Feb. 6, 1968 N. B. SMITH ETAL 3,367,150

APPARATUS FOR THE COLORATION OF FILAMENTS MELT SPUN FROM SYNTHETIC LINEAR POLYMERS

Original Filed Dec. 26, 1961 3 Sheets-Sheet 1

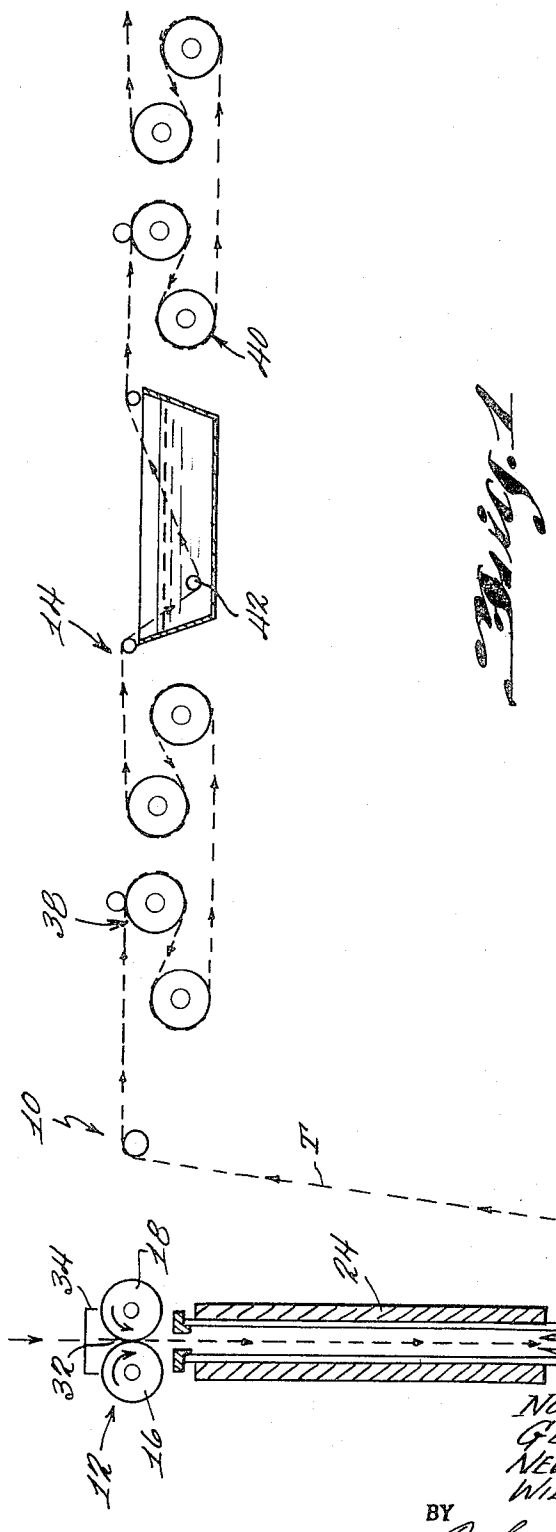


Fig. 1

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3 Sheets-Sheet 2

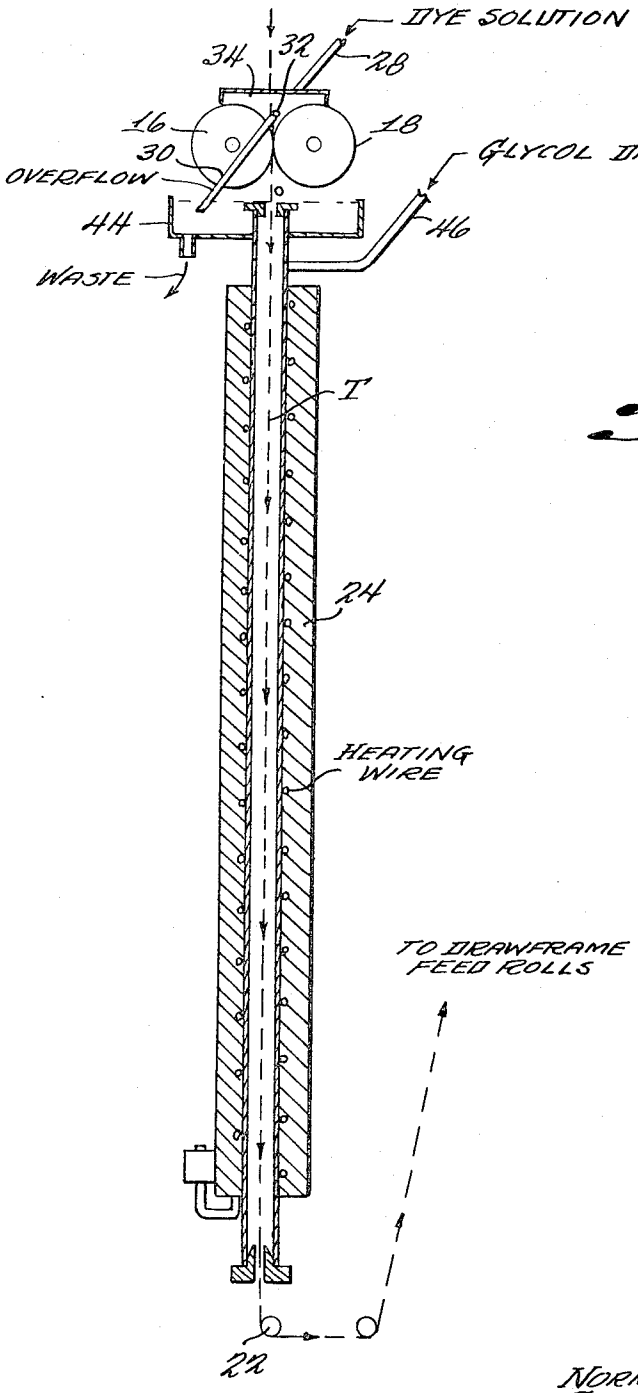


Fig. 2

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Fig. 3

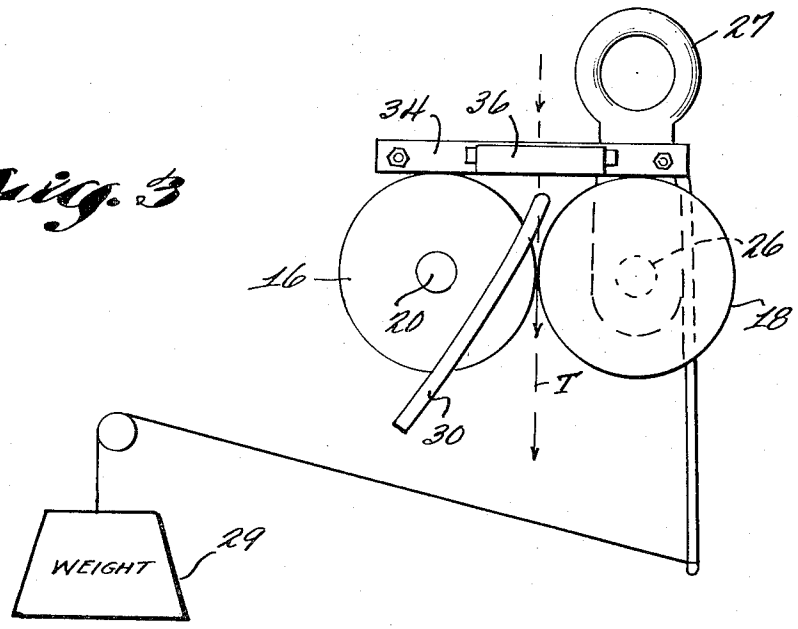
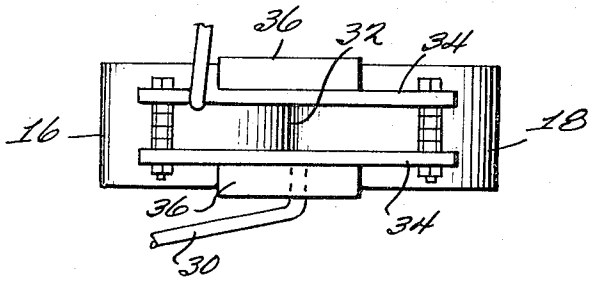


Fig. 4



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3,367,150

APPARATUS FOR THE COLORATION OF FILAMENTS MELT SPUN FROM SYNTHETIC LINEAR POLYMERS

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Original application Dec. 26, 1961, Ser. No. 162,248, now Patent No. 3,241,906, dated Mar. 22, 1966. Divided and this application Jan. 28, 1966, Ser. No. 544,322
Claims priority, application Great Britain, Dec. 28, 1960, 44,463/60
3 Claims. (Cl. 68—5)

ABSTRACT OF THE DISCLOSURE

A pad-mangling system for applying dye solution and a draw frame for drawing the filaments, comprising two resilient rolls, one fixed to a shaft driven fro mthe feed rolls of the subsequent draw frame and the other running on a floating shaft, which can be loaded to press the rolls together a controlled amount, side plates with heating and feed means for maintaining dye solution in a padding bath between the nip of the resilient rolls at a constant level and temperature followed by the draw frame with feed rolls driven at the same speed as the resilient rolls on the pad-mangling system, and draw rolls driven 3–8 times faster than the feed rolls with means for heating the filaments and means for removing dye solution which has not penetrated the filaments and means for winding or forwarding the dyed and drawn filaments.

The foregoing abstract is not intended to be a comprehensive discussion of all of the principles, possible modes or applications of the invention disclosed in this document and should not be used to interpret the scope of the claims which appear at the end of this specification.

Reference to related application

This is a division of our copending application Serial No. 162,248, filed December 26, 1961, and issued as U.S. Patent 3,241,906.

This invention relates to a novel apparatus for dyeing synthetic polymer filaments and fibres made e.g. from polyesters, copolyesters, polyamides and polyolefins.

Commercially available polyester filaments and fibres which are in their drawn condition are difficult to dye and many processes are used to overcome these difficulties. Thus it has been proposed to melt spin filaments, which are obtained from a polyester already coloured or pigmented in the melt. This process is now used, on a large scale, for the manufacture of filaments and fibres coloured white or black. It has the disadvantage that, for economic reasons, large batches of fibres or filaments have to be produced and therefore the range of colours which can be made commercially available must be limited.

It is usually preferred to colour fibres by application of dyestuffs. The best known dyes used for polyester fibres and filaments are disperse dyes, also known as acetate dyes. These are sold in finely divided form, together with a dispersing agent, and they are applied to the fibres, in commercial practice, from aqueous dispersions assisted by dyeing assistants, dye carriers or elevated temperatures

at superatmospheric pressure. The disperse acetate dyes can also be applied to polyamide and polyolefin fibres.

It is well known in the art that the strength of the filaments and fibres made from polyesters, polyamides and polyolefins can be considerably increased by a process, in which melt spun filaments are elongated to between 5 and 8 times their original length. Indeed, all such fibres and filaments have to be strengthened by a drawing process. During this process the polymer molecules in the filaments or fibres become oriented and more closely packed, so that access by other molecules, e.g. dyestuff molecules becomes more difficult and in the case of polyesters, much more difficult, Dyeing processes suggested hitherto have been intended to apply to fully drawn filaments and fibres, usually in yarn, tops or fabric form and commercially these processes have been carried out on such fully drawn material using high temperatures. Suggestions of dyeing undrawn melt spun material have not lead to successful exploitation because of accompanying changes in the filaments during the dyeing operation which render the filaments undrawable.

We now provide apparatus in which a novel colouring process is integrated into this necessary drawing process, so that both colouring and strengthening of the filaments or fibres can be performed in one continuous operation, and advantage can be taken of the permeability of the filaments or fibres in their undrawn condition.

This is a process which can be operated by the polyester yarn and fibre manufacturer because of its speed, effectiveness and relative ease of control.

According to our invention, we provide apparatus for rapidly, continuously colouring filaments melt spun from synthetic linear polymers in an integrated operation, comprising applying a dye, as hereinafter defined, dissolved, without dispersing agents or other diluents, in an organic substantially non-aqueous hot solvent to undrawn melt spun filaments having a birefringence of less than 10×10^{-3} derived from synthetic linear polymer, as hereinafter defined, under conditions such that penetration of the dye into the filaments is 60% of the cross-sectional area, or more, followed by drawing the filaments three to six times their length. The dye may be applied at temperatures up to 150° C. for a very short time, preferably less than 30 seconds using an organic solvent which dissolves the dye but does not cause embrittlement of the filaments or fibres in their undrawn condition. The dye must be free from any kind of harmful diluents, soluble in the organic solvent and substantive to the fibre.

We find that in the actual dyeing operation, the distribution of dye between solvent and fibre obeys the Distribution Law (Glaastone, "Texbook of Physical Chemistry," second edition p. 736). Whilst it is well known that this Law applies to the dyeing of fully drawn polyester fibres with disperse acetate dyes from aqueous dispersions (Vickerstaff, "The Physical Chemistry of Dyeing"), its application to undrawn yarn in a solvent dyeing system has not previously been disclosed. Thus in this dyeing system

$$\frac{\text{Concentration of dye in the fibre}}{\text{Concentration of dye in the solvent}}=\text{constant}$$

or

$$C_f/C_s=K$$

for immersion times greater than five seconds. At less than five seconds immersion the penetration of dye into

the fibre is not complete and the dyeing system has not reached practical equilibrium.

Heavy shades of colour on synthetic polymer filaments are produced when the concentration of dye in the fibre is about 2%, or more. Therefore, to obtain a full range of shades of colour up to heavy shades, in our solvent dyeing system, about 2% or more of dye should be dyed onto the fibre. Thus in Equation 1, the concentration of dye in the fibre must equal or be greater than 2%, i.e. $C_f \geqslant 2$ and hence the combinations of dyes and solvents which can be used are defined by the condition $KC_s \geqslant 2$.

The system works best when the dye is in true solution in the solvent, so that C_s should not exceed the saturation solubility of the dye in the solvent at the temperature of dyeing.

Thus $C_s \leqslant C_{sSat.}$ The condition for choosing dyes and solvents then becomes

$$KC_{sSat.} \geqslant \cdot 2 \qquad (2)$$

Dyes, of course, should be chosen from those dyes which are substantive (i.e. fixed and permanent) to the fibre being dyed. For polyester fibres and filaments these are usually in the class of dyes called the disperse acetate dyes. Solvents must be chosen from those which are sufficiently good solvents of the chosen dye to satisfy Equation 2 and which also have no adverse effect on any of the properties of the dyed, drawn fibre. For a commercial processs, solvents of low volatility, inflammability and tenacity are preferred. Solubility in water is an advantage in that water can be used to wash off solvent and unused dyestuff from the treated, dyed, undrawn or drawn fibre or filaments.

We find that high boiling organic liquids such as ethylene glycol, diethylene glycol, polyglycols and ethylene oxide condensates of average molecular weight of up to 6000, preferably between 200 and 1000, their esters and others and mixtures thereof, dimethyl and diethyl sebacate, oleic acid, meaitylene, triphenyl phosphate, and glycerol are all suitable solvents and work best in the region between 100 and 150° C., the filaments being in contact with the dye solution for a time less than 30 seconds, preferably between 5 and 15 seconds. Lower boling solvents such as trichlorethylene, carbon tetrachloride, acetone, benzene and glacial acetic acid, are also suitable and work best at or near their boiling points. Because of the higher volatility of these solvents it is necessary to fit the dye bath with means for condensing and returning to the bath vapours from the boiling solvents. Immersion times of up to 30 seconds, proferably between 5 and 15 seconds are again required.

Preferred solvents for use in apparatus are in the series from ethylene glycol, through diethylene glycol to polyethylene glycol of up to 1000 average molecular weight and from these we select ethylene glycol as the best solvent for use with polyester fibres. It will be appreciated that mixtures of these solvents may be used which are compatible with each other and which are liquid under treating conditions. The coefficient K in Formula 2 is preferably 0.2–1.6.

The shades of colour which can be obtained by our apparatus can be varied by altering the temperature of the dyestuff solution, or by increasing the concentration of the dyestuff in the solvent, but below saturation level. We find moreover that the dyestuff penetrates the spun undrawn yarn very rapidly, so that after 5 seconds immersion, only small improvements in shade can be obtained by increasing the immersion time. Because of this rapid penetration into the undrawn yarn, it is possible, if so desired, to remove excess dyestuff solution before the drawing stage of the process, without any deleterious effect on the colour of the drawn yarn.

We have found, however, that a number of organic liquids, whilst being excellent solvents for dyestuffs and being very suitable for transferring dyestuff into the undrawn fibre, have an effect on the undrawn polyester fibre whereby it is embrittled and rendered difficult or impossible to draw, after colouring. Such solvents are cyclohexanene, cinnamaldehydre, benzyl alcohol and chloroform. These solvents are all known to diffuse rapidly into polyesters but they affect the crystallinity of the material.

With polyamide and polyolefin fibres this effect was also apparent when solvents known to penetrate the fibres easily, were used.

Undrawn fibers and filaments from copolyesters such as polyethylene sebacate/terephthalate containing up to 15 mole percent of sebacate component, can also be treated and we find that they give improved shades of colour when treated acording to our invention.

Colours can be chosen from classes of dyestuffs, such as disperse acetate dyes and optical whiteners (e.g. "UVITEX" R.T.M.) the unsulphonated bases of acid wool dyes, or from pigments, such as the oil soluble pigments and the vat pigments. However, with regard to the conditions already defined for choosing colours for use in our process, disperse acetate dyes are the most substantive towards polyester filaments.

In applying the process described herein to the continuous dyeing of undrawn filaments, that is to filaments with a birefringence less than 10×10^{-3}, it is commercially advantageous to treat a large number of filaments at the same time, in the form of a tow. Because such tows have a high mechanical pick-up of liquid, it is necessary to restrict the pick-up of liquid from the solvent dye bath by mangling the tow as it leaves the dye bath so that the pick-up of solution is reduced from about 150% to about 10%. The pickup is defined here as the weight of the liquid present on a given length of the wet tow divided by the weight of the same piece of tow when dry. Alternatively and preferably, the solution of dyestuff can be applied to the tow of undrawn filaments by a pad-mangling system so that the amount of dye solution applied is controlled to a pick-up of 25–35%. The wet tow must then be maintained at the temperature required for dyeing and for the required time for example in a hot air furnace, or by sliding contact with a hot plate or in a radiative furnace until penetration of the dye into the filaments is 60% or more.

Exemplary apparatus according to the present invention is shown in the attached drawings wherein;

FIGURE 1 is a somewhat schematic side elevation view of apparatus embodying principles of the present invention;

FIGURE 2 is a side elevation view, drawn to an enlarged scale to illustrate further detail of the pad mangle and furnace of FIGURE 1;

FIGURE 3 is a side elevation view, drawn to an enlarged scale to illustrate still further detail, of the pad-mangle of FIGURE 2; and

FIGURE 4 is a top plan view of the pad mangle of FIGURE 3 with the resilient rolls shown sectioned along a horizontal plane intersecting their axes.

Referring to the drawings, a suitable apparatus **10** for dyeing filament tows T with a pad-mangling system **12** and a draw frame **14** for drawing the filaments comprises two resilient e.g. rubber covered rolls **16**, **18**, one fixed to a shaft **20** driven, e.g. by a gear box drive from the feed rolls **22** of the subsequent draw furnace **24** and the other running on a floating shaft **26** having a mounting **27** which can be loaded at **29** to press the rolls **16**, **18** and the filaments between the rolls together, by a controlled amount, means **28**, **30** for feeding and maintaining dye solution in a padding bath **32** between the nip of the resilient rolls **16**, **18** at a constant level and means for maintaining the bath at a constant temperature, such as side plates **34** containing the resilient rolls **16**, **18** with low voltage electric thermostatic or controllable cartridge heaters **36**, which float freely on the rolls, a feed pipe **28** for the dye solution and an overflow return pipe **30** in the

side plates **34** for maintaining the padding bath at a constant level and temperature; on the draw frame feed rolls **38** driven at the same surface speed as the resilient rolls **16**, **18** of the pad-mangling system **12** and draw rolls **40** 3–8 times faster than the feed rolls with means for heating the filaments just before or on the draw frame. The simplest form of heating means is a hot water bath **42** between the feed and draw rolls, but if desired alternatively or simultaneously the feed and/or the draw rolls may be heated, or any other known suitable heating means may be used during drawing. Dye solution which has not penetrated into the filaments may be removed before, during or after drawing by circulating liquid baths or by sprays. If the filaments become wet during drawing, i.e. if dry heating means are not used during drawing, it is necessary to complete the dyeing treatment before drawing. A suitable heating device comprises a thermostatically controlled heater tube mounted vertically below the pad-mangle. A heater tube 1 m. long has been found suitable in which the temperature is maintained as in the pad-mangle. Between the rolls and the heater tube is a drip tray **44** to collect any drips or splashes of the dye solution. A solvent, e.g. glycol, drip feed may be introduced at the top of the tube **24** through the conduit **46** to keep the tube-atmosphere saturated with solvent, e.g. glycol, vapour without directly contacting the filaments. The undrawn tow of filaments passes into the pad-mangling system where it picks up 25–30% of a solution of dye in solvent at a temperature appropriate to the solvent, passes out of the nip of the mangle directly into the heater tube, the whole tow running at a speed such that there is a dwell time of between 5 and 30 seconds in the hot zone, thereby substantially completing the dye treatment. The dyed undrawn tow T then passes directly onto a set of feed rolls **38**, through a drawing zone **14** and onto a similar set of drawing rolls **40** rotating at between 3 and 6 times the speed of the feed rolls **38** in the case of polyester and polyamide filaments and up to eight times in the case of polypropylene filaments. The dyed, drawn yarn may then be washed free of solvent and unused dyestuff by water sprays or by a circulating water bath, crimped, dried, heat set to reduce the residual shrinkage to one percent or less in boiling water for one minute and, if desired, cut into staple fibres.

The following examples illustrate, but do not limit our invention in which parts and percentages are by weight, as applicable.

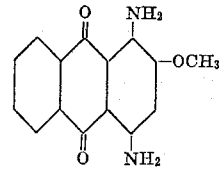
Example 1

Melt spun undrawn polyethylene terephthalate filaments in the form of 2000 denier about 200 filament tow is continuously immersed by passage through a dyebath solution containing 1 part of dye C.I. (Colour Index) No. 62015 in 99 parts of ethylene glycol, heated to 130° C. at about 150 feet/min., under conditions such that the dwell time in the dyebath is 5 seconds. The dye concentration and dyebath level are maintained to obtain a uniform colour on the filaments. The dyed tow is then continuously taken up by feed rolls of a draw frame where the filaments are elongated 3.6 times their length in steam at 95–100° C. The tow is then passed over a series of rolls and sprayed with hot water at 60–70° C. to continuously remove excess dye and solvent. The still wet tow is passed to a stuffer box crimper and crimped, dried and the crimped tow is heat-set at 140° C. in a relaxed condition, whereby the residual shrinkage in boiling water is reduced to less than 1%.

A crimped tow of filaments of an excellent shade of mauve-red is obtained. The birefringence of the undrawn uncoloured filaments is 0.005 and of the drawn filaments 0.21. The tow is cut into staple fibres which are mauve-red and which shrink less than 1% in boiling water.

Example 2

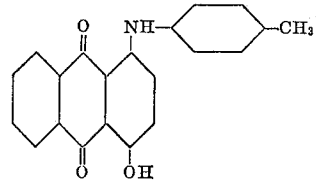
A solution of five parts of dyestuff C.I. (Colour Index) No. 62015



in 95 parts of ethylene glycol, used under the same conditions as Example 1, produces a very heavy red shade on the finished filaments, which when cut into staple fibre lengths shrink less than 1% in boiling water.

Example 3

A solution of two parts of the pigment C.I. Number 60725



in 98 parts of polyethylene glycol (molecular weight 600) used as in Example 1 produces a heavy shade of blue on the finished tow. Fibres cut from the crimped filaments when made up into fabrics do not pill and shrink less than 1% in boiling water.

It should be appreciated that by the means described herein it becomes possible for a fibre manufacturer to supply filaments and fibres which have been dyed uniformly in a wide range of colours and shades and which may be stabilised, e.g. by means of a crimp setting process, so that the final product maintains its tenacity and elongation and does not shrink, or shrinks, e.g. less than 1% in boiling water, depending on the stabilising treatment. As far as we are aware, all commercially available synthetic and particularly polyester staple fibres shrink a further amount during any subsequent commercial high temperature dyeing treatment, which is usually carried out on fabrics with a loss in tenacity and an increase in evolution. In contradistinction our dyed fibres obviously do not require dyeing but in their stabilised condition, in fabric form, they do not shrink. Thus using our dyed filaments and fibres which have been stabilised, it is possible to make the required design and colour in fabrics which do not require any further dyeing treatment and therefore do not shrink, moreover the original tenacity and elongation of the fibre is maintained.

Although the foregoing description relates to filaments and fibres, we believe the process to be applicable also to undrawn monofilaments, films and similarly shaped objects.

What we claim is:

1. An apparatus for the coloration of filaments melt spun from synthetic linear polymers which comprises a pad-mangling system for applying dye solution and a draw frame for drawing the filaments, comprising two resilient rolls, one fixed to a shaft driven from the feed rolls of the subsequent draw frame and the other running on a floating shaft, which can be loaded to press the rolls together a controlled amount, side plates with heating and feed means for maintaining dye solution in a padding bath between the nip of the resilient rolls at a constant level and temperature followed by the draw frame with feed rolls driven at the same speed as the resilient rolls on the pad-mangling system, and draw rolls driven 3–8 times faster than the feed rolls with means for heating the filaments and means for removing dye solution which has not penetrated the filaments and means for winding or forwarding the dyed and drawn filaments.

2. An apparatus according to claim 1 comprising a heating device for the filaments comprising a thermostatically controlled heater tube vertically below the padmangle.

3. An apparatus according to claim 1 comprising a tubular heating device for the filaments below the padmangle with means to keep the tube atmosphere saturated with solvent vapour without directly contacting the filaments.

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IRVING BUNEVICH, *Primary Examiner.*