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POLYESTER FILAMENTS AND LIKE STRUCTURES

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Fig. 1.

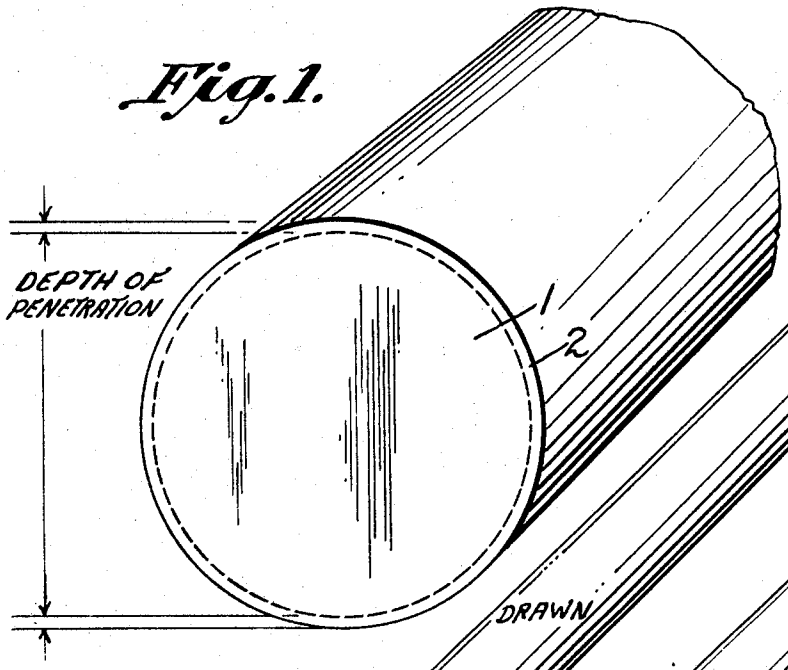


Fig. 2.

Fig. 3.

Fig. 4.

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POLYESTER FILAMENTS AND LIKE STRUCTURES

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ABSTRACT OF THE DISCLOSURE

Improved polyester filaments and fibres which have become dyeable with acid dyestuffs, characterised in that there is a substantially concentric outer layer which constitutes 30 to 80% of the fibre cross-sectional area, when viewed in transverse cross-section, which is dyeable with acid dyestuffs due to the presence of sites for such dyestuffs of nitrogenous compounds, as a result of a treatment with specified polyamines.

This invention relates to improved polyester filaments and like structures which become dyeable with acid dyestuffs.

It is well known that commercially available drawn polyester filaments and like structures which are derived from terephthalic acid, are more difficult to dye than yarns made from natural fibres or regenerated cellulose or protein fibres. This difficulty is associated with the highly oriented dense and crystalline structure of the polyester fibres which is not easily permeable by molecules of water and molecules of dyestuffs during conventional dyeing procedures. Although fabrics made entirely from polyester fibres can be dyed at elevated temperatures, for example 120 to 130° C. with disperse dyestuffs, the dyeing with other classes of dyestuffs, particularly acid dyestuffs, is difficult or impossible.

It is known (T. Vickerstaff, "Physical Chemistry of Dyeing," London, 1950, Oliver and Boyd) that an improvement in the rate of dyeing with temperature is due to an improvement in the rate of diffusion of dyestuffs into the oriented drawn fibre which in turn is due to an increase in the molecular mobility of the structure of the fibre with temperature, and we have found that whilst it is desirable to lower the transition temperature (T_g) of polyethylene terephthalate fibre to improve the dyestability, care must be taken that other valuable properties, for example, pleat retention, are not seriously impaired. Thus, it would be desirable to have a region of better dyeability with acid dyestuffs on the outside of the fibre which may be obtained by providing sites for such dyestuffs in the polyethylene terephthalate to produce a region which is modified to be dyeable with acid dyestuffs and an unmodified region which form the inner core of the fibre, so that improved dyeability and excellent pleat retention and crease resistance would be retained. Such a combination of desirable properties may be obtained by the use of a fibre with an outer layer or skin of material and an unmodified core. In U.S. Patent 3,251,913 these polyester structures may be obtained by treating the polyester structures in their undrawn or "as spun" condition, with an inert organic liquid e.g. polyethylene glycol, followed by drawing the structures two to six times their length. However these treated structures are not dyeable with acid dyestuffs.

We have now found that good and rapid penetration can be obtained if instead of the polyglycols, certain polyamines are used. Our proposed treatment should not be confused with known amine treatments for polyester fibres. The known treatments are carried out to impart antistatic properties or in some cases improved dyeability

and, as far as we are aware, are all carried out on commercially available filaments and fibres i.e. when they are in their drawn and oriented condition. Because of this, amine compounds having small molecules must be used to achieve penetration of the drawn oriented fibre and in the case of amine compounds having large molecules, penetration is slow and unattractive. Because of the dense structure of the oriented polyester fibres penetration is slow and must be promoted by the use of high temperatures and/or assistants, such as swelling agents. But even with the help of prolonged treatment times for the amine and with the help of assistants the results are disappointing. If penetration is insufficient the improvement in dyeability is insignificant; if penetration and good dyeability are achieved the drastic treatment brings about a deterioration of other properties of the fibres, such as a lowering of tenacity, abrasion resistance and with some amines discolouration, usually yellowing. Such a discolouration makes it of course impossible to achieve bright colours, particularly in the complementary region of the solar spectrum.

We have found that only certain amines with relatively large molecules are suitable and also that the treatment must be accurately controlled in order to obtain a penetration which is, after heating, more than 30% and less than 80% of the transverse cross-sectional area of the filaments or fibres. If penetration is substantially less than 30%, deep shades cannot be achieved and even lighter shades may be lost during processing, repeated washing and in use. If penetration is substantially above 75 to 80%, degradation and in some cases yellowish discolouration takes place because of the rather drastic conditions necessary to achieve such penetration.

We therefore prefer the treatment to be carried out on the undrawn filaments which do not have such a dense structure and this is followed by drawing the filaments and heating them to promote the required penetration. The filaments thereby become dyeable with acid dyestuffs and reaction with other treating agents is also improved.

According to our invention we provide improved polyester filaments and fibres which have become dyeable with acid dyestuffs, characterised in that there is a substantially concentric outer layer which constitutes 30 to 80% of the fibre cross-sectional area, when viewed in transverse cross-section, which is dyeable with acid dyestffs due to the presence of sites for such dyestuffs of nitrogenous compounds, as a result of a treatment with specified polyamines.

We also provide a process for the manufacture of improved polyester filaments and fibres comprising treating polyester filaments with an organic liquid comprising a polyamine as hereinafter defined, in their undrawn condition, drawing the filaments 2 to 6 times their length so that not more than 20% of the cross-sectional area of the so treated undrawn filaments are penerated by said amine, followed by heating the filaments in the presence of residual amine which is present on the filaments after drawing, until a substantially outer layer of the filaments constitutes 30 to 80% of the concentric cross-sectional area, when viewed in transverse cross-section, thereby becomes dyeable with acid dyestuffs.

The treatment must be accurately controlled, since a treatment leading to a final penetration i.e. after drawing and heating, of more than 80%, renders the filaments difficult to draw, and also impairs other properties, whilst a penetration of less than 30% does not provide sufficient sites for acid dyestuffs to be commercially acceptable. The percent penetration is based on the cross-sectional area of the filaments in their drawn condition and after heating.

Filaments which may be treated according to our invention include yarns and tows e.g. melt spun from polyesters derived from terephthalic acid, particularly polyethylene terephthalate or copolyesters of polyethylene terephthalate/sebacate, terephthalate/adipate, terephthalate/isophthalate, and other copolyesters and poly (hexa hydro-para-xylylene terephthalate). Filaments of the commercial range of denier and up to 30 denier in their drawn condition may be treated.

Temperatures suitable for the treatment of the undrawn filaments with the amine are above 80° C. and below 170° C., preferably 110 to 130° C. Suitable times of treatment are up to 1 minute, preferably 1 to 30 seconds. At room temperature the amines are very much less active and processing can therefore be continued without substantially impairing the filaments.

At temperatures in the preferred range and using yarns of about 6 denier per filament, a suitable immersion time is of the order of 5 seconds. Under these conditions, however, only slight acid dye uptake is obtained, if the temperature is reduced below 110° C., and at temperatures considerably above 130° C. the yarn cannot be drawn satisfactorily.

It should be appreciated that these temperatures apply only to filaments of approximately six denier per filament in the undrawn condition and a treatment time of 5 seconds; thus if the treatment time is reduced slightly, higher temperatures will become necessary, whereas if the treatment time is increased temperatures lower than 110° may be used. Conversely if the denier is increased either the treatment time should be increased or the treatment temperature.

After the treatment with the polyamines, which are specified hereafter, the filaments are preferably drawn immediately e.g. in water at temperatures between 60 and 100° C. in a continuous process, 2 to 6 times their length and this drawing is then followed by a heat treatment, preferably using heat setting conditions. Temperatures for the best treatment between 100 to 210° C., preferably 110 to 150° C. are suitable with times up to 40 minutes, preferably 5–20 minutes duration.

The filaments before the treatment should preferably be in their undrawn state defined in that the natural draw ratio at room temperature makes them capable of being elongated at least twice their length.

The polyamines which are suitable for our treatment are non ionic and should have an average molecular weight of about 110 to 1,000, preferably 200 to 600. These polyamines may be prepared from alkylene oxide condensates having at least two terminal hydroxyl groups. Examples of alkylene oxide condensates which are suitable for conversion to polyamines include the polyoxyethylene glycols, ethylene oxide condensates of polyhydroxy compounds such as glycerol, sorbitol or pentaerythritol, ethylene oxide condensates of amines such as methylamine, ethylamine and cetylamine. The molecular weight of the alkylene oxide condensate should lie within the range 110–1000.

Amines corresponding to the formula

$$NH_2—CH_2(CH_2—O—CH_2)_nCH_2—NH_2$$

where n is 3 to 12 are preferred, they are liquids or low melting solids. If higher molecular weights are used penetration is slow and difficult. At molecular weights substantially below 200 penetration is rapid, but the compounds become leached out during subsequent processing or when washing and scouring prior to dyeing.

It will be appreciated that with increasing cross-sections of the filaments treatment times must be prolonged to obtain sufficient penetration. It follows that the treatment should be carried out on filaments of substantially the same effective cross-section and differing by not more than 50% in cross-sectional area.

This means that when treating a multi-filament yarn each individual filament of any desired suitable cross-section, should be of a substantially uniform denier throughout its length and preferably the denier of each filament should be substantially the same and differ by not more than 50% from another, in the same yarn. It will be appreciated that unless there is such a uniformity, some of the filaments will be penetrated too deeply with the treating liquid and thereby become undrawable, or conversely that some filaments may become penetrated by less than 30% of their transverse cross-sectional area, which would render them commercially undesirable because of differences in shade and loss of colour during further processing and use, e.g. repeated washing.

The treatment may be carried out by immersion in the liquid but other methods of treatment may be used such as application by applicator rollers or by spraying, care being taken that at least 10%, preferably 20 to 40% of the liquid based on the dry weight of the structure, is available at the selected treatment temperature on the whole surface of the structure. If desired, various surface active agents may be added in small amounts to ensure a homogeneous treatment, and care should be taken to reduce the risk of entrapping air between the liquid and the surface of the filaments during treatment. It will be appreciated that the liquids may be applied at low temperatures, conveniently at room temperature, and that the structures may be subsequently heated to the required temperature for a sufficient time and before drawing, providing the required amount of liquid is present during heating to affect penetration of the structure and conversion after drawing, of 30–80%, preferably 45–75% of the structure to the modified constitution. After this treatment with the polyamine the filaments are drawn two to six times their length as spun, and heat set.

The attached drawing illustrates but does not limit our invention. FIGURES 1–4 show a filament in diagrammatic perspective view, partly in cross-section, in the successive stages of the process.

Referring to the drawing a polyester filament **1** is treated at an elevated temperature with a polyamine which penetrates only to a small extent through the outer periphery of the filament forming an annular outer layer **2**. As shown in FIG. 1, the filament is then drawn about 4 times its length and assumes the appearance as shown in FIG. 2 at **1B** with the annular layer **2B**, penetrated by the polyamine before drawing. On heat-setting the polyester fibre at e.g. 140° for 10 minutes, the polyamine penetrates and the fibre has the appearance shown in FIG. 3 at **1C** with the penetrated outer layer **2C** when the fibre is then dyed the fibre assumes the appearance shown in FIG. 4 at **1D** with the dyed area **2D**.

The following examples illustrate but do not limit our invention:

EXAMPLE 1

An undrawn tow of polyethylene terephthalate of intrinsic viscosity of 0.67, containing filaments of about six denier per filament, is passed through liquid polyalkylene oxide amine

$$NH_2CH_2(CH_2OCH_2)nCH_2NH_2$$

having a molecular weight of 300 at 125° C., at such a rate that the contact time is five seconds. The yarn is subsequently drawn in water at 95° C. to a draw ratio of 1:4. The drawn tow is crimped and heat set at 140° C. for ten minutes and dyed in an aqueous acid dye bath using azogeranine when a medium shade is obtained. An examination of dyed cross-sections of the filaments indicates a dye penetration of 75% of the cross-sectional area.

If desired, the treated structure may be quaternised e.g. with dimethylsulphate to minimise the tendency of the amine compound to diffuse out of the structure.

EXAMPLE 2

A polyamine as used in Example 1 is used for immersing polyethylene terephthalate filaments having a spun yarn filament denier of six, for 2 seconds at 130° C. The filaments are then drawn and crimped as in Example 1 and heat set again at 140° C. for 10 minutes and dyed. The dye penetration in a concentric outer layer of the circular cross-section of the filaments is found to be 45% of the total cross-sectional area.

EXAMPLE 3

The procedure of Example 1 is repeated also with a polyamine of the same average molecular weight for 14 seconds at 115° C. and but the polyethylene terephthalate filaments have a spun denier of 20 in their undrawn condition. After drawing, crimping, heating and dyeing as in Example 1 dye penetration is found to be 50% of the cross-sectional area.

EXAMPLE 4

The procedure of Example 1 is repeated but using polyethylene terephthalate undrawn filaments of denier 20 per filament and the immersion time in the polyamine is 24 seconds at 100° C. The dye peneration is found to be 30% of the cross-sectional area.

The following examples are given for comparison.

EXAMPLE 5

Polyethylene terephthalate undrawn yarn is treated with a polyamine of molecular weight 300 as in Example 1 but the temperature of the polyamine is kept below 100° C. and the immersion time at 5 seconds. After drawing, heat setting and dyeing as in Example 1 it is found that the dye uptake is only just detectably pink and penertation is less than 30% of the cross-sectional area of the fibres.

Since the filaments are processed in exactly the same way as in Example 1 it is clear that the heat setting process is in itself not effective because the same quantity of polyamine is present during heat setting and also the temperatures below 100° C. are insufficient for treatment times of 5 seconds.

EXAMPLE 6

A drawn yarn which has not been treated in the undrawn condition is heat-set in the presence of an amine as used in Example 1 at a temperature of 160° C. for 1 hour. The filaments again show no appreciable dye uptake i.e. they are only pust detectably pink.

Penetration of dye is less than 30% of the cross-sectional area in each filament.

This example therefore illustrates again the advantages of treating the filaments in their undrawn condition with the polyamine and that even a higher setting temperature than that used in Example 1 does not in itself bring about sufficient penetration of the amine on the drawn filaments.

EXAMPLE 7

A drawn yarn as used in Example 1 which is wet with the same polyamine (100% by weight of fibre) is heat set in an air oven at 170° C. After 10 minutes the sample has no dyeability with acid dyestuffs. After half an hour heating the sample is only partly dyeable with acid dyestuffs in places where degradation has also taken place. This degradation is apparent from an embrittlement of the filaments which would make it useless for conventional textile processing and in use. Even the parts that are dyeable only dye to a faint shade of pink.

This example illustrates that penetration is insufficient under these conditions and even higher heat setting temperatures and longer times of heating do not bring about an acceptable improvement in penetration. Moreover there is an increasing tendency of the polyamine to decompose.

The foregoing Examples 1–4 therefore illustrate the advantages of testing the polyester filaments with polyamine in their undrawn state followed by drawing and heat setting. Under these conditions good penetration of the polyamines and hence reasonable shades of acid dyes are obtainable, even at low subsequent heat setting temperatures and short heat setting times.

The comparative Examples 5–7 illustrate that heat setting temperatures and conditions alone, even in the presence of the polyamine do not appreciably improve dyeability with acid dyestuffs. If heat setting conditions are prolonged and the temperatures are raised to 160, 170 and even up to 180° C. in the presence of an amine, dyeability with acid dyestuffs can be improved but severe degradation of the fibre and the polyamine makes the former substantially useless for textile applications when it would be subject to wear, such as in garments.

What I claim is:

1. Improved filaments and fibres of polyesters having ester groups in the polymer chain which are dyeable with acid dyestuffs and which have

a substantially concentric outer layer which constitutes 30 to 80% of the filaments and fibre cross-sectional area, when viewed in transverse cross-section, said concentric outer layer comprising said polyester impregnated with polyamines and being dyeable with acid dyestuffs due to the presence of said polyamines, the polyamines providing sites for said acid dyestuffs and having the formula

$$H_2N—CH_2—(CH_2—O—CH_2)_n—CH_2—NH_2$$

where n is 3–12,

the interior of the polyester filaments and fibres also comprising said polyester but being free of amine.

2. The improved polyester filaments and fibres as claimed in claim 1 in which the polyester is polyethylene terephthalate.

3. Improved polyester filaments and fibres as claimed in claim 1 in which the polyester filaments contain at least one copolyester of terephthalic acid selected from the group consisting of polyethylene-terephthalate/sebacate, polyethylene terephthalate/adipate, polyethylene terephthalate/isophthalate, and poly (hexa-hydro-para-xylylene terephthalate).

4. Improved multi-filament polyester yarn comprising filaments as claimed in claim 1 in which all the filaments in a yarn are of substantially uniform denier throughout their length and the denier of each filament differs by not more than 50% from another in the same yarn.

5. Improved polyester yarn as set forth in claim 1 in which said outer layer constitutes 45–75% of said cross-sectional area.

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