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## PAPER COMPOSED OF FIBERS HAVING DIFFERENT TEMPERATURE-RESPONSIVE DIMENSIONAL-CHANGE CHARACTERISTICS, AND METHOD OF PRODUCING IT

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This invention relates generally to the manufacture of paper, and has particular reference to the conjoint employment of fibers having predetermined different characteristics, and to a procedure by means of which the special properties of the fibers are caused to manifest themselves and to impart new and unusual qualities to the paper.

It is a general object of the invention to provide a paper-making procedure whereby various properties of paper may be selectively enhanced or increased, and additional beneficial properties created, so that the field of usefulness of the paper may be enlarged. A more particular objective is to attain these results without material alteration of existing paper-making techniques and machines.

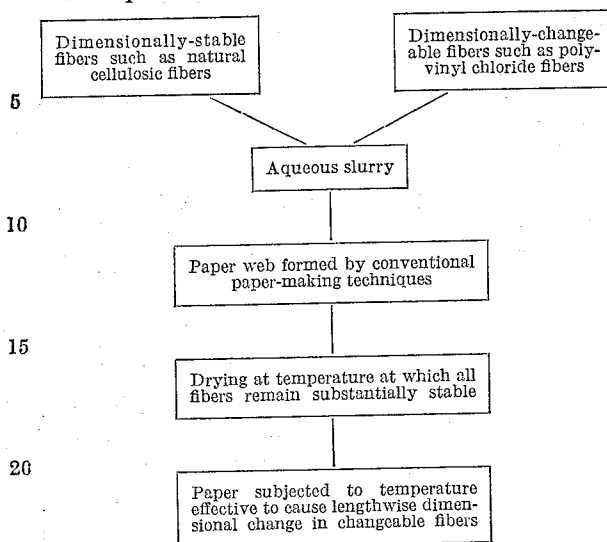
The invention is predicated upon the simultaneous employment, as components of a slurry from which a paper sheet is to be formed, of fibers having different temperature-responsive dimensional-change characteristics. As a result, after the paper-making process has proceeded to a stage at which the paper web is self-sustaining and a secure inter-fiber bond has been established, the paper may be subjected to a special treatment involving a temperature change so chosen that it brings about a substantial dimensional change in some of the fibers and a different dimensional change (or no change at all) in others. Because of the already bonded relationship existing among the fibers of which the sheet is composed, the differential changes in fiber dimensions create distorting forces which impart unique physical properties to the sheet.

By a judicious selection and proportioning of the fibers used, the changes that can be brought about in the paper are of various kinds. Among the special characteristics that can be created (singly, or more commonly in various combinations) are improved resilience, higher elongation, greater tear strength, increased surface area, greater permeability, reduced density, novel surface textures and appearance, more pleasant feel, softer texture and improved fabric-like draping qualities.

One way of achieving the benefits of the invention is to employ fibers of which one group has relative dimensional stability while another group is of the kind which undergoes a substantial shrinkage, lengthwise, under elevated temperatures. For the sake of convenience the fibers of the latter category will be referred to hereinafter as "shrinkable" fibers, while the more stable fibers will be termed "non-shrinkable." In a preferred procedure, the paper is formed in the usual way from an aqueous slurry of the fibers, and it is initially dried at a temperature so chosen as to be insufficient to shrink the shrinkable fibers to more than a minor degree. Thereafter the paper is subjected to a separate additional treatment calculated to bring about the desired shrinkage to maximum degree. This procedure has the advantage allowing the paper to be formed, in the first instance, by conventional paper-making techniques, and to be calendered or subjected to other finishing treatments before the special shrinking operation is carried out.

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A simplified flow diagram of the process is as follows:



The unusual effects produced by this invention are attributable to the fact that a marked and sudden reduction in length of the shrinkable fibers, after an inter-fiber bond with the non-shrinkable fibers has once been attained, exerts a pulling and distorting influence upon the non-shrinkable fibers and thus twists them into loops and coils which manifest themselves in various kinds of crinkles and wrinkles on the surface of the paper sheet. A large assortment of effects is attainable, creating marked changes in the basic properties of the paper, often imparting entirely new qualities to it. For example, it has been found that if the non-shrinkable fibers are long and of large diameter, they will be pulled into large, firm loops and coils by the shrinking action and the paper will have a pebbled texture with large deflections of the surface from the plane of the sheet. On the other hand, if the non-shrinkable fibers are short and of small diameter, the loops will be of much smaller amplitude and the texture of the paper will be finer and softer. Use of fine, soft non-shrinkable fibers in conjunction with a high proportion of shrinkable fibers can be made to produce papers with a flat rather than a pebbled surface, but with a fine internal crimp. Such papers resemble knitted fabrics in texture. If the fibers are randomly oriented, the pattern and texture produced will be isotropic. If the fibers are highly oriented, the pattern will be similarly oriented. It will be apparent that a great variety of desirable effects can be produced by proper selection of fibers and processing conditions.

The results attained will depend in each case upon a variety of factors among which are the nature of the fibers used, the proportion of shrinkable to non-shrinkable fibers, and the temperatures employed in drying the web and in subsequently bringing about the desired fiber distortions by shrinkage of the shrinkable fibers.

### FIBERS USED

Many different fibers are available for use in practicing this invention, and they may be employed in a large number of different combinations.

The fibers that are non-shrinkable, i.e., those having the dimensional stability required for the present purpose, may consist of any of the natural cellulosic fibers, of which manila hemp is an example. Rayon and other synthetic fibers are also useful, including pre-shrunk acrylic, polyester, and polyamide fibers. An example of pre-shrunk acrylic fibers is "Orlon" and an example of

pre-shrunk polyester fibers is "Dacron," both products of E. I. du Pont de Nemours & Co. Inc.

In the category of available shrinkable fibers, i.e., those having the shrinking characteristics necessary to produce the desired results, are most of the acrylic fibers, polyvinyl chloride fibers, polyester fibers, and polyamide fibers. Heat-set fibers, or synthetic fibers that have been pre-shrunk, are unsuitable for the purpose.

The shrinkable fibers must have the ability to shrink lengthwise, not in thickness. Where heat is the medium for initiating the shrinkage, the fibers to be used in practicing the invention should manifest a shrinkage of 10% (preferably at least 20%) at 212° F., and a shrinkage of 20% (preferably at least 35%) at 320° F.

Both the shrinkable and non-shrinkable fibers should generally be as long as can be used in obtaining good sheet formation on conventional paper-making machines. The preferred range is from one-eighth to one-half inch. In thickness the denier may vary from 1 to 6.

### FIBER PROPORTIONS

The ratio (by weight) of shrinkable to non-shrinkable fibers may vary from 1:4 to 4:1. The preferred range is from one-to-three to one-to-one. If the proportion of shrinkable fibers is too low, the distortions produced by them tend to become insignificant. Similarly, if the proportion of non-shrinkable fibers is too low, there is an insufficient dimensionally stable base upon which the shrinking of the other fibers may exert its effects.

### TEMPERATURES

The shrinkage in fiber diameter which normally occurs during drying of conventional cellulosic papers is not capable of producing the novel effects of this invention.

In order to produce the desired effect, the majority of the shrinkage of the shrinkable fibers must occur after all the fibers of the paper sheet have become firmly bonded together. Any fiber shrinkage occurring earlier than this produces merely a shortening of the individual shrinkable fibers, and the impact of the shrinking fibers is not transmitted to the product in the desired way. It is therefore necessary to adjust the drying temperatures so that the earlier stages of drying are carried out at relatively low temperature. When the sheet has been dried to the point at which secure inter-fiber bonding has been accomplished, it may be subjected to the higher temperatures at which shrinkage of the shrinkable fibers is brought about. This may be achieved by a blast of heated air or other gas, by passing the sheet through an oven or other heated chamber, by immersing the sheet in water maintained at the desired temperature, by passing the sheet over dryers set at the higher temperatures, or in any other appropriate manner. Tension on the sheet is preferably maintained as low as possible during this treatment.

The initial drying temperature may be of any magnitude adequate to effect complete drying at reasonable machine speeds. Generally a temperature between 150° and 220° F. is satisfactory, although under certain circumstances it may be as high as 270° F. In no case should the temperature be so high that insufficient residual shrinking capacity remains in the shrinkable fibers after the inter-fiber bonding has been established.

The subsequent heat treatment may be at any convenient temperature substantially higher than the maximum temperature to which the fibers were subjected during the initial drying of the sheet. Generally, the temperature at which the desired shrinkage of the shrinkable fibers is brought about will be between 210° and 300° F., although in some cases it may be as high as 350° F. In no case should the temperature be so high that serious degradation of the fibers occurs.

The following examples are illustrative of the various ways in which the invention may be practiced. The tabu-

lation lists the fibers and proportions used, and the procedural steps and results attained in each case are set forth thereafter.

	I	II	III	IV	V	VI	VII
Shrinking Fibers:							
Polyvinyl chloride.....	20	50					
Acrylic.....			50	50	75	50	25
Non-Shrinking Fibers:							
Manila hemp.....	80	50	50				
Rayon.....				50	25		
Polyester.....						50	
Acrylic.....							75

### Example I

The polyvinyl chloride fibers used were "Rhovyl 55" (The Rhovyl Company) having a shrinkage capacity of 55% at 212° F., and a weight of 3 denier per filament. The fibers were cut to about ¼" in length and were slurried in water with the unbeaten manila hemp fibers. Three parts by weight (dry basis) of trimethylol melamine acid colloid ("Parez 607"—The American Cyanamid Company) were added to impart wet strength, and the pH of the slurry was adjusted to about 3 with hydrochloric acid. The slurry was thoroughly mixed and the fibers were sheeted on the forming wire of a paper machine and dried at 160° F. At this point, the product was a smooth, porous paper weighing 0.7 ounce per square yard. The paper was then caused to shrink by immersing in water at 212° F. without tension, and was redried at 220° F. This treatment resulted in shrinkage of 15% (area basis) in the paper. The final product was a soft, fabric-like structure having a pleasing pattern of small random pleats.

### Example II

The ingredients and the procedure were the same as in Example I, but the larger proportion of shrinking fibers resulted in a shrinkage of 69% as compared with 15% in Example I. The final product was a soft relatively thick structure resembling a knitted fabric.

### Example III

The acrylic fibers used were "Type II Verel" (Eastman Chemical Products, Inc.) having a shrinkage capacity of 20% in 212° F. and 35% at 320° F. The acrylic fibers had a weight of 2 denier per filament and were cut to a length of about ½". In other respects the ingredients and procedure were the same as in Example I and II. A shrinkage in the paper of 23% was produced by the final treatment, and the product was a soft, fabric-like structure with a pebbled surface resembling seersucker.

### Example IV

The acrylic fibers used were the same as in Example III, except that the length was cut to about ¼". The rayon consisted of equal parts of fibers having a weight of 5½ denier per filament, and fibers having a weight of 1½ denier per filament, the former being about ¾" long and the latter about ¼" long. The slurry was thoroughly mixed and the fibers were sheeted on the forming wire of a paper machine and bonded with an acrylic resin latex. (In each of Examples I—III no special bonding agent was required since the natural cellulosic hemp fibers afforded adequate inter-fiber bonding.) The sheet was dried at 210° F. and calendered. At this point, the paper weighed 0.7 ounce per square yard, had a density of about 0.27 gram per cubic centimeter and two plies of this paper had an air permeability of 120 cubic feet per minute per square foot at a pressure drop equivalent to ½ inch of water. The paper was then heated for a few seconds to a temperature of 340° F. without tension on the web. This treatment resulted in a shrinkage of 36% (area basis). The final product had a density of .09 gram per cubic centimeter and the air permeability of two plies of

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the paper had increased to 372 cubic feet per minute per square foot.

#### Example V

The acrylic fibers were the same as those used in Example IV, but the rayon used consisted only of fibers having a weight of 1½ denier per filament and a length of about ¼". The procedure and treatment were the same as in Example IV but because of the larger proportion of shrinking fibers a shrinkage in the paper of 44% was produced, as compared to 36% in Example IV. Before shrinkage, the paper weighed 0.7 ounce per square yard, had a density of about 0.36 gram per cubic centimeter, and two plies had an air permeability of 75 cubic feet per minute per square foot at a pressure drop equivalent to ½ inch of water. The final product had a density of .09 gram per cubic centimeter and the air permeability of two plies of the paper had increased to 275 cubic feet per minute per square foot.

#### Example VI

The acrylic fibers were the same as those used in Example IV and V. The non-shrinking fibers used were "Dacron" (E. I. du Pont de Nemours & Co., Inc.) having a weight of 3 denier per filament, and cut to lengths of about ¼". The procedure was the same as in Examples IV and V. At the completion of the initial drying and calendering, the paper weighed 1.4 ounces per square yard, had a tensile strength of 6.7 lbs. per inch, an elongation at break of 15%, and an Elmendorf tear strength of 100. The subsequent heating of the paper to 340° F. resulted in a shrinkage of 28% (area basis) and a final product having a tensile strength of 6.7 lbs. per inch, an elongation at break of 26%, and an Elmendorf tear strength of 208.

#### Example VII

The shrinkable acrylic fibers used were the same as in Example VI. The non-shrinking fibers were "Orlon" (E. I. du Pont de Nemours & Co., Inc.) cut to a length of about ¼" and having a weight of 1 denier per filament. The slurry was thoroughly mixed and the fibers were sheeted on the forming wire of a paper machine and bonded with an acrylic resin latex. The sheet was dried at 270° F. and calendered. At this point, the paper had a tensile strength of 6.5 lbs. per inch, and an elongation at break of 10%. The paper was then heated for a few seconds to a temperature of 340° F. without tension on the sheet. This treatment resulted in a shrinkage of 23% on an area basis. The final product had a tensile strength of 8.6 lbs. per inch, and an elongation at break of 27%.

From the foregoing examples it will be apparent that the practice of the invention may be varied in a large number of ways, and that the changes brought about in the resultant paper will differ correspondingly. In addition to the ability, by means of this invention, to impart to paper a softer texture, better draping qualities, and a pleasanter feel than are usually found in conventional papers, it is possible to produce papers with improved resiliency, elongation, and tear strength. Such papers are particularly useful in the manufacture of industrial and electrical tapes. Increased bulk, permeability and surface area may also be produced. Papers can be made which have apparent densities less than 0.1 gram per cubic centimeter, and air permeability more than three times as high as conventional papers of the same types. The improved paper products may thus be useful as filter media in air filters, milk filters, and other installations in which these enhanced properties are of value.

The invention is not restricted to the use of fibers which are respectively "shrinkable" and "non-shrinkable," unless it be understood that these are relative terms. For example, both sets of critical fibers may be shrinkable but one may be so much more shrinkable than the other that the distortions contemplated by the invention, after inter-fiber bonding has been established, will result. Moreover, the range of temperatures effective to bring about the de-

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sired shrinkage of one set of fibers relative to the other may not necessarily be among the elevated temperatures. Fibers adapted to shrink under reduced temperatures are useful, in which case the dried paper would obviously be subjected to such reduced temperatures, rather than heat, to effect the desired distortion of the interengaged fibers. Heating of the paper sheet, to bring about the contemplated shrinkage, is however preferable because heat is commonly employed in the drying of paper, and is thus more readily available for use in carrying out paper-making techniques.

In many respects, therefore, the invention may be modified without necessarily departing from the spirit and scope of the invention as expressed in the appended claims.

What is claimed is:

1. In a paper-making process, the steps which consist in furnishing a slurry in which there are at least two sets of fibers having different temperature-responsive lengthwise dimensional-change characteristics, the ratio between said two sets of fibers lying in the range between 4:1 and 1:4, forming said slurry into a paper web and drying said web at a temperature below a predetermined maximum drying temperature to produce inter-fiber bonding in said web, and after said bonding has been established, subjecting the web to a temperature above said drying temperature effective to cause in one set of fibers a dimensional change appreciably different from that cause by said temperature in the other set.

2. In a paper-making process, the procedure defined in claim 1, in which the drying of the web to establish said inter-fiber bonding is carried out at a temperature at which both sets of fibers are dimensionally stable.

3. The procedural steps defined in claim 1, in which one set of fibers are selected from the group consisting of acrylic fibers, polyvinyl chloride fibers, polyester fibers, and polyamide fibers, and in which the other set of fibers are selected from the group consisting of rayon fibers, natural cellulose fibers, and non-shrinkable types of acrylic, polyester, and polyamide fibers.

4. A soft fabric-like paper product resulting from the paper-making procedure defined in claim 1.

5. In a paper-making process, the steps which consist in forming a paper web of a slurry containing shrinkable and non-shrinkable fibers, drying said web within a range of temperatures below a predetermined maximum drying temperature, said shrinkable fibers being adapted to shrink lengthwise when subjected to elevated temperatures and the ratio of shrinkable to non-shrinkable fibers lying in the range between 4:1 and 1:4, and after the web formation has progressed to the stage at which inter-fiber bonding has been established subjecting the web to an elevated temperature effective to cause an appreciable shrinkage in length of said shrinkable fibers, said elevated temperature being above said maximum drying temperature.

6. The procedural steps defined in claim 5, in which the ratio of shrinkable to non-shrinkable fibers lies in the range between 1:1 and 1:3.

7. The procedural steps defined in claim 5, in which the shrinkable fibers are polyvinyl chloride fibers, the non-shrinkable fibers are manila hemp, and the ratio of shrinkable to non-shrinkable fibers is in the range between 1:4 and 1:1.

8. The procedural steps defined in claim 5, in which the shrinkable fibers are acrylic fibers, the non-shrinkable fibers are manila hemp, and the ratio of shrinkable to non-shrinkable fibers is 1:1.

9. The procedural steps defined in claim 5, in which the shrinkable fibers are acrylic fibers, the non-shrinkable fibers are rayon, and the ratio of shrinkable to non-shrinkable fibers is in the range between 1:1 and 3:1.

10. The procedural steps defined in claim 5, in which the shrinkable fibers are acrylic fibers, the non-shrinkable fibers are pre-shrunk polyester fibers, and the ratio of shrinkable to non-shrinkable fibers is 1:1.

11. The procedural steps defined in claim 5, in which

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the shrinkable fibers are acylic fibers, the non-shrinkable fibers are pre-shrunk acrylic fibers, and the ratio of shrinkable to non-shrinkable fibers is 1:3.

12. In a paper-making process, the steps which consist in furnishing a slurry in which there are at least two sets of fibers one of which is dimensionally stable while the other undergoes lengthwise dimensional changes of appreciable magnitude in a range of predetermined effective temperatures, the ratio of dimensionally stable fibers to dimensionally changeable fibers lying in the range between 4:1 and 1:4, forming said slurry into a paper web, drying said web to establish inter-fiber bonding, said drying being carried out at a temperature outside said range, and thereafter subjecting the web to a temperature within said range so as to cause dimensional changes in the fibers affected thereby.

13. In a paper-making process, the steps which consist in furnishing a slurry containing a set of dimensionally stable fibers and also a set of fibers adapted to undergo lengthwise dimensional changes of appreciable magnitude at elevated temperatures, the ratio of dimensionally stable fibers to dimensionally changeable fibers lying in the range between 4:1 and 1:4, forming said slurry into a paper web, drying said web to establish inter-fiber bonding, said drying being carried out at a relatively low temperature

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below that at which said changeable fibers undergo dimensional change, and thereafter subjecting the web to an elevated temperature effective to cause said dimensional changes.

14. In a paper-making procedure in which a slurry containing dimensionally-stable fibers is formed into a web and the web is dried by heat to establish inter-fiber bonding, the steps which consist in introducing into said slurry a set of fibers adapted to shrink lengthwise when subjected to temperatures within an effective range higher than any temperature employed for drying of the web the ratio of dimensionally-stable fibers to shrinkable fibers lying in the range between 4:1 and 1:4, and subjecting the web after drying to a temperature within said effective range.

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