INTRODUCTION

Wood of trees

General description of wood:

Wood is a complex substance, both anatomically and chemically(1). The anatomical structure affects strength properties, appearance, resistance to penetration by water and chemicals. Wood of the common trees is composed of tubular cells, which are chiefly the type called *fibers* in paper technology. These hollow fibers are packed closely together, generally parallel to the direction of the grain (or to the stem or branch) that contains them. By their general properties these wood cells determine the properties of whatever woods they compose. If the walls of the fibers are in general thin, the wood is light in weight and relatively weak. Woods that are heavy and strong are characterized by thick-walled fibers. Also the arrangement of the fibers and other wood cells together with their particular markings, sculpture and structure are characteristics that, in addition to determining the physical properties of woods, serve to distinguish each different kind and permit the identification of woods by recognition of the cell structure.

General classification of woods:

Wood of coniferous trees is commonly known by the general term *softwood* and the conifers are commonly given the general designation *softwoods*. Wood of broad-leaved trees is commonly designated *hardwood*, and similarly the trees are commonly referred to as *hardwoods*. While some of the broad-leaved species furnish the hardest woods by mechanical standards, others of this group have the softest type of wood known, so that it should be understood that the designations *softwood* and *hardwood* are used merely to distinguish two different botanical classes of wood and are not otherwise accurately descriptive. Fibers or tracheids vary greatly in length within a tree and among species. Hardwood fibers average about 1 mm. in length; softwood fibers range from about 3 to 8 mm. in length. The fact that woods differ from each other in weight is generally due to differences in cell structure, since all the common woods are much alike in chemical composition except for small amounts of materials such as resin and stored or secreted substances. Dry wood cells may be empty or partly filled with deposits, such as gums or resins, intrusive growths from one kind of cell into another.

Chemical composition of wood:

Wood consists mainly of vertically oriented tubular fiber units or cells cemented together by the middle lamella see Fig. (1). The cells that make up the structural elements of wood are of various sizes and shapes and are firmly bonded together(2). The various chemical components are distributed in an interlocking network through this structure. In describing the chemical components of wood, it is common to differentiate between cell-wall components and extraneous materials as illustrated in Fig.(2). The components of cell wall are lignin and the total

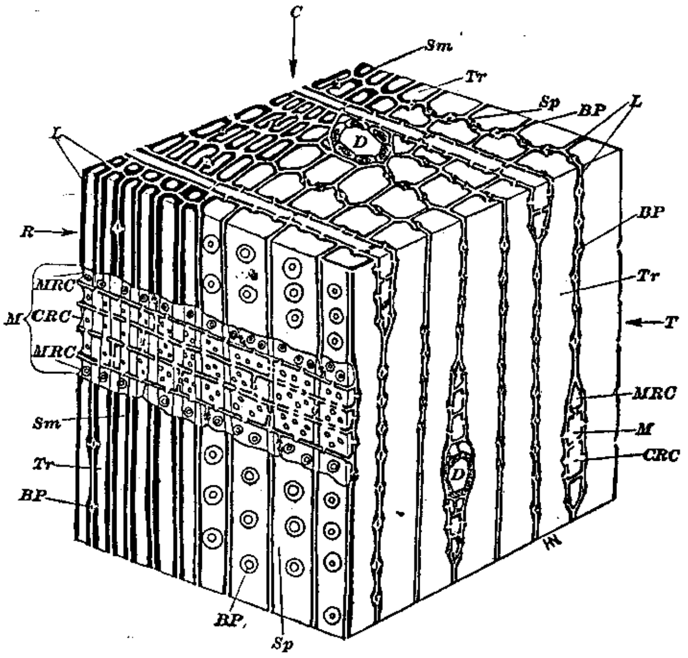


Fig. (1): Diagram of small block of a soft white pine . *C*, cross section; *R*, radial section; *T*, tangential section; *D*, resin duct; *Sm*, summerwood; *Sp*, springwood; *Tr*, Tracheid; *Bp*. bordered pit; *L*, middle lamella; *M*, ray; *CRC*, central ray cell; *MRC*, marginal ray cell.

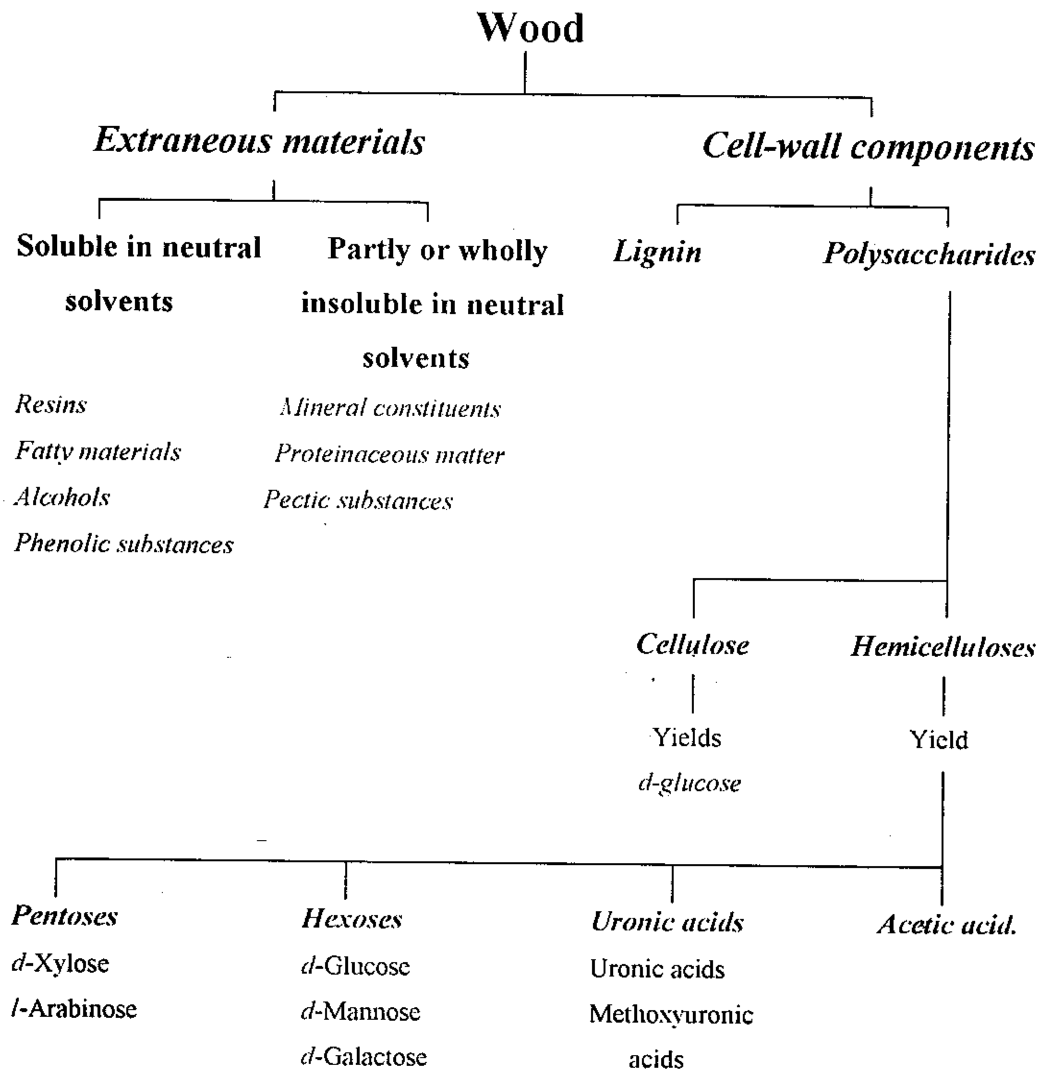


Fig. (2): General composition of wood carbohydrate fractions, consisting of cellulose and hemicellulose. The extraneous materials consist of substances that can be removed by extraction with non reactive solvents, protein residues from the protoplasm of the growing cell and the mineral constituents, some of which are difficult to remove,the main chemical components are:

(1) Cell wall carbohydrates

The cell-wall material is insoluble in all neutral solvents, hence the component can not be separated by the usual processes of solution and precipitation. Composition of a wood sample is determined by methods that are applicable generally to plants materials. Specific methods are given in **ASTM** standard, (American Society for Testing and Materials) and **TAPPI** standard, (Technical Association of the Pulp and Paper Industry). Cell- wall components include:

(a) Polysaccharides

The carbohydrates (polysaccharides) are the most prominent component of the cell wall, amounting in most cases to 65-75% of the weight of the wood. Hydrolysis of the total carbohydrate fraction yields mainly simple sugars and primarily glucose.

Polysaccharides divided into:-

(i) Cellulose

The main constituent of the cell-wall carbohydrate is cellulose, which in most respects is chemically similar to purified cotton cellulose. It consists of glucose residues joined through 1,4-β-glucosidic linkages. No wood cellulose has been prepared that does not contain traces of mannan and xylan.

(ii) Hemicellulose

The cell wall carbohydrates contain hemicellulose in addition to true cellulose. Historically hemicellulose was defined as the easily hydrolyzed portion of cellulose. Structurally the material is amorphous and includes as components mannose, galactose, arabinose, xylose, uronic acids and in some cases rhamnose. Analysis of wood celluloses made for technical purposes frequently express the composition in terms of α-, β-and γ-cellulose content. The distinction is based on solubility in alkali. In general terms, α-celluose is insoluble in 17.5% sodium hydroxide, β-cellulose is the soluble portion that is precipitated by acidification and γ-cellulose is the soluble portion no precipitated by acid.

(b) Lignin

The noncarbohydrate component of the cell wall, lignin, is a polymer based primarily on a substituted phenylpropane unit. It usually comprises from 18-28% of the wood and it is present in the middle lamella and the layered cell wall. The ultimate composition of lignin may vary from species to species.

(2) Extraneous components

The mineral constituent (inorganic extraneous) of wood vary greatly between species, between trees within a species and even within one tree. The most prominent cations found are calcium, potassium and magnesium. The common anions are carbonates, phosphates, silicates and sulfates.

The organic extraneous materials in wood consist of many classes of compounds, such as aliphatic and aromatic hydrocarbons, terpenes, (aliphatic and aromatic) acids and their salts, alcohols, phenols, aldehydes, ketones, quinones, esters and ethers, certain wood contain essential oils and alkaloides. Others contain tannins, coloring matter, water-soluble polysaccharides, gums and proteins.

Wood treatments

Treatments are designed to modify wood in order to change its physical(3), chemical(4) and biological(5) properties so as to be fire-resistance or flame retardant(6) and fire proof; in each case no feasible treatment prevent the combustion of wood at high temperature in the presence of oxygen, rather than the improvement in dimensional stability(7), mechanical properties(8) of wood, other wise the preservation from attack by fungi, termits and wood distroying insects(9).

Types of treatments

1- Pressure processes (Impregnation processes)

The preservative treatment of wood by pressure methods is the preferred commercial approach because of its greater efficiency and effectiveness than the non-pressure processes. Its effectiveness is due to the more uniform, deeper penetration and greater absorption of impregnant solution than can usually be attained by other means, these include:

(a) Full-cell processes (*Vacuum impregnation processes*)

The primary objective of a full-cell treatment is to attain maximum retention of preservative in the treated wood a preliminary vacuum is designed to remove as much air from the cells as possible (with the help of a vacuum pump), thereby removing that air cushion which resist the penetration of the impregnant solution. A further advantage is that there is a minimizing of preservative release "kick-back" caused by the expansion of trapped air when pressure is removed from the equipment.

Gohar and ***Guyonnet***(10) assist a new method for impregnating wood with monomers in which the process improves the dimensional stability of wood even on exposure to high humidity, the wood is subjected to controlled thermal treatment prior to vacuum impregnation with monomers so that curing is self effected by residual heat in the wood.

Another improved method for impregnation of wood was given by ***Nishio et al.***(11) .In which the impregnation is done via a pretreatment step in which wood is heated in a closed container to vaporize the moisture in wood and if needed heated steam is added prior to impregnating with liquid chemicals such as preservatives, synthetic resins or fire proofing agents.

(b) Empty-cell processes (pressure impregnation processes)

This is accomplished by applying compressed air to the wood samples before forcing the preservative into it (with the help of hydraulic pressure pump). The empty-cell process differs from full-cell process in that some means of recovering much of the preservative is used, leaving no liquid preservative in the cell lumens of the treated wood. This procedure traps air in the cells and when the pressure is released after treatment, the trapped air expands and forces the preservative out. A final vacuum serves to remove even more of the solution.

After the incorporation of a polymerizable monomers into the wood matrix by a suitable means, polymerization may be overcomed either by initiator-heat technique or by γ-radiation(12). The relative amounts of graft polymer and homopolymer formed in treated wood have not been established, the removal of homopolymers from the product by application of solvent indicates that some grafting does occur on the polysaccharides, probably on cellulose(13) and lignin(14) components. In such case polymerization of monomers were occur in situ leading to wood plastic composites(15) (WPC).

Impregnation of wood with liquids by the compression recovery method with improved liquid impregnation efficiency and treated or dyed wood and composites of wood with polymers therefrom was invented by ***Muraki et al.***(16) in which the impregnation process was carried out by immersing dry wood in a liquid in an autoclave, compressing wood at or above the softening temperature of wood by pressing the liquid in the autoclave and lowering the pressure of the autoclave to cause relaxation of the volume of wood in the liquid and injection of the liquid into the wood.

(2) Non-pressure processes (*Coating processes*)

Non-pressure processes include any method where no external pressure is applied to force the wood preservative into the timber. These include brushing or spraying and dipping.

Types of coating processes

(a) Brushing or Spraying

It is the simplest treatment available it requires a minimum investment in equipment and can be employed for any paintable material. The moderate penetration that results is seldom more than a few millimeters in depth including that surface cracks and checks are thoroughly filled and that generous quantities of coating material are applied over the entire surface of the wood.

(b) Dipping

Another non-pressure process for applying coating materials on wood. This method involves the immersion of the wood in a treating solution for a period of a few seconds to a few minutes. It provides little more effectiveness than brushing or spraying except that end penetration is frequently better in easily treated species.

Complete immersion provides greater uniformity of coverage than brushing and given more assurance that all checks are filled, dipping times are approximately three minutes.

It was shown by ***White***(17) that the use of coatings to improve fire resistance of wood, currently used fire retardant coatings for wood reduce flame spread. Fire resistive coatings designed for steel and foam plastics generally are not recommended for wood.

In all methods used in wood treatment the major factors influencing the choice of a particular method of treatment will be considered, cost is often the major consideration and simplicity of equipment is the other factor, the simplest processing method generally requires the least expensive equipment.

Types of fire-retardant paints and coatings

Fire-retardant paints and coatings are of two general types:
(1) Intumescent and **(2) nonintumescent.**

The main advantage of the intumescent coatings over a fire-retardant nonintumescing coating is the ability of the former to insulate the flammable substrate for substantial time periods from the high temperatures associated with a fire. The highly insulating character of a good intumescent coating can dramatically reduce the flame-spread rating of a flammable substrate to the incombustible range. Substrates protected by nonintumescing fire-retardant films often ignite readily as the unprotected material. Generally, the fire-retardant paint confines the fire to the immediate area of the building, whereas unprotected buildings are consumed in a matter of minutes.

(1) Intumescent Coatings:

Most of the fire-retardant coatings sold are intumescent because of the need for coatings suitable for use over combustible substrates(18). Since these coatings were originally developed primarily for use on wood, the fire retardant used in their preparation are largely those which had been found to be useful fire retardants on cellulosic materials.

The fire retardant ingredients are generally used in combination with a suitable film-forming binder in preparing intumescent coatings.

The ingredients are of three general types:

a- Phosphorus compounds capable of producing phosphoric acid on thermal degradation.

b- Nonresinous materials often called carbonifics, which produce large volumes of both nonflammable gas and carbon in the presence of phosphoric acid.

c- Gas-producing components, sometimes referred to aspumifics, which release large quantities of gas under the influence of the phosphoric acid produced at elevated temperatures, these components are often resinous in nature and act as binders in addition to forming gas.

Another fire-retardant intumescent coatings based on a copolymer of vinyl acetate and 2-ethyl hexyl acrylate resin emulsion has been developed for wood by ***Jain et al.***(19)

(2) Nonintumescent Coatings:

Perhaps the most important, if not the only, nonintumescent fire-retardant coatings being sold in any appreciable quantities are alkyd coatings containing chlorendic acid as the main fire retardant(20). In addition to their excellent and permanent fire retardancy, the alkyd enamels possess many of the advantages of conventional alkyd coatings. Because of their nonintumescent character, however the coatings only for noncombustible substrates.

Improvement of wood properties

(a) Dimensional stability of wood

Improvement of the dimensional stability of wood has been of primary interest, this because the tendency to shrink and swell with changes in humidity is the most unfavorable property of wood.

If wood were an isotropic material shrinking and swelling equally in all directions. However, its variable morphology, gross and submicroscopic, is the basis for unequal dimensional changes in the tangential, radial and longitudinal direction. Volumetric shrinkage can be very substantial in some wood but the more important factor is the differential shrinkage in the various directions that can lead to warping and distortion of all sorts and the swelling that accompanies the reabsorption of water.

Stamm(21) lists the successful procedures that can be used to reduce these volumetric changes. The method includes impregnating or coating wood with a substance that will retard moisture gain or loss, a substance that is insoluble in water. Another way is to bulk the cell walls while they are in the swollen state, thus physically preventing normal shrinkage. A third method is to change the wood chemically by replacing hydroxyl groups in the cellulose with others that are less hygroscopic.

Acetylation of wood is now possible commercially leading to a high dimensional stable wood. It involves the introduction of acetyl groups in place of the hydroxyl groups in wood that has been swollen chemically. Another stabilization technique is the thermal modification of wood. The chemical changes brought about by subjecting the wood to heat under controlled conditions does reduce its swelling and shrinkage.

Militz and Peek(22) reported that the impregnation of popular wood with water-soluble resins resulted in improving some technological properties of the wood. Most treatments considerably reduce swelling and shrinkage of the wood and antiswelling efficiency (ASE), depending on resin type. An air curing acrylate-modified alkyd resin and an air curing alkyd/polybutadiene oil system gave best results.

In addition, wood can be stabilized dimensionally through the impregnation with extracts from forest residues(23). Water extracts from Oak bark and wood chips and spruce needles were used to impregnate samples of beech and pine, which were dried and their shrinkage measured. The efficiency of the extracts was determined as a function of penetration into cell walls and ability to reduce water absorption by the wood samples.

Also dimensional stabilization of sungi wood by monomer and polymer impregnation was studied by ***Nobashi et al.***(24) in which sapwood was impregnated with several methacrylate monomers and thermocatalytically polymerized in situ. Polymer-impregnated wood were prepared by infusing the acetone solutions of several methacrylate polymers into the sapwood, followed by evaporating the solvent and by vacuum drying to a constant weight. When wood specimens of high moisture content were impregnated methacrylate monomers containing relatively bulky substituents, the wood-plastic composites (WPC) obtained should favorable dimensional stabilities toward moisture absorption. The addition of a proper amount of acetone to the monomers was effective to improve the dimensional stability of the (WPC). The dimensional stabilities were obtained with the impregnation of polymers having low molecular weight.

Tagawa et al.(25) showed that woods were impregnated with compounds comprising active OH-containing polymers and blocked isocyanate crosslinking agents and are cured to give improved durability and dimensional stability, methods may include:

a- Dissolving the above compounds in organic solvents,
b- Impregnating woods with these solutions, and
c- Diffusing the solvents from the woods.

A dimensional stable modified wood materials were manufactured by ***Kitagawa et al.***(26), through the impregnation of wood with inorganic alkoxides. Thus wood was impregnated with a 20% Si $(OEt)_4$ in iso Pr OH solution, then dried and cured to give a material having good shrinking and wet swelling compared to untreated wood.

Okamoto(27) can manufacture a dimensional stable wood by impregnating the wood with inorganic compounds and impregnating or coating the wood with resins. Thus, wood samples impregnated with an aqueous solution containing 42% $BaCl_2$ and 12% boric acid at 60°C for 24 hours to give 60 - 80% impregnated wood, which was coated with acrylic resin in vacuo by 40 – 70 g/m^2 then over coated with a polyester coating to give a material having good dimensional stability after soaking in H_2O at 20°C for 16 hours.

The dimensional stabilization of timber by impregnation with methyl methacrylate and polymerization by γ- radiation has been studied by ***Gibson et al.***(28) in which treatment with pure monomer yielded a product wherein the voids in the wood were filled with homopolymer, but introduction of the monomer in a solvent which swells wood enabled the methacrylate to penetrate the cell walls, giving a product which was not entirely extractable with polymer solvents such as chloroform. Both methods gave products with improved strength and stability.

(b) Compression strength of wood

The strength of a material depends on its ability of sustain load without undue deformation or failure. This property is inherent in the material itself and must be determined by experiment. As a result several types of tests have been developed to evaluate a material's strength under loads. In the United States the American Society for Testing and Materials (ASTM) has published guidelines for performing such tests. One of the most important tests to perform is the compression test. Although many important mechanical properties of a material (wood polymer composites) can be determined from this test, it is used to determine the relationship between average normal stress and normal strain in many engineering materials (composites). To perform this test a specimen of the material is made into a "*standard*" shape and size, a testing machine is then used to compress the specimen at a very slow constant rate until it reaches the breaking point(29). Compression strength was determined from the equation:

$$\delta = P/A$$

Where: δ = The compression strength *(kg/cm^2)*,

P = The maximum external force *(kg)* and

A = The cross section area *(cm^2)*.

The value of δ (delta) is then used to calculate the average normal strain in the specimen. The introduction of polymer in small amounts does not markedly affect the mechanical properties of wood; larger amounts lead to a products having higher desnity, greater rigidity, abrasion resistance and compressive strength and decreased permeability.

Yab et al.(30) can manufacture the wood-polymer composites (WPC) by using 10 vinyl monomers and mixtures of monomers and in situ polymerization by γ- radiation or the catalyst-heat treatment. (WPC) showed improvement in termite and fungal resistance and mechanical properties such as hardness, compression and static bending strengths.

The physical-mechanical properties of pinewood impregnated with polystyrene were investigated by ***Manrich et al.***(31), the incorporation of polystyrene into the wood matrix will improve the compression and static bending properties of pinewood. The micrographies confirmed that there distinct but continuous phases of polymer and wood cell wall, which granted the composites a better physical-mechanical behavior.

In addition an improvement in mechanical properties of pinewood achieved by impregnating wood with Ph OH – HCHO resins(32).

(c) Fire retardancy of wood:

Fire-Retardant-Treated wood: What is it, What it does and How it works(33). Attempts to produce fire-retardant wood have involve:

1- The impregnation of wood with agents that interact with the cellulose during pyrolysis.

2- The coating of wood with a substance can protect the wood through a physical insulating mechanism.

Fire-retardant paints present a surface coating which hinders the spread of flame and affords some protection in preventing rapid spread of a fire during its early stages.

A non-ignitable and non-combustible inorganic cemetitious binder system forms a fire – barrier coating for numerous types of flammable substrates(34). It imparts zero flame spread and zero smoke and prevents the penetration of flame for prolonged periods of time. Incorporating fire retardant fillers and additives increases the fire resistant properties of the system. The formulation can be formed into many types of products:

Coatings, insulating coatings, binders, adhesives, grouts, mastics, sealants, impregnants, laminates, millboards, foams, castings, tiles and fillers. Each type, whether standing alone or as component of a laminate, attacks fire at its most vulnerable points, viz. preventing initial ignition of a substrate, preventing flame spread along the surface by blocking access to fuel and preventing the penetration of flame through the substrate.

The combustible properties of wood treated with flame-retardant agents are tested according to ASTM:E (160)-crib test (35).

Most of the promising organic fire retardant systems evaluated in textile applications have probably been evaluated on wood. Polymerizable phosphorus and nitrogen-containing compounds have been prepared by reacting organophosphorus halides with allylamine or *m*-aminostyrene and organophosphoramidates with α, *β*-unsaturated acid chloride(36).

Wood in its untreated form has good resistance to the penetration of fire when used in thick sections for walls, doors, floors and roofs. This resistance exists because wood has low thermal conductivity, thus limiting the rate at which heat is transmitted to the interior of the member. Treatments of wood by a suitable fire-retardant may prevent ignition by a small source of fire or delay the development of a large fire. Fire-retardant treatments are used primarily for wood framing, roof-supporting members and decking, when permitted noncombustible buildings, also for all paneling in corridor and assembly areas of public buildings.

Lewin(37) reported that treating wood with acidified bromate-bromide solution (chemical modification) is capable of overcoming the flammability of untreated wood. The treatment is carried out in autoclaves with application of vacuum and pressure where the lignin component of the wood is brominated in the solid state by the treatment solution with a high yield of bromine.

Also a white ash specimen showed good fire retardancy(38) when impregnated with a mixture of adipic aicd-dibromopentyl-glycol-maleic anhydride coploymer, tris (2,3-dibromopropyl)-phosphate, methylmethacrylate and benzoyl peroxide and cured at 140°C .

Makano et al.(39) showed that, upon treating wood with solutions containing water-soluble inorganic substances, then immersing wood in H_2O to remove these substances from the surface and finally impregnating wood with water-soluble substances to form water – insoluble inorganic fire retardants, thus a wet wood veneer was immersed in 2.0 mol/L $BaCl_2$ for 24 hours at 60°C subsequently immersed in H_2O for 1 hour then immersed in 2.0 mol/L ($NH_4)_2$ SO_4 for 24 hours at 60°C, immersed in H_2O for 24 hours and dried to give a fire – resistance vener.

A flame-retardant wood was manufactured by ***Usui et al.***(40) by the precipitation of water-insoluble flame-retardant compounds into wood by impregnation with anion-containing solution and cation-containing solution, higher deposition with lower unreacted residue can be obtained by impregnation with either solution followed by other solution in 2 steps beginning with higher concentrated one first. Thus a veneer was saturated with water, impregnated with 2.0 mol/L $BaCl_2$ solution at 50°C for 24 hours, washed and impregnated with a solution containing 4.0 mol/L $(NH_4)_2$ HPO_4 and 60 mol/L H_3BO_3 for 1 hour followed by a solution containing 1.0 mol/L $(NH_4)_2$ -HPO_4 and 1.5 mol/L H_3BO_3 for 24 hours to give treated wood veneer with good flame retardance.

N- Alkenyl- and N-*m*-styryl-phosporamidates have been used to impregnate wood blocks(41) and polymerized in situ either by heat, chemical or irradiation initiation to impart flame – retardant properties to the wood.

Mechanism for fire-retardancy of cellulosic material

The application of heat on cellulosic materials causes pyrolysis of glucose units into combustible gases. These vapors are ignited under suitable conditions, the heat of combustion being sufficient in most cases to propagate the flame in the absence of external heat source. The mechanisms of combustion of cellulose and of fire-retardant cellulose have been reviewed by ***Browne***(42), ***Little***(43), and ***Schuyten***(44). It has been shown that the burning of cellulose occurs in two stages. Temperature of 300°C or above cause thermal degradation into gaseous, liquid, tarry and solid products. The volatile, flammable gases ignite and provide additional heat to further pyrolyze the liquid and tars into more flammable vapors, and also to form a carbonized residue which does not readily support combustion. This process continues until only the carbonaceous material is left. The second stage then begins, which consists of glowing of the carbonaceous material until this flameless combustion consumes the residue, leaving only an inorganic ash. Water is the first product given off during the pyrolysis of celluose(45). Pyrolytic scission occurs randomly a long the chain at the carbon-oxygen bonds, yielding fragments having either reducing or nonreducing end groups. In studies of the thermal degradation of glucose it has been shown that 1,2-anhydroglucose is formed, this then rearranges to 1,6-anhydroglucose as the temperature rises. Further pyrolysis of cellulose results in the formation of formaldehyde, acetone, glyoxal, glycoladehyde, lactic acid, glycolic acid, formic acid, acetic acid, water, carbon monoxide and carbon dioxide. Of greatest importance to the investigator in fire retardant cellulose, is the first step in the degradation of cellulose, i.e., the loss of water and the formation of the 1,6-anhydroglucose.

Thus, if cellulose could be made to decompose according to the equation:-

$$(C_6H_{10}O_5)_n \rightarrow 6n\,C + 5n\,H_2O$$

There would be no flammable gases and hence no flaming, during pyrolysis all effective fire retardants increase the quantity of carbon formed at the expense of the flammable tars, lower the decomposition point of cellulose and raise the temperature at which exothermic pyrolysis occur.

There is a good agreement on the fact that the reduction in tars and the increase in char is the property best correlated with nonflammability. The products of tar from treated cellulose is about one-fourth that obtained from untreated cellulose(46). The high hydroxyl content of cellulosic materials makes them amenable to somewhat different fire retardant techniques than those used in most other commercial polymers.

Fire-retardant polymers used in wood treatment(47)

(1) Definitions

With the continued and rapid expansion of the plastic production during the past decade the flammability or lake of it in these predominantly organic polymers have assumed increasing importance. Fire-retardant polymers must not only exhibit adequate and permanent fire retardancy, but must also posses other properties comparable to those of materials, which are not fire retardant. However, the following definitions have been generally accepted through common usage. The field of fire-retardant polymers has been plagued by a plethora of terms without clearly defined meanings such terms as fireproof, flame retardance, fire resistance, flame resistance and often interchangeably. The term "*flame-retardance*" and "*fire-retardance*" are commonly used in the industry to cover both the quality of retardancy and the act of retardation of the flame or fire. Such terms as fireproof, noncombustible and fire-resistance are somewhat ambiguous, unless qualified by a description of the fire conditions of a recognized test method. With few exceptions all commercial polymers burn pyrolyse or char at elevated temperatures, although their individual burning characteristic may vary widely. The development of suitable test methods for measurement of the flammability of polymer and treated wood were recognized standards organization as the American Society for Testing and Materials (ASTM-Standard).

On the bases of ASTM standard, the term fire retardant or fire retardancy will be used consistently to describe plastics whose flammability characteristics have been reduced to some degree measurable by commonly accepted test methods. Such terms such as fireproof and noncombustible will not be used because of misleading connotations when applied to polymers. The term inflammable meaning nonflammable is to be avoided under any circumstance. Many accepted test methods for meaning the burning characteristics of polymers are logically able to classify the polymer tested into one of he following:

a- ***"Burning"*** those samples, which are virtually, consumed under the test conditions.

b- ***"Self-extinguishing"*** those samples which burn for some limited period of time after removal of the test flame but become extinguished before the test specimen is completely consumed.

c- ***"Immediately self-extinguishing"*** are test specimens, which don't ignite under the test conditions or become extinguished so rapidly after removal of the test flame that self-extinguishing time can't be measured.

d- ***"Nonburning"*** applies to samples, which do not ignite under the test conditions. This is sometimes difficult to differentiate from self-extinguishing.

e- ***"Noncombustible"*** refers to refractory materials, which do not burn except under the most severe conditions.

(2) Requirements for fire-retardandcy of polymers

The molecule should be water-insoluble to achieve durability in laundering. A solvent-soluble organic molecule is proposed. The presence of orthophosphate group should be present in the molecule to dehydrate catalytically the cellulose substrate. The molecule should contain a polymerized group to effect a permanency of finish. The molecule should contain halogen or other group to reduce flammability of the gases of decomposition.

Since halogen and phosphorus radicals couple with free radicals produced in the combustion process and terminate the reaction, many flame retardant are halogen or phosphorus compounds, these may be:

(a) Additives, (b) External retardants, or (c) Internal retardants.

(a) Additives:

These flame– retardant agents are generally incorporated by physical blending with the base polymer. Included among these are ammonium bromide, diammonium phosphate, chlorinated waxes, poly (vinyl chloride) and tris –(2,3 – dibromopropyl) phosphate.

(b) External retardants:

These compounds which by themselves are ineffective flame retardants, but in the persence of halogens give good self–extinguishing properties the most important compounds of this group are oxides and sulfides of antimony, zinc borate and phosphorus esters.

(c) Internal retardants:

Involves the chemical combination of the flame-retardant agent into the basic polymeric structure compounds include in this group are bromoethyl acrylate, halogenated styrene, chlorendic acid, vinyl bromide, tetrachlorophthalic anhydride, tetrabromophthalic anhydride and tetrabromobispenol.

Fuel, oxygen and high temperature are essential for the combustion process. Thus some composites which have flame-retardant properties are not good fuel. Hydrate filler release water when heated and hence reduce the temperature of the combustion reaction. Also some compounds such as sodium carbonate, which release carbon dioxide, shield the reactants from oxygen. Char formed during the combustion processes, also shield the reactants from oxygen and retards the outward diffusion of volatile combustible products. Aromatic polymers tend to char and some phosphorus and boron compounds catalyze char formation. Synergistic flame retardant such as a mixture of antimony trioxide and an organic bromo compound are much more effective than single flame retardants(48).

A body of well-founded empirical data that is useful in formulating suitable fire-retardant compositions some of these are:

1- The incorporation of halogen atoms into a polymer decreases the flammability of the composition.
2- The efficiency of halogen in fire-retardant additives is F<Cl<Br.
3- Halogens on aromatic structures are less efficient than those in aliphatic hydrocarbons.
4- A combination of antimony oxide and halogen is more efficient than either of these compounds a lone.
5- Some combinations of phosphorus and halogen exhibit a considerable synergism in specific polymers.

6- The degree of effectiveness of fire-retardant varies markedly, depending upon polymer composition.

7- The amount of fire retardant required to obtain a constant degree of fire retardancy varies, depending on the physical form (i.e. molding laminates, foam or film) of the polymer composition.

8- Many fire-retardant compositions leave large amounts of charred, difficulty combustible residues when exposed to a flame.

9- The pyrolysis of halogen containing polymer composition, containing hydrogen generally results in conversion of most of the halogen into gaseous products, of which the largest constituent is hydrogen halide.

Thus flame-retardants like many other organic compounds may be toxic or they may produce toxic gases when burned. Hence extreme care must be taken when using fabrics or other polymers treated with flame-retardants.

(3) Action of fire retardant on cellulosic materials(47)

Starting with the hypothesis that all organic material can be destroyed by burning, an effective fire-retardant must retard ignition and inhibit subsequent flame spread. In the burning of any material, heat first reaches it by radiation, convection, or conduction. At the decomposition point, pyrolysis leads to the production of small, volatile fuel particles, which escape as a gas, creating porosity, and increasing the surface area. A greater surface accelerates the absorption of heat and the volatilization process.

With increasing temperature, the ignition points reached and a flame develops, producing additional heat for pyrolysis. Whether a self-sustaining flame develops depends upon the transfer of enough heat from the flame front to the hot substrate to maintain fuel production.

Four theories have been advanced for describing the action of fire retardant on cellulose, these are:

(a) ***Chemical,***
(b) ***Thermal,***
(c) ***Coating*** and
(d) ***Gas*** theories.

(a) Chemical theory:

During the pyrolysis, nearly all effective fire retardants increase the quantity of carbon formed at the expense of the flammable tars, lower the decomposition point of cellulose and raise the temperature at which exothermic pyrolysis occurs. It was noted that salts that dissociate to form acids or bases upon heating are usually effective fire – retardant. Most effective are the salts of strong acids and weak bases, and somewhat less effective are the salts of strong bases and weak acids.

(b) Thermal theory:

States that, fire retardancy could involve:

- An insulating effect,
- A thermal conductivity effect, or
- An overall reduction in exotherm.

The application to cellulose of compounds whose endothermic heat of pyrolysis is sufficient partially to offset the exothermic pyrolysis of cellulose could theoretically be an efficient method producing fire retardancy.

All evidence indicates that the last effect is only a minor contributing factor in fire retardancy of cellulose, although it undoubtedly plays an important role in fire retardancy of other substrates.

(c) Coating theory:

The coating theory states that the formation of an impervious coating around a cellulose fiber at combustion temperature effectively reduces the oxygen supply necessary for complete combustion. This causes formation of an increased amount of char, which act as a thermal barrier.

(d) Gas theory:

The gas theory states that combustion of cellulose can be halted by the emission of noncombustible gases from the fire retardants. These gases alter the flammability either by dilution of the combustible gases resulting from pyolysis or by the inhibition of flaming by the formation of free radicals which alter the normal combustion process.

Reactive fire retardants(47)

(i) Commercial fire–retardant additives

The perfect fire-retardant additive for most purposes should be cheap, colorless, easily incorporated into the polymer composition, compatible with it, stable to heat and light, efficient in its fire- retardant properties and have no adverse affect on the physical properties of the polymer. The fire –retardant additives of greatest commercial importance have been halogenated hydrocarbons, such as chlorinated waxes; various esters of phosphoric acid, such as tricresyl phosphate and triphenyl phosphate and solid antimony trioxide. Some common fire-retardant additives and their trade names are given in Table (1).

(ii) Commercial fire- retardant polymers

Some of the disadvantages of the fire- retardant additives can be overcome by the use of halogen or phosphorous containing polymers. Among the first reactive fire retardants and more commonly used are discussed below in more detail:

(a) Chlorendic acid

The best known and most widely used of the fire-retardant polyesters are based on chlorendic acid, 1,4,5,6,7,7- hexachloro-bicyclo (2,2,1) hept-5-ene-2,3-dicarboxylic acid. The success of

Table (1): Some common commercial fire-retardant additives.

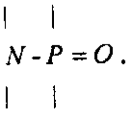
Additive	**Trade name**
Antimony trioxide	Thermograd
Chlorinated paraffins	Chlorowaxes Unichlor Halowax
Tributyl phosphate	Disflamol Kronflex TBP
Tris(2-ethylhexyl) phosphate	Disflamol TDF Kronflex TDF
Triphenyl phosphate	Disflamol TP TPP
Cresyl diphenyl phosphate	CDP Disflamol DPK
Tricresyl phosphate	Disflamol TKP Flexol TCP
Tris(2,3-dibromopropyl) phosphate	Celluflex CEF
Tris(2,3-dichloropropyl)phosphate	Celluflex FR-2
Poly-β- chloroethyl triphosphonate mixture	Phosgard C-22R

chlorendic acid as a reactive fire-retardant monomer in polyesters can be largely attributed to the high level of thermally and hydrolytically stable chlorine in this relatively inexpensive compound. In addition, esterification rates are comparable to those of phthalic anhydride, allowing ready substitution of this common reagent in commercial polyester preparations.

(b) Tetrabromophthalic anhydride

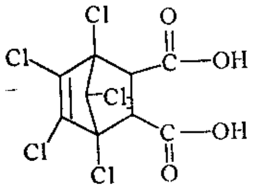
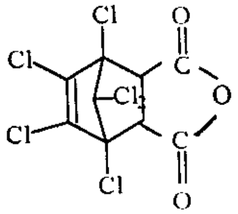
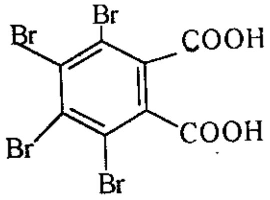
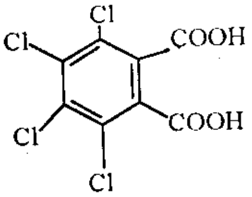
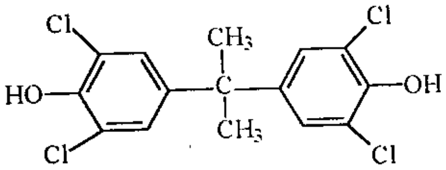
This compound is an excellent fire retardant monomer in thermoset polyester and epoxy resin. It shows fire retardancy at a bromine level of 12.5% compared with greater than 20% chlorine needed for chlorendic acid. It may be incorporated into a polymeric material to enhance its fire retardancy through ester formation by the reaction with excess alcohols(49) or it may be condenses with ethylenediamine in aquous acetic acid solution to give a white precipitate form N,N' - ethylene-bis (tetrabromophthalimide) as a flame retardant polymer(50).

(c) Phosphorus containing polyol and hydroxy alkylated urea(51)

Among the commercial nonhalogene fire retardant polymers are phosphorus-containing polyol and hydroxy alkylated urea and thiourea. Flame-retardancy of polyurethane resin foam can be improved by the incorporation into the foamable mixture nitrogen groups and phosphorus atoms which regarded as being phosphorous containing polyamide in which a phosphorus atom is usually directly linked to nitrogen, replacing the active hydrogen atom of amino or amido nitrogen. The material is insoluble in water and in most organic solvents, they contain the group  $\overset{|}{\underset{|}{N}}-\overset{|}{\underset{|}{P}}=O$.

This could be accomplished by the reaction of amonia or a derivative rich in nitrogen and contain active hydrogen attached to amino or amido nitrogen groups with orthophosphoric acid. Usually the molecule of the amino or amido compound will contain at least 18% of nitrogen, the rest of the molecule being atoms of hydrogen or carbon and hydrogen and in some instances atoms oxygen or sulfur(52). In other cases dimethyol urea can act as a flame retardant for cellulosic materials(53). Fire retardance of wood treated with basic nitrogen-compounds and orthophosphoric acid is improved related to a crosslinked structure created by orthophosphoric acid(54). Dilative transparent fire proof coatings were prepared from ethanol-modified urea-formaldehyde resin as a base material and orthophosphoric acid/starch a fire retardant(55), some common fire-retardants and their trade names are given in Table (2).

Table (2): Some common commercial reactive fire retardants.

Structures	**Trade name**
 Chlorendic acid	HET acid
 Chlorendic anhydride	HET anhydride
 Tetrabromophthalic acid	Firemaster PHT4
 Tetrachlorophthalic acid	Niagathal
 Tetrachlorobisphenol A	Firemaster CP4A