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MOISTURE RESISTANT PAPER

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This invention relates to water resistant or water repellent paper having desirable properties in the dry state, and to a method of manufacturing it.

Paper as it is normally manufactured is readily wetted and tends to lose practically all its strength and to disintegrate on thorough wetting thereof. Accordingly, it is of great importance to increase the "wet strength" of paper. Wet strength paper is ordinarily regarded as paper which retains 40–50% or more of its strength when it becomes thoroughly wet. Such high wet strength paper has assumed a place of considerable importance in the manufacture of bags and other wrappings for wet foods, construction and camouflage paper, map and blue-print paper, toweling, paper fabrics, twine, etc. Nevertheless, the loss of 50–60% of its strength which the available socalled "high wet strength" paper suffers on wetting thereof is appreciably more than is desirable for many purposes, and it is desirable to provide a paper which is not wetted when it is exposed to moisture and therefore retains, in contact with moisture, substantially its dry strength or which, even if possessed of a practical moisture pickup and retention capacity, does not disintegrate readily in the wet state.

Paper may be parchmentized by treatment with sulphuric acid, zinc chloride or the like, but while these treatments impart a certain wet strength to the paper, they also impart stiffness and harshness thereto, rendering the paper brittle in the dry state. Certain resin-forming materials may be incorporated with the paper making fibers in the beater, or may be used to impregnate the paper web, the resinous properties being subsequently developed into paper by aid of heat and a suitable catalyst. Such materials are relatively expensive and if the necessary conditions of temperature, time, concentration, etc. are not strictly controlled, curing of the resin is likely to be more or less incomplete, resulting invariations in the characteristics of the finished paper. Furthermore, these resin treatments tend to render the paper brittle and to make it difficult to fold or wrap it around packages without tearing the paper.

One object of this invention is to provide paper having a predetermined moisture pickup capacity, excellent wet strength when wet, and desirable characteristics in the dry state such as flexibility, softness, and the ability to be mainpulated without tearing. Another object is to provide such a paper economically. A further object is to provide paper having uniform high, dry and wet strength and substantially free from variations due to processes which depend upon curing operations.

These and other objects of the invention are accomplished by associating with the paper, either by incorporation into the paper stock by addition to the beater, or by application to the paper at a subsequent stage in the paper making or after treating processes, a dextran or dextran partial conversion product containing chemically bound radicals derived from higher fatty acids containing 8 to 18, preferably 12 to 18 carbon atoms.

The dextrans are high molecular weight, polysaccharides comprising anhydroglucopyranosidic units joined by molecular structural repeating alpha-1,6 and alpha-non-1,6 linkages, at least 50% of such linkages being apparently, alpha-1,6 linkages. The properties of the dextrans, including the structural repeating alpha-1,6 to alpha-non-1,6 linkages ratios, the molecular weight, the water sensitivity and the osmotic pressure in liquids may vary.

In one method of obtaining a dextran to be esterifield to produce the paper conditioning agents of the invention, there is first prepared an aqueous nutrient medium which may have the following composition:

	Percent by weight
Sucrose	20.0
Corn steep liquor	2.0
Monobasic potassium phosphates	0.5
Manganous sulfate	0.002
Sodium chloride	0.50
Water	Balance

This medium is adjusted to a pH of between about 6.5 and about 7.5, preferably 7.2, and the sterilized material is cooled to room temperature and inoculated with a culture of the dextran-producing bacteria, for instance, *Leuconostos mesenteroides* B–512 (Northern Regional Research Laboratory classification) and incubated at 20° to 30° C. (optimum 25° C.) until a maximum yield of dextran has been attained; normally a period of between 12 and 48 hours will be satisfactory for this procedure. The fermented product contains approximately 80–85% of water and is a thick turbid liquid.

Upon completion of the fermentation, which process renders the material somewhat acid, that is, to a pH of 3.5–5.5 (average 4.2), calcium chloride is added to the ferment to bring the pH thereof to about 7.0 to 8.0. This aids in the precipitation of phosphates. Thereafter, acetone or alcohol, which may be a water-miscible aliphatic, such as methyl, ethyl or isopropyl, is added in sufficient quantity to precepitate the dextran and this brings down, with the dextran, occluded and adsorbed bacteria, and nitrogenous and inorganic elements. To occasion complete precipitation of the dextran it may be desirable to allow the mix to stand for a relatively long period, such as about 6 hours. The precipitated dextran may be dried in any suitable manner, for example by drum drying. Thereafter, it may be reduced to particulate condition.

A purer dextran may be obtained by adding an aliphatic alcohol to the fermented culture at a pH between about 2.5 and 4.5. The precipitate thus obtained may be further purified by again precipitating it with the alchohol. Several precipitations may be performed.

The dextran thus produced is a so-called "native" dextran having a high molecular weight and being, in the particular case, soluble in water at ordinary temperatures.

The higher fatty acid radicals may be introduced into the molecule of high molecular weight dextrans such as the "native" product obtained as described above or an equivalent dextran, or dextrans of high molecular weight may be hydrolyzed to products of lower molecular weight prior to introduction of the fatty acid radicals. The hydrolysis may be effected in any suitable way, as by means of acid or enzymatically. For example, the dextran which is esterified may be obtained by hydrolyzing the initially water-soluble dextran obtained as described above, or a similar high molecular weight dextran, to a product having a molecular weight or average molecular weight in the range between 20,000 and 100,000, fractionating the hydrolysis product, if necessary, to obtain a fraction of preselected uniform or more nearly uniform molecular weight, and purifying the same by known methods for the removal of pyrogens and coloring materials. The

dextran may be a so-called "clinical" dextran such as may be used as a blood plasma extender. In general, the dextran may have a molecular weight between 5,000 and 50×10^6, as determined by light scattering measurements. The dextran to be esterified may be selected on the basis of whether it is to be applied to the paper as an after-coating or added to the heater, those of lower molecular weight being generally preferred when the ester is to be incorporated in the paper-making stock.

The dextran may be obtained by inoculating the culture medium with microorganisms other than that mentioned above. Thus it may be a water-soluble dextran obtained by the use of the microorganisms bearing the following NRRL classifications: *Leuconostoc mesenteroides* B–119, B–1146, B–1190, or a water-insoluble or substantially water-insoluble dextran obtained by the use of *Leuconostoc mesenteroides* B–742, B–1191, B–1196, B–1208, B–1216, B–1120, B–1144, B–523 *Streptobacterium dextranicum* B–1254 and *Betabacterium vermiforme* B–1139.

The dextran is not limited to one prepared under any particular set of conditions, including the microorganism used. It may be produced enzymatically, in the substantial absence of bacteria, by cultivating an appropriate microorganism, for example, *Leuconostoc mesenteroides* B–512 to obtain a dextran producing enzyme, separating the enzyme from the medium in which it is produced, and introducing the enzyme into a medium in which dextran is produced by the action of the enzyme. Also, the dextran may be obtained by bacterial conversion of 1, 4 linkages of dextrin to 1, 6 linkages of dextran. The dextran may be insoluble in water under ordinary conditions but soluble in aqueous alkali solution.

The higher fatty acid radicals may be introduced into the dextran molecule by any appropriate method, to produce the dextran fatty acid esters to be associated with the paper or paper-like product. The esters may be prepared by the methods described in our pending application, Serial No. 351,743, filed April 28, 1953. Thus, the dextran, in the form of a free-flowing, white powder, may be reacted with an esterifying derivative of the higher fatty acid, and preferably a halide such as the chloride thereof, in the presence of an acid acceptor or binding agent such as an organic base, as for instance a heterocyclic tertiary amine of the type of quinoline, pyridine, N-methyl morpholine, etc. and in the presence of a substance in which the reaction product is at least partially solvated, that is dissolved or swollen, as it is formed during the reaction, which results in the reaction mass being maintained in a highly swollen or dissolved state and thus insures substantially uniform, homogeneous reaction between the dextran and the esterifying agent. Substances which dissolve or swell the ester as it is formed are, for example, xylene, toluene, dioxane, etc. In general, the reaction may be carried out at temperatures between 100° C. and 155° C. for time periods varying inversely with the temperature between a half hour and three hours. The ester may be recovered from the crude reaction mixture by washing the latter with water to remove the hydrochloride of the organic base, removing the aqueous layer, adding a solvent for the ester to the residual mass, precipitating the solution into a non-solvent for the ester, such as a lower aliphatic alcohol, and filtering to obtain the ester.

Or the introduction of the higher fatty acid radicals into the dextran molecule may be effected by reacting the dextran with the selected acid in the presence of an "impeller" which may be the anhydride of a monohalogenated monobasic organic acid, e. g., monochloro acetic anhydride, and an esterification catalyst such as magnesium perchlorate at temperatures at which the reaction mixture remains in the liquid state, in general in the range between 50° C. and 100° C. and for a time varying inversely with the temperature between one-half hour and two hours. The ester may be isolated from the crude reaction mass by cooling the mass, dissolving it in a solvent therefor, precipitating it into a non-solvent for the ester, and filtering the ester.

The higher fatty acids which may be used as esterification agent, in the free acid form or in the form of their chlorides, are those containing from 8 to 18 carbon atoms and including caprylic, pelargonic, palmitic, margaric, and stearic acids, and the corresponding chlorides. Two or more of the substantially pure acids, or chlorides thereof, may be used, resulting in the production of mixed dextran esters. Or commercial acids, which comprise mixtures, may be used. For example, commercial or technical grade stearic acid, which comprises a mixture of stearic and palmitic acids, yields dextran stearate-palmitate.

Higher fatty acid esters of the dextran may be produced in which the D. S. (degree of substitution or ratio of the fatty acid radicals to anhydroglucopyranosidic units of the dextran) is from less than 1.0 up to 3.0, by using the fatty acid or its chloride in amounts varying between less than 1.0, say 0.1, and 10 parts thereof by weight per part of dextran. Unlike the dextrans, which are inherently more or less hydrophilic, the fatty acid esters are resistant to moisture to an extent which depends on the D. S., the higher the proportion of the fatty acid radicals per anhydroglucopyranosidic unit, the greater the water resistance. The particular ester or mixed ester associated with the paper may be selected, therefore, to render the paper water repellent or to control the amount of water which is picked up by the paper. Thus, the characteristics of the paper may be predetermined so that, when moisture absorption without disintegration is required, those properties may be imparted to the paper, and when a water repellent paper which is not readily wetted, such as construction paper, is desired, a paper having those properties may be readily produced.

The esters having a D. S. between about 2.5 and 3.0 are definitely hydrophobic and water repellent and are selected when a strongly water resistant paper is required. The partial esters, i. e. those containing free hydroxyl groups, and say, an average of between 1.5 and 2.0 fatty acid radicals per anhydroglucopyranosidic unit are both hydrophilic and hydrophobic. Such esters may be predominantly hydrophilic or predominantly hydrophobic, or the hydrophilic-hydrophobic properties may be essentially balanced. The hydrophilic-hydrophobic esters may be associated with the paper when a paper of high wet strength having the capacity to absorb a certain amount of moisture is desired.

The esters derived from fatty acids having the higher carbon content, i. e., acids having from 12 to 18 carbon atoms, possess a wax-like consistency and are particularly advantageous for the reason that they contribute to the flexibility and workability of the paper while conferring strength thereto coupled with either water repellency or a predetermined moisture absorption capacity.

The dextran ester and the paper making fibers may be mixed by a method suitable to the production of a particular type of paper. The mixture of fibers and the higher fatty acid ester of the dextran may be formed into a web in any suitable way, for example, by the use of machines of various types such as the "Fourdrinier," Harper, single cylinder or "Yankee" multi-vat machine, mold, "press pate" or the like.

Generally speaking, in preparing the furnish or load when dextran ester is mixed with the fibers in the beater it is preferable to disperse the ester in the aqueous suspension of the fibers, but in some cases the fibers and ester may be beaten together. In accordance with one embodiment of the invention, the dextran ester and the fibers are mixed and the mixture is stirred or beaten only long enough to insure that the ester is substantially uniformly distributed through the fiber suspension. The ester provides the fibers with a coating which serves as a binder for them, presenting the possibility of eliminating the prolonged conventional beating usually resorted to for

the purpose of hydrating and fibrillating the fibers, or of reducing the beating time, and thus producing paper products in which the fibers are non-hydrated and undergraded and bound together by waterproof or water resistant dextran fatty acid ester. The possibility of making a coherent paper without depending on fibrillation and interlocking of the fibrillae, permits the production of paper products comprising or composed of smooth-surfaced artificial or synthetic fibers which normally are not used in paper making for the reason that they do not fibrillate on beating and therefore do not comprise fibrillae which interlock and hold the fibers together when the furnish is laid down on a paper-making screen.

The amount of ester mixed with the fibers may be between 1% and 5% by weight, or higher.

In accordance with another embodiment of the invention, the paper is coated with the fatty acid ester of the dextran or dextran conversion product dispersed or dissolved in a suitable medium. For example, the paper, after calendering thereof may be coated with a solution of a higher fatty acid ester of a dextran, such as dextran palmitate or dextran stearate in a halogenated hydrocarbon such as chloroform or carbon tetrachloride, or with a solution thereof in an aromatic hydrocarbon such as benzene, toluene or xylene. The coating may be applied by passing the paper through the solution, or by spraying or brushing the solution on the paper.

The paper coated may be any conventional paper, such as that made by the sulfate, soda or sulfite process, or from rag pulp, cotton linters, or the base may be a web of discontinuous fibers such as the paper-like products which are sometimes described as "non-woven" fabrics.

Solutions of ester of from 1% to 5% or more by weight may be used, the higher concentration, as much as up to 10% by weight, being generally preferred if stiffer paper products are desired. On evaporation of the solvent, the paper product or base is provided with a more or less completely water resistant film which is firmly adherent to the base and which imparts a smooth surface to it, especially when the ester is derived from a fatty acid of the higher carbon content and exhibits the more pronounced wax-like properties.

The paper of this invention may be used in water, dried, and reused a number of times without disintegrating. It is useful as toweling, drapery substitute, filtering material, twisting paper, disposable sheet material, impregnating paper, etc. The esters may be used for modifying the moisture pick-up capacity and hence the wet strength of all kinds of paper including tissue paper, writing paper, book paper, bank note paper, wrapping paper; boards including Bristol board, wall board and box board, building felts and the like may be improved. The term "paper product" as used in the claims is intended to include all such papers, layers, tubes and molded articles of all kinds which are capable of being fabricated from paper making fibers and whether the ester is applied to the paper base as a coating or distributed through the base, or both.

The paper comprising the dextran higher fatty acid ester has satisfactory printing qualities.

By way of illustration, the following examples of specific embodiments of the invention are given:

Example I

To beaten paper stock there is added, at the wet end of the paper-making machine, an aqueous dispersion of dextran palmitate having a D. S. of about 1.2 palmitoyl radicals per anhydroglucopyranosidic unit of the dextran, and derived from a dextran having a molecular weight of about 20,000, to introduce about 5% by weight of the ester into the stock. The furnish or charge is then sheeted in a known manner on a Fourdrinier paper machine. The paper is processed in the usual manner. A finished paper having high dry and wet tearing and bursting strength and modified moisture-pickup and retention capacity is obtained.

Example II

A sheet of bleached kraft paper is passed through a treating bath comprising a 5% chloroform solution of dextran palmitate containing an average of 2.9 palmitoyl groups per anhydroglucopyranosidic unit of the dextran. The paper is passed between doctor blades arranged to remove excess treating medium from the opposite surfaces of the paper, and then dried. A finished water-repellant paper sheet having a smooth surface, good flexibility, and high dry and wet tearing and bursting strength is obtained.

Although the invention has been described in detail in connection with the higher fatty acid esters of the dextrans, esters of dextran conversion products may be used instead of or in addition to the dextran esters. By "dextran conversion products" is meant low-substituted dextran having at least some free hydroxyl groups and in which the substituent groups are groups or radicals other than the saturated fatty acid radicals of 8 to 18 carbon atoms. The low-substituted dextran or dextran partial conversion products contemplated are those which, prior to the introduction of the radicals derived from the fatty acids of 8 to 18 carbon atoms, contain other chemically bound radicals or groups such as lower acyl radicals, i. e. acyl radicals of from 1 to 5 carbon atoms, alkyl radicals of from 1 to 5 carbon atoms, aralkyl radicals containing a total of from 7 to 10 carbon atoms, and carboxyalkyl radicals in which the alkyl portion contains from 1 to 5 carbon atoms. The dextran conversion product may be a dextran acetate, propionate, butyrate, etc., an ethyl, methyl, or benzyl dextran, etc., or a carboxymethyl dextran. In the higher fatty acid esters of the dextran conversion product, the average ratio of lower acyl, alkyl, aralkyl or carboxyalkyl groups to anhydroglucopyranosidic units of the dextran may be from less than 1:1 to 1.5:1, and the average ratio of acyl radicals derived from fatty acids of 8 to 18 carbon atoms to anhydroglucopyranosidic units of the dextran may be from less than 1:1 to 2.9:1.

Preferably, in the esters of the conversion products, the ratio of the higher fatty acid radicals to anhydroglucopyranosidic units is from less than 1:1 to about 2.5:1. The dextran esters have a natural affinity for the paper base and adhere to it tenaciously.

It may be desirable, when the ester is added to the beater or at the wet end of the machine, and for more ready dispersion of the ester in the aqueous mass, especially when the ester is derived from a dextran of the higher molecular weights, to use a higher fatty acid ester of a carboxymethyl dextran.

Since modifications in the paper or paper-like articles embodying the invention, and changes in carrying out the process for producing the articles may be made without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of a dextran having, initially, at least some free hydroxyl groups, with a fatty acid containing from 8 to 18 carbon atoms.

2. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of a dextran having, initially, at least some free hydroxyl groups, with a fatty acid containing from 12 to 18 carbon atoms.

3. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of a dextran having, initially, at least some free hydroxyl groups, with palmitic acid.

4. Calendered paper characterized by increased mois-

ture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of a dextran having, initially, at least some free hydroxyl groups, with stearic acid.

5. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with a fatty acid containing from 8 to 18 carbon atoms, said ester containing an average of 2.5 to 3.0 radicals derived from the fatty acid per anhydroglucose unit of the dextran.

6. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with a fatty acid containing from 12 to 18 carbon atoms, said ester containing an average of 2.5 to 3.0 radicals derived from the fatty acid per anhydroglucose unit of the dextran.

7. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with palmitic acid, said ester containing an average of 2.5 to 3.0 palmitoyl radicals per anhydroglucose unit of the dextran.

8. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with stearic acid, said ester containing an average of 2.5 to 3.0 stearoyl radicals per anhydroglucose unit of the dextran.

9. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of carboxymethyl dextran with palmitic acid.

10. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of carboxymethyl dextran with stearic acid.

11. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with a fatty acid of 12 to 18 carbon atoms, said ester containing an average of about 2.9 radicals derived from fatty acids per anhydroglucose unit of the dextran.

12. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with palmitic acid, said ester containing an average of about 2.9 palmitoyl radicals per anhydroglucose unit of the dextran.

13. Calendered paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran with stearic acid, said ester containing an average of about 2.9 stearoyl redicals per anhydroglucose unit of the dextran.

14. The method of increasing the moisture resistance of calendered paper comprising the steps of applying to the paper a composition consisting essentially of a solution of an ester of dextran having, initially, at least some free hydroxyl groups with a fatty acid containing from 8 to 18 carbon atoms, in a halogenated hydrocarbon solvent for the ester, and then drying the product to leave thereon an adherent coating of the dextran ester.

15. The method of coating paper products according to claim 14, characterized in that the hydrocarbon solvent for the ester is an aromatic hydrocarbon.

16. The method of increasing the moisture resistance of calendered paper comprising the steps of applying to the paper products a composition consisting essentially of a solution of an ester of dextran with palmitic acid containing an average of 2.5 to 3.0 palmitoyl radicals per anhydroglucose unit of the dextran in the halogenated hydrocarbon solvent for the ester, and then drying the product to leave thereon an adherent coating of dextran palmitate.

17. The method of increasing the moisture resistance of calendered paper which comprises the steps of applying to the paper a composition consisting essentially of a solution of an ester of dextran with stearic acid containing an average of 2.5 to 3.0 stearoyl radicals per anhydroglucose unit of the dextran in the halogenated hydrocarbon solvent for the ester, and then drying the product to leave thereon an adherent coating of dextran stearate.

18. Paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran having, initially, at least some free hydroxyl groups, with a fatty acid containing from 8 to 18 carbon atoms.

19. Paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran having, initially, at least some free hydroxyl groups, with palmitic acid.

20. Paper characterized by increased moisture resistance imparted thereto by an adherent coating thereon consisting essentially of an ester of dextran having, initially, at least some free hydroxyl groups, with stearic acid.

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