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EXAMPLE I

IMPROVING THE DYEING UNIFORMITY AND
THERMOSTABILITY OF UNDRAWN ACRYLO-
NITRILE POLYMER FILAMENTS BY APPLYING
STEAM UNDER PRESSURE

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No Drawing. Application March 27, 1953,
Serial No. 345,234

4 Claims. (Cl. 8-130.1)

This invention relates to improving the uniformity of
fibers, filaments, yarns and similar articles prepared from
acrylonitrile polymers. More particularly, this invention
is directed to improving the short length dyeing uni-
formity and thermostability of continuous filament yarns
from such polymers.

Yarn may be produced by an evaporative spinning
procedure in which the acrylonitrile polymer is initially
in solution. The yarn is wound up at the spinning ma-
chine while it contains 20%, 30%, 40% or more of
residual solvent; it is then washed with water or with
water containing a small amount of solvent to reduce
the residual solvent to below 2.5%. Thereafter, the
yarn is drawn from 2 to 10 times or more in a pressure
steam drawing cell. Such yarn is frequently character-
ized by short length dyeing non-uniformities apparently
due to more porous or lower density sections which may
dye several shades deeper than the main portion of the
yarn. Moreover, these yarns, when subjected to treat-
ments at elevated temperatures, occasionally darken se-
verely and non-uniformly.

It is therefore an object of this invention to provide
an improved procedure for processing the spun yarn
prior to drawing it to improve dyeing uniformity and
to improve thermostability. Other objects will be ap-
parent from the description that follows.

The objects of this invention are accomplished by
subjecting the wound package of substantially undrawn
yarn, after the solvent has been extracted to reduce the
residual solvent therein to below 2.5%, to steaming
at a pressure between atmospheric and 40 pounds per
square inch gauge for a period of time of from a few
minutes to 2.5 hours or more, which time is roughly
inversely proportional to the pressure. The temperatures
used in the steaming are from about 100° C. to about
142° C. The steaming of the yarn cakes may be carried
out in an autoclave such as one constructed from a piece
of 8 inch pipe about 6 feet long, supported horizontally
and closed at its ends with flanges, one of which may
be made easily removable. At the top near one end,
a steam inlet pipe is connected through a pressure regu-
lator and at the bottom near the other end a drain con-
nection is located and provided with a steam trap and a
by-pass vent line around the trap. The cakes of yarn
can be easily slid into this pipe autoclave with ample
room for the steam to circulate around the outside of
the cakes, through the cake core and between the ends
of adjacent cakes. Other apparatus may be used as, for
example, autoclaves of other shapes and sizes. A large
diameter pressure vessel that permits loading of the cakes
vertically on spindles may be employed. In the steam-
ing of a plurality of cakes, the packages are sufficiently
separated to permit free access of steam with the cakes
at the ends and all around the cake.

The examples given below will serve to illustrate con-
ditions for carrying out this invention and are not limi-
tative.

1,370 denier-80 filament yarn produced by dry spin-
ning acrylonitrile homopolymer from solution in N,N-
dimethylformamide was wound up outside the spinning
cell on to a perforated core about 11 inches long and
3.5 inches outside diameter. The yarn cake itself was
about 10 inches long. As collected, the yarn contained
about 30% residual solvent and this was reduced to
about 1.7% solvent by pressure washing with water
containing a small amount of solvent and heated to
100° C. When this yarn without further treatment was
drawn in a steam pressure cell to 8 times its undrawn
length and thereafter heat relaxed 12%, a yarn of about
200 denier was obtained. The drawn yarn after twist-
ing to about 0.3 turn per inch was knitted into tubing
and dyed with Celanthrene Pure Blue BRS and numerous
short length dyeing flashes were noted throughout the
sample. These faults were more abundant in the yarn
from the outside 10% of the original spinning package,
and, therefore, this portion of the cake was selected for
the comparative tests that follow.

Cakes of washed yarn such as previously described
were subjected to steaming in the pipe autoclave de-
scribed above at the various conditions set forth below
and after the cakes were cooled, the yarn was drawn,
relaxed and twisted as earlier described in this example.
Yarn comprising the outside 10% of the spinning cake
was then knitted into tubing, dyed with Celanthrene
Pure Blue BRS and then compared with "control" sam-
ples which were similarly prepared except that the yarn
was drawn without being subjected to previous steam-
ing. Steaming removes about 90% of the short length
dyeing defects and the pressure and time conditions
that give this degree of improvement are set forth in
the chart below as well as conditions for a few cases
showing less improvement. The time of steaming shown
is from the time the pressure reaches 1 pound per square
inch less than the pressure of the test to the time the
autoclave is vented, which follows immediately after
shutting off the steam.

Percentage short length defect removal with steam

Steaming Pressure, Pounds/Sq. In. (Gauge)	Temp., ° C.	Steaming Time, Minutes								
		5	10	20	30	45	60	90	120	150
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
40	142	85	90							
25	131	45		90						
20	126				90					
15	121					90				
10	115						90			
5	108	None		30				90		
0	100			None			30		60	90

From these data was developed the empirical formula
that follows and subsequent tests on 675 denier-40 fila-
ment undrawn yarn as well as additional tests on 1,370
denier-80 filament undrawn yarn confirmed the accuracy
of the formula for gauge pressures between 0 and 40
pounds per square inch:

$$P\sqrt{t}=188\pm20$$

where P, the absolute pressure in pounds per square inch,
is equal to the gauge pressure plus 14.7 and t is the
time in minutes necessary to remove 90% of the short
length defects. There will, of course, be some minor
variations from a constant value, but within the pressure
limits previously specified this value will not vary a great
deal and the plus or minus 20 (about plus or minus 10%)
covers these minor variations i. e., between 168 and 208.

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EXAMPLE II

A washed package of undrawn 675 denier-40 filament polyacrylonitrile yarn such as described under Example I was subjected to steaming at 15 pounds per square inch gauge pressure for 40 minutes and thereafter was steam drawn and further processed as described under Example I. No dyeing irregularity could be found in the knitted dyed sample whereas a "control" sample subjected to the same processing steps but unsteamed showed numerous dye flashes. This pressure and time of steaming when substituted in the above formula gives a value of 188.

EXAMPLE III

A washed package of undrawn 1,370 denier-80 filament yarn of acrylonitrile/methylacrylate copolymer 94/6 prepared as described under Example I is subjected to steaming at 20 pounds per square inch gauge pressure for 30 minutes and thereafter is steam drawn and further processed as described under Example I. No dyeing irregularity can be found in a knitted dyed sample.

Steam pressures above about 40 pounds per square inch gauge are to be avoided because the time of treatment is so short that good control is impossible and not infrequently the short length dyeing irregularity was found to reverse itself and become a light dyeing streak instead of a dark dyeing streak relative to the bulk of the yarn. Prolonged steaming at pressures below 40 pounds per square inch gauge produces a yarn with poorer drawing continuity and is therefore undesirable. For reasons of control and reproducibility as well as economics, it is preferred that the pressure of steaming be maintained between about 10 and 25 pounds per square inch gauge which means the time of steaming is reasonable, being between about 20 minutes and about 60 minutes.

While the yarn packages are placed in a closed or pressure vessel containing steam, it is to be noted that the yarn is in static contact with the steam. The steam is not forced through the yarn windings. The packages and steam are so related that the steam can get all around the yarn body and steam does get into the body to some extent. If the steam is blown or forced through the package, a light dyeing (reverse) barré is invariably encountered in the final yarn. This adverse effect is not obtained in the process of this invention. The critical pressures and exposures used in the process of this invention not only produce the uniform dyeing and thermal stability desired, but prevent any adverse effects.

The yarns that are processed by this invention are generally substantially undrawn yarns produced by dry-spinning techniques. Some drawing does occur in this and in other methods for producing filaments. While certain drawn yarns can be treated with benefit in accord-

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ance with this invention, the process described herein is preferably applied to the as-spun yarns prior to their orientation by stretching. By so doing, rather than applying the process after orientation, the complexity of producing a drawn, void-free yarn is materially reduced and a yarn that dyes uniformly is attained.

This invention permits production of uniformly dyeable acrylonitrile polymer yarns without adding materially to their cost. While the acrylonitrile homopolymer yarns have been most difficult to dye uniformly, this invention may also be used to good advantage with yarns of copolymers of acrylonitrile, especially those having a major amount of acrylonitrile. Those acrylonitrile polymers having an acrylonitrile content of about 85% and more are preferred. The copolymers that can be used in this invention are many and are described in such patents as U. S. 2,404,714 to 2,404,727. Steaming in accordance with this invention also reduces thermal discoloration and reduces non-uniformity of discoloration which is highly desirable for uses wherein the yarns, fibers or similar items are bonded under heat and pressure to rubber as is done in the manufacture of automobile decking.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

We claim:

1. The process of improving the uniformity of filaments which have not been subjected to a drawing operation and which contain from 85% to 100% polyacrylonitrile and from 0% to 15% of an acrylate ester copolymerized therewith, which comprises placing the said filaments in an atmosphere of steam under a pressure of from 0 to 40 lbs. per sq. inch gauge for a time between 5 and 150 minutes.

2. The process of claim 1 in which the product of the absolute pressure and the square root of the time in minutes lies between 168 and 208.

3. The process of claim 1 in which the pressure is between 10 and 20 lbs. per square inch gauge.

4. The process of claim 1 in which the time is from 20 to 60 minutes.

References Cited in the file of this patent

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