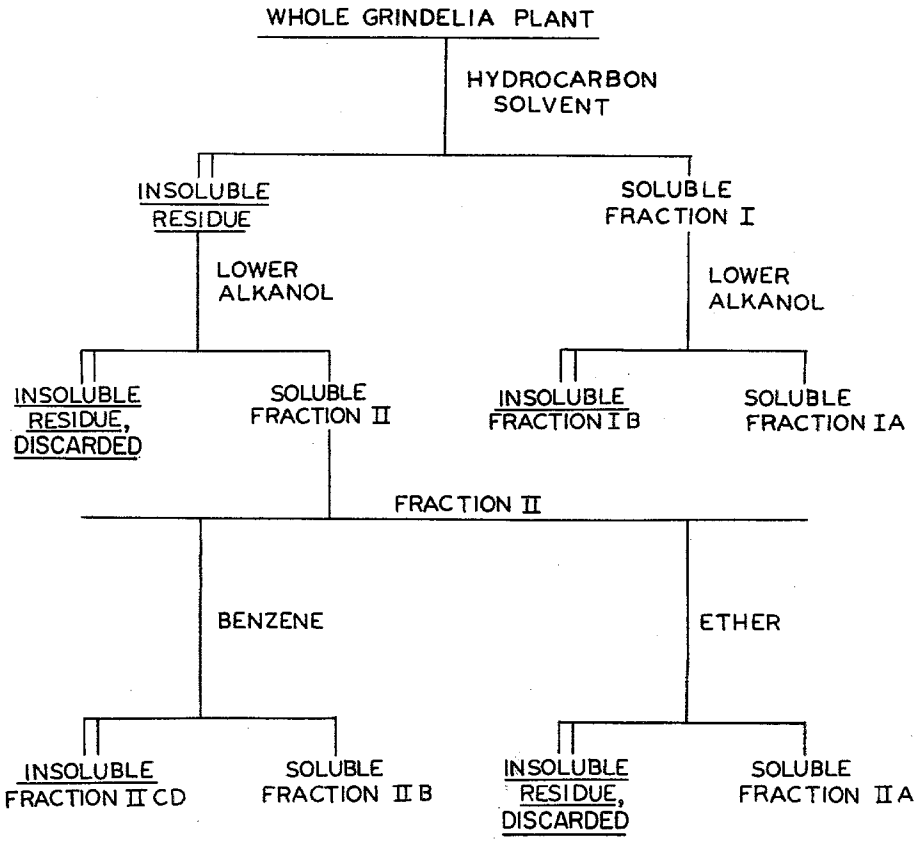
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METHOD OF SIZING CELLULOSE FIBERS WITH RESINOUS MATERIAL FROM THE PLANT GRINDELIA AND PRODUCT THEREOF

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This invention relates to novel methods of producing resin-coated cellulosic fibers, to novel fibrous products containing such fibers and particularly to internally sized, fibrous cellulosic materials, such as paper, board, shaped pulp articles and the like. The terms "cellulose" and "cellulosic fibers," as used in this specification and in the appended claims, refer to materials and fibers which are made up in whole or in part of cellulose, or modified cellulose or other substances which resemble cellulose in their ability to adsorb or absorb the sizing agents of the present invention.

At present, conventional sizing agents are usually derived from rosin. For various practical and economic reasons the raw material which is presently the predominant source of rosin in the United States is aged pine stumps, recovered from former forest lands which have been stripped of trees as a result of pulpwood lumbering operations. These stumps, which according to former practice were removed from the ground with the aid of dynamite, are now harvested with the aid of specialized tractors which pull them from the ground more or less by brute force. The harvested stumps are then sent to centrally located naval stores plants where they are reduced, by means of "hogs" and other types of shredding equipment to splinter-like chips. These chips are the starting material for the various chemical operations involved in producing a rosin size.

To begin with, the chips are usually treated with volatile organic solvents to extract their rosin content. Then the extracted chips are steamed to recover reusable solvent therefrom. After separation of the rosin from the volatile organic solvent, the rosin is converted to an aqueous dispersion which may be partly saponified by admixture with an alkali, such as caustic soda. Optional additives include protective colloids, such as casein, and filler or extender materials, of which kaolin is a representative example. Also, sizes containing rosin which has been chemically modified prior to saponification are now gaining favor.

Despite the wide-spread commercial acceptance of modified and unmodified rosin sizes, they are not without their disadvantages. The brute force removal of stumps from the ground and the grinding of large stumps to small chips consume a great deal of energy, require specialized equipment, incur high labor costs and are therefore unnecessarily expensive. When the above-described disadvantages are considered along with the fact that suitable stands of pine are found only in limited geographical areas and the fact that the forests are shrinking in size, it is apparent that there is a subsisting demand for sizing agents not derived from tree stumps.

Consequently, it is a principal object of this invention to fulfill this demand. It is a further object to provide a

source for sizing agents which does not necessitate the shredding of wood. Still another object is to provide paper sizing agents for application to cellulosic fibers without the aid of volatile solvents, such as are required with some of the synthetic resinous materials which have previously been proposed as substitutes for rosin sizes. A further object of the invention is to provide herein unrecognized sizing agents for application to water suspensions of hydrated or unhydrated pulp in the beater, stock chest, Jordan engine, fan pump, head box or at any other suitable point in the paper or board making process which is in advance of the sheet-forming step. Another object is to provide heretofore unrecognized sizing agents for application to cellulosic fibers either alone or in admixture with other sizing agents.

The above objects can be fulfilled in a surprisingly effective manner with the aid of a material which has heretofore been considered to have only limited usefulness in fields remote from the art presently under consideration. We have found that natural resinous materials derived from the plant Grindelia are useful in the sizing of cellulosic fibers. Our invention rests, in part, on the discovery that these natural resins may be converted, with or without prior modification, to alkaline solutions from which, under proper conditions, they can be made to precipitate on cellulosic fibers.

The plant Grindelia, from which our sizing agents are derived belong to the tribe Asteroideae of the natural family Compositae. The genus, Grindelia, includes some twenty-five species, six or eight of which are found in South America. The remainder occur in the United States mostly west of the Mississippi River, generally in arid and semi-arid plateau regions, although certain species also appear in regions where rainfall is more plentiful. A particularly prevalent plant in the United States is the specie *G. squarrosa,* commonly referred to as "Curly Cup Gumweed." Other well known species are *G. hummilis,* "Marsh Gumweed," *G. camporum,* "Field Gumweed," *G. robusta, G. nanna, G, fastigiata, G. perennis* and *G. Blakei,* among others. The varied species are perennial or biennial and produce, in varying amounts depending on the specie, a sticky resinous substance which manifests itself on the stem and leaves and especially on the flower heads. From this characteristic is derived the common name "gum plant" or "gum weed." Extracts of the plant have been shown to exhibit some utility in certain areas of the pharmaceutical field, but beyond this there has been apparently no further investigation of the plant for any purpose, except by the present inventors.

The various natural resinous materials produced in and on the growing plant Grindelia are essentially insoluble in water, but soluble in varying degrees in common hydrocarbon solvents, halogenated hydrocarbon solvents, ethers, lower alkanols, benzene, carbon disulfide and other organic solvents. These natural resinous materials can be readily separated from the other materials constituting the remainder of the plant. Such separation constitutes a necessary first step in the production of paper sizing solutions for use in the present invention. Separation of the natural resins from the plant is followed by an optional modification step. Then water, alkali, and the modified or unmodified resinous material are mixed together to form an aqueous, alkaline resin solution

containing saponified and/or unsaponified resin. Thus, the term "resin solution," as used in this specification and in the appended claims refers not only to homogeneous molecular mixtures of water and saponified resin ("true solutions"), but also to resin-in-water emulsions of unsaponified resin and to systems comprising water and both emulsified and dissolved resin.

The Grindelia resins contained in such a resin solution as is described above can be made to precipitate on cellulosic fibers with the aid of one or more coagulants, which will be described in some detail hereinafter. The invention is not restricted to any particular procedure for applying the coagulant(s). It is necessary only to form a water suspension by bringing together cellulosic fibers, a resin solution of the character described above, and an effective amount of the coagulant for the sizing agent. By an "effective amount" is meant any amount which is large enough to cause precipitation of the sizing agent on the fibers without being detrimental to the final product.

Various adjuvants may be incorporated in the sized fibrous articles produced according to our method, by adding such adjuvants either to the alkaline resin solution or to the aforesaid water suspension prior to, during or after deposition of the size. Included within the purview of the term "adjuvants" are: other sizing agents which can be applied to cellulosic fibers from water suspensions, pigments, dyes, fillers, extenders, protective colloids, viscosity control agents, wetting agents, anti-crystallizing agents, germicides, anti-oxidants, and, generally, any known additive for cellulosic fiber sizing compositions. It is understood, of course, that such adjuvants should be compatible with the sizing material of the present invention. After the addition of adjuvants, if any, and the deposition of the sizing material on the cellulosic fibers, water is removed from the suspension and the fibers are dried, with or without prior formation into shaped articles.

The novel products of the present invention include any and all articles formed of cellulosic fibers and carrying a size containing resinous material derived from the plant Grindelia. We contemplate the production of bulk fibers as well as the formation of shaped articles. Thus, the shape, volume and density of the finished fibrous product are of no consequence. Generally speaking, the novel products of the invention include not only sized paper, paper board, cardboard, hard board, molded pulp, papier mache and the like, but also coarse fibers in mats, in compressed blocks (such as are used in packing typewriters and the like), and in any other commercially useful form.

The production of the sizing agents used in connection with the present invention begins with separation of the natural resins from the plant Grindelia. Although other separation methods may undoubtedly be employed to derive our novel sizing agents from the plant Grindelia, we prefer to employ solvent extraction methods. A fairly good yield of resin can be obtained from the plant with a single extraction step, such as with a lower aliphatic clorinated hydrocarbon solvent. However, we prefer to employ a plurality of extraction steps, using different solvents, so that a more complete recovery of resin may be achieved. Multiple extractions with diverse solvents yield various rather specific fractions which can be used individually or in admixture with one another in making the novel sizing agents described herein. We will now describe a preferred extraction scheme with the aid of the accompanying drawing which constitutes a schematic diagram thereof.

In accordance with the representative extraction scheme shown in the drawing, dry, pulverulent plant solids, including pulverized leaves, flower heads and stems are leached with any common hydrocarbon solvent, such as by percolation. Some of the plant solids dissolve in the hydrocarbon solvent. This dissolved material constitutes a hydrocarbon solvent soluble fraction of the plant. The remainder of the plant solids constitute an insoluble residue.

The resultant liquor, containing solvent and both dissolved and undissolved material, is then filtered. The insoluble residue is caught on the filter. The hydrocarbon solvent soluble fraction passes through the filter with the solvent. Upon separation of the solvent from the filtrate, such as by distillation, a hydrocarbon solvent extract of the plant Grindelia is isolated. It is referred to hereinafter as "Fraction I," or as a hydrocarbon solvent soluble extract of Grindelia. At room temperature, it is a viscous oil.

Fraction IA can be obtained from Fraction I by the leaching thereof with a lower alkanol. The soluble portion of Fraction I is referred to as Fraction IA. Fraction IA is then a lower alkanol soluble, hydrocarbon solvent soluble fraction of the plant Grindelia and it resembles viscous oil at room temperature. The insoluble portion of Fraction I is referred to as Fraction IB. Fraction IB is then a wax-like lower alkanol insoluble, hydrocarbon solvent soluble fraction which melts at 71–82° C. By lower alkanol is meant any alkanol containing not more than about five carbon atoms, such as: methanol, ethanol, propanol, isopropanol, butanol, the isobutanols, amyl alcohol, the isoamyl alcohols, and mixtures thereof.

Although it is not essential that they be so derived, Fractions IA and IB are derived from Fraction I in this representative extraction scheme. Fraction I is simply extracted with a lower alkanol. That material which does not dissolve is Fraction IB. The solvent and dissolved material are then separated from Fraction IB by filtration and the filtrate is distilled to isolate Fraction IA.

The insoluble residue remaining after extraction of the whole Grindelia Plant with a hydrocarbon solvent can be further extracted with a lower alcohol to yield an alcohol soluble portion. From this soluble portion is derived soluble Fraction II. Fraction II is thus a hydrocarbon solvent insoluble, lower alkanol soluble fraction of the plant Grindelia and it has an acidic character. It is thus most readily obtained from the insoluble residue left over after leaching the whole plant with hydrocarbon solvent. This insoluble residue is mixed with lower alkanol and a portion of the residue dissolves. The remaining insoluble residue is separated from the liquor by filtering and is discarded. The resultant filtrate contains lower alkanol and Fraction II, a viscous oil which may be separated from the lower alkanol by distillation, and which will polymerize with itself when heated to temperatures approaching 150° C.

From Fraction II can be derived Fraction IIA by extraction with ether. Fraction IIA is thus an ether soluble, lower alkanol soluble, hydrocarbon solvent insoluble fraction, which is a viscous oil at room temperature. It may be obtained by extraction of Fraction II according to the procedure by which Fraction IA was obtained from Fraction I, except that ether is substituted for lower alkanol.

From Fraction II can also be obtained Fraction IIB by extraction with an aromatic hydrocarbon solvent, as for example benzene. Fraction IIB is thus a benzene soluble, lower alkanol soluble, hydrocarbon solvent insoluble fraction, also a viscous oil at room temperature. But, the insoluble portion remaining after extraction with benzene is also a useful material. This fraction, referred to as Fraction IICD, is a benzene insoluble, lower alkanol soluble, hydrocarbon solvent insoluble fraction, which material is solid at room temperatures. It will melt at 120° to 130° C. and will polymerize with itself when heated to temperatures approaching 150° C. Both Fractions IIB and IICD may be obtained from Fraction II, utilizing the same procedures used to isolate Fractions IA and IB from Fraction I, but using benzene instead of lower alkanol as the extracting solvent.

Following the separation of the plant resins from the plant, by extraction or otherwise, any one fraction or combination of fractions may be subjected to one or more treatments which for convenience are referred to herein by the collective term modification. The term "modifi-

cation" is used herein to refer generally to any and all physical and chemical treatments which might be applied to the plant resins to improve their characteristics for sizing purposes. Because those skilled in the art are well aware of various methods of treatment falling within the above definition, and because there is such a large variety of such methods of treatment available, it would be of little value to attempt an exhaustive listing. However, the following list is offered to illustrate a few of the many ways in which the Grindelia extracts may be modified: decoloration by bleaching with, for example, hydrogen peroxide, sodium hypochlorite or their equivalents, reduction of chromophores by treatment with one or more reducing agents, such as sodium hydrosulfite, hydrazine and sodium bisulfite; removal of chromophores by extraction or by adsorption on one or more surface-active materials such as activated carbon, Salka-Floc (trade name), which comprises finely divided wood cellulose, other allied cellulosic materials, cation and anion exchange resins, activated clay and activated alumina; hydrogenation; heat-treatment in the presence of a Lewis acid, such as Magnesium Chloride; transesterification with one or more alcohols and glycols; and chemically reacting part or all of the Grindelia extract with one or more fortifying agents.

We have found that Grindelia resin fractions can also be fortified with materials heretofore used in fortifying rosin. For example, a Grindelia adduct may be prepared by heating a Grindelia resin fraction with an α,β-unsaturated organic acid or anhydride in a weight ratio of resin to fortifier ranging from about 2:1 to about 20:1, preferably from about 3:1 to about 10:1. Among the various acids and anhydrides useful for carrying out these fortification reactions are: maleic acid, maleic anhydride, fumaric acid, dehydration products of citric acid, the half esters of maleic and fumaric acids, and others. The Diels-Alder reaction product may be subjected to various after-treatments or may be formed in the presence of other materials in addition to the α,β-unsaturated acid or anhydride.

After separation of the natural resins from the plant and after modification (if any) the modified and/or unmodified plant resins are converted into an alkaline aqueous resin solution, in which form the plant resin may be applied to the cellulosic fibers. In order to achieve a substantially complete utilization of the resinous content of the plant, it is believed most desirable to use Fractions I (containing IA and IB) and II (containing IIA, IIB and IICD) as the starting material for the aqueous alkaline resin solution. However, any one of the several modified or unmodified fractions (I, IA, IB, II, IIA, IIB or IICD) or any combination thereof may be used as the starting material. Furthermore, we contemplate the use of modified or unmodified plant resin fractions obtained with solvents and extraction procedures other than the ones mentioned herein. Consequently, it should be apparent that our novel method of sizing cellulosic fibers and the novel products of this invention are not restricted with regard to the use of all or any particular portion of the resinous material in the plant Grindelia, in the making of the sizing agents.

Formation of the alkaline resin solution or sizing agent begins with the preparation of an aqueous dispersion containing alkali and the modified or unmodified resinous material derived from the plant Grindelia. The term "alkali," as used in this specification and in the appended claims, refers to the hydroxides and carbonates of the ammonium radical and of the alkali metals. The alkali is slowly added to the aforesaid dispersion at room temperature with stirring. The pH of the dispersion is taken periodically. When the pH reaches a range of about 9.2 to about 11.5, preferably 9.8 to 10.5, the addition of alkali is discontinued. Water may then be added to bring the resultant alkaline resin solution to a convenient working strength.

Treatment in the above-described manner is effective to neutralize any and all of the resinous material from the plant. Fraction IB has a low acid number and does not dissolve; however, it is readily emulsifiable after neutralization. When preparing a resin solution using resinous material rich in Fraction IB, it is still possible to follow the procedure outlined above for forming a resin solution. This procedure should, however, be modified to the extent that the temperature is kept well above the melting point of Fraction IB (160° to 180° F.) until the emulsion has been formed. With this one change the above procedure is suitable for forming a resin solution containing significant amounts of Fraction IB in emulsified form.

Forming an aqueous alkaline solution of the modified and/or unmodified plant resin constitutes a convenient way of preparing the resin for application to the cellulosic fibers. This solution may readily be incorporated into or serve as the starting material for the water suspension in which precipitation of the size on the fibers is to be accomplished. In this connection, it should be understood that we have no desire to limit our invention to procedures involving a specific order of charging the fibers, size and coagulant to the aforesaid water suspension. It will readily be appreciated by those skilled in the art that the order of charging can be varied. For instance, the order can be: fibers first; size second; and coagulant third. Alternatively, the addition of fibers might be followed by addition of coagulant, then the size. Another possible procedure would include pre-mixing the size and coagulant and then adding them to a fiber suspension with violent agitation. The mixing and charging procedures may be carried out continuously or batchwise, preferably with continuous agitation, in any suitable variety of mixing equipment.

The preferred coagulant for our novel sizes is alum because it is economical, readily available and gives satisfactory results. However, the invention is not restricted in this regard. The term coagulant is intended to embrace mineral acids, acid salts and, generally, all of the known coagulants for rosin and modified rosin sizes. With alum, we have found that the amount of alum can be controlled in relation to the pH of the water suspension. If sufficient alum is added to produce a pH of about 4.5 to about 6, the amount so used will be an effective amount. With coagulants other than alum, the "effective" amount may be determined by routine control tests.

The weight ratio (dry basis) between the Grindelia resin sizes of the present invention and the cellulosic fibers treated therewith is not believed to be critical. Under most circumstances, the concentration of precipitated resin on the fibers will be from about 0.1 percent to 6 percent (based on the dry weight of the fibers) and, most commonly, it will be about 2 percent. However, there would be no departure from the scope of the present invention in using greater or lesser amounts than those falling within the above-stated range. Similarly, our invention is not restricted to treating aqueous fiber suspensions of any particular fiber concentration.

The usual mode of practicing our invention will involve applying one of our new sizing agents to water suspensions of hydrated or unhydrated pulp at some point in the paper making process in advance of the sheet-forming step, such as in the beater, the stock chest, Jordan engine, fan pump, or the head box. This step is most conveniently performed by adding the size solution to a turbulent stream of pulp at the head box or at some other point near the web-forming wire. When incorporating our novel sizing agents in the stock storage tank or at some other point where there is normally little turbulence in the pulp, the stock is most advantageously agitated during the addition of the sizing agent in rather dilute form. The coagulant may be added to the pulp at the same point at which the sizing agent is added or upstream or downstream thereof. However downstream addition is preferred. The addition of coagulant and sizing agent may

be carried out batch-wise or continuously—whichever is found the most convenient under the circumstances.

Sometime subsequent to the addition of the sizing agent coagulant, the pulp is run out on the wire or screen of a paper-making machine, such as a Fourdrinier machine and is formed into paper or board in the usual manner. Upon drying, the paper or board will be found to exhibit fair to excellent water repellency. Paper produced in accordance with the above procedure will be found to possess satisfactory resistance to blocking and will also be found to exhibit fair to good color and fair to very good inking characteristics, depending on the nature of the particular resin fraction employed in the sizing agent.

The following examples are presented with the intention of illustrating the invention without restricting it in any sense. All parts are by weight and the temperature is room temperature unless otherwise stated.

EXAMPLE 1

Fraction I

After pulverization in a hammer mill, 1,000 parts of the whole plant *G. squarrosa* are subjected to extraction by simple percolation at room temperature with 2,000 parts of commercially available Kuhn's VM & P CH47 (trade name) solvent, a naphtha containing about 83 percent aliphatic and 17 percent aromatic material and having a boiling range of 107 to 146° C. Upon filtration of the resultant slurry and distillation of the filtrate, 120 parts of a viscous oil, resin Fraction I, are isolated. The solid, hydrocarbon solvent insoluble material caught on the filter, having a weight (dry) of 880 parts, is dried and retained.

EXAMPLE 2

Fractions IA and IB

60 parts of Fraction I are mixed with 400 parts of methanol and the resultant slurry is filtered to remove therefrom about 5 parts of a waxy solid resin, melting at about 71° to 82° C., Fraction IB. Distillation of the filtrate to remove the methanol therefrom yields about 55 parts of a viscous oil, resinous Fraction IA.

EXAMPLE 3

Fraction II

The 880 parts of hydrocarbon solvent insoluble material retained from Example 1 are mixed with 1500 parts of methanol and the resultant slurry is filtered to remove the alcohol insoluble residue, which is discarded. The filtrate is found, upon distillation to remove methanol, to have contained 105 parts of a viscous oil, resinous Fraction II.

EXAMPLE 4

Fraction IIA

35 parts of Fraction II are extracted with 200 parts of ethyl ether. The resultant slurry is filtered to remove the ether insoluble residue which is discarded. The filtrate is found, upon distillation to remove ether, to have contained 30 parts of a viscous oil, resinous Fraction IIA.

EXAMPLE 5

Fractions IIB and IICD

35 parts of Fraction II are mixed with 70 parts of benzene and the resultant slurry is filtered to remove therefrom about 9 parts of a benzene insoluble solid resin melting at about 120° to 130° C., resinous Fraction IICD. Distillation of the filtrate to remove the benzene therefrom yields about 26 parts of a viscous oil, resinous Fraction IIB.

EXAMPLE 6

Chlorinated hydrocarbon solvent extract of whole Grindelia plant

1000 parts of the whole plant *G. squarrosa* are pulverized with a hammer mill and are subjected to extraction by simple percolation at room temperature with 4000 parts of chloroform. Upon filtration of the resultant slurry and distillation, 170 parts of a viscous oil are obtained.

EXAMPLE 7

Thermal polymerizate of Fraction II

A small sample of Fraction II is placed in a beaker and heated to 150° C. This temperature is maintained for 1 hour, at the end of which time the material is allowed to cool. A thermally polymerized product is obtained.

EXAMPLE 8

Thermal polymerizate of Fraction IICD

The procedure of Example 7 is repeated except that the starting material is Fraction IICD and the time is one quarter hour. Similar results are obtained.

EXAMPLE 9

Maleic anhydride adduct of Fraction II

10 parts of maleic anhydride and 90 parts of Fraction II are placed in a beaker. The beaker and contents are heated gently upon a hot plate until the resin and maleic anhydride have fused together. Heating is continued for 1 hour thereafter, the temperature being raised at a uniform rate to a terminal temperature of 150° C., whereupon heating is discontinued and the product is allowed to cool.

EXAMPLE 10

Maleic anhydride adduct of Fraction IA

The procedure of Example 9 is repeated with similar results, Fraction IA being substituted however for Fraction II.

EXAMPLE 11

Maleic anhydride adduct of Fraction IB

The procedure of Example 9 is repeated using Fraction IB instead of Fraction II. Similar results are obtained.

EXAMPLE 12

Preparation of sizing agent from Fraction IA

Neutralization of Fraction IA is carried out with continuous stirring at room temperature by the gradual addition of alkali (aqueous sodium hydroxide solution of 25 percent concentration) to an aqueous dispersion containing 100 parts of Fraction IA and 600 parts water. The pH of the mixture is taken frequently during the addition of alkali. Addition of alkali is continued until the pH of the mixture has risen to an end point of 11.0, whereupon the addition of caustic is discontinued. It is noted that the resin dissolves completely and that about 22.64 parts of sodium hydroxide solution have been used. Sufficient water is then added to bring the total weight of water present up to an amount corresponding to 99 times the amount of resin originally charged, i.e. to a solids content of 1.0 percent.

EXAMPLE 13

The procedure of Example 12 is repeated with similar results, the sodium hydroxide however being replaced by ammonium hydroxide.

EXAMPLE 14

The procedure of Example 12 is repeated, substituting potassium hydroxide for sodium hydroxide. Similar results are obtained.

EXAMPLE 15

Preparation of sizing agents from Fraction IB

Emulsification of Fraction IB is carried out with continuous stirring at a temperature of 82° C. by gradual addition of aqueous sodium hydroxide solution of 12 percent concentration to an aqueous dispersion containing

100 parts of Fraction IB and 600 parts water. The pH of the mixture is taken frequently. The addition of caustic is continued until the pH of the mixture rises to an end point of 11.0, whereupon the addition of caustic is discontinued. Sufficient water is then added to bring the total weight of water present up to an amount corresponding to 99 times the weight of resin originally charged, i.e. to a solids content of 1.0 percent.

EXAMPLE 16

Preparation of internally sized paper

Various sizing agents, alkaline resin solutions of modified and unmodified resins derived in accordance with procedures identical or similar to those employed in the above examples, are provided. Each of the various sizing agents is assigned a "test item" number for identification purposes. The various test items are then applied to bleached sulfite pulp according to a uniform internal sizing procedure, which involves preparing a water suspension of pulp, sizing agent and coagulant and then forming and drying handsheets of internally sized paper.

The origin of the various test items will now be set forth. Test item #1 is assigned to a blank run, that is, no size was present in the size solution. Test item #2 is assigned to a commercially available rosin type size, Hercules Staybelite (trade name) rosin size. Test item #3 and all of the remaining test items are alkaline solutions of modified or unmodified resin derived from the plant Grindelia. The derivation for the resin involved in these tests is as follows: Test items #3 and #4—Example 2; test item #5—Example 3; test item #6—Example 5; test items #7 and #8—Examples 7 and 8, respectively; test item #9—Example 9; test items #10–#12—same procedure as Example 9, but with increasing amounts of maleic anhydride; test item #13—same procedure as Example 9, but using Fraction IA instead of Fraction II; test item #14—same as for test item #13, but amount of maleic anhydride is increased; test item #15—same procedure as Example 9, but using Fraction IB instead of Fraction II; and test item #16—Example 6.

All of the resins used in test items 3–16 are neutralized in accordance with the procedure of Example 12, except test items #4 and #15. The latter test items are rich in Fraction IB and accordingly are treated in accordance with the procedure of Example 15. The resultant solutions are alkaline emulsions, rather than "true solutions." Test item #16, although treated in accordance with the procedure of Example 12, contains some of Fraction IB. As a consequence, the alkaline resin solution designated as test item #16 contains both emulsified and saponified (dissolved) resin.

In accordance with the uniform evaluation procedure adopted herein for illustrative purposes, 3.0 parts of pulp and 300 parts of water are beaten together in a blender until a good dispersion is obtained. Size solution (6 parts of each test item) is gradually added with further agitation. As agitation continues the pH is adjusted to approximately 5.0 by the addition of 9 parts of a 3 percent alum solution. Several TAPPI hand-sheets are then made up from the pulp sized with each test item. After drying for one hour at 105° C., the hand sheets are subjected to pre-evaluation conditioning in conformity with ASTM Standard Method D685–44 and to an ink test, a water repellency test, a blocking test. All tests were run under standard conditions of temperature (20° C.—except in blocking test) and humidity (2 percent). The color of the test sheets was also noted.

Testing procedure for the ink test involves making a cross on the sized paper with Sheaffer's (trade name) #42 washable blue ink. The degree of spreading of the ink is noted qualitatively. Water repellency is judged by observing the extent to which the sized sheets reject moisture when pressed down onto drops of water lying on a flat, non-porous surface. The blocking test involves compressing a stack of test sheets in a press for 16 hours under a pressure of 500 pounds per square inch and a temperature of 225° C. Color is judged visually.

The results of the evaluation tests show that blocking resistance is satisfactory with test items #2–16, no size having eben included in test item #1. The remainder of the test results are summarized in the following table, the heading "Resin" designating the particular type of modified or unmodified resin from which the alkaline resin solution is derived:

Test item No.	Resin	Ink Test	Water repellency	Color
1	No size	Poor	None	
2	Rosin	Good	Good	Good.
3	Fraction IA	do	Very good	Do.
4	Fraction IB	do	Excellent	Do.
5	Fraction II	Fair	Fair	Brown.
6	Fraction IIB	do	do	Lt. yellow.
7	Fraction II [1]	Good	Very good	Do.
8	Fraction IICD [1]	Very good	Excellent	Brown.
9	II(90)+M.A.(10) [2]	Good	Good	Yellow.
10	II(85)+M.A.(15)	do	do	Do.
11	II(80)+M.A.(20)	do	Very good	Do.
12	II(67)+M.A.(33)	Very good	Excellent	Do.
13	IA(90)+M.A.(10)	Good	Very good	Good.
14	IA(80)+M.A.(20)	do	Excellent	Do.
15	IB(90)+M.A.(10)	do	do	Do.
16	$CHCl_3$ Ext. [3]	do	do	Do.

[1] Thermally polymerized prior to neutralization.
[2] Alkalin resin solution derived from reaction product of 90 parts fraction II(II) and 10 parts Maleic Anhydride (M.A.). This symbolism is also utilized for the resins in test items 10-15.
[3] Alkaline resin solution derived from $CHCl_3$ extract of whole plant. The test results clearly demonstrate the benefits that can be obtained through the use of our novel methods and products.

We claim:

1. A method of producing resin-coated fibers, comprising: mixing together in an aqueous suspension cellulosic fibers, an aqueous alkali solution of resinous material including at least one fraction of the plant Grindelia selected from the group consisting of fractions soluble in hydrocarbon solvent and fractions insoluble in hydrocarbon solvent but soluble in lower alkanols containing from one to about five carbon atoms, and a coagulant in sufficient amount to precipitate said resin on the fibers; and recovering the coated fibers from the suspension.

2. A method according to claim 1 wherein the hydrocarbon solvent is a halogenated hydrocarbon solvent.

3. A method of producing resin-coated fibers, comprising forming a water suspension of cellulosic fibers, agitating said suspension, adding to said suspension an aqueous solution of resinous material, including at least one fraction of the plant Grindelia selected from the group consisting of fractions soluble in hydrocarbon solvent and fractions insoluble in hydrocarbon solvent but soluble in lower alkanols containing from one to about five carbon atoms, said aqueous solution having a pH of about 9.2 to about 11.5 and being furnished in an amount calculated to produce a resin content of about 0.1 to about 6 percent by weight on the dried fibers, adding an acidic coagulant to said suspension in sufficient amount to produce a pH of about 4.5 to about 6 in said suspension and to precipitate the resin on the fibers, draining the water from the fibers and drying them.

4. A method according to claim 3 wherein the addition of coagulant takes place subsequent to the addition of said aqueous solution of resinous material.

5. A method according to claim 3 wherein the resinous material is a solvent extract of the specie *G. squarrosa* modified by reaction with maleic anhydride in a weight ratio of about 2 to 20 parts of said extract per part of the maleic anhydride.

6. A method according to claim 3 wherein the hydrocarbon solvent is a halogenated hydrocarbon solvent.

7. A method according to claim 3 wherein the cellulosic fibers are wood pulp.

8. Cellulosic fibers having an adherent surface layer of resinous material including at least one fraction of the plant Grindelia selected from the group consisting of fractions soluble in hydrocarbon solvent and fractions insoluble in hydrocarbon solvent but soluble in lower alkanols containing from one to about five carbon atoms.

9. A shaped article formed from the fibers claimed in claim 8.

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