

UNITED STATES PATENT OFFICE

2,153,697

DYED PAPER AND PROCESS OF MAKING
THE SAMELaurence W. Porter, Westbrook, Maine, assignor
to S. D. Warren Company, Boston, Mass., a
corporation of MassachusettsNo Drawing. Application August 20, 1936,
Serial No. 97,078

10 Claims. (Cl. 8—7)

This invention relates to the art of coloring (dyeing) paper in the web, and is concerned more particularly with the fixing or mordanting of a normally water-soluble dyestuff in and on the fibers of the paper web. The invention embraces the process, the fixing means employed in the process, and the product produced thereby.

Colored paper is not ordinarily required nor expected to have the fastness, i. e., the freedom from bleeding, which washable fabrics must possess. A dyed paper is generally considered satisfactory if it can withstand a short contact with moist articles without having the dye run. For most uses, however, colored paper is desired that will stand some wetting without giving trouble. In such cases it heretofore has been customary to color the paper stock by adding dyestuff in the beating engine and mordanting the same to the fiber by the use of rosin size and alum. Direct dyestuffs are usually preferred, but some acid dyestuffs give satisfactory results when used in this procedure. Basic dyestuffs, generally speaking, are so fugitive that they are not commonly used for paper that is expected to have any considerable useful life under exposure to light.

Dyeing paper in the beater, however, has its disadvantages. In the first place the process is expensive when colors of other than very light shades are to be obtained. In the second place, it is practically impossible to obtain deep shades by beater-dyeing.

The easiest and, generally speaking, the only practicable way to obtain deep shades in dyed paper is to apply the dye to the paper web itself. Such dyeing is accomplished in practice by using dye boxes on the calendar rolls or by dipping the web in a dye bath.—This method of dyeing paper is often called staining. Acid dyestuffs are usually recommended for staining paper, for, as a class, these dyes are more soluble, have greater tinctorial power, and are cheaper than direct dyestuffs. Unfortunately, stained paper, especially paper stained with acid dyes, is badly affected by water. The dye dissolves to a considerable extent, and the paper is said to "bleed." Direct dyestuffs, which have an affinity for cellulose fibers, are much less affected by moisture than are acid dyestuffs, but in the high concentration required to give deep colors even they are not always satisfactory in respect to bleeding. Accordingly, in view of the advantages to be gained by staining paper in the web, it is apparent that a method of decreasing bleeding in stained paper, and especially in paper stained with acid dyes, is much to be desired.

Furthermore, paper stained in the web is usually unsized, since to insure even and deep staining the paper must be absorbent. An unsized condition in the finished paper, however, is undesirable: such a condition enhances the tendency of the dye to bleed; likewise, it materially lowers the wet strength of the paper itself, and interferes with subsequent operations, such as pasting, to which the paper may be subjected.

An object of the present invention is the provision of paper dyed in the web, the color thereof being resistant to bleeding. It is an object of the invention, also, to provide a sized paper product which has been dyed in the web. Another object is the provision of suitable mordanting or fixing agents for mordanting or fixing the dyestuff in and on the paper fibers. Still other objects include the provision of such fixing or mordanting means which are non-acid in action, and the provision of a treated paper web which is adapted subsequently to be stained or dyed to the production of a bleeding-resistant colored paper product. Other objects of invention will appear from a consideration of the following description.

In the description and in the appended claims I use the expression "fixing" to mean broadly a treatment the result of which is the diminishing of the tendency of the dyestuff to bleed when moistened or wetted with water. The result may or may not be what is technically known in the dyeing industry as "mordanting", and hence use of the latter expression herein is confined to the broad concept of diminishing bleeding.

By the method herein disclosed I have succeeded in producing colored papers stained in the web which are approximately equal in resistance to bleeding to usual papers dyed in the beater. At the same time I have produced a stained paper that is satisfactorily sized.

I achieve the desired increase in resistance to bleeding by including in the web a metallic compound other than or in addition to the alum used in the beater, said metallic compound acting as a setting agent, fixing agent, or mordant, for the dyestuff. The sizing may be produced by applying a size material to the web simultaneously with the dye solution or with the mordant material.

Details of an operable procedure for producing paper dyed in the web and enjoying improved resistance to bleeding are given immediately following. A furnish of papermaking fibers—for bright colors, bleached fiber is preferred—is prepared by any conventional means, as in a Hollander. A filler, such as clay or calcium carbonate, may be included if desired. Alum is or-

dinarly used as in usual paper-making practice, for although its use is not essential to obtain improved resistance to bleeding it is beneficial if sizing is to be imparted to the paper. The fibrous mix is formed into a web or sheet upon any conventional web-forming device, such as a Fourdrinier paper machine. A dye solution containing an acid and/or a direct or substantive dyestuff may be applied to the web on the paper machine, as in a dye bath or by other convenient means before the last press, or at a tub between sections of the driers, or at dye boxes on the calender; or it may be applied in a separate operation after the paper has left the paper machine. If no further treatment should be given the paper so produced, it would be comparable to usual grades of stained paper, and, especially if acid dyes had been used, would have little or no resistance to bleeding.

If to paper stained as described above there be applied a solution of a suitable metallic compound, the natural or normal bleeding tendency of the dyestuff is markedly reduced. The "setting" solution may be added immediately after the paper is stained, i. e., before it is dried, or the stained paper may be dried before the mordant is applied. The mordant solution may be applied by any convenient means, as by spraying, by dipping, or by means of rotating brushes or contact rolls. The concentration of the solution used will naturally depend somewhat upon the method of application. Usually, however, owing to the small quantity of metal compound required to set, fix, or mordant the dyestuff, a relatively dilute solution, say 10% or less, will be found satisfactory for use. The solution may be applied to one or both sides of the web, as desired.

When the staining is done at a size press, as it very advantageously may be done, it is convenient to apply the mordant at another size press immediately following. In such an organization the lower press roll may turn in a tank of mordant solution and carry the solution to the under side of the web as it passes through the squeeze nip between the rolls: in this case, excess liquid having been expressed, drying may be accomplished more easily and quickly than otherwise. Obviously, the top press roll instead of the bottom one, or both press rolls together, may be wet with the mordant solution if desired.

I prefer to use for surface mordanting or fixing a solution which is neutral or alkaline, as such a solution does not leave the paper acidic. Generally I use a solution made alkaline with ammonia, and especially a solution of a metal-ammonium complex. As bases for the mordant I select those metals of which the hydroxides or oxides are substantially insoluble in water but are soluble in ammonia water and/or in an aqueous solution of an ammonium salt. Such metals comprise cobalt, copper, nickel, and the magnesium-zinc group consisting of beryllium, magnesium, zinc, cadmium, and mercury. The particular compound chosen in any given case will depend in part upon the color desired to be obtained, as the shade yielded by a dyestuff is often noticeably affected by the particular mordanting or fixing agent used, though the dulling effect of the agent may be appreciably reduced in many cases by the inclusion in the dye bath of a colloid such as rosin, sodium silicate, casein, or the like. Then too, in some cases certain agents seem to have specific effectiveness for some dyestuffs and not for others. The choice of the particular agent will, therefore, be influenced to some extent by

the particular dyestuff or dyestuffs employed in a particular case. Speaking generally, however, and considering both the effect on the color of the dyestuff and the effectiveness in decreasing bleeding with a great number of dyestuffs, I prefer to use in this relation zinc compounds, and particularly the compound formed by dissolving a zinc salt, such as the chloride, nitrate, sulfate, or the like, in water and adding ammonia until the precipitate formed at first completely dissolves. I have found such solutions of zinc or its homologs to decrease to a marked degree the tendency to bleed, ordinarily shown by paper stained with acid dyestuffs. An appreciable improvement is also noticed when paper stained with direct dyestuffs is so treated, although of course the effect is not so marked, owing to the considerable resistance already possessed by direct dyestuffs.

In some cases the ammoniacal fixing or mordanting solution may be used in the dye bath itself, particularly if there be present a protective agent such as colloidal rosin, rosin soap, casein, sodium silicate, or the like. The single bath process is relatively sensitive however, varying considerably in effectiveness with the particular dyestuff used with the depth of color desired. For this reason I prefer to apply the agent in a separate subsequent step as previously described.

In some instances when it is inconvenient to resort to use of a mordant bath, or if it be desired to provide for sale a treated base stock in condition to be stained by the purchaser, the mordant may be included in the paper furnish with a fair degree of satisfaction. In such a case the ammoniacal zinc solution may be treated in the beater with alum, or zinc chloride treated in the beater with sodium aluminate. The mixed mordant so formed is more effective in reducing bleeding than is either aluminum hydrate or zinc hydrate alone.

To insure especial fastness, I may precipitate a zinc compound in the fibrous mix in the beater and then, after staining the web formed therefrom, treat the web with ammoniacal mordanting or fixing solution. Usually, however, I do not find such double treatment necessary, as a single application of agent to the stained web ordinarily gives sufficient resistance to bleeding for most purposes.

Light shades may be dyed with some degree of satisfaction on paper webs that contain some sizing. In dyeing deep colors, however, when it is desired that the web be colored throughout and not merely stained on the surface, it is practically necessary that the paper shall be absorbent at the time of staining, and preferably also at the time the agent is applied. It is usually advantageous to have the finished, stained paper well sized, since sizing, by increasing the paper's resistance to water penetration, likewise increases resistance to bleeding and decreases the tendency for the paper to disintegrate when wet.

I find it convenient to size the paper by incorporating a sizing material in the dye bath or in the mordant bath. I prefer to incorporate the sizing material in the dye solution, as the paper is usually more fully saturated by the dyestuff solution than by the mordant solution. The size used may be a wax emulsion or a mixture of ordinary rosin size (sodium resinate) and ammonium salt. I prefer, however, to include aluminum hydrate in the paper furnish, and then use a size composition comprising ammonium resinate, colloidal rosin, casein, and, optionally,

an ammonium salt. Such a size mixes well in either the dyestuff solution or the mordant solution and it imparts satisfactory sizing to the finished paper. Stained and mordanted webs sized in this manner are for practical purposes indistinguishable from beater-dyed paper except, of course, that they may have, if desired, a greater depth of color than is practicable in beater-dyed paper.

Specific embodiments of the invention follow:

Example 1

A. A furnish was made containing the following constituents:

	Pounds
Bleached sulfite fiber-----	1200
Bleached soda fiber-----	400
Aluminum sulfate-----	20

The mixture, at 5% consistency, was beaten moderately in a Hollander and the resulting stuff was then run out into a web upon a Fourdrinier machine, dried, and calendered lightly.

B. A dyestuff solution was made up in the following composition and concentration:

	Per cent
Crocein Scarlet N Extra (Color Index No. 252), an acid dye-----	1
Rosin as mixed ammonium resinate and unsaponified rosin-----	0.4
Casein, dissolved by ammonia-----	0.1
Remainder-----	Water

C. A mordant bath was made up by the following procedure: 50 pounds of zinc chloride was dissolved in 45 gallons of water, and strong ammonia water (about 14 gallons) was added until the zinc hydroxide at first formed was entirely redissolved. The solution was then made up to 60 gallons total volume.

The paper from item A was passed through the dye bath of item B, and then between press rolls. The paper took up about 1% of dyestuff by this treatment. The still wet paper was then run through another press of which both rolls were wet with the mordant solution of item C. The paper took up about 0.4% of zinc in this process. When the paper was dry it was found to have considerable resistance to bleeding, and was likewise satisfactorily sized.

Example 2

For the mordant-bath C of Example 1 I substituted the mordant-bath D following:

D. 20 parts of cadmium nitrate crystals and 2 parts of ammonium chloride were dissolved in 308 parts of water. The solution was then made alkaline with 50 parts of strong ammonia water.

Paper A was passed through dye bath B, pressed, passed through mordant-bath D, pressed, and dried. The sheet had considerable resistance to bleeding and was sized.

Example 3

For dye bath B of Example 1 I substituted a dye bath of the following composition:

	Per cent
E. Crocein Scarlet N Extra-----	1
Sodium silicate (having a SiO ₂ to Na ₂ O ratio of 3.8)-----	0.7

For the mordant-bath there was used a solution prepared as follows:

F. To 5 parts of cupric chloride crystals dissolved in 50 parts of water was added strong ammonia water until a clear solution resulted.

Water was then added to make a total of 100 parts.

Paper A was passed through dye bath E, pressed, passed through mordant-bath F, pressed, and dried.

The sheet was satisfactorily resistant to bleeding.

Instead of the sodium silicate of bath E above I may, with equally good results, employ therein a small but effective amount of ammonium carbonate, sodium carbonate, trisodium phosphate or other alkali, the advantageous function being due, apparently, to alkalinity left in the web after treatment with the dye bath. The alkalinity left in the paper by dye bath E or by a dye bath containing a corresponding amount of an equivalent minimizes any dulling effect of the mordanting or fixing agent on the tone of the dyestuff.

The fixed alkali content of the dyestuff bath should not be in excess of that amount necessary to provide a pH value of about 11.3, since I have found that at higher concentrations of fixed alkali the mordanting or fixing effect is largely destroyed. Increasing the pH value beyond 11.3 by addition of ammonia does not harm, however. Sodium zincate, I have found, is too alkaline to be effective in the present relation: the paper is damaged thereby, and the shade is ruined by such an application. Decrease in the dulling effect on the dyestuff of the mordanting or fixing agent by means of fixed alkali progresses with increase in the alkali content of the bath from nil to, say, the equivalent of a 2 to 2.5% solution of sodium carbonate.

Example 4

A furnish was made up comprising:

	Pounds
Bleached sulfite fiber-----	1000
Bleached soda fiber-----	600
Aluminum sulfate-----	55
Zinc chloride (dissolved in excess ammonia)-----	45

The furnish after moderate beating was made up into paper, dried, and calendered.

The paper web was passed through a dye bath, and then pressed and dried. The dye bath was of the following concentration:

	Per cent
Purpurine 4 B Conc. (Color Index No. 448), a direct dye-----	1
Crocein Scarlet N Extra, an acid dye-----	1/2

The paper was satisfactorily resistant to bleeding, but of course was not sized.

Example 5

The web A of Example 1 was passed through a bath of the following composition:

	Per cent
Pontacyl Fast Blue R (Color Index No. 208), an acid dye-----	0.83
Rosin, as mixed ammonium resinate and colloidal rosin-----	0.31
Casein, dissolved by ammonia-----	0.075
Zinc, as zinc-ammonium chloride-----	0.40

The web was pressed and dried.

The resistance to bleeding was satisfactory, and the paper was sized.

By the practice of the invention as herein disclosed a paper is produced which is satisfactorily and reliably stained and sized in the web and which is satisfactorily resistant to bleeding. Such paper is cheaper to produce than known colored papers of equal resistance to bleeding pro-

duced in the beater; for in the first place, to give any desired color value less dyestuff is required in staining than in the beater, and, in the second place, colors may be matched with much less waste and delay than when changes must be made in the stock-furnish. The use of acid dyestuffs is made feasible for staining paper that must stand contact with moist articles or handling by damp hands, and the paper so produced is left free from residual deleterious acidic salts.

Other dyestuffs which successfully have been mordanted or fixed or "set" in and on the fibers of the paper web by the practicing of my process are:

Dyestuff	Color Index No.
Picric acid	7
Guinea Green BA	666
Quinoline Yellow	801
Paper Yellow L	10
Pontacyl Green BL	666
Acid Blue B	707
Night Green A	667
Pontacyl Brilliant Blue E	671
Pontacyl Brilliant Blue RR	Not listed.
Pontacyl Violet S4B	698
Soluble Blue R	707
Supramine Pure Blue BL	Not listed.
Acid Navy Blue BN Conc.	246
Quinazol Blue BP	1054
Water Green S Extra	737
Acid Green 2 G Conc.	666
Soluble Pure Blue 3 G	Not listed.
Sulfon Acid Blue RA Extra Conc.	208
Picro-Carmine	Not listed.
Fast Wool Yellow 3 G 6	636
Tartrazine O	640
Acid Blue FFR	Not listed.
Acid Violet 4BNS	698
Patent Blue 2V	671
Anthraquinone Blue B	1054
Acid Blue R	707
Fast Wool Blue B	209
Acid Fast Violet BGP	699
Pontacyl Fast Violet 10 B	696
Pontacyl Green B	666
Alizarine Blue GS	Not listed.
Pontacyl Green SN	737
Fast Acid Green B	667
Soluble Blue 3RPA	707
Neptune Blue BRA Extra	671
Fast Wool Blue R	208

It is to be noted that, in my preferred process, i. e., treatment of the paper web in a dye bath followed by treatment with the ammoniacal metal oxide or hydroxide solution, the presence of aluminum sulphate in the paper or in the baths is wholly unessential from the standpoint of the fixing or mordanting of the dyestuff: it or an equivalent is necessary only for the sizing of the web. Thus, ashless filter paper treated in accordance with my preferred process shows a degree of fixing equal to that brought about in a paper containing aluminum sulphate or aluminum hydrate. However, where (as in Example 4 above) the ammoniacal metal oxide or hydroxide solution is incorporated into the beater contents whereby to produce a treated paper web adapted subsequently to be strained (dyed), it appears to be advisable for best results to coprecipitate aluminum hydrate with the metal hydrate of the ammoniacal fixing solution: neither the zinc hydrate alone nor the aluminum hydrate alone appears to be as effective for fixing dyestuff in and on the fibers as is the mixed precipitate. A possible explanation may be that the more gelatinous aluminum hydrate enmeshes the zinc hydrate and prevents loss of the latter during drainage through the wire as the sheet is being formed.

While ammoniacal solutions of salts of zinc and of copper have been specifically mentioned in the foregoing examples, and while my preferred species is an ammoniacal solution of a zinc salt, it is to be understood that the invention embraces also the use as the anti-bleeding agent of ammoniacal solutions of salts of other metals, as has been mentioned hereinbefore.

I claim:

1. In the process of making a colored paper which includes the steps of forming a cellulosic fibrous mix into a paper web and thereafter coloring the web by applying thereto an aqueous solution of a dyestuff of the group consisting of acid dyestuffs and direct dyestuffs, the improvement which consists in incorporating into the paper, at a stage not earlier than the dyeing step, an ammoniacal solution of an agent of the group consisting of oxides and hydroxides of metals of the group consisting of magnesium, beryllium, cadmium, mercury and zinc.

2. Improved process as defined in claim 1, according to which the dyestuff and metal oxide or hydroxide are incorporated into the pre-formed paper web simultaneously.

3. Improved process as defined in claim 1, according to which the metal oxide or hydroxide is incorporated into the paper web subsequently to incorporation of dyestuff into the latter.

4. Improved process as defined in claim 1, according to which the agent is zinc hydroxide in ammoniacal solution.

5. Process of staining paper which comprises applying to a paper web an aqueous solution of a dyestuff of the group consisting of acid dyestuffs and direct dyestuffs, and subsequently applying an ammoniacal solution of a salt of a metal of the group consisting of magnesium, beryllium, cadmium, mercury, and zinc.

6. Process which comprises applying to a cellulosic fibrous web containing an aluminum compound dispersed therethrough an aqueous mixture comprising dissolved dyestuff of the groups consisting of acid dyestuffs and direct dyestuffs and a rosin-size dispersion, and subsequently applying an ammoniacal solution of a salt of a metal of the group consisting of magnesium, beryllium, cadmium, mercury, and zinc.

7. Process as defined in claim 6, according to which the rosin-size dispersion comprises ammonium resinate and the metal content of the ammoniacal salt solution is essentially zinc.

8. Process of making colored paper which comprises applying to a pre-formed paper web containing dispersed alum an aqueous mixture containing in solution a dyestuff of the group consisting of acid dyestuffs and direct dyestuffs, a colloidal protective agent, and an ammoniacal solution of a hydrate of a metal of the group consisting of magnesium, beryllium, cadmium, mercury and zinc.

9. Process as defined in claim 8, according to which the aqueous mixture contains also a dispersion of sizing material including ammonium resinate.

10. Process of staining paper which comprises applying to a paper web an aqueous solution of a dyestuff of the group consisting of acid dyestuffs and direct dyestuffs, and subsequently applying an ammoniacal solution of a salt of zinc.

LAURENCE W. PORTER.