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PAPER

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This invention relates to a method for the preparation of an improved dyed paper and more particularly to a process of after treating surface colored paper.

Colored paper may be made by two processes. The color may be added to the paper before sheet formation by adding the color to the pulp in the beater. The more convenient and economical method is, however, the coloring of the sheet after it has been formed, by dipping or calendering. In the dipping process the sheet is dipped directly into a dye solution and allowed to drain, or the sheet is passed between rolls, one of which carries a film of dye solution to the surface of the paper, and is then passed through squeeze rolls for removing the excess dye solution from the paper. This latter rolls process is preferred to the process in which the sheet is passed into the dye solution. In the calendering process the dyeing is accomplished by placing dye boxes on the calender stack in contact with the calender rolls. In this process dyeing and calendering are accomplished in one operation.

Surface colored paper though much more economical to produce than that formed by the process wherein the coloring matter is added to the pulp before sheet formation, has the disadvantage of producing a color, even when basic or direct dyes are used, which will smudge or crock from the surface of the sheet and which is easily affected by contact with water or a moist object. This ready removal of the color is highly objectionable in that the color of the paper itself is affected with spots and streaks and any object coming in contact with the paper in the presence of water is badly stained.

Various classes of dyes have been used for the coloring of paper. Basic and direct dyes have an appreciable affinity for the cellulose fiber while acid dyes have very little affinity for the cellulose, but possess more satisfactory fastness to light than the basic colors and are more soluble than the direct colors.

Various methods have been suggested to overcome the disadvantage of surface colored papers outlined above. Thus, the moist sheet surface colored with basic dyes may be after treated with sulfurized phenolic compounds. This process is highly effective but is applicable only to the basic colors which are comparatively fugitive to light. Draves U. S. Patent No. 1,926,614 discloses a process for rendering paper surface dyed with direct or acid colors non-bleeding by means of an after treatment with a diaryl guanidine. Although improved results are obtained by this process still further improvement may be realized.

This invention has as an object the preparation of an improved surface colored paper. A further object is the preparation of a non-crocking surface colored paper. A still further object is the preparation of a non-bleeding surface colored paper fast to the action of water. A still further object is the fastness of the dye stuff on surface colored paper after the paper is after treated. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein the paper surface colored with a dye soluble in aqueous solutions and preferably surface colored with an acid or direct dye is subjected to an after treatment with an aqueous solution of deacetylated chitin.

Deacetylated chitin is a material which has only recently been available to the art. In copending application of George W. Rigby, Serial No. 731,600, filed June 21, 1934, there is disclosed a method for the preparation of a suitable deacetylated chitin. In this method shrimp, lobster or crab shells, freed from contaminant adherent material, such as flesh, by treatment with 1% solution of soda ash at the boiling temperature, then freed from lime salts by treatment with 5% hydrochloric acid followed by a second boiling with 1% soda ash solution, is deacetylated by treatment with caustic alkali at an elevated temperature for a considerable time, for example, with 40% sodium hydroxide at 110° C. for about four hours. Depending upon the conditions of this alkali treatment the material obtained contains from 20%–90% and preferably 70%–90% of its nitrogen in free amino groups.

The viscosity of the solutions made from the deacetylated chitin is markedly influenced by drying and other treatments to which the material is exposed. More drastic treatment than that exemplified above results in a material of low viscosity. Less drastic treatment than that above exemplified results in a material of increased viscosity. A material obtained by a given treatment may be increased in viscosity by heating for a considerable length of time or decreased by the addition of suitable deoxidizing agents, such as hydrogen peroxide, to an aqueous solution of a salt or to a suspension of the solid deacetylated chitin.

The Rigby application mentioned above discloses the preparation of numerous soluble salts of this material. The acetate of deacetylated chitin is preferred because of its ready availability, low cost and ease of use and the volatility of acetic

acid, but other acids which form water soluble salts with deacetylated chitin may also be used.

Having outlined above the general principle and purposes of the invention and described the unusual material which is used in the process of the present invention the following exemplifications of the process are given for purposes of illustration but not in limitation.

Example 1

A solution containing 20 gms. per liter of Crocein Scarlet (Colour Index 252) was prepared. Tissue paper was surface dyed by immersion, drained to remove superfluous dye solution and dried at 200° F. The tissue paper which was dyed a heavy red shade was very sensitive toward moisture. If sprinkled, the color ran badly and moistened paper or cloth brought into contact with it was badly stained.

The dried dyed tissue paper was immersed in a solution containing 0.78 gm. high viscosity deacetylated chitin per liter (dissolved with acetic acid). After draining to remove superfluous liquor, the treated tissue paper was dried at 200° F. This after-treatment completely eliminated the sensitivity toward moisture. Sprinkling with water caused no spotting and the color was not removed by contact with moistened cloth.

A much lighter shade of red was obtained by employing a dye solution containing 2 gms. of Brilliant Crocein per liter and a treating bath containing 0.3 gm. deacetylated chitin per liter. The resistance to moisture was equally satisfactory.

Example 2

The process was applied to calender dyeing by placing a box upon the calender stack in such a position that the paper, after being coated with a dye solution contained in one box was treated with a deacetylated chitin solution contained in a second box. Thus the process was satisfactorily applied to 16 point paper board by applying 50 lbs. Metanil Yellow (Colour Index 138) in 100 gallons water from the top box on the calender stack and 15 lbs. 10 oz. deacetylated chitin in 100 gallons water from a lower box on the calender stack after the board had been colored from the box on the upper roll.

The above examples illustrate the use of two acid dyes. Acid dyes in general may be employed in the process of the present invention. Further acid dyes which have been used and which are given in illustration of the wide range of the applicability of the invention are

	Colour Index
Fast Acid Blue	208
Acid Violet	698
Acid Green	666
"Pontacyl Blue Black SX"	246
Orange II	151
Tartrazine	640

The process is generally applicable to paper, including paper board, wrapping paper, tissue paper, crepe paper, absorbent paper, building paper, cardboard, cover paper, news print, printing paper and writing paper. The process is also of value in the after treatment of direct dye surface colored paper as is shown in the following example.

Example 3

A solution containing 10 gms. per liter of "Pontamine Sky Blue 6 BX" (Colour Index 518) was used for dip dyeing tissue paper. The dyed paper without drying was immersed in a deacetylated chitin solution containing 0.3 gm. per liter. The paper was subsequently dried at 200° F. The stability of the treated dyed paper was satisfactory. Satisfactory results were likewise obtained with Pontamine Fast Scarlet 4 BS (Colour Index 326) and Stilbene Yellow (Colour Index 622). Direct dyes in general may be used.

While the process is generally applicable to surface colored paper, even to paper surface colored by means of basic dyes so that an improvement is effected, even with basic dye surface colored paper by treatment with the process of the present invention, the results are by no means as striking as are the results obtained when the process is applied to paper surface colored with acid and direct dyes. These dyes therefore represent a very much more preferred embodiment of the invention.

The concentration of the dye liquor depends on the depth of shade desired and the absorbency of the paper. It varies from a small fraction of a per cent solution up to a saturated solution, the latter depending upon the solubility of the dyestuff. Dyeing and after-treating may be done at room temperature or at higher temperatures up to the boil. Drying may be done at any temperature that will not burn the paper. Best results were obtained in deep shades by using 21–30 oz. of a 5% solution of deacetylated chitin as the acetate in 10 gallons of water. Light shades required less deacetylated chitin and direct colors required less deacetylated chitin than acid colors.

While the examples show the use of acid and direct colors separately, they may be used together. Best results were obtained by using the color first and then the deacetylated chitin, the pretreatment with the deacetylated chitin followed by dyeing being less satisfactory. The paper may be dried after dyeing as shown in Example 1 or treated without drying as shown in Example 3.

The drying of the surface colored paper after treating with deacetylated chitin solution causes a reaction to take place wherein the deacetylated chitin acetate loses acetic acid with the formation of deacetylated chitin which is itself insoluble in water. This process may be accelerated by heating which may also cause a further chemical change, in that the deacetylated chitin acetate may react with the loss of water to form an amide type compound. Treatment with acid anhydrides or acid chlorides also has the same effect. The dried paper containing deacetylated chitin either as such or as the acetate may also be treated with a variety of reagents which react with the carbohydrate amine polymer and insolubilize the deacetylated chitin. Formaldehyde and glyoxal are examples of such material.

While the invention has been described in detail in terms of deacetylated chitin which is obtainable from shrimp, crab or lobster shells, which are preferred because of their ready availability, the comparative ease of preparation of the deacetylated chitin, and the convenience of its use, the invention is generally applicable to the use, in the treatment of surface colored paper to prevent smudging, bleeding and the like, of deacetylated chitin insoluble in water or alkaline media, but soluble in aqueous organic acid media and depositing coherent films therefrom, i. e, organic acid soluble deacetylated chitin. In-

stead of shrimp, lobster or crab chitin, chitin derived from the outer integuments of insects such as locusts, grasshoppers, and the like, may be used. Deacetylated chitin from vegetable sources such as mycelium from fungi such as *Aspergillus niger* may likewise be employed.

In the claims the phrase "surface-colored paper after-impregnated with deacetylated chitin" is used to denote a dyed paper which is impregnated with deacetylated chitin after dyeing, i. e., the paper is dyed and thereafter impregnated.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

We claim:

1. Process of preparing an improved colored paper which comprises immersing paper in a solution of Crocein Scarlet, removing excess dye solution, drying, immersing in a solution of deacetylated chitin and again drying.

2. Process of preparing an improved colored paper which comprises applying an aqueous solution of a deacetylated chitin acetate to a sheet of paper surface colored with an acid dye.

3. Process of preparing an improved colored paper which comprises applying an aqueous solution of a salt of deacetylated chitin to a sheet of paper surface colored with an acid dye.

4. Process of preparing an improved colored paper which comprises applying an aqueous solution of a salt of deacetylated chitin to a sheet of paper surface colored with a direct dye.

5. Process of preparing an improved colored paper which comprises applying an aqueous solution of a deacetylated chitin acetate to a sheet of paper surface colored with a direct dye.

6. Process of preparing an improved surface colored paper which comprises impregnating a surface colored paper with an aqueous solution of a salt of deacetylated chitin.

7. Process of preparing an improved surface colored paper which comprises impregnating a surface colored paper with an aqueous solution of an acetate of deacetylated chitin.

8. Surface colored paper after-impregnated with deacetylated chitin.

9. Acid dye surface colored paper after-impregnated with deacetylated chitin.

10. Direct dye surface colored paper after-impregnated with deacetylated chitin.

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