It is an object of this invention to provide an aqueous cationic dye-containing dyestuff composition which provides an improved dye uptake including both speed and amount of dye uptake when applied to acrylic shaped articles.

It is further object of this invention to provide a method for dyeing an acrylic shaped article utilizing an aqueous dyebath composition containing a water-soluble dyeing assistant.

SUMMARY OF THE INVENTION

These and other objects of the invention are achieved by providing an improved dyestuff composition for dyeing an acrylic shaped article comprising:

(a) an aqueous dyebath of a cationic dye, and
(b) a minor quantity of methyl cyanide sufficient to promote the dyeing of an acrylic shaped article.

In another aspect, the invention provides an improved process for dyeing an acrylic shaped article which comprises contacting the article to be dyed with an aqueous dyebath comprising:

(a) a cationic dye, and
(b) a minor quantity of methyl cyanide sufficient to promote the dyeing of the acrylic shaped article.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The acrylic shaped articles, e.g., fibers or films or the like, undergoing dyeing in the present invention are generally known in the art. These acrylic materials, and particularly polyacrylonitrile, one of the most important polymeric acrylic materials, may be formed by conventional solution spinning techniques (i.e., may be dry spun or wet spun) or by conventional solvent casting techniques, and are commonly drawn to increase their orientation. As is known in the art, dry spinning is commonly conducted by dissolving the polymer in an appropriate solvent, such as N,N'-dimethylformamide or N,N'-dimethylacetamide, and passing the solution through an opening of predetermined shape into an evaporative atmosphere (e.g., nitrogen) in which much of the solvent is evaporated. Wet spinning is concomitantly conducted by passing a solution of the polymer through an opening of predetermined shape into an aqueous coagulation bath. Casting is concomitantly conducted by placing a solution containing the polymer upon a support, and evaporating the solvent therefrom.

The acrylic polymer utilized as the starting material is preferably formed primarily of recurring acrylonitrile units. For instance, the acrylic polymer should preferably contain not less than about 85 mol percent of acrylonitrile units and not more than about 15 mol percent of units derived from a monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like, or a plurality of such monomers. The acrylic polymer utilized as the starting material may also be a modacrylic polymer, i.e., a long chain polymer containing less than 85 mol percent but more than 35 mol percent of acrylonitrile units. The term "acrylic shaped article" as used herein is meant to include modacrylic shaped articles also.

The acrylic shaped article is preferably provided as a continuous length of a fibrous material and may be in a variety of physical configurations. For instance, the fibrous material may be present in the form of continuous lengths of multifilament yarns, tows, tapes, strands, cables, or similar fibrous assemblages. Alterna-
tively, acrylic films of relatively thin thickness, e.g., about 1 to 10 mils, may be dyed. When the starting material is a continuous multilayered film, the dye is applied in the same, as known in the art, to improve the handling characteristics. The starting material may also be drawn in accordance with conventional techniques in order to improve its orientation. The starting material may also be scoured, bleached or otherwise physically or chemically treated in a known manner before dyeing.

The acrylic shaped articles have acidic sites which attract cationic dyes. The acrylic shaped articles may, for example, include acid-modified acrylic material and acrylic materials containing acid residues such as known in the art.

The aqueous dyebath with the exception of the methyl cyanide may be formed in a conventional manner containing the cationic dye, pH regulators, etc., as will be apparent to those skilled in the art. The cationic dyes utilized in the dyestuff composition of this invention can be any of the known cationic or basic dyes suitable for dyeing an acrylic article. Suitable basic dyes include the diphenylmethane and triphenylmethane derivatives, rhodamine dyes, azo dyes, anthraquinone dyes, thiazine dyes, oxazine dyes, xanthene dyes, polymethine dyes, azomethine dyes, said cyanine dyes. Specifically, dyes which are expected to function include: diphenylmethanes (ketone imines) such as auramine; triarylmethanedyes such as Color Index (hereinafter "C.I."), Basic Green 1, C.I. 42,040, fuchsinine (C.I. 42,500), roseviolet (C.I. 43,520) victoria blue (C.I. 44,040), basic violet (C.I. 42,557) (Suppi), rhodamine violet (C.I. 44,520), the basic dyes of U.S. Pat. 3,021,344, U.S. Pat. 3,032,561 and U.S. Pat. 2,083,888; xanthene dyes such as Pyronine G (C.I. 45,005), methylene red (C.I. 45,006), Rhodamine (C.I. 45,050), safranin (C.I. 45,070), Rhodamine 5G (C.I. 45,105), Rhodamine G (C.I. 45,150), Rhodamine 6G (C.I. 45,160), Rhodamine 12G (C.I. 45,310); acid dyes such as Acidine Orange NO (C.I. 46,005), Diamond Phosphine GG (C.I. 46,035), Rheonine AL (C.I. 46,075); methine dyes such as basic red C.I. 48,015, basic red C.I. 48,013, basic violet C.I. 48,020, basic orange C.I. 48,032; basic yellow C.I. 48,045; basic yellow C.I. 48,060; basic yellow C.I. 48,065, basic dyes prepared from 2-methylene-1,3-trimethyldiine (Fischer's Base) as disclosed in U.S. Pat. 2,734,901 and in "Synthetic Dyes" by Venkataraman, Academic Press Inc., New York, 1929, Vol. II, page 1174; basic methine dyes as described in British Pat. No. 462,238 and U.S. Pat. No. 2,164,793, basic azatrimethinecyanines dyes as those disclosed by J. Voltz in Angew. Chem. (English edition) pp. 532-537, October 1962; thiazole dyes such as Thioflavine T (C.I. 49,005); indamine basic dyes such as basic green C.I. 49,405; azine dyes such as Mauve (C.I. 50,245), Safranine T (C.I. 50,240); basic violet C.I. 50,055, basic blue C.I. 50,306, Induline 6B Base (C.I. 50,400); oxazine dyes such as basic blue C.I. 51,004, Mendola's Blue C.I. 51,175, basic black C.I. 51,213; thiazine dyes such as Methylene Blue C.I. 52,015; basic green C.I. 52,020; azo dyes such as the azoframine dyes described in British Pat. No. 942,844 and U.S. Pat. No. 3,121,711, chrysoildine C.I. 11,270, basic brown C.I. 21,010, the basic azo dyes of British Pat. Nos. 808,713, 785,958, 896,681, 894,389, 459,594, 502,728 and U.S. Pat. No. 2,973,272; 9,074,926; 3,053,591; 3,079,377; 2,099,525; 2,864,821; 2,864,813; 2,863,753; 2,889,315; 2,022,921; 2,238,485; 2,397,927; 2,906,747; 2,945,849; 3,096,318; 3,099,652 and 3,099,653; German Pat. Nos. 1,085,276; 1,088,631 and 1,135,589; French Pat. No. 1,295,862; anthraquinone dyes such as the basic violet mono and dicondensation products of quinizarin with 2-dimethylamino-ethanolamine and 3-dimethylamino-propylamine (British Pat. No. 489,172), the basic dyes dissolved in U.S. Pat. 2,716,655, the basic dyes dissolved in U.S. Pat. 2,153,012, the basic dyes disclosed in U.S. Pats. 2,701,801 and 2,701,802, the basic dyes of U.S. Pat. 2,888,467; 2,611,722; 2,737,517; 2,924,609; and 3,076,821; Canadian Pat. 624,035; British Pat. 459,594; 807,214; 824,530; 903,007; 889,374 and 295,111; German Patents 714,986; 1,073,129 and 1,082,916; French Patent 1,277,495 and Belgian Pat. 609,667; nitro basic dyes such as those disclosed in U.S. Pats. 2,834,793 and 2,934,794; and basic quinophthalone dyes such as those disclosed in U.S. Pat. 3,023,312; Sevron Yellow 3RL (C.I. basic yellow), Sevron Orange G (C.I. basic orange), Sevron Brilliant Red 4G (C.I. basic red 16), Sevron Red GL (C.I. basic red 18), Sevron Blue B (C.I. basic blue 21), Sevron Blue 2G (C.I. basic blue 22), Sevron Blue G (C.I. basic green 3), Astrazon Yellow 3G (C.I. basic yellow 11), Astrazon Blue BG (C.I. basic blue 3), Astrazon Blue 3RL (C.I. basic blue 47), Basacryl Yellow 5 GL (C.I. basic yellow 24), Basacryl Blue GL (C.I. basic blue 54), and Basacryl Blue 3RL (C.I. basic blue 55). Other suitable cationic dyes will be apparent to those skilled in the art.

In accordance with the present invention, the dyebath composition for dyeing shaped articles of acrylic polymers contains a cationic dye and an amount sufficient to promote dyeing of methyl cyanide. Methyl cyanide (acetonitrile) is soluble in water. Therefore, no dispersing and/or suspending media need to be added to the dyebath. The methyl cyanide can be added to the dyebath in an amount of from about 0.5 to about 10 percent, preferably from about 1 to about 5, weight percent based on the weight of the total dyebath composition.

Fast color dyeing of acrylic articles generally can be performed by contacting the articles with an aqueous cationic dye-methyl cyanide containing containing dyebath for a time sufficient to dye the articles. Generally, contact can be from about 1 to 3 hours at a temperature of from about 90° C. to about 100° C. Often, the dyebath can contain minor amounts of additives such as pH regulators, surface-active agents, etc., to assist in dyeing the articles. Dyeing of the acrylic articles with the dyebath composition of the present invention can be performed by using dyeing procedures as will be apparent to those skilled in the art.

The preceding example is given as a specific illustration of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the example.

**EXAMPLE**

An aqueous dyebath composition was prepared of 300 ml water, 150 mg Sevron Blue B dye, 2 g./l. of sodium acetate, 1/2 g./l. of an alkylaryl polyether surfactant commercially available as "Triton X-102" and sufficient glacial acetic acid to achieve pH of about 5.5. The sodium acetate is added to buffer the pH. Methyl cyanide was added to the dyebath in an amount of 3 ml. (0.78 weight percent of the total composition). A similar dyebath was prepared including 15 ml. of methyl cyanide (3.9 weight percent of the total composition). A third dyebath was prepared which was the same except that methyl cyanide was not added. The latter dyebath was used as a control sample.

Four acrylic fiber samples are added to each dyebath in an amount of 100 mg. of each fiber. Fiber A is a terpolymer of acrylonitrile, methacrylamide, and a minor quantity of sodium methallyl sulfonate. Fibers B, C and D are each a copolymer of acrylonitrile-methacrylate with acrylic fiber to acrylic fiber. Fiber B is of American origin while fiber C is of Japanese manufacture and fiber D is of German manufacture. Each of the fibers is contacted in a closed can for 2 hours at 97° C. with the dyebath compositions containing 0, 0.78 and 3.9 percent by weight of the total composition of methyl cyanide. The fibers after dyeing are evaluated to determine the amount of dye in each fiber. The results, expressed as the weight
percent of dye in each fiber for each dyebath composition are set forth in the table below.

<table>
<thead>
<tr>
<th>Acetonitrile, percent</th>
<th>0</th>
<th>0.78</th>
<th>2.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber A</td>
<td>12.8</td>
<td>12.6</td>
<td>13.8</td>
</tr>
<tr>
<td>Fiber B</td>
<td>6.3</td>
<td>6.9</td>
<td>6.1</td>
</tr>
<tr>
<td>Fiber C</td>
<td>3.7</td>
<td>3.9</td>
<td>6.5</td>
</tr>
<tr>
<td>Fiber D</td>
<td>2.6</td>
<td>3.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>

As may be seen from the table, the fibers which were contacted with the aqueous dyebath containing 0.78% by weight of the total composition of methyl cyanide surprisingly contained more dye than when they are contacted with an aqueous dyebath which contains 0 percent acetonitrile. The dye uptake resulting from contact with the 3.9 percent methyl cyanide-containing dyebath is even greater. These increases were found for every fiber sample. Sample D, for example, showed almost double the amount of dye at 3.9 percent methyl cyanide compared with the control sample. While the other fibers generally did not yield so dramatic an increase, the increase in uptake was substantial in every case. The data further indicates that when a predetermined amount of dye is desired in the fiber dying can be accomplished in a shorter time.

While the invention has been described with reference to the cationic dyeing, the methyl cyanide additive may also improve the dyeability of acrylic shaped articles with disperse or acidic dyes where the articles are otherwise dyeable with these types of dyes. The invention may be particularly applicable with highly drawn or industrial acrylic fibers or those having very low dye site concentrations.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended thereto.

I claim:

1. An improved composition suitable for dyeing polymers of acrylonitrile comprising:
   (a) an aqueous dyebath of a cationic dye, and
   (b) from about 0.5 to about 10 percent by weight based upon the weight of the total composition of methyl cyanide.

2. The improved composition of claim 1 wherein the acrylic shaped articles contain not less than about 85 mol percent of acrylonitrile units and not more than about 15 mol percent of units derived from a monovinyl compound polymerizable with acrylonitrile.

3. The improved composition of claim 1 wherein said methyl cyanide is present in said improved composition in a quantity of from about 1 to about 5 percent by weight based upon the weight of the total composition.

4. An improved process for dyeing polymers of acrylonitrile which comprises contacting the polymers of acrylonitrile to be dyed with an aqueous dyebath comprising:
   (a) a cationic dye, and
   (b) from about 0.5 to about 10 percent by weight based upon the weight of the total composition of methyl cyanide.

5. An improved process for dyeing acrylic shaped article in accordance with claim 4 wherein said acrylic shaped article is a fiber.

6. An improved process for dyeing an acrylic shaped article in accordance with claim 4 wherein said acrylic shaped article is a film.

7. An improved process in accordance with claim 4 wherein said acrylic shaped article contains not less than about 85 mol percent of acrylonitrile units and not more than about 15 mol percent of units derived from a monovinyl compound polymerizable with acrylonitrile.

8. The method of claim 4 wherein said methyl cyanide is present in said improved composition in a quantity of from about 1 to about 5 percent by weight based upon the weight of the total composition.

References Cited

UNITED STATES PATENTS

3,565,572 2/1971 Schneider et al. ---- 8—172 X
2,888,314 5/1959 Matlin et al. ------- 8—172 X
3,114,588 12/1963 Lewis ------------------ 8—93
3,493,981 2/1970 Noda et al. ------------- 8—172

LEON D. ROSDOL, Primary Examiner
T. J. HERBERT, Jr., Assistant Examiner

U.S. Cl. X.R.

8—83, 177 AB