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DYEING PLASTIC AND SOLUTION THEREFOR

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This invention relates to a dye solution for the dip staining of a plasticized polyvinyl acetal sheet, the method of preparing the dye solution and the method of dip staining the sheet using the dye solution.

In the manufacture of safety glass for windshields of automobiles and side windows of buses, as well as for other similar types of use, it is desirable to manufacture laminated safety glass, flat or curved, that is colored at least in a band portion of the safety glass by dyeing the plastic interlayer sheet to reduce the amount of visible light transmitted through that portion. For example, in windshields of automobiles it is customary to have a top colored graduated band in the safety glass to reduce the light transmission through that portion of the windshield. Also in buses it is desirable to use safety glass side windows that have upper and lower colored bands of uniform light transmission with a graduated coloration between these bands in which the graduation is such that there is no perceptible cut-off line for the top and bottom colored marginal bands. The graduation of color in the interlayer of the safety glass window is preferably chosen so that the transmission at the eye level when the window is mounted is about 20% and the upper and lower bands have 8 and 15% transmission in the visible range, respectively. In such windows the point of maximum transmission is about 35% and this is below the eye level point.

In the manufacture of the interlayer having the colored band with a graduated portion for use in windshields, the thermoplastic interlayer sheet is placed in a vertical plane and while thus maintained is rapidly lowered into a bath of dye solution so that the portion of the sheet to be dyed to a relative uniform intensity is immersed. Lowering of the sheet is continued but the rate of lowering is decreased until the sheet is moving slowly, then the rate of immersion is rapidly increased until the sheet has been immersed to the desired maximum point of coloration. The sheet is rapidly removed from the dye solution, rinsed in a liquid to remove excess dye solution and dried. The liquid is the solvent of the dye solution and this rinse treatment is followed by a water rinse.

In the manufacture of the safety glass side windows for buses the sheet is placed in a vertical plane and rapidly lowered in a bath of a dye solution until a portion of the sheet is immersed. Lowering of the sheet is continued at a decreasing rate until the sheet is being lowered very slowly, then the rate of immersion is gradually increased until the sheet is entirely immersed. As soon as the sheet has been completely immersed it is rapidly removed from the dye solution, rinsed in a liquid (the solvent of the dye solution) to remove excess dye solution, rinsed in water and dried. The sheet is next placed in a vertical position with the relatively uniform colored band at the top and immersed in the dye solution as previously described but with a small time of rapid immersion to provide a narrower marginal band of uniform coloration. The immersion is continued as described above for the first dip staining of the sheet but the time

is less when it is desired, as is customary, to have the intensity of color of the narrower marginal band less than the first band. The sheet after rapid removal from the dye solution is treated as previously described.

In this dip staining of thermoplastic interlayer sheet to obtain a dyed sheet suitable for safety glass side windows for buses previously mentioned, the apparatus and method described in my copending patent application Serial No. 401,980, filed January 4, 1954, entitled Dyeing Plastic Sheeting can be used. Of course, it will be apparent from the description below that best results are obtained when using the apparatus, especially the frame, and the method of mounting the sheet on the frame in the improved method of the present application including the use of the improved dye solution.

Safety glass is desired in which the thermoplastic interlayer of the safety glass has been dip stained to produce portions having a green color that absorbs part of the incident light but transmits light rays such that the colored objects, as viewed through the safety glass are seen in their natural colors. In order to provide this color heretofore, dye solutions containing a blue unsulfonated anthraquinone type dye, e.g., 1,4-di(aliphatically monosubstituted amino)-anthraquinone, has been used along with a yellow azo type of dye specifically, the azo coupling product of diazotized para-aminoacetanilide with paracresol. With regard to the blue 1,4-di(aliphatically monosubstituted amino)-anthraquinone, the term "aliphatic" is used in the sense of open-chain carbon compound. Such dye solutions usually contain also a pink dye such as an unsulfonated anthraquinone type dye, for example, 1-amino-4-hydroxyanthraquinone which is identified in Colour Index, 2d edition (published in 1956 by Society of Dyers and Colourists, published at Yorkshire, England), at page 3491, as C.I. Disperse Red 15, Colour Index No. 60710. Although it has been found possible to satisfactorily dip stain plasticized polyvinyl butyral sheeting by use of such a dye solution when utilizing a particular type of solvent, the safety glass utilizing such dyed sheet as the interlayer of the laminate with two sheets of glass would change color from the desired green to a blue color when subjected to a standard test for light fastness, e.g., by exposure in a Fadeometer. Similar color change occurred when the safety glass sheets were subjected to the direct sunlight for an extended period of time. This change in color was due to the fact that the yellow dye, although considered light fast for the usual intended purposes, was not sufficiently light fast for use with the other dyes in the colored safety glass for intense or long periods of exposure to light.

It is the object of this invention to provide a dye solution for dip staining polyvinyl acetal sheeting to produce colored sheeting in which the yellow component of the dye on the sheeting is stable to light for very long periods of time.

Another object of the present invention is to provide a method of utilizing a dye solution having a light fast yellow dye component for dip staining plasticized polyvinyl acetal sheeting.

It is another object of this invention to provide a dye solution for dip staining a plasticized polyvinyl acetal sheeting to produce a graduated coloration across a portion of the sheeting.

Still a further object of the invention is to provide a method of producing the improved dye solution.

These and other objects of the present invention will be apparent to one skilled in the art from the following description of embodiments of the present invention.

I have found that a particular type of yellow dye is suitable for imparting the yellow component of the coloring of a dye solution for use in dip staining of plasticized polyvinyl acetal sheeting. This type of dye is a yellow

dye of the unsulfonated pyrazolone azo type that is soluble in various organic solvents such as alcohols, ketones, esters, oils and plastics and is water insoluble. Examples of such pyrazolone dyes are:

4-phenyl-azo-1-phenyl-3-methyl-5-hydroxypyrazol;
4 - phenyl - azo - 1 - o,m - dichlorophenyl - 3 - methyl - 5-hydroxypyrazol;
4-o,m, dimethylphenyl-azo-1-phenyl-3-methyl-5-hydroxypyrazol;
4 - alpha - naphthyl - azo - 1 - phenyl - 3 - methyl - 5-hydroxypyrazol;
4 - p - diphenyl - azo - 1 - phenyl - 3 - methyl - 5 - hydroxypyrazol; and
4 - phenyl - azo - diphenyl - azo - 1 - o,m - dichlorophenyl-5-hydroxypyrazol-3-carboxylic acid.

These dyes are water insoluble. The preferred yellow dye is the azo coupling product of aniline and 1-phenyl-3-methyl-5-pyrazolone. This dye is listed above as 4-phenyl-azo-1-phenyl-3-methyl-5-hydroxypyrazol and is identified as Colour Index 12700.

In accordance with this invention it is necessary to use a particular solvent for the dye solutions containing the unsulfonated pyrazolone azo type dye. Although this type of dye is soluble in many classes of organic solvents as mentioned above, it is not possible to use such organic solvents alone as the solvent component of the dye solution. These solvents have a deleterious effect on the dimensional stability of plasticized polyvinyl acetal interlayer when the latter is immersed in such solvents for the time required to produce the desired intensity of coloration or intensity of stain. It was found to be necessary that the solvent of the dye solution be a mixture of water and an organic solvent. I have found that Cellosolve, which is ethylene glycol monoethyl ether, $C_2H_5OCH_2CH_2OH$, can be utilized when admixed with water within a narrow range of proportions to provide a suitable solvent for the unsulfonated pyrazolone azo type dye. The solvent extracts some plasticizer of the polyvinyl butyral sheeting but not to an extent that makes its use impossible for graduated dip staining. The use of too low a concentration of water in the mixture, i.e., too high a Cellosolve content, extracts too much plasticizer and attacks the acetal to a definitely adverse degree. Although more of the dye could be dissolved in such a high-Cellosolve type of solvent, graduated dip staining by the solution would not be possible because of the intense dip staining by such solutions even when the immersion time is brief. Thus the dye solution of the invention must be closely maintained with regard to water and Cellosolve content. The water content of the solvent must be maintained between 23 and 27 volume percent with the balance of the solvent being essentially Cellosolve. The use of a solvent having a higher content of Cellosolve is deleterious as mentioned above. The use of a higher water content will not permit adequate dissolution of the yellow dye of the invention to dip stain to the intensity required. For the dye concentration required such solvent will cause precipitation of the yellow unsulfonated pyrazolone azo type dye, when the solution has a pH that permits proper dip staining of the interlayer by this dye.

In the dye solution of the present invention formulation of the solvent of the solution is insufficient. In order to obtain a dye solution having a sufficiently high content of the unsulfonated pyrazolone azo type dye, it is necessary to provide a dye solution using the water-Cellosolve mixture described above and having a pH that is greater than 9 and less than 10.5.

In the preferred embodiment of the invention, in which the dye solution is used to dip stain plasticized polyvinyl acetal sheeting to a green color having a dominant wavelength of 549±2 millimicrons and an excitation purity of 27.5±2%, the yellow unsulfonated pyrazolone azo type dye, for example, the yellow dye Colour Index No. 12700, is used in the dye solution with a specified relative amount of a blue unsulfonated quinizarine type dye, such as the blue 1,4-di(aliphatically monosubstituted amino)-anthraquinone, with or without a pink unsulfonated anthraquinone type dye, such as the pink dye Colour Index No. 60710, i.e., 1-amino-4-hydroxyanthraquinone. In this formulation, the pH of the dye solution must be maintained at 9.5±0.05. A higher pH will produce a more blue stain while a pH below this range will produce a more yellow stain and if the pH is too low, i.e., 9 or below, a precipitation of the yellow dye from the solution will occur.

In the formulation of the dye solution for the dip staining of the present invention, it is necessary to use a nonionic wetting agent (about 0.05 to 0.5 weight percent of the dye solution) to improve the film-forming property of the dye solution on the interlayer being stained. In the absence of such a wetting agent, streaking will occur. Examples of suitable nonionic wetting agents are polyoxyethylene sorbitol tetralaurate, such as Atlas G–1044, polyoxyethylene lauryl ether, such as Atlas BRIJ–30 which contains 8 to 10 ethylene groups, and polyoxyethylene ether of sorbitan monolaurate, such as Tween 21.

In the method of the present invention a plasticized polyvinyl acetal sheeting is mounted on a frame in a manner described in my copending patent application mentioned above. The frame is maintained in a vertical position and is dipped into the dye solution of the invention at rates of immersion to produce graduated coloration with or without a uniform stained band. To obtain the type of bands of uniform stain with an intervening graduated stain to produce a sheet for use in a safety glass for a side window of a bus, a double immersion as described above is used. In the method of the present invention the rinsing differs from that heretofore used. After the sheet has been removed from the dye solution, the interlayer sheet on the frame is sprayed substantially simultaneously over the entire area of each side with water having a pH of about 4 to 5. Sprays that provide water with low impact are commercially available and are used. The use of acidified water prevents leaching of the dyes from the plastic. The acidified water rinse also contains a nonionic wetting agent, such as described above, to prevent any drainage streaks that would otherwise occur. The use of 0.01 volume percent of glacial acetic acid in the rinse water provides the pH of 4 to 5. About 0.01 volume percent of nonionic wetting agent, such as G–1044, in the rinse water is sufficient to prevent drainage streaks.

After water rinsing the plasticized polyvinyl acetal sheet on the frame, it is given a 15-minute soak in acidified water also having a pH of 4 to 5. The sheet while still on the frame is then placed in a drying oven maintained at 140–150° F. for about one-half hour to remove water and Cellosolve from the sheet. The sheet is then removed from the frame and is ready for use between two sheets of glass for laminating by any conventional process to produce a safety glass.

In the dip staining by the foregoing method of plasticized polyvinyl butyral sheet for the production of a green-colored sheet in which the green color of the sheet has a dominant wavelength of 549±2 millimicrons and an excitation purity of 27.5±2%, the following relative percentages of dyes are used: 17.04 weight percent pink dye Colour Index 60710; 56.62 weight percent 1,4-di(aliphatically monosubstituted amino)-anthraquinone; and 26.34 weight percent yellow dye Colour Index No. 12700. The total concentration of this mixture is 0.65 weight percent of the solution. Thus the solution contains 0.11 weight percent pink dye Color Index 60710, 0.37 weight percent 1,4-di(aliphatically monosubstituted amino)-anthraquinone and 0.17 weight percent yellow dye Colour Index No. 12700. In this preferred embodiment the amount of the wetting agent Atlas G1044 is 0.10 weight percent of the solution. The balance (99.25 weight per-

cent) is solvent which is a mixture of 25±2 volume percent water and 75±2 volume percent Cellosolve.

In the manufacture of this preferred dye solution concentrates of each of the three dyes is prepared. The commercial dyes which contain the 1,4-di(aliphatically monosubstituted amino)-anthraquinone and the pink dye Colour Index No. 60710 contain a large percentage of filler material and the filler is removed by dissolving the particular dye in Cellosolve without adjustment of pH and filtering the solution in each case through a filter that has a porosity of less than 15 microns. The commercial yellow dye Colour Index No. 12700 does not contain a filler and the concentrate of this material is prepared without any filtration. The yellow dye Colour Index No. 12700 in this preferred embodiment is dissolved in a solvent mixture of 25 volume percent water and 75 volume percent Cellosolve having a pH of 10.5 to 11. The pH is provided by the addition of a small amount of relatively concentrated, e.g., 5 N, aqueous sodium hydroxide solution. When the concentrate is 10 times stronger than the final concentration in the dye solution, the yellow dye Colour Index 12700 is used in an amount of 63.3 grams per gallon of the solvent mixture mentioned above. After dissolution of the yellow dye Colour Index 12700 in this solvent, it is used in the appropriate amount with the concentrated solutions of the 1,4-di(aliphatically monosubstituted amino)-anthraquinone and the pink dye Colour Index No. 60710 in Cellosolve. In the preferred embodiment these concentrates, also ten times the final concentration, contain 136 grams of the 1,4-di(aliphatically monosubstituted amino)-anthraquinone per gallon of Cellosolve and 40.9 grams of the pink dye Colour Index No. 60710 per gallon of Cellosolve. The appropriate amount of additional Cellosolve and water is mixed with these concentrates to provide with the nonionic wetting agent G–1044 a dye solution of the composition mentioned above. Adjustment of the pH to 9.5±0.05 is then accomplished by the addition of a small amount of glacial acetic acid. Acetic acid, as glacial acetic acid, is preferred to any other acid such as hydrochloric acid because yellow dye Colour Index 12700 and other yellow unsulfonated pyrazolone azo dyes are soluble in acetic acid. Any local concentration of the acetic acid in the dye solution will not cause a precipitation of the yellow dye from the solution.

During the use of the dye solution for the dip staining of a large number of plasticized polyvinyl acetal sheets the latter will cause a decrease in the pH of the solution because of the presence of some soda, i.e., sodium bicarbonate, on the surface of the interlayer sheeting. The sheeting contains soda on the surface initially to prevent adherence of surfaces of the interlayer sheeting in roll form. Although the sheets are cut from the roll, washed a couple of times with water and dried, a very small amount of soda remains and thus adversely affects the pH of the dye solution as mentioned above. Thus reuse of the dye solution requires a periodic addition of alkali to maintain the pH within the narrow range.

During use of the dye solution for staining, the dyes are used in staining at different rates according to optical analysis of the solution and the laminated safety glass, so that periodically the dye bath is adjusted to the initial concentrations of dyes by adding different ratios of the concentrates than used in the initial formulation of the dye solution. In this case also it is preferred in adjusting for a pH of 9.5±0.5 after the addition of makeup concentrates to add glacial acetic acid, rather than an acid such as HCl because localized precipitation of the yellow dye Colour Index No. 12700 and other unsulfonated pyrazolone azo dyes is prevented. Of course, if hydrochloric acid is added for pH adjustment, it is necessary to insure that the dye solution is stirred for a sufficient length of time to redissolve any of the dye precipitated in the local areas.

The dye bath should be maintained at a relatively fixed temperature to properly maintain an adequate rate of graduated stain development for a given rate of immersion of the sheet in the dye solution. It is preferred that the bath of dye solution be held at about 75° F. If the temperature is dropped, precipitation of dye occurs and the dye solution resulting therefrom would stain the plastic to a different dominant wavelength.

For some products it is desired to impart a higher intensity of coloration to the entire sheet than is obtained by immediately and rapidly removing the sheet from the dye solution after it is totally immersed. In such instances the sheet, when it has been totally immersed as described above, is allowed to remain immersed in the dye solution for an appropriate number of seconds to impart a higher intensity of coloration by staining. Then the sheet is rapidly removed from dye solution, rinsed by an acidified water spray, etc.

In the foregoing description of an embodiment of the method of the invention, the sheet, after being sprayed by the acidified water for the removal of excess dye solution and to prevent further staining, is prepared for use as a plastic interlayer for safety glass by soaking in the acidified water and then oven drying. The treatment of soaking in water and oven drying can be replaced as described by the following treatment of a preferred embodiment. The plasticized polyvinyl acetal sheet after the acidified water spray treatment is maintained on the frame, preferably held in a vertical position, in air at 90 to 100° F. until the surface of the sheet is dry. This drying operation requires approximately 10 minutes. The sheet is then cut off the frame and hung in a vertical position for a minimum of 32 hours in a room or chamber maintained at a low humidity, such as 10 percent relative humidity, and at a temperature of about 65° F. The room used for assembling the two sheets of glass with the plasticized polyvinyl butyral interlayer sheet preparatory to the laminating operation is maintained at such low humidity and at that temperature.

In the method previously described in which the acidified water spray or rinse stained sheet is followed by soaking in acidified water and then dried in an oven at elevated temperature, the relative amounts of the three dyes were chosen so that the final product after soaking and oven drying would have the required green color. Because the soaking in the acidified water removes some of the blue dye, e.g., 1,4-di(aliphatically monosubstituted amino)-anthraquinone, this dye solution is not completely satisfactory for the method of the preferred embodiment in which the soaking in water and the oven treatment are not used. When using the preferred embodiment in which the interlayer is surface dried by the storage for a short period of time, such as 10 minutes, at 90 to 100° F. followed by storage at low humidity and temperature of about 65° F., the dye solution contains the following relative amounts of the three dyes.

17.43 weight percent of pink dye Colour Index No. 60710
54.83 weight percent of 1,4-di(aliphatically monosubstituted amino)-anthraquinone
27.74 weight percent of yellow dye Colour Index No. 12700.

To make the dye solution for this mode of operation, concentrates of each of the three dyes are prepared as described above for use in the other method but the content of the dye in each case is as follows: 131.6 grams of 1,4-di(aliphatically monosubstituted amino)-anthraquinone per gallon of Cellosolve; 41.9 grams of pink dye Colour Index No. 60710 per gallon of Cellosolve; and 66.6 grams of yellow dye Colour Index No. 12700 per gallon of a mixture of 75 volumes/percent Cellosolve and 25 volumes/percent water adjusted to a pH of 10.5 to 11. Of course, in making a dye solution for staining plasticized polyvinyl acetal the appropriate amounts of these concentrates are used with the appropriate amounts of Cellosolve and water. The pH of the final solution is

adjusted to a value of 9.5±0.05 as described above in preparation of the dye solution for use in the other embodiment of the method in which the water soaking and oven treatment is utilized. The total amount of dye, as in the other dye solution, is 0.65 weight percent of the solution. In this solution, therefore, there is 0.18 weight percent of yellow dye Colour Index No. 12700, 0.36 weight percent of blue dye 1,4-di(aliphatically monosubstituted amino)-anthraquinone and 0.11 weight percent of pink dye Colour Index 60710.

In the embodiment in which there is acidified water soaking followed by an oven treatment of the water-rinsed stained sheet, the dye solution when examined in a glass cell having faces 0.11 mm. apart was found to have a dominant wavelength of 518.1 millimicrons with an excitation purity of 8.3 percent. The luminous transmittance of the dye solution in the glass cell was 31.4 percent. Using this dye solution in the manner described above, it was found that the safety glass prepared therefrom by laminating the resultant thermoplastic sheet having a thickness of about 0.015 inch between two sheets of Solex window glass each having a thickness of about .108 inch; had a dominant wavelength of 549.6 millimicrons and thus met the desired requirements for the green color. This was measured at a point in the laminate in which the luminous transmittance was 10 percent. The excitation purity was 27.5 percent.

In the embodiment of the method in which the sheet after acidified water spraying is surface-dried by maintenance at 90 to 100° F. followed by long-time hanging in air having a low relative humidity and a temperature of about 65° F., the dominant wavelength of the dye solution in the glass cell previously mentioned is about 524 millimicrons and has an excitation purity of about 9 percent with a luminous transmittance of about 30 percent. This solution will stain the interlayer sheet so that the final laminate will have the dominant wavelength, excitation purity and luminous transmittance substantially the same as that previously described for the laminate prepared from the dye solution utilizing the other embodiment of the method.

Laminates prepared with interlayer sheets stained in accordance with this invention had a lowering of the dominant wavelength of only 2.9 millimicrons when subjected to 200 hours of exposure in the Fadeometer apparatus, whereas the lowering of dominant wavelength was 47 millimicrons in a laminate using an interlayer stained with the dye solution containing the azo coupling product of diazotized para-aminoacetanilide with para-cresol in combination with pink dye Colour Index 60710 and 1,4-di(aliphatically monosubstituted amino)-anthraquinone as mentioned above. In the former case the visual color change was practically undetectable whereas in the latter case, with the 47 millimicrons lowering the change in color to blue was very apparent. Similar comparisons were obtained with long-time exposures in the sunlight in Florida and elsewhere.

In the foregoing description of the two dye solutions, the relative amounts of the three commercial dyes have been presented. In view of the presence of 48 and 58 weight percent of filler in the commercial dye containing 1,4-di(aliphatically monosubstituted amino)-anthraquinone and the commercial product containing pink dye Colour Index No. 60710, respectively, the relative amounts of the filler-free dyes in the solution used for staining followed by rinsing, water soaking and oven drying are: 11.36 weight percent of pink unsulfonated anthraquinone type dye; 46.77 weight percent of blue unsulfonated quinizarine type dye; 41.87 weight percent of yellow unsulfonated pyrazolone azo type. Thus filler-free dye concentrations in the dye solution are 0.05, 0.19 and 0.17 weight percent, respectively. Also in the dye solution used for dip staining followed by acidified water rinse, air drying at 90–100° F., etc., the relative amounts of the three filler-free dyes are: 11.53 weight percent of pink unsulfonated anthraquinone type dye; 44.84 weight percent of blue unsulfonated quinizarine type dye; 43.63 weight percent of yellow unsulfonated pyrazolone azo type. The filler-free dye concentrations in the dye solution are 0.05, 0.19 and 0.18 weight percent respectively.

The foregoing is a description of the preferred embodiments of the present invention and for purposes of illustrations only and the invention is not to be limited except as limited by the claims that follow.

I claim:

1. A method of coloring a plastic sheet which comprises placing a plasticized polyvinyl acetal sheet in a vertical plane, rapidly lowering the bottom marginal portion of the vertical sheet into a dye solution comprising an unsulfonated pyrazolone azo dye, a nonionic wetting agent and a solvent consisting essentially of about 23 to 27 volume percent water and about 73 to 77 volume percent ethylene glycol monoethyl ether, said solution being at a pH of greater than 9 and less than 10.5, continuing immersion of the sheet while first decreasing the rate until the sheet is being slowly immersed and then increasing the rate of immersion until the entire sheet is immersed, rapidly removing the entire sheet from the dye solution, spraying substantially simultaneously the entire area of each side of the sheet with a liquid consisting essentially of water, a nonionic wetting agent and an acid, said liquid having a pH of between about 4 and 5, and drying the liquid-sprayed sheet.

2. The method of claim 1 wherein the concentration of the unsulfonated pyrazolone azo dye in the dye solution is between about 0.17 and 0.18 percent by weight, the pH of the dye solution is 9.5±0.05, the unsulfonated pyrazolone azo dye is yellow dye Colour Index No. 12700 and the acid in the spray liquid is acetic acid.

3. The method of claim 2 wherein the drying step comprises maintaining the sheet in air at about 90 to 100° F. until the surfaces of the sheet are dry and then storing the sheet for at least 32 hours in air having a low relative humidity and maintained at a temperature of about 65° F. and wherein the 1,4-di(aliphatically monosubstituted amino)-anthraquinone dye is present in a concentration of about 0.18 weight percent of the dye solution and said dye solution also contains about 0.19 weight percent of a blue and about 0.05 weight percent of a pink dye Colour Index 60710.

4. A dye solution for staining of a sheet of plasticized polyvinyl acetal which comprises an unsulfonated pyrazolone azo dye, a nonionic wetting agent and a solvent consisting essentially of about 23 to 27 volume percent water and about 73 to 77 volume percent ethylene glycol monoethyl ether, said solution having a pH of greater than 9 and less than 10.5.

5. The dye solution of claim 4 wherein the concentration of the unsulfonated pyrazolone azo dye is between about 0.17 and 0.18 weight percent, the pH of the solution is 9.5±0.05 and the dye is yellow dye Colour Index No. 12700.

6. A dye solution for green staining of a sheet of plasticized polyvinyl acetal which comprises a yellow unsulfonated pyrazolone azo dye, a blue 1,4-di(aliphatically monosubstituted amino)-anthraquinone, a nonionic wetting agent, and a solvent consisting essentially of about 23 to 27 volume percent water and about 73 to 77 volume percent ethylene glycol monoethyl ether, said solution having a pH of 9.5±0.05.

7. A dye solution for green staining of a sheet of plasticized polyvinyl acetal which comprises a yellow dye Colour Index No. 12700, a blue 1,4-di(aliphatically monosubstituted amino)-anthraquinone, a pink dye Colour Index No. 60710, a nonionic wetting agent and a solvent consisting essentially of about 23 to 27 volume percent water and about 73 to 77 volume percent ethylene glycol monoethyl ether, said solution having a pH of 9.5±0.05 and the total concentration of the three dyes being 0.65 weight percent of the solution.

8. The solution of claim 7 wherein the concentration of the yellow dye in the solution is between about 0.17 and 0.18 weight percent.

9. The solution of claim 8 wherein the relative amounts by weight of the three dyes in the solution are about 41.87 parts of the yellow dye, about 46.77 parts of the blue dye and about 11.36 parts of the pink dye.

10. The solution of claim 8 wherein the relative amounts by weight of the three dyes in the solution are about 43.63 parts of the yellow dye, about 44.84 parts of the blue dye, and about 11.53 parts of the pink dye.

11. The method of preparing a dye solution comprising an unsulfonated pyrazolone azo dye, a nonionic wetting agent and solvent consisting essentially of about 23 to 27 volume percent water and about 73 to 77 volume percent ethylene glycol monoethyl ether which comprises forming a concentrated solution of said dye in a portion of said solvent adjusted to a pH of between about 10.5 and 11, adding the nonionic wetting agent and water and the ether in said volume percentages of the solvent to reduce the dye concentration to between about 0.17 and 0.18 weight percent of the solution and lowering the pH of the solution to 9.5 ± 0.05 by adding acid.

12. The method of claim 11 wherein the acid is glacial acetic acid.

13. A method of coloring a plastic sheet which comprises immersing at least a marginal portion of a plasticized polyvinyl acetal sheet in a dye solution comprising an unsulfonated pyrazolone azo dye, a nonionic wetting agent and a solvent consisting essentially of about 23 to 27 volume percent water and about 73 to 77 volume percent ethylene glycol monoethyl ether, said solution being at a pH of greater than 9 and less than 10.5, removing the sheet from the dye solution, spraying the immersed portion of the sheet with a liquid consisting essentially of water, a nonionic wetting agent and an acid, said liquid having a pH of between about 4 and 5, and drying the liquid-sprayed sheet.

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717,387 Great Britain ---------- Oct. 27, 1954

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,914,373

November 24, 1959

Raymond G. Rieser

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 38, for "have 8" read -- have about 8 --; column 8, lines 40 and 41, strike out "1,4-di(aliphatically mono-substituted amino)-anthraquinone" and insert the same after "blue" in line 44, same column.

Signed and sealed this 27th day of September 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents