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PHOTOGRAPHICALLY PRINTED FIBROUS PRODUCT AND METHOD OF PRODUCING THE SAME

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The invention relates to the production of pictures, designs, or the like by a photographic process within the texture of fabrics, paper, leather, or other substance capable of absorbing the dye. The object of the invention is to incorporate such pictures or designs within the body of the fibrous material so that the image will remain a permanent part of the fabric or fibrous structure to the same extent as when such material is subjected to an ordinary dyeing operation.

Paper and other fibrous materials have heretofore been coated by a film carrying a photographically sensitive medium so that upon developing and fixing photographically produced images the elements of the picture are carried upon the surface of the paper. The present invention, however, contemplates incorporating the design or picture directly within the body of the fibrous material itself and this result is accomplished by using what might be called a combination of a photographic and a dyeing method.

Previous attempts to accomplish a similar result have failed for a variety of reasons. In some cases, for example, it was attempted to sensitize the fibrous material by treatments which included exposure to nitrous acid. The action of nitrous acid, however, having an affinity for the fibre, causes a discoloration which cannot be washed out so that a white ground is not obtainable. Furthermore, the sensitivity to light of the fabric sensitized by the application of nitrous acid, is poor, even in those cases where the fabric was first dyed with primuline or other amine compound prior to treatment with nitrous acid. After printing and developing a fabric thus prepared, an additional disadvantage arises from the fact that the dye produced is not wholly fast. Attempts to sensitize a surface by application of a diazo compound led to no satisfactory result, not only because such solutions are not stable to heat or to subdued light, but because they have little or no affinity for the fibre of the material with which they are to be incorporated.

We have now found that excellent and satisfactory results can be obtained provided the fibrous material is not treated with nitrous acid at all, but the color bases are first completely diazotized independently of the fabric, are then enhanced with respect to speed of response to the effect of light and are then stabilized by being incorporated in a material or vehicle which will not only have the property of mechanically holding the diazotized bases upon the fibres until subsequent coupling is complete and the insoluble azo color is formed, but which will be sufficiently soluble to enable its removal when the dyeing process has been completed.

The result of this procedure is a product which is characterized by an absence of stain in the fibres constituting the fabric while insoluble azo color remains incorporated with the fibres of the fabric at those parts thereof where the presence of the color is desired as predetermined by the image of the negative through which the light rays are permitted to become effective. The product accordingly is readily identifiable by the clearness of the image as well as by its fastness to washing (soap test), fastness to light, and tenacious resistance to bleaching agents. The product produced according to our process can be distinguished at a glance from similar products attempted to be made by prior processes by the fact that the ground of the image or pattern possesses the natural color of the fabric while the image is and remains a clear azo color impregnation notwithstanding exposure to light, to the soap test, or to bleaching agents such as chlorine.

For the purpose of explaining the invention along the simplest lines, it will be particularly described in connection with textile material such as silks, but it is to be understood that the invention is also applicable to other fibrous or porous material capable of taking up the substances required for the practice of the invention.

A piece of silk textile material is impregnated with diazo solutions of insoluble azo colors. Such colors are well known for their remarkable fastness to light, washing, and chlorine. The usual method employed in the textile-dyeing industry in dyeing with such insoluble colors consists of impregnating the goods with naphthols and developing them in diazo solutions of color bases. According to the present invention, however, the goods are not first impregnated with naphthols before the addition of the diazo solutions of the color bases, but the color bases are first completely diazotized, diluted, associated with acutely light-sensitive substances and then incorporated in a stabilizer and vehicle capable of mechanically holding the light-sensitive materials upon the fabric until subsequent coupling is complete and the insoluble azo color is formed within the fibres and capable further of subsequent removal by treatment with a solvent which does not effect the dyed fabric. The composition thus formed is then not merely applied to the surface of the fabric but is worked into the fabric until an even im-

pregnation is achieved as, for example, by the use of a padding machine. After padding, the goods are dried in the dark, preferably by use of an air current and at temperatures not higher than ordinary room temperature. The dry, impregnated material is now exposed to light rays passing through a photographic positive or other transparent pattern or the image may be projected on the fabric directly from a projecting camera or by any other method.

The fabric, after being exposed to light, as described, is developed in a solution of naphthols of the AS group or any suitable body which produces insoluble azo compounds and is capable of being washed out of the fabric after the coupling is complete.

After developing the photographically produced image, the reagents are rinsed out and the picture or design is now a visible portion of the fabric, colored in accordance with any predetermined selection of azo color, but the image, instead of representing merely a surface condition of the textile material, is directly within the fibres of the material to the same extent as if each dot or line which composes the image had been separately embodied in the textile material by a dyeing process. The picture is visible from both sides of the fabric and is ingrained in the fibrous structure and is fast with respect to light, washing, friction, and chlorine, all substantially to the same degree as if the material had been dyed in solid colors with azo dyes.

The same process when applied to paper functions in approximately the same fashion and therefore makes it possible to produce photographically sensitized paper which will not only produce pictures having a desired tint but will anchor the picture in the fibrous structure of the paper itself. Designs may also be applied in this fashion and with generally similar results to fibrous structure such as leather, wood, and in fact any porous or fibrous material capable of impregnation with the dye components. It will be observed that throughout all of the treatments to which the fabric is subjected during the course of the process, the fabric is at no point exposed to the action of nitrous acid or affected by nitrous acid so that it is possible to obtain in those parts of the pattern or picture which were exposed to the most intense rays of light a clear white ground.

The process thus far generally described represents a sequence of steps as to which the following detailed information may be of assistance.

I. Impregnation

(*a*) *Diazotizing of the bases.*—A number of color bases are obtainable on the market under such names as fast orange GC base, fast red RBE base, fast violet B base, fast blue B base, fast blue 2 B base, etc. Directions for dissolving and diazotizing of those bases can be found in any standard manual of dyeing or can be obtained directly from the manufacturers of the bases. Coupling of these bases with different naphthols produces different shades of azo colors. As a specific example of the preparation and use of such bases an example of the application of the fast blue 2 B base which gives blue with naphthols AS and orange with AS—G will be described. 1.4 grms. of fast blue 2 B base are worked up into a paste with 30 cc. of cold water. 1.4 cc. hydrochloric acid of 32 Tw. is added to this paste. 0.35 grms. sodium nitrite is slowly added and the whole allowed to stand for thirty minutes. Before adding the sodium nitrite a few pieces of ice are introduced to keep the temperature from rising unduly. After thirty minutes, when the diazotizing is complete, the solution is filtered and brought to 100 cc. with cold water.

The color bases above referred to are standard and known and will be found illustrated for example in the publications concerning them issued in 1928, 1929, and 1930 by the General Dyestuff Corporation, 230 Fifth Avenue, New York city, sole distributors in the U. S. A. of the dye stuffs manufactured by General Aniline Works, Inc., Albany, N. Y. and Grasselli, N. J. and by I. G. Farbenindustrie Aktiengesellschaft, particular reference being made (*a*) to the book entitled "Naphtol AS and its Application" published 1929, wherein on page 1 naphthol AS is listed as No. 1, naphtol AS-G as No. 12 in the list of naphtols, while fast orange GC base appears as No. 2 and fast blue B base as No. 21 in the list of "Bases and fast color salts"; (*b*) to the December, 1928, publication of said General Dyestuff Corporation entitled "Fast Red RBE Base"; (*c*) to the March, 1929, publication of said General Dyestuff Corporation entitled "Fast Violet B Base"; and (*d*) to the April, 1930, publication of said General Dyestuff Corporation entitled "Fast Blue BB Base".

(*b*) *Increasing the sensitivity of the diazo solution.*—Diazo solutions are in themselves sensitive to light, but for the purposes of this invention it was found advisable to add different sensitizers to increase the sensitivity. The auxiliary sensitizers which have been satisfactorily used in connection with the invention are orthochrome T, rhodamine B, pinaverdol, ammoniacal solutions of silver chloride, ammonium iron citrate and a number of others which are used as sensitizers in photography. By the use of these auxiliary sensitizers the time necessary for exposure has been reduced to an extent of from ten to forty times the time that would be required if the auxiliary sensitizers were not used.

For the diazo solution of fast blue 2 B base, the sensitizer rhodamine B was employed in the proportion of 5 cc. of a 1:1000 solution in methyl alcohol, to 100 cc. of the said diazo solution.

(*c*) *Stabilizing the diazo solution.*—The diazo solutions, especially the sensitized diazo solutions, are not stable to heat nor to subdued light and they have little or no affinity for the fibre of the material with which they are to be incorporated. In order to increase their stability and to fasten them to the fibre in the first instance, and to prevent bleeding of the diazo compounds during the subsequent development, pastes of colloresine (water-soluble cellulose) or vinarol (polyvinyl-alcohol) are added. This type of products has the property of coagulating in alkaline solutions and accordingly will hold the bases mechanically upon the fibre until the coupling is complete and the insoluble azo color is formed. Referring again to the 100 cc. of the diazo solution of the fast blue 2 B base, an equal amount of colloresine DK 1:24 solution is added and thoroughly mixed.

(*d*) *Application of the paste to the fibre.*—The paste prepared in the above described manner is applied to the fibre with the help of a padding machine of well known type and construction. Such a machine ordinarily consists of two rubber rollers, one above the other, the pressure of the top roller being regulated. The bottom roller runs partly in a container which contains the impregnation paste. The fabric, after passing through the paste or padding liquor, runs between the rollers which insures an even impregnation through-

out the fibrous material. After padding, the material is dried, preferably by the use of an air current in the dark or at least in a darkened room. The antecedent operations are all preferably conducted under subdued light.

II. Exposure to light of the sensitized impregnated fabric

The exposure may be made in a printing frame behind a transparent positive or by projecting the image from a lens or through a screen or in fact in any suitable or desired manner. The sensitivity to light varies with different bases. In the specific example referred to, the time of exposure when printing behind a positive of medium opacity is 15 seconds in direct sunlight and from 10 to 15 minutes when printed with an electric bulb of 120 watts at a distance of 10 cm. The exact time of exposure in general depending as it does on the nature of the sensitizer, the concentration of the base, the density of the positive and the distance and power of light source, will, of course, be determined by the experienced operative who conducts this part of the process. In printing behind a diapositive the decomposition of the diazo compound proceeds in accordance with the transparency of the diapositive, thus tracing the pattern.

III. Developing

In developing thus exposed material, a full shade of azo colors is formed on the p'aces where the diazo compound was left intact. Half shades are obtained where the diazo compound was partly destroyed and at the places corresponding to the places of highest transparency of the diapositive the material is left undyed or, generally speaking, white. For developing, the use of the naphthol AS group is recommended. These substances are ordinarily the anilid of betaoxynaphthoic acid. For example, naphthol AS is anilid of betaoxynaphthoic acid. Naphthol AS—BS is nitroanilid of betaoxynaphthoic acid, while, as an exception, naphthol AS—G is diaceto acetic tolidid.

(a) Dissolving of naphthols

One part of naphthol is wetted out with two parts of alcohol and two parts of caustic soda 62 Tw. is added. 20 parts of boiling water is poured over and when the solution is clear, the whole is brought up to a hundred with cold water.

For materials sensitive to alkali, e. g., celanese, wool, silk, or the like, the naphthols are dissolved not in caustic soda as in other instances, but in triethanolamine which is harmless to the fabrics named. The naphthols are brought to a pasty state by the use of alcohol and thereupon 10 parts of triethanolamine are added. The paste is left to stand until it is clear and is then brought up to 100 parts with cold water. Some naphthols require a higher alkalinity to give a clear solution and in those cases 3 to 5 parts of monoethanolamine are added.

(b) Coupling

The exposed material is run through naphthol solution in connection with which the coupling takes place. When coupling is complete, usually in twenty to forty seconds, the material is aired for a short time, rinsed to remove the excessive alkaline and the colloresine thickening and soaped at boiling temperatures.

In the case of paper which cannot be washed nor boiled in soap the treatment is varied as follows: As soon as coupling is complete, the paper is given a short rinse in cold water to remove the excess of alkali, whereupon it is placed in a hot bath of 5% sodium bisulphite and then dried.

Prints made in accordance with the described process are fast to washing and light, thereby resulting in a permanent reproduction in a variety of colors selectable at will. The color is ingrained directly into the fibre. There is no coating and the material has all of its initial softness of texture.

We claim:

1. The method of dyeing a photographic image directly on to a textile, paper, leather, wood, or other impregnatable fabric which comprises preparing a solution of a completely diazotized base, incorporating said diazo solution in a stabilizer capable of mechanical adhesion to the fabric and of being removable therefrom by a solvent non-effective on the azo dye, mechanically working the thus prepared material into the texture of the fabric, exposing to selectively effective light, treating the fabric with a developing solution capable of forming azo colors where the diazo compound was left intact or was but partially destroyed during the exposure to light, washing out the excess of stabilizer and developing solution, and drying.

2. The method of dyeing a photographic image directly on to a textile, paper, leather, wood, or other impregnatable fabric which comprises preparing a solution of a completely diazotized base, associating said solution with a substance having the property of increasing the sensitiveness to light of the diazo compound, incorporating said diazo solution accompanied by the said light-sensitive substance in a stabilizer capable of mechanical adhesion to the fabric and of being removable therefrom by a solvent non-effective on the azo dye, mechanically working the thus prepared material into the texture of the fabric, exposing to selectively effective light, treating the fabric with a developing solution capable of forming azo colors where the diazo compound was left intact or was but partially destroyed during the exposure to light, washing out the excess of stabilizer and developing solution, and drying.

3. The method of dyeing a photographic image directly on to a textile, paper, leather, wood, or other impregnatable fabric which comprises preparing a solution of a completely diazotized base incorporating said diazo solution in a stabilizer capable of mechanical adhesion to the fabric and of being removable therefrom by a solvent non-effective on the azo dye, mechanically working the thus prepared material into the texture of the fabric, drying the same, conducting the drying and antecedent operations under subdued light, exposing the dried impregnated fabric to selectively effective light, treating the fabric with a developing solution capable of forming azo colors where the diazo compound was left intact or was but partially destroyed during the exposure to light, washing out the excess of stabilizer and developing solution, and drying.

4. The method of dyeing a photographic image directly on to a textile, paper, leather, wood, or other impregnatable fabric which comprises preparing a solution of a completely diazotized base, associating said solution with a substance having the property of increasing the sensitiveness to light of the diazo compound, incorporating said diazo solution accompanied by the said light-sensitive substance in a stabilizer capable of me-

chanical adhesion to the fabric and of being removable therefrom by a solvent non-effective on the azo dye, mechanically working the thus prepared material into the texture of the fabric, drying the same, conducting the drying and antecedent operations under subdued light, exposing the dried impregnated fabric to selectively effective light, treating the fabric with a developing solution capable of forming azo colors where the diazo compound was left intact or was but partially destroyed during the exposure to light, washing out the excess of stabilizer and developing solution, and drying.

5. A product comprising an impregnatable fibrous support having an image or pattern defined by an insoluble azo dye ingrained in the fibres thereof, the ground being the unstained original shade of the fibrous support, the support being free from nitrous acid effects, the image being one of clear definition of detail, fast to light, to washing, and resistant to the action of bleach, said product being the dried reaction product of an initial incorporation with the fibrous support, mechanically worked into the texture of the support, of a completely diazotized base in a stabilizer providing mechanical adhesion to the fibres of the support, followed by exposure to selectively effective light, development to form azo colors where the diazo compound was left intact or was but partially destroyed during the exposure to light, excessive stabilizer and developing solution having been washed out by a solvent non-effective on the azo dye.

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