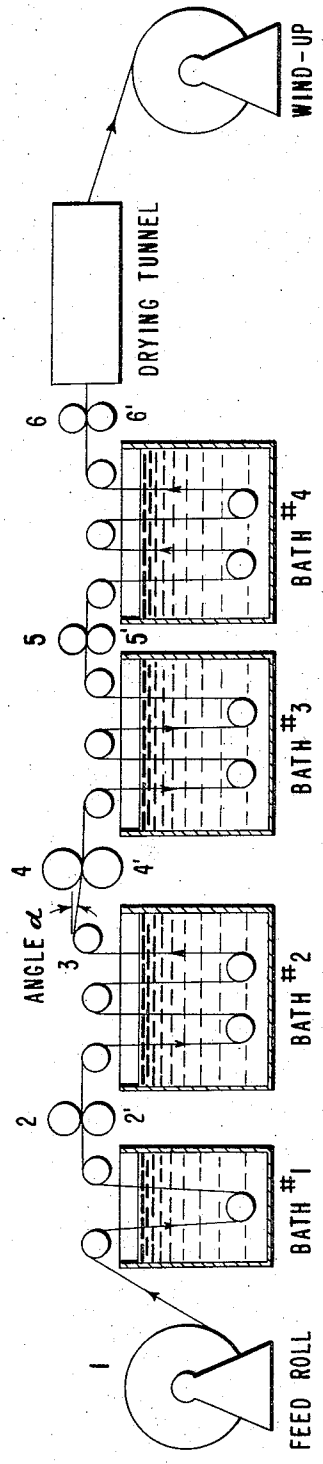
Aug. 22, 1967 W. F. MANWARING 3,337,289

PROCESS FOR DYEING MICROPOROUS SHEET MATERIAL

Filed Dec. 30, 1963



INVENTOR
WILLIAM F. MANWARING

BY Raymond E. Blomstedt

ATTORNEY

United States Patent Office 3,337,289 Patented Aug. 22, 1967

3,337,289

PROCESS FOR DYEING MICROPOROUS SHEET MATERIAL

William F. Manwaring, Cornwall, N.Y., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Filed Dec. 30, 1963, Ser. No. 334,423
4 Claims. (Cl. 8—4)

This invention relates to a process for dyeing microporous polyurethane sheet material and more particularly, to a process for dyeing microporous polyurethane sheet material with an acid or mordant dye and after-chroming the dyed material.

In the prior art, it has been the practice to color polyurethane materials by adding dyes or pigments to the polymer before it is foamed. This technique is not suitable for dyeing a microporous polyurethane sheet, which is primarily used as a leather replacement for shoe uppers, since only a limited number of colors can be obtained. This is of a particular disadvantage in the women's shoe industry in which a wide variety of colors are required and colors change from season to season.

Secondly, the prior art technique of adding color to the polymer does not lend itself to the continuous manufacturing of the microporous polyurethane sheet material. It is more economical to manufacture only one sheet material and then dye this material rather than to color the polymer, manufacture a quantity of material, and then change to another color of polymer. This prior art coloring technique becomes increasingly difficult and uneconomical when an impregnated non-woven web base, made in a separate operation, is utilized and the microporous polymeric topcoat is later applied. A process for dyeing the sheet after manufacture is much more desirable.

In dyeing materials such as wool, silk and nylon with acid and mordant dyes, after-chroming to increase color fastness is well known. But the dyes are usually applied by a batch process, such as Dyeback dyeing, in which large quantities of material are continuously rotated through a dye solution until the desired color is obtained. Then the material is after-chromed in a similar manner by rotating the material through a chroming solution. Batch processes are not as economical as a continuous process, but more important, these processes are not practical for relatively thick microporous thermoplastic material. To penetrate the thick web and the pores within the polymer, the sheet has to be contacted with the hot dye solution for a long period of time. Moreover, the heat of the dye solution along with the stresses placed on the sheet while it is rotated through the dye solution cause the surface of the polyurethane sheet material to deform, wrinkle, and crease, thereby giving an unsaleable product.

Pad dyeing, which is a continuous dyeing process, is well known for dyeing thin cloth material. However, pad dyeing is not used on thick heavy materials like carpets, pads and thick non-woven felts, nor are prior art padding processes useful in dyeing a microporous polyurethane sheet material since adequate dye penetration cannot be obtained in the time the material is in the dye solution. For heavy thick materials, the prior art teaches the use of batch processes, such as the Dyeback process or jig dyeing, so that the material can be kept in the dye solution until the desired color is obtained.

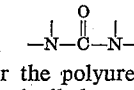
In a copending applictaion of J. A. Simms, U.S. Ser. No. 334,621, filed on Dec. 23, 1963, a process for dyeing a microporous polyurethane material after manufacture is described but only a particular group of dyes can be used to adequately color the microporous material. The dyes found useful in the process of the copending application are anionic water soluble dyes which have an equivalent weight of 200–600.

By the process of this invention thick microporous polyurethane sheet material can be dyed after manufacture. This invention allows for a wide selection of colors, is more economical than batch processes, and still more advantageously, this process dyes a microporous polyurethane sheet without deforming it. Therefore, the after-chroming of the colored sheet allows for the use of a wide variety of dyes and does not restrict the process to only a particular group of anionic water soluble dyes. After-chroming renders the dyes insoluble, makes the dyes color fast, and reduces water spotting caused by dye migration. Moreover, this invention overcomes the difficulty of inadequate dye penetration as experienced by the standard pad dyeing process by using additional treatment steps and by closely controlling process conditions, such as, time, temperature and solution concentration.

The dyeing process of this invention comprises treating a microporous polyurethane sheet material with water until the moisture content of the sheet is about 10–90% by weight, and immersing the wet sheet for about 20–120 seconds in an aqueous dye solution which contains about 0.002–3% by weight of either an acid or a mordant dye and is at a pH of about 1.5–11 and is at about 180-212° F. The dyed sheet is then squeezed which causes the dye to penetrate and give the sheet a uniformly colored surface. The dyed sheet is next immersed for about 1–4 minutes in an aqueous solution of a chromium compound. The solution contains about 0.1–5% by weight of the chromium compound and is at about 180–212° F. The dyed, after-chromed sheet is next washed in water at about 180–212° F. for about 2–20 minutes. The washed, after-chromed sheet is dried at approximately 200–300° F.

The steps of the preferred process are illustrated in FIGURE 1. A microporous polyurethane sheet 1 is unwound from a feed roll, dipped into Bath #1 containing hot water, passed between nip rollers 2 and 2′ to remove excess water, dyed in Bath #2, passed over turnroll 3 and into pressure controlled nip rollers 4 and 4′ at a downward angle α, immersed in Bath #3 containing an aqueous chroming solution, passed between nip rollers 5 and 5′, washed in Bath #4, passed between nip rollers 6 and 6 to remove excess water, dried and rewound.

The process for making a microporous polyurethane sheet material which can be dyed according to this invention is disclosed in U.S. Patent 3,100,721 to E. K. Holden. Polyurethanes either alone or int a mixture with other polymers, particularly vinyl chloride polymers, are useful in making the sheet material. One class of polyurethanes useful in this invention are polyureas, that is, polyurethanes containing the recurring structural unit:



The prepolymers for the polyurethanes are prepared by mixing one or more polyalkyleneether glycols or hydroxyl-terminated polyesters with a molar excess of organic diisocyanate and heating the mixture to a temperature of about 50–100° C. to form a prepolymer having terminal —NCO groups. An alternate procedure is to react the diisocyanate with a molar excess of polyalkyleneether glycol or polyester, then cap the resulting product, that is, react it with more diisocyanate to form a prepolymer having terminal —NCO groups.

The preferred polyurethanes are the chain extended polyurea type which are formed from aliphatic polyol segments which include the polyalkyleneether glycols having C_3–C_{12} alkylene segments and the hydroxyl-terminated polyester of C_3–C_{12} acyclic dicarboxyclic acid and C_3–C_{12} alkylene glycol. Polyalkyleneether glycols are the preferred active hydrogen containing material for the pre-

polymer formation. The most useful polyglycols have a molecular weight of 300 to 5000, preferably 400 to 2000; some of these polyglycols are, for example, polyethyleneether glycol, polypropyleneether glycol, polytetramethyleneether glycol, polyhexamethyleneether glycol, polyoctamethyleneether glycol, polynonamethyleneether glycol, polydecamethyleneether glycol, polydodecamethyleneether glycol and mixtures thereof. Polyglycols containing several different radicals in the molecular chain such as the compound $HO(CH_2OC_2H_4O)_nH$ wherein n is an integer greater than 1 can also be used.

The preferred polyurethanes are prepared with at least a major portion of an aromatic, aliphatic or cycloaliphatic diisocyanate or mixtures thereof; for example, tolylene-2,4 - diisocyanate, tolylene - 2,6 - diisocyanate, m - phenylene diisocyanate, biphenylene - 4,4' - diisocyanate, methylene bis-(4-phenyl isocyanate), 4-chloro-1,3-phenylene diisocyanate, naphthalene - 1,5 - diisocyanate, tetramethylene - 1,4 - diisocyanate, hexamethylene - 1,6 - diisocyanate, decamethylene - 1,10 - diisocyanate, cyclohexylene-1,4-diisocyanate, methylene bis-(4-cyclohexyl isocyanate) and tetrahydronaphthalene diisocyanate. Arylene diisocyanates in which the isocyanate groups are attached to an aromatic ring are preferred since these isocyanates react more readily than do alkylene diisocyanates.

Polyesters can be used instead of or in conjunction with the polyalkyleneether glycols, particularly those formed by reacting acids, esters or acid halides with glycols. Suitable glycols are polyalkylene glycols, such as methylene, ethylene, propylene, tetramethylene, decamethylene glycol; substituted polyalkylene glycols, such as 2,2-dimethyl-1,3-propanediol; cyclic glycols, such as cyclohexanediol and aromatic glycols, such as xylylene glycol. Aliphatic glycols are preferred when maximum product flexibility is desired and when making microporous articles. These glycols are reacted with aliphatic, cycloaliphatic or aromatic dicarboxylic acids or lower alkyl esters or ester forming derivatives to produce relatively low molecular weight polymers, preferably having a melting point of less than about 70° C., and molecular weights like those indicated for the polyalkyleneether glycols. Acids for preparing such polyesters are succinic, adipic, suberic, sebacic, terephthalic and hexahydroterephthalic acids and the alkyl and halogen substituted derivatives of the acids.

Hydrazine is preferred as the chain extending agent for the preferred polyurethanes, although C_1–C_6 (including cycloaliphatic) diamines, such as ethylene diamine, hexamethylene diamine and dimethyl piperazine and 1,4-diamino-piperazine can also be used advantageously either alone or in a mixture with hydrazine.

A particularly preferred chain extender that provides the microporous polyurethane product with improved dyeability, superior dye retention, and improved resistance to color fading and which can be reacted with the isocyanates terminated prepolymer has the structural formula

$$NH_2—R—\underset{\displaystyle R}{\underset{|}{N}}—R—NH_2$$

wherein R is an alkyl group containing 1–4 carbon atoms (i.e., a methyl, ethyl, propyl or butyl group). In the preferred compond, the R beneath the central N is methyl and the other two R's are propyl; thus, the preferred compound is N-methylamino-bis-propylamine.

This chain extender need not consist entirely of a compound having the formula shown above. It is usually best to use a blend of a minor proportion, preferably about 5–30 mole percent, of the above preferred chain extender with a major proportion, about 95–70 mole percent, of another compound having two active hydrogen atoms bonded to amino-nitrogen atoms, preferably hydrazine. Other chain-extending compounds which can be used along with the preferred compound are mono-substituted hydrazines, dimethyl-piperazine, 4-methyl-m-phenylene-diamine, m-phenylene-diamine, 4,4'-diamino-diphenyl-methane, 1,4-diamino-piperazine, ethylene diamine and mixtures thereof.

Polyurethane polymers made with more than about 5 mole percent of the preferred chain extender generally show the greatest improvement in dye retention and dyeability. More than about 20–30 mole percent of the preferred chain extender produces relatively little additional improvement in depth and retention of color and is usually not preferred for economic reasons. Best results are obtained with about 10–30 mole percent of the essential chain extender; a particularly preferred chain extender which gives excellent results comprises a mixture of about 80 mole percent hydrazine and 20 mole percent N-methyl-amino-bis-propylamine.

Mixtures of at least one vinyl polymer with a polyurethane can be used to prepare the microporous sheet material. Such mixtures, preferably containing polyvinyl chloride as the vinyl polymer, can contain from 1 to 2% of vinyl chloride polymer to about 50% thereof. Preferably such mixtures contain at least about 50% by weight of the polyurethane.

Microporous polyurethane sheet materials used as a leather replacement frequently contain a porous fibrous substrate to give the material the rigidity and strength required for this use. Such substrates are, for example, woven, twills, drills and ducks; jersey, tricot and knitted materials; felts, needle punched batts, porous batts impregnated with synthetic resins, such as styrene/butadiene, acrylic, vinyl halide, and polyurethane polymers. The choice of the particular fibers from which the substrate is made is not critical; they include those made from polyamides, polyesters, polyesteramides, acrylic polymers, viscous rayon, wool, cotton, glass and mixtures thereof. Elastomeric fibers and elastic fibers can also be used. Porous non-woven, needle punched, heat shrunk batts of polyethylene terephthalate fibers impregnated with the aforementioned polymers are particularly preferred. The preferred sheet material contains about 30–60% fiber by weight and about 70–40% of a microporous polyurethane polymer.

The difficulty in dyeing a thick sheet of a microporous polyurethane material and particularly a microporous polyurethane material adhered to an impregnated nonwoven web is in penetration of the coloring substance into the sheet. Adequate dye penetration is aided by the initial wetting of the sheet with hot water, by controlling the time, the dye concentration, temperature and acidity of the dye solution and also, by subsequently passing the sheet material through a set of nip rollers kept under a controlled pressure. The pass through the nip roller is extremely useful in forcing the dye to penetrate the center of the porous sheet material.

Following is a detailed discussion of each step in the process as shown in FIGURE 1.

The first step in the process consists of immersing the microporous polyurethane sheet material 1 in Bath #1 containing water. It is possible to dye a dry sheet of material without this initial wetting step; but in general a wetted sheet can be dyed more uniformly than a dry sheet. In many instances, however, the material is still wet from the manufacturing process and the water content within the sheet is uneven making this water pretreatment step necessary to equalize the water content throughout the sheet so that the material can be uniformly dyed. The temperature of the water is not critical, but warm water will penetrate the sheet at a more rapid rate than cold water. Water temperature should be above 160° F. and the preferred temperature is about 200–210° F.

The sheet is next passed between nip rollers 2 and 2' which squeeze the sheet uniformly and reduce the water content of the sheet to about 10–90% by weight with the preferred being about 30–50%. The water content of the sheet before it enters Bath #2, the dye bath, is not critical, but the moisture content throughout the sheet should be uniform to allow even penetration of the dye solution

which reduces color variation. A non-uniform water content within the sheet can cause spotting and streaking of the material.

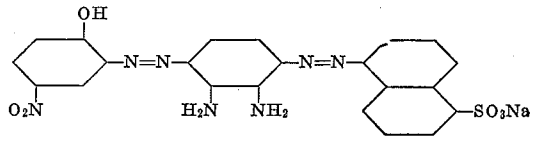
Many dyestuffs are affected by the hardness of water, therefore, it is important throughout the process to use softened water. Softening of the water can be accomplished by standard methods, such as passing the water through an ion exchange column or sequestration of the hardening agents.

After the water treatment, the sheet material is passed into the dye liquor. Dyes found useful in this process are of the acid and mordant type as classified by the Colour Index of the American Association of Textile Chemists and Colorists. The dyestuffs found particularly useful in this process are as follows:

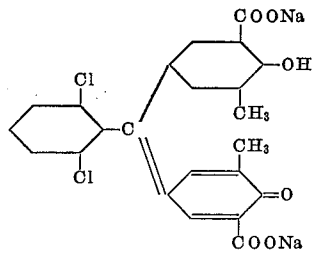
C.I. Mordant Brown 1
C.I. Mordant Brown 18
C.I. Mordant Brown 40
C.I. Mordant Blue 1
C.I. Mordant Blue 3
C.I. Acid Black 2
C.I. Acid Green 25
C.I. Acid Red 114
C.I. Acid Red 167
C.I. Acid Red 18
C.I. Mordant Black 9
C.I. Mordant Yellow 16

These dyes have the following structural formulas:

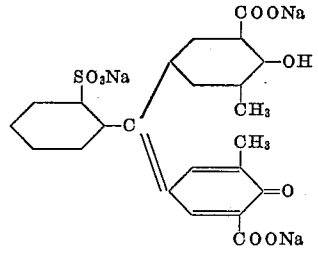
C.I. MORDANT BROWN 1



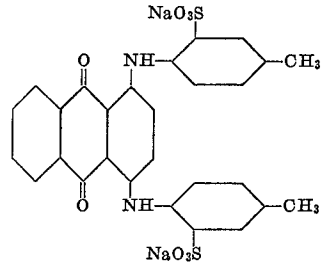
C.I. MORDANT BLUE 1



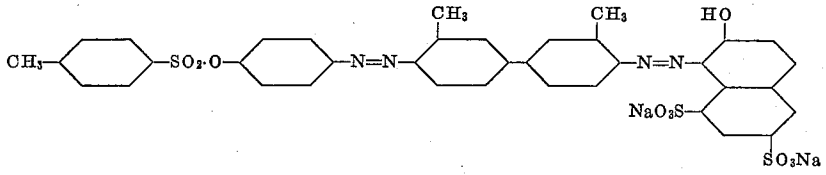
C.I. MORDANT BLUE 3



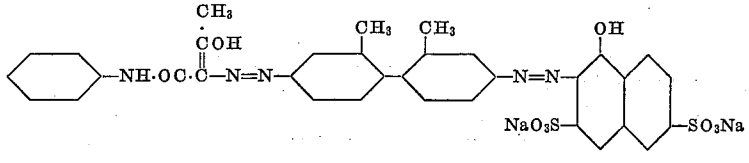
C.I. ACID GREEN 25



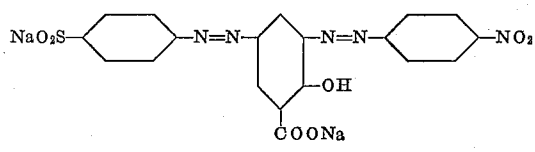
C.I. ACID RED 114



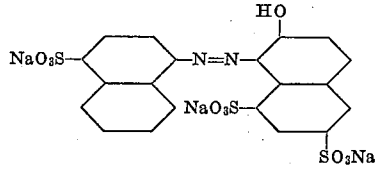
C.I. ACID RED 167



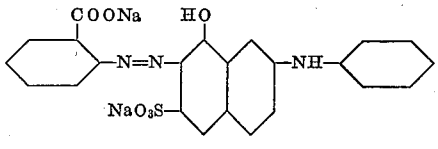
C.I. MORDANT BROWN 18



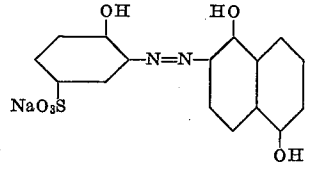
C.I. ACID RED 18



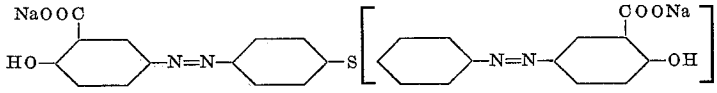
C.I. MORDANT BROWN 40



C.I. MORDANT BLACK 9



C.I. MORDANT YELLOW 16



C.I. ACID BLACK 2

Oxidation product of aniline and aniline hydrochloride witht nitrobenzene in the presence of ferric chloride reacted at 160–180° C.

At the time of this invention, the above dyestuffs gave the desired shade and tone of color used by the shoe industry. Any of the dyestuffs in the Colour Index grouping of acid and mordant dyes can be used in this process and this invention is not limited to the above list. However, some dyestuffs give a darker, deeper and richer shade than others in these groups, therefore, it is a matter of color choice as to which acid or mordant dyes are used.

The time the material is in the dye solution is from about 20–120 seconds. Less than 20 seconds usually results in inadequate dyeing of the sheet material, caused by inadequate penetration of the dye into the center of the sheet, and also the depth and the tone of the color are adversely affected. It is usually not desirable to use more than 120 seconds to dye the material because the process becomes uneconomical since either a slow speed of the material going through the bath would be required or an extremely large dye tank or several dye tanks would have to be used. Also, complete after-chroming of the dyed sheet requires about twice the time in the chroming solution as in the dye solution, i.e., 30 seconds in the dye solution requires about 60 seconds in the chroming solution.

The concentration of the dye in solution can be from 0.002–3% on a weight basis. Dye concentrations below 0.002% usually result in inadequate coloring of the material and dye solutions with concentrations over 3% generally give the product a muddy or mottled color. For efficient production, it is desirable to sustain a high dye concentration and pass the material through the dye solution at maximum speed, but each dyestuff has a different water solubility and, therefore, optimum operating concentrations for each dyestuff must be determined.

The temperature of the dye solution is about 180–212° F. It is preferable for efficient dye penetration and coloration to keep the temperature at about 200–210° F. If temperatures lower than 180° F. are used, the material is generally not adequately dyed because of lower dye concentrations caused by reduced dye solubility and also, because of reduced dye penetration into the sheet. Temperatures over 212° F. are not desirable since a pressure vessel is usually required to obtain these temperatures and would prove cumbersome in this process. Also, it is preferred to keep the temperature of the dye solution just below boiling at about 210° F., since this reduces losses of solution due to evaporation and boiling of the liquid out of the vessel.

The pH of the dye solution can be about 1.5–11; however, the pH is determined by the acidity or basicity of the dyestuff used. For optimium results, it is preferred to control the pH for most dyes between about 5.5–8. But, usually for wool dyeing operations need not be controlled at a preferred pH level and it is generally sufficient if it stays within pH 1.5–11 range. If a pH of below 1.5 is used, degradation of the base sheet material often occurs which shortens the life of the product by causing premature cracking of the microporous polyurethane topcoating and a breakdown in the polymeric impregnated substrate.

After dyeing, the material is passed between nip rollers **4** and **4'**. It is important, however, that the material is passed into the nip rollers at a downward angle. Angle α, as shown in FIGURE 1, should be about 5° downward or more from the horizontal. In the nip roller assembly, roller **4'** is permanently mounted and the roller **4** is movable and is attached to a device that controls the pressure applied to roller **4**. This subsequent squeezing operation is necessary since it forces the dye to penetrate the center portions of the sheet, and also gives the surface of the sheet an even and uniform color. To achieve these results, it is preferred to use rubber covered steel nip rollers, which are 10 inches in diameter and in which the rubber durometer value is about 75–80. The pressure applied to the roller is in the range of 50–125 pounds per lineal roll inch with the preferred range being about 75–100 pounds per lineal roll inch. Pressures lower than 75 pounds per lineal roll inch usually will not cause the dye to penetrate the sheets uniformly. Pressures higher than 125 pounds per lineal roll inch will generally cause removal of an excess amount of dye from the sheet, thereby lightening the color of the sheet and usually cause the microporous sheet to widen and reduce in thickness and have an adverse effect on the physical properties of the sheet.

Any means which can apply a constant pressure to the nip rollers can be used in this process. One practical and preferred method is to couple both ends of the axle of the movable roller **4** to separate air cylinders. This makes it possible to supply an even pressure across the web of material. The air cylinders are activated and deactivated by air under pressure supplied and controlled through a system of solenoid valves and switches. When the process is in operation, the solenoid valves are activated and the air supply depresses the piston in each cylinder which then actively engages the movable nip roller **4** with the sheet material. The roller is similarly disengaged by deactivating the solenoid and activating a second pair of solenoids which allows the air supply to raise the piston and disengage the roller.

It is desirable, but not absolutely necessary, throughout the process to use nip rollers which have a controlled pressure between 50–125 pounds per lineal inch. It is important, however, that nip rollers **2** and **2'**, used to press the sheet after the inital wetting step, nip rollers **5** and **5'** used after the chroming step and nip rollers **6** and **6'** used after the washing step, should not apply more than 125 pounds per lineal roll inch to the sheet material to prevent elongation in the transverse direction of the sheet.

After passing through nip rollers **4** and **4'**, the dyed sheet is next treated in Bath #3 containing an acidic aqueous solution containing a chromium compound. Chromium containing compounds such as chromic chloride, can be used but the preferred compounds are soduim dichromate or potassium dichromate because of their low cost. The concentration of chromium compound in the aqueous solution is about 0.1–5% by weight. The preferred after-chroming solution contains about 4 grams of sodium dichromate per liter of water and 2 grams acetic acid per liter of water.

The pH of the chroming solution should be about 3–7. A pH of about 3–5 is preferred for an efficient reaction when using a dichromate compound. Alkaline pH's reduce the dichromate ion's ability to react with the dye in the sheet material.

Treatment time in the chroming solution is about 1–4 minutes with the preferred time being 1–1½ minutes for efficient production. A treatment time below 1 minute generally does not allow for adequate chroming of the dye.

The temperature of the chroming solution is from

180–212° F. with the preferred range being about 200–210° F. Below 180° F. inadequate penetration of the chromium compound into the sheet usually occurs and also the reaction between the dye and the chromium compound is reduced with the result that the entire sheet is generally not adequately after-chromed.

After-chroming insolubilizes the dye which prevents dye migration from the sheet material, reduces water spotting, and renders the dye more stable to light, heat and effects of the atmosphere.

The dyed after-chromed sheet is passed between nip rollers 5 and 5′ to remove excess chroming solution and washed in Bath #4 containing hot water for about 2–20 minutes, the water temperature is about 180–212° F. The preferred conditions for efficient production are 2–6 minutes with the water at about 200–210° F. This washing step is necessary to remove any remaining solution of the chromium compound from the material which, if remaining in the material, would have a deleterious effect on the material and could injure those persons manufacturing the shoes from the material and also the wearer of the shoes. Wash temperatures below the 180° F. are usually inadequate to penetrate the sheet and generally fail to remove all of the residual chromium compound.

The dyed washed material is passed between nip rollers 6 and 6′ to remove excess water and dried for about 4–7 minutes by passing it through a hot air tunnel and by applying air with a temperature of 200–300° F. The preferred temperature is about 240–260° F. Temperatures higher than 300° F. will cause the microporous material to soften and the porous structure to collapse, and air temperatures lower than 200° F. usually do not dry the material adequately in the the desired time. Any hot air drying menas can be used to remove moisture from the dyed material, the preferred is a drying tunnel which is the more economical and practical method.

This invention is illustrated in the following examples.

Example I

A roll of microporous polyurethane sheet material is made in accordance with the teachings in Example I of U.S. Patent 3,100,721 to E. K. Holden, except the 50 parts of hydrazine extender are replaced with an 80/20 molar ratio of a mixture of hydrazine and N-methylamino-bis-propylamine. The resulting product is a porous impregnated non-woven mat of heat shrunk polyethylene terephthalate fibers impregnated with a microporous polyurethane polymer and uniformly coated with about 20 mils of a said polymer.

A roll of the above microporous polyurethane sheet material about 42 inches wide and about 250 feet long is advanced through the process of this invention at a rate of about 10 feet per minute.

The sheet material is passed through a hot water tank in which the water is about 205° F. and is controlled within plus or minus 5° F. The sheet is contacted with the water for about 20 seconds and then is passed between nip rollers applying a pressure below 125 pounds per lineal roll inch which reduce the water content of the sheet to about 40%.

The sheet is next treated with a dye solution which contains about 2.0% by weight of C.I. Mordant Brown 1. The pH of the dye solution is about 10.2. Temperature of the solution is controlled at about 205° F. After the sheet is contacted with the dye solution for about 48 seconds, it is passed between two steel nip rollers 10 inches in diameter and covered with rubber having a durometer of about 75. The pressure on the rollers is controlled at about 75 pounds per lineal roll inch.

The sheet is then passed into an aqeous dichromate solution which contains about 4 grams per liter of sodium dichromate and 2 grams per liter of acetic acid. The sheet remains in contact with the dichromate solution which is about 205° F. for about 80 seconds and is then passed between nip rollers applying a pressure below 125 pounds per lineal roll inch which remove excess dichromate solution.

Then the sheet is passed into a wash tank in which the water is maintained at about 205° F. and is washed for about 4 minutes. After passing the sheet between nip rollers applying a pressure below 125 pounds per lineal roll inch to remove excess wash water, the sheet is advanced to a drying tunnel. The sheet is dried for 5 minutes with hot air which is at a temperature of about 250° F.

Upon examination, the dye is found to have penetrated the entire sheet structure, is not removable with water, does not water spot and is resistant to fading by light. Shoes constructed of this material are found to have color fastness even after long periods of wear.

Example II

The microporous polyurethane sheet of Example I is dyed by the same process used in Example I, except that 0.0025% aqueous solution of C.I. Mordant Brown 18, pH 8.3, is used instead of the C.I. Mordant Brown 1 employed in Example I. The resulting dyed sheet has properties which are similar to those of the dyed sheet of Example I.

Example III

The microporous polyurethane sheet of Example I is dyed by the same process used in Example I, except that 2.5% aqueous solution of C.I. Mordant Black 9, pH 6.5, is used instead of the C.I. Mordant Brown 1 employed in Example I. The resulting dyed sheet has properties which are similar to those of the dyed sheet of Example I.

Example IV

The microporous polyurethane sheet of Example I is dyed by the same process used in Example I, except that 2.0% aqueous solution of C.I. Mordant Blue 3, pH 1.9, is used instead of the C.I. Mordant Brown 1 employed in Example I. The resulting dyed sheet has properties which are similar to those of the dyed sheet of Example I.

Example V

The microporous polyurethane sheet of Example I is dyed by the same process used in Example I, except that 2.5% aqueous solution of C.I. Acid Black 2, pH 10.0, is used instead of the C.I. Mordant Brown 1 employed in Example I. The resulting dyed sheet has properties which are similar to those of the dyed sheet of Example I.

Example VI

The microporous polyurethane sheet of Example I is dyed by the same process used in Example I, except that an aqueous dye mixture is used of 1.5% C.I. Acid Red 167 and 0.2% C.I. Mordant Yellow 16 with a combined pH of 8.25 instead of C.I. Mordant Brown 1 employed in Example I. The resulting dyed sheet has properties which are similar to those of the dyed sheet of Example I.

Example VII

The microporous polyurethane sheet of Example I is dyed by the same process used in Example I, except that an aqueous dye mixture is used of 0.6% C.I. Mordant Brown 1 and 0.2% of C.I. Acid Red 18 with a combined pH of 9.7 instead of the C.I. Mordant Brown 1 employed in Example I. The resulting dyed sheet has properties which are similar to those of the dyed sheet of Example I.

I claim:

1. A continuous process for dyeing a microporous sheet material which comprises

(1) treating the sheet with water until the moisture content of the sheet is about 10–90% by weight;

(2) immersing the wet sheet in an aqueous dye solution for about 20–120 seconds which solution contains about 0.002–3% by weight of a water-soluble dye selected from the group consisting of acid and

mordant dyes and has a pH of about 1.5–11 and at about 180–212°F.;

(3) squeezing the sheet with nip rollers with a nip pressure of about 50 to 125 pounds per linear inch to cause the dye to penetrate the sheet uniformly and to give the sheet a uniformly colored surface;

(4) immersing the dyed sheet for about 1–4 minutes in an aqueous acidic dichromate solution containing about 0.1–5% by weight of a dichromate compound and about 180–212°F.;

(5) washing the dyed sheet for about 2–20 minutes with water at about 180–212° F.; and

(6) drying the said dyed sheet for about 4–7 minutes at about 200–300° F.;

wherein said microporous sheet material comprises:

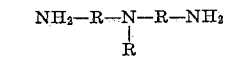
(a) a microporous surface layer of a polymeric material which is superimposed and tenaciously adhered to

(b) a porous fibrous substrate impregnated with said polymeric material

wherein said polymeric material comprises at least 50% by weight of a polyurethane polymer and up to 50% by weight of a polyvinyl chloride polymer, said polyurethane polymer being a chain-extended polyurethane which is the reaction product of an —NCO terminated dimer and a chain-extender having two amino nitrogen atoms each having an active hydrogen atom attached thereto, said isocyanate terminated dimer being the reaction product of an organic diisocyanate and active hydrogen containing polymeric material selected from the group consisting of a poly(alkyleneether) glycol and a hydroxy terminated polyester.

2. The process of claim 1 in which the —NCO terminated dimer is the reaction product of an arylene diisocyanate and poly(tetramethyleneether) glycol having a molecular weight of about 400–2000.

3. The process of claim 1 in which the chain-extender comprises hydrazine and a compound of the formula



wherein R is a C_1–C_4 saturated aliphatic group.

4. The process of claim 1 in which the porous fibrous substrate is a non-woven batt of polyethylene terephthalate fibers impregnated with said polymeric material and chain-extender consists essentially of hydrazine and N-methyl-amino-bis-propylamine.

References Cited

UNITED STATES PATENTS

2,300,445	11/1942	Weisberg	8—99
2,321,816	6/1943	Huss	8—46
2,459,813	1/1949	Grimmel	260—151
2,961,418	11/1960	Wilson	260—25
3,067,483	12/1962	Hollowell	28—80
3,097,044	7/1963	Skeuse	8—55
3,100,721	8/1963	Holden	117—135.5

FOREIGN PATENTS

591,284	1/1960	Canada.
543,198	2/1942	Great Britain.

OTHER REFERENCES

Ser. No. 391,542, Muller (A.P.C.), published Apr. 27, 1943.

Review of Textile Progress, 1962, vol. 14, pp. 276–279, published 1963, by Butterworth and Co., Washington, D.C.

Newman: American Dyestuff Reporter, Aug. 21, 1961, pp. 636–641.

NORMAN G. TORCHIN, *Primary Examiner.*

D. LEVY, *Assistant Examiner.*