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PROCESS FOR COLORING GLASS FABRICS

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This invention relates to the coloring or dyeing of fabrics having different surface structure or characteristics to obtain different tone effects.

Among the fabrics which may be dyed by the present invention are glass fiber fabrics, particularly those woven from glass yarns of lime-alumina-borosilicate relatively alkali free; fabrics made from cellulosic fibers, including cotton, rayon, cellulose acetate, and other cellulosic fibers; wool; silk; synthetic fabrics such as those prepared from acrylic (e.g. Orlon, Creslan, Acrilan, Varel, Zefran, Darvan and Dynel), polyester (e.g., ethylene glycol-terephthalic acid condensation polymers such as Dacron), polyamide (nylon), vinyl and vinylidene (e.g., Saran) fibers, polyethylene and polypropylene; and blends of two or more of any of the fibers enumerated above.

Fabrics of different surface structure or characteristics may be produced by any known procedure. For example, the fabrics may be woven from textured, nubbed, loop, knot, slub, bulked, bouclés, taslan, or filament-type yarns to produce loosely woven areas and tightly woven areas. The fabrics may be woven to produce a base having throws or loops thereon and thus provide two different surface structures or characteristics, one the base, and the other the throws or loops thereon. Fabrics may be woven in a conventional manner to provide a uniformly woven fabric and then napped to produce different surface characteristics. For example, a cotton fabric (100% cotton) or one woven from a blend of cotton and other fibers, after de-sizing, washing, bleaching and drying, as customary, is padded through a conventional softening bath, dried, printed in selected areas with a resin-resist formulation (e.g., 34% vinyl-acrylic copolymer, 5% melamine-formaldehyde resin, 32% sodium alginate containing 4% solids, 2% amine-hydrochloride catalyst, and the rest water), which formulation, if desired, contains dyes or pigments. Other areas are then printed with printing pastes containing dyes or pigments, but no resist, and still other areas, if desired, are left unprinted. The thus treated fabric is then passed through a flat calendar at 120° F. and loop cured for three minutes at about 320° F. It is thereafter napped by passage through a napping machine of any conventional type. The areas which were resist-printed remain flat and unaltered; the remaining areas are napped to produce a three-dimensional raised pattern thus forming a fabric having different surface structures or characteristics, one of which is the napped areas and the other the resist-printed areas.

Still another example of fabrics having different surface characteristics are flocked fabrics in which the flocking is applied to produce design or pattern effects. In such fabrics, the unflocked base fabric has one surface characteristic and the flocked areas another surface characteristic provided by the flocking.

This invention is particularly concerned with the dyeing of glass fiber fabrics. Heretofore, to produce glass fiber fabrics having dyed pattern effects, bulked yarns have been pre-dyed in two or more colors and woven in the desired pattern. This requires several time-consuming operations including the steps of pre-dyeing the yarn, weaving and finishing the pre-dyed yarn. These operations require the production of different batches of selected dyed yarns for each fabric pattern or style, which unnecessarily complicates the weave mill operations with consequent increased cost of producing the finished fabrics.

It is among the objects of the present invention to provide a process for selectively coloring or dyeing fabrics having different surface structures or characteristics to produce different tonal effects without the complications and consequent additional expenses, inherent in pre-dyeing the yarn, weaving and finishing the pre-dyed yarn.

A further object of the invention is to provide such a process for dyeing fabrics woven from textured, bulked, bouclé, taslan or filament type yarns, including glass fiber yarns, which process produces fabric pattern effects by selectively dyeing certain areas of the fabric, namely, the loosely constructed or float areas in preference to the more tightly constructed areas, usually the background areas thereof.

Still another object of this invention is to provide a process for dyeing fabrics having different surface characteristics involving the utilization of one and the same dye bath to produce different color effects on these fabrics, for example, to dye the base, background, or tightly woven areas one color while dyeing the float, throw, loop, or other areas of different surface characteristics a different color.

Other objects and advantages of the present invention will be obvious from the following detailed description thereof.

The process of this invention involves mixing a cationic flocculating agent with a dispersion of a pigment to produce a dispersion containing flocculated pigment particles and treating a fabric having different surface characteristics with this dispersion. This treatment results in the flocculated pigment particles dyeing the loosely constructed, float, raised or bulked areas of the fabric in preference to or to the exclusion of the areas of the fabric having different surface characteristics, e.g., the tightly constructed or background areas.

The dyeing bath used in the practice of the process of this invention comprises a dispersion of a pigment, including all or a substantial proportion of the pigment particles in agglomerated or flocculated form due to the addition of the cationic flocculating agent.

While anionic pigment dispersions are preferred, any pigment which can be charged anionically, can be used. Thus dry powdered pigments which can be charged anionically may be employed. In the presence of an anionic binder in the dye bath employed with such pigments, the pigments acquire an anionic charge and agglomerate upon addition of the cationic flocculating agent. In general, the pigment particles should have a particle size (the largest dimension of the individual particles) within the range of from 0.007 to 40 microns. In the case of oxide pigments the particle size is usually within the range of from 0.2 to 15 microns. The concentration of the pigments in the dye bath should be from 0.02 to 5%, preferably 0.05 to 4% by weight based upon the total weight of the bath.

Pigments useful in the practice of this invention are the inorganic pigments, chiefly the oxides, sulfites and sulfates of cobalt, chromium, aluminum, iron, zinc, cadmium, manganese, and selenium and organic pigments such as the phthalocyanine dyes; anthraquinone, thioindigoid, and indanthren vat dyes; azo coupling dyes; Hansa yellow and carbon black.

Examples of such pigments are given in Table I which follows:

TABLE I

Trade name:	Classification
Interchemical Corporation's—	
Padding Brown 9500–21	Indanthren Vat type.
Padding Brown R 9550–1	Iron Oxide Red.
Padding Yellow N 9851	Indanthren Vat type.
Padding Yellow K 9850	Iron Oxide Yellow.
Padding Green B 9450	Phthalocyanine.
Padding Violet 4B 9652	Indanthren Vat type.
Padding Red FG 9352	Indanthren Vat type.
Padding Orange 2R 9800–16	Molybdate Orange type.
Padding Chartreuse 9852	Lithosol Fast Yellow 3DB.
Padding Grey 2K 9250	Carbon Black.
Padding Blue 2G 9750	Phthalocyanine.
Kentucky Color & Chemical Company's—	
Cadmium Selenide Red WDP 10–73K	Cadmium Red.
Red Oxide WDP 10–9951	Iron Oxide Red.
Cadmium Yellow Lemon WDP 20–1575	Cadmium Yellow.
Yellow Iron Oxide WDP 20–8871	Iron Oxide Yellow.
Chromium Oxide WDP 30–9906	Chromium Oxide Green.
Phthalocyanine Green WDP 30–3820	Phthalocyanine.
Burnt Umber WDP 50–0525	Iron Oxide Brown.
Phthalocyanine Blue WDP 41–4852	Phthalocyanine.
du Pont's—	
Ponsol Yellow AR dbl paste	Anthraquinone Vat type.
Arnold Hoffman Company's—	
Ahcovat Olive T paste	Anthraquinone Vat type.
Ahcovat Jade Green B	Anthraquinone Vat type.
Ahcovat Olive Green BL	Anthraquinone Vat type.
Ciba's—	
Cibanone Brown 3B	Anthraquinone Vat type.
Cibanone Black DRB	Anthraquinone Vat type.
Microfix Golden Yellow G	Anthraquinone Vat type.
American Aniline's—	
Amanthrene Dark Brown BW	Indanthrene Vat type.
Putnam's—	
Lumatex Brilliant Orange G	Anthraquinone Vat.
Lumatex Dark Brown T	Iron Oxide.
Lumatex Brilliant Yellow	Azo-coupling.
Lumatex Scarlet B	Azo-coupling.
Lumatex Yellow Brown G	Iron Oxide.
Sandoz'—	
Graphtol Blue 6806–2	Phthalocyanine.
Graphtol Yellow 4882–2	Hansa Yellow.
Graphtol Black	Carbon Black.
Graphtol Brown G	Thioindigoid Vat.

The oxides, sulfites and sulfates of cobalt, chromium, aluminum, iron, zinc, cadmium, manganese and selenium sold by B. F. Drakenfeld Company, for example, the products sold by them under their trade names:

Egyptian Blue 10012
Yellow Brown 10017
Deep Yellow 10058
Turquoise 10119
Deep Brown 10184
Burgandy 10176

The preferred cationic flocculating agent employed in the dyeing bath is deacetylated chitin (polymeric acetamino carbohydrate), which is preferably employed in dilute acidic aqueous solution. This material may be obtained by heating crude chitin successively with soda ash and hydrochloric acid to remove the lime salts and adherent protein followed by digesting the sodium hydroxide or other alkali at an elevated temperature under conditions excluding oxidation, to produce deacetylated chitin. The deacetylated chitin thus produced is reacted with aqueous acetic acid, producing the water-soluble acetic acid salt. While it is preferred to use the acetic acid salt, other salts may be used such as, for example, those formed by reacting the purified deacetylated chitin with formic, pyruvic, or lactic acid. For a more detailed description of the production of such acid salts of deacetylated chitin, reference may be had to United States Patents 2,040,879 and 2,040,880, granted May 19, 1936.

Other cationic flocculating agents may be used, however, including for example, polyalkyl-polyamines (Sandofix WE sold by Sandoz, Inc.); polyalkyl-polyamine fatty acid reaction products (Ceranine HC(A) sold by Sandoz, Inc.); amino aldehyde condensate dye-fixatives (Lyofix EW, sold by Ciba); methylchloride quaternary of the stearic acid amide of 1-(2-aminoethyl) 2-heptadecenyl-2-imidazoline (Nalco D–1535 sold by Nalco Chemical Company); fluid oil in water type emulsions of low molecular weight polyethylene chemically stabilized with a cationic amine acetate derivative of a long chain fatty compound (Moropol A–164); dicyandiamide formaldehyde dye fixatives (Umefix F sold by Valchem); and colloidal cationic thermo-setting resinous reaction products of straight chain poly-functional amines and an aldehyde such, for example, as urea formaldehyde resins modified with (*a*) polyamines including ethylenediamine, diethylenetriamine, tetraethylenepentamine, guanidine, phenylbiguanidine, or bisguanidine, (*b*) hydroxylamines such as monoethanolamine or diethanolamine; (*c*) cyanoamines such as dicyandiamide, polyphenylbiguanide or polyphenyl methyl biguanide, (*d*) aminoamides such as guanidine, or (*e*) quaternary ammonium salts such as tetraethanol ammonium chloride, and methylated dimethyl aniline quaternary ammonium salts; and the reaction products of these resin-modifying agents with formaldehyde, in the absence of urea, such as tetraethylenepentamine-formaldehyde, bisbiguanidine-formaldehyde, polyphenolbiguanide-formaldehyde and guanylurea-formaldehyde.

The cationic flocculating agent is included in the bath in concentrations of from 0.005 to 5% based on the weight of the bath, preferably from 0.05 to 1%. The Lyofix EW may be used alone in amounts of 0.1% to 2% of the bath or with the addition of small amounts of the deacetylated chitin, particularly when dyeing the loose float areas of an all-filament yarn glass fabric. The use of Lyofix EW results in relatively small agglomerates of the pigment, particularly desirable in dyeing all-filament yarn fabrics. Upon the agglomeration of the dispersed pigment, or pigment and finish constituents present, agglomerates or flocculated particles having an average particle size of from about 10 microns to 2,000 microns result. The particle size of the agglomerates seldom exceeds about ⅛ of an inch.

The concentration of the cationic flocculating agent within the range hereinabove given depends chiefly upon the specific pigments employed in the dyeing bath, the rate of addition of the flocculating agent to the bath, the amount thereof added, the other constituents, if any, and the concentration thereof present in the dyeing bath, the bath temperature, the pH of the bath, the type of fabric dyed, and the degree of flocculation desired. While it is preferred to operate at atmospheric temperature conditions (65–105° F.), the temperature of the bath may be within the range of 35–200° F., or even higher, but below the boiling point of the lowest boiling constituent of the bath, usually the liquid.

The pH of the bath, produced by mixing the pigment, water, or other liquid and other additives and before the addition of the agglomerating agent, is within the range of 9 to 10.5. Should the pH fall below 9.5, ammonia is added to bring the pH within this range. Upon addition of Kylan or other acid agglomerating agent to a portion of this bath, say 20 to 40% by volume, the pH of this portion is usually within the range of 4.5 to 7.5. The pH of this portion, thus produced, is not critical. Upon remixing this portion with the remainder of the volume, a bath results having a pH of from 5 to 10.5. It is preferred to operate with an alkaline bath because the agglomerate dispersions are more stable under these pH conditions. On the acid side, the dispersion of agglomerates are relatively unstable; the greater the acidity the more unstable the agglomerate dispersion. Baths having a pH above 5.5 have been found satisfactory but, as noted, it is pre-

ferred to have the pH of the bath above 7. Ammonia is added for this purpose, if found necessary, to adjust the pH of the bath.

The optimum amount of cationic flocculating agent incorporated in the bath, desirably, is determined by adding predetermined amounts of the agent to be used to the dispersion of the pigment, applying the resultant dispersion by padding on a small sample of the fabric to be colored, and determining which concentration gives the desired shade.

The bath contains, in addition to the pigment and flocculating agent, a resinous film-forming binder for bonding the pigments to the fibers of the fabric to form fast colors. Any non-ionic or anionic film-forming material capable of dispersing in the liquid medium of the bath and providing an adherent pigment coating is employed. Examples of such binder resins include butadiene-acrylonitrile copolymers, such as Chemigum 248; polyethyl acrylate, Hycar 4501 (a product of the B. F. Goodrich Chemical Company); butadiene-styrene resins (Dow Latex 762–W); dimethylol ethylene urea resins, Umac EU (a product of Valchem); dimethylol triazone resins, Stanset 125 (a product of Standard Chemical Products Co.); polyvinyl chloride; polyvinyl acetate; polyvinyl alcohol; melamine-formaldehyde resins; acrylic resins, such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, ethyl methacrylate and copolymers of these acrylates and methacrylates including, for example, the acrylic acid ester polymers, copolymers sold by Rohm & Haas Company under their trade names Rhoplex FRN, WN–75, and Rhoplex AC–33; and water-insoluble linear copolymers, or salts thereof, of monoethylenically unsaturated monomeric units comprising 0.5 to 10 percent by weight of units containing carboxyl groups; the preferred salts are the ammonium salts, or salts of the water-soluble amines, such as methylamine, diethylamine, triethylamine, mono-, di-, or triethanolamine, morpholine, etc. (Rhoplex B-15). When dry pigment capable of being charged anionically is employed, the binder resin should be an anionic resin which will in effect impart an anionic charge to the pigment and result in the formation of agglomerates containing the pigment or pigments and binder resin. The amount of binder resin incorporated in the bath is from 0.25 to 5%, preferably from 0.5 to 2% by weight based on the weight of the bath.

In addition to the pigment, cationic flocculating agent and binder resin, the bath may contain conventional materials depending upon the fabric dyed, such as softeners, delustering agents, abrasive resistant agents, and agents to impart the desired finish. For example, when dyeing glass fiber fabrics, the bath may contain a dispersion of colloidal silica in amounts ranging from 0.3 to 4%, preferably from 0.6 to 2% solids present, based on the weight of the bath, to impart a non-slip and delustering finish to the fabric. It may also contain from 0.5 to 5% solids based upon the weight of the bath of an abrasion resistant additive, such as polytetrafluoroethylene (Teflon).

While passing the fabric through the bath, the latter is maintained in a state of agitation by any suitable means, for example, a suitable mechanical agitator, or by bubbling an inert gas through the bath. Such agitation maintains the pigment particles, including the agglomerates, dispersed throughout the bath.

While aqueous dye baths are preferred, the invention includes dye baths of other liquid media in which the pigment may be dispersed and which media, for all practical purposes, are chemically inert to the fabric being dyed and to the other constituents of the dye bath, including the cationic flocculating agent and the resin binder. Methanol, ethanol, isopropyl alcohol, and acetone are suitable media.

The constituents of the bath are mixed at any suitable temperature below the boiling point of the liquid constituents, below 212° F. in the case of aqueous baths, preferably at about room temperature.

A typical dyeing bath for glass fiber fabrics contains as solids from 0.02 to 5% pigment, from 0.005 to 5% cationic flocculating agent, from 0.25 to 5% of resin binder, from 0.03 to 3% non-slip agent, and from 0.5 to 5% abrasion resistant additive. The rest of the bath is water, i.e., the water content of the bath is from 77% to 99.195%.

A typical dyeing bath for other fabrics, including the synthetic fabrics, contains from 0.25 to 5% resinous binder, from 0.02 to 5% pigment, and from 0.005 to 5% cationic flocculating agent; the rest of the bath is water, but may be methanol, ethanol, isopropyl alcohol, or acetone. Thus the liquid content of the bath is from 85% to 99.725% by weight.

In producing the dyeing baths for the practice of the process of this invention, only a portion of the dispersed anionically charged pigments and finish constituents, if present, need be flocculated by the flocculating agent, leaving up to 50–90% of the pigment in the bath in finely dispersed non-agglomerated form. In such case, the flocculated or agglomerated pigment particles color chiefly or only the loosely constructed or float areas of the fabric, whereas the finely dispersed particles color the more tightly constructed or background areas of the fabric. By variation of the amount of the pigment agglomerated, and hence the concentration of the agglomerated pigment particles in the bath, different tonal effects are obtained. Similarly, by varying the concentration of the non-agglomerated pigment particles in the bath, different tonal background effects are obtained.

Alternatively, substantially all of the anionic pigment in a bath can be agglomerated or flocculated by the flocculating agent. The resultant bath functions to tone the loosely constructed fabric areas substantially to the exclusion of the more tightly woven portions thereof, leaving a substantially white background in the tightly woven areas to provide a sharply contrasting toned pattern when white fabrics are dyed; the original colored background is left undyed when colored fabrics are dyed by the process of this invention using such bath.

Still another procedure, according to the invention, involves adding to about 20–40%, preferably about 30%, of the total volume of dye bath, pigment particles for coloration of the relatively loosely constructed areas of the fabric, adding to this portion of the bath a cationic flocculating agent, then adding the remainder of the volume of the bath to the resulting mixture and introducing into the bath thus produced an additional finely dispersed pigment, if desired, of a different color from that employed initially. This finely dispersed pigment remains suspended in the bath in a non-agglomerated form. When the fabric is padded through this bath, multi-color effects are obtained, the agglomerated pigment particles dyeing essentially the relatively loosely constructed areas of the fabric and the dispersed non-agglomerated pigment particles dyeing the background or tightly constructed areas thereof.

The fabric on leaving the bath is passed through the padding or squeeze rollers, which squeezes out the dyeing liquor and causes it to flow over the fabric. During such flow the loosely constructed areas tend to trap the agglomerated pigment particles usually containing resin binder particles and other particles such as colloidal silica and abrasion resistant agent, if present, and cause the agglomerates to remain thereon while leaving the tightly constructed areas substantially free of the agglomerates. As the fabric passes through the padding rollers, the agglomerates are pressed into the loosely constructed areas and upon subsequent curing are bonded thereto. Employing a bath also containing non-agglomerated pigment particles, such particles adhere for the most part preferentially to the tightly constructed areas; while the

agglomerates are washed by the back-flow of liquid from such tightly constructed areas, the non-agglomerated colloidal pigment particles remain thereon. It will be understood that the above is offered as an explanation of why the present invention results in selective dyeing or two-tone dyeing and the invention is not to be limited to this explanation.

When treating long yardage, the agglomerated pigment in the bath is replenished from time to time, or continuously. Also a suspension of the non-agglomerated pigment particles may be added to the bath from time to time, or continuously, when coloring of the background area is desired to produce the desired shade or shades.

In the case of glass fiber fabrics, the average wet pick-up after leaving the squeeze rollers is 20 to 90% based on the weight of the fabric, depending upon the amount of textured, bouclé, filament, or other yarns of relatively loose construction in the fabric. In the case of cellulosic fabrics, particularly rayons, the average wet pickup after leaving the squeeze rollers is within the range of 60–75% based upon the weight of the fabric.

The fabric after leaving the squeeze rollers of the padder is passed through a drying or curing oven where it is subjected to temperatures of from 250 to 375° F. for from one to ten minutes. The longer times are used when heating at the lower temperatures or with high wet pickup fabrics and the shorter residence times when heating at the higher temperatures within this range.

If desired, when dyeing glass fiber fabrics, the fabrics are given a water-repellent treatment with a stearato-chromyl chloride or other Werner complex in which the acids group coordinated with the chromium atom has more than 10 carbon atoms, as described in United States Patents 2,273,040 and 2,356,161. The water-repellent is applied by passing the fabric through a bath containing from 0.2 to about 4 or 5% by weight chrome complex and then drying at 250–375° F. to set the water-repellent material on the fabric.

The following examples are given to illustrate specific embodiments of the dyeing process and bath of the invention. It will be appreciated that the invention is not limited to these examples.

Example I

A dyeing bath in amount of 48 gallons was prepared containing 3% colloidal silica (Syton DS added to the bath as a suspension of 30% of colloidal silica in water); 2% polytetrafluoroethylene (Teflon); 2½% polyethyl acrylate (Hycar 4501), the rest being water. The ingredients were mixed at 70° F. and the bath was then divided into two portions, one containing 30% of the bath by volume, and the other 70%. To the 30% portion was added 1 lb. of iron oxide yellow (Interchemical Corporation's Padding Yellow K–9850), and 0.84 lb. of phthalocyanine pigment (Interchemical Corporation's Padding Green B–9450) in the form of aqueous anionic pigment dispersions. The resultant mixture was stirred vigorously to disperse the pigment.

Six pounds of a 1% Kylan solution (containing the acetic acid salt of deacetylated chitin) were prepared by dissolving 0.06 lb. of Kylan flakes in 5.94 lbs. of 1% acetic acid. 5.6 lbs. of the Kylan solution was added slowly to the 30% bath portion; upon addition the pigment and finish (Teflon and Syton) particles agglomerated. The 30% bath portion thus produced was remixed with the 70% portion.

A glass fiber fabric comprising float areas of bulked yarn and background areas of filament yarn was passed through this bath at the rate of 39 feet per minute. The pickup was 32%. Thereafter the fabric was passed through a drying oven at 330° F. for a residence time of 2.3 minutes.

The fabric was dyed a brilliant mint green in the float portions; the background portions remained unstained white.

Example II

This example differs from Example I chiefly in that after the pigments and flocculating agent were added to the 30% volume, and the 30% and 70% volumes of the bath were combined, 0.99 lb. of indanthrene vat dye (Interchemical's Padded Yellow N-9851), and 2.82 lbs. of a second indanthrene vat dye (Interchemical's Padding Brown 9500–21) thoroughly mixed in a gallon of water were added to the dyeing bath.

A glass fiber fabric similar to that processed in Example I was dyed and finished in the same manner as the fabric in Example I. The float portions of the fabric were dyed a brilliant mint green and the background portions a champagne shade.

Example III

The bath in this example was made by adding 4 lbs. of metal oxide pigment (Drakenfeld's turquoise 10107) to 10 gallons of water. 2.4 lbs. of Nalco D–1535 was heated until the opaqueness disappeared and then slowly added to the pigment dispersion while stirring. The heating of the Nalco was for the purpose of dissolving lumps, the cold material could be added with the same results provided the mixture was stirred enough to eliminate lumps. Enough water was added to make a volume of 48 gallons thus obtaining a bath containing approximately 1% of agglomerated pigment. 1.6 lbs. of polyvinyl acetate emulsion was added to the bath.

An all-glass fiber fabric containing filament and bulked yarns was padded through this bath at a speed of 30 feet per minute; fabric wet pickup was 90%. The fabric was then dried at 320° F. with a residence time in the dryer of three minutes. It was then padded through a second bath containing 4% Syton and 3% Rhoplex HA–4 binder to impart to the fabric a deluster and crock and wash-fast finish. The fabric was then dried at 300° F. with a dwell time of three minutes in the dryer. The bulked yarns in the fabric were colored a bright turquoise and the filament yarns remained white.

Example IV

Into the 20% portion of a 48 gallon bath containing Hycar, Syton and Teflon, as in Example I, was dispersed 8 lbs. of phthalocyanine (Interchemical's Padding Green B–9450) and 0.12 lb. of carbon black (Interchemical's Padding Grey 2K–9250). To this dispersion was slowly added with agitation 1 lb. of Lyofix EW and 2 lbs. of a 1% Kylan solution. The resultant 20% bath portion was then combined with the remaining 80% by volume.

An all-filament glass fabric having raised float yarn was padded through this bath at a speed of 39 feet per minute with a wet pickup of 25%. The fabric was dried at 330° F. with a residence time of 2.3 minutes in the dryer. Fabric having a brilliant green tipped effect on the raised float yarns and a faint neutral green tint on the background portions resulted.

Example V

The bath in this example contained 1% yellow iron oxide in 10% water, 1% Kylan solution, 0.5% melamine formaldehyde resin, and about 87.5% methanol. The bath was produced by placing the dispersion of the dye in water in a container, adding the methanol and the Kylan, mixing until agglomerates resulted, and then adding the melamine resin to the resultant bath.

Upon padding an all-glass fiber fabric having bulked yarn through this dye bath and curing the fabric as in Example I, a two-tone fabric resulted having the bulked yarns colored a bright yellow and the background areas an off-white shade.

Upon repetition of this example, substituting a dye dispersion in methanol for the water in which the dye had been dispersed, and thus employing a bath substantially free of water, the contrast in color was appreciably more marked. The use of ethanol, and iso-

propyl alcohol instead of the methanol gives comparable results.

Example VI

This example involved the use of dry powder pigments instead of dispersions, as in the preceding examples.

Cobalt blue was pasted in water and the resultant paste dispersed in 20% of the total volume of the bath.

4 ml. of a 1% solution of Kylan was then added. The remaining 80% by volume of the bath was then mixed with the 20%, the former containing 2% Hycar–4501. Upon producing the bath in this manner, satisfactory agglomerates of the pigment resulted as evidenced by the dyeing of a glass fiber fabric having bulked yarns in this bath by passage therethrough and after treatment, as in Example I; the dyed fabric had a light blue shade in the bulked yarn areas while the background areas remained white having only a slight tint.

Example VII

Into 20% of a 48 gallon bath was added 0.8 lb. of Hycar, 1.6 lbs. of Syton, and 4 lbs. of indanthrene vat dye (Interchemical's Padding Yellow N–9851) and the mixture stirred to disperse the dye particles. To this dispersion was added 9.82 lbs. of a 1% Kylan solution prepared as in Example I. The remaining 80% of the water content of the bath was then added and 8 lbs. of Moropol ARF resin binder introduced into the bath.

A synthetic fabric consisting of 100% spun rayon having floats was padded through this bath at a speed of 15 yards per minute, with a wet pickup after leaving the padding rolls of 73% by weight. The fabric was dried at 330° F. with a residence time of two minutes in the dryer. The float areas of the fabric were colored a golden yellow and the background portions a much lighter shade of yellow.

It will be noted that the present invention provides a process and dyeing bath for selectively dyeing fabrics having different surface structures or characteristics, simply and economically, and for producing desired tonal effects. The invention is particularly useful in dyeing bulked, bouclé, or filament glass fiber fabrics producing contrasting shades or tones on the bulked or loosely constructed areas as compared with those in the tightly constructed, usually the background areas.

Heretofore to produce multi-colored glass fiber fabrics, it was necessary to use pre-dyed fibers dyed with colorants able to withstand temperatures of 1200° to 1300° F. The present invention can be practiced with pigments or anionic pigment dispersions having melting or decomposition points above the temperature of the drying or curing, which temperature depends upon the residence time in the curing or drying zone and may be as low as 200° F. and in general is from 300 to 400° F. Thus the present invention permits of a much greater choice of pigments to produce a vastly larger range of shades and colors.

All percentages employed in this specification, unless otherwise specified, are given on a weight basis.

Since different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for coloring glass fiber fabrics having relatively tightly and loosely constructed surfaces, which comprises forming a padding bath containing at least 77% by weight of liquid, from 0.005% to 5% by weight of a cationic flocculating agent from the group consisting of deacetylated chitin; polyalkyl-polyamines; polyalkyl-polyamine fatty acid reaction products; amino aldehyde condensate dye-fixatives; methylchloride quaternary of the stearic acid amide of 1-(2-aminoethyl) 2-heptadecenyl-2-imidazoline; fluid oil in water type emulsions of low molecular weight polyethylene chemically stabilized with a cationic amine acetate derivative of a long chain fatty compound; dicyandiamine formaldehyde dye fixatives; colloidal cationic thermo-setting resinous reaction products of straight chain poly-functional amines and an aldehyde; and a mixture of such agents, from 0.02% to 5% by weight of anionic pigment particles and binder for said pigment particles, the amount of said cationic flocculating agent within said range being sufficient to effect the flocculation of at least a substantial proportion of said pigment particles, maintaining the solid constituents of said bath including the flocculated pigment particles suspended and uniformly dispersed throughout said bath, padding the glass fiber fabric through said bath to deposit the flocculated pigment particles preferentially on the loosely constructed surfaces leaving the tightly constructed surfaces substantially free of said flocculated pigment particles, and thereafter heating the fabric to cause the binder to bond the flocculated pigment particles to the loosely constructed surfaces to produce contrasting tonal effects on the respective tightly constructed and loosely constructed surfaces of said glass fiber fabric.

2. The process as defined in claim 1, in which the anionically charged pigment particles initially have a particle size of from 0.007 to 40 microns and upon flocculation produce agglomerates having an average particle size of from 10 to 2000 microns.

3. A process for coloring glass fiber fabrics having relatively tightly and loosely constructed surfaces, which comprises forming a padding bath containing at least 77% by weight of water, from 0.005% to 5% by weight of a cationic flocculating agent from the group consisting of deacetylated chitin; polyalkyl-polyamines; polyalkyl-polyamine fatty acid reaction products; amino aldehyde condensate dye-fixatives; methylchloride quaternary of the stearic acid amide of 1-(2-aminoethyl) 2-heptadecenyl-2-imidazoline; fluid oil in water type emulsions of low molecular weight polyethylene chemically stabilized with a cationic amine acetate derivative of a long chain fatty compound; dicyandiamine formaldehyde dye fixatives; colloidal cationic thermo-setting resinous reaction products of straight chain poly-functional amines and an aldehyde; and a mixture of such agents, from 0.02% to 5% by weight of anionic pigment particles, and from 0.25% to 5% by weight of resin binder, agitating said bath to effect the flocculation of at least a substantial portion of said pigment particles in said bath by the cationic flocculating agent and to maintain the flocculated pigment particles and resin binder suspended in and uniformly distributed throughout said bath, padding the glass fiber fabric through said bath thereby preferentially depositing on the loosely constructed surfaces flocculated pigment particles and resin binder with substantially no deposition of said flocculated pigment particles on the tightly constructed surfaces, and thereafter heating the fabric to effect the bonding of the flocculated pigment particles to the loosely constructed surfaces by the resin binder and thus producing contrasting tonal effects on the loosely and tightly constructed surfaces.

4. The process as defined in claim 3, in which the amounts of cationic flocculating agent and anionic pigment are proportioned so that substantially all of the pigment is flocculated by the cationic flocculating agent and only the loosely constructed surfaces are colored with said pigment.

5. The process as defined in claim 3, in which after the formation of said bath by mixing said cationic flocculating agent, aqueous dispersion of pigment particles, resin binder and water, a dispersion of a pigment of a different color than the first mentioned pigment having a particle size smaller than that of the flocculated pigment particles is added to the bath and upon padding the fabric through said bath the flocculated pigment par-

ticles are deposited on the loosely constructed surfaces and the said pigment of different color is deposited on the tightly constructed surfaces.

6. A process for coloring glass fiber fabrics woven to provide tightly and loosely constructed surfaces, which process comprises, producing a padding bath containing from 0.05% to 5% by weight of a cationic flocculating agent from the group consisting of deacetylated chitin; polyalkyl-polyamines; polyalkyl-polyamine fatty acid reaction products; amino aldehyde condensate dye-fixatives; methylchloride quaternary of the stearic acid amide of 1-(2-aminoethyl) 2-heptadecenyl-2-imidazoline; fluid oil in water type emulsions of low molecular weight polyethylene chemically stabilized with a cationic amine acetate derivative of a long chain fatty compound; dicyandiamide formaldehyde dye fixatives; colloidal cationic thermo-setting resinous reaction products of straight chain poly-functional amines and an aldehyde; and a mixture of such agents, from 0.02% to 5% by weight of anionic pigment particles, from 0.25% to 5% of a binder resin and at least 85% by weight of water, in which bath at least a substantial proportion of the anionic pigment is in an agglomerated condition, agitating said bath to maintain the agglomerated pigment particles in suspension and dispersed uniformly throughout said bath, padding said glass fiber fabric through said bath to deposit preferentially on the loosely constructed surfaces the agglomerates of said pigment particles and resin binder, and thereafter heating the fabric to a temperature to cause the resin binder to bond the agglomerated pigment particles to the loosely constructed surfaces, thus coloring the loosely constructed surfaces preferentially to the tightly constructed surfaces.

7. The process as defined in claim 6, in which an aqueous dispersion of a second pigment having a different color from that of the first mentioned pigment is added to the bath and dispersed therein, upon padding the glass fiber fabric through the resultant bath the loosely constructed surfaces have deposited thereon the said agglomerates of the pigment particles admixed with resin binder and the tightly constructed surfaces have deposited thereon the second mentioned pigment admixed with resin binder, and upon heating the thus treated fabric the pigment agglomerates are bonded to the loosely constructed surfaces and the second mentioned pigment to the tightly constructed surfaces.

8. The process as defined in claim 6, in which the bath also contains from .3% to 4% by weight of colloidal silica, from .5% to 5% by weight of polytetrafluoroethylene and the fabric after padding through said bath is heated to a temperature of from 200° to 400° F. for from 1 to 10 minutes.

9. A process for coloring glass fiber fabrics woven to provide tightly and loosely constructed surfaces, which process comprises, mixing with at least 77% by weight of water a dispersion of anionically charged pigment particles having a particle size of from 0.007 to 40 microns, a cationic flocculating agent from the group consisting of deacetylated chitin; polyalkyl-polyamines; polyalkyl-polyamine fatty acid reaction products; amino aldehyde condensate dye-fixatives; methylchloride quaternary of the stearic acid amine of 1-(2-aminoethyl) 2-heptadecenyl-2-imidazoline; fluid oil in water type emulsions of low molecular weight polyethylene chemically stabilized with a cationic amine acetate derivative of a long chain fatty compound; dicyandiamide formaldehyde dye fixatives; colloidal cationic thermo-setting resinous reaction products of straight chain poly-functional amines and an aldehyde; and a mixture of such agents, and a resin binder to produce a padding bath containing from .02% to 5% by weight of said pigment particles in which at least a substantial proportion of said pigment particles is agglomerated and the agglomerates have an average particle size

of from 10 to 2000 microns, from .005% to 5% by weight of said cationic flocculating agent, from 0.25% to 5% by weight of said resin binder, and at least 77% by weight of water, agitating said padding bath to maintain said agglomerated pigment particles in suspension therein and uniformly dispersed therethroughout, padding the fabric through said bath thereby preferentially depositing on the loosely constructed surfaces flocculated pigment particles and resin binder with substantially no deposition of said flocculated pigment particles on the tightly constructed surfaces, and thereafter heating the fabric to effect the bonding of the flocculated pigment particles to the loosely constructed surfaces by the resin binder and thus producing contrasting tonal effects on the loosely and tightly constructed surfaces.

10. A process for coloring glass fiber fabrics woven to provide tightly and loosely constructed surfaces, which comprises, forming a padding bath by mixing with about 20% to 40% of the volume of said bath a dispersion of anionic pigment particles, a cationic flocculating agent from the group consisting of deacetylated chitin; polyalkyl-polyamines; polyalkyl-polyamine fatty acid reaction products; amino aldehyde condensate dye-fixatives; methylchloride quaternary of the stearic acid amide of 1-(2-aminoethyl) 2-heptadecenyl-2-imidazoline; fluid oil in water type emulsions of low molecular weight polyethylene chemically stabilized with a cationic amine acetate derivative of a long chain fatty compound; dicyandiamide formaldehyde dye fixatives; colloidal cationic thermo-setting resinous reaction products of straight chain poly-functional amines and an aldehyde; and a mixture of such agents, to produce a dispersion of agglomerates of said pigment particles in water, adding the dispersion of agglomerated pigment particles to the remaining 60% to 80% of the volume of said bath, incorporating in said bath a resin binder, then adding to said bath a dispersion of anionic pigment particles of a different color, the said pigments, cationic flocculating agent, water and binder being introduced into said bath in amounts to produce in the total bath, by weight, from .005% to 5% of said cationic flocculating agent, from .02 to 5% by weight of said pigments, from 0.25% to 5% by weight of said resin binder and at least 77% by weight of water, agitating said bath to maintain said flocculated pigment particles and the said pigment particles of different color suspended therein and uniformly dispersed throughout said bath, padding said glass fiber fabric through said bath to deposit the said pigment agglomerates and resin binder upon the loosely constructed surfaces and the said pigment particles of different color and resin binder upon the tightly constructed surfaces, and thereafter heating the fabric to cause the resin binder to bond the agglomerated pigment particles to the loosely constructed surfaces and the pigment particles of different color to the tightly constructed surfaces.

11. The process as defined in claim 10, in which the said padding bath contains from .05% to 1% by weight of said cationic flocculating agent, from .05% to 4% by weight of said pigment, from .05% to 2% by weight of resin binder, from 0.6% to 2% of colloidal silica, and from 0.5% to 5% polytetrafluoroethylene, the agglomerated particles have a particle size of from 10 to 2000 microns, and the pigment particles of a different color have a particle size of from 0.007 to 40 microns.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,108,897 October 29, 1963

William L. Hamiter et al.

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

Column 5, line 27, for "ethyl methacrylate" read -- ethyl ethacrylate --; line 43, for "pigments" read -- pigment --.

Signed and sealed this 14th day of April 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents