April 13, 1937. E. C. SCHACHT 2,077,016

PAPER

Filed Oct. 27, 1932

Fig. 1.



Fig. 2.

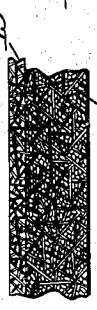


Fig. 3.



Fig. 4.



Fig. 5.

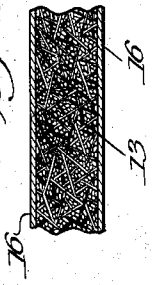


Fig. 6.



Fig. 7.

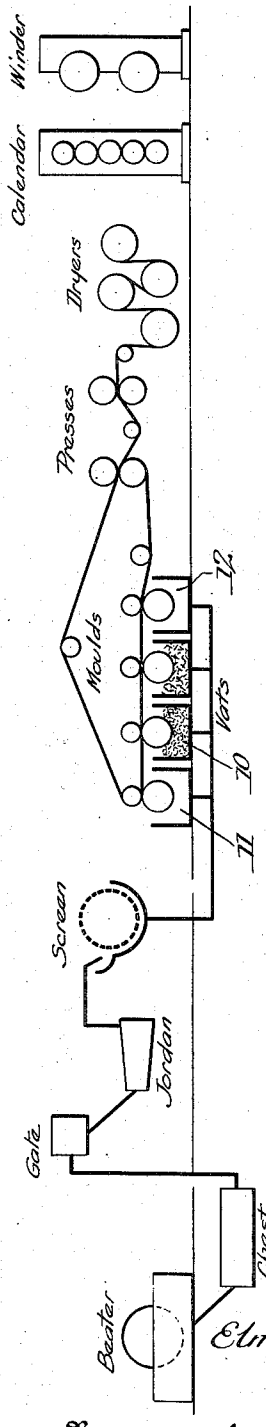
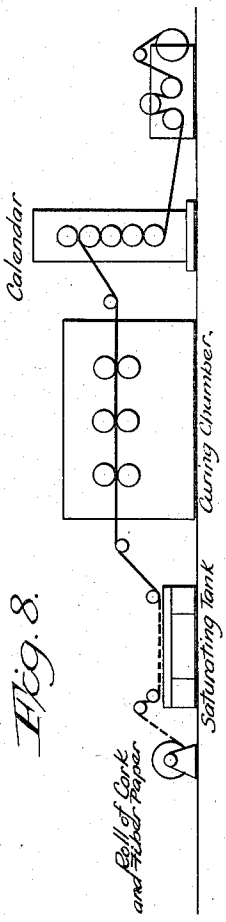


Fig. 8.



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2,077,016

PAPER

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Application October 27, 1932, Serial No. 639,907

8 Claims. (Cl. 92—21)

The present invention relates to the method of manufacturing paper-like or sheet material products, particularly the products of my Patents Nos. 1,888,409, November 22, 1932; 1,888,410, November 22, 1932; and 1,904,087, April 18, 1933, and this application is a continuation-in-part of the applications which matured into said patents.

The principal object of the invention is to produce the sheet materials and particularly those of my aforesaid applications, that is, flexible materials comprising (1) a web of a mixture of separators such as comminuted cork and fibre having a rubber-like binder incorporated therein in accordance with my earliest application and (2) a web the laminae of which comprise cork or other separator and fibre and fibres respectively and in which is likewise incorporated a rubber-like binder in accordance with the second of the above-mentioned applications. To obtain these sheet materials, I have developed a method which is efficient for large scale production and enables uniformity to be obtained in the final product.

Broadly speaking, I am particularly concerned with producing these various paper-like materials by a method wherein the sheets are formed as single ply webs, i. e., non-laminated webs on the usual Fourdrinier machine or are built up of plies after the manner of paper making practice in which a cylinder paper-making machine or multiple Fourdrinier machine is employed and wherein the respective stocks are formed into laminated webs and felted together in the machine.

Thus I will follow this invention in producing (1) single ply webs; and (2) multi-ply webs, the latter having its lamina composed of (1) a mixture of separators and fibres; (2) fibres exclusively, and (3) certain laminae composed of fibres and separators and other laminae of fibres exclusively. I incorporate in the webs of these various structures binder materials in predetermined percentages, so that the respective laminae of the ultimate sheet will contain:

(*a*) The same percentages of the same binder;

(*b*) Different percentages of the same binder;

(*c*) The same percentages of different binders; and

(*d*) Different percentages of different binders, whereby the characteristics of the respective plies can be controlled.

The binder preferably employed is rubber-like and comprises rubber or a rubber composition, that is normal latex, balata or gutta percha, or a rubber compound of one or more of these raw materials with or without suitable vulcanizing agents, coagulants, activators and accelerators. I find that by coating the components of the respective webs with a rubber-like binder, that a very acceptable article can be produced.

Again, I obtain a single ply or integral stratified web in which the lamination or laminations of the built-up structure are controlled as to (1) relative density, and (2) components, that is the kind and amount of (*a*) fibres, (*b*) comminuted cork or other separator and (*c*) binder present. The relative densities of the layers will be controlled by the size of the cork particles, the type of fibre used, and the length of time that the stock is subjected to beater action and the percentage of the respective components. The structural components of one layer may be composed solely of fibres and that of another layer of comminuted cork and fibres; the layers may be formed solely of fibres and of respectively different types, or solely of a mixture of cork and fibres and of variable mixtures respectively. The binder employed may be the same throughout the stratified web or each layer may have a different binder incorporated therein. The amount of binder present is regulated with respect to concentration and also with relation to the density of the web.

In this way, control of the coefficients of (1) absorbency, (2) strength, and (3) resiliency, i. e., compressibility and rebound, may be had and varied at will (as well as relative flexibility and stiffness) in the ultimate product.

A very important object of the invention, therefore, is to produce sheet materials of the character of my aforesaid applications wherein a very precise control may be had of the structure of the sheet.

The method embodies paper making practice as described with either of several final or intermediate steps which are each efficient to incorporate the binder. Thus I proceed (1) by a method of saturation after the web is formed; (2) by recourse to pre-mixing, i. e., mixing the binder with the other components before the stock is beaten, or (3) by beater addition, that is adding the binder to the stock in the beater.

In each case the control features outlined above are available, can be operated with exactness and enable a uniform sheet to be obtained.

Sheet material according to this invention may be formed to have the following alternative structures:

(*a*) Facing layer and bottom layer

(*b*) Facing layers and intermediate layers

(*c*) Alternative layers corresponding to the re-

spective facing layers and bottom or intermediate layers.

(a) (b) (c) Wherein the facing layers are

(1) Thin, equal to or of less thickness than the bottom layer or intermediate layers, or vice versa.

(2) Of less density than the bottom layer or intermediate layers, or vice versa.

(3) Of the same structural components or mixtures as the bottom layer or intermediate layers or vice versa.

(4) Of a different structural component or mixture than the bottom layer or intermediate layers, or vice versa.

(5) Permeated with the same binder as the bottom layer or intermediate layers, or vice versa.

(6) Permeated with a different binder than the bottom layer or intermediate layers.

(7) Permeated with a greater amount of binder than the bottom layer or intermediate layers, or vice versa.

(8) Permeated with a binder of greater concentration, i. e., having a higher percentage of binder than the bottom layer or intermediate layers, or vice versa.

(9) Permeated with a binder compatible or harmonious with a desired surface coating or finish.

(d) Each of the products of (1) to (9) inclusive provided with (1) a facing, (2) a backing, (3) a facing and backing and (4) a core of flexible or stiff preformed material such as paper, cardboard, vulcanized fibre, cloth or open mesh fabric, synthetic resin, or vulcanized latex or rubber, forming a flexible or stiff permeable or impervious reinforcement.

It is an object of the present invention to produce sheet material capable of wide application, which may be decorated, is light in weight, soundproof, abrasion or wear resistant, inert with respect to the action of water or organic and inorganic solvents, and porous and absorbent or impervious and non-absorbent.

The products of the present invention are useful in the manufacture of gasket and sealing material, rug anchors, press blankets for impression cylinders of printing machines, floor coverings, artificial leather, wall board, panel material, breaker strip for doors and jambs, i. e., for refrigerators, electric and heat insulating material, anti-squeak material, channel material, soundproof material, insoles, and table tops, as well as numerous other applications. The sheet materials are characterized by (1) high tensile strength, (2) resilience, i. e., compressibility and rebound, and (3) flexibility and pliability in that the sheets may be sharply flexed or creased without cracking or the formation of weakened areas.

I attribute the excellent qualities of these products in part to the method employed in their manufacture. Webs of the structure described without a specially incorporated material will be resilient and cellular by reason of the presence of the cork, and strengthened because of the fibres, but are subject to cracking and formation of permanent weak areas under sharp flexing.

I prefer paper making practice because the web obtained may be controlled very exactly, and likewise the incorporation of the binder which is essential to the production of my sheeted articles can be precisely regulated and accomplished. In addition to these advantages, the paper making practice enables a sheet to be obtained wherein the fibres and cork are interlaced and intimately associated in what may be described as hinging or pivoting of the fibres on the cork particles, thereby forming a strong and resilient web characterized by numerous voids and interstices. In other words, from a careful examination of the sheeted articles having the binder incorporated therein and formed by this method, it has been determined that when the cork fibre sheet is bent, cracked, or deformed, what actually occurs is that the fibres at the point of deformation are relieved to cause the cork particles which separate the fibres to compress. This allows the fibres to accommodate themselves or become aligned instead of being forced to absorb the entire strain and therefore become ruptured. The cork being highly compressible, returns to its original shape after the strain has been removed, and this causes substantially all of the fibres to resume their original positions in an unbroken state. Thus the sheeted articles under abnormal strains will not retain permanent lines of cracking or breakage. The sheet materials are moreover cellular and absorbent, i. e., capable of exerting capillary effect and the web may be treated uniformly throughout its interstitial mass to improve the inherent characteristics and enhance its flexibility, strength and resistance to bending strains. By reason of the method of this invention, the stratified web will have its respective layers simultaneously produced and bonded together as by felting. In other words, I find that by controlling the make-up of the web and the incorporation and selection of the rubber-like binder, that the normal characteristics of the web are improved and such weaknesses as lack of resistance to bending strains and tearing strains are effectively corrected.

It is an aim of the invention to produce a web or sheet adaptable for floor coverings or other applications where a wear resistant surface is required. In such a case the facing layer will be provided with a rubber-like binder having (1) a very strong bonding coefficient, (2) abrasion resistant and resistant to the effect of water, solvent or chemical action and (3) present in large enough amount to insure the desired result. The bottom or intermediate layer may have any suitable type of binder or the same binder, but the binder will be present preferably in much less amount in the unexposed portion of the web.

Thus a floor covering made as a cork fibre product will have its top layer made as a highly absorbent structure which would, in a saturating process, take up a great deal of resin, rubber latex, or some glutinous adhesive so as to give the covering a high wear coefficient, and plain fibres will also in some cases be used in this top ply so as to also get a smooth surface for coating with ornamental designs with such material as enamel, paint or lacquer. The center section will be more dense so as to be less absorbent during the saturating process and thereby save on the cost of the saturant during the manufacturing process. The bottom layer will be composed of coarse cork particles and fibre so as to have a good non-slip surface, as where it is used for small rugs.

Similar floor coverings would likewise be made by introducing a high percentage of resin or rubber by pre-mixing or beater addition during the paper-making process in the top ply at which time a lower concentration of resin or rubber will be

introduced in the intermediate or bottom plies, thus saving on the cost of saturant, while producing a very acceptable product that has a high wear coefficient on its surface.

In the manufacture of artificial leather I preferably resort to the laminated structure having a cork and fibre mixture layer or layers wherein the top surface is composed exclusively of fibre and of high density, so as to absorb just as little of the saturant and give the high native paper strength. This all-fibre ply may be calendered so as to give a very nice surface for coating or embossing, and the cork fibre ply gives a fine suede-like or leathery surface, after saturation with a rubber-like binder. This product will be pliable like leather, will have a smooth surface for receiving a finishing coating, will have a leathery appearance on the exposed side, and will have considerable resistance to tear because of the high native tensile strength of the all-fibre ply which is enhanced during the saturating process. A very acceptable artificial leather is made in the same manner by the use of rubber latex or resins introduced either during the paper-making process by pre-mixing or beater addition or by subsequent saturation.

A further important object of the invention is to produce press blankets for impression cylinders in the printing industry. Thus I use a single ply web of cork and fibres as produced on the single Fourdrinier, or a built-up web obtained by using a multiple Fourdrinier or cylinder paper-making machine and permeated with a suitable binder, i. e., glutinous adhesive, resin, etc., in accordance with this invention. With one or preferably both sides of the resilient web of appropriate flexibility will be combined a backing of preformed material such as paper, cloth, and/or vulcanized fibre, i. e., hard fibre or fish paper, if desired.

In the manufacture of insole material, I will produce either a single ply web of cork and fibres, a multi-ply web of cork and fibres, or a multi-ply web of layers of cork and fibres and fibres respectively, and having an incorporated binder such as resin, latex or glutinous adhesive as herein recited. The principal requirements of such material are (1) strength and ability to withstand stitching and sewing, (2) flexibility to maintain the shape of the insole in use, (3) resilience and smoothness so as to be comfortable, and (4) absorbency to take care of perspiration, and all of which I obtain with this invention. The surface layer, whether of cork and fibres or fibres alone, will be controlled as to density, i. e., absorbency, and may be calendered if required. Also a layer of pressure sensitive or heat sensitive adhesive is applied to the undersurface of the sheet or any suitable adhesive or gummed surface will be desirable in some cases. Again, a backing or facing, or both, of muslin or other open web fabric, may be combined with the sheet and in fact thin leather, paper or cloth may be utilized. The backing of course in such case may carry the adhesive.

A further object of the invention is to produce sheet material for anti-slip rug anchors or bases for floor coverings. Thus a thin sheet of cork and fibre permeated with a rubber-like binder in accordance with this invention is highly satisfactory to prevent slipping of small rugs on highly polished floors. If desired, the upper surface of the anchor may have a backing or reinforcement of cloth or paper, the cork fibre surface being presented to the floor and by reason of the cellular or porous nature of the web, firmly grips the floor surface. I believe this may be due to the compressibility and porosity of the web forming a multiplicity of vacuum cups or to the frictional coefficient of the cork and fibre layer and its relative spongy roughness.

It is a further aim of this invention to produce a decorated finish on the sheet as described in my Patent 1,888,410. For example, the web will have a facing layer composed solely of beaten fibres and a bottom or intermediate layer of cork and fibre mixture. With such a facing layer there results a product which is particularly useful in receiving finishing coatings on the fibre facing. I have discovered that the saturation or permeation of a laminated product of this type affords a means of producing a very improved coated sheet material. Some saturants, such as rubber, interfere with the application of certain finishing coatings. However, the fibre facing layer when applied to the cork fibre may be readily regulated in characteristics which affect the condition of its surface intended to receive a finishing coating. For example, it may be regulated as to density, as by selection of proper fibres or control of the period of working the mass in the beater. This permits the permeation thereof by the binder to be reduced to a minimum or otherwise regulated by controlling the density of the fibre layer. Again the condition of the surface of the fibre facing layer, as well as the condition of its body, may be varied as desired in any other respects independently of the cork fibre layer, since its mass is prepared and may even receive its binder, in whole or in part, separately from the cork fibre layer, as described. The combination, therefore, of the paper fibre layer with the cork fibre layer in a product saturated with a binder, enables me to produce a surface which may receive a finish unimpaired in character by the saturant or binder, regardless of the nature of the finish or of the saturant. For example, if the finish to be applied is one which does not coact well with the binder, the fibre facing may be made very dense, so that it has a very small amount of the rubber-like saturant therein, or may be separately impregnated, e. g., in the beater or by pre-mixing with a binder harmonious with the finishing material, as well as with the binder of the cork fibre layer. On the other hand, if the finish to be applied is one which is improved by or is compatible with the binder, a fibre facing less dense than in the former instance may be utilized and having a proportionately increased amount of saturant therein. In any event, a fibre facing denser than the cork fibre layer is usually preferred.

The above and additional objects and advantages will appear as the description of the invention proceeds.

Figure 1 is a view showing a single ply web of cork and fibre.

Figure 2 is a view showing a built-up web, one layer of which is formed of fibres and the other layer of cork and fibre mixture.

Figure 3 is a view of a multi-ply web of cork and fibres.

Figure 4 is a view of a multi-ply web of cork and fibres and a facing layer of fibres.

Figure 5 is a view showing facing layers of preformed material and a core of material made in accordance with any of the forms of Figures 1 to 5.

Figure 6 is a similar view of a laminated web having a core of the preformed material.

Figure 7 is a diagrammatic view of a paper-making machine.

Figure 8 is a diagrammatic view showing the method followed for an immersion treatment and also the type of curing chamber employed with any of the several methods.

In referring to paper-making machines, it will be understood that while I have represented for purposes of illustration in the drawing a cylinder type of machine, a multiple Fourdrinier may be used with equal facility, and I use a regular or single Fourdrinier machine where single ply webs are being produced.

The vats for the stock are indicated at **10**, **11** and **12**, and feed the respective cylinders, the web being felted together and built-up as understood in the art. In other respects, the various parts of the apparatus have been lettered to describe their function.

With reference to Figure 8, it will be noted that a bath is used in which the rubber-like or other binder is disposed and through which the web is entrained.

The present invention is not restricted to immersion or impregnation since I have found it equally satisfactory to incorporate the binder by pre-mixing or beater addition as above described. In Figure 8 also I have illustrated a curing and drying chamber wherein instead of festooning the web, which I also do in some cases, it is passed between rolls which may be hot or cold as desired, and this procedure is adopted where the web as completed on the machine contains the incorporated binder. Of course, in some cases I may incorporate the binder by premixing or beater addition, and thereafter give the web a saturating treatment, from whence it may be carried over drying racks or drying rollers, as desired. The curing or vulcanizing chamber, of course, may take various forms, depending upon the particular binder utilized, and its temperature will be suitably controlled to effect a setting of the binder.

As a further condition of the method of operation, the speed of travel of the web through the drying and curing station can be controlled, and likewise in the case of the saturating treatment, the web may be wound onto rolls and thereafter, at any suitable time, passed through the bath, or the web may be formed and continuously fed through the saturating apparatus.

With respect to the vats **10**, **11** and **12**, there may be any number of these, and I have simply shown four by way of illustration. The vats **11** and **12** will contain the stock for the surface layers, while the vats **10** will feed the cylinders to produce the intermediate layers or plies. Thus I may control the stratified or laminated structure of the web by disposing in the various cylinder vats such wet stocks with or without incorporated binder as will produce the desired web.

It will be understood that by "wet stocks" I mean a mixture of fibres or pulp or fibres and cork in water. All such paper-making components are thoroughly mixed with water and put in suspension before being made into a felted sheet.

For example, the vats **10** may contain a stock composed of a mixture of cork and fibres while the end vats **11** and **12** will contain a stock which is exclusively fibres. Such a disposition may be reversed, and also each of the vats may contain a stock composed of a mixture of cork and fibres or of fibres alone to produce the stratified web and the nature of the respective stocks can be varied to accord with the ultimate product desired.

It will be understood that the web is built-up, i. e., simultaneously formed and bonded by felting to produce a substantially integral structure, characterized by the nature of the stocks fed to the respective cylinders. As I have hereinbefore set forth, webs which are not provided with a binder are resilient, cellular, and strong, but in accordance with the present invention these inherent characteristics are materially enhanced, and more important, the web is rendered strongly resistant to tearing strains and bending and creasing strains.

In carrying out the invention, I prepare the various stocks and feed them to the cylinder vats. For example, I will prepare the stock consisting of a separator, that is, comminuted cork, fibres and sufficient water, and feed such stock to the intermediate vats **10**; also I will prepare a stock composed substantially exclusively of paper fibres and feed the same to either of the end vats **11** and **12** to produce a surface layer or layers.

The broader phases of the process defined in the claims appearing hereinafter, may be carried out with the use of other separators than comminuted cork having substantially similar characteristics, for example comminuted barks other than cork, leather chips and rubber particles. By separators, I mean materials of low specific gravity which are compressible and/or elastic, which preferably can be screened to a size and which are of a character which retain compressibility and size when wet or compressed and which continue to separate the contiguous fibres and tend to cause these fibres to return to their original position when pressure has been released.

The separator or comminuted cork should be of a size which may be termed "effective". That is to say, the cork granules to be effective should not exceed, in cross-section, the desired thickness of the finished sheet, nor should they be smaller in cross-section than the cross-sectional diameter of the fibres. Finer cork than this will act as a filler, thereby preventing the formation of voids and air cells, and also will be lost to a larger extent in the paper making process; likewise smaller particles would be ineffective in acting as separators and hinges about which the fibres can flex. I have used successfully cork particles of a grade from 50 to 150 mesh and 30 to 50 mesh.

The fibres with which the cork particles are mixed to form the web **10**, should be sufficiently long (*a*) to contribute tearing strength to the finished product, (*b*) to mesh and hold the "separating" particles, i. e., the cork, and (*c*) to make an absorbent paper, quickly permeable to saturating solutions. Specific examples of the fibres which I employ are:

Jute	Absorbent alpha cellulose
Rope	Wood pulp fibres
Hemp	Cotton
Sisal	Linen
Kraft pulp fibres	Asbestos.
Long wood pulp fibres	

The requirements for a successful binder are that it be capable of coating the cork particles and the fibres in such manner that the sheet will constitute a very strongly bonded structure in which the resilience and strength will be enhanced and the finished web will be substantially resistant to deformation.

Referring to Figure 1, I have illustrated a web constructed in accordance with this invention and composed of a mixture of cork and fibres, and comprising a single layer or ply 13, for example as produced on the single Fourdrinier machine. A built-up structure of cork and fibre mixture is shown in Figure 3, the respective strata 14 of which are bonded together by the felting operation of the paper-making machine. The webs shown in Figures 1 and 3 will have the fibres and cork in intimate interlaced relation, producing a porous or absorbent structure capable of exerting capillary effect.

Either of the webs of Figures 1 and 3 will be permeated by a selected binder and most important, the density of the single ply or the density of the respective strata of the multi-ply web may be controlled so as to regulate the amount of binder present when the web is subsequently saturated.

In the case of the stratified article, the thickness of the respective layers or plies 14 may be regulated on the paper-making machine in accordance with the product desired by varying the number of cylinders employed, by varying the machine speed or the type of felt employed, and by changing other control factors which are well known in the paper-making art.

In Figures 2 and 4, the paper-like layer 15 is composed exclusively of fibres and may be relatively thin with respect to the cork and fibre layers, as shown, and controlled as to density as heretofore explained if subsequent saturation is to be resorted to. The layers may be of any desired thickness and density equal to each other, or the fibre layer of greater thickness than the cork and fibre layer or different amounts of binder may be present in the different layers or different amounts of different binders may be used in the various layers, all in accordance with the ultimate product desired.

The final webs obtained, that is, the single ply web or the composite web, will have the characteristics above enumerated, but will tend to crack or exhibit weakened areas if sharply flexed or creased. In other words, this product will have a tendency toward brittleness and will not possess a flexibility or rigidity comparable to the saturated material.

In order to obtain the products of my aforesaid applications, i. e., flexible material, I permeate the web by permanently and insolubly incorporating therein a rubber-like flexible binder. This binder will be selected in accordance with the intended purpose of the material.

The binder creates a stronger union between the fibres and cork particles, increases the strength and resilience of the respective webs and has the particular function or capacity of overcoming any tendency of the web to crack or weaken under creasing or folding strains. Also, according to the specific requirements of the resultant saturated product, a rubber-like or other binder can be selected which will render the product substantially oilproof or waterproof or both, abrasion and wear resistant, and which will be harmonious with regard to a desired coating or finishing material.

The binder will uniformly coat the cork particles and impregnate the fibres throughout the cellular structure of the web and will be present in sufficient amount to permanently insure and preserve a maximum of strength, resilience and flexibility in the web.

The binder employed will be described as a flexible binder but it will be understood that variations in stiffness or rigidity in the final product can be obtained by choosing a binder with the required characteristics, by varying the amount of the binder present and in some cases by varying the subsequent treatment of the binder. For example, I may incorporate a large amount of a binder which when dried or cured throughout each of the layers of the integral web will produce a stiff sheet. Such a sheet will have the characteristics of resilience and strength of the more flexible article and will be resistant to deformation in that it may be cut, punched, sawed or otherwise worked. The qualities in the final product are usually determined both by the choice of impregnant and by the amount of binder present and it should be understood that the control features of this invention include the use of different binders in different layers and which are controlled as to percentage or amount present.

The binder which I will describe as a rubber-like material may comprise any natural India-rubber-containing-latex or any India-rubber-containing-latex preserved by ammonia, formaldehyde and the like, or any gutta-containing-latex or balata-containing-latex, singly or combined. Likewise, I will employ compositions of one or more of the above-mentioned latices, with suitable vulcanizing agents, accelerators, activators, antioxidants and coagulants.

It will be understood that the binder fundamentally accomplishes the purpose of bonding the cork and fibres together and its incorporation by any of the several methods is accomplished in such a manner that a construction is produced in which the resilience and strength of the particular web is enhanced and, moreover, the web is rendered substantially resistant to deformation.

In order that the operation of the invention may be clear, I will describe several of the binders which I have found successful, but it will be understood that there are various commercial compositions which will be of equal value.

I will use as the binder a water solution or dispersion of normal latex having a content of rubber up to substantially 20% to 25% and to which solution is added sodium polysulphide in the amount of substantially 5% of the rubber present and 1% to 2% of piperidine pentamethylene dithiocarbamate of the rubber present, as well as an antioxident such as Neozone L (du Pont) in amount equivalent to substantially 2% of the rubber content. This composition is useful where an immersion treatment is employed. The impregnated sheet is dried at about 135° F. and subsequently heated to about 160° F. for about twenty minutes, to vulcanize the rubber.

Where rubber is used as the permeating medium, I may employ vulcanized latex or vulcanized rubber which has been dispersed or vulcanized rubber dissolved in a suitable organic solvent. If a bath saturation process is used, the web can be saturated with rubber latex to which has been added sodium polysulphide or colloidal sulphur and a suitable antioxidant and the web subsequently dried at about 135° F.

A preferred solution for use as a bath saturant consists of normal latex containing 25% to 30% rubber, 2% colloidal sulphur (based upon rubber present), 1% to 2% (based upon the content) of a suitable low temperature accelerator such as piperidine pentamethylene dithiocarbamate, 2% (based upon the rubber content) of a suitable activator such as colloidal zinc oxide, and 2%

(based upon rubber present) of Neozone L (du Pont). The sheet saturated with this solution may be dried at 135° F. and heated to about 160° F., to cure the rubber. This solution produces a very flexible product. The final sheet may have a rubber content up to substantially 65% of the finished product. To increase the rigidity of the product I may resort to the use of larger percentages of colloidal sulphur and longer times of curing.

I have also used re-dispersed vulcanized rubber or prevulcanized rubber commercially known as "Vultex" which requires only a drying to cure.

Since I also utilize with the rubber-like binders, other binders, the following additional examples of this component are described. In this connection, I may pre-mix a rubber-like binder with one stock, and one of the resin and/or glutinous binders to be mentioned with another stock or stocks and felt the same together on the paper-making machine to produce the built-up layer having the respective laminations each provided with a different binder. Again, I may, by pre-mixing or beater addition, incorporate a binder in the web which will be a rubber-like binder and thereafter pass the web through a bath of one of the other types of binders to be now referred to.

With respect to permeation and saturation with a rubber composition as herein described, the respective plies of the sheet will be controlled as to density, i. e., absorbency. As for instance, a more absorbent furnish may be used to form the surface ply of paper on the cylinder machine. The resulting web when subjected to the rubber impregnating bath will absorb a high percentage of rubber in the surface layer, thus furnishing resistance to wear at the point of contact when the product is in use.

These rubber-like binders afford the result that the sheet is strengthened, its tendency to crack or weaken is replaced by flexibility resistant to sharp creasing and folding, and the compressibility and rebound not only are not disturbed, but are made effective to a greater degree.

Examples of other binders are glutinous adhesives, such as casein, hide, bone, albuminous and similar glues capable of being rendered insoluble, and which can be treated or tanned, so as to become permanently and insolubly incorporated in the structure of the sheet.

As tanning agents, I resort to one or more of such materials as formaldehyde, paraformaldehyde, hexamethylenetetramine and sodium bichromate. In connection with the glutinous binder and tanning agent, I utilize plasticizers of which glycerine, sulphonated castor oil, diethylene glycol, and aquaresin, are examples. Thus I employ a plasticized adhesive or binder, and I find that with such a saturant the single ply or laminated structures are strengthened so as to be resistant to tearing, are rendered flexible, in that they will not crack under sharp creasing or folding and are pliable, in that regardless of the degree of flexing, to which they are subjected, they will return to the normal sheet-like condition without noticeable creases or any indication of the lines of bending. Moreover, such saturant being permanently and insolubly incorporated throughout the cellular structure of the webs not only lends a resilience and pliability to the sheet, but enhances, to a remarkable degree, the inherent compressibility and rebound.

Further examples of satisfactory flexible binders are natural or synthetic resins of which innumerable varieties are commercially available and which may be treated by conventional processes and with modifying agents as understood in the art, to impart the necessary flexibility and elastic characteristics.

Of the natural resins, I resore to kauri and copal resins, degelled linseed and China-wood oils, as well as modified China-wood oil, and of the synthetic resins, I find those of the alkyd, furfural and phenol-formaldehyde types, such as bakelite, are very acceptable, as well as polymerized isoprene and chlorinated rubber. For certain uses, a satisfactory product can be obtained by impregnation with cheap material such as bituminous matter or pitches, that is bitumens which may be secured from the natural pitch lakes or as by-products from coke ovens.

Of the flexible plasticized adhesives above mentioned, it will be observed that many of them, such as the glutinous and resin binders are not only resistant to moisture, but are, moreover, inert with respect to various organic and inorganic solvents, of which mineral oils and distillates are examples and the rubber-like binders herein are similarly inert or may be rendered so when required.

In selecting the various saturants or binders, the particular use of the material is the determining factor. In gasket materials it is essential that the article resist the action of water and oil so that it will not disintegrate when used to seal joints in pipes or containers conveying these fluids. In the manufacture of artificial leather, as well as floor coverings comparable with linoleum and artificial linoleum, it is essential, in most cases, that the article be moisture resistant.

The finished web when permeated with rubber latex or natural and synthetic resins, for example, will produce flexible floor coverings and artificial leather not affected by water.

In the manufacture of gasket material, a rubber-like binder is quite satisfactory if the finished product is to be used for water or weak alkalis or acids.

With respect to binders adapted to produce stiffness in the sheet, I will use resins both natural and synthetic, rubber latex containing a high percent of sulphur and subsequently cured by a high degree of vulcanization, animal and vegetable glues with or without the hardening or setting agents to produce the required stiffness.

With respect to the resinous binders above mentioned, I will use, for example, the flexible alkyd resins or bakelite types (that is, phenol-formaldehyde types) or other kinds of suitable resins available in the trade. It will usually be found advantageous to use both heat and the commonly indicated solvents for the type of resin employed in order to secure the proper degree of fluidity for ready saturation in case the bath method is employed. The exact procedure will depend upon the method of impregnation and the properties of the resin used. In some cases, the resin will be substantially pure but in other cases modifying agents such as polymerized linseed oil or China-wood oil may be present or suitable drying oils alone such as polymerized China-wood oil may be used as saturants. Subsequent curing of the permeating oils and resins will depend upon the nature of the specific saturant or saturants used and the properties of the product desired. Thus the permeated web

may be subjected to both heat and pressure to cure the binder or to heat alone or to heat and oxygen (air) according to whether the permeating medium is heat reactive, oxygen reactive or both heat and oxygen reactive. Some saturants such as air drying varnishes or resins may be air cured at ordinary temperatures, but in general, higher temperatures with shorter curing times will be preferable. As illustrations of the above types, I prefer bakelite which is most advantageously cured with heat and under pressure, but which may be cured by heat alone; the modified alkyd resins as for example, the alkyd resins combined with China-wood oil and suitable driers which are readily cured by heat and oxygen (air) and the so-called air drying varnishes with either natural or synthetic resins, which may be air-dried at ordinary temperatures.

It will be observed that all of these various binders are capable of being cured or vulcanized in the sheet, by heat, pressure or both.

By reason of the pliability and resilience of the web, particularly with an incorporated binder such as described herein, it forms an excellent base for such plastic and flexible coatings as cellulose lacquers, or oleo resin varnishes, of which there are innumerable commercial varieties available. Such lacquers utilize, as a base, a cellulose derivative, such as cellulose nitrate or cellulose acetate, together with a gum and plasticizer, and the present sheet material will cooperate with such a coating to prevent cracking of the coating film. I will also employ China-wood oil varnishes and linseed oil varnishes which likewise are flexible and of which a number of commercial varieties are obtainable.

Furthermore, substantially all of the binders will enable cellulose derivative or varnish coatings and films to be applied to the sheet without difficulty.

In the case of artificial leather, I utilize coatings of pyroxylin, alkyd resins and similar substances which will produce the desired surface, and these, by reason of the flexible and resilient character of my laminated base, will be prevented from cracking or scarring in use.

In the manufacture of floor coverings, such as linoleum and artificial linoleum, I employ the varnishes and lacquers above mentioned, with equal success since the elastic and flexible nature of the coatings will be retained because of the flexibility and resilience of the laminated base.

I have set forth above the various components of the web, namely the fibres, the cork and fibre mixture, the binders, and examples of coating materials and finishes.

The method of carrying out the invention to produce the final binder incorporated sheet will now be described. I will have recourse to any one of three steps, and in some cases will combine one or more of these steps in accordance with the type of sheet desired.

In the drawing, I have illustrated in Figure 8 a saturating treatment. That is to say, the web either formed on a single or multiple Fourdrinier machine, or upon a cylinder type machine, is entrained through the saturating bath as shown in Figure 8.

In this method, the density of the web will be controlled and moreover its character will be determined by the nature and size of the cork, the nature of the fibres, and the amount of beating to which the mixture is subjected. Also the structure of the web will be regulated by the percentage of cork to fibre or vice versa, and it will be understood that I may produce a web in which either of these components predominates.

Another step and one equally preferable to the saturating treatment for incorporating the binder, is by the beater addition. That is to say, the stock will have admixed with it in the beater a proper percentage of the binder for the final article. Another process of incorporating the binder into the web is by pre-mixing, wherein the binder is mixed with the components of the stock before they are submitted to the beater action.

By these methods not only may the structure of the web be controlled, as previously described, but also, in the case of the stratified sheet, the percentage of binder and the type of binder may be controlled in the respective layers of the web. In each case I am enabled to control the density of the web, the character of the components and their amount, i. e., their relative percentage with respect to each other and the amount and character of the binder or binders present in the individual layers of the final web.

With respect to pre-mixing and beater addition, it will be understood that the components may be individually pre-mixed with the binder, or a mixture of the components pre-mixed with the binder and the same procedure followed in the beater.

I may also add one or more of the components of the binder to the cork and/or fibres before mixing or to the beater mass, and the further treatments may take place during the formation of or after the web is formed. In other words, I may resort to the single use of pre-mixing, beater addition, or subsequent bath saturation in order to impregnate the web with the binder, or I may utilize a combination of any two or three of the above processes. As an illustration, I may add a binder by pre-mixing and add more of the same binder or another or a modifying agent in the beater or by subsequent immersion in the bath. In other words, independent consecutive treatments with the components of the saturant may be resorted to according to the binder employed and the specific qualities required in the resultant product.

Immersion treatment

The web will be produced on the apparatus shown in Figure 7 or a multiple or single Fourdrinier. In the case of a single ply web of cork and fibers, its density will be controlled and the speed of travel through the bath regulated whereby the amount of impregnation, i. e., percentage of rubber-like or other binder present, will be accurately and uniformly maintained. If the web is dense, a smaller amount of binder will be absorbed. The quantity of binder absorbed will vary in inverse proportion to the density of the web and the speed of travel of the web.

In the case of the laminated integral and composite web, i. e., built-up web, the same conditions apply except that the layers will usually be of different density and therefore less binder will be present in the layer or layers of greater density than in the one or more of less density, subject, of course, to the limitation that I could not efficiently in all cases introduce a high percentage of binder in the inside plies by the saturating process, where the outside plies are very dense, since these would present some difficulty to the introduction of the binder through them into the more absorbent inner plies. There-

fore, in a final product of this kind, I preferably resort to beater addition or pre-mixing in order to introduce a high percentage of binder in the core and lower percentages in the outside plies. As an alternative, of course, I will resort to pre-mixing or beater addition to introduce the binder into the plies of the core and introduce the binder in the surface layers by an immersion treatment.

Specifically, and for purposes of illustration, since I have saturated webs of the various structures above set forth, (see (*a*) (*b*) (*c*) (*d*)) and have employed the various binders exemplified, the web will comprise a thin surface layer of fibres constituting a paper-like web and a layer of cork and fibre mixture. The thin paper-like layers are of greater density than the cork and fibre layer or vice versa.

The web will be fed either continuously from the paper making machine or from storage rolls of the untreated material as shown in the drawing.

In Figure 8 the tank contains, as the impregnating bath, normal latex containing 25% to 30% rubber, 2% colloidal sulphur (based upon rubber present), 1% to 2% (based upon the content) of a suitable low temperature accelerator such as piperidine pentamethylene diathiocarbamate, 2% (based upon the rubber content) of a suitable activator such as colloidal zinc oxide, and 2% (based upon rubber present) of Neozone L (du Pont). The sheet saturated with this solution may be dried at 135° F. and heated to about 160° F., to cure the rubber. This solution produces a very flexible product. The final sheet may have a rubber content up to substantially 65% of the finished product. To increase the rigidity of the product I may resort to the use of larger percentages of colloidal sulphur and longer times of curing. The respective proportions indicated may be departed from as desired and are simply given by way of illustration.

Also by way of illustration I will treat similarly a single ply web of cork and fibers as herein described, the density of which has been suitably controlled.

The webs so treated are dried in any suitable manner, as on the drying rack or rolls as shown. The web is thereupon wound up into commercially distributable rolls. The final products are excellent for sealing materials and gaskets, being substantially resistant to water and weak acids and alkalis.

The web treated by immersion, as just described, has permanently and insolubly incorporated throughout its cellular structure, the flexible or rubber-like binder. This complete saturation is attained by reason of the interstitial nature of the web. That is to say, the presence of the separator, i. e., the cork particles, and their interlaced relation with the fibres, produces cells, air spaces and voids, whereby the web exerts a maximum capillary effect and the fibres are impregnated and the cork particles coated. In fact, both the fibres and cork are encased in the binder, and the thorough permeation of the web assures the presence uniformly throughout the web structure of sufficient binder to obtain and preserve the qualities of strength, resilience and flexibility or stiffness.

In this connection, a single bath may be employed or several independent immersions resorted to. Thus, in a laminated structure I may incorporate the glue and glycerine in one bath and paraformaldehyde in another, or place all in a single bath, with a suitable retardant, i. e., oxalic acid, to delay the glue formaldehyde reaction, to saturate the outside plies after a resinous or rubber binder has been incorporated by pre-mixing or beater addition in the inside plies.

Further, the resinous and latex binders are capable of being cured in the sheet by means of heat and pressure or heat alone without producing any deleterious results. This is particularly true with bakelite resins as well as the rubber saturants, and I have described above specific baths composed of these two materials. In some cases suitable dryers may be added to the varnishes or resins respectively, in order to decrease the temperature and time of curing.

Therefore, without describing them in detail, I refer to Figure 8 wherein the single ply or multiple ply web is passed through a single bath of a rubber or resin saturant and then through a curing and drying chamber over racks or rolls to vulcanize or cure the binder. The temperature of the chamber and the temperature and/or pressure of the rolls will be regulated in accordance with the particular saturant solution or mixture employed, according to its determined amount in the sheet and the setting or hardening required.

By way of illustration, since I use any of the structures mentioned above (see (*a*) (*b*) (*c*) (*d*)) and the binders exemplified in the impregnating method, the cylinder forming the top ply of paper is fed with a mixture of cork and fibre which has been subjected to a severe beating in order to decrease the porosity and subsequent absorption of this part of the web. The paper web is formed and dried in the usual manner and then passed through a bath containing a solution of a suitable rubber-like composition as described above to saturate the web and then passed to a suitable drying arrangement as shown to evaporate the solvent and cure, i. e., vulcanize the rubber.

In the case of the stratified web having a layer or layers 15 exclusively of fibres, i. e., a paper-like web, this thorough and uniform permeation is obtained, since such layers are porous in accordance with their density, permitting capillary action and the fibres are absorbent and capable of impregnation.

Any of the above mentioned binders may be used, as determined by the product desired, and prepared as a bath with their modifying agents, through which the sheet is passed.

With respect to saturation with a bath of a rubber or resinous composition as herein described the respective plies of the sheet will be controlled as to density, i. e., absorbency. As for instance, a more absorbent furnish may be supplied to the vats feeding the cylinders to form the surface ply or plies. The resulting web when subjected to the rubber or resin impregnating bath will absorb a high percentage of rubber in the surface layer or layers than in the intermediate or concealed layers, thus furnishing resistance to wear at the point of contact when the product is in use.

In other words, the density of the outer layers would be so low, so as to permit the introduction of a high percentage of rubber in the surface. The density of the inner or intermediate plies could be increased so that less rubber would be located in the center section where it is not needed.

Thus by controlling the density of the outer layers, I increase the rate of absorption during

the saturating process, so as to get a high percentage of rubber on the surface.

For wear resistant material, as floor coverings, I select a resin or rubber saturant as above mentioned. These can be cured in the sheet to give a hard finish, and a sheet which will be abrasion resistant and resistant to the action of water, mineral oils, as well as organic and inorganic solvents. The amount present will be determined by the density of the web and the method of binder incorporation employed. Thus when wear resistant material is desired, it can be made by putting a high percentage of the selected binder in the top surface which can be accomplished by making the surface ply very absorbent if saturation is to be resorted to or by putting in a high percentage of binder in the top ply during the paper-making process by beater addition or pre-mixing. In other words, I rely on density control to get the high percentage of binder on the top ply when saturation is employed whereas I preferably put the binder in during the paper-making process by pre-mixing or beater addition in most other instances to accomplish the result. As above explained, I also resort to a combination of both methods.

Beater addition

A preferred method of incorporating a rubber-like binder in the webs which have been described is by beater addition wherein the binder is incorporated with the fibre or cork and fibre mixture as a final step in the beater process before the stock passes on its way to the vats. A typical example of this process is as follows:

The well-beaten and well-purified (especially from calcium salts) fibres or fibres and cork, made ready for the addition of latex, are treated per 1200# fibre or fibre and cork mixture, with 7 lbs. of dissolved flake caustic soda to insure definite alkalinity for complete dispersion of the latex before coagulation. I insure a pH of 11.0 or over at this stage. Next, 6 lbs. of hemoglobin dissolved in a ¼ bbl. of water is added as a protective colloid, for which purpose the addition of the silicate and casein, which are later added, is used. At this stage, I make sure of the precipitation, as insoluble salts, of any residual calcium, by the addition of 5 lbs. of dry oxalic acid and 1¼ gallons of ammonia water.

Next, 29 lbs. of commercial ("A" or "U" grades) of silicate of soda are added, after which 3 lbs. of casein dissolved in ammonia water are added to the beater.

After mixing the above ingredients, a sufficient quantity of latex solution is quickly added to the circulating stock in the beater to give the desired amount of rubber in the finished sheet. Before the addition of the latex, the beater roll is raised to reduce danger of poor latex coagulation. As soon as the latex emulsion is furnished, sufficient 8% solution of paper-maker's alum, that is, aluminum sulphate, is added to coagulate the latex, which coagulation is evidenced by the clarification of the water surrounding the fibres. An average of 160 lbs. dry alum per beater is necessary to coagulate 18% of dry rubber. Higher percentages of rubber will require more alum.

At this stage, the circulation of the stock in the beater is stopped and the stock is allowed to stand for five minutes. At the end of this time, circulation is again started when about 120 lbs. of alum in a 15% solution is added to the beater to make the mixture strongly acid. When about one-half of this quantity of alum has been furnished to the beater, the valve in the latter is removed and the stock is at once emptied into the chest on its way to the machine.

Also in lieu of using different or equal percentages of the same binder in the stock in various vats feeding the cylinders on a cylinder machine, we may use entirely different binders in the respective stocks supplied to the separate vats, since it is possible to prepare the stock for each vat by a separate pre-mixing and beater operation. As an example of this method of operation, a top or surface ply of paper containing rubber may be formed in the same manner given above for the top surface ply of the first previous example having a rubber-like binder. The other plies of paper may be made of a furnish prepared by pre-mixing and consisting of 40 parts by weight of petroleum base asphalt, flow point approximately 180° F., 30 parts by weight of 30 mesh cork and 30 parts by weight of suitable rag fibre. The resulting mix or furnish after proper dilution is then beaten for one-half hour in an ordinary beater and the respective stocks diluted and fed to the vats in the usual way.

In the manufacture of floor coverings and the like, a low percentage of the binder may be placed in the cork fibre mixture used to feed the vats forming the center and, in some cases, the bottom layers, while a high percentage of a hard finishing binder may be placed in the stock fed to the vats forming the surface layer so as to offer a sufficient resistance to wear. Also, where a high percentage of the hard binder is used in all the plies, then the material will be relatively stiff. Thus equal or different percentages of the same binder or a different one may be incorporated in the separate plies by the beater addition process.

It will be observed that by the beater addition process I am able to have a relatively thin paper-like layer provided with a relatively small percentage of one of the binders above referred to, and of high or low density, and a layer of cork and fibre mixture of greater or less density than the paper-like layer and containing a greater or less percentage of the binder. Furthermore, I will incorporate any of the several binders above referred to, and in addition the concentration of the binder, that is, its adhesive effect, may be different from the respective layers.

Also, I will use for some of the layers a binder capable of giving a hard finish, and I may incorporate in the respective layers different binders selected from those listed above, whereby when the sheet is subjected to a curing action, one thereof will become hard and wear resistant while the other will become resilient.

By the beater addition process I am enabled to produce flexible materials, absorbent materials, materials having a hard finish and abrasion resistant and also I am able to produce a relatively stiff product.

Pre-mixing

With respect to pre-mixing, the same control is available as just described in connection with beater addition. The step of pre-mixing, however, comprehends adding the rubber-like binder to the paper-making components before they are submitted to the beaters.

By pre-mixing, the binder may be mixed with the components of the web individually, as a mixture, or both.

The invention contemplates the introduction of different or equal percentages of the same or different binders into the respective plies of the web, by a combination of the pre-mix and beater addition processes. The following is a specific illustration of the method of carrying out this process:

For the surface layer or No. 1 furnish, 50 parts by weight of rope fibre is saturated with an equal amount of water and placed in a steam jacketed mixer, together with 60 parts by weight of phenolic resin having a flow point of 70° C. to 80° C., and 50 parts by weight of cork, 30 to 150 mesh. The entire mass is then mixed at a temperature of 90° C. for forty-five minutes. Hot water, 50 parts by weight, is added and the mixing continued for fifteen minutes, whence the entire mass is removed and placed in a suitable beater. The concentration in the beater is so adjusted as to give the proper beating consistency, that is, approximately 5% solids, and beaten for one-half hour. The resulting furnish is then suitably diluted and used to feed the cylinder forming the surface ply in the final paper-like material.

A No. 2 furnish for the bottom or intermediate layers will be prepared by incorporating a rubber-like binder by beater addition after the method previously described. Thus, the final product may be made to contain a surface layer or layers of resinous material while the remaining layers will be permeated with a rubber-like binder. It will be seen that various modifications and combinations are readily available. The surface and bottom plies may be the same, i. e., rubber or resin furnish, and the intermediate plies resin or rubber furnish.

The furnishes suitably diluted are fed to the cylinders in accordance with the desired sheet, that is, to appropriate cylinders for forming the surface ply and intermediate and bottom plies. The cylinders so fed, as described above, are operated to give a paper-like product with a surface layer or layers containing a high percentage of resin or rubber and other plies containing less binder or vice versa. The resulting paper is dried and cured in order to set up the binder.

Likewise, the curing treatments will be substantially the same, that is, the web will be formed from the respective stocks and thereafter presented to the curing chamber over racks or rolls and at appropriate temperatures and pressures or both, to obtain the desired setting of the binder.

By resorting to pre-mixing and/or preferably beater addition, a product desirable for insoles can be formed, which has high resistance to tear due to a high percentage of rubber or other binder in the inner layers but which has absorbent surface layers due to the decreased percentage of resin and/or rubber added to the beaters supplying the vats which make up these particular plies. Where heretofore it has been customary to produce a laminated article of this type by forming the layers individually and by bonding them by a rubber or other cement, the effect has been that the cement between the respective preformed layers acts as a seal between the respective layers and prevents moisture from passing from one side to the other, which is corrected by the present process and article. For example, on the paper making machine I would produce by beater addition or pre-mixing, a laminated sheet having a small percentage of rubber on the top layer which would insure the insole absorbency as required. I could not efficiently introduce a high percentage of rubber in the inside plies by the saturating process, because where the outside plies were very dense they would present some difficulty to the introduction of the binder through them to the more absorbent inner plies. Therefore, if the final product is to have absorbent outside plies and still contain the binders, I preferably resort to beater addition and make the completed product on the paper-making machine, so that its outside layers will contain less binder and therefore be more absorbent as to perspiration when used as inner soles, for example.

As modifications of the three methods which are embodied in the paper-making process, I may subject the respective stocks or any one of them to a pre-mixing or beater addition treatment and thereafter to a saturating treatment using different types of the binders herein mentioned.

Summing up the control features of the invention and regardless of the components, the control of the qualities of the finished sheets are secured by—first, the regulation of the density of the individual layers, second, by the control of the percentage and type of binder present in the layers, and third, by the combination of these two control features. The density of a layer of paper composed of plain fibre or of cork and fibre or any other components from which the paper will be made, can be varied in the paper-making process (without the introduction of a binder of any kind) by varying the time of beating, length of fibre, size of cork particles and relative proportions of these or other components employed. A multiple ply paper made on a cylinder paper-making machine can therefore be made by laminating several plies of paper having a different density in each ply. When this completed sheet is saturated, the amount of saturant which the various plies will absorb will be different, depending upon the varying rates of absorption resulting from the variation in density from ply to ply, subject to the practical limitations heretofore disclosed. That is, for example, a large amount of binder cannot be introduced into a porous center ply if the outside plies are of greater density. Therefore, a means of controlling the amount of binder or saturant present in the different plies is presented by the density control of the individual plies, although as in the illustration just given, no binder is introduced into the plies during the paper-making process.

Where pre-mixing and/or beater addition are resorted to, I not only vary the amount of binder present in the individual plies but vary as well the type of binder or binders in the individual layers. For example, I use different amounts of the same binder in vats 11—10 and can use different percentages of an entirely different binder in vats 10—12. The binder is incorporated in the paper-making process either by pre-mixing or beater addition or both.

As a third variation, I can have a combination of the cases just outlined above whereby I control the density of one or more plies of paper (unimpregnated) and combine these plies on the paper-making machine with other plies containing controlled amounts of binder or binders, adding by pre-mixing or beater addition or both. This product is then passed from the paper-making machine and saturated, in which process the controlled densities of the plies which were not impregnated with a binder in the paper-making

process, will control the final amount of saturant absorbed by these plies during the saturating process.

In other words, we have three definite means of control—

1. That, presented as in the bath treatment, by regulating the amount of binder absorbed due to varying the densities of the paper plies during the paper making process.

2. By varying the percentages or amounts of binders and the type or types of binders present in the individual plies or layers when such binder or binders are added by the pre-mixing and/or beater addition processes, and

3. By the combination of these two methods.

It will be understood that the coating treatment will preferably take place after the binder incorporated web has been formed and the coating may be applied by immersion, brushing, spreading or spraying.

With each of the several methods I am enabled to obtain a flexible product, and by varying the type and percentage of binder and the curing treatment, one which will have relatively greater stiffness.

It will be seen that by the control of the density of the stock, the nature of the cork particles and fibres and the beating action, as well as the percentage relationship of the components there is produced the structures herein described. In other words, I obtain a uniform product having the requisite amount of binder distributed throughout the interstitial structure in exactly the amount required to form the finished sheet.

With each process above outlined, the paper or board as formed is passed through a heated chamber over a drying rack or preferably rolls as shown in the drawing to remove the solvent or solvents. In cases where a heat convertible binder is present, the heat treatment is continued sufficiently to set the binder. In practically all cases a temperature of from 80° to 140° C. was found preferable, the time, of course, varying with the particular material.

Suitable coloring agents, for example, dyes or suspended pigments, may be added to the binders in order to obtain any desired color effects.

In connection with the examples given, other fibres will be used, as for example, rope, jute, wood, kraft, sulphite, hemp, alpha cellulose, rag, and the like; the proportion of fibre can be varied as desired.

Although 50 mesh cork was specified in the above examples, this can be varied over wide limits, and we have successfully used mesh ranges from 30 to 200.

In order to obtain different flexibilities, other rubber compounds than the examples given above can be used. Again, in the case of the rubber-like or phenolic binder, this can be varied over wide limits, as for example, from 20 to 80 per cent of the finished product.

By adjusting the proportions of binder with any of the methods described, a material suitable for use in the plastic field can be prepared. However, in this case, the material is not given any severe heat treatment, care being taken that the paper is simply dried, in order that a subsequent molding operation can be carried out (165° C., 1,000 lbs. pressure per square inch).

The rubber-like binder compositions per se with their modifying agents mentioned herein are all commercial products and I have set them forth as illustrative instances of binders which I have utilized with success and which are capable of permitting curing and setting of the binder in the sheet. The same is true with the coating materials.

Another very acceptable product which I make in accordance with this invention is a new gasket material and I use any or a combination of the steps of binder incorporation explained above. Thus I will prepare a web composed exclusively of asbestos fibres having relatively dense and impervious surface layers and intermediate layers of less density and greater compressibility. This structure may be reversed and the gasket provided with a core of dense, impervious layers and surface layers of greater compressibility and less density and impermeability. The relatively dense layers will be relatively thin with respect to the more compressible layers although they may be equal to or of greater thickness, or the more compressible layers of less thickness than the relatively denser layers.

A single binder may be used or several different distinct ones for the respective laminae, and selected from those above mentioned, preferably in accordance with physical and chemical conditions surrounding the particular gasket application.

The gasket material may have any desired surface coating, as for example a layer of graphite as well known in the gasket art.

A similar structure, i. e., one having a relatively dense, incompressible and impervious layer or layers and a layer or layers of less density, greater compressibility and less imperviousness, is formed exclusively from any of the fibres herein listed, asbestos being given as a further concrete example, and likewise the exact structure can be formed exclusively from mixtures of cork and fibres. Again the structure is formed from layers composed of asbestos fibres mixed with one or more of the other fibres mentioned, as rope fibre, or mixed with comminuted cork, or comminuted cork and rope fibre or one or more of said other described fibres. Furthermore, the structure is formed with layers respectively exclusively of asbestos fibres and (1) layers exclusively of one or more of the other fibres mentioned or of cork and fibres and (2) of the asbestos mixtures just described.

As one concrete example the surface layers may be of asbestos and the compressible intermediate layers of cork and fibre mixture.

In each case the product will have a suitable binder incorporated therein, if required, a surface coating where desired, and/or a layer of graphite or similar material.

In some instances, as where the surface layer is not required to be smooth, calendering may be omitted, and in other instances the thin paper-like web or the thin surface layer of cork and fibre will not require any calendering. However, for certain decorative purposes where a very high finish is required, I resort to calendering.

Referring to Figures 5 and 6, the sheets in accordance with this invention are combined with a preformed material 16, such as a layer of cloth, paper, synthetic resin, vulcanized fibre or rubber. Such layers will be flexible or relatively stiff, as desired, serving as a reinforcement for the web and may be permeable or impervious. The preformed material will be (see Figure 5) (1) a backing, (2) a facing, and (3) both, or (see Figure 6), a core. As to the core structure, this also may have a facing or backing, or both, of the preformed material.

That is to say, the sheets will be constructed

in accordance with either of the webs of Figures 1 to 4. The combining may take place on any suitable combining machine, as for example, between opposed rolls.

A preformed facing and backing material may be applied as the permeated webs issue from the paper making machine or bath, and the combining takes place simultaneously with the curing of binder and the drying of the web, i. e., the combining rolls will be suitably heated.

The adhesive may be applied to the surface of the preformed material or the surface of the web. Pressure or heat sensitive adhesives are employed as well as glues and binders of the type recited above. In certain cases the web will have excess binder present on its surface so that additional adhesive will not be required. Again the web and preformed nonpermeated material will be combined and then the composite sheet saturated in a bath of the binders herein described. Also the permeated or non-permeated webs may be formed and wound into rolls, and thereafter combined with preformed material as required, or the combining will be a continuous or consecutive step after or before drying of the web. Also, the combining may be accomplished with pre-cut sheets as with the manufacture of veneers.

These faced and backed products have a variety of uses and particularly are useful for printing press blankets, insoles and rug anchors, as well as floor coverings. They may be suitably coated for any desired purpose with lacquers or varnishes as herein described.

For press blankets I may use any of the permeated webs herein described, but I prefer to use for printing press blanket material a single or double ply web of cork and fibre in accordance with this invention. I saturate the web with a rubber-like binder or other binder, as for example a glutinous adhesive, i. e., glue and glycerine and set the glue with formaldehyde. This will give a flexible blanket of required strength and resilience.

I will in some cases, where added strength is needed, apply a flexible backing of paper, cloth or vulcanized fibre. Also I apply the backing to both surfaces of the web as shown in Figure 5 as a further reinforcement.

While I have indicated rubber and glutinous adhesives, I also find the resin binders satisfactory for press blankets.

As a modification, a non-permeated web of cork and fibre has one or both surfaces united to a backing as above described.

As a further modification a core of the backing material will be employed such as cloth or paper and the webs united to opposite sides thereof. A backing and/or facing will also be used in some cases.

As a further form of printer's blanket or make ready, and particularly with reference to the use of vulcanized fibre, I will employ a relatively thin sheet of this material, and adhesively unite it to one of the sheeted products of this application, or to a layer wholly of comminuted cork particles and a binder, preferably one of those herein mentioned. This material (i. e., cork and binder) may be sheeted or may be spread upon the vulcanized fibre sheet.

The outside surfaces of the blanket material will be treated in such manner as to be smooth and impervious and non-adhesive to printing ink.

For insole material I will use any of the various webs herein described and any of the several binders to obtain a flexible, strong and absorbent material which likewise is resilient.

Preferably the exposed portion or tread surface will be freely absorbent to perspiration and hence will have only a minimum of binder present.

A premeable facing or backing such as muslin or other open web fabric will sometimes be applied to one or both surfaces of the web as a reinforcement.

The undersurface will also in some cases carry a pressure sensitive or heat sensitive adhesive of which many varieties are commercially available.

The insoles will be stamped out of the sheet in the usual manner.

As one illustration, I will, by pre-mixing or beater addition, put a small percentage of binder such as rubber latex in the top plies (fibre alone or cork and fibre) in order to produce absorbency of the finished insole on account of perspiration. In the intermediate and bottom plies, I introduce a high percentage of a binder such as a resin and/or rubber latex in order to increase the strength of the product, its resistance to wear and ability to stand sewing.

Other of the binders are equally applicable.

A new and important use for treated cork fibre (single ply or multi-ply) resides in its application as a rug anchor. Tests with a sheet of cork fibre impregnated with a rubber-like binder as well as with glue, glycerine and formalhehyde under small rugs on polished floors were very satisfactory. The rug does not slip on the cork fibre surface and the cork fibre grips the polished floor so that there is no movement of the rug relative to the cork fibre or the cork fibre relative to the floor, or both the cork fibre and the rug relative to the floor.

Cork fibre treated with the various binders mentioned produces a very acceptable rug anchor with or without the addition of a reinforcing material such as a layer of paper or cloth. This expedient is used in some cases in order to prolong the life of the anchor because small rugs are constantly being removed from the floor for cleaning purposes, and in the handling, a thin sheet of cork fibre might ultimately become torn. I use a combination of cork fibre and cloth, and cement the cloth on the side of the cork fibre which is in contact with the bottom side of the rug. I also put two layers of cork fibre on either side of a core of reinforcing cloth. Instead of impregnating with a rubber-like binder, I also use a resinous binder.

The products of this invention, especially treated cork and fibre, are adapted for use as anti-squeak material on automobiles. In this application, the compressibility and resilience of the product insure a tight joint between the adjacent surfaces and at the same time due to sound absorbency prevent noise and squeaking. It is readily processed into the desired form, that is, cut, slit, or folded. It is also substantially weatherproof and does not disintegrate when wet.

Another automotive application is the use of window channel material. The compressibility and resilience of the cork and fibre products make possible a tight joint with glass and at the same time afford a yielding or cushioning support to prevent window breakage. Other desirable attributes for this purpose are availability in various colors, weatherproofness, resistance to disintegration when wet, sound absorbency and ease of processing.

It will be understood that the various structures set forth herein will be permeated with various of the binders, for example, the surface layer will be permeated with a glutinous binder, i. e., glue, glycerine and formaldehyde, and the intermediate plies and bottom plies with a resinous material or a rubber-like material. Thus also one layer will contain a rubber-like binder and another layer a resinous binder. Similarly other sheets will be formed in which either the resinous binder or the rubber-like binder will permeate the surface layers and the other binders the intermediate and bottom layers. In some cases the top and bottom layers will be permeated with the same binder.

In referring herein to a resinous binder, I mean various natural and synthetic resins and compositions thereof which are well-known commercial articles, and in connection with rubber-like materials, I mean latex and similar latices, i. e., balata and gutta-percha and various rubber compositions, all of which are available in the trade.

The term "paper-like" is intended to cover the webs produced in accordance with this invention on a paper-making machine.

I claim:—

1. The process of making sheet material comprising a laminated web having paper-like layers felted to produce an integral composite structure which comprises preparing separate stocks of different densities, each of a mixture of separator and fibres, felting the stocks on a paper making machine into an integral web, the laminae of which have different coefficients of absorbency and saturating the web with a rubber-like binder to include such binder in the web in accordance with the absorbency of the layers thereof.

2. The process of making sheet material comprising a laminated web having paper-like layers felted to produce an integral composite structure which comprises preparing separate stocks of different densities, each of a mixture of comminuted cork and fibres, felting the stocks on a paper making machine into an integral web, the laminae of which have different coefficients of absorbency and saturating the web with a rubber-like binder to include such binder in the web in accordance with the absorbency of the layers thereof.

3. The process of making sheet material comprising a laminated web having paper-like layers felted to produce an integral composite structure which comprises preparing separate stocks for the individual layers, incorporating in some of said stocks predetermined percentages of a rubber-like binder material, felting the stocks into a laminated web and saturating the web to incorporate a binder material in other of the layers of the web.

4. Sheet material comprising a laminated paper-like web having the laminae thereof felted together into a substantially integral structure, rubber-like binder material in the laminae of said web, one of said laminae having a greater percentage of binder than another thereof and the binders being of respectively different types whereby to provide laminae of different characteristics.

5. Sheet material comprising a laminated paper-like web having the laminae thereof felted together into a substantially integral structure, rubber-like binder material in the laminae of said web, the said laminae having equal percentages of respectively different types of binders whereby to provide laminae of different characteristics.

6. Integrally laminated sheet material of paper-like form having one of its layers permeated with a rubber-like binder and another with a glutinous adhesive.

7. Integrally laminated sheet material of paper-like form having one of its layers permeated with a rubber-like binder and another with a bituminous binder.

8. Integrally laminated sheet material of paper-like form having one of its layers permeated with a rubber-like binder and another with a glutinous adhesive and another with a bituminous binder.

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