DYING OF CELLULOSIC FIBERS WITH CATIONIC DYE AND MONTMORILLONITE CLAY AND ResultING PRODUCT

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Int. Cl. D21h 3/80

U.S. Cl. 162—162

13 Claims

ABSTRACT OF THE DISCLOSURE

Cellulosic fibers are dyed by treatment with an aqueous solution of a cationic dye such as Methyl Violet and an alkali metal or acid montmorillonite clay, such as bentonite. The bentonite clay increases the retention of the cationic dye onto the fibers.

The present invention relates to a process of dyeing cellulosic fibers and to the resulting product. In one specific aspect, it particularly relates to the production of colored paper from cellulosic fibers wherein a cationic dye is used in combination with an alkali metal or acid montmorillonite clay.

Perhaps the most used procedure for preparing colored paper is to add a dye to the fibers prior to their being formed into sheets. Such procedure is commonly referred to as “beater dying.” The open top and vigorous mixing action of the beater makes it an excellent place to add the dye. However, the term “beater dying” is taken to include also dyeing in Hydrodulpers, Dynodupers, Jordan’s mixing chest, mixing tanks, fan pumps, head boxes and the like where mixing conditions exist.

The main classes of dyes used in the production of colored papers, and especially in beater dying, are the acid, direct and basic dyes. The first two classes, namely the acid and direct dyes, are anionic in nature and are generally sodium salts of color acids. Basic dyes are salts of color bases and in most cases are either the hydrochlorides or oxalates. They are cationic in nature and are readily soluble in water, especially under acid or neutral conditions. While these basic dyes have strong tintorial value and brilliance, they are not always retained to the desired extent by the fibers and especially by bleached fibers. Additionally, many of such dyes have a tendency to give “teethers” or “hairs” when used to dye even unbleached fibers. This effect, sometimes also termed “mottling,” can be undesirable, especially in the pastel shades. It is apparently caused by a small amount of the fibers coming into contact with an excessive concentration of dye or by certain fibers dyeing more readily than other fibers. The fibers absorb and retain such a quantity of dye that they are very heavily colored. Since there is little, if any, transfer or distribution of dye from the colored to the uncolored fibers, subsequent mixing of these heavily dyed fibers with the rest of the furnish does not result in a uniform distribution of the dye.

We have now discovered that the retention of cationic dyes by cellulosic fibers can be improved if the fibers are treated with a combination of the cationic dye and an alkali metal or acid montmorillonite clay. In addition to improving dye retention, our process also eliminates or substantially eliminates undesirable mottling in most instances. The process is especially valuable in dyeing the cellulosic fibers prior to their formation into sheets although it is also useful in dyeing already formed sheets as well as fabrics and the like derived from cellulosic fibers such as cotton.

As indicated, the cationic dye and alkali metal or acid montmorillonite clay are preferably added to dilute dispersions of the cellulosic fibers prior to the formation of sheets from such dispersions. Preferably, the addition is made to the beater or refiner or to the already beaten or refined fiber. In the latter case, the dye and montmorillonite clay are thoroughly mixed with the beaten or refined fibers. Any of the wide variety of commercially available beaters and/or refiners can be used. The cellulosic fibers can be any of those used in papermaking, such as those commonly referred to as sulfite, soda, sulfate, and ground wood stock, or fibers derived from rag, cotton, bast, flax and hemp fibers such as straw, or from repulped broke. The fibers may be bleached or unbleached. In this latter respect it is to be noted that our process has special utility in the dyeing of bleached fibers or mixtures of bleached and unbleached fibers—i.e. mixed furnish. The concentration of the fibers in the aqueous dispersion is generally less than about 4.0% by weight and preferably in the range of 0.5 to 3.0% by weight.

Any of the alkali metal montmorillonite clays can be used but the sodium clays are preferred over the lithium and potassium clays for example. It is also to be understood that the alkali metal montmorillonites occur naturally in an impure form, that is they are mixed with other clay materials. Such mixtures containing substantial amounts of the montmorillonite clays are suitable for the practice of the invention and are included in the term alkali metal montmorillonite clay. Of course, the alkali metal montmorillonites can be used in various purified forms if desired. The acid (or hydrogen) clays are easily obtained by passing an aqueous suspension of the alkali metal clays through a column containing the hydrogen form of a cation exchange resin.

The alkali metal or acid montmorillonite clay is used in an amount sufficient to increase the retention of the cationic dyes on the fibers. Preferably, such clays are used in an amount of about 0.05 to 1.0% by weight based on the dry weight of the fibers.


The amount of dye added to the cellulosic fibers is not critical and, of course, depends on the strength of the dye and color desired. Preferably the dye is used in an amount of about 0.05 to 1.0% by weight based on the dry weight of the fibers.

Both the alkali metal or acid montmorillonite clay and the cationic dye are added to the fibers as dilute aqueous dispersions or solutions. Preferably, the dispersions or solutions contain less than about 10% by weight of the montmorillonite clay and/or dye. When the said materials are to be added to the fibers prior to the formation of sheets therefrom, they are also preferably made as dilute dispersions or solutions and then added to the aqueous fiber dispersion. In many instances, it is preferred that the montmorillonite clay is first added to the fibers followed by addition of the cationic dye. Where the materials are added to already formed sheets or fabrics derived from cellulosic fibers, the montmorillonite clay dispersion is also first preferably applied. In paper making, such addi-
tion can take place at the calendar. But generally, any method of dipping, spraying, etc. of the sheets or fabrics can be employed.

In the preferred procedure wherein the alkali metal or acid montmorillonite clay and cationic dye are thoroughly mixed with an aqueous pulp or fiber dispersion, sheets can then be prepared using conventional techniques. In this respect, the relatively uniform dispersion of the pulp fibers containing the cationic dye and the montmorillonite clay is filtered through a screen which leaves a wet sheet on the screen. This sheet can then be dried and otherwise processed to make paper which can be used for a variety of purposes including use as a non-woven fabric. Any of the conventional paper-making machines can be used including the Fourdrinier and cylinder machines. The wet sheets are preferably dried at temperatures of 200° F. to 250° F., to a moisture content of less than about 10%. Any conventional drying technique can be used such as steam-heated dryers.

It is to be understood that conventional additives such as fillers and the like can be added. Representative fillers are talc, CaCO₃, silica, TiO₂ and so forth.

The following examples are illustrative of the process and products of the present invention and are not to be considered as limiting. Unless otherwise indicated all parts and percents are by weight.

**EXAMPLE I**

One liter samples of an aqueous dispersion of moderately refined bleached kraft pulp at 0.8% solids adjusted to a pH of about 4.5 were first prepared. To one sample was added 2 cc. of a 1% slurry of sodium montmorillonite clay (Wyoming bentonite) in water. Such slurry was prepared by dispersing 7% of the bentonite with water, passing the mixture through a centrifuge to remove grits and diluting with water to a 1% slurry. To a second sample of the fiber dispersion was added 2 cc. of a slurry of china clay (kaolin). To each of the above samples and a third sample containing no clay was added 4 cc. portions of a 0.2% aqueous solution of the basic dye New Fuchisine (available from American Cyanamid). The dispersions were thoroughly mixed and then single handsheets were made from such pulp samples on a Noble and Wood Handsheet machine at 0.025% pulp consistency. The wet sheets were dried on a rotary dryer at between 200 to 250° F., until they were dry—i.e. contained less than 10% moisture. The sheet containing the sodium montmorillonite clay was deeply and evenly dyed while the sheets containing no clay and the china clay were approximately the same color and very pale. They also showed feathering or motting.

**EXAMPLE II**

Example I was repeated except that the pH of the fiber dispersion was maintained at about 8.5. Substantially the same results were obtained with the sheet containing the sodium montmorillonite clay being far superior—i.e. more deeply and uniformly dyed with little or no motting.

**EXAMPLES III–XII**

Examples I and II were repeated except that the New Fuchsine dye was replaced by the following dyes: Green MX (Examples III and IV), Auramine O (Examples V and VI), Chrysoidine Y (Examples VII and VIII), Methyl Violet (Examples IX and X), and Methylene Blue (Examples XI and XII). The sheets containing the sodium montmorillonite clay had the same excellent dyeing as in Examples I and II with the exception that the Chrysoidine Y was apparently insoluble at pH 8.5 and thus the handsheet of Example VIII was not dyed to any appreciable extent. The sheets containing the sodium montmorillonite clay were all vastly superior to those containing the kaolin clay with the exception that the handsheets prepared using Methylene Blue at a pulp pH of 4.5 were approximately the same.

**EXAMPLE XIII**

Six by six inch cotton twill swatches were treated in the following manner.

(A) Eight swatches were wet and two of same dipped into each of 0.2% aqueous solutions of Methylene Blue 2B dye, Methyl Violet 4BX dye, Green MX dye and New Fuchsine dye. These eight swatches were marked as the controls.

(B) Eight swatches were dipped into a 1% clay dispersion as used in Example I and dried by hanging at room temperature. The said swatches were then rinsed in clean water and two of same dipped into each of the dye solutions identified in (A).

After the above procedures were completed (each dipping being for approximately ½ hour), the edges of the swatches were sewn to prevent unraveling and the cloths were subjected to five washings using Tide as the detergent. Each color was washed alone on the first wash and all together on the last four washes. The controls were all badly faded after one wash. After five washes the Green MX controls had no color, the Methylene Blue 2B controls were very light blue. The Methyl Violet 4BX controls were light violet and the New Fuchsine controls were faded even more than after one wash. In contrast, the clay treated swatches were only slightly faded after one washing. After five washings, the Green MX dyed swatches were green, the Methylene Blue 2B swatches were dark blue with some fading, the Methyl Violet 4BX swatches were dark violet and the New Fuchsine swatches were considerably darker than the controls. Similar results were obtained where swatches were dipped in the clay dispersion and rinsed before dipping into the dye solutions or rinsed and dried prior to being dipped into the dye solutions. However, the results were best where the clay dipping was followed by drying without the intermediate rinsing step.

It is apparent from the above examples that the montmorillonite clay greatly improves the dyeing of cellulosic fibers with cationic dyes. Where the dye is insoluble at a particular pH, the treating solution or pulp pH should be adjusted accordingly. The data of the examples also show that the montmorillonite clay is unexpectedly superior to other clays, such as kaolin, improving dyeing with a wide variety of basic dyes at various pH's. Example XIII shows the value of the present invention in the dyeing of already formed cellulosic materials, namely fabrics.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. **The process of dyeing cellulosic fibers which comprises treating such fibers with an aqueous dispersion of an alkali metal or acid montmorillonite clay and an aqueous solution of a cationic dye, said clay being used in an amount sufficient to increase the retention of the cationic dye by the fibers.**

2. The process of claim 1 wherein the clay is sodium montmorillonite.

3. The process of claim 1 wherein the fibers are first treated with the aqueous dispersion of the montmorillonite clay and then with the aqueous cationic dye solution.

4. The process of claim 1 wherein the cationic dye is a basic dye.

5. The process of claim 1 wherein the montmorillonite clay is used in an amount of about 0.1 to 1.0% by weight based on the dry weight of the fibers.

6. In the process of preparing colored paper from an aqueous dispersion of cellulosic fibers and a cationic dye, the improvement comprising adding an alkali metal or acid montmorillonite clay to the dispersion before forming the dispersion into sheets, said clay being used in an amount sufficient to increase the retention of the cationic dye by the cellulosic fibers.

7. The process of claim 6 wherein the clay is sodium montmorillonite.
8. The process of claim 6 wherein the montmorillonite clay is added to the dispersion before the cationic dye.

9. The process of claim 8 wherein both the montmorillonite clay and the cationic dye are added to the fiber dispersion as dilute aqueous dispersions or solutions.

10. The process of claim 6 wherein the montmorillonite clay is added in an amount of about 0.05 to 1.0% by weight based on the dry weight of the fibers.

11. The process of claim 6 wherein the fibers are bleached fibers or a mixture of bleached and unbleached fibers.

12. The product prepared by the process of claim 1.

13. The paper product prepared by the process of claim 6.

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