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METHOD OF IMPROVING THE WET STRENGTH OF PAPER BY ADDITION OF ETHYLENE-VINYL ACETATE COPOLYMER THERETO

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This invention relates to a process for improving the wet strength of fibrous materials, such as paper, textiles and the like. More particularly, but not by way of limitation, the present invention relates to a process of stock sizing fibrous sheet materials, such as paper and the like, to impart to such materials a higher mechanical strength in a water-wetted condition.

In the paper-making industry, it is the usual practice in the manufacture of a great many types of paper to incorporate a sizing agent in the paper by the process known as stock sizing. Stock sizing may be contrasted with external or surface sizing in that the size material in the former process is incorporated internally in the paper or fibrous sheet during the process of manufacture. Surface sizing, on the other hand, is used to apply a coating or film of the sizing agent to the sheet of paper or fibrous material after it has been formed. Both types of sizing procedures are utilized to improve the resistance of the fibrous sheet to penetration by water or other liquids.

In addition to the primary object of reducing the moisture penetration susceptibility of fibrous material, the application of an internal or surface size may be intended to achieve certain other objects, such as imparting a high degree of flexibility to the fibrous sheet, improving the mechanical strength properties of the paper when in a wetted or moist condition and improving the reception of the paper or other fibrous material to printing ink, dyes, etc. Although two of the most widely used internal sizing materials have heretofore been rosins and waxes, such materials, while imparting to the paper or other fibrous stock a high resistance to moisture penetration, have afforded less than optimum improvement in the wet tensile strength and other mechanical strength properties of fibrous sheets when in a moistened or wetted condition. The greatest improvement in the latter respect has heretofore been afforded by certain synthetic resin sizing materials. However, these sizing agents generally lack the highly moisture-resistant properties of waxes and rosins.

It is proposed by the present invention to provide an improved stock sizing process utilizing a novel sizing agent which imparts to the fibrous material in which it is incorporated a high resistance to water penetration and results in a substantial upgrading of the wet tensile strength of such fibrous material. Broadly, the present invention comprises first preparing an aqueous emulsion of a mixture of wax and a high molecular weight copolymer produced by the copolymerization of ethylene and vinyl acetate. The aqueous emulsion of the described character is incorporated as an internal or stock sizing material in the interstices and on the fibers of a sheet of paper or other fibrous material to impart to such material a high resistance to penetration by liquids and a substantial improvement in the wet tensile strength of such materials. In general, the emulsion constituting the size material may be incorporated in the fibers of the material treated by any of a number of stock sizing techniques well understood in the art, but a preferred method of incorporating the emulsion of the present invention is by initially preparing a slurry of the fibers and water

and then adding the wax-copolymer emulsion to the slurry under pH conditions at which the emulsion is not destroyed. A predetermined amount of alum is next added to the slurry-emulsion mixture to break the emulsion and deposit out the wax and copolymer in intimate admixture on the fibers in the slurry. The fibers are then dewatered by a suitable technique, and then pressed into an integrated sheet with the wax-coplymer mixture remaining evenly and effectively distributed in the interstices of the fibers and on the fibers as a thin coating.

The sheets of fibrous material produced in the manner described by the present invention are characterized in having a substantially higher tensile strength when wet or damp than sheets not subjected to the sizing treatment, and also have a higher wet tensile strength than sheets which have been sized with wax emulsions alone. Since the latter technique has been widely used to impart resistance to moisture penetration, and to achieve some improvement in the wet tensile strength of paper and similar fibrous materials heretofore, the present invention constitutes a technically improved and economically competitive method for producing sheets of fibrous materials having generally superior properties for many uses than the types of fibrous sheets which have been previously prepared using wax emulsions as an internal sizing material.

From the foregoing summary description of the invention, it will have become manifest that it is an object of the present invention to provide an improved process for manufacturing sized fibrous materials, such as paper and the like, in which the fibrous product is characterized in having a higher tensile strength when moist or wet than other fibrous materials manufactured without benefit of the invention.

An additional object of the present invention is to provide an improved sizing composition for internally or stock sizing sheets of fibrous material for the purpose of improving the wet tensile strength and resistance of such sheets to penetration by liquids.

A further object of the invention is to provide sheets of paper and similar fibrous materials having a high resistance to moisture penetration and characterized by a relatively high wet tensile strength.

Additional objects and advantages of the invention will become apparent upon reading the following detailed description of the invention.

In more specifically describing the present invention, the types of materials suitable for use in preparing the aqueous wax-copolymer emulsions used to internally size the sheets of fibrous material will first be considered. A variety of types of waxes may be employed with the main requirement of such waxes being a high degree of compatibility with the ethylene-vinyl acetate copolymer which constitutes the second major ingredient of the emulsion. Most of the materials qualifying as waxes under commonly accepted definitions are satisfactory for use in the invention with both naturally occurring and synthetic waxes being broadly operable. Suitable waxes may be of either animal, vegetable or mineral origin with such materials being defined broadly as opaque or translucent organic thermoplastics having a melting point between about 100° F. and 195° F. with such thermoplastics melting to relatively low viscosity liquids and not exhibiting thread-spinning phenomena, forming paste or gels with organic non-polar solvents, having water-resistant properties and possessing illuminant power. All of the waxy materials which are operative in the present invention have the common characteristic of a long saturated carbon chain and most of them are fatty acid esters of alcohols other than glycerols. However, in addition to

the latter type of waxy maerials, the exceptions to the latter definition which are yet commonly recognized as waxes are also generally applicable in the invention. These include, for example, the Japan waxes and the Myrica waxes.

Although, as indicated, a variety of waxes can be employed for pretreating fibrous stock in accordance with the process of the present invention, the waxes derived from petroleum such as microcrystalline, semimicrocrystalline, and crystalline waxes are preferred. The most preferred waxes for use in the invention are the paraffin crystalline waxes which occur in various fractions of most types of crude petroleum. Since the paraffin crystalline waxes are derived from the fractionated cuts obtained upon distillation of the crude petroleum, they are frequently referred to as petroleum distillate waxes to distinguish them from the so-called microcrystalline waxes which are derived from certain tarry or more viscous residues remaining from certain fractionations occurring in the petroleum refining processes. The latter waxes consist of mixtures of isoparaffins, naphthenes and small amounts of aromatic and straight chain hydrocarbons. Usually, the microcrystalline waxes are separated by solvent recrystallization methods from the non-distillable pot or still residue obtained as a result of the fractional distillation of petroleum. They may be differentiated from the paraffin crystalline waxes in that they are characterized by higher molecular weights and higher boiling points than paraffin wax. Also, the microcrystalline waxes are generally more ductile and exhibit higher viscosities and higher refractive indices than paraffin waxes.

The paraffin waxes preferred for use in the present invention are derived from the overhead distillate fractions of petroleum, and manifest melting points in the range of from about 117° F. to about 150° F. and Saybolt viscosities in the range of from about 35 S.U. to about 45 S.U. at 210° F. The paraffin waxes are further visibly characterized by crystallizing into large, well-formed distinct crystals of the plate and needle types. The physical characteristics of a paraffin wax may vary over the range indicated, depending upon the crude petroleum source, the portion of the crude which is used for wax producion and the differences in refining techniques. The paraffin waxes are unsaponifiable but can be readily emulsified in water in the presence of a suitable emulsifying agent. In order to illustrate further the various types of paraffin waxes that are preferably utilized in this invention, a brief description will be given of the procedure employed in the manufacture of paraffin wax.

A customary fractionation of crude petroleum stocks yields light fractions or cuts comparatively rich in wax components which, as hereinbefore indicated, are termed paraffin or distillate wax. These paraffin rich fractions are normally liquid at elevated temperatures and upon cooling to lower temperatures, the wax content readily precipitates. After satisfactorily cooling a wax distillate, the precipitate is removed by a filtering process in the form of slack wax. Slack wax normally contains from about 20 to about 40 percent by weight oil content. Next, the slack wax is sweated, which operation merely consists of heat treating the wax whereby the oil therein drains from or sweats out of, the solid wax as the temperature is slowly raised. The sweating operation yields a crude scale wax containing about 2 percent by weight oil. Fully refined paraffin wax is then obtained by merely further sweating the crude scale wax to a specific melting point range followed by treatment with a suitable adsorbent. The fully refined product usually contains less than 0.5 percent by weight of oil. In the practice of the present invention, scale wax or mixtures of the refined wax with either slack wax or scale wax can be employed.

The second major component of the emulsion used as a size material in the practice of the present invention is a copolymer of ethylene and vinyl acetate having a polymerized vinyl acetate weight content of from about 10 percent by weight to about 40 percent by weight and, preferably, from about 20 percent by weight to about 35 percent by weight. These copolymers can be conveniently prepared by copolymerizing a mixture of ethylene and vinyl acetate in the presence of a free-radical catalyst, e.g., tertiary butylhydroperoxide, in a suitable reactor at a pressure of from about 1500 to about 3000 pounds per square inch, and at a temperature of from about 150° C. to about 250° C. Varying conditions of temperature, pressure and reactant concentrations, as well as variations in the type and amount of catalyst, will give copolymers of varying molecular weight, ethylene to vinyl acetate ratio and melt index.

Ordinarily in this art, the molecular weight of the resulant copolymer is not expressed as such because of the difficulty and uncertainty of reliably ascertaining this property. Accordingly, the preferred manner of specifying the molecular weight characteristics of such copolymers is in terms of the copolymer's melt index as determined by ASTM D–1238–57T. Briefly stated, this test consists of determining the amount in grams (melt index value) of the copolymer that can be pressed through a standard orifice in 10 minutes at 190° F. with a piston weighing 2160 grams. The ethylene-vinyl acetate copolymers useful in the present invention exhibit melt indices ranging between about 3 and about 500 and, preferably, between about 3 and 30.

In general, the emulsions which constitute the sizing material used in the practice of the present invention will include, in addition to the copolymer and wax hereinbefore described, a suitable emulsifying agent and water. Additionally, small amounts of various well-recognized modifying or filler materials which are compatible with the wax and copolymer components of the emulsion may be added to the composition for the purpose of modifying some of the specific properties of the fibrous sheets fabricated by the process of the invention. These materials and their effect are, however, well known to those skilled in the art and it is not proposed in this application to detail their particular characteristics, or the amounts which it may be desirable to add in a specific instance.

The relative amounts of wax and copolymer which are used in the emulsion compositions employed in the invention may vary over a wide range with the wax-copolymer weight ratio extending from about 1:1 to 99:1. Preferably, on a weight basis, between about 4 parts of wax to 1 part of copolymer, and 3 parts of wax to 2 parts of copolymer are used in preparing the emulsion.

The amount of the emulsifier which is employed in preparing the emulsion used in practicing the invention is not particularly critical, provided only that a sufficient amount of the emulsifier be employed in each case to produce a relatively stable homogeneous emulsion in which all of the wax-copolymer globules are retained in suspension in the water. Amounts of the emulsifier which substantially exceed the minimum required to effect good emulsification can be tolerated but serve no useful purpose in most instances and are therefore generally undesirable. Preferred emulsifying agents for use in practicing the invention are the amine soap types of emulsifier and these may, in general, be employed in weight percentages (based on the total weight of the emulsion) of from about 7 percent up to about 11 percent. In the case of some wax-copolymer systems, an amount of this type of emulsifier as high as 15 percent by weight can be tolerated.

In addition to the amine soap types of emulsifiers, other well-known emulsifiers, such as a mixture of 60 percent by weight of a polyoxyalkylene derivative of sorbitan palmitate and 40 percent by weight of sorbitan palmitate function suitably in the invention. In the preferred method of practicing the invention, the preferred amine soap emulsifying agent is formed in situ during the preparation of the emulsion. The procedure of preparing the emulsion, including the formation of the emulsifying

agent in situ, will be hereinafter described in greater detail.

The amount of water employed in forming the described aqueous emulsions is not critical to the practice of the invention provided that a sufficient amount of water be utilized to assure the suspension of all of the wax-copolymer mixture in the emulsion. In general, at least about 3 parts by weight of water for each part by weight of the total solids content of the emulsion is employed. Above this minimum amount of water generally required, the emulsions may be diluted with up to about 15 parts by weight of water for each part by weight of the dispersed phase.

As a final consideration relative to the ingredients of the emulsion used in practicing the invention, it is preferred to include in the emulsion a small amount of a protective colloidal material, such as a polyvinyl alcohol resin, or fine clay for the purpose of stabilizing the emulsion and assuring against the premature breaking thereof. Such protective colloidal materials are well known in the art and their function well understood. It should be noted that although the process of the invention is preferably practiced by including a relatively small amount of such protective colloid in the emulsion, the emulsions may be formulated without such inclusion and may, in such instances, be effectively utilized as an internal size material in the fabrication of sheets of paper and other fibrous materials.

The general procedure which is preferably followed in preparing the emulsions used in the invention comprises initially mechanically mixing in the weight ratio hereinbefore described, finely divided particles of the ethylene-vinyl acetate copolymer with particles of the wax to be used. The mixture of wax-copolymer is then heated to a temperature exceeding about 205° F. and, preferably, when the heating is carried out at atmospheric pressure, between about 205° F. and 215° F. The water to be employed in the emulsion is brought to a boil and the hot wax-copolymer mixture and boiling water are combined in a suitable blending device capable of developing high shear forces in the mixture.

Preferably, the wax-copolymer mixture is initially added to a preheated mixing device prior to the addition of the water and is subjected to a sort period of agitation to assure thorough mixing of the wax and copolymer particles. At this time, the emulsifying agent may be either added to the wax-copolymer mixture, or it may be formed in situ therein by adding a suitable amine to a wax-copolymer mixture to which has previously been added a sufficient amount of a fatty acid to produce, upon addition of the amine, the desired amount of emulsifying agent. The boiling water, to which has been added a protective colloid, such as polyvinyl alcohol resin, if one is used, is then added to the mixture and is thoroughly agitated therewith for a sufficient period of time to assure complete emulsification of the wax-copolymer mixture. The protective colloid may be added to the mixture prior to, at the time of or following the addition of the water. Following the period of agitation in the mixing device, the mixture is poured into a cooled container and is brought rapidly to ambient temperature while continuing the agitation of the mixture to prevent the growth therein of wax crystals.

The internal or stock sizing techniques by which the aqueous emulsion of the present invention may be incorporated in sheets of fibrous material are generally well understood in the art and, as is well known, are subject to considerable variation in conditions depending upon the final characteristics or properties desired in the paper or fibrous sheets, the type of equipment used in fabricating the sheets, the type of pulp or fibers from which the sheets are to be made and a multitude of other factors which may be different in each particular sizing situation. In evaluating the properties imparted to hand sheets of kraft paper prepared for laboratory testing, however, a preferred sizing procedure was employed, and is believed to be generally applicable to the incorporation of the wax-copolymer emulsion in fibrous sheets as an internal size.

At the outset of the stock sizing procedure, an aqueous slurry of the pulp fibers from which the sheet stock is to be made is prepared by thoroughly mixing about 20 grams of the pulp with water in a pulp fiber concentration of about 1 percent by weight. In preparing the hand sheets of kraft paper used in the wet tensile strength tests hereinafter described, unbleached kraft pulp fibers were employed. Soft water is preferably used when available. The aqueous slurry of the unbleached kraft pulp is agitated for a sufficient period of time to uniformly distribute the fibers in the water and engender uniformity of fiber size. In commercial paper manufacture, the slurry may be that which normally exists in the paper manufacturing process in the beater, in the jordan, in the beater chest or in the machine chest. The wax-copolymer emulsion may be added to the slurry of the fibrous stock at any of these points in the commercial process, but is preferably added at the beater.

After beating or agitating the slurry for an extended period of time, the slurry is cooled to ambient temperature (the temperature is raised slightly by the agitation) and its pH is adjusted to avoid breaking of the emulsion and precipitation of the wax and copolymer on the fibers of the stock immediately upon addition of the emulsion to the slurry. In the preparation of the hand sheets used in the tests hereinafter described, the slurry was prepared using soft water and was therefore slightly acidic. When the wax-copolymer emulsion is slightly basic in nature as, for example, when an amine soap emulsifying agent is utilized, and therefore has a pH higher than 7, it is desirable to adjust the pH of the pulp slurry up to a neutral or basic value. This may conveniently be accomplished by the addition of a soda ash solution or other suitable basic material, such as caustic soda, sodium silicate or sodium aluminate. In commercial paper manufacturing, acid conditions in the beater generally prevail in mills where white water is used to furnish the beater and, in such cases, the pH of the pulp slurry is adjusted in the manner described.

After adjusting the pH of the slurry to neutral or slightly basic, the emulsion is diluted with several parts of water ranging from about 3 parts up to about 15 parts by weight and the diluted emulsion is then added to the slurry in an amount sufficient to give a total wax-copolymer-emulsifier content in the mixture of from about 0.25 percent by weight to about 40 percent by weight based on the weight of the dry pulp fibers in the slurry. In other words, the percentage of the constituents of the emulsion, other than water, in the total weight of the slurry and emulsion, with water excepted, may range from about 0.25 percent by weight to about 40 percent by weight. The amount of the active size material (wax-copolymer) required to obtain a desired sizing effect varies with the furnish or grade of paper which is to be made, the fibrous material being used and with mill conditions. For example, some pulps, such as unbleached kraft pulp, are easier to size than others. The effectiveness of the sizing does not increase in direct proportion to the amount of sizing agent added. Generally, the maximum sizing effect is realized when from about 0.75 to 1.5 percent by weight of size is used, based on the weight of the dry pulp fibers.

The mixture of emulsion and pulp slurry is next thoroughly agitated to assure that the size is well dispersed in the stock prior to the addition of the coagulating or precipitating agent and/or alum (aluminum sulfate). However, as is well known in the art, there are occasional instances where it is preferred to add all or a part of the precipitating agent and an amount of aluminum sulfate prior to the addition of the size material. Thus, on occasions when the water used in preparing the slurry is very hard, it is advisable to adjust the pH to about 7 with alum prior to the addition of the size.

In preparing the hand sheets used in testing the size material of the present invention, the precipitating agent, consisting of 3 grams of aluminum sulfate for each gram of solids in the added emulsion, was introduced to the slurry-emulsion mixture after the mixture had been well agitated. The alum (aluminum sulfate) is added in the the form of an aqueous solution. In general, when the unbleached kraft pulp is the type of fibrous material employed and the emulsion is added in the manner above described, the prescribed weight ratio of alum to emulsion solids will yield a mixture having a pH of between about 4 and 5.5. However, if the pH should fall outside this range following the addition of the alum, it is desirable to add suitable acidic or basic materials to bring the mixture within this range since better fixing of the size appears to result when it is precipitated from a solution of this pH. Moreover, precipitation of the size from a slurry-emulsion mixture having a more acidic pH than about 4 appears to impart an undesirable brittleness to the sheets of fibrous material fabricated from the pulp.

Following the addition of the alum to the slurry-emulsion mixture, the mixture is then agitated for a slightly longer period of time to assure contact of the alum with all of the dispersed phase of the emulsion. The whole mixture is then subjected to any of the treatments ordinarily used for preparing sheet stock of fibrous material from pulp slurries. In preparing the hand sheets hereinbefore described, the mixture was poured on a fine mesh screen (about 100 mesh) and air was drawn through the screen by vacuum to remove a substantial portion of the water from the mixture. The web which was formed upon the screen by the described de-watering was then removed, placed between two layers of felt and passed between a heated roller and hot plate to remove substantially all of the remaining water and to fix the size upon the cellulose fibers.

In order to evaluate the effect of stock sizing unbleached kraft paper using the wax-copolymer emulsions hereinbefore described, a plurality of sized hand sheets 11 inches in width and 11 inches in length were made and were cut into strips 6 inches in length by 1 inch in width. The unbleached kraft paper was selected for testing because of its use in the manufacture of liners and medians for corrugated board which is frequently used in the packaging industry for containing high moisture content foods and other moist materials, and which is also frequently subjected in shipment to exposure to water and high moisture conditions. A plurality of the hand sheets were prepared using emulsions which contained a paraffin wax having a melting point of between 124.2 and 126 and an oil content not exceeding 0.25 percent. The Saybolt color of the wax was between 28 and 30 and its tensile strength was between 350 and 360 p.s.i.

The ethylene-vinyl acetate copolymer employed in the emulsion used in preparing the hand sheets contained about 28 percent vinyl acetate, was characterized by a melt index of about 25, a molecular weight of approximately 300,000 and a density at 30° C. of 0.95 gram per cubic centimeter. The weight ratio of paraffin wax to copolymer used in preparing the emulsions was 70:30.

For purposes of comparison, the emulsion sized hand sheets were subjected to both wet and dry tensile strength tests and, additionally, an unsized hand sheet was similarly tested. Tensile strength tests were also conducted on hand sheets which had been stock sized using an aqueous emulsion containing only paraffin wax of the type used in the wax-copolymer emulsion. In the case of both the wax and the wax-copolymer emulsions, triethanolamine stearate was the emulsifying agent employed and soft water was utilized in preparing the emulsions. The constitution of the two emulsions used in stock sizing the unbleached kraft pulp for comparison wet tensile strength tests are tabulated in Table I.

TABLE I

Wax emulsion:	Weight percent
Paraffin wax	17.90
Triethanolamine stearate	7.30
Soft water	74.80
70% wax, 30% copolymer emulsion:	
Wax-copolymer blend	15.30
Triethanolamine stearate	7.46
Polyvinyl alcohol resin (protective colloid)	0.76
Soft water	76.48

In the wet tensile strength test, the sheets of paper were immersed for a period of 24 hours in water prior to conducting the tensile strength test. In all of the tensile strength tests, the tests were performed on an Instron instrument following the procedures prescribed in ASTM–D–1320–57T. The results of both the wet and dry tensile strength tests are tabulated in Table II.

TABLE II

Specimen Tested	Tensile Strength, lbs./square inch	
	Wet	Dry
Unsized	76	4,266
Sized with 40 percent* of Wax Emulsion	449	1,136
Sized with 40 percent of Wax-Copolymer Emulsion	508	1,250
Sized with 30 percent of Wax Emulsion	275	968
Sized with 30 percent of Wax-Copolymer Emulsion	384	1,030
Sized with 10 percent of Wax Emulsion	221	890
Sized with 10 percent of Wax-Copolymer Emulsion	273	1,429
Sized with 5 percent of Wax Emulsion	220	1,242
Sized with 5 percent of Wax-Copolymer Emulsion	369	2,192
Sized with 2 percent of Wax Emulsion	159	1,167
Sized with 2 percent of Wax-Copolymer Emulsion	298	3,764

*Percentage figures in this column refer to the weight percent of dry ingredients of the emulsion in the sized sheets based upon the weight of the dry fibers in the sheet.

It may be perceived in referring to Table II that the hand sheets which were stock sized using the emulsion containing wax and the ethylene-vinyl acetate copolymer (in a weight ratio of 7:3) gave a much higher wet tensile strength than the hand sheet which was not subjected to treatment with any size, as well as the hand sheets which were sized using an emulsion containing only the paraffin wax and using the same amount of sizing. Moreover, the treatment of the hand sheets with the wax-copolymer size imparted to the finished sheets a higher dry tensile strength than those sheets which had been treated with an emulsion containing only an equivalent amount of wax even though both types of sized sheets did not possess a dry tensile strength as high as the dry tensile strength of the unsized paper. The latter characteristic is generally true of sized fibrous materials with the sacrifice in dry tensile strength being tolerated in order to obtain the benefit of the moisture-resistance imparted by the size.

From the foregoing description of the invention, it will have become apparent that the present invention provides a novel procedure for improving the wet tensile strength of sheets of fibrous material which have been subjected to an internal sizing treatment to reduce the water permeability thereof. The novel fibrous sheets produced by the invention are useful for a variety of purposes which will be well understood and appreciated by those skilled in the art.

Although certain specific examples of exemplary methods of practicing the invention have been outlined in the foregoing description by way of example, it will be apparent to those skilled in the art that certain modifications and innovations may be made in the suggested conditions and chemical materials employed. For example, the described method of incorporating the wax-copolymer

emulsion in the slurry of pulp fibers is intended to be merely illustrative of one method by which such addition may be accomplished. The paper-making technology is well aware of other stock sizing techniques which may be employed with equal efficacy. It is thus intended that insofar as the broad principles of the present invention are relied upon in stock sizing fibrous materials to achieve the useful results attributed to the invention, any innovations and modifications which may be adopted in the method of stock sizing utilized, the particular types of emulsifiers and dispersing agents used, and the particular conditions and procedures used in finally fabricating the sheets of fibrous material with the size incorporated therein shall not remove such practice from the spirit and scope of the invention as defined by the following claims.

What is claimed is:

1. A method of improving the wet strength of paper which comprises mixing with the paper pulp which is to be used for making said paper an emulsion composition comprising water, an emulsifying agent and from about 0.25 percent by weight to about 40 percent by weight, based on the dry pulp, of a wax-copolymer mixture comprising from about 50 parts by weight to about 99 parts by weight wax and from about 1 part by weight to about 50 parts by weight of an ethylene-vinyl acetate copolymer containing from about 10 percent by weight to about 40 percent by weight vinyl acetate and having a melt index of from about 3 to about 500, and forming the treated paper pulp thus obtained into paper.

2. The method of claim 1, characterized further in that said wax is a petroleum-derived wax having a melting point of between about 117° F. and about 150° F.

3. The method of claim 2, characterized further in that said ethylene-vinyl acetate copolymer contains from about 20 to about 35 percent by weight vinyl acetate and has a melt index of from about 3 to about 30.

4. The method of claim 3, characterized further in that the wax-copolymer mixture comprises in the range of from about 4 parts wax to about 1 part copolymer to from about 3 parts wax to about 2 parts copolymer.

5. The method of claim 4, characterized further in that the wax-copolymer mixture is used in an amount to provide from about 0.75 percent by weight to about 1.5 percent by weight based on the dry pulp.

6. The method of claim 5, characterized further in that said emulsifying agent is selected from the group consisting of amine soaps and a 60:40 weight ratio mixture of a polyoxyalkylene derivative of sorbitan monopalmitate and sorbitan palmitate.

7. The method of claim 6, characterized further in that said emulsion is prepared by:

(a) mixing between from 60 percent by weight to about 80 percent by weight wax with from about 20 percent by weight to about 40 percent by weight copolymer;

(b) heating the wax-copolymer mixture to at least 205° F.;

(c) adding the emulsifying agent to the wax-copolymer mixture;

(d) adding boiling water to the hot wax-copolymer mixture in a weight ratio of at least 3 parts by weight of water to 1 part by weight of wax-copolymer mixture;

(e) thoroughly mixing the wax-copolymer mixture and water to form an aqueous emulsion; and

(f) cooling the aqueous emulsion to ambient temperature while agitating the emulsion to prevent growth of wax crystals.

8. A sheet of paper having improved wet tensile strength, said sheet of paper being characterized in that the preparation thereof includes the step of mixing a wax/ethylenevinyl acetate copolymer blend with the paper pulp which is used for making said paper, said wax-copolymer blend being used in an amount in the range of from about 0.25 percent by weight to about 40 percent by weight, based on the dry pulp, and comprising from about 50 parts by weight to about 99 parts by weight wax and from about 1 part by weight to about 50 parts by weight of an ethylene-vinyl acetate copolymer containing from about 10 percent by weight to about 40 percent by weight vinyl acetate and having a melt index of from about 3 to about 500.

9. A sheet of paper as described in claim 8, characterized further in that:

(a) the wax of said wax-copolymer blend is a petroleum-derived wax having a melting point of from about 117° F. to about 150° F.; and

(b) said ethylene-vinyl acetate copolymer contains from about 20 to about 35 percent by weight vinyl acetate and has a melt index of from about 3 to about 30.

10. A sheet of paper as described in claim 9, characterized further in that:

(a) said wax-copolymer blend comprises in the range of from about 4 parts wax to about 1 part copolymer to from about 3 parts wax to about 2 parts copolymer; and

(b) said wax-copolymer blend is used in an amount to provide from about 0.75 percent by weight to about 1.5 percent by weight based on the dry pulp.

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