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3,116,199 WATER-LAID WEB

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14 Claims. (Cl. 162—146)

This invention relates to a method of forming water-laid fibrous products containing fibers formed of carboxyalkyl cellulose ethers.

In the conventional production of water-laid fibrous products such as papers, naturally occurring cellulose fibers such as wood pulp, cotton linters and the like are mechanically hydrated as by heating and mixing in a paper mill beater in the presence of a large excess of water. In forming a pulp slurry as by a beating operation, the fibers become hydrated and exhibit a microscopic and sub-microscopic peeling of individual fibrils along the surface of the fibers and at the ends of the fiber bundles without chemically altering the fiber. The slurry is then passed to a suitable screen to lay down the fibers as a sheet or mat. The physical properties of the sheet such as strength, tear and burst are dependent to a large extent on an interlocking of the hydrated fibers and of the fibrillae on the fibers and a fiber-to-fiber bonding which develops upon drying. The physical properties of the water-laid sheets are directly dependent upon the properties of the fibers and the paper-making process. In general, the natural cellulosic fibers classed as paper-making fibers vary in both diameter and length generally being from about 0.030 mm. to about 0.012 mm. in diameter and from about 0.5 mm. to about 4 mm. in length. The fibers are produced by nature and their physical properties cannot be altered at will although the properties may be altered within a given narrow range as by the choice of the raw material, the specific pulping process and the specific paper-making process variables.

Synthetically produced organic fibers offer many functional advantages in the production of water-laid products because it is possible to accurately provide fibers of any desired diameter and length and of an extremely wide range of physical properties. In general, however, the synthetic organic fibers do not have the fibrillatable structure which characterizes natural cellulose fibers and, accordingly, they do not exhibit natural fiber characteristics when beaten and mixed in a large excess of water as in a paper mill beater. Hence, in this sense, the formation of water-laid sheets of these synthetic non-fibrillatable fibers per se is unattainable because of intimate interlocking of the fibers can be effected and there is very little, if any, fiber-to-fiber bonding prior to drying or after drying such water-laid sheet. Many of the synthetic organic fibers are difficult to disperse in water and tend to agglomerate so that when they are laid down from a slurry as a water-laid sheet, they are said to exhibit a very poor sheet formation, particularly where the fibers are of a length greater than about 1/4 inch. In some methods, synthetic fibers are employed in the manufacture of water-laid sheets but it is necessary to employ dispersing agents and adjust the paper-making process variables if uniform sheet formation must be attained. This is a rather costly operation particularly when dispersing agents are em-

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ployed because a large portion of the dispersing agent is lost in the white water.

In order to obtain desired physical characteristics of water-laid sheets and impart desired characteristics, it is often necessary to utilize costly high grade paper pulps and incorporate in the sheet various types of binding or bonding materials. Where the binding materials are incorporated in the fiber slurry, a large portion of the binder is lost in the white water during sheet formation. Alternatively, the binding material, where it is water-soluble or water-dispersible, may be incorporated in the wet or dry sheet by impregnation. Impregnation, however, requires additional operational procedures and equipment. As further alternatives, the binding or bonding agent may be in the form of a powder-like material which is dusted on the sheet, or thermoplastic fibers may be incorporated in the sheet. Where thermoplastic binding or bonding agents are utilized, it is necessary to subject the sheet at some stage in its manufacture to a heating and pressing operation to activate the agent. In general, the incorporation of binding materials or agents particularly gel-type binding materials reduces the porosity of water-laid products and thermoplastic-type binding or bonding agents impart certain stiffness and harshness which for many purposes is undesirable.

In the copending application of Battista, Cruz and Reichel, Serial No. 67,019, filed November 3, 1960, there is disclosed and claimed water-laid fibrous sheets and methods of forming such sheets by utilizing a synthetic, homogeneous, hydrophilic fibrous binder having predetermined physical characteristics and bonding power. This type of fibrous binder is formed of water-insoluble, alkali-soluble cellulose ethers having a degree of substitution of from at least about 0.10 to about 0.60, one group of which is water-insoluble, alkali-soluble carboxyalkyl cellulose ethers. In accordance with the disclosure of this copending application, the water-laid fibrous sheet is formed by incorporating in a fiber slurry the fibrous binders without any other alteration in the conventional methods employed in normal paper-making operations. The products may consist entirely of the fibers constituting the fibrous binder or the products may include other natural or synthetic fibers or mixtures of the various classes of fibers.

One of the purposes of the present invention is to provide a method of forming water-laid fibrous sheets comprising fibers formed of carboxyalkyl cellulose ethers as hereinbefore described whereby the sheets have improved physical properties.

Other objects and advantages of the present invention will become apparent from the description and claims which follow.

The present invention is based upon our discovery that water-laid fibrous sheets comprising synthetic, homogeneous, hydrophilic fibrous binders formed of water-insoluble, alkali-soluble carboxyalkyl cellulose ethers having a degree of substitution of from at least about 0.10 to about 0.60 have enhanced physical properties when the water-laid products are formed from a fiber slurry having a pH above substantially neutral pH to about pH 10.5.

As pointed out in the above-identified copending application, it has been proposed to utilize chemically altered natural cellulose fibers in forming water-laid webs. In

many respects, only the surfaces of such fibers are altered chemically and the composition of the fibers is therefore not homogeneous throughout the fiber. This type of fiber may replace some of the binding or bonding agents which are frequently employed in increasing the dry strength of water-laid fibrous sheets. Where the water-laid fibrous sheet is formed entirely of the chemically altered natural cellulose fibers, such as etherified natural fibers, the optimum physical properties of the water-laid sheets are obtained when the etherified fibers have a degree of substitution of about 0.20. The physical properties of the sheet level off or decrease from the optimum values as the degree of substitution increases above this figure. In this prior art practice, it was essential that the ether formed on and with the cellulose of the fiber be a hydroxyalkyl ether.

As disclosed in the copending application, the strength characteristics of water-laid fibrous sheets formed from the synthetic, homogeneous, hydrophilic binder fibers increase with an increase in the degree of substitution of the cellulose ethers from which the binder fibers are formed and the strength characteristics of water-laid sheets formed in accordance with the present invention follow the same general pattern.

The present method is applicable only to the fibrous binders which are synthetically formed from a carboxyalkyl ether of cellulose such as carboxymethyl cellulose, carboxyethyl cellulose, carboxypropyl cellulose and the like. The homogeneous, fibrous binders are formed synthetically from an alkali solution of a water-insoluble, alkali-soluble carboxyalkyl ether of cellulose having a degree of substitution of at least about 0.10 to about 0.60 preferably between about 0.30 and about 0.50. The degree of substitution, commonly designated as D.S., is the number of substituent groups per anhydroglucose unit of cellulose. For the purposes of the present invention, it has been discovered that when the D.S. is below about 0.10, the synthetically produced binder fibers do not have a sufficient hydrophilic bonding action to appreciably affect the properties of the water-laid sheets. On the other hand, where the D.S. exceeds about 0.60, the fibers when mixed in water tend to lose their fiber characteristics.

The carboxyalkyl ether of cellulose may be formed by any desired method. Examples of methods for the preparation of this class of cellulose ether as disclosed in U.S. Patents 2,511,060 and 2,577,844. An alkali solution of the ether is extruded through a spinneret into a conventional coagulating and spinning bath such as an aqueous solution of sulfuric acid and sodium sulfate to form filaments of predetermined diameter which are then cut to any desired length. As is well known, the diameter and lengths may be varied at will and the strength characteristics of the filaments and fibers may likewise be varied within limits by the selection of a specific cellulose ether, by the degree of substitution of the ether and by the spinning conditions. The properties and characteristics of the synthetic fibers may be accurately and reproducibly predetermined. These variations and modifications are well known to those skilled in the art and, since they form no part of the present invention, no detailed discussion is included herein. The length of the fibers for the purposes of the present invention may be from about 1/4 inch to 2 and 3 inches or any other desired length. Normal paper-making methods generally employ fibers of not more than 1/4 inch. However, this length is based largely upon historical development because paper-making fibers are generally of a length of not more than about 1/4 inch.

The synthetic, homogeneous, hydrophilic binder fibers formed of the carboxyalkyl cellulose ethers differ in many respects from chemically altered natural fibers in that they will be homogeneous in chemical composition, uniform in physical properties, uniform in diameter and uniform in length for any particular application whereas chemically altered natural cellulose fibers will vary in

composition, properties, diameter and length. Advantageously, the carboxyalkyl cellulose ether binder fibers are preferably, but not necessarily, employed in the wet gel state, that is, in a never-dried condition, and when added to the fiber slurry or to the water, they are in a swollen or highly swollen condition. The synthetic, fibrous binders do not become fibrillated as do natural paper-making fibers so that when they are to be mixed or blended with natural paper-making fibers, they may be added in the heater after the natural fibers have been beaten, the beater then serving solely as a mixer. When these synthetic binder fibers are blended with other non-fibrillatable fibers, all of the fibers may be blended in the beater, the beater serving solely as a mixer.

The degree of swelling and the gelatinous condition of the particular carboxyalkyl cellulose ether fibrous binder will be dependent largely upon the degree of substitution of the cellulose ether from which the fibers were formed. For example, undried synthetic fibers formed of a carboxyethyl cellulose having a D.S. of about 0.135 are in a swollen state; synthetic fibers formed of a like ether having a D.S. of about 0.3 are in a highly swollen, semi-gelatinous state; and synthetic fibers formed of a like ether having a D.S. of about 0.5 are in a very highly swollen, almost gelatinous state.

The synthetic binder fibers are readily dispersed in water and appear to aid in dispersing other fibers, both natural and other forms of synthetic fibers, in preparing the fiber slurry and are highly compatible with both naturally occurring fibers and with other synthetic fibers. Because of the swollen or almost gelatinous condition and their ready dispersibility, their presence results in an exceedingly uniform sheet formation when sheeted either by themselves or when mixed or blended with other fibers.

Upon drying the water-laid fiber sheets comprising or containing the carboxyalkyl cellulose ether fibrous binder, a high degree of fiber-to-fiber bonding occurs because of the initial swollen and somewhat gelatinous state of these synthetic fibers. The amount of fiber-to-fiber bonding varies directly with the D.S. of the carboxyalkyl cellulose ethers from which the binder fibers are formed. This property or characteristic is readily demonstrated by measuring certain physical properties of handsheets formed from such synthetic fibers. Standard paper laboratory techniques utilizing the Noble and Wood cycle beater to form the fiber slurry and the Noble and Wood sheet-mold to form handsheets in accordance with the standard TAPPI methods may be employed.

Handsheets were prepared from fibers produced from carboxyethyl cellulose ethers formed in accordance with the method disclosed in Patent No. 2,577,844. Briefly, viscose containing 9% cellulose, 6% caustic soda and 31% carbon disulfide based on the weight of the cellulose and having a sodium chloride salt test of 5 was mixed with acrylonitrile, the amount of acrylonitrile being 2%, 4% and 6% based upon the weight of the viscose. After each sample was mixed at room temperature for one hour, the acrylonitrile-viscose mixtures were held for 24 hours at atmospheric pressure and room temperature. The viscoses were then mixed again for one hour to complete the reaction and to drive off ammonia gas. After deaeration overnight at 18° C., the reacted viscoses were spun into an aqueous spinning bath containing 12% sulfuric acid, 5% zinc sulfate and 20% sodium sulfate at a temperature of 50° C. and at a spinning speed of 50 meters per minute to form a tow of about 1100 denier, 980 filaments. From the spinning bath, the filaments were passed through a cascade, the bath containing about 4% sulfuric acid, 1.3% zinc sulfate and 3% sodium sulfate maintained at 85° C. where they were stretched approximately 100%. The filaments were then washed and dried on drums and collected on cones. The filaments thus formed had diameters of 12 to 13 microns and were cut to 1/4 inch lengths.

In Table I which follows, it will be noted that the

handsheets prepared from the viscose to which 2% acrylonitrile had been added (carboxyethyl cellulose, about a D.S. of 0.02) were too weak for test purposes. Sample B formed from the viscose to which 4% acrylonitrile (carboxyethyl cellulose, about a D.S. of 0.063) had been

at Marcus Hook, Pennsylvania had a pH of about 7.5. In the course of a year, the pH of the tap water varies between about 6.5 and about 7.5 and, for the purposes of this invention, this range is considered as "a substantially neutral pH."

Table II

Sample	pH	Agent	Ream Weight (lbs.)	Breaking Length (meters)	Tear Factor	Burst Factor	Elongation (percent)	Caliper (mils)	Specific Vol.
D-----	4.4	H ₂ SO ₄ -----	44.3	2,929	201	20	3.1	6.3	2.6
E-----	4.6	Alum.-----	44.3	2,550	234	17	2.3	7.2	2.0
F-----	7.5	H ₂ O-----	43.9	2,015	287	21	2.1	7.6	3.1
G-----	8.2	Ca(OH) ₂ -----	42.9	3,546	101	30	3.5	5.8	2.4
H-----	8.7	NaOH-----	43.4	3,626	88	30	3.6	5.7	2.4

added, formed sheets which could be tested but such sheets do not have satisfactory strength characteristics. On the other hand, Sample C fibers formed from the viscose to which had been added 6% acrylonitrile formed satisfactory handsheets. It will be noted that this modified viscose formed carboxyethyl cellulose having a degree of substitution of approximately 0.135 which is somewhat above the lower limit of a satisfactory degree of substitution for the purposes of this invention. The data as noted above also indicates that as the D.S. increases, the dry bonding power increases. The ream weight is the calculated weight for 500 sheets each 25 inches by 40 inches. The tensile strength is expressed as breaking length in meters (based on a 15 mm. strip) and is calculated using the formula

$$\frac{47,400 \times p}{\text{Ream weight in lbs.}} \text{ or } \frac{21,500 \times p}{\text{Ream weight in lbs.}}$$

where *p* is the breaking load of a 15 mm. strip in kilograms or where *P* is the breaking load of a 15 mm. strip in pounds. The

$$\text{Burst factor} = \frac{50 \times \text{Mullen burst in p.s.i.}}{\text{Ream weight in lbs.}}$$

These factors are used herein to convert the actual measurements to the TAPPI standard ream weight.

Table I

Sample	Percent ACN	D.S.	Ream Wt., lbs.	Breaking Length (meters)	Tear Factor	Burst Factor	Percent Elongation	Caliper (mils)	Specific Vol.
A-----	2				Too weak to test				
B-----	4	0.063	42.9	1,142	144	8	1.2	8.6	3.62
C-----	6	0.135	42.0	2,327	296	18	1.9	6.6	2.84

Percent ACN—percent acrylonitrile added to the viscose.

Handsheets cannot be prepared by standard TAPPI methods from all carboxyalkyl cellulose fibers wherein the ether has a D.S. at or close to the upper portion of the range because the sheeted fibers on collection are so highly swollen and gelatinous in nature that they become extruded through the screen upon application of pressure.

The effect of the pH of the slurry or furnish upon the physical characteristics of water-laid webs containing the carboxyalkyl cellulose fibrous binders is readily demonstrated by the measurement of the strength characteristics of handsheets prepared from fibers formed from carboxyethyl cellulose fibers of the type described hereinbefore. Carboxyethyl cellulose fibers having diameters of 12 to 13 microns and formed from viscose to which had been added 6% acrylonitrile were prepared as described in connection with Table I. The cellulose ether had a D.S. of approximately 0.135. Handsheets were formed from slurries whose pH values were adjusted by the use of various agents and the handsheets then subjected to conventional physical test methods. The results of these tests are presented in Table II. No adjustment of the pH of the slurry was made in the case of Sample F, the water being ordinary tap water which at the time of the tests

Similarly, for any specific proportion of fibrous binder, the strength characteristics of the products of the fiber blends will vary directly with an increase in the pH above substantially neutral pH of the fiber slurry or furnish, and with the degree of substitution of the cellulose ether. The strength characteristics relative to the pH will vary as illustrated in Table II.

In Table III which follows, there is illustrated the increase in physical properties with an increase in the proportion of carboxyalkyl ether fibers. Handsheets were formed from viscose rayon fibers (designated as Fiber R) and from blends of viscose rayon fibers (Fiber R) and carboxyethyl cellulose fibers (designated as Fiber X) having a D.S. of 0.135 as described hereinbefore. The rayon fibers were of a high tenacity, textile grade viscose rayon having a relatively thick skin and relatively smooth surfaces. All of the fibers had diameters of 12 to 13 microns and were cut to ¼ inch lengths. The handsheets were prepared in accordance with standard TAPPI procedures and were subjected to the standard physical testing procedures as described. The slurries from which the handsheets were formed were prepared with tap water having a pH of about 7.5. As the pH of the slurries is in-

creased, the improvements in strength characteristics increase as illustrated in Table II.

boxyalkyl cellulose ether fibrous binders with viscose rayon or with natural paper-making fibers, the improve-

Table III

Fiber X (percent)	Fiber R (percent)	Ream Weight (lbs.)	Breaking Length (meters)	Tear Factor	Burst Factor	Elonga- tion (percent)	Caliper (mils)	Specific Vol.
100-----	0	42.0	2,327	299	18	1.9	6.6	2.84
75-----	25	42.9	1,872	295	12	1.8	7.5	3.16
50-----	50	43.4	1,353	262	12	1.5	8.2	3.41
25-----	75	43.9	664	146	6	1.3	9.0	3.70
0-----	100		No measurable strength					

Like results are obtained with other types of rayon fibers and other synthetic organic fibers. The specific physical characteristics will vary because of variations in the physical characteristics and properties of the different specific forms of viscose rayon or other synthetic fibers. For example, when low tenacity, thin skinned viscose rayon fibers are substituted for the high tenacity rayon fibers, the physical properties of the blends of fibers will, of course, be lower than those set forth in the table.

Like results are also obtained when the carboxyalkyl cellulose ether fibers are blended with natural paper-making fibers. The physical strength characteristics of the fibrous products will vary directly with the proportion of the carboxyalkyl cellulose ether binder fibers, with the degree of substitution of the cellulose ether from which the binder fibers are formed and will also vary directly as the pH is increased above substantially neutral pH. The specific strength characteristics will, of course, be dependent upon the specific natural paper-making fibers employed in the blends and the relative proportions of the cellulose ether fibers and paper-making fibers.

As pointed out in the above-identified copending application, synthetic fibers, such as, for example, rayon fibers, are difficult to disperse in water because they tend to agglomerate. Various dispersing agents may be incorporated in a slurry to aid in their dispersion and the fibers then deposited on a screen to form a fairly uniform sheet. The fibrous binders formed of the carboxyalkyl cellulose ethers may replace the dispersing agents and they aid in dispersing rayon and other synthetic fibers. Wet water-laid sheets formed of all viscose rayon fibers of the conventional textile types require special handling to permit their removal from a collecting screen. If such sheets are first dried and then removed from the screen, the sheets have no measurable tensile strength, tear factor and burst factor. Fibrous binders formed of the carboxyalkyl cellulose ethers, when incorporated in the slurry with rayon fibers in an amount as low as 1% by weight of the rayon fibers, provide wet water-laid sheets having sufficient strength to permit ready removal from a collecting screen and the dried sheets so formed have measurable strength characteristics and the strength characteristics may be enhanced by sheeting the fiber mixture from a furnish having the contemplated higher pH's.

Many different embodiments of the invention will be apparent and obvious to those skilled in the art and may be made without departing from the spirit and scope of the invention. It is to be understood that the foregoing specific embodiments are included merely as illustrative and are not intended as limitations. For example, in the foregoing discussion and in the specific examples, the fibers employed had diameters of from 12 to 13 microns and were cut to 1/4 inch lengths. These dimensions were selected merely as a matter of convenience. As pointed out hereinbefore, the fibrous binder may be of any desired length and any desired diameter. Likewise, the products may be of any desired thickness and may vary from soft, porous, non-woven webs to harsh, relatively non-porous, parchment-like webs, the latter being formed of substantially all carboxyalkyl cellulose ether fibers having degrees of substitution in the upper portion of the stated range. Although specific reference is made to blends of the car-

ment in strength characteristics are also obtained when the fibrous binders are blended with other synthetic fibers and other natural fibers or mixtures of synthetic and natural fibers and the water-laid products are laid down from slurries or furnishes having pH's within the stated range.

We claim:

1. In a method of producing water-laid, fibrous products from dispersions containing synthetic, homogeneous, hydrophilic fibrous binders formed of a water-insoluble, alkali-soluble carboxyalkyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, the step of sheeting the fibers of the dispersion to form a water-laid fibrous product from a dispersion having a pH above substantially neutral pH but not exceeding about pH 10.5.

2. The step in the method as defined in claim 1 wherein the carboxyalkyl cellulose ether is carboxymethyl cellulose ether.

3. The step in the method as defined in claim 1 wherein the carboxyalkyl cellulose ether is carboxyethyl cellulose ether.

4. The step in the method as defined in claim 1 wherein the carboxyalkyl cellulose ether is carboxypropyl cellulose ether.

5. In a method of producing water-laid fibrous products, the steps which comprise forming a dispersion of fibers in an aqueous medium having a pH above substantially neutral pH but not exceeding about pH 10.5, at least 1% by weight of the dispersed fibers being formed of a water-insoluble, alkali-soluble carboxyalkyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, sheeting the fibers to form a fibrous product and drying the product.

6. The steps in a method as defined in claim 5 wherein the carboxyalkyl cellulose ether is carboxymethyl cellulose ether.

7. The steps in a method as defined in claim 5 wherein the carboxyalkyl cellulose ether is carboxyethyl cellulose ether.

8. The steps in a method as defined in claim 5 wherein the carboxyalkyl cellulose ether is carboxypropyl cellulose ether.

9. In a method of producing water-laid fibrous products, the steps which comprise forming a dispersion of fibers in an aqueous medium having a substantially neutral pH, at least 1% by weight of the dispersed fibers being formed of a water-insoluble, alkali-soluble carboxyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, adjusting the pH of the aqueous medium to a pH above substantially neutral pH but not exceeding about pH 10.5, sheeting the fibers to form a fibrous product and drying the product.

10. The steps in a method as defined in claim 9 wherein the carboxyalkyl cellulose ether is carboxymethyl cellulose ether.

11. The steps in a method as defined in claim 9 wherein the carboxyalkyl cellulose ether is carboxyethyl cellulose ether.

12. The steps in a method as defined in claim 9 wherein the carboxyalkyl cellulose ether is carboxypropyl cellulose ether.

handsheets prepared from the viscose to which 2% acrylonitrile had been added (carboxyethyl cellulose, about a D.S. of 0.02) were too weak for test purposes. Sample B formed from the viscose to which 4% acrylonitrile (carboxyethyl cellulose, about a D.S. of 0.063) had been

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H-----	8.7	NaOH-----	43.4	3,626	88	30	3.6	5.7	2.4

added, formed sheets which could be tested but such sheets do not have satisfactory strength characteristics. On the other hand, Sample C fibers formed from the viscose to which had been added 6% acrylonitrile formed satisfactory handsheets. It will be noted that this modified viscose formed carboxyethyl cellulose having a degree of substitution of approximately 0.135 which is somewhat above the lower limit of a satisfactory degree of substitution for the purposes of this invention. The data as noted above also indicates that as the D.S. increases, the dry bonding power increases. The ream weight is the calculated weight for 500 sheets each 25 inches by 40 inches. The tensile strength is expressed as breaking length in meters (based on a 15 mm. strip) and is calculated using the formula

$$\frac{47,400 \times p}{\text{Ream weight in lbs.}} \text{ or } \frac{21,500 \times p}{\text{Ream weight in lbs.}}$$

where p is the breaking load of a 15 mm. strip in kilograms or where P is the breaking load of a 15 mm. strip in pounds. The

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These factors are used herein to convert the actual measurements to the TAPPI standard ream weight.

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Percent ACN—percent acrylonitrile added to the viscose.

Handsheets cannot be prepared by standard TAPPI methods from all carboxyalkyl cellulose fibers wherein the ether has a D.S. at or close to the upper portion of the range because the sheeted fibers on collection are so highly swollen and gelatinous in nature that they become extruded through the screen upon application of pressure.

The effect of the pH of the slurry or furnish upon the physical characteristics of water-laid webs containing the carboxyalkyl cellulose fibrous binders is readily demonstrated by the measurement of the strength characteristics of handsheets prepared from fibers formed from carboxyethyl cellulose fibers of the type described hereinbefore. Carboxyethyl cellulose fibers having diameters of 12 to 13 microns and formed from viscose to which had been added 6% acrylonitrile were prepared as described in connection with Table I. The cellulose ether had a D.S. of approximately 0.135. Handsheets were formed from slurries whose pH values were adjusted by the use of various agents and the handsheets then subjected to conventional physical test methods. The results of these tests are presented in Table II. No adjustment of the pH of the slurry was made in the case of Sample F, the water being ordinary tap water which at the time of the tests

It is quite apparent from this table that the strength characteristics particularly as measured by the breaking length and by the burst factor are substantially improved as the pH is increased above "a substantially neutral pH." Although this example merely illustrates the effect of the pH of the furnish on handsheets formed of carboxyethyl cellulose fibers having a D.S. of 0.135, like improvements are obtained with other carboxyalkyl cellulose ethers within the D.S. range as set forth hereinbefore.

The improvements are not limited to water-laid webs formed entirely of the carboxyalkyl cellulose ether fibers. This group of fibers may be utilized as fibrous binders in combination with other fibers, both synthetic and natural fibers. In such blends of fibers, the dry bonding power of the carboxyalkyl cellulose fibrous binders also varies with the increase in the pH of the slurry or furnish above a substantially neutral pH and with the degree of substitution of the carboxyalkyl cellulose ether.

It is well known that water-laid sheets, such as handsheets prepared in accordance with standard TAPPI procedures and formed entirely of viscose rayon filaments have no measurable strength characteristics. By incorporating fibrous binders formed of carboxyalkyl cellulose ethers, water-laid products may be formed having strength characteristics which will be dependent directly upon the proportion of the fibrous binder in the blend of fibers.

Similarly, for any specific proportion of fibrous binder, the strength characteristics of the products of the fiber blends will vary directly with an increase in the pH above substantially neutral pH of the fiber slurry or furnish, and with the degree of substitution of the cellulose ether. The strength characteristics relative to the pH will vary as illustrated in Table II.

In Table III which follows, there is illustrated the increase in physical properties with an increase in the proportion of carboxyalkyl ether fibers. Handsheets were formed from viscose rayon fibers (designated as Fiber R) and from blends of viscose rayon fibers (Fiber R) and carboxyethyl cellulose fibers (designated as Fiber X) having a D.S. of 0.135 as described hereinbefore. The rayon fibers were of a high tenacity, textile grade viscose rayon having a relatively thick skin and relatively smooth surfaces. All of the fibers had diameters of 12 to 13 microns and were cut to 1/4 inch lengths. The handsheets were prepared in accordance with standard TAPPI procedures and were subjected to the standard physical testing procedures as described. The slurries from which the handsheets were formed were prepared with tap water having a pH of about 7.5. As the pH of the slurries is in-

creased, the improvements in strength characteristics increase as illustrated in Table II.

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50-----	50	43.4	1,358	262	12	1.5	8.2	3.41
25-----	75	43.9	664	146	6	1.3	9.0	3.70
0-----	100		No measurable strength					

boxyalkyl cellulose ether fibrous binders with viscose rayon or with natural paper-making fibers, the improve-

Like results are obtained with other types of rayon fibers and other synthetic organic fibers. The specific physical characteristics will vary because of variations in the physical characteristics and properties of the different specific forms of viscose rayon or other synthetic fibers. For example, when low tenacity, thin skinned viscose rayon fibers are substituted for the high tenacity rayon fibers, the physical properties of the blends of fibers will, of course, be lower than those set forth in the table.

Like results are also obtained when the carboxyalkyl cellulose ether fibers are blended with natural paper-making fibers. The physical strength characteristics of the fibrous products will vary directly with the proportion of the carboxyalkyl cellulose ether binder fibers, with the degree of substitution of the cellulose ether from which the binder fibers are formed and will also vary directly as the pH is increased above substantially neutral pH. The specific strength characteristics will, of course, be dependent upon the specific natural paper-making fibers employed in the blends and the relative proportions of the cellulose ether fibers and paper-making fibers.

As pointed out in the above-identified copending application, synthetic fibers, such as, for example, rayon fibers, are difficult to disperse in water because they tend to agglomerate. Various dispersing agents may be incorporated in a slurry to aid in their dispersion and the fibers then deposited on a screen to form a fairly uniform sheet. The fibrous binders formed of the carboxyalkyl cellulose ethers may replace the dispersing agents and they aid in dispersing rayon and other synthetic fibers. Wet water-laid sheets formed of all viscose rayon fibers of the conventional textile types require special handling to permit their removal from a collecting screen. If such sheets are first dried and then removed from the screen, the sheets have no measurable tensile strength, tear factor and burst factor. Fibrous binders formed of the carboxyalkyl cellulose ethers, when incorporated in the slurry with rayon fibers in an amount as low as 1% by weight of the rayon fibers, provide wet water-laid sheets having sufficient strength to permit ready removal from a collecting screen and the dried sheets so formed have measurable strength characteristics and the strength characteristics may be enhanced by sheeting the fiber mixture from a furnish having the contemplated higher pH's.

Many different embodiments of the invention will be apparent and obvious to those skilled in the art and may be made without departing from the spirit and scope of the invention. It is to be understood that the foregoing specific embodiments are included merely as illustrative and are not intended as limitations. For example, in the foregoing discussion and in the specific examples, the fibers employed had diameters of from 12 to 13 microns and were cut to 1/4 inch lengths. These dimensions were selected merely as a matter of convenience. As pointed out hereinbefore, the fibrous binder may be of any desired length and any desired diameter. Likewise, the products may be of any desired thickness and may vary from soft, porous, non-woven webs to harsh, relatively non-porous, parchment-like webs, the latter being formed of substantially all carboxyalkyl cellulose ether fibers having degrees of substitution in the upper portion of the stated range. Although specific reference is made to blends of the car-

ment in strength characteristics are also obtained when the fibrous binders are blended with other synthetic fibers and other natural fibers or mixtures of synthetic and natural fibers and the water-laid products are laid down from slurries or furnishes having pH's within the stated range.

We claim:

1. In a method of producing water-laid, fibrous products from dispersions containing synthetic, homogeneous, hydrophilic fibrous binders formed of a water-insoluble, alkali-soluble carboxyalkyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, the step of sheeting the fibers of the dispersion to form a water-laid fibrous product from a dispersion having a pH above substantially neutral pH but not exceeding about pH 10.5.

2. The step in the method as defined in claim 1 wherein the carboxyalkyl cellulose ether is carboxymethyl cellulose ether.

3. The step in the method as defined in claim 1 wherein the carboxyalkyl cellulose ether is carboxyethyl cellulose ether.

4. The step in the method as defined in claim 1 wherein the carboxyalkyl cellulose ether is carboxypropyl cellulose ether.

5. In a method of producing water-laid fibrous products, the steps which comprise forming a dispersion of fibers in an aqueous medium having a pH above substantially neutral pH but not exceeding about pH 10.5, at least 1% by weight of the dispersed fibers being formed of a water-insoluble, alkali-soluble carboxyalkyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, sheeting the fibers to form a fibrous product and drying the product.

6. The steps in a method as defined in claim 5 wherein the carboxyalkyl cellulose ether is carboxymethyl cellulose ether.

7. The steps in a method as defined in claim 5 wherein the carboxyalkyl cellulose ether is carboxyethyl cellulose ether.

8. The steps in a method as defined in claim 5 wherein the carboxyalkyl cellulose ether is carboxypropyl cellulose ether.

9. In a method of producing water-laid fibrous products, the steps which comprise forming a dispersion of fibers in an aqueous medium having a substantially neutral pH, at least 1% by weight of the dispersed fibers being formed of a water-insoluble, alkali-soluble carboxyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, adjusting the pH of the aqueous medium to a pH above substantially neutral pH but not exceeding about pH 10.5, sheeting the fibers to form a fibrous product and drying the product.

10. The steps in a method as defined in claim 9 wherein the carboxyalkyl cellulose ether is carboxymethyl cellulose ether.

11. The steps in a method as defined in claim 9 wherein the carboxyalkyl cellulose ether is carboxyethyl cellulose ether.

12. The steps in a method as defined in claim 9 wherein the carboxyalkyl cellulose ether is carboxypropyl cellulose ether.

13. In a method of producing water-laid fibrous products, the steps which comprise forming a dispersion of fibers in an aqueous medium having a substantially neutral pH, at least 1% by weight of the dispersed fibers being formed of a water-insoluble, alkali-soluble carboxyalkyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, the balance of the fibers being viscose rayon fibers, adjusting the pH of the aqueous medium to a pH above substantially neutral pH but not exceeding about pH 10.5, sheeting the fibers to form a fibrous product and drying the product.

14. In a method of producing water-laid fibrous products, the steps which comprise forming a dispersion of fibers in an aqueous medium having a substantially neutral pH, at least 1% by weight of the dispersed fibers being formed of a water-insoluble, alkali-soluble carboxyalkyl cellulose ether having a degree of substitution of from about 0.10 to about 0.60, the balance of the

fibers being natural paper-making fibers, adjusting the pH of the aqueous medium to a pH above substantially neutral pH but not exceeding about pH 10.5, sheeting the fibers to form a fibrous product and drying the product.

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