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# FIBROUS WEBS, INCLUDING PAPER, FORMED FROM WATER INSOLUBLE DEXTRAN FIBERS

Leo J. Novak, Dayton, Ohio, assignor to Commonwealth Engineering Company of Ohio, Dayton, Ohio

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This invention relates generally to non-woven fibrous webs. More particularly, it relates to such webs, including paper, comprising fibers of water-insoluble dextran.

A particular application of the invention is in the production of cigarette paper.

The paper used as wrapper for machine made cigarettes is commonly made from flax fibers and is loaded with an alkaline filler, usually calcium carbonate (chalk), incorporated in the paper sheet during manufacture thereof. Thus, the calcium carbonate is added to the paper pulp suspension comprising the flax fibers while the suspension is in the beater or in the machine chest, or just prior to formation of the pulp into a continuous paper web or sheet on the paper machine. The chalk filler is normally used in an amount such that it constitutes about 20% to 30% of the total weight of the filled paper.

The chalk filler has been used for other purposes in addition to insuring continuous steady burning of the paper.

It makes the paper more opaque, giving a cigarette of improved appearance, and also cuts down the time required to dry the paper.

A known disadvantage of the calcium carbonate filler is that the paper containing it normally does not have the most desirable ashing characteristics. On burning the filled paper there are formed carbonized paper particles that commonly appear as black curling ashes that tend to flake off and fall from the cigarette onto the smoker's clothes. To avoid this insofar as possible, the paper is subjected to special chemical treatment to produce a clinging ash which is cohesive and adheres to the tobacco ash. Various materials including water-soluble borates, tungstates, sulfates and phosphates, such as guanylurea phosphate, have been added to the filled paper before it leaves the machine, for this purpose.

Another established disadvantage of the chalk-filled flax paper is its relative weakness when wet. During smoking of the cigarette, if the saliva in the smoker's mouth wets the paper, the wet portion tends to pull away from the remaining dry portion and adhere to the smoker's lips, sometimes disintegrating in the smoker's mouth. To improve the wet strength of the paper, it is common to incorporate in the partially dry paper water-resistant materials such as urea-formaldehyde resin precondensates together with an acid to catalyze insolubilization of the resin during drying or on subsequent heat treatment of the paper.

Recently, it has been found that benzpyrene long known to be carcinogenic hydrocarbon, is a combustion product of the conventional cigarette paper. This complex hydrocarbon has been shown to be a product of cellulose degradation and re-arrangement on burning. Not only is the benzpyrene a definitely harmful chemical but, obviously, the more extraneous chemical substances that are required to be added to the paper to render it acceptable as wrapper for the tobacco, and the greater the variety of those substances so far as chemical structure is concerned, the greater is the risk incurred that, on smoking of the cigarette, other harmful, or at least undesirable, tars and volatile products will be produced.

The primary object of this invention is to provide improved cigarette paper formed from non-cellulosic fibers and an organic filler, and having the opacity, ashing



characteristics and wet strength required for a satisfactory cigarette paper.

Another object is to produce, continuously, new and novel fibrous webs of indefinite length and width and suitable for use as non-woven fabric.

These and other objects are accomplished by providing a fibrous web, including paper and more especially cigarette paper, formed from or comprising water-insoluble dextran fibers bonded by water-insoluble dextran which is also a filler for the cigarette paper.

The dextrans are high molecular weight polysaccharides made up of anhydroglucopyranosidic units, characterized in that those units are joined by molecular structural repeating linkages of which at least 50% and usually a higher proportion are 1,6 linkages, and obtained by the action of specific microorganisms such as those of the *Leuconostoc mesenteroides* or *L. dextranicum* types on sucrose. The ratio of 1,6 to non-1,6 linkages, which influences the physical properties of the dextran, depends on the particular microorganism (or enzyme thereof) used to effect the biosynthesis. Microorganisms which convert sucrose to a dextran that is inherently water-insoluble include those bearing the following NRRL (Northern Regional Research Laboratory) designations: *Leuconostoc mesenteroides* B–523, B–1118, B–1120, B–1139 and B–1144.

The procedure is to inoculate a suitable aqueous sucrose-bearing nutrient medium with a culture of the microorganism or with an aqueous dilution of the enzyme filtered from the culture, incubate the mass until the dextran is produced in maximum yield, and then separate the dextran from the fermentate and purify it. The dextran may be used at its native normally very high molecular weight or partially hydrolyzed to a lower molecular weight at which it is still insoluble or substantially insoluble in water.

The water-insoluble dextrans produced by the microorganisms are soluble in aqueous alkaline solutions such as 0.5% aqueous sodium hydroxide. Aqueous alkaline solutions of the dextran or xanthates thereof may be used to obtain the water-insoluble dextran in fiber form.

The fibers are obtained for instance by extruding the aqueous alkaline solution of the dextran into an aqueous acid setting bath at 50° C.–60° C. or at room temperature. The setting bath may have a pH of 1.0 to 4.5 and be an aqueous solution of any suitable acid such as one of the non-volatile organic acids, for instance oxalic, tartaric or citric acid. The bath may also be an aqueous solution of strong mineral acid such as hydrochloric, sulfuric or phosphoric acid, although the milder organic acids are preferred when the spinning solution is an aqueous alkaline solution of the water-insoluble dextran.

When the aqueous alkaline solution of the dextran is extruded into the aqueous acid bath, the resulting dilution and neutralization causes precipitation of the dextran and coagulation thereof in the form of filaments or a monofil. The monofil or filamentary bundle is withdrawn from the bath, washed to remove any residual acid, stretched and dried. Conventional equipment for forming, after-treating and drying the monofil, or filamentary bundle may be used. The processing, including the drying, may be continuous.

In another embodiment of the invention, the spinning solution or "dope" is dextran xanthate. The xanthate may be obtained by first reacting the dextran with a strong alkali metal hydroxide such as sodium hydroxide, and then reacting the sodium dextran thus obtained, in aqueous slurry, with liquid or gaseous carbon disulfide, until a xanthate containing from 0.2 to 3.0 xanthate groups is obtained. The xanthation reaction may be performed at a temperature of 20° C. to 25° C. for 2 to 4 hours, using a molar ratio of alkali dextran to $CS_2$ of 1:3 to 12:1,

The xanthate is extruded through a spinneret into an aqueous acid solution as described above, preferably an aqueous sulfuric acid solution. The monofil or bundle of filaments withdrawn from the bath are washed, stretched and dried in the usual way.

The filaments may be collected as a tow or filamentary bundle of large cross-section, processed, including stretched, in the tow or bundle form, and then cut or otherwise disrupted to obtain a mass of discontinuous fibers for use in making the paper or fibrous web.

The discontinuous fibers, however obtained, may be of normal papermaking length or may be shorter or longer than the normal length.

The fibers are suspended in water acidified to pH 1.0 to 5.0. Suspension of the fibers to obtain a pulp may be accomplished by simply stirring the fibers into the acid solution in a conventional paper beater, without resort to actual beating. The water may contain a small amount, 0.1% to 0.5% by weight, of a neutral or acid anionic dispersing agent, but dispersing agents are not required for effecting distribution of the dextran fibers in the acidified water.

After the suspension is obtained, an aqueous dilute alkaline solution of a water-insoluble dextran, such as an aqueous solution of native *L.m.* B–523 dextran in 1%–2% aqueous sodium hydroxide, is added. Dilution of this solution by the acidified water (pH 2.0–5.0) results in precipitation of the dextran on the dextran fibers in the form of discrete colloidal particles.

The suspension is then laid down on the papermaking screen to form a coherent web in which the discrete dextran particles adhered to the dextran fibers act as a binder for the fibers. On drying, there is obtained a coherent porous web the fibers of which are bonded together wherever the dextran particles occur therein. The dextran constituting the bonds between the fibers constitutes about 5% to 30% of the total weight of the finished web.

In making cigarette paper, it is preferred to use fibers all of which are water insoluble dextran fibers. In such papers, the dextran particles serving as bonds between the fibers, constitute a wholly organic filler for the paper. The paper is an all-dextran paper, and has satisfactory opacity, ashing characteristics, and wet strength without incorporation of extraneous modifying agents.

Instead of adding the aqueous alkaline solution of the dextran to the fiber suspension in the beater, it may be added in the stock line between the Jordan and the paper machine headbox.

On running the suspension containing the dextran fibers having the discrete dextran particles adhered to the surface thereof over the paper machine in the conventional way, a substantially neutral, white paper or fibrous web is obtained. The paper or web is finished in the usual manner, and in its final state is insoluble in water and capable of absorbing an appreciable amount of moisture without disintegration.

In some instances, depending on the purpose for which the paper is intended, the dextran fibers are mixed with conventional fibers such as beaten cellulose fibers or non-beaten, smooth, artificial and synthetic fibers of the type of regenerated cellulose, cellulose acetate, nylon, "Orlon," "Dacron," cellulose esters and ethers, dextran esters and ethers such as dextran acetate or benzyl dextran, etc. The water-isoluble dextran fibers may comprise 5% to 95% of the fiber mixtures. Webs containing 50% of the water-insoluble dextran fibers and 50% of beaten cellulose fibers have numerous uses.

The cigarette paper consisting of the dextran fibers and water-insoluble dextran filler and binder is combustible. It burns steadily and continuously once the cigarette is lit. At temperatures above 200° C. in the presence of moisture the dextran is depolymerized to dextran having a molecular weight in or approaching the range for clinical arrangement. The heat-degraded dextran usually has a somewhat different structural arrangement than native dextran either as a result of cross-linking or of a more extensively branched condition.

The following examples are illustrative of specific embodiments of the invention, it being understood that these examples are not limitative.

*Example I*

Fibers of water-insoluble dextran regenerated from xanthate native *L.m.* B–523 dextran and of conventional papermaking length are suspended in water containing 2% acetic acid in a paper beater, to a consistency of about 2.5% without beating. A solution of 10% of the native *L.m.* B–523 dextran in 2% sodium hydroxide in an amount to provide 10% by weight dextran in the finished paper is added with stirring. The dextran precipitates out of solution and adheres to the fibers in the form of discrete colloidal particles. The furnish is run over the paper machine in the conventional manner of paper manufacture, in the course of which it is dried to obtain a coherent, opaque sheet of the dextran fibers bonded and filled or loaded by the dextran particles. The paper is very suitable for use as cigarette paper.

*Example II*

To a 2.0% suspension of beaten cellulose fibers in water to which 3% of acetic acid has been added after the beating there are added 2% of the water-insoluble dextran fibers of Example I. A solution of 10% of the water-insoluble dextran in 2% sodium hydroxide solution is added in an amount to provide 5% by weight in the finished product of the precipitated particulate dextran as binder for the fibers. The furnish is run over the paper machine and finished, including calendered, to obtain a coherent, smooth, relatively porous web consisting of the cellulose fibers and the dextran-bonded fibers. The web is adapted for use as wrapping and for other purposes for which coherent fibrous webs or non-woven fabrics are adapted, and which is capable of absorbing moisture in appreciable amount without disintegration.

*Example III*

In this instance paper is made which comprises establishing a suspension of cellulose fibers such as fibrous wood pulp and to the suspension of the fibers in water is added acetic acid and water-insoluble dextran fibers; thereafter there is introduced alkaline metal hydroxide solution to provide approximately 5% by weight of precipitated dextran particles as a binder for the water-insoluble dextran fibers; the resultant aqueous suspension of fibers is then flowed onto a screen to remove excess water and form a continuous fibrous web, the web is then calendered to obtain a smooth relatively porous sheet composed of cellulose fibers and water-insoluble dextran fibers bonded together with dextran. A solution of 10% of the water-insoluble dextran in 2% sodium hydroxide solution is used to provide the binder for the water-insoluble dextran fibers as in Example II.

In the present invention it has been found that a mixture of cellulose fibers and dextran fibers can be bonded together with precipitated dextran and formed in situ. The resultant aqueous suspension of fiber is then flowed onto a screen and formed into a paper web similar as in the manufacture of paper. Such paper containing both cellulose fibers and dextran fibers, which latter are insoluble in water, provides a paper which has important utility in the manufacture of cigarette paper and overcomes the disadvantages of ordinary cellulosic paper as used heretofore for this purpose. By the incorporation of dextran fibers the wet strength and ashing characteristics of the paper is improved over the conventional cellulose types. The paper made in accordance with this invention does not deteriorate upon being wetted with water and maintains its wet strength without the need for incorporating extraneous reinforcing material as has been suggested heretofore to improve the wet strength of cigar-

ette paper and the like. The paper as made in accordance with this invention is not only water-insoluble by reason of the dextran fibers and binder but forms a paper which burns evenly and continuously during smoking of the cigarette and overcomes the disadvantages of rapid deterioration and loss of strength as occurs with the use of ordinary cellulose papers. The ashes from such a cigarette remains substantially coherent with the fiber even after the same is consumed so that the ashes can be retained over a substantial period of time without removal. These advantages are important in the case of smoking tobaccos, cigarettes and the like.

Other methods of shaping the fibrous suspension may be employed. For instance, the suspension may be pulled down by suction onto a form the shape of which it assumes, and dried on the form.

The products may be dyed to any desired shade in any desired color using aqueous or non-aqueous dye solutions or dispersions.

Since various changes and modifications may be made in practicing the invention without departing from the spirit and scope thereof, it is to be understood that it is not intended to limit the invention except as defined in the appended claims.

What is claimed is:

1. The method of making a coherent fibrous paper sheet which comprises preparing an aqueous acid suspension of discontinuous fibers comprising water-insoluble dextran fibers, adding to the suspension an aqueous alkaline solution of water-insoluble dextran whereby as a result of dilution and neutralization of the alkaline solution by the acid containing water of the suspension the dextran is precipitated on the surfaces of the fibers, laying the suspension down on a reticulated screen to remove water therefrom and collect the fibers in the form of a sheet, and drying and finishing the sheet.

2. A method of making fibrous paper web useful as a cigarette paper wrapper which consists in preparing an aqueous acid-containing suspension of discontinuous water-insoluble dextran fibers, distributing an aqueous alkaline solution of water-insoluble dextran, introducing therein an aqueous alkaline solution resulting from dilution and neutralization of an acid-containing water suspension of water-insoluble dextran which is precipitated on the fiber surfaces and bonds the fibers together, forming the suspension into a paper sheet, and drying and finishing the sheet to obtain a paper sheet in which the fibers are bonded together by the water-insoluble dextran carried on the fiber surfaces, said precipitated dextran providing a filler for the cigarette paper.

3. A method of making a cigarette paper which consists of the steps of establishing an acetic suspension of water-insoluble dextran fibers acidified to pH 1.0 to 5.0, introducing an alkali metal hydroxide solution to said suspension to provide approximately 5% by weight of precipitated dextran particles as a binder for said water-insoluble dextran fibers, and flowing the resultant aqueous suspension of fibers onto a screen to remove the excess water and form a continuous fibrous web, calendering the resultant web to obtain a smooth, relatively porous sheet composed of said fibers and which consists of water-insoluble dextran fibers bonded together with dextran.

4. A cigarette paper made in accordance with the method of claim 3.

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