To relax the synthetic-fiber goods and garments prior to heat-setting, that is, to relieve internal tensions or stresses in the fibers resulting from weaving or knitting the fabric to avoid heat-setting them in the fibers, they can be dry tumbled or wet treated at temperatures substantially below the heat-setting temperature, for example, in a tumble dryer at about 220° F. for about 20 minutes or in a wet bath at about 115° F for a similar period.

After heat-setting of the goods or garments as described above, they are dyed. However, it is estimated that seconds, that is, goods or garments rejected because of creases and the like defects set therein, range as high as 5% to 10% in large-scale commercial heat-setting operations. Such goods, of course, cannot be dyed and sold as top grade products. Inconsistent heat-setting in the fabric itself, for a variety of reasons including poor heat transfer through the mass of goods rolled into tubular or drum heat settings in an autoclave, could cause poor dyeing, such as barre which is streaking on the fabric of different shades of dye as a result of slight differences in the nature of the fibers and slightly different taking of the dye. The problem of barre is especially of concern with acid dyeing colors or neutral dyeing acid colors in some fibers and with disperse colors with others, and is caused in part by the virtual inability to manufacture filaments and fibers of synthetic resins having highly consistent characteristics.

It is accordingly an object of this invention to provide an improved process for the heat-setting of goods and garments of fabrics woven and knitted from synthetic fibers of various types. It is also an object of this invention to provide a process that eliminates the need for separate processing to internally relax synthetic-fiber goods and garments prior to heat-setting them. A further object of this invention is to provide a process whereby fabrics of woven and knitted nylon, polyester, acrylic, modacrylic or triacetate of all their various types can simultaneously be heat-set and dyed. A still further object is to provide a process for full internal relaxation of goods and garments of synthetic fibers and for heat-setting them while simultaneously dyeing them. Another object is to provide a process for stabilizing the dimensions of un-sized and sized goods and garments without substantial internal relaxation, and then simultaneously heat-setting to stabilize the new dimensions and dyeing them. These and other objects of the invention will be in part apparent and in part pointed out in the remainder of the disclosure and the claims hereinafter.

In accordance with the foregoing objects, the invention comprises a novel process whereby fabrics such as woven or knitted, including both tubular and open-width knitted, fibers or filaments of synthetic resinous materials that must be heat-set such as nylon, polyester, acrylic, modacrylic, and triacetate in their various forms can be heat-set and simultaneously dyed in the form of goods or garments while in relaxed condition substantially free of external tensions in a single heat-setting and dyeing bath. The goods or garments can either be fully relaxed in the heat-setting and dyeing bath, or they can be treated without internal relaxation to stabilize their dimensions as un-sized and sized goods. Alternatively, stretched or stretched and relaxed garments having enlarged dimensions can be heat-set, stabilized and simultaneously dyed in the dye bath. The process enables all conventional types of dyeing apparatus to be used, such as wash wheels, paddle wheels, beck and pressure machines. Furthermore, conventional dyestuffs including acid dyeing colors, natural dyeing acid colors, basic dyes and disperse dyes can be used in accordance with the dyemakers' recommendations for each specific type of synthetic-resin fiber. Blended or combination fabrics of the synthetic fibers and other substances such as
cotton, rayon and the like can also be heat-set and dyed by the process. The process permits the simultaneous use of cleaning, scouring, desizing and softening agents in the heat-setting and dyeing bath, thereby offering the possibility of fully treating and finishing the goods or garments in essentially a one-step operation unless it is necessary to do wet-finishing, for example, of woven goods and combination fiber goods.

"Nylon" is used herein to refer to long-chain synthetic polyamides having recurring amide groups

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\text{\( -\text{CH}_2-\text{NH-} -\text{CH}_2- \text{ON} \)}
\]

including its various forms identified as nylon-6 nylon-6,6 and nylon-6,10. Similarly, "polyester" is used to refer to long-chain synthetic polymers having a major portion by weight of esters of dihydric alcohols and terephthalic acid, e.g., the 50, 60 and 80 series. "Acrylic" refers to long-chain synthetic polymers having at least 85 by weight of acrylonitrile groups

\[
\text{\( -\text{CH}=\text{CH}- \text{ON} \)}
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while "modacrylic" refers to similar polymers having at least 35% but less than 85% by weight of acrylonitrile groups. "Triacetate" is used to refer to fibers composed of cellulose acetate in which not less than 92% of the hydroxyl groups are acetylated.

An important advantage of the process of this invention is its eminently suitable for the dyeing of nylon with acid dyeing colors which in general have better washing fastness, light fastness and gas-fading fastness properties than more expensive processes using disperse dyes. That is so because acid dyeing colors can be used in the process without the disadvantages usually associated with applying them to nylon, such as blotching, streaking, crack marks, shading and barre. Another important advantage of the process is that polymers heat-set and dyed thereby with disperse dyes, which tend to wet crock and dry crock and to have poor light-fastness, have superior light fastness and color fastness to bleeding and crocking. In addition, less expensive kinds of disperse dyes can successfully be used in the process. A further important advantage of the process is that it enables modacrylics to be dyed with good fastness with acid dyes, which are generally less expensive than the disperse dyes ordinarily used, and which have heretofore been successfully used only with considerable difficulty. That advantage coupled with the natural flame-retardant properties of modacrylics enhances their attractiveness for domestic uses such as for upholstery and drapery.

For heat-setting and dyeing of synthetic-fiber goods or garments in tension-free relaxed condition, especially for tubular or open-width knit goods and full-fashioned garments, a dyebath is prepared containing water to which is added a quantity of a sulfonated animal oil or a sulfonated vegetable oil obtained by treating the animal or vegetable oil with a sulfonating agent, such as sulfuric acid, to prepare a sulfonated derivative of the animal or vegetable oil. The exact nature and composition of the sulfonated animal oil or the sulfonated vegetable oil is not known and does not presently appear to be critical to the success of the process. Certain sulfonated animal and vegetable oils, however, are known to provide especially good results and are therefore utilized preferred. Such oils of and vegetable oils include coconut oil, soybean oil, castor oil and marine mammal oils such as sperm oil and porpoise oil, and fish oils. In general, different sulfonated oils can be blended together. Particular commercially available sulfonated oils that are effectively utilized in the process are those sold under the trade designations "Marset RK" by March Chemical Products, Inc., of New Milford, N.J., "Aliphatic Ether Sulphate" by Onyx Oil and Chemical Company of Jersey City, N.J., and "Tanalene 200" and "Tanalube" by Tanatex Chemical Corporation of Kearny, N.J. The first-mentioned material is a blend of sulfonated animal oil and blended sulfonated vegetable oils stabilized by hexylene glycol, and is a preferred sulfonated oil that provides excellent results.

An important feature of the sulfonated vegetable oils and sulfonated animal oils is that in the sulfated form they are, preferably, completely non-substantive to the synthetic resin fibers. Furthermore, they provide a lubricating action for the goods or garments in the heat-setting and dyeing bath, and at the same time provide generally good to excellent levelling action and dispersment of the dyestuff. The sulfonated animal and vegetable oils are used effectively in the dyebath in an amount of at least about 0.05% by weight of active material based on the amount of water. There appears to be no limit on the amount of sulfonated oil in the dyebath except perhaps practical and economic considerations. A preferred range is about 0.05% to about 5% by weight of active material, and for a blend of sulfonated oils such as "Marset RK" the optimum amount is about 4%.

For full internal relaxation of the goods or garments in the dyebath, a relaxing and softening agent is advantageously used. Materials known in the art as swelling agents can be used with the exception of certain aromatics such as benzene and phenols. Suitable swelling agents include, for example, chloroethylene, trichloroethylene, carbon tetrachloride and similar cleaning solvents. A particularly good swelling agent is a blend of o-dichlorobenzene and trichlorobenzene which provides a good balance between high and low volatility materials for use under the processing temperatures and times of the invention discussed hereinafter. It is apparent from their nature that the swelling agents also provide a cleaning action. The amount of swelling agent used in the dyebath is based on the weight of fabric (o.w.f.) to be treated, and should be in the range of about 0.5% to about 25% o.w.f., depending upon the particular synthetic-fiber fabric being processed. For example, up to about 4% o.w.f., and preferably about 0.7% to about 2.0% is advantageously used with nylon whereas more than about 3% o.w.f., and preferably between about 5% and 20%, desirably should be used with fibers of the other resins because the agent provides the swelling and levelling action required to carry the dyestuff into those fibers to dye them. Color and depth of shade of the dyeing, of course, are factors in the amount of swelling agent used, and here too, higher amounts of active material would not hinder the process.

An emulsifier should be used with swelling agents because they are not sufficiently soluble in the essentially aqueous dyebath. Anionic or non-ionic emulsifiers known to the art are satisfactory and can be used. The emulsifier and swelling agent are desirably blended prior to their addition to the dyebath. Emulsifier in an amount of up to about 50% by weight of the swelling agent can be used in the blend. The emulsifiers are, or have many of the characteristics of, detergents and therefore provide a cleaning and scouring action in the dyebath. A particular suitable emulsifier and swelling agent combination containing blended chlorinorated benzenes and anionic and non-ionic emulsifiers is sold under the trade name "Marsolve FR" by March Chemical Products, Inc.

The dyebath should be maintained slightly alkaline during the heat-setting operation of at least about 7.5, and up to about 8.5. Greater alkalinity requires correspondingly greater amounts of acid for subsequent neutralization. A buffer to control the pH can advantageously be used. Such buffers include tetrasodium pyrophosphate, trisodium phosphate, soda ash and sodium bicarbonate as well as the corresponding potassium and calcium compounds and similar buffers. Generally, in the order of up to about 1% o.w.f. of buffer can be used although higher amounts would not be harmful.
To heat-set and dye internally relaxed synthetic-fiber goods or garments, a dyebath as described is made up and is heated to about 100° to about 120° F., after which the goods or garments to be heat-set and dyed are entered into the dyebath. The dyebath machine is turned on and the goods are internally relaxed at a temperature in that range, and preferably at between about 107° and 117° F. At lower temperatures the relaxing is too slow and at higher temperatures partial setting of the fabric may occur. The relaxing time varies depending on the particular dyeing machine used, and desirably is about 15 to 20 minutes on a paddle wheel, about 12 to 15 minutes on a wash wheel, and about 40 to 60 minutes on a bec or pressure machine. Less time may result in less than full relaxation, which of course may be desired, while longer times are generally unnecessary. The choice of machine depends on the type of goods or garments to be heat-set and dyed, e.g., a paddle wheel is suitable for tubular knit goods and full-fashioned garments, a wash wheel for those as well as for certain laces, and a bec or a pressure machine is suitable for open-width knit goods, spun goods, certain laces and openwork, and combination fabrics as well as for tubular knit goods.

After internally relaxing the goods or garments, the dyebath is heated slowly at a rate less than about 2° F. per minute, and preferably at about 1° F. per minute, to the temperature recommended by the dyemaker for the particular dye to be used. That temperature usually is about 135° to about 160° for cotton. The dye is then added in the recommended quantity for the amount of goods or garments to be dyed, and dispersed in the dyebath. The dyebath temperature is then raised slowly at the rate above mentioned up to the boil and held at the boil for at least about 30 minutes and, except for polyesters, preferably for about 45 to 90 minutes. During that time the goods or garments are heat-set and dyed. If either acid dying colors or basic dyes are used, the acid to neutralize the dyebath and to exhaust the dye can be added to the dyebath in accordance with the dyemakers' recommendation as to the kind of acid and the required pH level. It is desirable to add the acid during a period of about 10 minutes on a paddle wheel, about 6 to 9 minutes on a wash wheel, and about 30 to 45 minutes on a bec or pressure machine after the dyebath is brought to the boil. Acetic acid should preferably be used to neutralize disperse dyes.

For the sake of caution to avoid shocking the heat-set and dyed resin fibers, the dyebath should be cooled slowly and rinsed by overflow to reduce the temperature to about 120° F. after which the dyebath can be dropped and the goods or garments can be rinsed with water at about 100° F., to which, especially for rinsing knitted fabrics, a conventional substantive softener can be added for finishing. Thereafter, the goods or garments can be dried, e.g., in a tumble dryer if a wash or paddle wheel dyeing machine was used or otherwise in a loop or closed frame dryer, especially for open-width knitted fabrics, at a temperature of about 170° to about 250° F.

Another embodiment of the invention enables goods or garments of synthetic-fiber fabrics to be simultaneously heat-set and dyed as well as to stabilize their desired or unsized dimensions, that is, heat-set and dyed without substantial internal relaxation of the fibers. For polyester, acrylic, modacrylic and triacetate fibers, a dyebath as described above is prepared.

For nylon fibers, however, a dyebath is prepared as described above except that no swelling agent to promote relaxation and shrinkage is added. Instead, a levelling agent with little or no swelling properties is used to assist in dispersing the dyestuff in the dyebath and on the fibers. Suitable agents include having high ionic points, such as naphthia with an open-test rated flash point of about 420° F. Cleaning solvents such as the chlorinated aliphatic and aromatic ones mentioned hereinbefore having swelling properties are to be avoided. Like the swelling agents, however, the levelling agent is used in an amount of about 0.5% to about 4% o.w.f. and should be blended with an emulsifier. Also, a penetrating agent, such as a petroleum base, may advantageously be used. A commercially available blend of those ingredients eminently suitable for use in this process is sold as "Marnsolve GD" by March Chemical Products, Inc. Acrylic fibers can similarly be treated without the use of a swelling agent, but such processing is less desirable.

The dyebath is held at the temperature recommended for the addition of the dyestuff, e.g., 135° to 160° F., preferably at the high end of that range or even higher, and the dyestuff is added and dispersed in it. Thereafter the goods or garments are entered into the dyebath and wetted-out, that is, completely saturated with the bath. The temperature of the dyebath is then raised to the boil as rapidly as possible, for example, by the injection of steam into the dyebath. Delay between the time the goods or garments are entered into the dyebath and the time the dyebath reaches the boil should be minimized so the goods or garments will not be internally relaxed to any significant extent. Alternatively, the goods or garments can be entered into the dyebath at or near the boil if care is taken to maintain the pH of the dyebath above at least about 7.5, and preferably about 8, when using acid or neutral dyeing acid colors. After reaching the boil, the process is completed by following the procedure for full relaxation as previously described.

Because slight relaxation might occur in the goods or garments, it may be of advantage to stretch them a small amount, e.g., in the order of up to about 4% before entering them into the dyebath.

To dye and heat-set garments and goods of greater than desired or unsized specifications, the same type of dyebath and process described above for maintaining desired or unsized dimensions can be used. However, the greige goods or garments are first dimensionally enlarged by conventional means, such as on a tenter frame or other stretching devices, to the desired dimensions, and preferably up to about 5% in excess thereof. Thereafter they are heat-set and dyed, as described, as quickly as possible to avoid substantial internal relaxation and to stabilize the enlarged dimensions.

Acid dyeing colors, neutral acid dyeing colors and disperse dyes should be used in the process for fibers of nylon, and those dyes as well as basic dyes can be used for acrylic and modacrylic fibers. Polyester and triacetate fibers, of course, should be dyed with disperse dyes that exhaust neutral or, in the case of polyesters, especially those of other than the 5 series, with basic dyes. The superior fastness of disperse dyes obtained by this process, particularly on fibers of polyester, appears to be due to avoiding the use of swelling agents containing phenolics and benzoates and to using an alkaline dyebath.

It is of course to be understood that numerous changes can be made in the ingredients, proportions and conditions of the process as set forth herein without departing from the scope of the invention as defined in the claims appended hereto.

I claim:

1. A process for the heat-setting, dyeing and stabilizing of dimensions of a substantially externally tension-free synthetic resin fiber selected from the group consisting of nylon, polyester, acrylic, modacrylic and triacetate fibers which comprises adding the fiber in a condition substantially free from external tension to an aqueous dyebath at a temperature at least as high as 135° F. containing a sulfonated vegetable oil, a sulfonated animal oil or a blend thereof, which sulfonated oil is substantially non-substantive to said fiber in said dyebath, and heating said fiber in said dyebath to dye and heat-set said fiber.

2. A process as defined in claim 1 wherein said fiber is added to the dyebath at a temperature at or near the boil.
3. A process as defined in claim 1 wherein said fiber is added to the dyebath at a temperature in the range of about 135° F. to about 160° F., and the dyebath is rapidly heated at least substantially to the boil.

4. A process as defined in claim 1 wherein the dyebath is rapidly heated at least substantially to the boil after said fiber is added.

5. A process as defined in claim 1 wherein said fiber is heated in the dyebath at or near the boil.

6. A process as defined in claim 1 wherein said dyebath contains at least about 0.05% by weight of said sulfonated oil calculated on the weight of water therein.

7. A process as defined in claim 1 wherein said dyebath contains from about 0.05% to about 3% by weight of said sulfonated oil calculated on the weight of water therein.

8. A process as defined in claim 1 wherein said dyebath has a pH of between about 7.5 and about 8.5.

9. A process as defined in claim 1 which further comprises adjusting the pH of said dyebath to between about 7.5 and about 8.5 by addition of a buffer.

10. A process as defined in claim 1 wherein said fiber is nylon and said dyebath contains from about 0.5% to about 4% by weight of said fiber of a levelling agent.

11. A process as defined in claim 1 wherein said fiber is polyester, acrylic, modacrylic or triacetate and said dyebath contains from about 3% to about 25% by weight of fiber of a swelling agent.

12. A process as defined in claim 1 wherein the dimensions of the fiber to be stabilized are the unsize or desired dimensions.

13. A process as defined in claim 1 which further comprises enlarging the unsize or desired dimensions of said fiber prior to adding said fiber to the dyebath, whereby the enlarged dimension is substantially stabilized.

14. A process for heat-setting, dyeing and substantially stabilizing the dimensions of goods or garments made of a fabric of a synthetic resin fiber selected from the group consisting of nylon, polyester, acrylic, modacrylic and triacetate fibers without substantial internal relaxation of the fibers in the fabric which comprises: preparing an aqueous dyebath containing (1) at least about 0.05% by weight of active material calculated on the weight of water in the dyebath of a sulfonated vegetable oil, a sulfonated animal oil or a blend thereof, which sulfonated oil is substantially non-substantive to said fiber in the dyebath, (2) a dyestuff for said fiber, (3) a buffer to adjust the pH of the dyebath to between about 7.5 and about 8.5, and (4) a buffer from about 0.5% to about 4% by weight of nylon goods or garments of a levelling agent or (b) from about 3% to about 25% by weight of polyester, acrylic, modacrylic or triacetate goods or garments of a swelling agent; adding said goods or garments in a substantially tension-free relaxed, folded or roped condition to said dyebath at a temperature of at least about 135° F.; and heating said goods or garments in said dyebath to dye and heat-set the fibers thereof.

15. A process as defined in claim 14 wherein said goods or garments are added to the dyebath at a temperature at or near the boil.

16. A process as defined in claim 14 wherein said goods or garments are added to the dyebath at a temperature in the range of about 135° F. to about 160° F., and the dyebath is rapidly heated at least substantially to the boil.

17. A process as defined in claim 14 wherein said dyebath is rapidly heated at least substantially to the boil after said goods or garments are added.

18. A process as defined in claim 14 wherein said goods or garments are heated in said dyebath at or near the boil.

19. A process as defined in claim 14 wherein said dyebath contains from about 0.05% to about 3% of said sulfonated oil.

20. A process as defined in claim 14 wherein said swelling agent (4)(b) is substantially free of phenolics and benzoxazoles.

21. A process as defined in claim 14 wherein the dimensions of said goods or garments to be stabilized are the unsize or desired dimensions.

22. A process as defined in claim 14 which further comprises enlarging the greige dimensions of said goods or garments prior to adding them to the dyebath, whereby the enlarged dimensions are substantially stabilized.

23. A process as defined in claim 14 wherein said dyestuff is an acid dyeing color, a neutral dyeing acid color, a basic dyestuff or a disperse dyestuff.

24. A process as defined in claim 14 wherein said fabric is woven or knitted from polyester, acrylic, modacrylic or triacetate fibers and said dyebath contains from about 5% to about 20% of said swelling agent (4)(b).

25. A process as defined in claim 14 wherein said fabric is woven or knitted from modacrylic fibers and said dyestuff is an acid dyeing color or a neutral dyeing acid color.

26. A process as defined in claim 14 wherein said goods or garments added to the dyebath are folded in a machine, folded in a bag, open relaxed or in relaxed dyeing equipment.

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