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RESEARCH ON WOOD, CELLULOSE, AND LIGNIN

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During the last few years a number of commodities made from wood by chemical means have quietly assumed positions of great importance in the lives of everyone in this country and have exerted a great influence on national economics and living standards. We have come to accept such things as rayon, lacquers, artificial wool, artificial lumber, artificial sponges, cellophane, cellulose sausage casings, road binders, plastics, and many others as commonplace and have given little thought as to how they were developed. We may safely assume that they are but forerunners of the many that will appear in the future. All and more of these products are the result of intensive laboratory research and not one of them can be attributed to the work of a single man or laboratory. They represent the combined work of hundreds of research workers in this country and abroad and over a period of years. The earliest work on synthetic cellulose fiber was done nearly one hundred years ago. Since then countless successful and unsuccessful experiments have been made until now we have fabrics surpassing the fondest dreams of a relatively few years ago.

The diversity of developments in the cellulose industry makes it difficult to point out specifically contributions of fundamental research. The Forest Products Laboratory believes it has contributed through its fundamental research, at least indirectly, toward the development and improvement of many of these products and has assisted in paving the way for new developments. This paper will attempt to briefly discuss recent research at this institution and cooperating agencies.

The recent isolation from wood of the total lignin-free carbohydrate fraction, which contains the hemicellulose as well as the cellulose, promises to be of great value in developing and expanding the uses of cellulose. This work has already thrown a new light on the chemistry of wood, on the composition of the carbohydrates contained in wood, and on possible means of utilizing more of the carbohydrate fraction than is now being utilized in the production of pulp and rayon. It has even found application outside the field of forest products. Researchers in animal nutrition have wanted to find out the effect of lignin on the assimilation

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of plant carbohydrates but have never been able to remove the lignin without also removing part of the carbohydrates. The isolation of the total carbohydrate fraction, lignin-free, was the answer to their problem.

The chemical dissection within recent years of the wood fibers under the microscope into fibrils, fusiform bodies, and ultimately into the tiny spherical bodies has been of great assistance in explaining to the pulp and paper maker and to the manufacturer of synthetic fibers certain behaviors of the cellulose fiber. The early work on the location of the lignin in and around the fiber was directly responsible for the development of the semichemical pulping process. It has also aided the paper maker in explaining why beaten fibers produce a stronger paper than do unbeaten fibers. At least a part of this effect is due to the fibrillation of the ends of the fiber and to the development of a hydrated cementing material which, because of its greater adhesiveness, produces a firmer sheet. It is of interest to the rayon manufacturer because of the need for knowledge regarding the dispersion of cellulose fibers in suitable media into very small particles which are ultimately recombined to form fibers at the spinnerette. Further information, such as the molecular size and shape of these still smaller dispersed particles, is now being obtained. These small cellulose units are so small that they cannot be seen even under the highest powered microscope and their size and shape can be determined only by indirect measurement, such as viscosity, osmotic pressure, diffusion, spreading, and dielectric measurements. The fact that they are rod-shaped explains in a measure why they can be recombined into long fibers. Lignin, on the other hand, is made up of smaller and more nearly spherical molecules. These molecules can be made to form resins but cannot be spun into long fibers.

Perhaps less fundamental, but none the less important, is the research work of the Forest Products Laboratory in pulp and paper, of which only a brief description can be given here. Some 90 American species have been pulped by the standard processes -- mechanical, sulphite, sulphate, and soda. New processes, such as the semichemical, semikraft, and semisulphite, have been developed and are in commercial use. The recent commercial development of southern pine pulps was preceded many years by our experimental work on all of these species. The suitability of these woods, and of southern gums and other hardwoods for newsprint, book, bond, and wrapping papers was demonstrated on a laboratory basis long before their commercial production was realized. The production of bleached papers from southern pine was accomplished in the laboratory more than 15 years ago. Improvements in bleaching processes were worked out there. The current trend toward use of southern pine semi-bleached kraft in proposed southern newsprint mills was first suggested and such papers were made experimentally. The use of southern gum for newsprint was accomplished on a laboratory scale before 1930. Present work on the influence of growth conditions on chemical characteristics, and fiber properties of pines and other species are strongly influencing the trend of pulping throughout the country and aiding in the objective of making the United States independent as to its pulpwood resources. In recounting these developments we must not fail to acknowledge the

accomplishments of contemporary workers. In this connection the research of Dr. Herty and of the A. D. Little Laboratories deserves special mention.

Work on the chemical nature of lignin has also been in progress in many countries for nearly 100 years and although considerable progress has been made in the last few years, chemists are still unable to prove definitely its chemical constitution or to devise profitable ways of utilizing it. In recent years the Forest Products Laboratory and other laboratories have succeeded in learning a good bit concerning the fringes of the lignin molecule, particularly the nature of certain groups which give it the few known chemical properties that it possesses. We also know now that hardwood and softwood ligning are quite different. It was formerly believed that acetic acid resulted from the decomposition of the lignin when wood is destructively distilled; it is now known that it arises almost entirely from the holocellulose. When lignin is destructively distilled or treated with alkali, phenolic or aromatic materials are obtained. Because of this, many investigators have concluded that the lignin is made up largely of aromatic constituents. The Forest Products Laboratory does not feel that these reactions are sufficient evidence for such conclusions. Evidence obtained from many other reactions indicates that lignin is not aromatic but must be aliphatic or terpene in nature or composed of rings containing bridge oxygens. A recent careful examination by means of X-ray of specially prepared pure lignin revealed a definite crystalline structure. This is contrary to all previous conclusions which hold lignin to be amorphous in character and should add impetus to the study of the chemical nature of lignin.

These facts regarding the chemical nature of lignin seem to be of relatively little practical importance, but they have been responsible for several very interesting developments. Among them are the use of sulphonated lignin or sulphonated hydrolyzed wood in the negative plate of storage batteries. Although only comparatively small quantities of lignin are required, it makes possible the reduction in size and weight of the battery and increases its efficiency about twelve times at 0° F.

During the early work of the Forest Products Laboratory on the chemical nature of lignin, it was observed that formaldehyde had a pronounced softening effect upon lignin. Upon drying the softened lignin a hard resinous product was obtained. This led to the development of a process for the production of a plastic that depends upon the removal of part of the cellulose from wood by cooking with dilute acid, with the consequent increase of the lignin content in the residue. The softening point of the lignin is lowered by the addition of plasticizers, such as aniline and furfural, so that the mixture can be pressed at 155° C. and at a pressure of 3,000 pounds per square inch to give a hard, dense, brilliant black molded product at low cost. A number of industries are now interested and the prospects of an entirely new low-cost plastic are very bright.

When wood is cooked with dilute acid for the production of a plastic material, sugars are formed. These sugars and the acid are

removed by washing with water. The sugars may be fermented to alcohol, acetone, butyl alcohol, and other products by means of suitable organisms. Recent experiments at the University of Wisconsin indicate that the sugar solution may be used as a new preservative for the "canning" of alfalfa and clover in the form of silage. This silage, after six months' storage period, had a pH of 4.0, carried less than 10 percent of its total nitrogen in the form of ammonia, and contained about 130 micrograms of carotene per gram of silage. Another investigation indicates that lignin obtained from waste pulping liquors offers promise as an agent for softening boiler-feed water. When added to a lime-soda softened water it hastens the flocculation of the precipitated chemicals and permits them to be readily removed by skimming or filtering.

Many of the properties of wood are due to its colloidal nature. Colloids are materials that exhibit properties different from those of massive solids because of their large internal surface. The importance of the colloidal or surface properties in the case of wood can perhaps be appreciated better when we realize that the internal surface, which can be seen under the microscope, of a cubic inch of wood is about 10 square feet. Although this surface seems large, it is small in comparison with the surface on which water is adsorbed. This amounts to about one acre per cubic inch of wood.

A knowledge of the capillary structure of wood is of importance from a number of standpoints. Wood may be likened to a sponge with many microscopic and submicroscopic openings. The removal of water from wood in seasoning involves the passage of water and water vapor through the capillary structure. The treatment of wood with preservatives, fire retardants, and antishrink chemicals and the treatment of chips with pulping chemicals involves the penetration of the capillary structure of wood. Even painting and gluing involve the penetration of materials into the capillary structure near the surface.

Wood contains four different capillary size classes: (1) pores and resin ducts which are often visible to the naked eye, (2) fiber cavities which are visible under low-powered magnification, (3) pit-membrane pores which serve as the means of communication from the fiber cavity to fiber cavity and are, in general, below microscopic visibility, and (4) cell-wall capillarity, which exists only when the walls are swollen and approaches molecular dimensions in size. The last two size classes are of major importance in the treatment of wood. When you pour liquid from a bottle, it is not the diameter of the bottle that determines the rate of flow but the diameter of the neck. In the same way it is the pit-membrane pores and cell-wall pores that are the bottle necks in wood. As these bottle necks cannot be seen they can only be measured by indirect means. From studies of the flow of liquids through wood under hydrostatic pressure, and an electrical potential, from pressures required to displace a liquid within the structure with a gas, and from studies of the condensation of vapors in the capillary structure, the dimensions of these minute capillaries can be determined. These studies

have shown that seasoning of wood is a diffusion phenomenon, occurring chiefly through the cell walls, whereas pressure treatment is confined to passage from fiber cavity to fiber cavity through the pit-membrane pores. This information is proving invaluable in choosing the proper treating method and conditions for all kinds of wood treatment.

Wood, when dry, is one of the best electrical insulators. The electrical conductivity increases about a millionfold from the dry condition to that at which the fibers are saturated. These findings have led to a simple electrical means of determining the moisture content of lumber.

Studies of wood-liquid relationships and the bonding force of wood for water have given an insight into the mechanism of swelling and shrinking and have led to a means of its control. The permanent reduction of the swelling and shrinking of wood to one-fourth of normal has resulted from these fundamental studies. Wood is treated with synthetic resin-forming constituents that have a strong bonding force for the wood. They are then caused by heat to react within the fibers of the wood, forming a permanent chemical bond with the wood groups which normally bond water. Application of this treatment to plywood greatly reduces moisture trans-fusion through the wood and surface checking and also gives an appreciable decay resistance, acid resistance, and an increase in hardness.