The subject of this invention is the manufacture of impregnated sheet products wherein novel types of prefabricated fibrous webs serve as foundations or carriers for the impregnant. More especially, the fibrous webs comprehended by the present invention are those webs which are waterlaid, i.e., deposited from aqueous suspension, on machinery of the papermaking class, such as a Fourdrinier or cylinder machine, and which, while capable of undergoing impregnation with aqueous dispersions of binders like rubber latex, are intended for impregnation with impregnants that can be introduced into the web in heat-liquefied condition and then caused to set or coagulate as a continuous phase imparting thereto such desired properties as body, stiffness, strength, tear resistance, moldability, water repellency, and weathering capacity.

In making certain types of impregnated sheet products, it is customary practice to start with a suitable prefabricated fibrous web and to immerse the web in a bath of heat-liquefied impregnant of sufficient fluidity to enter into and through the web and then to remove the web from the bath and cause the impregnant to set or harden to its normally solid state. Such, for example, is the practice in making waterproof sheet products for roofings, flooring, and other building purposes, a bath of molten asphalt or other bitumen constituting the medium into which the starting web is dipped. Such is also the practice in making shoe stiffener material of the so-called thermoplastic variety, which is prepared by impregnating a suitable fabric with molten compositions, such as resin or the like, which upon setting impart stiffness and resiliency to the impregnated sheet. The shoe stiffener blanks cut from the impregnated sheet are softenable and moldable under the application of moderate heat non-injurious to leather, wherefore they can be moulded into the desired shape during assembly with the shoe upper, and then allowed to stiffen in such shape. In accordance with the present invention, I prepare a waterlaid fibrous web preeminently serviceable as a carrier for an impregnant, and more especially one which is to be associated in a molten state with such web. There are factors which I have found to be of great importance in preparing the web of the present invention, especially when comparatively short-fibered cellulose fibers, such as wood pulp, are employed as the raw material on account of their low cost and easy availability. Thus, I have found that one should not strive primarily for the securement of a strong web as it comes off in dry condition from the paper machine. On the contrary, one may advantageously deposit the web from the aqueous fiber suspension and then dry it with the air far under conditions of little, if any, outside pressure either during forming or drying. Other than the drawing together of the fibers on account of the action of surface tension during drying, the web may, therefore, be in practically the same condition of compactness as deposited from aqueous suspension with its fibers only loosely interfelted. The web may hence be tender or lacking in much tensile strength, but it may be fluffly or bulky and so highly porous and absorbent that it can readily take up far more of its own weight in molten asphalt or other liquid impregnant. In making the webs of the present invention, I use substantially unbleached, preliberated cellulose pulps as raw material, preferably substantially unbleached wood pulps, such as kraft or sulphite, or mixtures of such pulps. Preferably, also, these wood pulps, although substantially unbleached, have undergone refining to a higher alpha cellulose content than that associated with the raw pulp liberated from the wood. The refining treatment may be carried out in a suitable alkaline liquor and under conditions to produce an unbleached product having a high alpha cellulose content, say, about 93% to 96%, as is now known to those skilled in the art. These raw or refined pulps in substantially unbleached condition are preferably used in a practically unbeaten or unhayed form in making the webs of the present invention, as beating not only shortens the fibers but generates cellulose hydrate and thereby detracts from the absorbency in the resulting web. Even though it makes for greatest tensile strength in the web. As already indicated, however, I am not primarily interested in securing a web of initial high strength at the sacrifice of web absorbency, for reasons which will presently appear. I have found that webs made as hereinbefore described are far superior to the kinds of webs hereofore used as the carriers for heat-liquefied impregnants. Heretofore, waterlaid webs were prepared with a view toward securing considerable initial strength in the web at the expense of web absorbency. I have found, however, that the waterlaid webs of the present invention are so highly absorbent that, despite their low initial strength, they can be drawn continuously through one or more baths of heat-liquefied impregnants, e.g., molten asphalt, without much trouble on account of breakage. I attribute this success to the high rate at which the asphalt enters into and diffuses throughout the web, there-
by serving to bind together the fibers so that the web immediately upon entering the bath is so greatly strengthened that it can endure the further stresses in its journey without rupturing. I attribute this success also to the substantially bleached state of the fibers and, if they have been refined, further to their high alpha cellulose content. In unbleached state, the fibers are notably freer from xyloglucans or other degraded celluloses which are unstable, especially under application of heat. This applies especially to raw pulps, but it holds true even in connection with refined pulps. Under the application of considerable heat, bleached pulps may lose much more of their strength than would be the case if the same pulps were in substantially unbleached condition. Consequently when, as is true of my web, it is made up of unbleached pulp fibers, it is not weakened appreciably in passing through a bath of hot, liquid impregnant. Moreover, unbleached pulps invariably yield "freer" aqueous pulp suspensions than do similar bleached pulps whose xylan content apparently becomes more or less dispersed as fine or colloidal particles in the water of suspension, especially under agitation. The unbleached pulp suspension which I use enhances the porosity of the resulting web, for "freeness" in a pulp suspension is consonant with porosity in the web derived theretofrom, whereas "slowness" in the pulp suspension makes for density in the web. When the web is made from unbleached, refined pulp, it is especially resistant to being weakened by heat on account of the higher proportion of heat-resisting alpha cellulose in the refined pulp fibers. Moreover, the refined pulp fibers also conduct to a web of enhanced absorbency by virtue of the greater "freeness" possessed by refined pulps as compared with similar unrefined pulps.

Any one of the species of webs made in accordance with the present invention can imbibe more than 250% of its own weight in molten asphalt, without having a superfluity of asphalt on its surfaces. This imbibition of asphalt may take place even more rapidly than when webs of lower asphalt-holding capacity, such as heretofore made, are treated to the limit of their capacity. Accordingly, the webs of the present invention need be in contact with the heated asphalt for a shorter period of time, to attain a given asphalt content. There is thus less danger of scouring the fibers and causing their embrittlement.

Non-cellulosic fibers, especially those like wool and asbestos, which are more resistant to heat than the cellulose fibers, may be blended with the aqueous suspension of cellulose pulp used in fabricating my web. The cellulose pulp may be pre-liberated wood pulps or longer-fibered pulps, such as derived from manila, sisal, ramie, or the like, or mixtures of such pulps. Wood pulps offer the advantages of low cost and easy availability, but the blending with such pulps of the longer-fibered pulps derived from manila, sisal, ramie, or otherwise is desirable, in that the web attainable from such a blend has higher initial strength. A portion of the pulp may be mercerized, as mercerized fibers approximate the porosity and bulkiness of the web, although it is preferable to use a substantial portion, if not most, of the pulp in un-mercerized condition, because of the difficulty in realizing a web of good formation or texture from a pulp furnish unmercerized in entirety. I shall now give an example of procedure practiced in accordance with the present invention to produce a bituminized web designed for roofing, flooring, building, and analogous purposes. I can take as raw material a Kraft pulp which has been refined to an alpha cellulose content of about 85% to about 96%, but which is in essentially unbleached condition. The pulp is suspended in practically unbeaten condition in water to form a homogenous dilute suspension, which is run off on a paper machine operated under conditions leading to a dry web having a compactness falling within the range of about 30 to 55. This means that in making the webs whose compactness lies at the lower end of the range, there must be little, if any, pressure applied to the web during its traverse of both the wet and dry ends of the paper machine. The compactness values given are obtained by dividing the basis weight in pounds by the thickness in inches and multiplying by the factor $10^{-2}$. The expression "basis weight," as shown in papermaking circles, represents the weight in pounds of 480 sheets whose dimensions are 24 x 36 inches, this being equivalent to 2880 square feet of sheet material. In other words, the compactness value really represents the weight of material per unit volume of sheet material. The dry starting web thus produced is tender and tears readily under much stress. Nevertheless, it can undergo bituminization satisfactorily as a continuous sheet by running it through one or more baths of molten asphalt, 105 for instance, at a point of about 150°F. (ball and ring test) and heated to about 300°F to 350°F. The stretch of web in contact with the fluid asphalt may be as short as 3 feet at a web speed of about 100 feet per minute to ensure a uniform and complete impregnation into a product containing about 300% or more by weight of asphalt, based on dry fiber, and yet possessing a "dry" surface, that is, free from superfluous asphalt, after the continuous phase carried by the web has been allowed to cool and no re-solution or transformation of the impregnation can occur. Necessity for the product to be uniformly impregnated with asphalt is secured.

The resulting product has high moisture and weather resistance, which properties are traceable to the high proportion of asphalt present therein as a continuous phase. The high asphalt-to-fiber ratio reduces the cost of the finished product on a pound basis, because asphalt is considerably cheaper than fiber. The product has such remarkably high resistance against tearing, especially against the initiation of tear, that the tender starting web would hardly be associated in one's mind with such a different product. Because the product contains a refined, substantially unbleached wood pulp, it stands up against the action of moisture and weathering, by reason of the high stability of the fibers, as well as of their complete encasement by asphalt. The foregoing exemplary procedure, with only a change in the material used as an impregnant, can serve in the manufacture of thermoplastic shoe stiffener material for cutting into shoe stiffener blanks, e.g., box toe blanks. In place of the bath of asphalt, a suitable thermoplastic stiffening composition, like rosin, should be melted at a 140°C temperature of, say, about 250°F. This temperature is sufficient to liquefy the rosin to a flouncy ensuring quick and uniform impregnation of the web. If desired, the asphalt may be blended in the proportion of, say, 50% with the 100
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A dried, porous, bulky, waterlaid web of preliberated but substantially unbleached cellulose fibers made up in part of wood pulp and in part of longer-fibered pulp of the nature of manila and sisal, said wood pulp being in a substantially unhydrated condition and having an alpha cellulose content of at least about 93%.

2. A dried, porous, bulky, waterlaid web of preliberated but substantially unbleached cellulose fibers blended with non-cellulosic fibers, said cellulose fibers being in a substantially unhydrated condition and having an alpha cellulose content of at least about 93%.

3. A dried, porous, bulky, waterlaid web of preliberated but substantially unbleached cellulose fibers blended with wool fibers, said cellulose fibers being in a substantially unhydrated condition and having an alpha cellulose content of at least about 93%.

4. A dried, porous, bulky, waterlaid web of preliberated but substantially unbleached cellulose fibers blended with asbestos fibers, said cellulose fibers being in a substantially unhydrated condition and having an alpha cellulose content of at least about 93%.

5. A dried, porous, bulky, waterlaid web, comprising non-cellulosic fibers and a preponderant proportion of preliberated and refined but substantially unbleached wood pulp having an alpha cellulose content of at least about 93%.

6. A dried, porous, bulky, waterlaid web, comprising wool and a preponderant proportion of preliberated and refined but substantially unbleached wood pulp having an alpha cellulose content of at least about 93%.

7. A dried, porous, bulky, waterlaid web, comprising asbestos and a preponderant proportion of preliberated and refined but substantially unbleached wood pulp having an alpha cellulose content of at least about 93%.

GEORGE A. RICHTER.