

[54] FUGITIVE COLORATION OF SOLID MATERIALS WITH DYES

[72] Inventor: Jerry A. Cogan, Jr., Spartanburg, S.C.
[73] Assignee: Deering Milliken Research Corporation, Spartanburg, S.C.
[22] Filed: Feb. 12, 1969
[21] Appl. No.: 798,815

2,819,179 1/1958 Barnard et al.....117/139.5 R
2,920,975 1/1960 Livak.....8/164
2,959,461 11/1960 Murray.....8/164
3,227,510 1/1966 Bridgeford.....8/31
3,236,685 2/1966 Caldwell et al.....117/138.8 F

OTHER PUBLICATIONS

Moore et al., IBM Technical Disclosure, Vol. 7, No. 6 Nov. 1964

Primary Examiner—William D. Martin
Assistant Examiner—M. R. Lusignan
Attorney—Norman C. Armitage and H. William Petry

[52] U.S. Cl.117/62.1, 8/164, 117/138.8 A, 117/138.8 F, 117/143 A, 117/4, 117/63, 117/66, 117/93.31, 117/100 S, 117/161 UN, 117/161 UT, 117/161 UC, 117/161 UZ
[51] Int. Cl.B44d 1/44
[58] Field of Search.....8/164; 117/102, 76 T, 161 UC, 117/138.8 F, 62.1, 138.8 A, 143 A, 4, 63, 66, 93.31, 100 S, 161 UN, 161 UT, 161 UC, 161 UZ

[57] ABSTRACT

A process for repeatedly tinting and changing the color of solid materials which comprises applying a polymeric composition to the material and thereafter contacting the treated material with a dye which has a higher affinity for the polymeric composition than the material. In this manner the dye is temporarily fixed on the material and can be removed by washing in a detergent solution. The dyeing and removing steps can be repeated.

[56] References Cited

UNITED STATES PATENTS

2,683,647 7/1954 Hagan.....8/164
2,690,953 10/1954 Livak et al.....8/164

14 Claims, No Drawings

FUGITIVE COLORATION OF SOLID MATERIALS WITH DYES

BACKGROUND OF THE INVENTION

This invention relates to a process for repeatedly tinting and changing the color of solid materials, and more particularly, to a process whereby the change of color can be easily effected.

Methods for coloring solid materials such as paper, wood, plastics and textile fabrics are well-known and have been the subject of many patents. The choice of a particular coloring technique is most generally determined by the nature of the substrate being colored although many other factors are involved, such as desired shade and color. Moreover, some dyeing techniques result in a more permanent coloration of fabrics than others. For example, in U.S. Pat. No. 2,955,900, a process is described for the application of basic dyestuffs and dyestuffs containing ternary and quaternary salt groups to textile materials. In particular, this patent describes the treatment of the dyed material with an alkali which results in dyeings having good light- and wash-fastness.

It has also been known that although certain colors can be made permanent to washing, it is possible to strip the colors from fabrics by acid treatments. However, this acid treatment is rigorous and results in permanent damage to the fibers of the fabric. Moreover, even though strong acids may be used, complete removal of the dye is not often accomplished, and subsequent dyeing with a different color creates problems in predictability and reproducibility.

One coloring technique which has been utilized with some degree of success for producing changeable color fabrics involves the use of the so-called "indicator dyes." The nature of these dyes is not well understood, and so these dyes are commonly categorized by their ability to undergo a color change on treatment with a solution capable of influencing the relative acidity of the colored fabric. That is, the indicator dyes undergo a color change in response to a variation in the hydrogen-ion concentration. Such processes with relation to changing the color of hair on toys is described in U.S. Pat. No. 3,382,607. U.S. Pat. No. 3,030,227 utilizes color formulations for application to all types of fabrics and articles which are capable of undergoing a color change by the application of a relatively weak acid such as citric acid. However, this latter process is irreversible since the color change on application of the acid is due to a decomposition of the dye component of the composition.

One problem encountered in using such dye systems is the inability to provide a large variety of colors. For example, as shown in U.S. Pat. No. 3,030,227, a maroon colored fabric can be changed to a red colored fabric by a dilute acid treatment. No other color changes on this fabric are possible, and the process is not reversible. On the other hand, where indicator dyes such as those described in U.S. Pat. No. 3,382,607 are used, the color change is reversible in response to a variation in the hydrogen-ion concentration. For example, a fabric dyed with methyl red is a bright red color when on the acid side, but upon the addition of a basic solution to raise the pH of the fiber above 6, the color of the fabric changes dramatically to a golden yellow. Treatment with an acid changes the color back to red. One of the difficulties of these changeable colors is that only two colors are possible since further variation in the pH of the fabric does not result in a change in color.

Colored inorganic salts such as copper sulfate and iron oxides might be deposited into or on solid materials to tint the material. However, such a deposition could not be repeated after the fabric is converted to a garment since the color developed would most likely be very uneven due to seams, creases, etc. in the garment. Similarly, the use of known fugitive tints would also result in uneven deposition of color. Moreover, both of these techniques result in colors which are susceptible to water spotting.

SUMMARY OF THE INVENTION

The process of the present invention provides a method for repeatedly dyeing and tinting solid material, especially textile fabric, in a manner which results in a colored material which can be easily stripped of its color without damaging the material or fibers of the fabric. That is, the dye is fugitive when washed in a detergent solution. The process which results in these unique properties comprises applying to the solid material a polymeric composition, contacting the treated material with a dye which has a higher affinity for the polymeric composition than the material whereby the dye is temporarily fixed on the material, and removing the dye by washing the material in a detergent solution. This solid material can be subsequently and repeatedly dyed with other dyes to provide additional colors which also can be removed by washing in a detergent solution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention is applicable to all types of solid materials and especially fabrics and articles made therefrom including garments of all types such as ladies' and children's blouses and dresses, sheets, pillow cases, drapery and upholstery materials, table cloths, doll clothes, etc. The color of these articles can be repeatedly changed to suit the owner's fancy at any particular time thus avoiding the necessity of having a wide variety of colored articles on hand at any one time. The process also is sufficiently simple and harmless to enable children to carry out the coloring steps of the process without adult supervision.

Solid materials which can be repeatedly colored in accordance with the process of the invention include a wide variety of materials including metal, wood, paper, textiles, leather, glass and plastics. These materials can have any shape or configuration, and all or part of the material can be colored.

The textile fabrics which are useful in this invention may be prepared from virtually all types of fibers ranging from fabrics containing 100 percent natural fibers such as cotton, to fabrics composed exclusively of synthetic fibers such as polyesters and polyamides. Blends of these fibers also are contemplated as useful in the invention since fabrics comprising such blends are so readily available. Synthetic fibers which are useful either alone or in blends with natural fibers include polyamides such as polyhexamethylene adipamide; polyesters such as polyethylene terephthalate; acrylic fibers such as polyacrylonitrile and homopolymers or copolymers of acrylonitrile such as acrylonitrile/methylacrylate (85:15); and cellulosic derivatives such as cellulose acetate and viscose Rayon. Polyester/cotton fabrics are particularly useful in the process of the invention. Although the discussion of this specification relating to textile materials is directed generally to textile fabrics, the process is applicable to fibers in all forms such as yarn, roving, sliver and thread. All forms of fabrics may be treated including woven, non-woven, knitted, etc.

As mentioned previously, the process of this invention results in a tinted or dyed solid article whose color can be easily removed or changed as desired. This controllable dye removability is obtained as a result of the nature of the compositions applied to the fabric and the sequence in which the compositions are applied. In this process, the solid material is first treated with a polymeric composition and thereafter contacted with a dye which has a higher affinity for the polymeric composition than the solid material. Since the dye is affixed to the polymer rather than the substrate, fugitivity of the dye is obtained when the dye is capable of forming some type of complex with the polymeric composition, which complex dissociates in a detergent solution. In the absence of the polymer, the solid materials either do not pick up significant amounts of the acid and basic dyes or the coloration is more permanent once it adheres to the substrate.

The most common combinations of polymer and dye which have been found to be useful for providing the desirable con-

trolled sensitivity include basic polymers with acid dyes and acid polymers with basic dyes. The latter combination is preferred, especially on textile fabrics since many fabrics today contain basic polymers to improve their permanent press and wrinkle recovery and these basic polymers can provide dyeability with acid dyes which cannot be removed. Moreover, the addition of a basic polymer on a fabric already containing another basic polymer could result in compatibility problems.

Addition polymers of N-vinyl lactams are examples of basic polymeric compositions useful in this process. More particularly, polymers of N-vinyl pyrrolidone and copolymers thereof with ethylenic compounds such as acrylonitrile, vinyl chloride, ethyl acrylate, etc. are contemplated.

Other polymeric compositions useful in the process include one or more of a large number of the so-called soil release compounds such as synthetic acid polymers, low molecular weight polyesters and fluorochemicals.

Synthetic acid polymers suitable as the polymeric composition of the present invention may be prepared from any of the polymerizable organic acids, i.e., those having reactive points of unsaturation, e.g., one of the acrylic acids. These polymers may be homopolymers of the acids or interpolymers of an acid and other monomers copolymerizable therewith so long as at least 10 percent by weight acid is present in the polymer. Examples of polymerizable acids that may be used are acrylic acid, maleic acid, fumaric acid, methacrylic acid, itaconic acid, crotonic acid, cinnamic acid, polymerizable sulfonic acids, polymerizable phosphoric acids, etc. Monomers that may be interpolymerized with the above acids include monomers capable of copolymerizing with the acids which will not adversely affect the polymer. Suitable monomers include esters of the above acids prepared by reacting the acid with an alkyl alcohol, e.g., acrylic esters such as ethyl acrylate, methyl acrylate, propyl acrylate, isopropyl acrylate, 2-ethylhexyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, etc.; alkyl fumarates, maleates, crotonates, cinnamates, etc.; vinyl halides; monomers having vinylidene groups, e.g., styrene, acrylonitrile, methyl-styrene; substituted vinyl monomers, e.g., chlorostyrene, butadiene, etc. Various mixtures of the above polymers also may be employed in the process of the present invention as well as salts of the acid polymers, e.g., sodium, potassium, lithium, ammonium salts, etc.

Examples of synthetic acid polymers that may be used according to the present invention are the following combinations:

ethyl acrylate : acrylic acid;
ethyl acrylate : acrylic acid : acrylamide;
butyl acrylate : acrylic acid;
ethyl acrylate : methacrylic acid;
ethyl acrylate : itaconic acid;
methyl methacrylate : acrylic acid;
2-ethyl hexyl acrylate : acrylic acid;
acrylamide : acrylic acid;
butyl acrylate : acrylic acid : acrylamide;
ethyl acrylate : acrylic acid : N-methylol acrylamide;
ethyl acrylate : acrylic acid : styrene;
ethyl acrylate : acrylic acid : hydroxypropyl methacrylate;
ethyl acrylate : acrylic acid : divinyl benzene;
ethyl acrylate : acrylic acid : allyl acrylamide;
ethyl acrylate : acrylic acid : glycidyl acrylate;
ethyl acrylate : sodium styrene sulfonate;
ethyl acrylate : crotonic acid;
styrene : acrylic acid;
ethyl acrylate : acrylic acid : hydroxyethyl methacrylate;

and
hydroxyethyl methacrylate : acrylic acid : acrylamide; and
butyl acrylate : ethyl acrylate : acrylic acid.

As noted above, the acid polymer should contain at least about 10 percent by weight acid calculated as acrylic acid and preferably at least about 20 percent by weight acid. Copolymers of acrylic acid or methacrylic acid with an acry-

late ester such as ethyl acrylate are considered to be especially useful.

The polymeric composition is preferably applied to the solid material as an aqueous dispersion or emulsion. Advantageously, between about 2% and 40% and preferably between about 5% and 35% by weight of the polymer is present in the aqueous dispersion. When applied to textile fabrics, it is desirable to have between about 0.2% and 7% by weight thereof based on the dry weight of the textile material and preferably between about 0.5% and 4% by weight.

The polymers utilized in the process of this invention are generally those which form a hydrophilic film upon drying although a continuous film is not necessary. It has been observed that the fugitivity of the dyed fabrics is improved if the fabric having the polymer thereon is subjected to textile resin curing conditions. Such treatments especially improve the durability of the desirable properties. Moreover, the presence of a textile resin catalyst and optionally, an aminoplast textile resin during the curing results in even further improvement. Although it is believed that there is some reaction between the polymer and the textile resin, the reaction mechanism has not been definitely ascertained. Thus, in a preferred embodiment, the first step of the process involves treating a textile material with an aminoplast textile resin, a textile resin catalyst and a polymer, preferably an acid polymer.

The term "textile resin" is intended to include both monomers and polymers which when applied to a textile material and reacted under proper conditions undergo polymerization and/or condensation to the thermoset state. Aminoplast resins present a group of particularly preferred textile resins. These nitrogen-containing resins, when applied to a textile material in the presence of a catalyst at a temperature of about 130° to about 200° C., are transformed into the thermoset state.

Examples of the aminoplast resins include urea formaldehydes, e.g., propylene urea formaldehyde and dimethylol urea formaldehyde; melamine formaldehydes such as pentamethylol melamine; ethylene ureas such as dihydroxy dimethylol ethylene urea; carbamates; alkylol amides such as methylol formamide; acrylamides such as N-methylol acrylamide; diureas such as trimethylol acetylene diurea; triazines such as dimethylol-N-ethyl triazines, etc. Mixtures of aminoplast textile resins also are contemplated. Additional aminoplast resins and mixtures thereof are described in more detail in U.S. Pat. No. 3,377,249.

The amount of textile resin applied to the fabric is determined primarily by the ultimate use of the garments or articles prepared from the fabric. For purposes of the present invention, the amount of textile resin in the pad bath may vary between about 2 and 30 percent. The resin applied to the fabric should be in the range of about 2 to 20 percent based on the dry weight of the fabric and preferably in the range of about 4 to 9 percent. The catalyst which may be employed in the process of the present invention in combination with the polymer and textile resins will depend upon the specific resin that is applied to the material. For instance, if the textile resin has a functional group that is reactive under acidic conditions, then an acid catalyst is used. Likewise, the base catalysts are used when a functional group is present which is reactive under alkaline conditions. The catalysts are those conventionally used to activate the reaction of textile resins with the hydroxy groups of cellulose. Preferably, latent acid or base acting catalysts are utilized. The most common acid acting catalysts are the metal salts, for example, magnesium chloride, zinc nitrate and zinc fluoroborate and the amino salts, for example, monoethanolamine hydrochloride.

The latent base acting catalysts utilized comprise alkali metal salts such as sodium carbonate which will decompose to form the stronger base sodium oxide during curing. Additional base acting catalysts include potassium bicarbonate, potassium carbonate, sodium silicate, alkali metal phosphates and quaternary ammonium hydroxides.

The amount of catalyst to be utilized is that conventionally used in other processes. For example, up to about 15 percent by weight of an acid acting catalyst in the pad bath is usually utilized with a preferred range being from about 1 to 7 percent. The amount of catalyst to be utilized will further depend in part on the temperature at which the reaction is conducted and the amount of catalyst consumed in the reaction. For example, when base catalysts are utilized and if a highly acidic group is released during the reaction, the amount of base applied to the textile material should be at least sufficient to provide an excess of base in addition to that which is consumed by the highly acidic group.

The polymer dispersion or emulsion utilized in the process of the invention may include other ingredients in addition to the polymer such as emulsifying agents, wetting agents, softeners, fluorocarbon, water, oil repellent materials, etc. The bath can be applied to the solid substrate in any suitable manner although padding of the bath onto the solid material is preferred because of ease of operation. Alternatively, the ingredients may be sprayed on as liquids, the substrate may be treated with the vapors of the compounds, or the substrate may be dipped in the emulsion. In general, the applicator is adjusted to provide from about 30 to 100 weight percent wet pickup on fabrics from the bath.

After the acid polymer and optionally, textile resin catalyst, etc. are applied to the fabric, the fabric is dried and optionally, subjected to textile resin curing conditions. The drying temperatures are dependent upon the particular catalyst utilized in the process, and where it is desired to prepare a garment from the fabric prior to curing, the drying temperature should be insufficient to activate the catalyst.

Irradiation techniques may be employed when an aminoplast resin having ethylenic unsaturation is applied to a fabric. An insulating core transformer, operated at a potential varying between 100,000 electron volts and 500,000 electron volts may be successfully used to irradiate the textile material. Such a transformer is commercially available from High Voltage Engineering Corporation, Burlington, Massachusetts. The amount of ionizing radiation necessary is at least 32 electron volts for each ion pair formed. Thus, irradiation of 32 volts and above is effective. Both high energy particle and ionizing radiation are useful in this invention. The preferred dosage of radiation is in the range of 1,000 rads to 100 megarads, a rad being the amount of high energy radiation of the type which results in energy absorption of 100 ergs per gram of fabric. More preferably, the irradiation dosage ranges from 0.5 to 5 megarads. Further details concerning the curing and irradiation of polymer treated fabrics are contained in U.S. Pat. No. 3,377,249.

The following examples illustrate the first step in the process of the invention, namely, the application of the polymer system to the fabric. Unless otherwise indicated, all parts are by weight.

EXAMPLE 1

Samples of Dacron/cotton (65/35) fabric are treated with a pad bath emulsion comprising 20% N-methylol acrylamide (50% aqueous solution); 10% emulsion copolymer of ethyl acrylate : acrylic acid (70/30); 5% magnesium chloride catalyst; and 65% water. This pad bath is padded onto the fabric at 50% pickup whereupon the fabric is dried at a temperature ranging from about 90° to 138° C. to reduce the fabric moisture content to approximately 5%. The dried fabric is then given an irradiation dosage of 2 megarads in an insulated core transformer manufactured by the High Voltage Engineering Corporation of Burlington, Massachusetts. The fabric is cured by heating at a temperature of 163° for 15 minutes.

EXAMPLE 2

The procedure of Example 1 is repeated except that a 100% cotton fabric is used in lieu of the Dacron/cotton fabric.

EXAMPLE 3

The procedure of Example 1 is repeated except that the following pad bath is utilized:

24% dihydroxy dimethylol ethylene urea (50% aqueous solution); 10% copolymer of ethyl acrylate : acrylic acid (70:30); 5% zinc nitrate hexahydrate, 6% of a mixture of glycerol monostearate and polyethylene glycol monostearate; 0.2% wetting agent; and 54.8% water.

EXAMPLE 4

The procedure of Example 1 is repeated except that the following pad bath is utilized:

10% copolymer of ethyl acrylate : acrylic acid (70:30); 5% zinc nitrate hexahydrate; and 85% water.

EXAMPLE 5

The procedure of Example 4 is repeated except that 100% Dacron fabric is used in lieu of the Dacron/cotton fabric.

EXAMPLE 6

The procedure of Example 1 is repeated except that the emulsion copolymer is a copolymer of ethylacrylate : acrylic acid comprising 50% ethyl acrylate and 50% acrylic acid.

EXAMPLE 7

A fabric made from a blend of 65% polyester/35% cotton fiber is treated with a pad bath comprising 2.4% of a copolymer of vinyl pyrrolidone and ethyl acrylate (40% aqueous solution; Polecron 130, sold by General Aniline and Film Corporation); 0.024% succinic acid; 24% dihydroxy dimethylol ethylene urea (50% aqueous solution; Reactant 100 sold by American Cyanamid Company); 6% magnesium chloride (30% aqueous solution; Catalyst MX sold by American Cyanamid Company); 0.1% nonyl phenol polyoxyethylene ether (Surfonic N-95 sold by Jefferson Chemical Company); and 67.5% water. The fabric is padded, dried, and cured 90 seconds at 325° F. A thin coating of the basic polymer is obtained.

EXAMPLE 8

A hollow glass sphere is sprayed with an emulsion comprising 10% of a copolymer of ethyl acrylate : acrylic acid (70/30), 5% zinc nitrate hexahydrate and 85% water, and air dried. A thin coating of the acid polymer is deposited thereon.

EXAMPLE 9

A fabric is treated as in Example 7 except that the copolymer of vinyl pyrrolidone and ethyl acrylate and the succinic acid are omitted from the pad bath. After curing, the fabric is treated with a second pad bath comprising 0.20% diethylene triamine; 0.38% acetic acid; 0.90% diglycidyl ether of diethylene glycol (70% aqueous solution); 10% isopropyl alcohol; 0.05% nonyl phenol polyoxyethylene ether (Surfonic N-95 sold by Jefferson Chemical Company); and 88.47% water.

The second step in the process of the invention involves contacting the solid materials which have been treated with the polymeric compositions with a dye which has a greater affinity for the polymeric composition than it does for the substrate. In this manner, the dye is temporarily fixed to the substrate and it can be easily removed by washing in a detergent solution. It is believed that the dye forms some type of semistable complex with the reactive groups of the polymer, but which dissociates when brought into contact with a detergent solution. In addition to providing the desired fugitivity, the polymeric composition on the solid material improves the build up of the dye on the material which provides for deep shades of colors which have been heretofore difficult to obtain on certain fabrics.

As mentioned previously, it has been found that acid dyes are useful when the polymeric composition is basic, whereas

basic dyes should be employed when the polymeric composition is acidic.

The acid dyes which can be employed in this invention include such commercial dyes as illustrated in the following table.

ACID DYES

| Color Index No. | Commercial Name |
|-----------------|-------------------------------------|
| Acid Yellow 17 | Xylene Light Yellow 2G |
| Acid Yellow 42 | Sylphon Yellow RS |
| Acid Yellow 128 | Cibalan Yellow FGL |
| Acid Red 1 | Azo Rhodine 2G |
| Acid Red 85 | Benzyl Fast Red GRG |
| Acid Red 251 | Cibalan Bordeaux EL |
| Acid Red 253 | Cibalan Brilliant Scarlet RL |
| Acid Blue 45 | Alizarine Sapphire BLN |
| Acid Blue 80 | Brilliant Alizarine Milling Blue BL |
| Acid Blue 158 | Palatine Fast Blue GGNA |
| Acid Blue 183 | Cibalan Brilliant Blue GL |
| Acid Brown 19 | Cibalan Brown BL |
| Acid Black 107 | Cibalan Black BGL |

The basic dyes also are well-known in the art being characterized as salts of colored organic cations with simple anions which are usually inorganic in nature. Generally, such dyes are devoid of sulphonic and carbocyclic acid groups and are instead characterized by the presence of an amino group or a quaternary ammonium structure in which the anion is derived from a strong acid such as chloride, bromide, sulphate or sulphonic acid. The anions of stronger acids generally yield more water soluble dyestuffs. The colored cations may, however, also be present as salts with weaker acids such as the anions of acetic acid, formic acid, lactic acid, etc.

As mentioned above, these basic dyes are well-known in the art and are commercially available. The following list is exemplary of some commercially available basic dyes:

| Commercial Name | Color Index No. |
|-------------------------------|-----------------|
| Astrazon Yellow 7GLL | Basic Yellow 21 |
| Sevron Brilliant Red 4G | Basic Red 14 |
| Sevron Blue 5G | Basic Blue 4 |
| Safraine A Conc. | Basic Red 2 |
| Maxilon Pink GA | Basic Red 13 |
| Sevron Brilliant Red D | Basic Red 19 |
| Rhodamine 6G DN | Basic Red 1 |
| Sevron Brilliant Red 3B | Basic Violet 15 |
| Auramine | Basic Yellow 2 |
| New Blue ND Conc. | Basic Blue 6 |
| Sevron Blue 2G | Basic Blue 22 |
| Victoria Green Small Crystals | Basic Green 4 |

The dyeing procedure is carried out in the usual manner whereby the material to be dyed is placed in the dye bath liquor at temperatures ranging from room temperature up to the boiling point and then maintained at a selected temperature until the dye bath is substantially exhausted. In general, higher temperatures result in an increased rate of dyeing although it has been found that satisfactory rates are obtained even at room temperature or lower.

The pH of the dye bath is not critical but it is preferred to maintain substantially neutral or slightly acidic conditions to avoid any possibility or tendency of the basic dyestuffs used in the dyeing procedure to precipitate. Acids such as acetic acid and boric acid are useful for this purpose, and it has been observed that the presence of boric acid in the bath increases the buildup of the dye on the fabric. Further, in addition to the acids, the dye solutions may also contain any of the conventional well-known additives such as softening agents, wetting agents, etc.

It should be understood, of course, that uniform application of the dyestuff is not required since it may, in some instances,

be more desirable to apply the dyestuff to limited portions of the article such as printing techniques. The nature of the application method and the extent of tinting and dyeing depend upon the particular results desired.

The following examples illustrate the procedure for dyeing solid materials which have been treated with a polymer. Unless otherwise indicated, all parts are by weight.

EXAMPLE A

The fabric treated with the acid polymer in Example 1 is dyed by placing the fabric in the washing machine containing about 42 liters of water at 140° F. and adding 100cc. of a basic dye solution containing 1.5 grams of Sevron Blue 5G, 25 grams of boric acid and 3 grams of wetting agent. The washing and rinsing cycle is completed and the fabric is tumbled dried. The fabric obtained in this manner is uniformly dyed blue.

EXAMPLE B

The procedure of Example A is repeated except that the dye solution contains 1 gram of Sevron Red 4G. A red fabric is obtained.

EXAMPLE C

The procedure of Example A is repeated except that the dye solution contains Auramine (yellow) in the amount of 1 gram. The fabric obtained in this manner is yellow.

EXAMPLE D

The fabric of Example 7 is dyed with an anionic dye (for example Xylene Light Yellow 2G) in an exhaustion procedure. The buildup of yellow dye is much greater than a fabric which has not been treated as in Example 7.

EXAMPLE E

The coated glass sphere of Example 8 is placed in a one-liter container half filled with water. A basic dye solution (10 cc.) comprising 0.01 gram of Sevron Blue 5G, 0.1 gram of acetic acid and a small amount of a commercial wetting agent is added to the container which is then shaken gently for 3-5 minutes. The sphere is removed and rinsed in tap water. A blue ball is obtained.

In addition to dyeing fabrics in washing machines, it is possible by the process of this invention to carry out the dyeing process at room temperature in smaller containers. For example, a sample of the fabric prepared in Example 1 is placed in a 1-quart jar about one-half full of tap water to which has been added 10 cc. of a basic dye solution comprising 0.015 gram of Safraine A, 0.1 gram of boric acid and a small amount of a wetting agent obtained by reacting 9.5 moles of ethylene oxide with 1 mole of phenol. The cap is placed on the jar which is shaken for approximately 1 to 2 minutes. The fabric is then removed from the jar and rinsed in tap water to remove excess dyestuff. The fabric prepared in this manner is a deep shade of red.

As mentioned previously, one of the unique characteristics of the dyed articles of this invention is the fugitivity of the dye under relatively mild conditions. It is observed that materials which have been treated with the polymer compositions and dyed in accordance with the process of this invention, for example, the products of Examples A-E, can be stripped of the color without damage to the material simply by subjecting the material to an aqueous detergent solution. It must be noted that the dye is not fugitive to water alone which allows these materials to be exposed to moisture and water without the loss of color.

The dye may be removed from a textile fabric such as those described in Examples A-D by a washing in the usual manner either in a washing machine or in some other suitable container where sufficient agitation can be obtained to provide contact between the detergent solution and the fabric. Thus, large amounts of dyed fabric can be stripped of the color by

washing in a home washing machine using a normal cycle at 130° F. and an amount of detergent recommended for the particular washing machine. Alternatively, smaller amounts of colored fabric may be stripped by placing the fabric in jars containing water and detergent and thereafter shaking the jar for about 5 to 15 minutes to effect the removal of the dye from the fabric. The fabric is then rinsed and dried, and this fabric can subsequently be repeatedly dyed and stripped in accordance with the procedure described above.

The detergents which are utilized in the detergent solutions of this invention may be any of the commercially available detergents and soaps. As will be expected, the rate of removal of the dye will depend upon the temperature of the detergent solution, the concentration of the detergent in the solution, and the extent of agitation. All of these conditions will be readily apparent to one skilled in the art. In some instances, it is desirable to increase the rate of removal of the dye by utilizing two or more detergent solutions in succession and replacing the first solution with a second solution after a shorter contact time, such as, for example, 1 to 2 minutes. In this manner, the colored fabrics are in contact with stronger detergent solutions for shorter periods of time resulting in an overall more rapid rate of removal.

One of the advantages of the process of this invention is that a fabric can be dyed with a particular color as desired, and subsequently dyed with a second color since the first color can be removed by washing in a detergent solution. For example, the blue fabric prepared in Example A is washed in a detergent solution to remove the blue color, rinsed and dried. This fabric is then subjected to a basic dye solution containing Seron Red 4G to produce a red fabric (which red color also is fugitive in a detergent solution).

Alternatively, it is possible to carry out the process of the invention on fabrics which have already been permanently dyed. In this way the color can be changed as desired by applying the polymer and particular dye on top of the permanently dyed fabric to give a new color which can be removed at will to leave the original color. This utility is best explained with an example. A fabric can be permanently dyed yellow when finished at the mill and converted to an article such as a dress, blouse, tablecloth, etc. When it is desired to change the color of the blouse, for example, the yellow blouse is treated with an acid polymer followed by application of a basic dye such as Safraine A. This results in a red blouse. Later the article is washed in a detergent solution whereby the red dye is removed leaving a yellow blouse. In this manner, the consumer does not have to re-dye the blouse after every washing, but only when she wishes some color other than yellow.

The process of this invention provides a method for varying the color of fabrics by a simple technique readily adaptable to equipment available in every home once the polymeric composition has been applied to the fabric. The invention makes it possible for anyone to change the color of said fabrics easily and to any color desired. Unlike the presently known methods, the change is effected without the necessity of utilizing harsh chemicals which can be dangerous to the consumer as well as the fabric. The process of this invention is completely harmless to the consumer and to the fibers of the fabric being treated. Additionally, the invention provides a method whereby the fabric can be treated with the polymer converted to a garment, doll clothes or other article such as table cloths, draperies, etc. having a specified size, shape and design, which

article can thereafter be repeatedly dyed a variety of colors provided that each color is removed by washing in a detergent solution before the next color is applied. Of course, it is possible to place a second dye over the first dye, or to use a combination of dyes. In this instance, the predictability of color obtained is reduced, but the fugitivity is not affected.

That which is claimed is:

1. A process for repeatedly changing the color of solid materials comprising:

- a. coating the material with an acidic or basic polymeric composition,
- b. contacting the acidic or basic polymer-coated material with a basic or acidic dye, respectively, which has a higher affinity for the polymeric coating than the material whereby the dye is temporarily fixed on the polymeric coating by forming a complex which can dissociate in a detergent solution,
- c. removing the dye from the polymeric coating by washing the coated material in a detergent solution, and
- d. subjecting the washed polymer-coated material to a second dye which has a greater affinity for the polymeric coating than the material.

2. The process of claim 1 wherein the polymeric composition is a basic polymer and the dyes are acid dyes.

3. The process of claim 1 wherein the polymeric composition is an acid polymer and the dyes are basic dyes.

4. The process of claim 3 wherein the acid is a synthetic acid polymer comprising at least 10 weight percent acid calculated as acrylic acid.

5. The process of claim 1 wherein the solid material is a textile fabric.

6. The process of claim 5 wherein the fabric comprises a blend of cellulosic and synthetic fibers.

7. The process of claim 6 wherein the synthetic fibers are polyester fibers.

8. The process of claim 4 wherein the acid polymer is prepared from a monomeric mixture comprising an acrylic ester and an acrylic acid.

9. The process of claim 8 wherein the monomeric mixture comprises from about 10 to 80 parts of ethyl acrylate and about 20 to 90 parts of acrylic acid.

10. The process of claim 3 wherein the acid polymeric composition also contains an aminoplast textile resin and a textile resin catalyst, and the coated material is subjected to textile resin curing conditions before dyeing.

11. The process as defined in claim 1 wherein said solid material comprises a fabric and wherein said fabric is coated with a synthetic acid polymer comprising at least 10 weight percent acid calculated as acrylic acid, the fabric is converted into a desired article, and thereafter, the coated fabric is contacted with a basic dye having a greater affinity for the polymeric composition than the fabric.

12. The process of claim 11 wherein the fabric comprises a blend of cotton and polyester fibers.

13. The process of claim 11 wherein the fabric initially is treated with an aminoplast textile resin and a textile resin catalyst prior to the application of the acid polymer, and the fabric is subjected to textile resin curing conditions after application of the acid polymer or after formation of the article of wearing apparel.

14. The process of claim 13 wherein the textile resin is an acrylamide or an ethylene urea.

* * * * *

65

70

75