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PROCESS OF COLORING CELLULOSIC FIBERS

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This invention relates to a process of coloring cellulosic fibers. More particularly, this invention pertains to a process for the manufacture of colored papers, paperboards and the like by adding to an aqueous slurry of cellulosic fibers a liquid coloring composition and thereafter forming paper from the resulting slurry.

As is well known, papermaking fibers are usually colored by incorporation into fibrous aqueous slurries of water-soluble colorants, i.e., dyestuffs. On the other hand, water-insoluble colorants, i.e., pigments have been used in the paper industry only to a limited extent. The main reasons for a rather limited usage of pigments in coloring cellulosic fibers are: (1) unsatisfactory coloring efficiency, as compared to water-soluble dyestuffs; (2) uneven distribution of the pigment throughout the paper, causing an undesirable effect, known as two-sidedness in the papermaking art; (3) relatively low retention of water-insoluble colorants by the cellulosic fibers, even though employed in the form of aqueous suspensions containing surface active agents, thus causing marked losses of the colorants in the sewer system and contributing to stream pollution.

Accordingly, the present invention has as a principal object an improved process for coloring cellulosic fibers by adding a water-insoluble colorant in admixture with a dialkyl sulfoxide to an aqueous slurry of papermaking cellulosic fibers in the presence of a cationic agent in such a manner that the disadvantages enumerated hereinabove are avoided.

Another object of this invention is to provide an improved process for the manufacture of colored paper, paperboard and the like fibrous material by incorporating a liquid dispersion of a water-insoluble colorant in a dialkyl sulfoxide into an aqueous papermaking slurry in such a manner as to produce a colored paper web characterized by a high coloring efficiency and a substantially complete retention of the colorant incorporated therein.

Still another object of this invention is to provide an improved process of coloring cellulosic fibers in the form of an aqueous pulp slurry by adding thereto a cationic dispersion of a water-insoluble colorant in such a manner as to attain a substantially uniform distribution of the colorant throughout the pulp slurry and thus produce a uniformly colored paper web having no undesirable two-sidedness.

These and other objects and advantages of this invention will be apparent from the following description and the appended claims.

The process of this invention broadly comprises providing an aqueous slurry of cellulosic papermaking fibers, adding to said slurry (*a*) a composition comprising, as essential ingredients, a dialkyl sulfoxide and a water-insoluble colorant, and (*b*) a cationic agent, under such conditions that the colorant particles will be deposited or affixed on individual fibers and such fibers will retain their property of forming into a paper web on conventional papermaking equipment. The resulting colored paper web has colorant particles uniformly distributed throughout and contains substantially the entire amount of the colorant incorporated into the pulp slurry.

Accordingly, the invention is based on the discovery that it is possible to produce a paper colored with a water-insoluble pigment, provided that such pigment is added

in admixture with a dialkyl sulfoxide to an aqueous system containing papermaking fibers and deposited on the fibers with the aid of a cationic agent.

The process of this invention is applicable to coloring compositions containing any dialkyl sulfoxide capable of being used as a carrier for the insoluble colorants. Thus the coloring compositions may comprise dialkyl sulfoxides where the two alkyl groups are the same or different, including methyl-alkyl sulfoxides, such as methyl-decyl sulfoxide, methyl-dodecyl sulfoxide, as well as lower dialkyl sulfoxides containing up to 8 carbon atoms, such as dimethyl sulfoxide, methyl-ethyl sulfoxide, methyl-n-propyl sulfoxide, diethyl sulfoxide, and dibutyl sulfoxide. A particularly suitable representative of these is dimethyl sulfoxide manufactured and supplied by Crown Zellerbach Corporation of San Francisco, California.

The type of colorant employed in admixture with dialkyl sulfoxide in accordance with the present invention is immaterial so long as it is substantially water-insoluble. Thus the colorants suitable for incorporation into pulp slurries include an endless variety of inorganic and organic pigments which differ from each other in chemical composition or physical properties. Exemplary of inorganic color pigments are red, brown, yellow, orange, green, blue, white pigments, etc. The organic colorants cover essentially the complete color range and are prepared from practically all types of colored organic compounds. Exemplary of these are phthalocyanine pigments, vat pigments of the indigoid and quinonoid series, anthraquinone derivatives and the like.

In addition to the two essential constituents of the coloring composition, namely the dialkyl sulfoxide and a water-insoluble colorant, two auxiliary constituents may be incorporated therein, if desired.

First, water may be added to dilute the coloring composition to a desired solids concentration.

Secondly, a dispersing agent may be incorporated primarily in order to facilitate a uniform dispersion of the colorant in the sulfoxide.

The dispersing agents which may be employed in preparing a suitable coloring composition are: cationic agents such as quaternary ammonium salts or bases, long chain amine salts, tertiary sulfonium salts or bases, and the like. The quaternary ammonium compounds are examples of especially satisfactory dispersants. Exemplary of these is a quaternary ammonium salt containing 2 long straight hydrocarbon chains within the same molecule, supplied by the Harshaw Chemical Co. under the trademark "Uversoft D."

Similarly, a wide variety of non-ionic dispersing agents may be employed. Such dispersing agents are, in general, derivatives of aliphatic alcohols containing at least one free hydroxy group, particularly aliphatic polyhydroxy substances or polyhydric alcohols incompletely esterified with higher molecular weight aliphatic acids, particularly fatty acids. Exemplary of these are stearic acid monoester of diethylene or triethylene glycol, polyoxyethylene sorbitan stearates and the like.

Typical anionic dispersing agents which are suitable in preparing compositions in accordance with this invention are the soaps of aliphatic acids, alkyl aryl sulfonates, alkyl aryl polyether sulfonates, fatty alcohol sulfates, sulfonated aliphatic compounds, and the like. It should be noted that these and other anionic dispersants are used as aids in preparing the coloring compositions. However, their electrical charge will be destroyed in acidic medium after the composition has been admixed with the aqueous slurry of fibers in the presence of a cationic agent.

A wide variety of cellulosic fibers may be used in the process of the present invention. Such fibers in the form of aqueous slurries may be derived from softwoods, hard-

woods, or annual plants and may be produced by conventional chemical pulping procedures as well as by mechanical defibering procedures. Such procedures are conventionally employed in the manufacture of paper, paperboard, fiberboard, particle board and the like fibrous materials.

A coloring composition suitable for use in the process of this invention may be prepared by simply admixing together a dialkyl sulfoxide and a water-insoluble colorant with or without the above mentioned auxiliary constituents and then vigorously stirring in a suitable mixing or dispersing apparatus until a uniform dispersion is obtained.

The respective amounts of the various constitutents described hereinabove which may be employed in the preparation of the coloring compositions are shown in the following Table 1 in which the figures are expressed in percent by weight.

TABLE 1

	Broad Range	Preferred Range
Colorant	1–90	20–60
Dialkyl Sulfoxide	10–99	15–50
Dispersing Agent	0–25	5–15

It should be noted that water may be incorporated in the composition in an amount sufficient to produce a dispersion of a desired solids concentration which may range broadly from 0.1% to 50% and preferably from 5 to 25% by weight.

The coloring composition may be added to an aqueous slurry of paper-making fibers at any point prior to the paper web formation. Thus, it may be added at the beater, mixing chest, or paper machine headbox. A very convenient method of incorporating the composition into the pulp slurry is at the beater where the pulp is being circulated, thereby insuring a rapid and uniform distribution of the pigment throughout the pulp slurry.

The cationic agent may be incorporated into the pulp slurry either prior to, or simultaneously with, or after addition of the coloring composition to the slurry. In some instances, where a sufficient amount of a cationic dispersing agent has been admixed with the coloring composition, further addition of a cationic agent to the pulp slurry may be omitted.

A number of cationic agents may be used in the process of this invention. These include the cationic dispersing agents enumerated hereinabove, as well as melamine-formaldehyde resin, urea-formaldehyde resin, polyvalent metal salts such as aluminum sulfate, and the like. After the cationic agent has been incorporated into the pulp slurry, the pigment particles are affixed or deposited on the individual fibers very rapidly and their retention is substantially complete.

Also, if desired, other materials conventionally employed as pulp additives may be incorporated into the pulp mixture. Such materials may includes starches, gums, sizes, such as sodium rosinate or sodium aluminate, and the like.

Although the pH of the fibrous slurry is not too critical for deposition of the colorant on the fibers, best results are obtained if the pH of the slurry is adjusted to a value between 3 and 8, preferably between 4 and 6.5. The choice of pH level will depend primarily on such factors as the character of the pulp, the type of the colorant and the type of the cationic agent employed. The pH of the pulp slurry may be adjusted, if necessary, by adding thereto any suitable acidic agent such as an acid or a salt of strong acid and weak base or a polyvalent metal salt.

It will be understood by those skilled in the art that the amount of colorant added to a pulp slurry in the form of a liquid dispersion containing the colorant and a dialkyl sulfoxide may vary depending on the type of fibers, the type of the colorant and the degree of color intensity desired in the final paper product. Usually, an amount from 0.01% to 10% of the colorant, preferably from 0.05% to 3% of the colorant, based on the weight of oven-dry fibers will produce a highly satisfactory tinctorial strength in the resulting colored paper.

Also, the amount of the cationic agent incorporated into pulp slurry may vary broadly from 0.1% to about 4% based on the weight of oven-dry fibers. In any event, the amount of the cationic agent must be sufficient to insure a substantially complete deposition of the pigment particles on the fibers.

The aqueous slurry of cellulosic fibers treated with a colorant in accordance with this invention is then run on the paper machine wire or cylinder and the resulting paper web is passed through the drying section of the paper machine in the usual manner. Other properties may be imparted to the paper web by creping and/or calendering.

The hereindescribed invention will be further illustrated by means of the following examples which are intended to be descriptive of the invention in preferred embodiments thereof, percentages or parts being expressed by weight unless otherwise specified.

Example 1

A liquid coloring composition was prepared by placing in a mixing apparatus 25 parts of a pigment, i.e., titanium dioxide together with 45 parts of dimethyl sulfoxide heated to 75° C. and mixed vigorously until a uniform dispersion was obtained.

To an aqueous slurry of cellulosic fibers at 4% consistency comprising a mixture of 70 parts sulfite pulp and 30 parts groundwood, there was added sufficient of the resulting coloring composition to incorporate 1.25% of the pigment, based on the weight of the oven-dry fibers. After the resulting mixture was agitated for 30 minutes, a cationic agent, i.e., a quaternary ammonium salt containing 2 straight hydrocarbon chains of 16 to 18 carbon atoms in length within the molecule (Uversoft D), was incorporated into the mixture in an amount corresponding to 3% of the cationic agent based on the weight of oven-dry pulp. Thereafter sufficient aluminum sulfate in form of an aqueous solution was added to adjust the pH of the slurry to 6 and the slurry was formed into paper in a conventional manner. The resulting paper retained substantially all of the pigment incorporated into the pulp slurry and was characterized by uniform color.

Example 2

In a manner essentially similar to that described in Example 1, a coloring composition was prepared by admixing 70 parts of a pigment, i.e., Pigment Green B, 30 parts of dimethyl sulfoxide and sufficient water to produce a dispersion having 20% solids by weight.

The dispersion was incorporated into the same paper-making fibrous slurry as described in Example 1 in an amount corresponding to 2.75% of the pigment based on the weight of oven-dry pulp. Thereafter the same cationic agent as described in Example 1 and aluminum sulfate were incorporated into the pulp slurry to adjust its pH to 7.2. The resulting paper was colored entirely satisfactorily.

Example 3

An aqueous pigment dispersion was prepared by admixing together 60 parts of the pigment, i.e., phthalocyanine blue, 35 parts of dibutyl sulfoxide, 5 parts of a non-ionic dispersing agent, i.e., an alkyl aryl polyether alcohol and sufficient water to produce a dispersion of 10% solids concentration. The resulting dispersion was added to bleached kraft pulp slurry in an amount sufficient to incorporate 3% of the pigment based on the weight of oven-dry pulp. Sufficient aluminum sulfate was then added to adjust the pH of the slurry to 5.5. Paper formed from

the resulting slurry had a color of excellent fastness to light and a superior water- and oil-bleed fastness.

Example 4

A coloring composition was prepared by admixing together 75 parts of a water-insoluble pigment, i.e., Hansa Yellow, 15 parts of methyl-ethyl sulfoxide, 10 parts of an anionic dispersing agent, i.e., sodium rosinate and sufficient water to produce a dispersion of 20% solids concentration. After having added sufficient of the resulting dispersion to incorporate 1% of the pigment (dry fiber basis) to an unbleached sulfite pulp slurry, 1% of cationic melamine-formaldehyde resin, based on dry fiber, was added to the slurry followed by addition of sufficient hydrochloric acid to lower the pH of the slurry to 4.5. The retention of the pigment was substantially complete and the color of the resulting paper was excellent.

Example 5

A coloring composition was prepared by admixing together 40 parts of a pigment, i.e., Permanent Red 2–B, 40 parts of methyl-dodecyl sulfoxide, 20 parts of a cationic dispersing agent, i.e., "Uversoft D," described hereinabove, and sufficient water to produce a uniform dispersion of 20% solids concentration. The resulting dispersion was added to an aqueous pulp slurry of 1% consistency consisting of 60% bleached softwood kraft and 40% bleached hardwood kraft in an amount sufficient to provide 4% of the pigment based on the weight of oven-dry pulp. Following addition of the dispersion, 1% of cationic urea-formaldehyde resin, based on the weight of dry fiber, was added thereto together with sufficient aluminum sulfate to adjust the pH of the slurry to 6. The resulting paper was colored very uniformly.

Example 6

A liquid coloring composition was prepared by mixing together 55 parts of a pigment, i.e., Vat Yellow, 35 parts of methyl butyl sulfoxide, 15 parts of a cationic dispersing agent, i.e., "Uversoft D," described hereinabove, and sufficient water to produce a dispersion of 20% solids concentration. The resulting dispersion was added to a pulp slurry at 2% consistency consisting of 50% softwood kraft pulp bleached and 50% of bleached soda bagasse pulp. Thereafter 0.5% of cationic melamine-formaldehyde resin, based on oven-dry pulp, was added thereto, followed by addition of a mixture of equal parts of sodium aluminate and sulfuric acid in an amount sufficient to adjust the pH of the slurry to 5.8. The color imparted to the resulting paper was highly satisfactory.

Accordingly, it is apparent that by the present invention we have provided an improved process for the manufacture of colored papers and the like fibrous materials, which process includes incorporating into an aqueous slurry of cellulosic fibers of a coloring composition comprising essentially a water-insoluble colorant and a dialkyl sulfoxide, in the presence of a cationic agent. Through interaction of the dialkyl sulfoxide and of the cationic agent, the process results in a rapid, uniform, and a substantially complete deposition of pigment particles on the fibers, which in turn results in the formation of paper products characterized by a substantially complete pigment retention, highly satisfactory shades and superior color value which could not be attained heretofore using water-insoluble pigments.

The foregoing specification contains only a limited number of preferred embodiments of the present invention. It will be understood by those skilled in the art, that this invention is not limited thereto and it embraces numerous variations, modifications, and equivalents without departing from its spirit and scope. Rather, it is to be interpreted in the light of what is set forth and defined in the hereto appended claims.

We claim:

1. A process for coloring cellulosic fibers which comprises adding to an aqueous slurry of said fibers (*a*) a liquid dispersion comprising 10 to 99 parts by weight of a dialkyl sulfoxide and 1 to 90 parts by weight of a water-insoluble colorant and (*b*) a sufficient amount of a cationic agent to effect a substantially complete deposition of the colorant on the fibers.

2. The process of claim 1 wherein the dialkyl sulfoxide comprises an alkyl-methyl sulfoxide.

3. The process of claim 1 wherein the dialkyl sulfoxide contains up to 8 carbon atoms.

4. The process of claim 1 wherein the dialkyl sulfoxide comprises dimethyl sulfoxide.

5. The process of claim 1 wherein said dispersion includes a nonionic dispersant.

6. The process of claim 1 wherein said dispersion includes a cationic dispersant.

7. The process of claim 1 wherein said dispersion includes an anionic dispersant.

8. The process of claim 1 wherein said dispersion includes water.

9. The process of claim 1 wherein said cationic agent is added to said slurry prior to addition of said dispersion.

10. The process of claim 1 wherein said cationic agent is added to said slurry after addition of said dispersion.

11. The process of claim 1 wherein said dispersion and said cationic agent are added simultaneously to said slurry.

12. The process of claim 1 wherein the pH value of said slurry after addition of said dispersion and said cationic agent is from about 3 to about 8.

13. The process of claim 1 wherein the pH value of said slurry after addition of said dispersion and said cationic agent is from 4 to 6.5.

14. The process of claim 1 wherein the amount of the cationic agent is from 0.1% to about 4% based on the weight of the oven-dry fibers.

15. A process for the manufacture of colored paper which comprises adding to an aqueous slurry of papermaking fibers an aqueous dispersion comprising essentially 15 to 50 parts by weight of dimethyl sulfoxide, 20 to 60 parts by weight of a water-insoluble colorant and a sufficient amount of a cationic dispersing agent to effect a substantially complete deposition of the colorant on the fibers, the amount of said colorant added to said slurry being from 0.01% to 10% based on the weight of the oven-dry fibers, distributing said dispersion substantially uniformly throughout said slurry, adjusting the pH of the slurry to a value between 4 and 6.5, and forming a paper web from the resulting slurry.

16. The process of claim 15 wherein the amount of said colorant is from 0.05% to 3% based on the weight of the oven-dry fibers.

17. A process for the manufacture of colored paper which comprises adding to an aqueous slurry of papermaking fibers (*a*) a liquid dispersion comprising essentially 10 to 99 parts by weight of dimethyl sulfoxide and 1 to 90 parts by weight of a water-insoluble colorant, and (*b*) a sufficient amount of a cationic agent to effect a substantially complete deposition of the colorant on the fibers, and thereafter forming a paper web from the resulting slurry.

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