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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Dyeing Shaped Articles made from Oxymethylene Polymers

We, CELANESE CORPORATION OF AMERICA, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to dyeing shaped articles made from oxymethylene polymers.

Oxymethylene polymers can be produced in a form in which they are sufficiently thermostable to be shaped by the action of heat and pressure. Such polymers also yield filaments having properties rendering them highly satisfactory for textile purposes apart from the fact that they have heretofore been regarded as resistant to colouration with dyes. Thus, acid dyes, direct dyes, premetallized dyes and basic dyes fail to develop a full shade as the polymers do not take up as much as 0.1% of their weight of such dyes from baths containing practical amounts of dyestuff in reasonable dyeing periods of up to two hours.

According to the present invention, a process for dyeing shaped articles made from solid thermoplastic oxymethylene polymers comprises maintaining the article to be dyed in contact with an aqueous dispersion of a disperse dyestuff at an elevated temperature until the article assumes the desired depth of colour. It has been found that the polymers respond to treatment with disperse dyestuffs so as to yield products having any desired depth of the desired colour.

The invention is chiefly concerned with the dyeing of the polymer in filamentary form, e.g. as a tow yarn, roving, sliver, batting or knitted or woven textile fabric, but may be

applied also to the colouration of other shaped articles, e.g. films, made from the polymer.

The invention is applicable to shaped articles made not only from oxymethylene homopolymers but also from copolymers, including copolymers comprising recurring

units having the formula $(-O-CH_2-(C)_n-)$,

wherein n is an integer from zero to 5 and is zero in from 75 to 99.5 percent of the recurring units; these particular copolymers, which are especially satisfactory for filament production, may be obtained by copolymerising trioxane with, for instance, ethylene oxide or dioxolane.

The disperse dyes which are applied in accordance with the invention include as azo dyes, anthraquinone dyes and arylamine dyes often referred to as acetate dyes. Specific examples of these dyes are 2-nitro-4-sulphon-anilido diphenylamine; 4-ethoxy-2-nitro-diphenylamine - beta - hydroxypropylamide; 4-nitro-2-methoxyphenyl azo 4'-bis (beta-hydroxyethyl) amino-2'-acetylaminobenzene; 4-nitro-2-methylsulphonophenyl azo 4'-(N-beta-hydroxyethyl - N - difluoroethyl) aminobenzene; 4-nitro-2-chlorophenyl azo 4'-bis (beta-hydroxyethyl) amino-2'-methylbenzene; 1 - hydroxyethyl - amino - 4 - hydroxyethylamino - 5 - hydroxy - 8 - hydroxy anthraquinone; 4'-nitrophenyl azo 4-di-beta-hydroxyethylamino-2'-acetaminobenzene; a mixture of 1,4 - di(hydroxyethylamino) - 5,8 - dihydroxy anthraquinone and 1-amino-4-anilido anthraquinone; 1,5 - dihydroxy - 8 - nitro - 4-(meta-alpha-hydroxyethyl) anilido anthraquinone; 1,8-dihydroxy-4-(para-beta-hydroxyethyl) anilido-5-nitro anthraquinone; 1- amino-4-anilido anthraquinone; and 2,4-dinitro-6-chlorophenyl azo 4'-bis (hydroxyethyl) amino-2'-acetyl-amino-5'-methoxy benzene; 1-amino-

[Price 4s. 6d.]

4-hydroxy anthraquinone; and 1-methylamino-4-beta-hydroxyethylamino anthraquinone. These dyestuffs, as sold, are in the form of mixtures of the actual dye with a dispersing agent, such as sodium ligno-sulphonate or the sodium salt of a formaldehyde-naphthalene sulphonic acid condensation product, and usually contain about 30 to 45 percent of the actual dye.

Preferably filamentary material, treated in accordance with the invention is prepared from the oxymethylene homopolymer or copolymer by melt spinning, although products made by dry and wet spinning methods may also be used. Usually one or more thermal stabilisers are incorporated into the polymer in order to reduce degradation during spinning, a proportion between about 0.05 and 10 weight percent (based on the weight of polymer) being suitable for most stabilisers.

The filamentary material is usually prepared for dyeing by scouring. The material may be scoured in a hot aqueous solution of a detergent or, in the case of the copolymers specified above, of alkali. Trisodium phosphate or tetrasodium pyrophosphate is generally used in solution of about 1 to 5 weight percent, based on the weight of the filamentary material. The temperature of scouring is generally between about 70° and about 90° C. and the scouring operation is usually continued for at least 30 minutes.

In the dyeing operation any equipment and techniques suitable for the thorough impregnation of the filamentary material may be used. The disperse dye is usually maintained in the dye bath in a concentration between 0.01 and 500 weight percent, based on the weight of the filamentary material, between 0.01 and 10 weight percent being preferred for a finite dye bath and between 100 and 500 weight percent being preferred for a simulated infinite dye bath. The dye bath temperature is preferably between 80° and 100° C. and the residence time of the filamentary material in the dye bath is preferably between $\frac{1}{2}$ hour and 4 hours.

Carriers, such as ortho-phenyl phenol, benzoic acid and methyl para-toluate, may be included in the dye bath, for instance in concentrations between 2 and 20 weight percent, based on the weight of the fibre.

Dispersing agents and water softeners may be added to the dye bath to promote optimum dyeing conditions, according to the nature of the particular disperse dye and the hardness of the available water. After impregnation, excess dyestuff is removed by scouring and the filamentary material is dried.

The following Examples illustrate the invention:—

EXAMPLE 1

The filamentary material used was made from a trioxane-dioxolane copolymer containing 4 percent by weight of monomeric units

derived from dioxolane, having an inherent viscosity of 1.2 (measured at 60° C. in a 0.1 weight percent solution in p-chlorophenol containing 2 weight percent of alpha-pinene) and stabilised with 1 weight percent each of 2,2'-methylene bis-(4-methyl-6-tertiary butyl phenol) and malonamide. 91 parts by weight of this stabilised copolymer were blended with 27.3 parts of dimethyl formamide by heating in a closed container in an oven for 4 hours followed by rolling on a mill for 5 minutes. The rolls of the mill were maintained at about 160° C. The polymer was removed from the rolls, cut up and ground into pellets and the pellets were melt spun through a jet having 10 holes of 0.020 inch diameter at a temperature of 175 to 180° C. The filaments were collected at a take-up speed of 200 metres/minute as a yarn having a denier of 231. The yarn was drawn over a 12 inch long shoe heated to 133° C. at a draw ratio of 9.05 to 1 and a draw speed of 11 metres/minute. The drawn yarn had a denier of 25.6 and a tenacity of 6.0 grams per denier with 21 percent elongation.

100 mg of this yarn, after scouring, was immersed in a simulated infinite dye bath containing 300 mg of disperse dye in 600 ml of water and maintained at 97° C. for 1 hour. The dye used was Eastone Red NGLF (C.I. Disperse red 35). After extraction with perchlorethylene and drying, the fibre was found to have taken up 1.1% of its weight of the dye to be coloured a full red shade.

EXAMPLE 2

Ladies' stockings were knit from a 20 denier monofilament of an oxymethylene copolymer. The copolymer contained 2 weight percent of monomeric units derived from ethylene oxide and was stabilised with 0.1 weight percent of cyano-guanidine and 0.5 weight percent of 2,2'-methylene bis-(4-methyl-6-tertiary butyl phenol). The filament was melt spun at 190° C. and drawn to 7.6 times its original length over a shoe heated to 140° C.

The stockings were dyed in a dye bath containing 0.125% Celliton Brown 3—RA (CI 11100), 0.05% Eastman Blue BNN (CI 61505), 0.5 g/l sodium N-methyl-N-oleyl laurate, 0.5 g/l Calgon (sodium metaphosphate), 3 g/l orthophenyl phenol and the rest water. The dyeing time was 30 minutes and the dyeing temperature was 95° C. The stockings were dyed to an even shade and did not bleed or change shade upon being subjected to steam at 20 pounds per square inch gauge.

To obtain a similar shade under the same dyeing conditions in the absence of the orthophenyl phenol required 0.5% of Celliton Brown and 0.2% of Eastman Blue BNN. Celliton is a Registered Trade Mark.

WHAT WE CLAIM IS:—

1. Process for dyeing shaped articles made from solid thermoplastic oxymethylene polymers which comprises maintaining the article

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1. Process for dyeing shaped articles made from solid thermoplastic oxymethylene polymers which comprises maintaining the article



to be dyed in contact with an aqueous dispersion of a disperse dyestuff at an elevated temperature until the article assumes the desired depth of colour.

- 5 2. Process according to Claim 1, wherein the dyebath contains from 0.01 to 10.0 weight per cent of dyestuff, based on the weight of the article to be dyed, and is maintained at a temperature of from 80 to 95° C. and the
10 article is kept in contact with the hot dyebath for a period of from 30 minutes to 4 hours.

3. Process according to Claim 1 or 2, wherein the article is made from an oxymethylene polymer comprising recurring units
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having the formula $(-\text{O}-\text{CH}_2-(\text{C})_n-)$,

wherein n is an integer from zero to 5 and is zero in from 75 to 99.5 per cent of the recurring units.

4. Process for dyeing shaped articles made from solid thermoplastic oxymethylene polymers substantially as hereinbefore described. 20

5. Filaments, yarns and fabrics and articles made therefrom whenever dyed by a process as claimed in any of the preceding claims. 25

6. Dyed filamentary materials and stockings made from an oxymethylene polymer, whenever dyed substantially as hereinbefore described with reference to the accompanying examples. 30

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