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SAFETY PAPER

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This invention relates to identifiable paper and other cellulosic materials, and to the process of making the same, wherein the mark of identification comprises fibers which are fluorescent in ultra-violet light, soluble in solvents that have no effect on the cellulosic fibers and capable of being colored so that they are completely fast to acids, alkalis, bleaching agents, etc.

An object of the invention is the economic and expeditious production of cellulosic materials, such as paper, cardboard, felts, etc., which have incorporated therein fluorescent fibers, made of or containing an organic ester of cellulose, as a mark or means of identification or as a decoration. A still further object of this invention is the production of paper to be used as bank-note paper, stock certificates, revenue stamps, labels and the like, the authenticity of which paper may be determined by a plurality of simple tests since the paper contains fibers which are fluorescent in ultra-violet light or near ultra-violet light and which fibers may be dissolved out of the paper by means of solvents which have no effect upon the fiber and since the fibers may have one or a plurality of definite diameters.

Identifiable paper, as heretofore commonly manufactured, had incorporated therein short lengths of silk fibers as a means of identification. This paper has been used mostly as bank-note or currency paper. The silk fibers are of two-fold importance, firstly, for the reason that they show the paper to be of a certain type and, secondly, because colored fibers in the paper make more difficult the photographic reproduction of printed matter on the paper. I have found that by incorporating in paper fibers made of or containing an organic ester of cellulose that has been treated with a tertiary amine, there are obtained many advantages which are not obtainable with paper employing silk fiber. One advantage of employing an organic ester of cellulose treated with tertiary amine, which gives to the organic ester of cellulose the property of being fluorescent in ultra-violet and near ultra-violet light, is that photographic reproductions with various color filters becomes more difficult. Another advantage of employing such fibers is that there may be incorporated in the paper several types of fibers, that is, fibers having different denier, different color and different composition, and the fibers may be present in various proportions, some or all of which are fluorescent, such that upon a microscopic examination of the paper in various lights the authenticity of the same is easily ascertained. Another advantage of the pres-

ent invention is that the threads may be dissolved from the paper without effecting the paper, thus giving rise to a very simple test for the authenticity of the paper. Furthermore, by employing this invention, identification marks may be made resistant to or unaffected by bleaching agents, or the paper may have some identification marks which cannot be removed by a bleaching operation and others which can be removed by a bleaching operation.

In accordance with my invention, I form sheet cellulosic material, such as tissue paper, writing paper, cardboard or other types of material from any suitable cellulosic material and incorporate in said cellulosic material fibers, formed of or containing an organic ester of cellulose and a tertiary amine having at least two aryl substitution groups, of any desired denier, color, length, or mixtures of such fibers. The fibers made from or containing an organic ester of cellulose may be incorporated in the cellulosic material in any suitable manner. However, in accordance with this invention, I prefer to incorporate the organic ester of cellulose treated with the tertiary amine in the paper stock or pulp, either before the beater or before or after the Jordan, by feeding to the stock a uniform amount of the fibers. This may be accomplished by feeding a lap or roving formed of organic ester of cellulose fibers to the paper stock or by forming a suspension of the said fiber and flowing it into the paper stock.

The base material of the paper or other cellulosic article may be any suitable stock normally employed in the formation of such cellulosic articles. For instance, the paper or other cellulosic article may be made from wood or vegetable pulps made by the mechanical method, soda method, sulphate method, sulphite method or combinations of these, or from cotton and linen rags or masticated paper or mixtures of these. The paper or other cellulosic article may be formed on the same machines and in the same manner as such articles have been previously manufactured. For instance, this invention is applicable to hand methods of making paper, cardboard and the like or to the machine methods wherein the pulp is mixed, then passed through a beater, a Jordan, blending tanks and onto a sluiceway to the screens or to the Fourdrinier. The paper or other cellulosic article may be of any suitable thickness from tissue paper up to felts and blocks. This invention is of particular importance, however, with cellulosic articles of writing paper thickness or wall paper thickness. This inven-

tion, moreover, is of some importance in the manufacture of cardboard for containers as the identifiable characteristic of the same makes possible the ready detection of counterfeit or spurious packages.

As stated, this invention relates to the production of identifiable paper or other cellulosic materials that are to be used for any purpose where ready identification is desirable. This invention is also of importance in the manufacture of cardboard for boxes or closure members of containers, for pass cards and the like. In the above applications of the invention the problem of ready identification and the difficulty of duplication is of major importance.

The invention, however, has also another object, i. e. that of decoration. In the above applications of the invention the decorative feature may be incorporated along with the protective feature, or the invention may be used purely for decorative effects in, for example, tissue paper either of the soft or glazed variety used as wrappings for bottles, packages, and, in fact, articles of all kinds. Here also the protective feature may be of some importance in that each manufacturer may have a particular color, denier or mixtures of colors and deniers which make the origin of the wrappings easily determinable. This invention may be used in the production of wall paper, coverings for individual packages or boxes and the like. For instance, I may produce paper, such as wall paper, or coverings for cardboard boxes, by employing a mixture of organic ester of cellulose fibers and printing or dyeing the organic ester of cellulose fiber after it is in the paper. Wall paper made in accordance with my invention may include organic ester of cellulose fibers of different color, denier and pigmentation, as well as organic ester of cellulose fiber of natural color. A design may be printed on the paper by employing dyes having affinity for cellulose fiber and no affinity for an organic ester of cellulose fiber and/or dyes having affinity for organic ester of cellulose fiber only and not for cellulosic materials. Multiple color effects in paper are thus produced through a differential dyeing or printing operation and through the pigment or coloring matter already in the organic ester of cellulose fibers. This differential or multiple color effect coupled with the fluorescent property of the treated organic ester of cellulose fibers would be impossible to duplicate without starting with the formation of the paper and then only when the percentages of the various components are known.

Any suitable type of organic ester of cellulose fiber may be employed in making identification marks in or on the cellulosic material, for instance, fibers formed of cellulose acetate or other organic esters of cellulose, such as cellulose formate, cellulose propionate and cellulose butyrate.

The organic ester of cellulose fibers may be formed by spinning into the form of substantially continuous filaments a solution of an organic ester of cellulose in a suitable solvent therefor. The solution of the organic ester of cellulose may be extruded through suitable orifices into any suitable solidifying medium, such as a drying atmosphere according to the dry method of spinning, or into a precipitating bath as in the wet method of spinning. The substantially continuous filaments as individual filaments,

bands, bundles or hanks, may then be cut or torn into suitable lengths.

The fibers incorporation in the cellulosic article may be of any suitable length, for instance, from $\frac{1}{32}$ of an inch to 3 or more inches. The organic ester of cellulose fibers may be relatively straight or the same may be embossed or treated in liquids to impart to the fiber a curl, print or other configuration. If desired, the fibers, or filaments, before being cut or torn into fibers, may be intermittently embossed by such means as heated embossing rolls to form segments which have a predetermined configuration, while other segments have their natural fiber-like shape. As the organic ester of cellulose fibers are thermoplastic, this embossing is permanent and the configuration is more or less carried into the finished article regardless of the drastic action in the Jordan and sluiceway.

The organic ester of cellulose fiber may contain, besides the organic ester of cellulose base material and the tertiary amine, effect materials such as pigments, plasticizers, dyes, lakes, filling materials, fire retardants and the like. These materials may be incorporated in the fibers by adding the effect materials to the solution of organic ester of cellulose prior to its formation into filaments, or the effect materials may be added to the formed filaments or fibers in any suitable manner. For instance, the fibers may be dyed by means of dye baths with or without the aid of swelling agents and the like. Pigmented fibers are of exceptional value for identification purposes. The pigmented fibers may be of any suitable color from white to black. They may be formed by mixing with the spinning solution from which the fibers are formed such pigments as the metal oxides, hydroxides, carbonates, phosphates, etc. For instance, a white fiber may be formed by incorporating titanium, zinc or lead oxide in a fiber, while red fibers may be produced by incorporating iron oxide or the like in a fiber, while blue fibers may be formed by incorporating Prussian blue therein. Besides the metal oxides, hydroxides or metal salts, there may be employed as pigments insoluble or relatively insoluble organic compounds.

The fibers of an organic derivative of cellulose employed in the making of the cellulosic materials may be of any suitable denier, or a mixture of fibers of different deniers may be used. For instance, fibers having a denier of 0.3 up to 20 or more may be employed or mixtures of fibers of any desired deniers may be employed. In the manufacture of the organic derivative of cellulose fiber by means known in the art, the fibers may be made to have a denier which varies in any desired amount over a given length. When these fibers are cut into the length desired in the finished paper, the fibers show this varying denier which gives rise to a still further means of determining the origin of a paper. In stamps, stock certificates, currency and the like it is often desirable to incorporate in the cellulosic base material a low denier fiber, say fiber having a denier of 0.5, as a means of making difficult the photographic reproduction of the article, and then large denier fibers, say 3 to 10 denier, for a ready or more visible determination of the authenticity of the article. The fibers of the same denier or of each denier may be of the same or of a different color.

The fibers of an organic derivative of cellulose may be dyed any suitable color prior to incor-

poration in the cellulosic material or the fibers may be of natural color. I have found that organic derivative of cellulose fiber containing a white or colored pigment is of exceptional value in this respect in that the color of the fiber is unaffected by acids, alkalis, bleaching agents and the like, although the fiber may readily be dissolved by solvents such as acetone, chloroform, ethyl dichloride, a mixture of diethylene chloride and ethyl or methyl alcohol and the like. Thus, by placing the cellulosic material or paper in the solvent, there is provided a ready test as to whether the identifiable fibers are formed of an organic ester of cellulose or not, whereas placing the cellulosic material in a bleaching agent is a ready test as to whether the fibers are pigmented or dyed. The organic ester of cellulose fibers may be partially saponified or intermittently saponified, whether they be pigmented or not, to change their affinity for printing inks, dyes, etc. The use of the intermittently saponified fibers gives rise to still another possibility of identifying the origin of the certain cellulosic material since the saponified segment of the fiber of identification can be dissolved only by the use of solvents different from those which are capable of dissolving the other segment.

Fibers other than organic esters of cellulose which have been treated with a tertiary amine such as, for example, benzyl ethyl aniline do not fluoresce in near ultra-violet light. This property is particular to the organic esters of cellulose. Therefore, by intermittently saponifying fibers of organic esters of cellulose a single colored fiber may be made to fluoresce on one portion of its length and not on another portion of its length.

Thus, in accordance with my invention, the origin of the cellulosic material is ascertained by easy and simple tests such as the character of fluorescence in ultra-violet or near ultra-violet light, the size of the identification fibers, the number of different sizes or whether the fibers are bleach-proof or easily bleached. For instance, there may be placed in a paper different types of fibers, such as large denier fibers, small denier fibers having a curl or a crimp to interfere with photographic reproductions or, say, a black fiber unaffected by bleaching mixed with red fibers easily bleached, some or all of these fibers being fluorescent, or any other combination of fibers described above.

The fluorescent property may be imparted to the organic ester of cellulose fiber by incorporating with the fiber a small amount of a tertiary amine having at least two aryl substitution groups. Examples of such tertiary amines are besides the benzyl ethyl aniline noted above, dibenzyl aniline, benzyl phenyl aniline, phenyl ethyl aniline, etc. After incorporating the tertiary amine with the organic ester of cellulose the same is subjected to ultra-violet light for from 5 to 60 minutes after which period it becomes fluorescent and this property is permanent. The organic esters of cellulose absorb these tertiary amines and, therefore, the tertiary amine may be incorporated with the yarn during the dyeing operation where the tertiary amine is in suspension or in a dispersion of the dye bath. The tertiary amine may be incorporated with the fibers by mixing the same with an oily substance and lubricating the fibers with this mixture during a winding operation or by batching the material in a bath of the same. The tertiary amine may also be incorporated with the organic ester

of cellulose fiber by applying the same to the organic ester of cellulose prior to forming it into filaments or fibers. Thus, the tertiary amine may be added to the stabilizing bath in the preparation of the organic ester of cellulose or the tertiary amine may be added to the spinning solution. Any amount of the tertiary amine may be employed, for instance, from 0.05% to 10% or more based upon the weight of the organic ester of cellulose fiber, the preferred amount being from 0.3% to 1%.

The organic ester of cellulose fiber may be incorporated in the paper in any suitable manner. However, I have found it of advantage to form the organic ester of cellulose fiber into a sliver of fairly uniform weight. By this means where more than one type of organic ester of cellulose fiber is employed the proper distribution or mixing of the product is easily obtained. This sliver whether in spool form or canned is drawn to the stream of paper stock either before it enters the Jordan or after it has passed through the Jordan prior to reaching the screens and there it is broken down into the individual filaments by means of water jets, beaters, air or other means and mixed into the paper stock.

In place of forming the fibers into a roving, I may form the fibers of organic ester of cellulose into a lap by means of a cotton or wool carding device. This lap is pulled between nip rolls to a point above a flowing stream of paper stock and by means of beaters, air jets or other means broken down to the individual fibers, and the fibers forced into the stream of paper stock passing therebeneath. If it is desired to place the marks of identification only on predetermined sections of the paper, this may be done by feeding the organic ester of cellulose fiber to the paper stock where the paper stock meets the screens. Here the organic ester of cellulose fibers may be fed to the paper stock in rows, bunches or otherwise.

I have also found that the organic ester of cellulose fiber may be mixed with the paper stock by forming a slop of the organic ester of cellulose fiber in water by the addition of from 1 to 5% on the weight of organic ester of cellulose fiber of tapioca, starch, dextrin and the like. Tapioca, starch, dextrin and the like gives to the mixture of water and organic ester of cellulose fibers sufficient body and viscosity so that the fibers move with the water and stay evenly dispersed or suspended in the liquid in such a manner that the mixture may be poured over the edge of a tank into a stream of water pulp. If tapioca, starch, dextrin or the like is not employed there is a tendency for the water in the mixture to drain from the organic ester of cellulose fibers which are left in the tank. Tapioca, starch and dextrin also act as a protective colloid for the fibers.

Any suitable percentage of organic ester of cellulose fibers may be mixed with the cellulosic fiber stock. A suitable amount for stock certificates, bonds and revenue stamps, when employing a dark colored fiber, is a 5 denier organic ester of cellulose fiber in an amount equal to about 1 to 4% based on the weight of the cellulosic fiber. Obviously, smaller or greater percentages of each may be employed according to the result desired. In the manufacture of wall paper, coverings for cardboard or the cardboard boxes themselves as high as 20 to 30% of organic ester of cellulose fiber, based on the weight of the product, may be employed.

As an illustration of this invention, but without being limited thereto, the following example is given:

Example

- 5 By means of a cotton card a lap is formed from 5 denier cellulose acetate fibers containing 0.5% on the weight of the fibers of benzyl ethyl aniline. A slurry of a sulphite wood pulp containing about
- 10 10% of linen or rag pulp is formed in the usual manner. To the stream of sulphite pulp flowing from the Jordan onto the screen is added the cellulose acetate fiber in an amount equal to 3% on the weight of the air dried paper. The addition
- 15 of the cellulose acetate fiber to the stream of sulphite pulp is accomplished by drawing the lap through nip rollers at a constant speed to give the desired percentage of fibers and beating with mechanical beaters the end of the lap as it comes
- 20 through the nip rollers in a manner to knock the fibers free from each other and into the stream of sulphite pulp. The fiber is found to have the cellulose acetate fibers evenly dispersed therein. The cellulose acetate fibers are readily visible,
- 25 individually fluorescent in ultra-violet light, and may be dissolved from the paper by dipping the paper in acetone. There is no tendency for the paper at those parts not containing cellulose acetate fiber to fluoresce.
- 30 It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of my invention.
- 35 Having described my invention, what I desire to secure by Letters Patent is:
1. A safety paper comprising a felted body of cellulose fibers and having embedded therein from 1 to 4%, based on the weight of the cellulose
 - 40 fibers, of organic ester of cellulose fibers containing benzyl ethyl aniline.
 2. A safety paper comprising a felted body of cellulose fibers and having embedded therein from 1 to 4%, based on the weight of the cellulose fibers,

of cellulose acetate fibers containing benzyl ethyl aniline.

3. A safety paper comprising a felted body of cellulose fibers and having embedded therein from 1 to 4%, based on the weight of the cellulose fibers, of organic ester of cellulose fibers containing $\frac{1}{2}$ %, based on the weight of the organic ester of cellulose fibers, of benzyl ethyl aniline.

4. A safety paper comprising a felted body of cellulose fibers and having embedded therein from 1 to 4%, based on the weight of the cellulose fibers, of cellulose acetate fibers containing $\frac{1}{2}$ %, based on the weight of the cellulose acetate fibers, of benzyl ethyl aniline.

5. A safety paper comprising a felted body of cellulose fibers and having embedded therein 3%, based on the weight of the cellulose fibers, of organic ester of cellulose fibers containing $\frac{1}{2}$ %, based on the weight of the organic ester of cellulose fibers, of benzyl ethyl aniline.

6. A safety paper comprising a felted body of cellulose fibers and having embedded therein 3%, based on the weight of the cellulose fibers, of cellulose acetate fibers containing $\frac{1}{2}$ %, based on the weight of the cellulose acetate fibers, of benzyl ethyl aniline.

7. A safety paper comprising a felted body of cellulose fibers and having embedded therein from 1 to 4%, based on the weight of the cellulose fibers, of organic ester of cellulose fibers, said organic ester of cellulose fibers being a mixture of such fibers having at least two deniers, at least two colors and at least one component thereof containing benzyl ethyl aniline.

8. A safety paper comprising a felted body of cellulose fibers and having embedded therein from 1 to 4%, based on the weight of the cellulose fibers, of cellulose acetate fibers, said cellulose acetate fibers being a mixture of such fibers having at least two deniers, at least two colors and at least one component thereof containing benzyl ethyl aniline.

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