FORTIFIED PAPER

By J. A. VAN DEN AKKER

PAPER in its ordinary forms is so commonplace and has been with us for so long that one is apt to overlook its very great importance in all phases of our economy. During the desperate days after Pearl Harbor, when industry was mobilized for total war, the pulp and paper industry was almost neglected. However, the men of the industry, aware of the rapidly developing shortages of steel and wood, and sanguine of the possibilities of cellulosic fiber reinforced with modern resins, reacted to the emergency with a combination of zeal and ingenuity that proved to be remarkably prolific. During 1942 and '43, pulp and paper were considered "reasonably available," and many articles needed in the war effort and in the maintenance of civilian life were fabricated with various forms of "fortified paper," thus releasing large tonnages of steel and other critical materials to war industry.

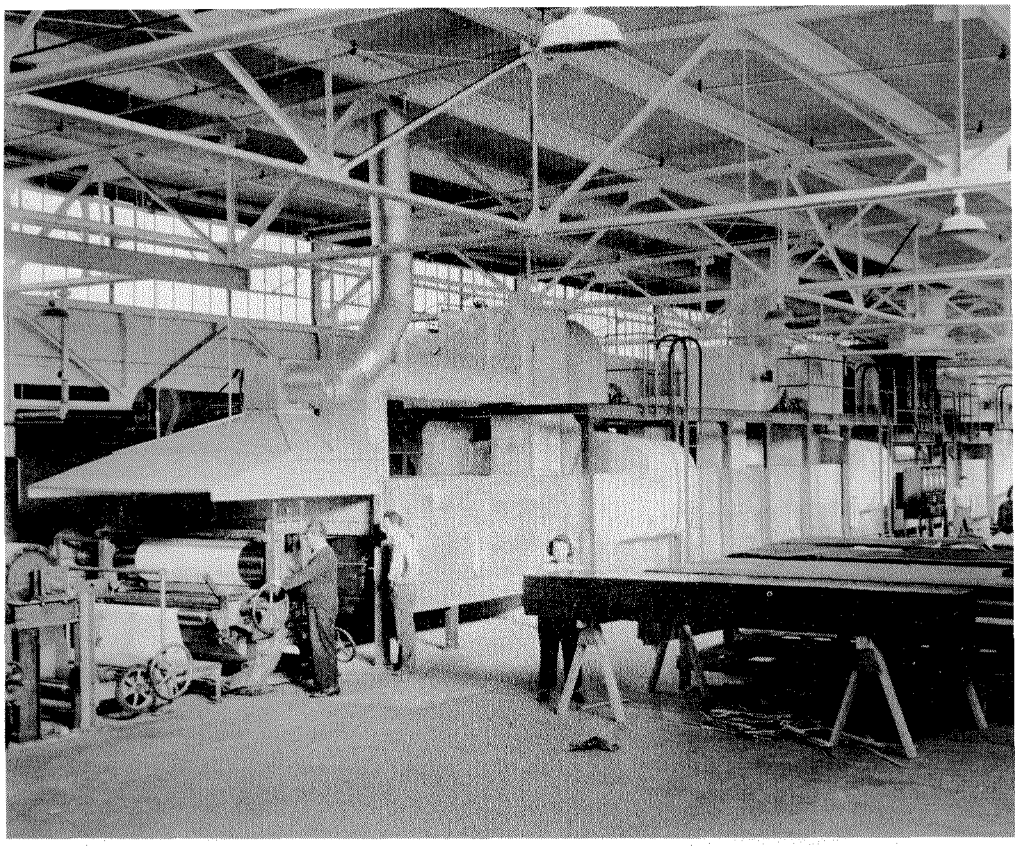
The growing substitution of paper for other materials, together with inadequate allotment of manpower to the paper industry and to the cutting of pulpwood, eventually resulted in the paper shortage, which is still with us. The **normal** uses of paper accounted for huge tonnages. Some of the data are illuminating. During the later months of the war, 90 per cent of the 700,000 articles necessary for the maintenance of our troops overseas were packaged or protected by paper, and a majority of those articles included paper as an integral part. Thirty tons of blueprint paper are required in the construction and fitting of one battleship. Four billion more tabulating cards were used in 1943 than in the preceding year.

A description of the normal uses of paper would require a "five-foot shelf" of books. The importance of a material is not, of course, always measured in terms of volume of production. The electrical industry requires various classes of dielectric and insulating papers ranging from dense condenser paper of thickness less than 0.0003 in. in certain grades (the decimal point is in the right place!) to heavy, porous high-voltage cable paper and vulcanized or impregnated fiberboard. Although the total tonnage of electrical papers is not inconsiderable, the technical value of such papers is far out of proportion with their listing in a tabulation of business statistics of the whole paper industry. One is prone to think of paper as something on which to write or print—there is very little publicity on the industrial applications of the many grades of paper designed for specific applications. The technical reader may find interest, during the coming months, in making mental note of special applications which have hitherto escaped his attention.

BONDING IN TYPICAL PAPERS

It is an age-old fact that a strong sheet of paper cannot be formed unless the cellulosic fibers of which it is composed have been subjected, in the presence of water, to a mechanical beating action. The **beater** causes a partial disruption of the fibers, as manifested by the formation of microscopic and sub-microscopic fibrils (electron micrographs reveal that some of the finer filaments released from the fiber are of diameter less than 100 Angstroms), and, although the entwining of fibrils resulting from the beating contributes to the strength of the paper, it is erroneous to think of the papermaking process as essentially a felting together of the fibers. The important result of beating is believed to be a bonding together of the fibers at points of contact during the drying operation. During the last stages of drying, contacting fibers are pulled together by large localized pressures of capillary origin, and, according to one theory, the hydroxyl groups of the cellulose molecular chains (exposed by the beating action) are brought sufficiently close together for their force fields to be effective; this cohesive bonding is aided by the adhesive effect of a colloidal dispersion of cellulose and of the hemicelluloses formed during the beating process.

In view of the fact that the strength of the fiber-to-fiber bonds is greatly inferior to the tensile strength of the fibers, the strength of paper is determined by (among other things) the number and nature of the bonds. The **dry strength** of paper, in the vast majority of uses, is more than adequate. However, the nature of cellulosic bonding is such that water produces a great weakening; the **wet strength** of untreated paper is a minute fraction of the dry strength. This unhappy but intrinsic weakness of untreated papers is well known through such common vexations as the paper towel which disintegrates while one dries his hands, the paper bag which fails in its job of carrying home a precious lot of eggs because one egg happens to break and leak, and the newspaper, left in the rain a moment too long, which falls apart if its reader



Impregnating machine for the treatment of paper to be used in phenolic paper-base laminates. Courtesy of the Consolidated Water Power and Paper Company.

is imprudent enough to fling it open before the paper dries.

For many years, a number of kinds of paper have been made with sizing agents (such as rosin and wax) added to the beater. Such papers resist penetration by water and, hence, display a measure of wet strength if not placed in contact with water for a long period of time. There is a surprisingly large number of uses of paper in which strength is required over short periods of contact with water or aqueous media and, in consequence, the generally employed sizing techniques have been fairly successful.

It is obvious, however, that wet strength of paper towels and other absorbing papers cannot be achieved through the use of agents which act through imparting water resistance to the paper. During the decade before the war, the technology of adding low percentages of polymerizing resins was developed. The resin (usually urea- or melamine-formaldehyde) is added to the fiber in a water soluble form (monomer or low degree of polymerization) and is subsequently cured on the driers of the paper machine. Paper fabricated by this process can be made both absorbent and adequately strong when wet. The better paper towels, in which the fibers are bonded together with a polymerized resin, can be used as wash cloths, and may be re-used a number of times.

WARTIME DEVELOPMENTS

Some of our earliest shipments of supplies to the South Pacific in domestic-type paperboard containers suffered tragic losses. In many instances the conditions of battle were such that cargoes could not be transferred in normal manner to lighters or docks. It was necessary for our supply ships to speed to a supply point, drop their cargoes into the sea, and make a hopeful dash for safety. Subsequently, our men on shore fished the supplies from the water. Containers of the domestic type simply disintegrated. It appeared that wooden boxes and crates would be required for all overseas shipping; however, analysis of the lumber supply showed that there would not be sufficient lumber to satisfy the needs of global shipping.

The industry met the challenge of producing paperboard boxes of strength, rigidity, and durability at least the equal of nailed or wirebound wooden boxes in the so-called "V-board" boxes. The "solid-fiber" kraft board (so named to distinguish it from corrugated board) was comprised of laminations bonded together with waterproof glues such as the rather remarkable combination of urea-formaldehyde resin and starch. V-board, of thickness of about 0.1 in., was manufactured to a specification of more than 750 lb/in.^{2} dry bursting strength (pressure differential over a circular orifice of one square inch area) and more than 500 lb/in.^{2} after a 24-hour immersion in water. It was conservatively estimated in 1943 that the V box program was equivalent to conserving 1500 carloads of lumber per month. Improvements were made in the V boxes and, eventually, it was found that a number of classes of supplies could be shipped more satisfactorily in them than in wooden boxes.

The conservation of steel during the war by substitution of paper products is noteworthy. The steel grommets employed for the handling and protection of bombs were replaced by laminated chipboard rings which, except for a thin outer band of steel, were made from waste paper; it has been estimated that the metal conserved by the paper rings was more than 50,000 tons per year. Cylindrical paper containers for oil and paint conserved about 90,000 tons; a variety of new folding and set-up boxes replaced about 125,000 tons of metal per year, and large tonnages of pliofilm, rubber, and cellophane were also conserved. The molded fiber industry employed phenolics in the production of such items as flash-light cases, alarm-clock cases, walky-talky battery cases, special cannisters, and instrument cases. Huge tonnages of steel (in the form of drums) and of burlap, cotton, and wood were released through the successful development of the multiwall paper bag, which has been used for the shipment of many commodities formerly shipped in drums or slack wood barrels, such as calcium chloride, soda ash, bicarbonate of soda, ammonium nitrate, and rosin. These bags are used by the hundreds of millions for the shipment of chemical fertilizer, and a larger number is consumed by the cement industry. The complete list of wartime substitutions of paper for critical materials is impressive. One of the most interesting exhibits in Washington during the war years was that prepared by the Pulp and Paper Division of WPB's War Products Development Section, to which credit is due for an effective job in serving as a clearing house for the armed forces and industry and in co-ordinating the efforts of the paper industry.

Great improvements had to be made in paper itself. Battles cannot be won if the maps and other vital papers carried by the troops fail to withstand repeated wetting by rain, mud, and swims in jungle streams or ocean water. It is necessary that such papers withstand, without danger of failure, the wiping off of mud, blood, or grease. Papers for maps, charts, and manuals having amazing wet strength and durability were fortified with resins which were polymerized on the paper machines in a manner similar to that previously mentioned. Only small percentages of resins (just sufficient to produce strong, water-resistant bonds between the cellulosic fibers) were employed, so that the paper retained its essential physical and structural properties.

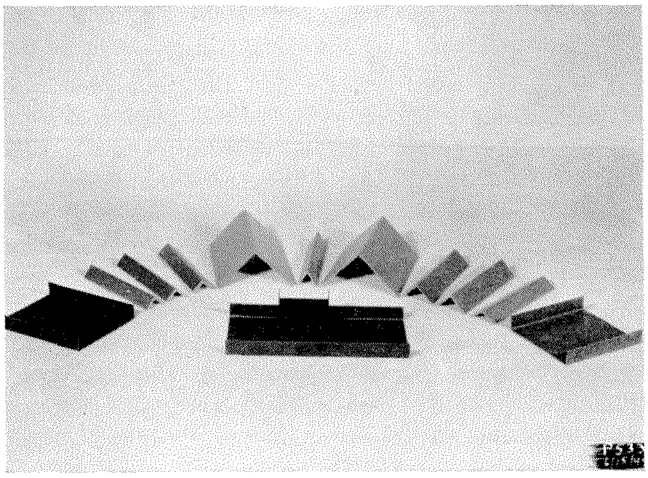
Some people like to think of paper as a skeletal web, the voids of which may be filled with an opacifying agent such as clay, titanium dioxide, or other "filler," and the surfaces of which may be coated with the conventional "coating color" (essentially an aqueous slurry of casein and clay) to improve the printing quality—or the surfaces may be sealed with a continuous film of wax, asphalt, or moisture-impervious plastic to yield a moistureproof sheet. During the war the manufacturers of rag-content map paper developed the technology of filling the voids of the paper with fluorescent pigments. The fluorescent map papers so produced were of considerable value in night military operations; by the use of small ultraviolet lamps equipped with filters which eliminate the visible radiation, the deleterious effect of map reading on the dark adaptation of the observer's eyes was mitigated, and the chance of attracting the enemy's attention was rendered negligible. When printed with two or more inks containing fluorescent pigments displaying different colors, fluorescent maps are beautiful to behold. (Needless to say, the choice of colors and pigments was such that the maps could be employed in ordinary light!)

Lens paper was one of the tremendous trifles of the war. The pre-war rate of production of lens paper was, of course, completely inadequate for the job of cleaning the large number of optical devices and instruments used by the Navy and Army. Moreover, lens paper was composed of Mitsumata fiber, the supply of which was cut off by hostilities in the Pacific. A number of experts must have shuddered at the thought of wiping fine optical parts with tissues prepared from domestic fibers. However, one of the large tissue mills produced satisfactory, grit-free lens paper by the carload on huge, high-speed equipment.

Paper has long been employed as a base for Bakelite and other plastics. During the war a considerable amount of developmental research was done on resin-impregnated paper which, in the form of many layers, could be cured at **low pressure** to produce a dense, hard, and strong plastic laminate*. Used on a limited scale by war industries, the new paper-base plastics were not sufficiently well developed early in the war for widespread use in aircraft, marine craft, and materiel. However, their mechanical and physical properties, some of which are presented later, indicate numerous, interesting peacetime applications.

"LOW-PRESSURE" PAPER-BASE LAMINATES

In a general way, it was expected that the strength of a laminate would depend upon the elastic constants



Angle and channel pieces fabricated with "Consoweld." Courtesy of the Consolidated Water Power and Paper Company.

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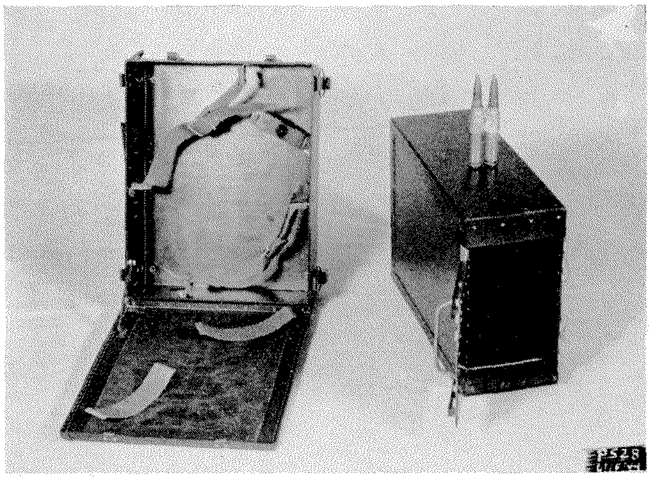
*Designated "papreg" by the Forest Products Laboratories; concurrently, that organization, located in Madison, Wisconsin, the Consolidated Water Power and Paper Company of Wisconsin Rapids, Wisconsin, the McDonnel Aircraft Corporation of St. Louis, and the Institute of Paper Chemistry of Appleton, Wisconsin carried out intensive research on the development and application of low-pressure laminates.



"Consoweld" Galvin and ammunition boxes. Courtesy of the Consolidated Water Power and Paper Company.

of both the resin and fiber (but not on the strength characteristics of the unimpregnated paper), and that the moduli of elasticity of the resin should be comparable with those of the fiber. The fiber-resin system is not amenable to mathematical analysis and, therefore, the successful development of papreg involved numerous experiments of the typical "experiment station" variety. At length, optimum factors relative to sheet composition and characteristics were found. Research on resins was, of course, vitally concommitant with the work on paper.

In the manufacture of papreg, a continuous web of suitable paper is impregnated with resin (usually phenol- or urea-formaldehyde) in soluble or depolymerized form. After passage through the impregnating bath and squeeze rolls, most of the solvent is driven from the web in a drying operation. The product obtained—now ready for any one of a variety of hot pressing operations—contains a substantial percentage (usually 30 to 40 per cent) of incompletely polymerized resin; it is fairly hard and is not tacky or sticky, so that it may be shipped and stored in rolls or in the form of packages of cut sheets.

In the production of flat stock, a number of sheets of the resin-impregnated paper are placed between the platens of a hydraulic press, and the pressure and temperature are elevated in accordance with a definite schedule. During the initial stages the resin is thermoplastic and the sheets, then quite flexible, become intimately bonded together. The pressure employed depends, of course, on the type of product employed, but is relatively low, being less than 250 lb/in.^{2} and, in certain types, less than 100 lb/in.^{2} In a short time the molecules of the resin polymerize (as a result of the elevated temperature) to produce the desired hardness and mechanical properties in the papreg; the material, no longer thermoplastic, may then be removed from the press without cooling. As in the production of resin-bonded plywood, the only limitation on the thickness of flat stock obtainable with steam-heated platens is that associated with the conduction of heat to the central plane. Without doubt slabs of considerable thickness could be produced with presses equipped for dielectric heating.

A most important advantage of the new plastic laminates is the fact that they can be formed with bag-molding operations like the Vidal and Duramold processes, using low-pressure equipment. As is well known, bag-molding of plastic laminates eliminates the need, in many operations, of employing large and excessively expensive dies. Large, curved bodies of complex shape (such as the hull of a rowboat) are formed in an autoclave. Although there are several bag-molding techniques, the general principle may be illustrated by two methods. In one procedure, the sheets of resin-impregnated paper are laid over a wooden die (the process of cutting and laying on is something of an art), the whole is enclosed in a rubber bag and placed in an autoclave, and steam of the desired pressure and temperature is admitted to the autoclave. The other method utilizes a semi-cylindrical autoclave resembling a Quonset hut. In this case, the bottom surface of the wooden die is flat and is placed in contact with the floor of the autoclave. A rubber bag occupying the space between the die and the inner surface of the autoclave is then inflated with steam, thus being made to exert pressure against the laminations. In these operations the small thickness of the resin-impregnated paper permits the latter to be bent around sharply curved surfaces.

In a qualitative manner a phenolic laminate may be described as being hard, stiff, strong, wear-resistant (in the presence of water as well as when dry); its color, usually light brown, is dependent upon the color of the resin and fiber and may be adjusted, through the use of dyestuffs, in an appreciable area of chromaticity; its density is about twice that of ordinary paper, but only half the density of aluminum. It is not ductile and cannot be formed in dies, but it can be machined. The brittle nature of phenolic resins is offset by the toughening action of the cellulosic fibers and, although the impact resistance of phenolic laminates (Charpy or Izod) leaves something to be desired, ruptures are not readily propagated by cracks. The material is anisotropic, *exhibiting different mechanical* properties in the three principal directions if not cross-banded (the fact that the fibers in a paper sheet are not randomly oriented accounts for a "grain" effect); however, in building up a laminate, the individual sheets may be cross-banded, as in the fabrication of plywood, to yield equality of mechanical properties in the two principal directions parallel with the laminations.

Some of the important characteristics of phenolic

"Kimpreg" surfaced plywood tables in the "Quonseteria." Courtesy of the Kimberly-Clark Corporation.

paper-base laminates are presented in Table I. The values given are not exact, but are intended only to give the reader the orders of magnitude of the properties.

Of special interest is the high ratio of strength to weight of papreg. To be comparable on this basis, a light-metal alloy having twice the density of papreg should have a tensile strength in the range of 50,000 - 70,000 lb/in.^{2}. The stiffness of bar or plate of papreg is especially noteworthy. It is well known that the flexural rigidity of a plate or curved member increases with the cube of its thickness; that is to say, for the same weight, the stiffness of members of different materials should be compared on the basis of the ratio of the modulus of elasticity to the cube of the density. As an illustration, a light-metal alloy of density twice that of papreg would not be comparable on this basis unless its modulus of elasticity were of the order of 20,000,000 lb/in.^{2} This underscores the value of paper-base laminates in stressed - skin and monocoque structures where weight is an important consideration, as exemplified by prefabricated houses, mobile craft of all sorts, household and business articles, concrete forms, etc. This advantage is recognized in plywood, which was used extensively in the production of high-speed aircraft in England during the war. Announcement is made, at the time of writing, of the commercial construction in Milwaukee of a 19-ft cabin cruiser in which the hull, cabin, decking, flooring, and many other parts are fabricated from paper-base laminate. It is said that the weight of the finished cruiser, 900 lb, is more than 50 per cent less than that of a conventional wooden cruiser of the same size. An advantage claimed in the announcement is the avoidance of caulking through the use of the new water-proof resin glues. The company making the announcement states that a number of row, sail, and outboard boats have been built with the

TABLE I

Some Properties of Phenolic Paper-Base Laminate

	Parallel Laminated	Cross Laminated
Molding Conditions		
Pressure, lb/in.^{2}	75	75
Temperature, °F	325	325
Time (1/8 in. thick), min	12	12
Specific gravity	1.4	1.4
Tension, lb/in.^{2}		
Ultimate, with grain	36,000	25,000
Ultimate, across grain	18,000	
Modulus of elasticity, with grain	3,000,000	2,200,000
Modulus of elasticity, across grain	1,500,000	
Compression, lb/in.^{2}		
Ultimate, flatwise	40,000	40,000
Ultimate, edgewise with grain	19,000	18,000
Ultimate, edgewise across grain	17,000	
Flexure, lb/in.^{2}		
Modulus of rupture, with grain	32,000	26,000
Modulus of rupture, across grain	20,000	
Modulus of elasticity, with grain	3,000,000	2,000,000
Modulus of elasticity, across grain	1,500,000	
Shear, Johnson double, lb/in.^{2}		
Edgewise, across grain	15,000	14,000
Edgewise, with grain	13,000	
Flatwise, across grain	15,000	14,000
Flatwise, with grain	13,000	
Impact, Izod, ft lb/in. notch		
Flatwise, with grain	5.0	4.0
Flatwise, across grain	2.0	
Hardness, Rockwell	M100	M100
Water absorption, per cent		
1/8 in. x 2 in. x 2 in. specimen, 24 hr	3	3

plastic laminate, and that "high reports on their durability under severe usage" have been received.

Another advantage of papreg lies in its internal friction or damping capacity, which is high, relative to that of metals of the types employed in structures. Vibrations originating in engines, for example, are readily transmitted throughout metal structures, and stresses may rise to perhaps dangerously high values where a condition of resonance or near-resonance exists. These undesirable phenomena are greatly reduced in plastic structures. Of course, a structural element which is directly linked with a strongly oscillating member, and is thereby subjected to intensive vibrational stress, should be of a metal alloy having high fatigue endurance—a property ordinarily associated with low internal friction.

Plywood surfaced with paper-base laminate is attractive in both appearance and technical properties. In the production of this interesting material, the plywood is sandwiched between layers of the partially cured resin-impregnated paper, and the combination is bonded together between the heated platens of a hydraulic press. In the case of woods (like Douglas fir) used in the manufacture of plywood having excellent strength properties but poor appearance, the surfacing with the paper-base laminate greatly extends the range of application. In all cases, however, surface layers of the strong laminate (applied in optimum thickness) greatly increase the flexural strength of the material—the laminate is applied at the greatest possible distance from the neutral plane of the combination, where it can do the most good. Recalling our considerations of density, we note that we are here dealing with a material having a core of quite low density and, hence, for a given weight, great stiffness.

Plywood surfaced with paper-base laminates is available from a number of plywood manufacturers, and is finding wide application in such diversified fields as aircraft, automotive vehicles, boats, boxes, trunks, building construction (including a variety of farm structures), furniture, freight and passenger cars, and refrigerators. It is greatly superior to ordinary plywood in the following properties: water absorbtion (very low), abrasion resistance, resistance to weathering, water-vapor permeability (considerably lower than that of asphalt-laminated building paper), hardness, strength, chemical stability, resistance to termites, fungus, etc., and appearance.

It is sometimes helpful, in appraising a new development, to obtain an overall picture of what has been done. The industry starts with wood (pulpwood—much of which is not suitable for lumber), in which the cellulosic fibers are bonded together with lignin. In the chemical pulping process, the lignin is taken into solution, and the fibers are separated, screened and washed, and built into a web of paper. Resin is then added to bond the fibers together to form a paper-base laminate. What has been gained in obtaining a product more expensive than wood? The trend in the process is somewhat analogous to that in the manufacture of plywood. The cost of producing plywood is balanced by the advantages gained, some of which are greatly improved uniformity of the material (resulting from the multiplicity of plies), greater strength, more nearly uniform strength in all directions of the material, and elimination of warping and splitting. In the production of paper-base laminate, these improvements are intensified. Uniformity of the product is much greater, because the fibers from tons of wood pulp are mixed, and because all steps in the process are controllable. Most important, however, is the fact that lignin, which is water-sensitive, has been replaced by a bonding agent which is stronger and does not lose its strength in the presence of water.

Plywood surfaced with paper-base laminate is an excellent example of the application of engineering economics to the optimization of factors involved in the combination of products of substantially different cost to obtain an excellent material which can be feasibly employed in a wide variety of applications.

"Kimpreg" surfaced plywood used for the manufacture of pre-cast stone. These forms will withstand in excess of 100 casting operations. Courtesy of the Kimberly-Clark Corporation.