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METHODS OF MAKING FIBROUS MATERIALS

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This invention relates to improved fibrous materials and more especially to improvements in paper materials and in methods of making paper.

It is a principal object of the invention to improve paper and its methods of preparation, and to devise a procedure for incorporating special modifying materials with paper pulp fibers with a view to imparting novel wet strength and other desirable properties to paper obtained from the fibers. It is a further object of the invention to bring together special sizing materials with wet cellulose coatings of well-beaten pulp fibers, and while thus associated to subject the sizing materials to novel heating operations, thereby to bond the fibers more strongly one to another. Another object is to prevent the occurrence of foaming and sticking in connection with the use of special sizing materials. Another object of the invention is to reduce or eliminate losses in connection with the use of special sizing materials and to overcome the formation of lumps of finely divided sizing materials in finished paper. Another object is to provide improvements in combining vinyl compounds, and other substances, with sheet materials, both during and after formation of the sheet materials. Another object of the invention is to present novel heating and washing operations in connection with the use of finely divided cold-water-swallowable compounds. Still another object of the invention is to provide an improved paper product which includes a water-receptive sizing. The invention also aims to provide a method of making paper which is simple, cheap and efficient.

The nature of the invention, and its objects, will be more fully understood from the following description relating thereto.

In carrying out the method of the invention, there are employed finely divided materials which swell in cold water and which dissolve in hot water. One example of such a sizing material is a polyvinyl alcohol. In the presence of cold water (water at 50° F. for instance), this material, in some forms, passes from a powder state into a water-swollen phase and in this state exhibits a definite stickiness. The water-swollen polyvinyl alcohol further has the property of more or less abruptly changing, in the presence of water, and upon application of heat, to a viscid or plasticized state in which water-swollen particles of the polyvinyl alcohol lose their entity and tend to flow into one another. If heating is continued in the presence of suitable amounts of water, the flowed mass becomes completely dissolved. The polyvinyl alcohol material, in a viscid or plasti-

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cized state, is adapted to set into solids or films which are greatly superior to masses obtained from cold-water-swollen particles of this material. The solids or films may be further strengthened by heat and pressure.

The word "plasticized" as employed in the specification refers to a condition resulting from converting water-swollen particles, by means of heat and small amounts of water, to an intermediate fluent state, occurring before the particles dissolve.

As illustrative of application of a cold-water-swallowable material in a web or sheet in accordance with the method of the invention, the following procedures are noted:

Example I

A water-receptive polyvinyl alcohol is provided in a finely divided state in which substantially all of the particles are of a size such that they will pass through a 140-mesh screen and will be retained on a 160-mesh screen. In an ordinary run of bleached kraft paper, amount of paper of, for example, 2500#, may be produced. For such an amount, approximately 2700# of dry pulp and approximately 250# of polyvinyl alcohol may be utilized for making paper on a Fourdrinier machine.

The polyvinyl alcohol particles are washed in cold water to remove cold-water-solubles and other impurities. There are thus obtained water-swollen particles which may be prepared and handled either as an aqueous suspension or in a solid state.

The water-swollen vinyl particles, for example in aqueous suspension, are then added to a suspension of well-beaten or hydrated pulp fibers. The addition is preferably made at the stuff box of the paper machine, at which point very substantial dilution of the pulp fibers takes place. A pulp consistency of 2.71% at time of adding polyvinyl alcohol, and subsequent dilution to about .271% consistency on the wire are suitable.

The fibers and the sticky swollen vinyl particles are agitated together for a suitable period, to incorporate these materials intimately together, and to increase retention of the water-swollen particles by the hydrated cellulose coatings on the pulp fibers while the materials are in suspension. A web or sheet of paper is then formed in the usual manner, as by passing the pulp and adhering swollen particles through a papermaking machine, which includes screens on which the fibers are arranged and felted together.

The newly formed web of paper, containing

10% by weight of polyvinyl alcohol, is carried to drying rolls of the type generally employed in drying a wet web of paper. The web is subjected to gradually increasing temperatures of from 120° F. up to 220° F. for periods of from 60 to 90 seconds or longer. During this period, the moisture content of the web decreases from 75-85% down to 5-10%; the water-swollen particles are carried to or slightly beyond a point at which they are plasticized or fluent; and the plasticized or fluent material sets into separated masses in localized areas of the web.

Example II

Particles of a smaller size than those noted in Example I, as for example particles retained by a 300-mesh screen, are incorporated with raw pulp fibers, or fibers which have not been hydrated by beater treatment, and a web of paper is formed therefrom in the same general manner described in connection with Example I. Thereafter the web is subjected to the heating conditions of a conventional paper machine as set forth in Example I, for a length of time sufficient for the swollen particles to reach a plasticized or fluent state, for example 30-60 seconds. Upon reaching a plasticized or fluent state, the particles start to flow and spread out around the paper fibers as thick, viscid masses. While still in a relatively thick, viscid state and before they are dissolved to any appreciable extent, the masses are allowed to set by interrupting or substantially reducing heat applied from the drying rolls of the paper machine. This is preferably carried out by passing the web completely out of contact with a heated roll surface for a short interval. Drying is continued to form a web of finished paper which contains vinyl compound in the form of separated masses bonded about groups of fibers.

The paper product obtained by the procedures just above described is characterized by several new and useful properties. One of the more important of these properties is relatively high wet strength which has been found to range from 30 to 70 percent of the dry strength of the paper, as measured by an Ashcroft or Mullen paper tester. The usual wet strength of paper obtained from conventional papermaking operations in which alum and rosin are employed is approximately 20 to 25 percent of the dry strength of such a paper. It will be seen therefore that exceedingly high wet strength is obtained in comparison with the wet strength of conventional papers.

The water-swollen particles, when heated to a point at which they become plasticized or fluent, are viscid and flow in between and around the points of contact of the fibers, acting as a cement for joining the fibers together at localized areas in a web of paper, thereby developing the high wet strength noted. Separated masses obtained from the fluent material have the property of becoming highly elastic when exposed to moisture. If paper, in which such masses of polyvinyl alcohol occur, is utilized in a moist state, this elasticity of the masses becomes important as it tends to hold the fibers resiliently together in much the same manner as a plurality of rubber bands. It is pointed out that the thickness of each separated mass determines to some extent its gripping power. Therefore it is desirable to prevent each water-swollen particle from being flowed to a point where only a very thin spread-

out mass is obtained which would not exert as great gripping action as thicker masses.

An important feature of the invention is to secure at localized areas in the paper, relatively thick masses of polyvinyl alcohol obtained from this material while in a plasticized or fluent state, and before it has dissolved to any appreciable extent. This may be accomplished by the procedure indicated in Example I, in which the particle size is regulated with respect to the moisture and heating conditions of a paper machine. A somewhat similar result may also be arrived at by employing particles of various sizes and by controlling or interrupting the heating operation, as illustrated by the procedure set forth in Example II.

Important moisture and heating conditions in a paper machine include the degree of heating which is permissible in drying a wet web of paper; the time during which the paper is subjected to heat; the amount of moisture in paper during the heating period; and the maximum temperatures normally available in a paper-making machine. Paper as it comes from the screens in a wet, newly formed state, contains from 75% to 80% moisture by weight. Heating should be controlled to prevent this moisture from turning into steam and causing "cockling," or the formation of bubbles or imperfections in the finished paper. Temperatures below 200° F. are suitable for avoiding cockling, and conventional paper machine dryers usually operate at temperatures of from 130° F. to 220° F. A period of from 30 seconds to 90 seconds, and in some cases longer, is usually required in passing paper through the drying rolls of a paper machine.

In Example I a preferred procedure was outlined in which it will be observed that a range of particle size is employed (140 to 160-mesh size) which, under paper machine conditions such as those just above noted, provides for the water-swollen particles being brought to a fluent state and then set into separated masses. It is pointed out that the method of Example I does not require any substantial change or interference with the conventional paper-making process, and control of particle size is relied upon to provide desired results in wet strength.

In Example II, the small particle size is compensated for by controlling the heating operation, either by interrupting the heating, or in other ways, to obtain relatively thick separated masses which provide desirable wet strength. It should be observed that the procedure of Example II makes possible the use of sizes of particles which could not be used in the procedure of Example I.

While the use of particles of the 140-160-mesh screen size is preferred, desirable results may be obtained, especially by the procedure of Example II, with particles of from 100-300-mesh screen sizes, and in some cases 50-500-mesh screen sizes. In all cases, it is preferable to employ particles of as uniform size as possible as this facilitates control of heat and moisture.

The use of very small particles, for example 500-mesh particles, is in most instances less desirable as they tend to provide less wet strength and are too readily plasticized in the residual water of the web under paper machine temperatures. It is also more difficult to determine the point at which the plasticizing or melting of relatively small particles occurs, in accordance with the procedure of Example II.

The use of relatively large particles requires

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longer periods of heating and more moisture in order to obtain complete plasticization of the particles. If sufficient moisture is not available, or if adequate heating is not carried out, parts of the swollen particles which do not become plasticized appear in the finished web of paper and cause lumps, commonly referred to as "fish eyes." By using particles which are small enough to be flowed readily by the conditions of the paper-making process (Examples I and II), the occurrence of lumps, or "fish eyes," is avoided.

By the use of sizing material of the type illustrated, it is possible to secure a very desirable sizing of raw pulp fibers and to eliminate hydrating or beating pulp fibers and thus reduce the normal cost of papermaking. This procedure of forming paper of raw pulp fibers sized with a water-swellaible material is of highly efficient and useful character.

The steps of heating finely divided materials, of suitable size, up to or slightly beyond the point at which they become plasticized, and allowing them to set into relatively thick masses, may be desired to be practiced without first swelling the material, but by adding it in a powder form, or in other ways at various points during or after the formation of the paper web as, for example, to pulp fibers in a beater machine, the fan pump, the head box and the like, or to a web of paper. Also the procedures may be utilized in making other materials than paper, as textiles and others.

Another important feature of the invention is the preliminary washing of the finely divided vinyl compound in cold water. According to the invention, it has been found that some cold-water-swellaible, finely divided materials, and in particular the vinyl compound noted, contain a cold-water-soluble fraction which, to a very large extent, is responsible for the frothing or foaming. This fraction may vary and in the case of polyvinyl alcohol amounts to as much as from 6% to 50% of the weight of the polyvinyl alcohol in a powder form. By washing the polyvinyl alcohol in cold water before adding the material to the pulp fibers, the cold-water-solubles may be substantially eliminated and a very substantial reduction in foaming may be obtained, and in some cases foaming may be completely eliminated. As a result, interference with the formation of the paper web and losses of the polyvinyl alcohol are both overcome and the introduction of this sizing material with pulp fibers is made practical.

Swelling of the particles as obtained by the washing step or in other ways is important since it develops stickiness which greatly assists in holding the particles to the fibers while they are being felted together on the screen of a paper machine.

In addition, it has been found possible to further reduce foaming or frothing by adding chemical agents in conjunction with the finely divided material and a pulp suspension. One excellent reagent of this type is a chromium compound, such as ammonium bichromate. Ammonia is also useful for this purpose. The chemical reagents may be used in such amounts as are necessary to eliminate the need of removing the cold-water-soluble fraction of the vinyl compound and to establish a pH-value of at least 8.3.

In cases where a finely divided material is found to have a small cold-water-soluble fraction, the chemical reagent is most efficiently employed in small amounts to overcome foaming, since the use of excess amounts of the chemical reagents may be objectionable for other reasons. In other

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cases, both of the procedures may be resorted to. If polyvinyl alcohol is provided in a form in which no cold-water-soluble fraction is present, little, if any, defoaming treatment may be required.

The methods described in Examples I and II provide a maximum wet strength obtainable in paper under the normal heating conditions provided for in most paper drying rolls. This wet strength runs around 60% to 90% of the dry strength of the paper, and in many cases is highly satisfactory, especially where only a range of heating common to a paper machine (130° F.-220° F.) is available. In some instances, however, it is desirable to increase this wet strength figure to even higher values. In accordance with the invention, procedures for further improving the wet strength of paper are provided, of which the following examples are illustrative:

Example III

A web of paper is made in the manner above described, in which water-swollen particles are incorporated in and around fibers in the web and heated up to, or slightly beyond, a point at which the particles become plasticized and flow around fibers, in localized areas, and the paper is dried to a desired point. Thereafter the web is subjected to temperatures in excess of those usually permissible on a paper machine, as for example temperatures of from 220° F. to 300° F., and in some cases as high as 450° F. Heating at these temperatures is carried out for short periods in the presence of small amounts of moisture to prevent the paper fibers from becoming dried out to a point where they would be brittle. Small amounts of moisture are successively or continuously added to the web during or between applications of heat at the high temperatures noted.

Example IV

A suspension of water-swollen particles is mixed with pulp fibers and a web of paper formed therefrom. The web of paper is then heated to a temperature of from 130° to 220° F., for a period suitable for plasticizing the water-swollen particles in the residual water of the web, to provide a substantially continuous body of the plasticized material extending throughout the fibers of the web. Heating under 220° F. is continued until a relatively small amount of moisture is present in the web, as for example 30% or less, at which point the temperature is raised to 300° F. and in some cases as high as 450° F. This high temperature heating is maintained for a short period in the presence of small amounts of moisture in the web. Intermittent or continuous heating and moistening may be thus carried out several times.

The procedures of Examples III and IV rely on temperatures which are in excess of those utilized to dry newly formed webs of paper containing relatively large amounts of moisture, and which are in excess of temperatures usually available in a paper-making machine. Special heating means are required and provided for, either in conjunction with the paper machine or at some other point. For example, a special high temperature drying roll may be furnished at the end of the paper machine. The use of pressure, as for example by calendar rolls in conjunction with heat, may also be desirable.

Heating at high temperatures (230°-450° F.) in the presence of moisture, tends to toughen and strengthen the plastic masses and the paper has greatly improved wet strength as compared with a paper prepared by the procedures of Examples

I and II. By heating at the temperature noted, wet strength of from 100% up to 150%, of the dry strength of the paper, and even higher may be obtained under some conditions. Where these high wet strengths are desirable and heating facilities are available, a preferred method of the invention therefore is to resort to the high temperatures noted (220° F.-450° F.). The step of adding fresh amounts of moisture to the web from time to time, while heating at temperatures in excess of 220° F., especially tends to strengthen the polyvinyl alcohol, and may in some instances be employed to continue or complete the changing of relatively coarse particles from a water-swollen state to a plasticized condition. Also, relatively high temperature heating may be advantageously carried out in some cases without resorting to obtaining an optimum plasticized condition of the water-swollen particles.

An important feature of high temperature heating is the saving in sizing material which may be effected in obtaining a desired wet strength. For example, if a 90% wet strength paper is desired, it may be obtained, using a 10% suspension of polyvinyl alcohol, by the procedure of Example I. However, by the high temperature method (230° F.-450° F.), only a 3% suspension of polyvinyl alcohol would be necessary to obtain 90% wet strength.

The high temperature heating, in addition to toughening and increasing the bonding strength of the polyvinyl alcohol in the paper fibers, also tends to impregnate the polyvinyl alcohol in the fibers to a greater extent than is obtained by a heating operation such as that of Example I. Impregnation of the paper fibers by the polyvinyl alcohol, when heated to the relatively high temperatures noted, is also greatly increased by the use of very well hydrated pulp fibers.

The extent of heating at high temperatures may vary from 220° F. up to 450° F., depending upon the particular character of the polyvinyl alcohol being employed. Alcohols containing polymers of different character may require different heat treatment. Various other changes may be resorted to.

Polyvinyl alcohol, incorporated into paper in the manner described, is useful for other purposes than to increase wet strength. For example, it may be utilized to obtain improved retention of filler materials such as clays. In accordance with the method of the invention, clay is added to a suspension of pulp fibers in the presence of water-swollen polyvinyl alcohol particles. The polyvinyl alcohol in its sticky swollen state tends not only to stick to the pulp fibers but to hold the clay, both on itself and on the fibers, as they are felted together on the screens of a paper machine. As high as 30% to 50% of clay by weight may be successfully introduced into paper by the use of the polyvinyl alcohol.

Water-swollen vinyl particles may also be utilized in association with sizing materials such as papermakers' alum or rosin. It has been found that the polyvinyl alcohol particles provide a paper of greatly increased wet strength when combined with alum or rosin, as compared with the wet strength of a paper in which only the alum and rosin are employed.

The use of polyvinyl alcohol is also important in reducing sticking of sizing materials. A particular instance of a sticky sizing is water-swollen casein. This substance, when wet, tends to stick the fibers too greatly, so that they fail to become properly felted together on the screens of a papermaking

machine. In addition, casein tends to stick to the felts of the drying rolls.

In accordance with the invention, polyvinyl alcohol is mixed with a suspension of water-swollen casein particles prior to or while adding the casein to pulp fibers. The polyvinyl alcohol serves as a protective colloid, minimizing the adhesiveness of the casein and yet allowing it to exercise a considerable bonding effect throughout the pulp fibers. The reduction in adhesiveness or stickiness on the part of the casein thus obtained also eliminates sticking or other undesirable reaction with the felts, after the web of paper has been formed and is being dried.

In connection with swelling the particles to render them sufficiently sticky for adhering to pulp fibers, we may employ certain chemical agents, of which particularly desirable examples are ammonium bichromate or ferric chloride. These compounds may be added to a suspension of pulp fibers mixed with the finely divided materials. Preferably solutions of from 5% to 10% of these hardening or gelling agents should be employed. The chemical agents noted increase stickiness of the swollen particles, thereby to facilitate retention of the particles on pulp fibers.

In addition to wet strength, the paper product obtained by the method of the invention presents various other novel and useful properties, one of which is its water-receptive and water-retentive character. The vinyl compound is combined with the paper fibers in a water-receptive state to provide a water-receptive and water-retentive sizing in the paper. The word "sizing" as employed in the specification is used in the broad sense of a modifying material combined with paper fibers without any special reference to water-repellent character being intended. It is pointed out that a water-receptive sizing material which imparts strength, flexibility, grease-repellent character, and other desirable properties to paper, is of a highly novel character, as compared with water-repellent sizing materials.

The vinyl impregnated paper of the invention, with the vinyl compound occurring in a water-receptive state, insures permanent retention of small amounts of moisture in the paper, and the vinyl compound itself when containing moisture acts as a plasticizing agent to preserve a highly developed flexibility. This flexibility is particularly important in using the paper as a substitute for metal in making lithographic printing plates which in use are required to be bent and clamped around printing rolls.

A moisture-retentive vinyl resin, when impregnated in paper, may also facilitate sticking or bonding, to the paper, of coatings obtained from aqueous suspensions. This is important in making printing plates, particularly in respect to plates of the type described in an earlier Patent No. 2,230,981, issued February 4, 1941, in which water-receptive resin materials are utilized to form the non-printing portions of a lithographic printing plate. The sticking is likewise important in connection with the general application of coating materials of an aqueous character.

The paper of the invention also may have increased dry strength, relative to the dry strength of conventional rosin-sized papers, and is particularly adapted to resist being pulled apart by the suction of a printing press when the paper is employed as a printing plate.

A particular instance of the use of paper in a wet state is in connection with the use of paper as a substitute for metal utilized in forming lith-

ographic printing plates. Lithographic plates require exposure to water in their preparation and use. The paper of the invention presents a wet strength which is well adapted to withstanding the immersion in water customarily encountered in making and using lithographic plates.

There are obtained in the impregnated paper a very substantial resistance to disintegration by water and a very high cohesion when saturated with water. For example, the impregnated paper may be saturated with water, placed on a supporting surface and rubbed a number of times by the thumb under pressure, without appreciable roughing or attrition of the paper surface occurring.

In addition, the presence of the vinyl compound in the paper web, in a water-receptive state as noted, allows the paper to be glazed without undesirable heating or tearing effects, and more especially without requiring that the paper be separately coated before the glazing operation is carried out, as is now necessary.

The use of a water-receptive sizing in paper renders the paper particularly resistant to curling. The paper, by means of the water-receptive sizing, absorbs and gives off moisture at a substantially uniform rate throughout the sheet. This tends to prevent curling when subjected to variable moisture conditions. Elimination of curling is desirable in many uses of the paper, and especially in connection with paper to be used as a substitute for metal in making lithographic printing plates.

It will be seen that improved materials and heating operations of the invention provide a number of advantages such as greater wet strength, dry strength, and other properties. Also, increased retention of modifying materials and more efficient methods of incorporating various types of materials in paper.

While we have disclosed specific materials and procedures of the invention, it should be understood that various other materials, changes and modifications may be resorted to, in keeping with the spirit of the invention as defined by the appended claims.

We claim:

1. A method of making fibrous material which comprises mixing together water-swollen particles of polyvinyl alcohol from which impurities tending to cause frothing and foaming and which are soluble in water below 50° F. have been removed with a suspension of pulp fibers, said polyvinyl alcohol being soluble in water at tem-

peratures above 130° F., forming a web in which the fibers are felted together, with the particles being distributed therein, subjecting the web to limited heating at temperatures between 130° F. and 220° F. during a period in which the moisture content of the web is reduced from 75-85% moisture to 5-10% moisture to plasticize the water-swollen polyvinyl alcohol and cause it to set into relatively thick separated masses which are characterized by elasticity when moistened.

2. Method of making paper which comprises incorporating into a suspension of fibers, water-swollen particles of polyvinyl alcohol, which particles will swell in cold water and will dissolve in water at temperatures above 130° F., forming a web in which the fibers are felted together, and water-swollen particles are distributed therein, subjecting the web to limited heating at temperatures between 130° F. and 220° F. during a period in which the moisture content of the web is reduced from 75-85% moisture down to 5-10% moisture to plasticize the water-swollen particles, continuing the heating operation at temperatures above 130° F. to cause the plasticized particles to merge into one another and form a continuous mass connecting constituent fibers of the web, and then heating at temperatures of from 220° F. to 450° F. for short intervals in the presence of small additional amounts of water added to the web, in order to toughen the web and increase the bonding strength of the polyvinyl alcohol in the fibers.

3. A method of making fibrous material which comprises adding water-swollen particles of polyvinyl alcohol to a suspension of pulp fibers, said polyvinyl alcohol being swellable in cold water and which dissolves at temperatures above 130° F., forming a web in which the fibers are felted together with the particles being distributed therein, subjecting the web to limited heating at temperatures between 130° F. and 220° F. for a period of from 60 to 90 seconds to plasticize the water-swollen particles, and cause them to set into relatively thick separated masses surrounding groups of constituent fibers of the web, then heating the web at temperatures between 220° F. and 450° F. in the presence of small additional amounts of moisture applied to the web, in order to toughen the web and increase the bonding strength of the polyvinyl alcohol in the fibers.

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