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METHOD OF LAMINATING POLYVINYL ALCOHOL FILM TO PAPER AND PRODUCT

Jay F. Strawinski, Philadelphia, Pa.

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This invention relates to paper and methods of making the same, and more particularly to paper having improved characteristics not heretofore available.

It has heretofore been proposed to provide a paper retardant to water, oils, grease and most common organic solvents. For this purpose, the paper or its surfaces were impregnated or coated with various selected materials for rendering the paper impervious or retardant to these liquids or semi-liquids. The resultant product obtained in that manner was greatly stiffened, and required the application of plasticizers in order to reduce the stiffness. While the plasticizing produced a paper having certain desirable characteristics, the original softness and pliability of the unprocessed paper were not attained and the impregnated or coated product was relatively non-absorbent, depending upon the degree of coating or impregnation accorded the paper. The resultant paper obtained in this manner tended to be repellent to particular liquids or semi-liquids (including greases). At the same time, in many instances, the finished product exhibited a glossy sheen which changed the appearance of the original paper and was frequently not desirable.

It has also heretofore been proposed to provide a water, oil, and organic solvent resistant paper of increased strength which included a lamination of a pre-cast film of cellulose acetate or the like. The laminating has usually been effected by the use of heat or solvents and pressure. The degree of heat required or the amount of solvent used to soften the film and the pressure employed usually resulted in some of the molten or softened plastic being forced between and around some of the fibers of the paper employed. Upon cooling or drying a mechanical bond was formed. While certain types of dense and relatively non-porous papers have been employed for this purpose, it has not heretofore been practicable to bond extremely light weight, porous and absorbent papers or sheets because the molten or softened plastic was forced through the pores of the paper, and was visible on the outer surfaces. A very stiff product was thus obtained, even if plasticizers were added, and the exposed surfaces no longer exhibited their previous absorbency. The original character of the unprocessed paper was completely changed.

It has also heretofore been proposed to employ hot melts and cold or hot adhesive solutions or pastes applied to one or more of the surfaces of sheets to be bonded and then effect the

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union by the application of pressure, and also to employ adhesive solutions or pastes applied to interposed sheet material and united to outer covering sheets by the application of pressure.

In the prior use of bonding materials, the bonding material tended to penetrate between the fibers and to a considerable extent into the heart of the sheets being laminated. In many cases the material tended to strike through to the outer surfaces of the paper, even if heavy paper was employed and the paper was sized. The strike through of the bonding material frequently changed the appearance of the original unprocessed sheets and objectionably modified its color, light reflection, pH value and absorbency, and the qualities of the bonding material were imparted in large part to the fibers of the sheets. Where the strike through was irregular this also resulted in an objectionable mottled appearance of the outer sheets. These objectionable features were particularly noticeable where thin, porous, and absorbent tissues were utilized.

It has heretofore been proposed to increase the strength of light weight, soft, porous, absorbent, cellulosic tissues by the addition of small quantities of sizing, either as water soluble sizing, such as starch, cellulose ethers, gelatin and the like, or as water insoluble sizing such as resins, waxes, latex and the like. The quantity of sizing which can be added without impairing other desired qualities, such as softness and absorbency, is very limited. The appreciable addition of the sizing also appears to introduce a rattle which may be readily heard when the paper is shaken or folded.

It has heretofore been proposed to increase the wet strength of thin, light weight, soft, porous, absorbent cellulosic tissues by the addition of suitable materials, such as small quantities of melamine urea or urea formaldehyde resins. The quantity of such materials must be kept limited or the original qualities of the paper are impaired.

It has been observed that even with addition of sizing or wet strength additive materials the paper is still relatively weak in the cross direction, whether dry or wet.

It has also heretofore been proposed to provide paper having a degree of water repellency, while maintaining some of the softness and flexibility of the paper prior to treating. For this purpose it has been proposed to crepe and impregnate or coat the fibers of the tissues with water insoluble resins, waxes, latex and the like. The paper thus obtained is relatively repellent to water, but is not resistant to water under moderate pressure

or water of reduced surface tension (soapy water) or to oils, greases, alcohol and other organic solvents. Such paper also lacked strength in the cross direction.

It is the principal object of the present invention, therefore, to provide a paper which will overcome the objections heretofore encountered and which will be light in weight, soft, with porous and absorbent surfaces, and which will have a good hand.

It is a further object of the present invention to provide a paper of laminated character in which the exterior laminations will retain substantially their original characteristics of softness and appearance, but which will have added strength, both when wet and when dry.

It is a further object of the present invention to provide a paper having greater tensile strength in all directions whether wet or dry than that of the constituent parts and which will have such strength without the necessity for including sizing.

It is a further object of the present invention to provide a paper having the exterior surfaces absorbent to liquids such as water, oils, alcohol, gasoline, greases, and the like, but which will retard the passage of such materials from one face of the paper to the other.

It is a further object of the present invention to provide a paper which will be soft, light in weight, and relatively free from rattle, pliable, and which will serve to replace textile fabrics in many applications and uses.

It is a further object of the present invention to provide a paper which is suitable for a wide variety of uses and which is particularly suitable for use as toilet tissues, facial tissues, paper toweling, dentists' bibs, dress shields, hatband liners, shoe liners, table covers, and as package wrapping paper.

It is a further object of the present invention to provide improved methods of laminating light weight sheet materials to provide a paper having improved characteristics.

It is a further object of the present invention to provide improved methods of preparing a constituent of a laminated light weight sheet material.

It is a further object of the present invention to provide improved and economical methods of fabricating paper.

Other objects and advantageous features of the invention will be apparent from the specification and claims.

The nature and characteristic features of the invention will be more readily understood from the following description, although it will, of course, be understood that various changes and modifications may be made in the structure and methods disclosed without departing from the spirit of the invention.

The paper, in accordance with the present invention, preferably is formed of an interior web or layer having on each face thereof an exterior web or layer, the exterior layers or webs preferably each being of the same or similar materials. The exterior layers preferably each comprise a single web or layer which may be non-fibrous, such as regenerated cellulose, metal foil, and the like, or may be fibrous material, such as paper. In a preferred application of the invention for each of the exterior layers there is employed a single web or layer of a thin, soft, absorbent, porous paper creped or not, as desired, which is preferably relatively non-sized, of the type

known as facial cleansing tissue or cellulose wadding. The interior layer or web preferably consists of a pre-cast or pre-formed film or sheet of a hydrophilic colloid, organic or inorganic, which has the characteristic of absorbing water and swelling, but not dissolving or dispersing in cold water or water at room temperature when in film or sheet form. The film or sheet should also have the ability to maintain its integrity during the combining with the exterior webs or layers so that it is free from undesirable cracks or holes and so that the fibers in the outer layers of paper are kept separated with respect to each other.

For the interior layer or web I prefer to use, as a material possessing the desired characteristics, commercially available previously plasticized polyvinyl alcohol film or sheet material of the type which is relatively insoluble in cold water or water at ordinary room temperature and which is conditioned as hereinafter explained.

I have found that such a polyvinyl alcohol film of the order of 1 mil (.001") in cross section thickness may be utilized after suitable treatment, although a thicker or thinner film could be employed so long as it is suitably treated to obtain, or so that it has, the desired characteristics hereinafter referred to. In order to condition such a film or sheet of the thickness indicated and to provide a very thin, highly pliable and soft finished paper, the film or sheet is preferably given a predetermined stretch in each of two directions at right angles to each other. For this purpose, a stretch in each direction at right angles of the order of three and a half times the original dimension is applied to yield a film area approximately twelve times that of the original film area, as this has been found satisfactory for most applications. I have found that for the purposes of the present invention the stretching may be satisfactorily effected at ordinary room temperature by the careful application of dilute solutions of one of the well known softeners for the film, which for polyvinyl alcohol include formamide, glycerine, sorbitol, ethylene glycol, diethylene glycol and others, and also by the careful application of water alone.

In this connection it has been ascertained that a one percent solution of glycerine in water is satisfactory if applied in sufficient amount only to moisten each film surface during the stretching operation, two applications having been found satisfactory in most instances. If excessive softener is applied during the stretching operation the film may be softened excessively or become excessively hygroscopic. If an excessive amount of the moistening liquid is present in or on the film at the time of stretch, it has been observed that additionally there is a tendency of the film to break.

It has also been found that if the film is moistened with a one percent solution of glycerine in water, followed by moistening with water alone, with sufficient time allowed for absorption and subsequent partial drying to take place between applications, and this treatment alternated that a satisfactory result is obtained. The stretching is effected after each application of moistening material and before thorough drying has occurred.

While it is not entirely certain as to the exact character of change which takes place in the film, it is believed that the stretching effects a molecular orientation in and on the surface of the

film and that this tends to set in the drying. It has been found that the toughest and yet thinnest film is obtained by this alternate wet stretching and drying. The use of a very thin film of this character also contributes to lower cost of production. If the film is permitted to dry while in the stretched condition it will tend to maintain its new area, and even though the film itself is still elastic, this effect being more permanent after the film has been bonded between the exterior layers.

After the film has been brought to the desired stretched condition and with the moisture then present, or with remoistening if necessary, the exterior layers of thin, soft, pliable, absorbent sheet material in moistened condition are brought into contact with the moistened faces of the film and the whole is then dried under a low pressure of the order of one to five pounds per square inch. The interior layer or film, in partially moistened condition, is tacky and the exterior layers are adherent thereto.

During the drying the laminated material may be maintained in stretched condition. The application of the exterior layers or webs to the interior layer or web in this manner provides between the layers a non-penetrating bond which appears to differ from the usual mechanical type of bond dependent upon penetration between and around the fibers. This non-penetrating bond may be effected as a result of some form of physico-chemical attraction between the components of the bonding material and the paper fibers.

If desired, and after the exterior layers have been brought into contact with the moistened faces of the film, the laminated material may be permitted to contract in one or more directions and at the desired angles to provide a creped effect without the necessity for or employing any other creping operation.

After drying and in the laminated material the exterior webs or layers are relatively inelastic, while the interior web or layer is relatively elastic. The bonding of the exterior webs appears to prevent shrinkage of the interior layer. The laminated sheet has a moderate degree of elasticity.

An appreciable degree of softness and good hand is attained by dry crumpling of the laminated sheet after fabrication, and without the use of softeners. In this treatment some of the fibers of the outer layers may be broken but the strength of the sheet is not materially reduced.

At the time of moistening the outer webs or at any other desired stage, such as after the drying of the laminated material, it has been found desirable in some instances to employ a softening agent, such as a dilute solution of glycerine, sorbitol, ethylene glycol, diethylene glycol or the like, or a relatively non-hygrosopic softener, such as diethylene glycol stearate or the like, for the exterior webs.

The gauge and pliability of the paper will depend upon the gauge of the film before stretching, the degree to which the film is stretched and the gauge of the exterior layers employed.

The paper which is thus obtained is soft and pliable and very closely resembles in appearance the materials used as the outer layers prior to the lamination. The paper, however, has a greater tensile strength, whether wet or dry, than the combined tensile strengths of the individual components. With this increased strength the paper has a considerable degree of elasticity, has

a good hand and has a clothlike appearance and feel. The paper also has an ability to drape similar to that of textile fabrics.

The paper has a low permeability to gases, such as hydrogen sulphide, air, oxygen, hydrogen, carbon disulphide, and the like, and accordingly is suitable as a wrapping for food products, silverware, and other articles where it is essential to exclude gases.

The faces of the paper are absorbent to liquids, but strike through or transfer of water or aqueous solutions from one face to the other is retarded. Other materials, such as oils, greases, fats, alcohol, and most of the common organic solvents are greatly retarded in their passage from one face to the other face, the retarding being such that the paper is essentially proof against the passage of these materials. The continuous character of the interior layer is particularly important in preventing the passage of oil, alcohol and organic solvents from one face to the other face.

The film or interior layer being hydrophilic provides greater total water absorbency than that of the exterior layers separately considered. The speed of liquid absorption also appears to be increased.

Where an increased water resistance is desired the interior layer may be treated, before, during, or after the laminating has been effected, with suitable insolubilizing agents, such as paraformaldehyde, sodium dichromate, cuprammonia, dicarboxylic acids (such as sebacic, citric, tartaric, etc.), and others.

If it is desired to modify the absorbent character of one or both of the exterior layers by the addition of water-repellent or waterproofing materials, this may also be effected, prior to or after the laminating, to modify the characteristics of the finished product to the desired extent, and without change in the softness and pliability thereof.

If the paper is made water-repellent on one or both faces, the face will, however, retain their ability to absorb oil, alcohol and most common organic solvents, while at the same time greatly retarding their passage from one face to the other face.

If one or both of the exterior layers have been treated to render the same water-repellent, the lamination of such layers as herein pointed out provides increased strength not obtainable with soft water-repellent porous paper heretofore available, and also provides increased resistance to the passage of water under moderate pressure of water whose surface tension has been reduced, and has a very high degree of resistance to the passage of oils, greases, alcohols and most other solvents, in the same manner as heretofore pointed out where the paper is not water-repellent treated.

The paper thus prepared will still retain the soft and pliable characteristics and the clothlike appearance, but has other uses, such, for example, as a backing sheet for disposable baby diapers or for catamenial pads, or for making window drapes, table covers, and the like.

I claim:

1. The method of making laminated sheet material which comprises moistening a sheet of polyvinyl alcohol, increasing the area of the sheet to a plurality of times the original dimensions by stretching the sheet in a plurality of directions, and applying directly to the surfaces

of the stretched sheet, with moistening, exterior webs of porous thin flexible sheet material.

2. The method of making laminated sheet material which comprises increasing the area of a sheet of polyvinyl alcohol film by stretching the sheet in a plurality of directions, applying directly to the surfaces of the stretched sheet with aqueous moistening exterior webs of porous thin fibrous sheet material, and restraining the laminated material from shrinking during drying.

3. The method of making laminated sheet material which comprises increasing the area of a sheet of polyvinyl alcohol film by stretching the sheet in a plurality of directions, applying directly to the surfaces of the stretched sheet with aqueous moistening exterior webs of porous thin fibrous sheet material, and permitting the shrinking of the laminated sheet during drying.

4. The method of making laminated sheet material which comprises applying directly to the surfaces of a sheet of polyvinyl alcohol which has been prestretched in a plurality of directions to a plurality of times its original dimensions, with aqueous moistening, exterior webs of thin cellulosic sheet material.

5. The method of making laminated sheet material which comprises applying directly to the surfaces of a sheet of polyvinyl alcohol which has been prestretched in a plurality of directions to a plurality of times its original dimensions with aqueous moistening, exterior webs of thin water-repellent cellulosic sheet material.

6. The method of making laminated sheet material which comprises applying directly to the surfaces of a sheet of polyvinyl alcohol which has been prestretched in a plurality of directions to a plurality of times its original dimensions exterior webs of thin porous cellulosic sheet material, and applying to the exterior webs water-repellent material.

7. The method of making laminated sheet material which comprises applying directly to the surfaces of a sheet of polyvinyl alcohol which has been prestretched in a plurality of directions to a plurality of times its original dimensions with aqueous moistening, exterior webs of thin cellulosic sheet material, and softening the laminated sheet.

8. The method of making laminated sheet material which comprises applying directly to the surfaces of a sheet of polyvinyl alcohol which has been prestretched in a plurality of directions to a plurality of times its original dimensions with aqueous moistening exterior webs of thin

cellulosic sheet material, and softening the laminated sheet by dry crumpling.

9. A soft pliable laminated sheet material relatively free from rattle and capable of draping comprising an uninterrupted web of a polyvinyl alcohol film prestretched a plurality of times its original dimensions in more than one direction and in which the integrity of the web is retained having, in direct adherent engagement with the faces thereof and separated by said film, exterior coverings of thin porous single ply fibrous cellulosic sheet material, said sheet material being resistant to separation of the laminations in the presence of water.

10. A soft pliable laminated sheet material relatively free from rattle and capable of draping comprising an inner uninterrupted web of a polyvinyl alcohol film prestretched a plurality of times its original dimensions in directions normal to each other and in which the integrity of the web is retained having, in direct adherent engagement with the faces thereof and separated by said film, exterior coverings of thin fibrous single ply liquid-absorbent cellulosic sheet material free from gloss, said sheet material being resistant to separation of the laminations in the presence of water.

JAY F. STRAWINSKI.

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