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PROCESS OF PHOTO-PRINTING

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18 Claims. (Cl. 95—6)

This invention relates to a process of photo-printing colored designs, and relates more particularly to the formation of azo dyes upon sensitized carriers of organic origin by the action of light, the dye being formed upon the portions of the carrier that are exposed to the light.

It is necessary to distinguish my process clearly from the known "diazo-type process", used principally for the purpose of reproducing drawings from tracings by the action of light, and in which azo dyes are also formed upon a sensitized carrier. In view of the differences between my process and the diazo-type process, I have adopted as a distinctive name for my process, the title "diazo photo-printing".

Diazo compounds may be divided into two general classes, the first class comprising those diazo compounds that display the characteristic property of coupling with coupling components such as amines, phenols and amido-phenols, and the second class comprising those diazo compounds that do not show this characteristic reaction. Diazo compounds of the first class may be termed syn-diazo compounds or iso-diazo compounds, and those of the second class may be termed anti-diazo compounds or normal diazo compounds. I shall use these terms herein in the foregoing sense.

As is well known, azo dyes may be formed by coupling two components under suitable conditions, one component being a syn-diazo compound, and the other being a so-called "azo dye-forming coupling component", or, more briefly, a "coupling component", principally an amine, phenol or amido-phenol.

Diazo compounds may be decomposed by light to form phenolic bodies, which are of course not capable of forming azo dyes with coupling components. This reaction is the basis of the diazo-type process. In one embodiment of the diazo-type process, paper is coated with a light-sensitive anti-diazo compound alone, and then exposed under a negative or tracing, the diazo compound being decomposed where the light strikes. The sensitized paper after exposure is developed with an alkaline solution of a coupling component. The alkali converts the anti-diazo compound into a syn-diazo compound, which then couples with the coupling component so that an azo dyestuff is formed on the unexposed portions of the paper. There are various modifications of the diazo-type process, but in all of them the fundamental reaction is the conversion of a light-sensitive diazo compound into a phenolic body by the action of light.

Diazo photo-printing, on the other hand, is based on the reactions exhibited by diazo sulphites and certain analogous diazo compounds. The diazo sulphites, when properly prepared from other diazo compounds in the absence of strong actinic light, do not display the characteristic property of coupling with coupling components and hence belong to the class of anti-diazo compounds. Upon exposure to strong actinic light under suitable conditions, however, a syn-diazo compound is formed.

In the diazo photo-printing process, therefore, the carrier may be sensitized in the absence of strong actinic light with a mixture of a coupling component and a light-sensitive diazo sulphite, and the sensitized carrier may then be exposed to light, whereupon the diazo sulphite is decomposed with the formation of a syn-diazo compound which proceeds to couple with the coupling component to form an azo dye directly on the portions of the carrier exposed to the light.

The discovery that certain diazo sulphites possess the property of coupling with dye-forming components only after exposure to light, was made by Adolf Feer in Germany and disclosed by him in German Patent No. 53,455, published August 19, 1890. Feer neglected to give any description of the preparation of his sulphites, but a general method for the preparation of these compounds was given by Lumiere in a paper published in the Bulletin Soc. Francaise de Photographie for 1896, at page 195. Lumiere's general method is as follows: To a neutral diazo compound, in aqueous solution at 10° C., is slowly added a cold, concentrated aqueous solution of sodium sulphite in excess of molecular proportions, preferably two molecules of sodium sulphite to one molecule of diazo compound. The mixture at first displays the property of coupling with coupling components to form azo dyes, but rapidly loses this property. The reaction product may be precipitated by salting out with sodium chloride, filtered off, and purified, if desired, by redissolving, filtering the solution and reprecipitating. Upon exposure to strong actinic light, the reaction product shows the characteristic syn-diazo reaction of coupling with dye-forming components to form azo dyes.

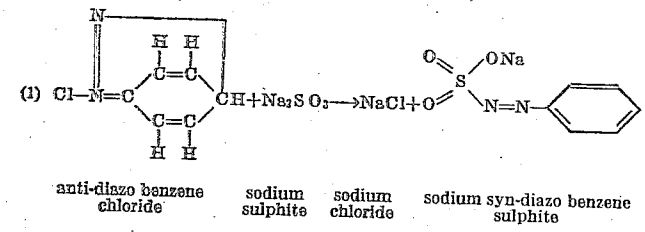
Feer considered the compound formed to be a diazo sulphonate having the general structural formula $R—N=N—SO_3Na$, and Lumiere followed him in this terminology. I consider the term "diazo sulphonate" not properly applicable to these products, because the free diazo sulphonic acids are not known. What might be considered the standard method of obtaining diazo sulphonic

acids (by acting on a diazo compound with concentrated or fuming sulphuric acid) leads to the formation of complicated bodies of quite different characteristics. I prefer to consider these compounds as double metalo-organic salts of sulphurous acid formed by the substitution of one of the sodium atoms of the sodium sulphite by diazo compound. I shall therefore employ the term "diazo sulphite" for these products, but I wish to point out that I use this term not as defining any particular structural configuration of the compound, but rather to indicate the product obtained from a diazo compound by the action of neutral sulphites such as sodium sulphite in cold neutral or alkaline solution.

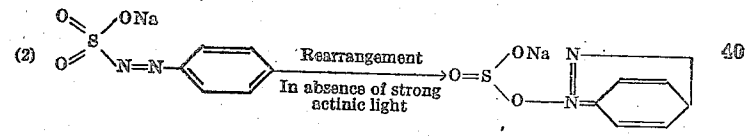
In my opinion the peculiar properties displayed by diazo sulphites are due to the desmotropic or tautomeric character of sulphurous acid. It has been shown that sulphurous acid may exist in two structural forms, the one symmetrical and the other unsymmetrical. My explanation is that the diazo sulphites formed are themselves desmotropic and capable of existing in two isomeric structural forms, one the syn form and the other the anti form. The syn-diazo sulphite is first formed, but in the absence of strong actinic light, a rearrangement promptly takes place, forming the more stable anti-diazo sulphite. The anti-diazo sulphite may be converted into the syn isomer by the action of strong actinic light, but this isomer, being unstable, readily decomposes, losing sulphur dioxide and forming another syn-diazo compound. This theory explains the fact that the reaction product at first still shows the property of coupling with coupling components and only loses this property after a short interval of time, and also explains why diazo sulphites show this peculiar property and salts of simple acids, such as diazo chlorides, do not.

For the purpose of illustration, I shall show the reactions which may be presumed to take place between benzene diazo chloride and sodium sulphite. These reactions may be shown graphically according to either the diazonium salt theory of Hantsch, or the more modern theory of the quinonoid configuration of diazo compounds. I believe that the quinonoid theory fits the known facts regarding the properties of diazo compounds better than the diazonium salt theory, but for the purpose of comparison, I am showing the essential reactions below in accordance with both theories.

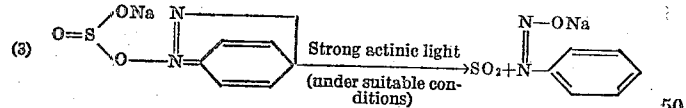
Quinonoid theory



anti-diazo benzene chloride — sodium sulphite — sodium chloride — sodium syn-diazo benzene sulphite

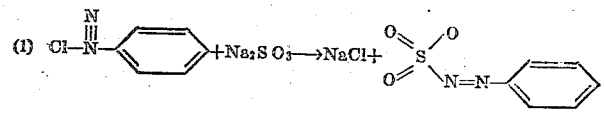


sodium anti-diazo benzene sulphite

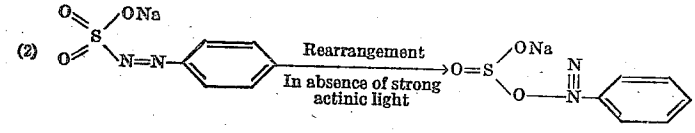


sodium syn-diazo benzene hydroxide

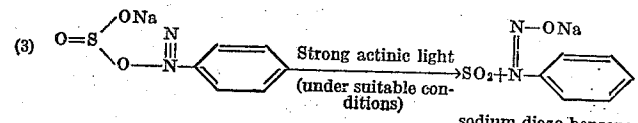
Diazonium salt theory



sodium diazo benzene sulphite (syn-diazo compound

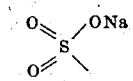


sodium diazonium benzene sulphite (anti-diazo compound)

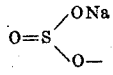


sodium diazo benzene hydroxide (syn-diazo compound)

Reaction (1) according to each theory indicates the temporary formation of the reactive and unstable syn-diazo compound. Reaction (2) shows the rearrangement of this compound into the isomeric anti-diazo compound, which is stable in the absence of strong actinic light. It should be noted that the asymmetrical group



in reaction (1) is positive and displays basic properties, while the symmetrical isomeric group



in Reaction (2) is negative and displays acid properties. These reactions thus agree with the well-known conversion of anti-diazo compounds into syn-diazo compounds by transfer from an acid to an alkaline medium. It will be understood that Reaction (3) in each case is merely symbolical, and will not take place except under suitable conditions, such as the presence of reagents as discussed below.

The correctness of the foregoing theory is evidenced by my discovery that diazo selenites display the same properties as diazo sulphites. Selenous acid, like sulphurous acid, is a desmotropic acid capable of existing in two isomeric forms, one symmetrical and the other unsymmetrical. In fact, I have discovered that diazo selenites possess the advantage over diazo sulphites of being in general more sensitive to light, and one of the features of my invention resides broadly in the use of diazo selenites in diazo photo-printing. Tellurous acid likewise displays the same properties, but its salts are too expensive for ordinary commercial use.

Although I do not wish to be limited to the theory just described, I am sufficiently persuaded of its accuracy that, for the sake of convenience, I shall designate the non-reactive diazo sulphites and diazo selenites and like compounds existing in the absence of strong actinic light as "desmotropic anti-diazo compounds". The term "diazo" as used herein is usually intended to include tetrazo and polyazo compounds as well as diazo compounds in the strict sense. It will be understood that the reactive isomers of these desmotropic anti-diazo compounds are unstable and can exist for only a short period of time, being decomposed entirely almost as rapidly as formed under the conditions of my diazo photo-printing process.

Both Feer and Lumiere were interested solely in color photography. Feer disclosed only a few azo dyes capable of being formed by diazo photo-printing, and Lumiere, while he extended the field somewhat, directed his efforts principally toward obtaining azo dyes capable of use in color photography to give the three primary colors, blue, yellow and red.

Langguth and Hummel appear to have attempted some work in color photography along the lines indicated by Feer and Lumiere, as evidenced by their German Patent No. 465,413 published September 19, 1928, and the corresponding United States Patent No. 1,710,455, dated April 23, 1929. Langguth and Hummel followed the erroneous nomenclature of Feer and Lumiere.

All of these workers were interested only in color photography, and so far as I am aware, this reaction has not been employed outside of that field. The processes of these workers do not appear to have progressed beyond the laboratory stage and are not sufficiently developed to be applicable to the photo-printing of colored designs in competition with known methods of mechanical printing on vegetable or animal fiber fabrics.

The principal object of my invention is to provide a convenient, practical process of diazo photo-printing applicable to the commercial production of colored designs on any carrier of organic origin.

Both Feer and Lumiere dry their sensitive paper before exposing to the light. I have discovered that the action of the light is much more rapid and complete in the presence of water, and may be further expedited by the use of a reagent capable of taking sulphur dioxide out of the reaction. Such a reagent may be termed a chemical sensitizer. Furthermore, the amount of water used must be, for best results, within very definite limits, as will be pointed out hereinafter. The Langguth et al. patents mentioned above disclose the exposure of the sensitive paper in a moist condition, but no instructions are given as to the limits of the moisture nor is any reason for its use mentioned, nor are any other reagents employed. One of the features of my invention, therefore, is the employment of water in definite proportions, either with or without the addition of a chemical sensitizer as above defined.

Other objects and advantages of my invention will be apparent from the following description of my invention and from the appended claims.

In carrying out my process, I preferably impregnate a carrier, for example paper or cloth, with a water solution of a desmotropic anti-diazo compound and an azo dye-forming coupling component, the diazo compound being incapable of coupling with the azo component, but generating under the action of strong actinic light a syn-diazo compound capable of so doing. I preferably incorporate a chemical sensitizer such as one of the reagents mentioned below in the sensitive mixture in addition to the water in order to insure the completion of the reaction in the desired direction. The sensitized carrier is then exposed in moist condition, the degree of moisture being carefully regulated as hereinafter disclosed, to the action of light under a suitable negative, tracing or other translucent pattern, whereupon an azo dye is formed on the portions of the carrier exposed to the action of light. I then fix the dye on the carrier, if necessary, and remove the unexposed light-sensitive mixture by washing, preferably with hot water. The carrier is then dried and is ready for use, or, if desired, a further design may be superimposed upon the design already formed by repeating a similar series of steps.

It will be observed that the foregoing process results in the direct formation of the azo dye on the exposure to light. This may therefore be called direct diazo photo-printing. It is also possible to carry out my process of diazo photo-printing in an indirect manner. In order to do so, the carrier is coated with the light-sensitive desmotropic anti-diazo compound alone, then exposed to light, and subsequently treated with the coupling component. This may be termed the indirect method, since the dyestuff is not produced directly upon the exposure but by subsequent development. The indirect method of diazo photo-printing has a disadvantage of giving only a weak impression or thin coating of the dye, for reasons which will be made apparent

hereinafter, and in practice requires a white background. The indirect method, therefore, has little practical value for obtaining a strong color as compared with mechanical methods of printing. In carrying out my process, therefore, I prefer to utilize the direct method of diazo photo-printing, except where pale shades are desired.

My process is generally applicable to the formation by photo-printing of any azo dye capable of being formed by the coupling of a diazo compound and an azo dye-forming component, and possessing the following characteristics:

1. The diazo compound component of the dye must be capable of forming desmotropic compounds having two isomeric forms with desmotropic acids, such as sulphurous and selenous acids. With certain easily identified exceptions, practically any soluble diazo compound can be converted into a desmotropic diazo sulphite or selenite.

2. The desmotropic diazo compound must be light-sensitive, that is to say, it must be converted by the action of light from the anti form incapable of reacting with a coupling component into the syn isomer capable either of so doing or of being converted into a syn-diazo compound capable of so doing. Not all diazo compounds of desmotropic acids meet this condition, for example, the diazo compounds of hydrocyanic acid are either not sufficiently light-sensitive, or the two isomeric forms do not have sufficiently pronounced acid and alkaline characteristics to provoke the corresponding change of nitrogen valence in changing anti-diazo compound to syn-diazo compound.

3. The solubility of the dye must be less than the solubility of the components from which it is formed, except in the case of soluble dyes which readily combine with the material of the carrier to produce a new insoluble compound.

My process can be used to apply any azo dye possessing the foregoing qualifications, whether it be acid, basic, or neutral, and whether it be a direct or substantive dye, or a mordant or adjective dye. The characteristics of the dye, however, determine the treatment necessary to fix the dye on the carrier and its applicability to different kinds of fabrics. With cotton fabric and direct or substantive dyes insoluble in hot water, no fixing is necessary. With other dyes, the dye should be fixed on the cotton fabric before washing the fabric with hot water to remove the undecomposed sensitive mixture after exposure to the light. In general, it may be stated that the fixing treatment may be the same as would ordinarily be used in dyeing with the same azo dye on a carrier of the same type.

The speed of formation of the azo dyes in diazo photo-printing depends upon (1) the chemical nature of the components, (2) the relative solubility of the components to the solubility of the azo dye, (3) the sensitivity of the components to light, (4) the presence of water in the sensitive mixture, (5) the use of chemical sensitizers in the sensitive mixture, (6) the quality of the printing light, and (7) the temperature at which the reaction is conducted.

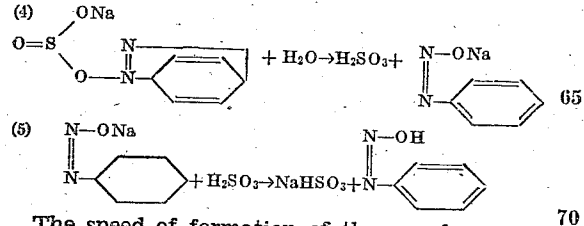
Factors one and two above depend, of course, upon the particular dye that it is desired to form, the selection of the dye being governed by the color desired, the nature of the carrier, and the special requirements of the dyed article, such as fastness to light, and so forth. For a given dye, therefore, these factors are fixed. Where a choice is to be made between certain dyes, however, in general, more satisfactory results will be obtained, the more readily the dye fixes upon the fabric to be dyed and the more insoluble the dye as compared to the solubility of the components. The chemical nature of the components determines the character of the formed dye as to whether it is acid, basic or neutral, and hence determines the ability of the dye to fix on the particular fabric to be dyed. In general, the more readily the dye fixes on the fabric, the more completely it will be taken out of the reaction and hence the more rapid the reaction will be. Likewise, the more insoluble the dye, the more quickly it will be taken out of reaction and consequently the speed of the reaction in the direction of forming the dye will be increased.

Factor three, the sensitivity of the components to light, is, of course, dependent largely upon the chemical nature of the components. To some extent, however, it depends upon the nature of the desmotropic anti-diazo compound, that is to say, whether a diazo sulphite or diazo selenite is employed. It is preferable, of course, to employ the more sensitive form of the diazo compound.

Factor four, the presence of water in the sensitive mixture, determines to a great extent both the speed and the completeness of the formation of azo dyes in diazo photo-printing. There are a few coupling components, such as naphthylamine, which will form azo dyes by reaction with diazo sulphites when exposed to strong actinic light in a dry condition. Generally speaking, however, sensitive mixtures containing coupling components and diazo sulphites are decomposed by light only very slowly in the dry condition, thus rendering the use of such dry mixtures impracticable commercially. The presence of water not only makes the action of the light more rapid, but renders the formation of the dye more complete. If a sensitized fabric contains less than about 50% of its weight of water, the formation of the dye will not be complete. But an excess of water is also detrimental, because water is to some extent at least a solvent for the dye formed, and the capillarity of the fibers of the fabric tends to spread the dissolved dye, thereby staining parts of the fabric which were not exposed to the light. The best results are obtained when the sensitized fabric during exposure contains from 65% to 125% of water by weight based on the weight of the dry fabric.

Just as water aids the sensitivity of the mixture, dehydrating agents destroy its sensitivity. The presence of such materials as alcohol, calcium chloride and acids in the sensitive mixture should be carefully avoided.

When diazo sulphites in water solution are exposed to the action of strong actinic light, the reaction may be presumed to take place in two stages as indicated below:



The speed of formation of the azo dyes may be still further increased by the use of suitable chemical sensitizers as mentioned in factor five above. It will be evident that the speed of Reactions (4) and (5) may be enhanced by the re-

moval of the sodium hydrogen sulphite from the zone of reaction. By so doing, the completeness of the reactions in the direction of forming the diazo hydroxide is encouraged, and the diazo hydroxide, in turn, readily couples with the coupling component to form the azo dye. Furthermore, the prompt removal of sodium hydrogen sulphite from the reaction zone avoids the possibility of the sulphurous acid and the syn-diazo compound formed according to Equation (4) reacting to produce hydrazines or other compounds, thus resulting in a decreased formation of dye.

The reagents that may be used for the purpose of removing sodium hydrogen sulphite or sulphur dioxide in one form or another from the reaction, are many and varied in character, among them being acetone, sodium stannate, sodium aluminate, soap, tri-basic sodium phosphate and borax. I shall designate all such substances as chemical sensitizers, since they do not enter into the main reaction, that is, the formation of the azo dye, but simply speed this reaction by the removal of sulphur dioxide or its compounds. The term "sensitizer" as used in this specification and the appended claims should, therefore, be understood as meaning a substance possessing this property of removing sulphur dioxide under the required conditions. Obviously, the sensitizer must be one which has no deleterious effect on the azo dye or its components.

The sensitizers mentioned act in different ways. Acetone forms an addition product with sodium hydrogen sulphite, thus withdrawing the latter from the reaction. The aldehydes and many other ketones resemble acetone in possessing this property, but acetone is particularly useful because it is relatively inexpensive, an excellent solvent for organic substances and miscible with water in any proportion. The inflammability of acetone is the only drawback to its extensive use. These addition products are known as bisulphite compounds.

Sodium stannate is a very energetic sensitizer, and even permits diazo sulphites to be decomposed by strong actinic light in the absence of a coupling component. Sodium aluminate is less important and may be used only with amines. Soap is a useful sensitizer when the fixing of the dye requires a weak alkaline medium. Its use has the disadvantage of producing a slight coloring on the unexposed portions of the fabric.

The salts of weak, non-volatile inorganic acids and strong bases, such as tri-basic sodium phosphate and borax, when used as sensitizers readily combine with sulphurous acid or hydrogen sulphite to form neutral sulphites, and can frequently be used to better advantage than soap. Free alkali could, of course, be used to accomplish the same result, but might have a disadvantageous effect upon the dye or the carrier.

The quality of the printing light, factor six above, has a good deal to do with the speed of the reaction. The initial velocity of the photochemical reaction is determined by the light absorbing ability of the components of the sensitive mixture. The light absorption of the sensitive mixture, which is generally of yellow or brownish-yellow color, is chiefly in the blue, violet and ultra-violet parts of the spectrum. The printing light should therefore be rich in light of this character, that is to say, it should be strongly actinic. I have found that if the formed dye absorbs considerable light during the reaction, this absorption of light by the formed dye increases the speed of the reaction. This may be due either to the additional light energy thus made available in the reaction zone for the photo-chemical reaction, or merely to an increase of temperature in the reaction zone. Whatever the cause, the fact is that the best results are obtained when light absorption by the formed dye is encouraged. The light absorption of the formed dye depends upon its color and may be in any part of the spectrum. The source of printing light should therefore radiate all rays from ultra-violet to infra-red.

From the foregoing it will be apparent that light filters are not only unnecessary but undesirable, and that the sensitized fabric should be subjected to the direct action of the printing light, except for such interference as is intentionally provided by the negative or other pattern. The use of a light filter greatly increases the time required for exposure, since it reduces the light absorption both by the components of the sensitive mixture and by the formed dye, and particularly because it cuts out the infra-red rays and their attendant heat energy.

The richness of the printing light in ultra-violet and infra-red rays has a decided effect upon the time of exposure. Using a low pressure mercury vapor lamp, with an intensity of illumination of 100 candle-feet per square foot, the exposure required may vary from one to five minutes. Using a high pressure mercury vapor lamp or an open carbon arc lamp with so-called ultra-violet carbons, with the same intensity of illumination, the time of exposure required is only about one-quarter as long. The latter sources of light require a shorter time because of their richness in ultra-violet and infra-red rays.

The effect of the reaction temperature, factor seven above, on the speed of formation of the azo dyes has already been mentioned in connection with the absorption of light. I have found that increased temperature favors the formation of the azo dye, provided, of course, that the temperature does not exceed the temperature of decomposition of the components of the sensitive mixture, say 100° C. I have also found that the rise in temperature of the fabric during ordinary periods of exposure is not sufficiently great to cause decomposition of the components of the sensitive mixture. It is therefore neither necessary nor desirable to use cooling frames during the exposure. In fact, the fabric may advantageously be heated during the printing operation, or may be warmed prior to exposure.

In the preferred embodiment of my invention, therefore, I expose the sensitized fabric in a warm condition to the direct action of strong actinic light, such as that provided by a high pressure mercury vapor lamp as described above, the negative, of course, being placed between the lamp and the fabric.

My complete process of diazo photo-printing comprises the following steps:

(1) Preparing a solution of the desired light-sensitive desmotropic anti-diazo compound;

(2) Preparing a solution of the desired coupling component;

(3) Preparing the sensitive mixture;

(4) Impregnating the fabric with the sensitive mixture;

(5) Regulating the moisture content of the fabric to secure the proper degree of humidity;

(6) Exposing the fabric to strong actinic light under a negative;

(7) Fixing the formed dye on the fabric if necessary;

(8) Washing the fabric;

(9) Drying the fabric.

The general method advanced by Lumiere and described above may advantageously be used for preparing the light-sensitive desmotropic anti-diazo compound to be used in making up Solution 1. The choice of the particular diazo compound from which one prepares the desmotropic anti-diazo compound depends upon the particular azo dye which it is desired to form on the fabric. Ordinarily, I convert the diazo compound into either a sulphite or a selenite, but mixtures of the two may be employed if desired. I have found that a convenient strength of solutions of diazo compound is 5 centigram-molecules in 1000 c. c. of water for tetrazo sulphites or selenites, and 10 centigram-molecules in 1000 c. c. of water for diazo sulphites or selenites. These compounds when dissolved in water and kept in tightly corked bottles are very stable and do not decompose under ordinary temperature and light conditions for at least six months. Some such solutions have shown no marked decomposition after standing for a year.

The coupling component to be used also depends upon the azo dye to be formed. The method of preparation of such coupling components is no part of my invention and is well known, and hence need not be described herein. The quantity of the coupling component in the sensitive mixture should preferably be either just sufficient or slightly less than enough to combine with the desmotropic anti-diazo compound present. An excess of the coupling component should be avoided, as should also too great concentration of the coupling component in the sensitive mixture. With too great concentrations of some coupling components, the unexposed parts of the design may be tarnished by a combination of the coupling component with the fabric being dyed. Coupling components so combined with the fibers of the fabric are sometimes very difficult to remove by washing. I have found a concentration of the coupling component in the sensitive mixture of four centigram-molecules in 1000 c. c. of water to be convenient and practical. It is of great importance to use freshly prepared solutions of coupling components, inasmuch as many coupling components are susceptible to hydrolysis and a few to photolysis.

The sensitive mixture may be made up by mixing appropriate volumes of the solutions of the desmotropic anti-diazo compound and of the coupling component. The density of the color obtained depends to a certain extent upon the concentration of the sensitive mixture; the more concentrated the sensitive mixture the deeper the color. It is usually inadvisable, however, to increase the concentration of the sensitive mixture materially above the limits mentioned above. In many instances deep colors may be obtained readily by the addition of salting-out agents, such as sodium sulphate and sodium chloride, to the sensitive mixture. The addition of salting-out agents is especially to be recommended when the dyeing of the fabric with the corresponding azo dye requires the addition of such agents.

The sensitive mixture may be completed by the addition of a sensitizer as described above. The choice of the sensitizer likewise depends upon the dye to be formed, some of the sensitizers mentioned giving better results with some dyes than with others. The more important conditions regulating the choice of the sensitizer have been outlined above. The sensitizer may be added to the combined solutions of the desmotropic anti-diazo compound and the coupling component, or to either of these solutions before mixing.

The impregnation of the fabric with the sensitive mixture may be accomplished simply by dipping the fabric in the sensitive mixture. The excess sensitive mixture is then removed by wringing or pressing.

I have already pointed out the desirability of having the amount of water in the fabric within definite limits. The regulation of the percentage of moisture in the fabric may readily be accomplished by placing the fabric in a closed steam chamber full of saturated steam. The temperature of the chamber is then regulated to produce humidity conditions corresponding to the desired percentage of water in the fabric. A condition will very quickly be reached in which the amount of water in the fabric is in equilibrium with the steam in the chamber, and the fabric may then be removed. In most cases, the temperature should not be over 100° C., because at this temperature some of the components begin to decompose.

The exposure may be performed in the ordinary manner of making blue prints and the like, the sensitized fabric being placed in a printing frame under a negative or other pattern bearing the desired design. The use of a reflecting surface beneath the fabric considerably decreases the required time of exposure. For large scale commercial operations, special printing machines are necessary, but such machinery forms no part of the process invention herein described. As pointed out above, it is neither necessary nor desirable to use light filters or cooling frames during the exposure.

As has also been pointed out above, the sensitized fabric should preferably be warm during the exposure. Where the humidity of the fabric has been regulated in a steam chamber as described above, the fabric may simply be placed in the printing frame before it has had an opportunity to cool greatly. In some cases, it may be desirable to provide the printing frame with heating means, which may take any conventional form. The temperature of the fabric at the instant of exposure may advantageously be between 30° C. and 60° C. Some rise in temperature probably takes place during the exposure, but will be only beneficial, since during the short exposures mentioned, the temperature cannot rise as far as the decomposition temperature of the components.

Whether or not it is necessary to fix the dye formed during the exposure on the fabric depends upon the particular azo dye formed and the character of the fabric. With certain dyes and fabrics, no fixing is necessary, as has already been pointed out. With others, the fixing procedure to be followed should be exactly the same as that customarily followed in dyeing with the same azo dye in the ordinary manner.

The washing of the fabric is ordinarily done with hot water at a temperature of 50° to 80° C. The washing is continued until all or substantially all of the sensitive mixture is eliminated. Acetic acid, sodium acetate or soap may be added to the wash water in cases where they are effective in removing the undecomposed sensitive mixture and do not affect the dye. The final rinsing of the fabric should be with cold water.

The drying of the fabric may be accomplished

in the manner ordinarily employed in dye plants.

Steps 4, 7, 8 and 9 as outlined above may be performed in regular dyeing machines.

The final product of the process just described is a dyed fabric having all of the properties of any fabric dyed with the same azo dye in the ordinary manner. The dyed fabric may therefore be subjected to any after treatment capable of being used in connection with that azo dye in ordinary dyeing operations. These after treatments include: (1) treatments with metallic salts, such as salts of copper, chromium and barium; (2) coupling with diazo compounds followed by the usual development; (3) formation of polyazo dyes by diazotizing the dye already obtained on the fabric followed by development with the proper developer; (4) topping the azo dye with aniline dyes.

In general, in diazo photo-printing all of the rules for the treatment of the azo dye under consideration are to be strictly followed. Thus, the rules for fixing and after treatment, the use of salting-out agents, and so forth, all follow the corresponding rules for ordinary azo dyeing.

Where multi-color printing is to be employed, any after treatments to be applied to the printed dye should be carried out before applying any subsequent dye to the fabric, since these treatments increase the fastness of the dye originally printed.

The following specific examples are illustrative of the way in which my invention may be applied. It is to be understood, however, that the specific examples given are merely by way of illustration, and that my process is by no means limited to the application of the specific azo dyes mentioned in these examples:

EXAMPLE A—DYEING WITH FLAVAZINE YELLOW L

Step 1.—Preparing a solution of the light-sensitive desmotropic anti-diazo compound

Dissolve 9.3 grams of aniline in 10 c. c. of hydrochloric acid (specific gravity 1.18). Add 100 c. c. of water and 50 grams of crushed ice to the resulting solution of aniline chloride.

Dissolve 7 grams of sodium nitrite in 50 c. c. of water and add 50 grams of crushed ice. Pour 10 c. c. of hydrochloric acid (specific gravity 1.18) into the solution of sodium nitrite. Add another 50 grams of crushed ice. Stir the resulting solution of nitrous acid until it reaches a temperature of about 8° C.

Add the cool solution of aniline chloride gradually to the nitrous acid solution with continuous stirring. Allow the resulting diazo benzene solution to stand for about fifteen minutes.

Dissolve 25.2 grams of anhydrous sodium sulphite (or 26.8 grams of anhydrous sodium selenite) in 100 c. c. of water. Cool the solution to about 10° C. by the addition of 50 grams of crushed ice.

The diazo benzene solution prepared as described above is slowly added to the sodium sulphite (or sodium selenite) solution with continuous stirring. After twenty minutes, test a sample of the solution with an alkaline solution of a phenol or a naphthol. If the test shows the characteristic diazo reaction, add more sodium sulphite (or selenite) solution, until a repetition of the test shows no diazo reaction.

Then dilute the solution with water to a volume of 1000 c. c. The concentration of this solution is 10 centigram-molecules of benzene diazo sulphite (or selenite) in 1000 c. c. of water.

Step 2.—Preparing a solution of the coupling component

Dissolve 27.5 grams of 1-p-sulpho-phenyl-3-methyl-5-pyrazolon in 100 c. c. of a 4% solution of sodium hydroxide. The concentration of this solution is 10 centigram-molecules in 100 c. c. of water.

Step 3.—Preparing the sensitive mixture

Mix 10 parts by volume of the benzene diazo sulphite (or selenite) solution with one part by volume of the pyrazolon solution, preparing only enough of the sensitive mixture to meet immediate requirements.

Step 4.—Impregnating the fabric with the sensitive mixture

The piece of wool, silk or cotton to be dyed (previously thoroughly washed to remove grease, oil and dirt) is dipped in the sensitive solution and saturated therewith. The piece of fabric is then gently pressed to remove the excess sensitive mixture.

Step 5.—Regulating the moisture content of the fabric to secure the proper degree of humidity

The fabric may be allowed to dry in an open room at ordinary room temperature for about twenty minutes. For more exact results, the pressed fabric may be placed in a closed steam chamber filled with saturated steam at a suitable temperature, say 85° C., and the temperature raised a few degrees. The fabric may be removed after, say, a quarter of an hour, the time not being important as the equilibrium condition is quickly reached and thereafter the moisture content of the fabric does not change.

Step 6.—Exposing the fabric to strong actinic light under a negative

The moist fabric is placed in a printing frame under a negative and exposed to strong actinic light from a 120 volt high pressure mercury vapor lamp at a distance of 18 inches for a few seconds. The time of exposure under the negative depends, of course, on the density of the negative. The time given is for a negative having clear transparent parts and dense opaque parts. Using a low pressure mercury vapor lamp at the same distance, the time required would be from two to three minutes, and for a 150 watt nitrogen filled tungsten filament lamp the time required would be five to ten minutes.

Step 7.—Fixing the formed dye on the fabric

With silk and wool fabrics, no fixing treatment is necessary prior to washing. For cotton fabrics, the fabric should be washed in a 10% solution of barium chloride in water. This barium chloride treatment converts the formed dye into an insoluble colloidal lac, which is very fast to light. This fixing treatment may advantageously be employed even for silk and woolen fabrics.

Step 8.—Washing the fabric

The fabric is then thoroughly washed with hot water at a temperature of from 60 to 80° C. for ten to fifteen minutes to remove all of the unexposed sensitive mixture. It is preferable to acidify the water slightly with hydrochloric or acetic acid.

Step 9.—Drying the fabric

The fabric may then be dried in a conventional manner.

The design thus formed on the fabric is of a yellow color, and the formed dye is known as flavazine yellow L.

EXAMPLE B—DYEING WITH CONGO 4R (RED)

Step 1

Prepare a solution of ditolyl tetrazo-sulphite having a concentration of 5 centigram-molecules in 1000 c. c. of water. This solution may be prepared from 21.2 grams of commercial tolidine in the manner given in the preceding example for the preparation of benzene diazo sulphite from aniline.

Step 2

Dissolve 2.45 grams (1 centigram-molecule) of sodium naphthionate in 40 c. c. of water, separately dissolve 1.54 grams (1 centigram-molecule) of sodium resorcinate in 10 c. c. of water, and then mix the two solutions together.

Step 3

Mix 200 c. c. of the ditolyl tetrazo-sulphite solution and 50 c. c. of the coupling component solution, and dissolve 2.12 grams of sodium stannate in the resulting sensitive mixture.

Steps 4, 5 and 6

These steps may be performed as in Example A, except that the exposure should be somewhat longer. For example, using a low pressure mercury vapor lamp at a distance of 18 inches, the exposure should be from 4 to 5 minutes.

Steps 7 and 8

No special fixing treatment is required if the silk, wool or cotton fabric is washed with hot water as described under 8 in Example A. A very fast brownish red color may, however, be obtained by treatment with a solution of diazo-p-nitro-benzol before washing, and then washing with cold water.

Step 9

As in Example A.

EXAMPLE C—DYEING WITH OXAMINE BLUE 4R

Step 1

Prepare a solution of ditolyl tretrazo-sulphite having a concentration of 5 centigram-molecules in 1000 c. c. of water as specified in Example B.

Step 2

Dissolve 2.63 grams (1 centigram-molecule) of sodium 2-amido-5-naphthol-7-sulphonate and 2,5 grams (1 centigram-molecule) of sodium 1-naphthol-4-sulphonate in 50 c. c. of water.

Step 3

Mix 200 c. c. of the ditolyl tetrazo-sulphite solution and 50 c. c. of the coupling component solution, and dissolve 4 grams of sodium tri-basic phosphate in the resulting sensitive mixture.

Steps 4, 5 and 6

These steps should be performed as in Example A.

Step 7

The dye should be diazotized on the fabric in the usual way, using nitrous acid solution, and should then be developed with alkaline beta-naphthol solution. This gives a very fast deep blue color.

Steps 8 and 9

Same as in Example A.

EXAMPLE B—DYEING WITH DIAMINE BORDEAU

Step 1.

Prepare a solution of dianisol tetrazosulphite having a concentration of 5 centigram molecules in 1000 c. c. of water. This solution may be prepared from 24.4 grams of dianisidine in the manner given in Example A for the preparation of benzene diazo sulphite from aniline.

Step 2.

Dissolve 2.44 grams of meta-toluylendiamine in 100 c. c. of hot water at a temperature of 70–80° C.

Step 3.

Pour 200 c. c. of the dianisol tetrazo-sulphite solution into the 100 c. c. of the coupling component solution. If the liquid is not transparent and clear, it should be heated until all of the components are dissolved. Add 15 c. c. of acetone.

Steps 4, 5 and 6.

These steps may be performed as in Example A.

Step 7.

No fixing treatment is required with silk fabrics because the dye is basic and fixes well on silk without treatment. With cotton and woolen fabrics, the dye should be fixed on the fabric by washing in a solution containing 25% of tannic acid and 10% of tartar emetic. This acid bath forms an insoluble lac and thus fixes the dye on the fabric. If desired, the dye may be diazotized on the fabric and gives very dark brown colors after development with naphthols.

Steps 8 and 9.

These steps may be performed as in Example A.

The term "pattern" as used in the appended claims is intended to include any pattern or design having transparent or translucent parts, whether a photographic negative, tracing, stencil, or any other medium capable of modifying or regulating the exposure of the carrier to light.

It will be apparent to those skilled in the art that my process may be modified in many particulars without departing from the spirit of my invention, and I desire to be limited, therefore, only by the scope of the appended claims.

I claim:

1. The process of diazo photo-printing which comprises preparing a water solution of a light-sensitive desmotropic anti-diazo compound and an azo dye-forming coupling component, impregnating a carrier with the said solution, exposing the carrier while containing at least 50% of water by weight of the dry carrier to the action of actinic light under a pattern, removing the undecomposed sensitive mixture, and drying the carrier.

2. The process as claimed in claim 1 in which the water content of the carrier during exposure is between 65% and 125% by weight of the dry carrier.

3. The process as claimed in claim 1 in which the actinic light contains all rays from ultra-violet to infra-red.

4. The process as claimed in claim 1 in which the moist carrier is at a temperature of at least 30° C. at the commencement of the exposure.

5. The process of diazo photo-printing which comprises preparing a sensitive mixture contain-

ing water, a light-sensitive desmotropic anti-diazo compound and an azo dye-forming coupling component, impregnating a carrier with the sensitive mixture, regulating the water content of the carrier between the limits of 50% and 125% by weight of the dry carrier, exposing the carrier so moistened to the action of actinic light under a pattern, removing the undecomposed sensitive mixture, and drying the carrier.

6. The process as claimed in claim 5 in which the light is a strong actinic light containing all rays from ultra-violet to infra-red.

7. The process as claimed in claim 5 in which the moistened carrier is substantially above room temperature at the commencement of the exposure.

8. The process as claimed in claim 5 in which the moistened carrier is at a temperature above 30° C. and not greatly exceeding 60° C. at the commencement of the exposure.

9. The process of diazo photo-printing which comprises preparing a sensitive mixture containing water, a light-sensitive desmotropic anti-diazo sulphite, an azo dye-forming coupling component and a chemical sensitizer adapted to remove sulphur dioxide from the reaction, impregnating a carrier with the sensitive mixture, exposing the carrier in moist condition to the action of actinic light under a pattern, removing the undecomposed sensitive mixture, and drying the carrier.

10. The process as claimed in claim 9 in which the sensitizer is sodium stannate.

11. The process as claimed in claim 9 in which the sensitizer is acetone.

12. The process as claimed in claim 9 in which the water content of the carrier during exposure is between 50% and 125% by weight of the dry carrier.

13. The process as claimed in claim 9 in which the light is a strong actinic light containing all rays from ultra-violet to infra-red.

14. In a process of diazo photo-printing, the steps of impregnating a carrier with a water solution of a light-sensitive anti-diazo compound, and exposing the carrier to the action of actinic light under a pattern while containing at least 50% of water by weight of the dry carrier.

15. In a process of diazo photo-printing, the steps of impregnating a carrier with a water solution of a light-sensitive anti-diazo compound, and regulating the water content of the carrier between the limits of 65% and 125% by weight of the dry carrier.

16. In a process of diazo photo-printing, the step of impregnating a carrier with a water solution of a light-sensitive desmotropic anti-diazo sulphite and a chemical sensitizer adapted to remove sulphur dioxide from the reaction.

17. The process of diazo photo-printing which comprises sensitizing a carrier with a water solution of a light-sensitive desmotropic anti-diazo sulphite and an azo dye-forming coupling component, and forming the dye on the moist carrier by the action of actinic light, the water content of the carrier during exposure to the actinic light being between 50% and 125% by weight of the dry carrier.

18. The process of diazo photo-printing which comprises sensitizing a carrier with a water solution of a light-sensitive desmotropic anti-diazo selenite and an azo dye-forming coupling component, and forming the dye on the moist carrier by the action of actinic light, the water content of the carrier during exposure to the actinic light being between 50% and 125% by weight of the dry carrier.

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