymerization to strong, brittle, resin-like substances which are insoluble
in benzene, toluene, chloroform, petroleum ether and tetrahydrofuran. Bonding
between inert glass fibres must evidently depend on sufficient wetting and
adhesion at the glass-oil polymer interface. With chemically reactive sub-
stances covalent linkage formation under favourable conditions must be con-
sidered. With high lignin content pulps the level of extra strength increase
does not exceed 150\%, but is somewhat lower. Although delignification of
groundwood with sodium chlorite to approximately 15\% weight loss increased
untreated paper strength almost five times, further treatment by oil satu-
ration and heat polymerization gave only an additional 22\% strength increase.
Results of sodium chlorite delignification of Asplund pulp followed by sheet
formation and oil polymerization gave similar values (179). In fact, such low strength increases were observed on pulps with only 5% weight loss had by mild oxidative delignification. Since commercially purified pulps were not tested at that time, the above result led to the hypotheses that oil polymerization within lignified tissues is chemical in nature and depends on lignin quality rather than lignin quantity. Furthermore, the strength of oil-tempered experimental hardboards was significantly reduced when hot water soluble hemlock bark tannins were precipitated onto the Asplund fibre prior to treatment. Evidence of a lignin-tannin condensation was immediately evident on hot-pressing of the fibre mat by development of the characteristic purple color known for the complex. Other fibre treatments such as hot caustic and alcohol-benzene extractions, as well as cellulose degradation by irradiation did not influence oil condensation within the experimental hardboards to any degree.

The present study contained three types of residual lignin in fibres. The alkali lignin of the kraft pulp showed lowest reactivity as measured by increase in tensile strength following the irradiation treatment. With this pulp there is still room for strength improvement as evidenced by the large proportion of fibre pull-outs within the fracture zone. On the other hand, oil polymerization with groundwood and sulfite sheets produced tensile strength values of approximately maximum strength capacity of the particular fibres. Thereby, intrinsic fibre strength became the limiting factor with such paper sheets.

The increased methoxyl content of irradiated, untreated pulps may be a competing mechanism for the very site of oil copolymerization within and between fibres. Reactive sites terminated by addition of methyl radicals
could account for the lower efficiency of irradiation grafting compared to that produced with thermal curing. This theory seems to be substantiated by higher extractability of oil residues following irradiation treatment. Further, maximum strength was not obtained by heat treatment of irradiated samples (Treatment G). This is to say, that the number of sites available for bond formation could be reduced by some associated factor of irradiation. The effect appears to be less pronounced with the kraft sheets, whereas the increase in methoxyl content is highest for this pulp (17%).

The increase of methoxyl content may be due to formation of formaldehyde as degradation product from residual lignin (194) or carbohydrates and recondensation with the same.

6. Polymerization with Handsheets Prepared from Pulp Fibre Blends

Most previous work done on effect of fibre length and sheet strength properties is not applicable when chemical pulps are mixed with groundwood. This is due to the large difference in bonding capacities of the two fibre ingredients. With sulfite pulps removal of fines had little effect on regular tensile strength, but reduced stretch and burst slightly as observed by Thode and Ingmanson (219). In similar experiments with kraft pulps, removal of fines shifted the tear-tensile strength relationship in direction of higher tear for a given fibre breaking length. The change was rather small by adding more fines, since bonding capacity and flexibility of the fibres was not altered materially.

Blending chemical fibres with groundwood involves another phenomenon. Although effects of blending have not been investigated in detail,
indications (32) are that strength of the resulting papers is not a direct function of blending between the two extremes. The breaking load of fibre mixtures is dependent upon the ratio of long fibres to fines in the mixtures, as well as upon the breaking load of each component. If these were the only effects present with such mixtures a linear relationship between breaking load and groundwood content would be expected.

The effect of fibre blending is examined in the present study as shown in Fig. 9 and 10 (Plot A). The relationship between tensile strength and extent of blending is exponential for both sulfite and kraft mixtures. Equations are presented in Table XX (Eq. 1 and 17). Thus, there must be additional factors influencing breaking load of the blends. Brecht and Erfurt (32) suggest sheet density as a contributing factor, since density of the sheet increases with a larger proportion of fines.

Although curves obtained for the two types of blends are mirror images (sulfite: convex - concave, kraft: concave - convex) they both have inflection points at the 50% blend level. These represent quite different tensile strengths (Fig. 9 and 10) with values higher for the sulfite-groundwood mixture. The same holds for modulus of elasticity (Fig. 11 and 12). Simple parabolic relationships were obtained for ultimate tensile strain (Fig. 13 and 14), since strain is generally higher for the sheets containing kraft fibres. Variation of tensile energy absorption was linear with increasing amounts of groundwood pulp. Slope of these regressions is negative, generally with higher values for the sulfite - groundwood mixtures.

Addition of small amounts of groundwood lowered the strength of sulfite handsheets drastically, possibly due to the large difference in tensile
strength of the individual components. The strength difference is nearly fourfold for sulfite vs. groundwood, whereas it is only twofold for unbeaten kraft. Thereby, groundwood addition reduced bonding of sulfite pulps much more than with kraft pulps. The greater bonding capacity of sulfite fibres, however, was retained throughout the whole series of mixtures. It is possible that the higher tensile strength of sulfite papers is derived from fibre breakage up to the inflection point, whereafter the strength is determined by the strength of interfibre bonds rather than the fibre strength. At the point of 50% mixture Brecht and Klemm (33) found that all long fibres were surrounded by fines (groundwood) so that the fines alone determined the breaking load of these papers. They believed that properties of high yield, long-fibred unbeaten pulps are, in principle, similar to those of groundwood since the long fibres are relatively stiff or brittle and little fibrillated. According to these findings there should be a sharp drop in tensile strength at the 50% blending ratio. No such phenomena were observed with either blend series prepared for this experiment. Strength of sulfite sheets at the 50% blend level was about the same as that found for pure kraft handsheets in this experiment. It appears that long fibres contribute considerably to paper strength throughout the whole blending range, with limiting factor being mostly determined by the bonding capacity and to some extent the strength of the parent chemical pulp. It is of interest that the same relationship holds for modulus of elasticity (Fig. 11 and 12), and to some extent for tensile energy absorption (Fig. 15 and 16).

Tensile strain properties, on the other hand, are quite dissimilar. The lower degree of allowable deformation seems to be indicative of better
conformity and more effective stress distribution within paper webs made from sulfite fibres even in mixtures with groundwood (Fig. 13). This is also expected from the substantially higher modulus of elasticity values indicated above.

From an industrial point of view the above findings have very critical meaning. By taking the case where certain strength standards have to be met with either of the two chemical pulp furnish, it would be easier to maintain the desired strength feature with kraft blends due to the small change over the 40 to 70% range of groundwood content used as blend. On the other hand, blending proportions would have to be more exactly metered with sulfite-groundwood pulp mixtures if properties are to be controlled, due to the rather large strength change (approximately 400 psi for every 10% increase in sulfite pulp between 30 to 100% sulfite pulp content) with this series. It should be noted, however, that based on pulp behavior similar to the one observed here, it could be still more economical to produce a certain paper strength with sulfite-groundwood mixture due to the substantially higher strength had from such mixtures. In other words, relatively smaller amounts of expensive chemical pulp would be necessary to achieve a desired strength with sulfite-groundwood than with kraft-groundwood mixtures.

Within the irradiation dosage range investigated no measurable loss in tensile strength occurred up to $10^3$ to $10^5$ rad dosage (Plot C, Fig. 9-16). After slight initial strength increase the loss was approximately 21 to 30% following a $2 \times 10^7$ rad integral irradiation dosage for the sulfite-groundwood series. This decreased with increasing amounts of groundwood. On the other hand, strength losses seemed to have increased for the kraft-
groundwood series from 17 to 21% with increasing groundwood content. These observations may be in line with theories on radioprotection of wood carbohydrates by lignin, since a more intimate chemical mixture of wood carbohydrates with lignin can be expected on lignin grafting onto cellulose following alkaline pulping as observed by Kleinert (108).

Modulus of elasticity was relatively unaffected within the irradiation range studied. However, both tensile strain and energy absorption followed similar patterns as had with ultimate tensile strength.

The equations calculated for tensile strength change of oil dipped sulfite- and kraft-groundwood blends (Fig. 9 and 10, Plot D and Eq. 5 and 21) predict straight line relationships for both blend series at a slightly lower level than had for control specimens (Fig. 9 and 10, Plot A). Reduction in tensile strength was not followed by modulus of elasticity (Fig. 11 and 12), but is evidenced by a decrease in tensile strain (Fig. 13 and 14) and tensile energy absorption (Fig. 15 and 16).

Decrease in tensile strength due to oil absorption has been ascribed by others (146) to lubrication of the fibres permitting easier deformation. Increased deformation, however, should result in lower modulus of elasticity and higher strain. The fact is, that neither lubrication nor swelling of the polymer network can account for the higher modulus of elasticity since the final effect should be the same in both cases.
a. Thermal treatment

Considerable improvements in all strength properties were observed following thermal treatment of oil dipped handsheets prepared from the pulp blends. Behavior of the saturated papers were strongly affected by properties of the basic pulps. There is strong indication from this that oil polymerization by heat is strongly influenced by lignin quality and fibre properties. As postulated in earlier sections, limitations to oil polymerization effects appear to be due to intrinsic fibre strength in case of sulfite fibres, to surface chemistry with kraft fibres and to physical limitations for groundwood fibre fragments.

The actual effectiveness of polymerization is difficult to measure with sulfite papers since practically no interfibre failures occur on tensile testing (Fig. 71). An effectiveness of 80 to 85\% is estimated for kraft sheets accepting equal intrinsic fibre strength for sulfite and kraft fibres. Under the present circumstances, more than 100\% reinforcement efficiency was estimated for groundwood sheets.

Change in tensile strength of oil treated sulfite-groundwood sheets shows a sharp initial drop (Fig. 9, Plot E) following addition of small amounts of groundwood, possibly due to ease of weak spot formation in paper with heterogeneous groundwood distribution. This large sensitivity of tensile strength to disturbances in the paper network is due to the fibre strength dependence of oil polymerized sulfite papers to a level where characteristics of oil polymerized groundwood become strength controlling factors. This occurs between 40 to 60\% groundwood in pulp blends comprising the handsheets.

The same process shows surprising uniformity of strength
improvement for the kraft-groundwood blend series (Fig. 10, Plot E), almost as if treated sheet strength depends on factors similar to those of untreated sheets. This allows more accurate prediction of strength improvement due to oil polymerization within the kraft-groundwood series.

Of interest with regard to oil polymerization within chemical pulp-groundwood sheets is the fact that a common strength level can be observed at 50% blend regardless of whether sulfite or kraft pulp is used for blending. The strength increase at this point is only 37% for sulfite and 110% for the kraft series. It is believed that this result is due to the effect exerted by oil polymer reinforcement of interfibre bonding between long and short fibres comprising these blends. It is also possible that the energy required to break all the fibres in tension within a sheet containing 50% groundwood strongly welded to the chemical fibres is the same as that required for pulling out 50% of kraft fibres from the groundwood network. However, comparing results in Table XV and XIX and Fig. 15 and 16 (Plot E) for these samples shows that the tensile energy absorption was some 50% higher for the kraft-groundwood series following oil polymerization than had with the sulfite-groundwood series. Full explanation requires further treatment of these phenomena.

Modulus of elasticity (Fig. 11 and 12, Plot E) changed significantly and in similar fashion to tensile strength, with largest improvements occurring with high groundwood-content (up to 50%) blends.

It should be noted also that while tensile strain decreased in a regular fashion for the kraft-groundwood series (Fig. 14) an increase is noted with increasing amounts of groundwood in the sulfite blend series. (Fig. 13)
b. Gamma-ray irradiation treatment

Much of that discussed in the foregoing section could be repeated here, since effects had by irradiation polymerization within sheets made of blends between chemical pulps and groundwood are much the same as those with thermal treatment. Some results are more modest. Nevertheless, properties from irradiation oil polymerization are in some cases directly comparable to those had with prolonged heat treatment. In Fig. 9 and 10 maximum tensile strength values obtained within 10 to $10^5$ rad dosage are plotted (Plot Fm) for comparison with effects had from thermal treatment. The same results expressed as per cent of absolute strength increase are plotted in Fig. 17. These plots show polymerization efficiency by gamma-irradiation for both pulp blend series compared to those had with thermal treatment. Thereby, it is found that based on absolute strength increase oil polymerization by irradiation was least effective (for reasons already discussed) on sulfite handsheets and most effective on handsheets made from pure groundwood pulp. Handsheets prepared from kraft-groundwood pulp blends show an intermediate position. On an absolute strength basis, oil polymerization by irradiation was most effective for papers made from sulfite groundwood blends. However, these required higher levels of irradiation. For both types of pulp blend the increase in tensile strength of oil dipped handsheets increased exponentially with increase in integral irradiation dosage as described by equation 5 for sulfite and equation 21 for the kraft blend series (Table XX). Unfortunately, there is no common blend level at which effectiveness of polymerization by irradiation would be the same for the two types of pulp mixtures. In fact, equation 13 predicts a 15% higher strength value for oil treated handsheets
made of pure groundwood pulp, suggesting the importance of sulfite fibres in the high groundwood content blends. Thereby, on an absolute strength basis oil polymerization by gamma-irradiation favours blending with sulfite pulps to such an extent that at 60% groundwood content the level of tensile strength obtained with thermal treatment of oil dipped handsheets is surpassed. This result suggests that lignin quantity may be only of secondary importance for the proposed strength reinforcement by oil condensation. Since sulfite pulp residual lignin is retained in a less degraded and condensed state than kraft pulp lignin, such response was expected. Superior behavior of residual sulfite lignin may be ascribed to a more open structure, as well as improved hydrophilic properties acquired during processing.

Similar plots (Plot Fm) are produced for modulus of elasticity (Eq. 14 and 26) and tensile energy absorption (Eq. 16 and 28) for both types of pulp blends. Plots for tensile strain are not given, since correlation between tensile strain and pulp blend for the samples showing maximum tensile strength within 10 to 10^5 rad.integral irradiation dosage were non-significant.

Significance of treatment effects on ultimate tensile strength was tested by a combined analysis of variance for the three pulps. Results of the analysis are presented in Table XI. Both treatments (blending = Per.; and irradiation = Treat.) and their interaction had a highly significant effect on development of ultimate tensile strength. In curvilinear regression analyses, on the other hand, it was shown that the independent variables (blend per cent and irradiation) are completely unrelated.

The tensile strength level resulting from interaction of pulp type and extent of blending was calculated from the analysis of variance for both sulfite-and kraft- groundwood series and is plotted in Fig. 19. The
highly significant difference between the two blends is due to the overall
difference in slopes between any two levels of blending. Significance of
these differences have been discussed in the foregoing sections.

Relationship between dependent variables is determined by calculat-
ing simple regression equations for various groups of treatments that
appeared as close groups. Thus, it was found that controls (A) and irradiated
controls (C) formed one group, oil dipped (D) and irradiation polymerized (F)
samples formed another group and finally thermally polymerized (E) and irradiation
plus thermally polymerized (G) samples represented a third distinctive group. The
various regressions for both pulp blends are presented in Fig. 20 to 24.
Relationships were drawn for ultimate tensile strength ($Y_1$) vs. modulus of
elasticity ($Y_2$), ultimate tensile strain ($Y_3$) and tensile energy absorption
($Y_4$) and for $Y_2$ vs. $Y_3$ and $Y_4$. Values obtained for the highly irradiated
samples ($2 \times 10^7$ rad dosage) are omitted from the plots since they fell beyond
the prediction. Reasons for this are found in advanced cellulose degradation,
since the lower tensile strength was not accompanied by substantial change
in modulus of elasticity. Interestingly, the level of strain within these
samples remained practically constant as tensile strength increased to a
maximum. Generally, the two types of blends behaved similarly in this regard.

A significant relationship was obtained between tensile strength
and modulus of elasticity for the sulfite-groundwood blend as shown in Fig.
20. This relationship is indicative of the good bonding quality of sulfite
fibres used for this experiment. It was found that improvement in tensile
strength on thermal grafting is proportional to fibre quality. With irradia-
tion grafting there was a definite increase in modulus of elasticity as
related to tensile strength. This effect gives evidence for loss in tensile strength at even intermediate irradiation levels (possibly at $10^5$ rad), and has significance in that at this dosage level cellulose degradation may have taken place. Relationships like these may be of some assistance in determining the allowable degradation of products when exposed to irradiation treatment. Trends seem to be similar with kraft blends although not quite as decisive. Of interest here is the difference in average slope indicating a much larger allowable deformation of bonds within the kraft papers even after thermal polymerization. Fig. 20 is believed to be a good demonstration of the wide range of strength parameter that can be covered by blending and the proposed copolymerization procedure.

The rather strong relationship between $Y_1$ and $Y_2$ can be observed with all relationships they enter. The similarity between Fig. 22 and Fig. 24 is also striking. Relationships with ultimate tensile strain (Fig. 21 and 23) are difficult to follow due to limited accuracy of strain measurements. It is obvious, however, that while there was little change in strain pattern with increasing tensile strength (or modulus of elasticity) for the sulfite-groundwood samples in any particular treatment, there was a definite increase in strain in the kraft-groundwood samples. This may be due to weakened interfibre bonds caused by swelling, if solvent swelling is accepted as more detrimental to kraft-groundwood interfibre bonding. It can also be observed that such solvent effects must be permanent within these types of sheets, since thermal treatment gave similarly increasing strain to that observed with irradiation polymerized samples. It seems that strain falls off rapidly with decreased amounts of groundwood and increased amounts of irradiation.
(Fig. 21, Plot D and F).

Tensile energy absorption in relation to tensile strength and modulus of elasticity is influenced favorably for the treated high groundwood-content sulfite pulps and for the thermally polymerized kraft pulps. This is obviously due to the effective welding effect by oil polymerization within the handsheets. Lower relative effectiveness of irradiation on kraft blends is also evident from Fig. 24.

At this point it seems appropriate to review homopolymer versus graft copolymer effects as shown by the study. Results from solvent extractions included in this experiment certainly do not prove this point either way, since the homopolymer produced within the web of glass filterpaper could not be dissolved by usual organic solvents. Further, the larger strength increases observed with handsheets made from high purity cellulose fibres and with glass filterpaper suggest that lignin has detrimental effect to extra strength development. However, it should be remembered that oil polymerization in these cases was carried out with heat alone. It is also pointed out, that the oil is sufficiently stable at room temperature to prevent homopolymerization for long periods of time (perhaps one or two years). Effects on polymerization by irradiation must be due to formation of either homopolymer, graft-copolymer, or to a combination of these. However, these cannot be partitioned from the present data.

The effect of lignin oxidation by sodium chlorite treatment in Asplund (175) and groundwood pulps pointed toward a chemical reaction between residual lignin and the drying oil. The fact that treated fibres were strongly inhibited in strength reinforcement suggests lowered reactivity of
the fibre surface and preferential destruction of lignin reactive sites, since the oxidation treatment is specific to lignin and when properly practiced has little effect on carbohydrates. The same was demonstrated within this experiment.

Unfortunately, preferential attack of oxidizing agent on lignin may have caused an erroneous conclusion by Koshijima and Muraki (116), who reported proof for a methyl methacrylate-hydrochloric acid lignin copolymer by application of a mild sodium chlorite treatment to the copolymer. Thereby, the graft polymethyl methacrylate was dissolved from the copolymer. The separated polymethyl methacrylate had a molecular weight at least fifty-fold that determined for the parent polymer, hydrochloric acid lignin. Thus, it was concluded that only a few long-chain polymethyl methacrylate molecules were grafted onto the parent polymer. However, fragmentation and degradation of the parent polymer by sodium chlorite could also liberate the branch polymer. It is not known whether recovery of copolymers was quantitative or involved total destruction of hydrochloric acid lignin by sodium chlorite.

The present work could be expanded in two main directions:

1. Further investigation of the basic polymerization mechanism by blocking conceivable reactive sites on the lignocelluloseic fibres through acetylation or selective methylation, or both. It is known (31) that these treatments provide substituted lignocellulosic pulp derivatives, wherein hydrogens of potential primary and secondary hydroxyls, as well as carbonyl groups are replaced by acetyl or methoxyl groups. Possibly methylation would be the more useful treatment due to selective control of sites by choosing different methylating agents. A brief summary of selective
methylation on the phenyl propane lignin building unit is presented in Fig. 25. Three methylating agents could be used, diazomethane, aqueous alkaline dimethyl sulfate and methanol-hydrochloric acid (1% by volume). Any combination of these could provide the desired degree of substitution. The methylation treatments should be carried out on the pulps at not greater than 10% consistency. It is expected that the anhydrous conditions required for diazomethane and methanol-hydrochloric acid treatments would cause pulp strength loss, as well as require extensive water soaking before handsheet formation. Effectiveness of methylation can be followed by determination of methoxyl content or determination of phenolic hydroxyls by some suitable method. Kraft pulp should show lower reactivity than either sulfite or groundwood pulp.

Handsheets prepared from pulps treated as described should be further processed in the way described herein. Due to poor reproducibility of strength results by a single irradiation dosage, at least three levels of irradiation dosages, i.e., $10^3$, $10^4$ and $10^5$ rad, should be used. Control specimens (similar to Treatment A of this experiment) would be required.

2. A second avenue of investigation could include maximizing the effect of strength increase by irradiation polymerization of the drying oil. This could include formulation of a more selective oil (possibly by gaschromatographic determination of oil components before and after irradiation, aided by I.R. spectra), removal of stabilizing agents and investigation of effect of peroxide formation on irradiation.

Each approach could comprise the subject of a separate experiment. It would be hoped that with the aid of such information the oil copolymerization
mechanism could be adequately described. Efficiency of oil polymerization by the irradiation technique could be estimated by the use of glass filter-paper as a substrate which resists degradation by gamma-rays.
SUMMARY

Means for improving mechanical strength of papers made from high yield sulfite, kraft and groundwood fibres, as well as blends of the chemical pulps with groundwood, are described. The treatment involves saturation of handsheets with CTIA Polymer (a commercial hydrocarbon drying oil) and subsequent oil polymerization within the fibre webs by high temperature heating or by the novel method of gamma-irradiation.

Effects with the various treatments examined in the study are summarized as follows:

A. In spite of the relatively high residual pulp lignin, handsheets made from high yield sulfite fibres gave highest tensile strength and modulus of elasticity. Kraft sheet strength was slightly more than one-half of that had with sulfite and twice that with groundwood. Lower strength is attributed to weaker interfibre bonding within kraft papers and to poor fibre conformity and low average fibre length with groundwood. Evidence for lower bond strength in kraft sheets is indicated by excessive fibre pull-out on failure.

Significantly different effects were experienced when blending sulfite and kraft fibres with groundwood. The higher bonding capacity of sulfite fibres was clearly preserved, even with high groundwood content sheets. Basic fibre strength was not the only factor operating in chemical pulp mixtures with groundwood.
B. Prolonged heating (1.5 hr at 145°C) of non-impregnated hand-sheets gave 10 to 15% increase in tensile strength, as well as slightly increased stiffness and tensile energy absorption. Largest improvements were obtained with the more heat resistant kraft pulps followed by sulfite and groundwood. This behavior is probably due to improved hydrogen bonding and additional cross-link formation within dry fibre webs.

C. Exposure of non-impregnated handsheets to increasing amounts of gamma-ray irradiation had little effect on sheet strength parameters up to $10^5$ rad integral dosage. At $2 \times 10^7$ rad dosage only sulfite pulp handsheets were adversely affected, possibly due to advanced cellulose depolymerization and decreased intrinsic fibre strength.

D. Oil saturation without curing reduced tensile strength by up to 20%, but slightly increased modulus of elasticity especially for the low groundwood content kraft blends. Slight reductions in ultimate tensile strain and tensile energy absorption were also noted. These effects are believed to result from swelling by the diluted oil (benzene plus some oil component) which is capable of wetting cellulose or lignin. A second factor, lubrication of interfibre bonds, may permit larger deformation before tensile failure.

E. No cellulose treatment known confers all properties that occur as a result of oil copolymerization within fibre webs. Substantial strength increases were recorded for all types of handsheets following prolonged thermal treatment of oil saturated samples. Relative effectiveness of treatment seems to be limited by: 1. state of residual lignin and 2. intrinsic fibre strength. Maximum strength was obtained on sulfite sheets.
as evidenced by exclusive fibre failures on tensile testing. Both modulus of
elasticity and tensile energy absorption were high following such treatment.
Maximum strength development was also observed with groundwood handsheets,
although only one-third as high as had with untreated handsheets following
sodium chlorite delignification of the initial pulp.

Although strength of kraft handsheets was almost double that of
untreated sheets, only partial fibre failure was observed. This suggests that
chemical reactivity of kraft residual lignin is not sufficient to allow a
maximum increase of bond strength within such paper webs. Nevertheless, the
strength improvements were substantial. A common tensile strength level was
observed with the sulfite- and kraft-groundwood blends at 50% groundwood
addition. The point was reached rapidly by increasing groundwood in sulfite
sheets, due to the large difference in basic sheet strengths. The strength
equilibrium between the two types of blends must be due to physico-chemical
effects accentuated by the treatment and limited by intrinsic fibre strength.
Reinforced bond strength within fibre webs may also contribute additional
strength. In sulfite-groundwood blends all fibres were broken in tension.
Since groundwood fibres may not contribute more strength than in pure ground-
wood sheets, their presence must promote weak-spot development in blended
papers. Development of kraft-groundwood sheet strength was due to comparable
strength contributions of individual pulp components. Fibre breaking was
found to occur more extensively in sulfite than kraft paper. Since intrinsic
fibre strength and bond strength cannot be separated completely with paper
webs, other evidence must be used. The larger number of fibres broken in
tensile testing of treated sulfite papers indicated a larger number of fibres
taking part in the stress distribution as compared to kraft papers.

Modulus of elasticity of treated papers was raised to a very high level. Limit of proportionality on the stress-elongation curves was greatly extended for such fibre webs.

F. Gamma-irradiation as energy source for copolymerization gave comparable results although slightly lower (30-50%) than polymerization by thermal treatment. Tensile strength increases by thermal treatment of oil impregnated handsheets were 118% for groundwood, 52% for sulfite and 84% for kraft sheets. Values were 76%, 38% and 42%, respectively, by gamma-irradiation. Efficiency with sulfite papers was difficult to assess, since practically no interfibre failure occurred on tensile testing following oil polymerization by thermal treatment. Copolymerization efficiency was estimated at 65% with groundwood, 73% with sulfite and 50% with kraft paper sheets indicating some correlation with reactivity of respective fibre surfaces in paper. Maximum efficiency was observed with an irradiation dosage below that known to cause detectable degradation of wood carbohydrates.

The discontinuous structure of paper was retained, although a slight swelling was evident with irradiation polymerized papers. Whether normal fibre bonding with hydroxyl hydrogens is disrupted by the copolymerization treatment, is not known. The initial effect of swelling was evident by decreased tensile strength, increased elasticity, tensile strain and energy absorption. It is possible that the higher strength of thermally polymerized samples is due to a partial flow of CTLA Polymer and reduced plasticization temperature of the lignin, as well as to a higher value of permanent set obtained on heating. Just to what proportion covalent bonding, as
compared to mechanical adhesion, between the lignin-oil copolymer is responsible for the increased strength in sheets made from high yield pulps, was not investigated. Based on evidence from sodium chlorite oxidation of groundwood, approximately 80% of the strength increase is due to covalent bonding and 20% to mechanical adhesion by homopolymer formation between the wood fibres.

G. The synergistic effect of oil polymerization by gamma-irradiation and thermal after-treatment suggests a similarity of reaction end products although kinetics and mechanism of extra strength development may involve entirely different principles. No efforts were made to characterize either type of reaction.

Application of irradiation as energy source could replace thermal treatment as being comparably effective and faster, whereby it is more suited for continuous processing of long paper webs. Added advantage of irradiation processed oil treated papers is less discoloration, especially with high lignin content papers, and lower modulus of elasticity, a factor clearly objectionable for some paper uses.

By use of glass filterpaper, highly purified commercial celluloses and groundwood oxidation, a dual role of the drying oil was demonstrated. In the inert glass filterpaper bonding is evidently mechanical adhesion. It is also possible that the same type of bonding takes place with highly purified cellulose fibres. Laboratory purification by sodium chlorite treatment, which mostly affects lignin (approximately 50% of the lignin was removed), improved groundwood sheet tensile strength tremendously, while only 22% additional strength was observed on handsheets following oil saturation and thermal treatment. This is in direct line with earlier observations made by
the author (179) on Asplund fibre. The same inhibiting effect was not observed when high purity cellulose fibres were chlorited.

As further work, the substitution of reactive hydroxyl groups in both cellulose and lignin by selective acetylation and methylation and by reduction followed by methylation could better reveal identity of reactive sites and respective reactivities of cellulose and lignin towards copolymerization with hydrocarbon drying oils. If no site is found by these or other means the possibility of pure mechanical bonding would be favoured, although the inhibition observed on oxidation of high lignin content mechanical pulps would still have to be explained.

Partial solubility of the oil saturant following polymerization treatment suggests covalent bonding between some fibre constituent and drying oil. An especially good relationship was observed between oil fractions resisting extraction and tensile strength of irradiation polymerized samples. Since irradiation has been shown to reduce unsaturation of olefins and polymerization requires larger irradiation dosages, a reduction in solubility at 10 rad dosage could hardly be due to homopolymerization. However, extent of true graft copolymerization cannot be determined by simple extraction techniques since the homopolymer was also insoluble in the usual organic solvents. Application of the sodium chlorite treatment and I.R. spectras of collected precipitates might be expected to reveal presence of lignin fragments with the liberated oil polymer as demonstrated by Koshijima and Muraki (116).
CONCLUSIONS

Oil polymerization within handsheets made from chemical pulps, groundwood and chemical pulp-groundwood combinations strengthened interfibre bonding without noticeable effect on intrinsic fibre strength.

With wood fibres effectiveness of the treatment as initiated by heat or gamma-ray irradiation was related to surface colloidal and basic fibre properties. Maximum strength parameters (ultimate tensile strength, elasticity, ultimate tensile strain and tensile energy absorption) were observed only with sulfite sheets following copolymerization as revealed by tensile failures. The relatively lower efficiency in extra strength development with kraft pulps could be a result of the more condensed nature of alkali lignin, as well as of the pre-existing lignin-cellulose graft formed during the alkaline pulping process. Thereby, as anticipated the limit of strength improvement was not set entirely by intrinsic fibre strength. Consequently, the experimental copolymerized sulfite fibres withstand 30% more stress than the corresponding kraft fibres. This phenomena may be related to difference in reactivity and strategic location on or within the fibre wall rather than to difference in the total amount of lignin. Groundwood behaved differently and cannot be compared directly to chemical pulps due to the limitation of excessive short fibre fragments of low conformity. Contribution of groundwood to paper strength in mixtures with chemical fibres was somewhat proportional to the basic sheet strength.
Advantage of irradiation processed papers in comparison to those thermally treated includes improved speed of polymerization, less discoloration and somewhat lower stiffness.
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TABLES AND FIGURES
Table XII. Mean ultimate tensile strength (psi) \((Y_1)\) values for handsheets made from sulfite-groundwood pulp blends.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Per cent groundwood in handsheet ((X_1))</th>
</tr>
</thead>
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<tr>
<td></td>
<td>0.</td>
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<td>A</td>
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</tr>
<tr>
<td>B</td>
<td>4319</td>
</tr>
<tr>
<td>D</td>
<td>3730</td>
</tr>
<tr>
<td>C10(_{\text{rad}})</td>
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</tr>
<tr>
<td>C10(_{\text{2rad}})</td>
<td>4720</td>
</tr>
<tr>
<td>C10(_{\text{3rad}})</td>
<td>4409</td>
</tr>
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<td>C10(_{\text{5rad}})</td>
<td>4342</td>
</tr>
<tr>
<td>C2x10(_{\text{7rad}})</td>
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</tr>
<tr>
<td>E</td>
<td>6352</td>
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<tr>
<td>F10(_{\text{rad}})</td>
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<tr>
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<td>G2x10(_{\text{7rad}})</td>
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1. Each value represents an average of 5 measurements for particular \((X_1)\) blends.

* Maximum strength value for particular \((X_1)\) blend following irradiation grafting \((F_m)\).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control; D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted; G. Irradiation plus thermally grafted.
<table>
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</thead>
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<td>C₁₀³ rad</td>
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</tr>
<tr>
<td>C₁₀⁵ rad</td>
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</tr>
<tr>
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<td>G₂₀¹₀ rad</td>
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</table>

1. Each value represents an average of 5 measurements for particular (X₁) blends.

* Maximum strength value for particular (X₁) blend following irradiation grafting (Fₘ).

Treatment:  
A. Untreated control; B. Heat treated control; C. Irradiated control; D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted; G. Irradiation plus thermally grafted.
Table XIV. Mean values for ultimate tensile strain (in./in.) \( \times 10 \) \( (Y_3) \) for handsheets made from sulfite-groundwood pulp blends.

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<th>70</th>
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<td>.172(^1)</td>
<td>.165</td>
<td>.160</td>
<td>.157</td>
<td>.173</td>
<td>.154</td>
<td>.148</td>
<td>.151</td>
<td>.136</td>
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<td>.133</td>
</tr>
<tr>
<td>D</td>
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<td>.178</td>
<td>.173</td>
<td>.177</td>
<td>.169</td>
<td>.156</td>
<td>.147</td>
<td>.146</td>
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<td>.147</td>
<td>.165</td>
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<td>.139</td>
<td>.160</td>
<td>.141</td>
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</tr>
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<td>C(_{10}^2) rad</td>
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<td>.156</td>
<td>.159</td>
<td>.159</td>
<td>.133</td>
<td>.141</td>
<td>.133</td>
<td>.133</td>
</tr>
<tr>
<td>C(_{10}^3) rad</td>
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<td>.157</td>
<td>.155</td>
<td>.169</td>
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<td>.148</td>
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<td>C(_{10}^5) rad</td>
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<td>.160</td>
<td>.165</td>
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<td>.171</td>
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<td>.150</td>
<td>.145</td>
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<td>.152</td>
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<td>F(_{2}\times)10(^7) rad</td>
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<td>.083</td>
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<td>.106</td>
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<tr>
<td>G(_{10}) rad</td>
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<td>.141</td>
<td>.142</td>
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<td>.121</td>
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<td>G(_{2}\times)10(^7) rad</td>
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1. Each value represents an average of 5 measurements for particular \((X_1)\) blends.
2. * Maximum strength value for particular \((X_1)\) blend following irradiation grafting \((F_m)\).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control; D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted; G. Irradiation plus thermally grafted.
Table XV. Mean values of maximum tensile energy absorption (in. lb/cu in.) \( (X_4) \) for handsheets made from sulfite-groundwood pulp blends.

<table>
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<th>Treatment</th>
<th>Per cent groundwood in handsheet ( (X_1) )</th>
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<tr>
<td>B</td>
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</tr>
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<td>D</td>
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<tr>
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<td>C10⁵ rad</td>
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<tr>
<td>F10 rad</td>
<td>146.2</td>
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<td>F10² rad</td>
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<td>G2x10⁷ rad</td>
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</tr>
</tbody>
</table>

1. Each value represents an average of 5 measurements for particular \( (X_1) \) blends.

* Maximum strength value for particular \( (X_1) \) blend following irradiation grafting \( (F_m) \).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control; D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted; G. Irradiation plus thermally grafted.
Table XVI. Mean ultimate tensile strength (psi) ($Y_1$) values for handsheets made from kraft-groundwood pulp blends.

<table>
<thead>
<tr>
<th>Treatment</th>
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<td>1951</td>
<td>1919</td>
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</tr>
<tr>
<td>B</td>
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<td>2398</td>
<td>2179</td>
<td>1983</td>
<td>1815</td>
<td>1835</td>
<td>1689</td>
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</tr>
<tr>
<td>C</td>
<td>2354</td>
<td>1763</td>
<td>1712</td>
<td>1595</td>
<td>1410</td>
<td>1351</td>
<td>1347</td>
<td>1259</td>
<td>1083</td>
<td>1117</td>
<td>1011</td>
</tr>
<tr>
<td>C10 rad</td>
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<td>2060</td>
<td>1939</td>
<td>1739</td>
<td>1699</td>
<td>1654</td>
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<tr>
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<td>2282</td>
<td>1983</td>
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<td>1635</td>
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<td>1247</td>
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<td>1964</td>
<td>1904</td>
<td>1733</td>
<td>1680</td>
<td>1463</td>
<td>1713</td>
<td>1103</td>
<td>1097</td>
<td>1307</td>
</tr>
<tr>
<td>C105 rad</td>
<td>2720</td>
<td>2305</td>
<td>1955</td>
<td>1902</td>
<td>1666</td>
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<td>1204</td>
</tr>
<tr>
<td>C2x107 rad</td>
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<td>1890</td>
<td>1651</td>
<td>1485</td>
<td>1366</td>
<td>1417</td>
<td>1290</td>
<td>1245</td>
<td>945</td>
<td>958</td>
<td>1090</td>
</tr>
<tr>
<td>E</td>
<td>4935</td>
<td>4416</td>
<td>4059</td>
<td>3818</td>
<td>3510</td>
<td>3646</td>
<td>3625</td>
<td>3405</td>
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<tr>
<td>F10 rad</td>
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<td>3331</td>
<td>3129</td>
<td>3050</td>
<td>3267*</td>
<td>2607</td>
<td>2466</td>
<td>2136</td>
<td>1952</td>
<td>1987</td>
<td></td>
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<tr>
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<td>3817*</td>
<td>3445*</td>
<td>3332*</td>
<td>3300*</td>
<td>2715</td>
<td>2683</td>
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<td>2914*</td>
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<td>2797</td>
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<td>2567</td>
<td>2090</td>
<td>2133*</td>
<td>2166*</td>
</tr>
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<td>2747</td>
<td>2557</td>
<td>2466</td>
<td>2235</td>
<td>2206</td>
<td>2248</td>
<td>2090</td>
<td>1744</td>
<td>1784</td>
<td>1881</td>
</tr>
<tr>
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<td>4219</td>
<td>3893</td>
<td>3749</td>
<td>3550</td>
<td>3599</td>
<td>3141</td>
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<td>2649</td>
<td>2758</td>
<td>2748</td>
</tr>
<tr>
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<td>3993.</td>
<td>4021</td>
<td>3872</td>
<td>3677</td>
<td>3339</td>
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<td>2768</td>
<td>2500</td>
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</tr>
<tr>
<td>G2x107 rad</td>
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<td>2661</td>
<td>2328</td>
<td>2633</td>
<td>2511</td>
<td>2401</td>
<td>2136</td>
<td>2174</td>
<td>1941</td>
<td>1824</td>
<td>1850</td>
</tr>
</tbody>
</table>

1. Each value represents an average of 5 measurements for particular ($X_1$) blends.
2. Maximum strength value for particular ($X_1$) blend following irradiation grafting ($F_m$).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control;
D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted;
G. Irradiation plus thermally grafted.
Table XVII. Mean elasticity (psi/100) ($Y_2$) values for handsheets made from kraft-groundwood pulp blends.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>0.</th>
<th>10.</th>
<th>20.</th>
<th>30.</th>
<th>40.</th>
<th>50.</th>
<th>60.</th>
<th>70.</th>
<th>80.</th>
<th>90.</th>
<th>100.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2702</td>
<td>2623</td>
<td>2162</td>
<td>2154</td>
<td>2113</td>
<td>1926</td>
<td>1915</td>
<td>1848</td>
<td>1530</td>
<td>1406</td>
<td>1534</td>
</tr>
<tr>
<td>B</td>
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<td>2967</td>
<td>2588</td>
<td>2370</td>
<td>2264</td>
<td>2227</td>
<td>2062</td>
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<td>1529</td>
<td>1456</td>
<td>1469</td>
</tr>
<tr>
<td>C</td>
<td>3278</td>
<td>2626</td>
<td>2500</td>
<td>2277</td>
<td>2133</td>
<td>2001</td>
<td>2147</td>
<td>1848</td>
<td>1530</td>
<td>1406</td>
<td>1534</td>
</tr>
<tr>
<td>D</td>
<td>3274</td>
<td>2757</td>
<td>2449</td>
<td>2385</td>
<td>2220</td>
<td>2086</td>
<td>2200</td>
<td>1940</td>
<td>1582</td>
<td>1362</td>
<td>1743</td>
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<td>C10 rad</td>
<td>3473</td>
<td>2847</td>
<td>2404</td>
<td>2335</td>
<td>2071</td>
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<td>1362</td>
<td>1743</td>
</tr>
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<td>C10^2rad</td>
<td>3487</td>
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<td>2469</td>
<td>2255</td>
<td>2198</td>
<td>2220</td>
<td>1948</td>
<td>1988</td>
<td>1427</td>
<td>1511</td>
<td>1580</td>
</tr>
<tr>
<td>C10^3rad</td>
<td>3604</td>
<td>3467</td>
<td>3132</td>
<td>2957</td>
<td>2816</td>
<td>2554</td>
<td>2552</td>
<td>2579</td>
<td>2182</td>
<td>2052</td>
<td>2148</td>
</tr>
<tr>
<td>C10^4rad</td>
<td>3890</td>
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<td>3506</td>
<td>3569</td>
<td>3484</td>
<td>3241</td>
<td>3102</td>
<td>2817</td>
<td>2552</td>
<td>2322</td>
<td>2303</td>
</tr>
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<td>3850</td>
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<td>3258</td>
<td>3210</td>
<td>2821</td>
<td>2862</td>
<td>2904</td>
<td>2848</td>
<td>2337</td>
<td>2242</td>
<td>2154</td>
</tr>
<tr>
<td>C2x10^7rad</td>
<td>4319</td>
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<td>3288</td>
<td>2975</td>
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<td>2881</td>
<td>1396</td>
<td>2277</td>
<td>2290</td>
</tr>
</tbody>
</table>

1. Each value represents an average of 5 measurements for particular ($X_1$) blends.

* Maximum strength value for particular ($X_1$) blend following irradiation grafting ($F_m$).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control; D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted; G. Irradiation plus thermally grafted.
Table XVIII. Mean values of ultimate tensile strain (in./in.)\(^2\) for handsheets made from kraft-groundwood pulp blends.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Per cent groundwood in handsheet (X(_1))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.</td>
</tr>
<tr>
<td>A</td>
<td>.210</td>
</tr>
<tr>
<td>B</td>
<td>.218</td>
</tr>
<tr>
<td>D</td>
<td>.192</td>
</tr>
<tr>
<td>C(_{10}) rad</td>
<td>.204</td>
</tr>
<tr>
<td>C(_{10})(^2) rad</td>
<td>.203</td>
</tr>
<tr>
<td>C(_{10})(^3) rad</td>
<td>.175</td>
</tr>
<tr>
<td>C(_{10})(^5) rad</td>
<td>.192</td>
</tr>
<tr>
<td>C(<em>{2})(^x)(</em>{10})(^7) rad</td>
<td>.117</td>
</tr>
<tr>
<td>E</td>
<td>.260</td>
</tr>
<tr>
<td>F(_{10})(^2) rad</td>
<td>.255*</td>
</tr>
<tr>
<td>F(_{10})(^3) rad</td>
<td>.253</td>
</tr>
<tr>
<td>F(_{10})(^5) rad</td>
<td>.250</td>
</tr>
<tr>
<td>F(<em>{2})(^x)(</em>{10})(^7) rad</td>
<td>.132</td>
</tr>
<tr>
<td>G(_{10}) rad</td>
<td>.220</td>
</tr>
<tr>
<td>G(_{10})(^2) rad</td>
<td>.212</td>
</tr>
<tr>
<td>G(<em>{2})(^x)(</em>{10})(^7) rad</td>
<td>.097</td>
</tr>
</tbody>
</table>

1. Each value represents an average of 5 measurements for particular (X\(_1\)) blends.

* Maximum strength value for particular (X\(_1\)) blend following irradiation grafting (F\(_m\)).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control; D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted; G. Irradiation plus thermally grafted.
Table XIX. Mean values of maximum tensile energy absorption (in. lb/cu. in.) ($Y_4$) for handsheets made from kraft-groundwood pulp blends.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Per cent groundwood in handsheet ($X_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.</td>
</tr>
<tr>
<td>A</td>
<td>117.6</td>
</tr>
<tr>
<td>B</td>
<td>124.5</td>
</tr>
<tr>
<td>D</td>
<td>101.8</td>
</tr>
<tr>
<td>C10 rad</td>
<td>107.2</td>
</tr>
<tr>
<td>C10^2 rad</td>
<td>116.5</td>
</tr>
<tr>
<td>C10^3 rad</td>
<td>105.9</td>
</tr>
<tr>
<td>C10^5 rad</td>
<td>114.5</td>
</tr>
<tr>
<td>C2x10^7 rad</td>
<td>50.4</td>
</tr>
<tr>
<td>E</td>
<td>251.9</td>
</tr>
<tr>
<td>F10 rad</td>
<td>150.2</td>
</tr>
<tr>
<td>F10^2 rad</td>
<td>205.7*</td>
</tr>
<tr>
<td>F10^3 rad</td>
<td>201.5</td>
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<tr>
<td>F10^5 rad</td>
<td>198.7</td>
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<tr>
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<td>80.2</td>
</tr>
<tr>
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<td>191.7</td>
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<tr>
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<tr>
<td>G2x10^7 rad</td>
<td>53.3</td>
</tr>
</tbody>
</table>

1. Each value represents an average of 5 measurements for particular ($X_1$) blends.

* Maximum strength value for particular ($X_1$) blend following irradiation grafting ($F_m$).

Treatment: A. Untreated control; B. Heat treated control; C. Irradiated control;
D. Oil dipped control; E. Thermally grafted; F. Irradiation grafted;
G. Irradiation plus thermally grafted.
Table XX. Equations for calculated response surfaces.

Symbols:

- $Y^1 =$ Ultimate tensile strength, psi.
- $Y^2 =$ Modulus of elasticity, psi/100.
- $Y^3 =$ Ultimate tensile strain, (in/in)$_{10}$.
- $Y^4 =$ Tensile energy absorption, in.lb/cu in.

- $X_1 =$ Pulp blend, %.
- $X_2 =$ Log. Radiation dosage, rad.

- $(X_1)_n =$ $X_1$ vs. $Y_n$ plane;
- $(X_2)_n =$ $Z$ vs. $Y_n$ plane.

Series: G--SG--S ($X_1$), GR--SGR--SR ($X_2$) = ($Z$), $N = 66$.

1. $Y_1 = 4507.86 - 28.4606X_2^2 - 0.3631X_2^2 + 0.1766X_1X_2^2 -$
   - 2.6048$X_1^3 + 0.003179X_2^2$. 
   SEE = 156.35 psi,
   $R = 0.99028$, $R^2 = 0.98066$.

2. $Y_2 = 4973.80 - 28.5883X_2^2 - 0.36347X_2^2 + 0.350389X_1^3 +$
   + 0.0031514$X_2^3$. 
   SEE = 153.15 psi/100,
   $R = 0.99171$, $R^2 = 0.98349$.

3. $Y_3 = 163472 + 0.0030322X_1^2 - 0.000003244X_2^2 - 0.0007458X_1X_2^2 -$
   - 0.0061297$X_1^3 + 0.000002278X_2^3$. 
   SEE = 0.0902 (in./in.)$_{10}$,
   $R = 0.94783$, $R^2 = 0.89838$. 
Series: G--SG--S \( (X_1) \); GR--SGR--SR \( (X_2) = (Z) \) Continued:

4. \( Y_4 = 141.959 - 1.13543X_2 + 2.3156X_1^2 - 0.15699X_1X_2 + \\
+ 0.03464X_1^2X_2 - 0.53524X_1^3 \)

\[ \text{SEE} = 9.64 \text{ in.lb/cu in.} \]

\[ R = 97414, \quad R^2 = 0.94894. \]

Series: GD--SGD--SD \( (X_1) \), GRT--SGRT--SRT \( (X_2) = (Z) \). \( N=66 \).

5. \( Y_1 = 3826.36 + 883.615X_1 + 28.0439X_2^2 = 114.593X_1^2 - \\
- 3.07294X_1X_2 + 0.00074254X_1^2X_2 \)

\[ \text{SEE} = 300.76 \text{ psi} \]

\[ R = 96693, \quad R^2 = 0.93494. \]

6. \( Y_2 = 5257.31 + 261.834X_1 - 48.5655X_2 - 27.3388X_1^2 + \\
+ 0.0013174X_2^3 \)

\[ \text{SEE} = 220.77 \text{ psi/100} \]

\[ R = 98424, \quad R^2 = 0.96872. \]

7. \( Y_3 = 0.15675 + 0.003979X_1^2 - 0.000007858X_1X_2 - \\
- 0.0007256X_1^3 \)

\[ \text{SEE} = 0.0135339 \text{ (in./in.)} \]

\[ R = 0.89499, \quad R^2 = 0.80100. \]

8. \( Y_4 = 112.677 + 7.1469X_1^2 - 0.010735X_2^2 + 0.00579X_1X_2^2 - \\
- 1.1329X_1^3 + 0.0002259X_1^2X_2^3 - 0.002274X_1^2X_2 \)

\[ \text{SEE} = 17.871 \text{ in.lb/cu in.} \]

\[ R = 0.90679, \quad R^2 = 0.82226. \]
Series: GO--SGO--SO \(X_1\), GRTH--SGRTH--SRTH \(X_2\) = (Z). N = 44.

9. \[ Y_1 = 5622.90 - 164.311X_1 - 88.4973X_2 + 1.23041X_2^2 - 0.006216X_2^3 \]
\[ \text{SEE} = 287.29 \text{ psi}, \]
\[ R = 0.9585 \quad R^2 = 0.91862. \]

10. \[ Y_2 = 5950.86 - 27.0099X_1 - 110.196X_2 + 1.5556X_2^2 - 0.008047X_2^3 \]
\[ \text{SEE} = 164.15 \text{ psi/100}, \]
\[ R = 0.98822, \quad R^2 = 0.97659. \]

11. \[ Y_3 = 0.15333 - 0.038808X_1 + 0.01537X_2^2 + 0.00000201X_2^3 - 0.001561X_1^2 \]
\[ \text{SEE} = 0.010668 \text{ (in./in.)}.10, \]
\[ R = 0.93548, \quad R^2 = 0.87513. \]

12. \[ Y_4 = 168.08 - 114.14X_1 - 1.6364X_2 + 55.118X_2^2 + 0.00772X_2^3 + 1.2696X_1X_2 - 0.7013X_1^2X_2 - 5.691X_1^3 \]
\[ \text{SEE} = 15.08 \text{ in.lb/cu in.}, \]
\[ R = 0.92564, \quad R^2 = 0.85682. \]

Series: GRT_m--SGRT_m--SRT_m \(X_1\); N = 11.

13. \[ Y_1 = 5655.87 - 57.942X_1 + 0.23989X_1^2 \]
\[ \text{SEE} = 195.58 \text{ psi}, \]
\[ R = 0.9773, \quad R^2 = 0.9545. \]
Series: GRT --SGRT --SRT \( X_1 \) (Continued):

14. \( Y_2 = 5951.61 - 57.204X_1 + .19655X_2 \)
    \[ \text{SEE} = 116.28 \text{ psi/100,} \]
    \[ R = .9932, \quad R^2 = .9865. \]

15. \( Y_3 \) = Non-significant regression.

16. \( Y_4 = 213.66 - 4.56778X_1 + 7.2108X_2^2 - 406.69X_1 \)
    \[ \text{SEE} = 9.61 \text{ in.lb/cu in.,} \]
    \[ R = .9615, \quad R^2 = .9253. \]

Series: G--KG--K \( X_1 \), GR--KGR--KR \( X_2^2 \) = (Z), \( N=66 \).

17. \( Y_1 = 2629.12 - 35.2337X_2 + .4148X_2^2 - .80955X_1^3 - .002062X_2 \)
    \[ \text{SEE} = 120.49 \text{ psi,} \]
    \[ R = .96648, \quad R^2 = .93408. \]

18. \( Y_2 = 3056.09 + 40.0408X_1 - 41.4928X_2 + .52704X_2^2 - .56911X_1X_2 - .002603X_2^3 \)
    \[ \text{SEE} = 168.27 \text{ psi/100,} \]
    \[ R = .94968, \quad R^2 = .90189. \]

19. \( Y_3 = .215269 - .02023X_1 + .00793X_1^2 - .00007028X_2^2 - .0009497X_1^3 + .000 000 000 107X_1X_2 \)
    \[ \text{SEE} = .008889 \text{ (in./in.)}^{10}, \]
    \[ R = .97026, \quad R^2 = .9441. \]
Series: G--KG--K ($X_1$), GR--KGR--KR ($X_2$) = (Z). Continued:

20. $Y_4 = 110.57 - 0.7991X_2 - 0.1242X_1^2 + 0.00006370X_1X_2^2$.
   \[ \text{SEE} = 7.364 \text{ in.} \text{lb/cu in.,} \]
   \[ R = 0.96465, \quad R^2 = 0.93055. \]

Series: GD--KGD--KD ($X_1$), GRT--KGRT--KRT ($X_2$) = (Z). \(N=66\).

21. $Y_1 = 2318.97 + 1038.51X_1 - 14.8641X_2 - 243.06X_1^2 +$
   \[ + 15.696X_1^3. \]
   \[ \text{SEE} = 231.71 \text{ psi,} \]
   \[ R = 0.94548, \quad R^2 = 0.89394. \]

22. $Y_2 = 3155.96 + 156.573X_1 - 17.1211X_2 + 4.8819X_1X_2 -$
   \[ - 2.1967X_1^2X_2 + 0.1474X_1^3X_2 + 0.003861X_1^2X_2^2. \]
   \[ \text{SEE} = 251.983 \text{ psi/100,} \]
   \[ R = 0.92458, \quad R^2 = 0.85484. \]

23. $Y_3 = 0.2030 + 0.03117X_1 - 0.00000968X_2^2 - 0.000769X_1^3 +$
   \[ + 0.0000001165X_1^2X_2. \]
   \[ \text{SEE} = 0.0164 \text{ (in./in.).10,} \]
   \[ R = 0.95684, \quad R^2 = 0.91555. \]

24. $Y_4 = 101.28 + 69.703X_1 - 0.7819X_2 - 9.9704X_1^2 -$
   \[ - 0.004643X_1X_2^2 + 0.0007023X_1^2X_2^2. \]
   \[ \text{SEE} = 14.74 \text{ in.} \text{lb/cu in.,} \]
   \[ R = 0.96873, \quad R^2 = 0.93843. \]
Series: GRT - KGRT - KRT \((X_1)\). N=11.

25. \(Y_1 = 3691.67 - 16.938X_1\)  
SEE = 122.15 psi,  
\(R = .95918,\)  \(R^2 = .9198.\)

26. \(Y_2 = 3715.50 - 15.632X_1\)  
SEE = 151.11 psi/100,  
\(R = .9287,\)  \(R^2 = .8646.\)

27. \(Y_3 = \) Non significant regression

28. \(Y_4 = 218.21 - 3.229X_1^2 + 178.645X_1^3\)  
SEE = 11.28 in, lb/cu in.,  
\(R = .96448,\)  \(R^2 = .9302.\)

Series: GO--KGO--KO \((X_1)\), GRTH--KGRTH--KRTH \((X_2)=(Z)\). N=44.

29. \(Y_1 = 4818.92 - 250.782X_1 - 27.7596X_2 + .06584X_2^2 + 1.3862X_1X_2\)  
SEE = 171.462 psi,  
\(R = .97863,\)  \(R^2 = .95771.\)

30. \(Y_2 = 3990.06 - 38.5345X_2 + .058669X_2^2 + 7.1266X_1X_2 - .06789X_1^2 - .8726X_1^2X_2 + .003583X_2^3 + .001101X_1X_2^2\)  
SEE = 138.13 psi/100,  
\(R = .96433,\)  \(R^2 = .92994.\)
Series: GO--KGO--KO ($X_1$), GRTH--KGRTH--KRTH ($X_2$) = (Z). Continued

31. $Y_3 = 0.26028 - 0.06238X_1 - 0.00091662X_2 + 0.02453X_1^2 -$
   $- 0.002576X_1^3 + 0.0000001491X_1^2X_2^2.$
   
   $\text{SEE} = 0.00932\ \text{(in./in.^2)}.$
   
   $R = 0.98582,\ \ \ \ R^2 = 0.97185.$

32. $Y_4 = 235.964 - 31.571X_1 - 2.2018X_2 + 1.02377X_1^2 +$
   $+ 0.006165X_2^2 + 0.18348X_1X_2.$
   
   $\text{SEE} = 17.5832\ \text{in.lb/cu in.},$
   
   $R = 0.9451,\ \ \ \ R^2 = 0.8938.$
Table XXI. Effect of thermal and irradiation grafting on strength properties of handsheets made from the three basic pulp types.

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<th>Sample</th>
<th>Max. Tensile Strength</th>
<th>Strength Increase from</th>
<th>Modulus of Elasticity</th>
<th>Strength Increase from</th>
<th>Ul. Tens. Strain</th>
<th>Strength Increase from</th>
<th>Max. Tens. Energy</th>
<th>Strength Increase from</th>
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<td></td>
<td>psi</td>
<td>%</td>
<td>psi</td>
<td>%</td>
<td>in/in</td>
<td>%</td>
<td>Lbs.</td>
<td>%</td>
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<td>1534</td>
<td>-</td>
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<td>-</td>
<td>33.0</td>
<td>-</td>
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<tr>
<td>B</td>
<td>1277</td>
<td>+ 4</td>
<td>1469</td>
<td>- 4</td>
<td>.147</td>
<td>+10</td>
<td>36.9</td>
<td>+ 9</td>
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<tr>
<td>D</td>
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<td>- 21</td>
<td>1584</td>
<td>+ 3</td>
<td>.106</td>
<td>+25</td>
<td>18.9</td>
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<tr>
<td>G</td>
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<td>+ 6</td>
<td>1743</td>
<td>+14</td>
<td>.142</td>
<td>+ 6</td>
<td>35.2</td>
<td>+ 6</td>
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<td>+118</td>
<td>2566</td>
<td>+67</td>
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<td>+20 +8</td>
<td>82.2</td>
<td>+149 +123 +335</td>
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<tr>
<td>E</td>
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<td>+ 76</td>
<td>2242</td>
<td>+46</td>
<td>.176</td>
<td>+32</td>
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<td>+129 +300</td>
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<td>F max</td>
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<td>+55 +61 +50</td>
<td>.157</td>
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<td>S</td>
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<td>4776</td>
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<td>4961</td>
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<td>.162</td>
<td>- 6</td>
<td>117.4</td>
<td>- 23</td>
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<tr>
<td>C max</td>
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<td>+ 13</td>
<td>5143</td>
<td>+11</td>
<td>.188</td>
<td>+ 9</td>
<td>166.9</td>
<td>+15</td>
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<td>E</td>
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<td>6184</td>
<td>+33 +30 +25</td>
<td>.177</td>
<td>+ 3 +10 +9</td>
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<td>+52 +67 +87</td>
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<td>F max</td>
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<td>5995</td>
<td>+29 - +20</td>
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<td>220.9</td>
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<td>+25 +21 +16</td>
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<td>3463</td>
<td>+28</td>
<td>.218</td>
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<td>124.5</td>
<td>+ 6</td>
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<tr>
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<td>3278</td>
<td>+21</td>
<td>.192</td>
<td>- 9</td>
<td>101.8</td>
<td>-16</td>
</tr>
<tr>
<td>K</td>
<td>2733</td>
<td>+ 2</td>
<td>3473</td>
<td>+28</td>
<td>.204</td>
<td>- 3</td>
<td>116.5</td>
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<td>+ 84 +67 +110</td>
<td>4240</td>
<td>+57 +22 +29</td>
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<td>+24 +19 +35</td>
<td>251.9</td>
<td>+114 +106 +147</td>
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<td>+ 42 +62</td>
<td>4035</td>
<td>+50 - +23</td>
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<td>+ 75 - +102</td>
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<td>+46 +14 +21</td>
<td>.220</td>
<td>+ 4 +1</td>
<td>191.7</td>
<td>+63 +54 +88</td>
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</tbody>
</table>

A: Control; B: Heat treated control; D: Oil dipped control; C max: Irradiated control; E: Thermally grafted; F: Irradiation grafted; G: Irradiation plus thermally grafted.
Table XXII. Per cent tensile strength increase on some purified pulps before and after sodium chlorite and oil polymerization treatments.

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Treatment</th>
<th>Tensile Strength</th>
<th>Strength Increase, %, from</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>D</td>
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<td>Glass Paper</td>
<td>A</td>
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<td>-</td>
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<td></td>
<td>E</td>
<td>2446</td>
<td>3490</td>
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<td>Bleached Kraft</td>
<td>A</td>
<td>3257</td>
<td>-</td>
</tr>
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<td></td>
<td>B</td>
<td>3527</td>
<td>+8.3</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>2788</td>
<td>-16.8</td>
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<tr>
<td></td>
<td>E</td>
<td>7752</td>
<td>+138</td>
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<td></td>
<td>H</td>
<td>1838</td>
<td>-77</td>
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<td>HD</td>
<td>1720</td>
<td>-</td>
</tr>
<tr>
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<td>HE</td>
<td>7442</td>
<td>+128</td>
</tr>
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<td>TAPPI Standard</td>
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<td>-</td>
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<td>B</td>
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<td></td>
<td>D</td>
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<td>E</td>
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<td>+332</td>
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<td>HD</td>
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<td>HE</td>
<td>5316</td>
<td>415</td>
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<td>High-Alpha Viscose</td>
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<td>-</td>
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<td>D</td>
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<td>E</td>
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<td>713</td>
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<td></td>
<td>HD</td>
<td>394</td>
<td>-</td>
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<td>468</td>
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<tr>
<td>Ground-wood</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1277</td>
<td>+4</td>
</tr>
<tr>
<td></td>
<td>D</td>
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<td>-21</td>
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<td>HD</td>
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<td>-</td>
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<td></td>
<td>HE</td>
<td>8929</td>
<td>+545</td>
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</table>

Treatment: A: Control; B: Heat Treated Control; D: Oil dipped control; E: Thermally grafted; H: Delignified by acidic sodium chlorite (NaClO₂); HD: NaClO₂ + oil dip, HE: NaClO₂ + oil dip + heat.
Table XXIII. Equations for calculated dependent variable correlations, \( Y = a + bX + cX^2 + dX^3 \).
Scaling \( Y_1 = 10^{-2}, Y_2 = 10^{-3} \).

<table>
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<tr>
<th>Pulp Type</th>
<th>Treatment</th>
<th>( X )</th>
<th>( Y_1 )</th>
<th>( Y_2 )</th>
<th>( Y_3 )</th>
<th>( Y_4 )</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
<th>( R^2 )</th>
<th>SEE</th>
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<td>A&amp;C</td>
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<td>.138578E-01</td>
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<td>.102481E+01</td>
<td>.358926E+01</td>
<td>-.430658E-03</td>
<td>.449922E-05</td>
<td>.991</td>
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<td>D&amp;F</td>
<td>( Y_1 )</td>
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<td>.991</td>
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<tr>
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<td>E&amp;G</td>
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<td>.138578E-01</td>
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<td>Kraft</td>
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<td>.991</td>
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<tr>
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<td>( Y_1 )</td>
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<td>.105421E+00</td>
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<td>A&amp;C</td>
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<td>.991</td>
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Earlywood:

Figure 6. Scanning electron photomicrographs of wood tensile fractures before and after irradiation and thermal grafting (150 X).

Latewood:

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<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Position in Increment %</th>
<th>Sp. Gr. g/cm³</th>
<th>Number of Replicates</th>
<th>Sample Thickness cm</th>
<th>Ultimate Tensile Strength psi</th>
<th>Strength Increase %</th>
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<td>7330</td>
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</table>
Figure 7. Scanning electron photomicrographs of paper tensile fractures before and after grafting (150 X).

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<th>Sample</th>
<th>Treatment</th>
<th>Photomicrograph</th>
<th>Tensile Strength psi</th>
<th>1,000 psi</th>
<th>Modulus of Elasticity (in/in).10⁻¹</th>
<th>Tensile Strain</th>
<th>Tensile Energy Absorption in.lb/cu in.</th>
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<tr>
<td>Groundwood</td>
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<td></td>
<td>F</td>
<td>h</td>
<td>2166</td>
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<td>224.2</td>
<td>.176</td>
<td>75.6</td>
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A: Control, F: Gamma-ray irradiation grafted, E: Thermally grafted.
Figure 8. Deep tensile fracture of kraft paper (150 X).
Figure 9. Sulfite-groundwood handsheet tensile strength ($Y_1$) as a function of blending and post-sheet formation treatments.

Figure 10. Kraft-groundwood handsheet tensile strength ($Y_1$) as a function of pulp blending and post-sheet formation treatments.
Figure 11. Change of sulfite-groundwood handsheet elasticity ($Y_2$) as a function of blending and post-sheet formation treatments.

Figure 12. Change of kraft-groundwood handsheet elasticity ($Y_2$) as a function of pulp blending and post-sheet formation treatments.
Figure 13. Effect of pulp blending and post-sheet treatments on ultimate tensile strain ($Y_3$) of sulfite-groundwood handsheets.

Figure 14. Effect of pulp blending and post-sheet formation treatments on ultimate tensile strain ($Y_3$) of kraft-groundwood handsheets.
Figure 15. Maximum tensile energy absorption ($Y_4$) of sulfite-groundwood handsheets as a function of pulp blending and post-sheet formation treatments.

Figure 16. Maximum tensile energy absorption ($Y_4$) of kraft-groundwood handsheets as a function of pulp blending and post-sheet formation treatments.
Figure 17. Absolute strength increase due to thermal and irradiation grafting onto sulfite- and kraft-groundwood handsheets.
Figure 18. Effect of extractable monomer residues and homopolymer fractions (expressed as percentage of sample weight) on initial tensile strength of oil dipped (D) specimens following thermal (E) and gamma-irradiation grafting (F,G).
Figure 19. Tensile strength of sulfite- and kraft-groundwood handsheets as calculated from the significant interaction between pulp type and level of blending.
Figure 20. Relationship between ultimate tensile strength ($Y_1$) and modulus of elasticity ($Y_2$) for handsheets made from sulfite- and kraft-groundwood blends.
Figure 21. Relationship between ultimate tensile strength \( (Y_1) \) and ultimate tensile strain \( (Y_3) \) for handsheets made from sulfite- and kraft-groundwood blends.
Figure 22. Relationship between ultimate tensile strength ($Y_1$) and tensile energy absorption ($Y_4$) for handsheets made from sulfite- and kraft-groundwood blends.
Figure 23. Relationship between modulus of elasticity ($Y_2$) and ultimate tensile strain ($Y_3$) for handsheets made from sulfite- and kraft-groundwood blends.
Figure 24. Relationship between modulus of elasticity ($Y_2$) and tensile energy absorption ($Y_4$) for handsheets made from sulfite- and kraft-groundwood blends.
Figure 25. Scheme for selective methylation of lignin in wood.
Figure 26. Discoloration of groundwood, sulfite and kraft papers due to irradiation and thermal grafting.

Groundwood Pulp:

- Control
- Irradiated C. 2x10^7 rad dose
- Radiation Copolymer 10^5 rad dose
- Thermal Copolymer 145°C, 1.5 hr.

Sulfite Pulp:

- Control
- Irradiated C. 2x10^7 rad dose
- Radiation Copolymer 10^5 rad dose
- Thermal Copolymer 145°C, 1.5 hr.

Sulfate Pulp:

- Control
- Irradiated C. 2x10^7 rad dose
- Radiation Copolymer 10^5 rad dose
- Thermal Copolymer 145°C, 1.5 hr.
Figure 27. Characteristic stress-elongation curves for 50:50 sulfite-groundwood blend.