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PROCESS OF MAKING COLORED PAPER

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This invention relates to colored papers, and especially to such papers that are fast to bleeding and to processes of coloring the papers.

Heretofore colored papers have been made by two general methods, namely by surface coloring in which water soluble dyestuffs of various kinds were applied to the surface of the formed sheet and beater dyeing in which insoluble pigment or a soluble dyestuff was mixed with the paper pulp before it was formed into a sheet.

Pulp which was colored with insoluble pigments was generally fast to bleeding but the coloring was not always completely satisfactory with respect to tinctorial strength. Only a limited number of shades could be made by this process, many of which were not particularly bright.

Formed sheets were generally surface colored either by running the sheets through water solutions of water soluble dyes or by passing the sheets between two rollers, one of which dipped into a solution of the dye. The dyeing of paper was also combined with the calendering operation in accordance with which one or more rolls of the calender stack was equipped with a color box so that a film of the water soluble dye solution would be carried into the nip where it would be taken up by the paper. In all of the processes in which soluble dyes were used the colored dyestuff was only loosely associated with the fibres. Any contact of the paper with water caused resolution of dye, spotting of the paper and bleeding onto other objects which came in contact with the wet paper.

It was possible to obtain good light fastness and brightness in a limited number of colors with water soluble dyes but all such colored papers bled. In general the best light fastness was accompanied with poor brightness, and the bright shades were poor in light fastness. Consequently it was not possible to obtain colored papers in bright shades with fastness to bleeding and good light fastness.

Attempts have been made to prevent spotting and bleeding of surface colored papers by after-treating with tannic acid lakes and the like. While an appreciable decrease in water bleeding has been accomplished by this means the weakening of the tinctorial strength of the dye, the dulling effect of the after-treatment, the excessive cost of the after-treatment and generally the inferior light fastness of the products made these processes impracticable. As far as we are aware no process of surface dyeing paper has been provided which produces a colored paper of good light-fast and good bright shades and one which is free from spotting and bleeding.

It is among the objects of the present invention to provide colored paper which is free from spotting and bleeding when contacted with water, and to provide processes for making the colored paper. Another object is to provide colored paper in bright shades having excellent light-fastness. Another object of the invention is to provide surface colored paper having the improved fastness properties referred to. Another object is to provide processes for the surface dyeing of paper which provide non-bleeding colored papers which have satisfactory light fastness and brightness. Still other objects of the invention will be apparent from the following description.

The objects of the invention are attained generally by wetting the paper stock or a paper sheet throughout or in a surface layer with a solution containing a compound which has no or unsatisfactory tinctorial value but which will combine chemically with another substantially non-tinctorial compound in solution to form a colored composition which is insoluble and has high tinctorial value, and then applying a solution of said other compound to the sheet of paper. The solution which is applied initially to the paper may be a solution of a diazo salt or a solution of a coupling component of an insoluble azo dye, a solution of a dyestuff which upon oxidation produces an insoluble color or a solution of an oxidizing agent for developing such a dye, a solution of an inorganic salt which will combine with another organic or inorganic salt to form an insoluble colored compound or a solution of said other compound. The second solution applied to the paper contains whichever component of the colored insoluble substance that was not initially applied.

The invention is illustrated by, but not limited to the following examples:

Example 1

1000 lbs. of bleached sulfite of 6% consistency were treated in the beater with 20 gallons of a solution made by dissolving 10 lbs. of acetoacetanilide with 2 lbs. 5 oz. of sodium hydroxide. 5 lbs. of rosin size and 35 lbs. of alum were added and the fibers were formed into a sheet on the paper machine and partially dried. This sheet was then passed through a solution of stabilized diazo salt containing 1% by weight of diazotized meta nitro para toluidine, through squeeze rollers and dried.

The sheet was surface colored a brilliant yellow of very good fastness to light and complete bleeding fastness.

Example 2

Bleached sulfite tissue was passed into a bath containing ½% by weight of beta naphthol. The bath was made by adding one pound of beta naphthol to one pint of denatured ethyl alcohol and then adding 4½ oz. of sodium hydroxide dissolved in two quarts of water. In making the solution it is preferable, though not essential, to apply heat. When solution was complete the volume was made up to 12 gallons.

The bleached sulfite tissue was passed between two felt covered rollers, the bottom one of which rotated in the beta naphthol bath. The paper was then passed between two additional felt covered rollers, one of which rotated in a solution of stabilized diazo salt, containing 0.8% by weight of diazotized para chlor ortho nitroaniline. The diazo solution had been buffered by adding sodium acetate and 0.75% acetic acid giving a pH value of approximately 4.0. The sheet was then dried or creped and dried.

The tissue was colored a moderately bright orange of excellent fastness to light and complete bleeding fastness. The sheet was deeply colored on the surface and less deeply colored in interior portions.

Example 3

Bleached sulfite cover paper was passed through a bath containing a 1% solution of the meta nitro anilide of beta hydroxy naphthoic acid. This bath contained the anilide, alcohol and sodium hydroxide in the proportions of one quart of denatured ethyl alcohol and 4 oz. of sodium hydroxide to the pound of the anilide. After passing between squeeze rollers the paper was passed through a water solution of a stabilized diazo salt containing 1.5% by weight of diazotized para nitro ortho anisidine. The paper was again passed between squeeze rollers and then dried.

Surface coloration in medium depth scarlet of excellent fastness to light and complete bleeding fastness was attained.

Example 4

Bristol board was calender colored on one side by using in the first box an 0.8% solution of the anilide of beta hydroxy naphthoic acid. This solution consisted of one quart of denatured ethyl alcohol and 6 oz. of sodium hydroxide per pound of the anilide. In the second box was a solution of stabilized diazo salt containing 1.25% by weight of diazotized 5-nitro ortho anisidine.

The board was colored a wine shade of fairly good light fastness and complete bleeding fastness.

Example 5

Semi-bleached kraft wrapping paper was dyed on a two bath dipping machine. The first bath contained a 0.75% solution of the beta naphthalide of beta hydroxy naphthoic acid. This solution was made by dissolving equal weights of sodium hydroxide and the naphthalide in one quart of denatured ethyl alcohol per pound of the naphthalide. The second bath was a solution of a stabilized diazo salt containing 0.6% by weight of diazotized 2:5 dichlor aniline and 0.6% by weight of diazotized para nitro ortho anisidine.

The sheet was colored a pale scarlet of good light fastness and complete bleeding fastness.

Example 6

Unbleached sulfite tissue was colored on a two bath dipping machine and subsequently creped. The first bath contained 0.5% by weight of acetoacetanilide and 0.5% by weight of the ortho toluidide of beta hydroxy naphthoic acid each of which was dissolved with one quart of denatured ethyl alcohol and 4 oz. of sodium hydroxide per pound of the coupling component. The second bath was a solution of a stabilized diazo salt containing 1.5% by weight of diazotized 5-nitro ortho anisidine.

The dull orange surface coloring had moderately good light fastness and complete bleeding fastness.

Example 7

Bleached sulfite tissue was colored on a creping machine which was equipped with containers for two baths ahead of and in addition to the bath commonly used under the creping roll. The sheet was passed through the first bath which was acidic and contained a 1.5% by weight solution of diazotized para chlor ortho anisidine and a small amount of a compatible wetting agent. After squeezing the sheet was passed through the second bath which was a solution containing 0.5% by weight of diacetoacetyl tolidine sulfone and 0.5% by weight of beta naphthol. The latter bath contained 4½ oz. sodium hydroxide and 1½ pint of denatured ethyl alcohol per pound of each of the components.

The sheet was passed through the third bath under the creping roll which contained 0.1% acetic acid and the customary amount of glue which is commonly used in producing crepe. The sheet was then creped and dried. The third bath served to neutralize any alkali which was carried by the sheet upon leaving the second bath. Any acetic acid remaining in the paper after passing through the creping bath was volatilized when the sheet was dried, thus giving a neutral paper.

The brilliant orange surface coloring had good fastness to light and complete bleeding fastness.

Example 8

Bleached sulfite crepe was made and colored on the machine described in Example #7. The first bath contained 0.8% by weight of the sulfuric acid ester of Jade Green and 0.5% by weight of diaceto acetyl tolidine sulfone which had been dissolved with 5 oz. of sodium hydroxide and one quart of denatured ethyl alcohol per pound of the coupling component.

The second bath was a solution of a stabilized diazo salt containing 0.8% by weight of diazotized para chlor ortho anisidine and 0.1% by weight of acetic acid. The bath under the creping roll contained 0.05% by weight of potassium permanganate, 0.2% by weight of acetic acid and the customary quantity of glue used in producing crepe.

The tissue was surface colored a yellowish green of good light fastness and complete fastness to bleeding.

Alakaline solutions of other diazo dye coupling components can be mixed with other alkali soluble leuco esters of vat dyes and used for the first bath, and acid solutions containing diazo

salts and an oxidizing agent can be used for the second bath to produce variations in colors and colorings of excellent fastness and non-bleeding properties.

As an example of such a combination the sulphuric acid ester of "Ponsol" Blue BF may be used with aceto-acetanilide and diazotized meta-nitro-para-toluidine is mentioned.

In coloring with azo dyestuffs alone or in conjunction with other colors either component of the azo color may be applied first to the paper fibre or sheet. In general either of the components of the colors can be applied first.

Paper can be surface colored by using any diazotized or tetrazotized aryl amine compound, but only those which are free from solubilizing groups can be diazotized and used for the diazo base to produce colored papers which are absolutely fast to bleeding. Among the large number of such compounds which are free from solubilizing groups and have given satisfactory results when diazotized and coupled with azo dye coupling components, are mentioned meta-, ortho- and para-nitro-anilines, meta- and ortho-chloraniline, 2:5-dichlor-aniline, para-chlor-ortho-nitro-aniline, 4-nitro-2-amino-toluene, 3-nitro-2-amino-toluene, 3-nitro-4-amino-toluene, 4-chlor-2-amino-toluene, 5-chlor-2-amino-toluene, 6-chlor-2-amino-toluene, 4-nitro-2-amino-anisole, 5-nitro-2-amino-anisole, 4-chlor-2-amino-anisole, alpha naphthylamine, amido-azo-toluol, benzidine, dichlor-benzidine, dianisidine, 4:4'-diamino-diphenylamine. Many other diazotizable arylamine compounds which are devoid of solubilizing groups can be used.

Instead of solutions of stabilized diazo salts, the diazo baths can be made from the solutions of the desired arylamine. It is generally more convenient in practice to make the baths containing the diazo salts by way of dissolving stabilized diazo salts in water than by diazotizing the primary aryl amines at the location where the baths are to be used. Stabilized diazo salts are virtually dry compositions, usually in the form of powders which are stable in air, soluble in water and yield aqueous solutions containing the diazo salt, the stabilizing agent and other constituents of the composition. The term, stabilized diazo salts, as used in the specification and claims refers to such compositions. Various compositions of the kind are known. For example, such compositions can be made by adding to the diazotization medium a compound, such as 1:5 naphthalene disulfonic acid which forms with the diazo salt a type of double salt that precipitates in the diazotization medium. The precipitate is then separated from the diazotization medium as a damp solid or paste which is then mixed with a suitable dehydrating agent, such as partially dehydrated alum or magnesium sulfate. In this virtually dry condition the composition can be handled in air without decomposing and it can be kept for immediate use over long periods of time. Upon dissolving this composition in water, the diazo salt is contained in the solution in a condition to couple with azo dye coupling components. The acidity of the diazo baths is regulated so that when the solution of diazo component and the solution of the other component or components of the dye are mingled on the fibres, a neutral to slightly acid residual solution eventually results. The residual solution on the fibres should in no case be alkaline.

It is preferable to apply a dilute solution of a weak volatile acid, such as acetic acid to the colored fibres before they are dried, when residual alkali may be present, especially when the solution of coupling component is a relatively strong alkali solution or when it is applied to the paper after the diazo solution is applied. Exact neutrality is not necessary. A mildly acid residual solution is preferable, especially when the acid is a mild volatile acid since the residue of acid will be volatilized in the drying operation without harmful effect to the paper.

In all cases the coupling component of azo dyestuffs can be applied first but this is not essential since the component of the dyes can be applied in either order. In cases where the components couple as well in alkaline solution as in acid or neutral solutions good results are produced whether one or the other component is applied first. Depending upon whether the coupling can be made more advantageously in acid, neutral or alkaline solution a convenient order of applying the components may be selected.

Likewise a large variety of azo dye coupling components can be used to give non-bleeding colors. In general the azo dye coupling components which are devoid of sulfonic acid groups can be used to give non-bleeding colors. Among the coupling components useful for producing non-bleeding colored papers the following are mentioned as representative. The aryl amides of beta-hydroxy-naphthoic acid, the anilides of beta-hydroxy-naphthoic acid, meta-nitro-anilide of beta-hydroxy-naphthoic acid, beta-naphthalide of beta-hydroxy-naphthoic acid, ortho-toluidide of beta hydroxy-naphthoic acid, para-anisidide of beta-hydroxy-naphthoic acid, 6-chlor-ortho-toluidide of beta-hydroxy-naphthoic acid, ortho-phenetidide of beta-hydroxy-naphthoic acid, ortho-anisidide of beta-hydroxy-naphthoic acid, aceto-acetanilide, aceto-acetyl-ortho-chlor-anilide, diaceto-acetyl-toluidine-sulfone, aceto-acetyl-para-phenetidine, alpha-naphthol, beta-naphthol, phenol, resorcinol, 2:6-dihydroxy-naphthalene, 1:5-dihydroxy-naphthalene and beta hydroxy naphthoic acid. Still other arylamides of beta-hydroxy-naphthoic acids, aceto-acet-arylides, substituted naphthols, and ethers of beta-hydroxy-naphthoic acids can be used to produce colored paper which is fast to bleeding. Coupling components which contain sulfonic acid and carboxylic acid groups can be coupled on the paper fibre in accordance with the described procedure to produce colored paper of good brightness and light fastness but when sulfonic acid groups are present the colors are not absolutely fast to bleeding, such as naphthylamine-sulfonic acids, hydroxy-naphthylamine-sulfonic acids, 1:5-naphthalene-oxy-sulfonic acid, 1:4-naphthalene-oxy-sulfonic acid, para-amino-benzoyl-J-acid, sulfanilic acid and H-acid. By suitably selecting a coupling component it is evident that many variations in shade may be produced by coupling with a series of diazotized amine compounds.

Colored papers made by the preferred processes of the invention have excellent fastness to light, complete fastness to bleeding and are essentially fast to rubbing. The term "fast to rubbing" in the specification and claims means that when the colored material is rubbed with a clean cloth or paper, the color is not removed onto the cloth and the cloth is not colored unless or until fibre substance is detached from the body of colored fibre. For example the effect of combinations of diazotized amines and coupling components which are free from solubilizing groups when ap-

plied to paper fibres and sheets does not appear to be the same as the effect of such components on textile fibres. When applied to paper, the color does not rub off or become detached from the paper fibre when rubbed with a piece of clean cloth or paper, whereas same of the initially applied color on textile fibres crocks or rubs off until some other treatment is applied to remove the excess of color. When applied to paper none of the color can be removed by boiling water, whereas boiling water will generally remove some of the initially applied color from textile material. The surprising characteristic of these colors to combine immediately and permanently with paper fibres when such permanent fixation was not attained initially on textile fibres was unexpected notwithstanding the related but somewhat different compositions of the fibres. Thus the dye combinations used in accordance with applicants' invention produce properties when they are applied to paper fibres which the dyestuffs do not generally produce when they are applied to cotton textile fibres. These properties make the dyeing of paper practicable when such color combinations are used. In the dyeing of textiles with ice colors it was necessary to dye the fibre with the coupling component and then develop with the diazo component but in the coloring of paper either solution can be applied first. The action of the solutions on the paper fibres apparently produces a new composition of paper fibres and color material and is somewhat different than the action of the components on textile fibres. Whether the differences are due to differences in the chemical constitution or to differences in the mechanical structure between textile and paper fibres is unknown, and it is to be understood that the invention is not necessarily limited to any suggested theory.

Since from the foregoing description of the invention it will be apparent to those skilled in the art that many embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific illustrations herein set forth.

We claim:

1. The process which comprises consecutively wetting a surface layer of a formed article of paper fibres with a solution comprising an azo dye coupling component and a solution comprising a diazotized aryl amine, and drying, the total acid remaining on the fibre before drying being not in excess of that which produces a combined residual mixture on the fibre which is neutral to slightly acid.

2. The process which comprises consecutively wetting a surface layer of a formed article of paper fibres with a solution of an azo dye coupling component which is free from water solubilizing groups and a solution of a diazotized aryl amine which is free from water solubilizing groups, and drying, the total acid remaining on the fibre before drying being not in excess of that which produces a combined residual mixture on the fibre which is neutral to slightly acid.

3. The process which comprises wetting a surface layer of a formed article of paper fibres with an alkaline solution of an azo dye coupling component, applying an acidic solution of a diazotized aryl amine to the surface of said article, and drying, the acid in said solution of diazotized arylamine being sufficient to produce a residual solution which is neutral to slightly acid.

4. The process which comprises wetting a surface layer of a formed article of paper fibres with an acidic solution of a diazotized arylamine, applying an alkaline solution of an azo dye coupling component and drying, the total acid applied to the fibres being sufficient to make a residual solution on the fibre which is neutral to slightly acid.

5. The process which comprises wetting a surface layer of a formed article of paper fibres with an acidic solution of a diazotized arylamine, applying an alkaline solution of an azo dye coupling component, applying a solution of a weak volatile acid and drying, the total acid applied to the fibres before drying being sufficient to make a residual solution on the fibre which is neutral to slightly acid.

6. The process which comprises consecutively wetting a surface layer of a formed article of paper fibers with a solution comprising an azo dye coupling component and a solution comprising a stabilized salt of a diazotized arylamine, and then drying, said solutions being applied in such amounts that the total acid remaining on the fiber before drying is not in excess of that which produces a combined residual mixture which is neutral to slightly acid.

7. The process which comprises consecutively wetting a surface layer of a formed article of paper fibers with a solution comprising an azo dye coupling component and a solution comprising a stabilized salt of a diazotized arylamine, and then drying, said arylamine being free from solubilizing groups, and said solutions being applied in such amounts that the total acid remaining on the fiber before drying is not in excess of that which produces a combined residual mixture which is neutral to slightly acid.

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