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3,534,540

COMPOSITE MULTI-COLOR OR COLORABLE YARN STRUCTURES

George H. Collingwood, Hopewell, Harry J. Demas,
Richmond, and George F. Bryant, Colonial Heights,
Va., assignors to Allied Chemical Corporation, New
York, N.Y., a corporation of New York

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ABSTRACT OF THE DISCLOSURE

This invention relates to multi-color or colorable composite-yarn structures and to the method of preparing same which comprises simultaneously crimping, entangling and twisting a plurality of continuous, synthetic filaments comprising at least two nylon filaments obtained from polyamides, each differing from the other by at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer.

This is a continuation-in-part of application Ser. No. 628,371, filed on Apr. 4, 1967, now U.S. Pat. 3,460,336.

This invention is directed to multi-colored or colorable texturized composited-yarn structures and to a process of preparing same. More specifically, this invention is directed to multi-colorable yarn structures which are particularly useful in preparing tweed-like textiles of improved heatherness and are relatively free of coring or streaking and chevroning. Still further, this invention relates to improved multi-colorable yarns useful in the manufacturing of tweed carpets and the like.

Heretofore, tweed-like or multi-dye single-end filament yarns were produced by combining two or more differently dyed textured yarn in a knitting, commingling, twisting and/or weaving operation. In producing, however, the continuous filament multi-dyed single-end yarns in accordance with any one or a combination of the above-stated operations, certain construction or surface streaks were formed in the final dyed product. For the most part, these surface streaks were due to the unequal distribution of each of the differently dyed filaments on the surfaces of the yarn bundles in the product. Thus, these streaks were prevalent primarily because of the deficiencies in the construction or combining processes used in preparing the multi-dyed filament ends.

Because of these deficiencies, it was almost impossible to prepare a streak-free, multi-dyed, tweed-like textile, e.g., tweed carpets and the like. Consequently, due to the inability to produce a substantially streak-free, multi-dyed yarn for commercial use, the public acceptance of tweed-like products has been significantly reduced.

To avoid these and other problems and to provide substantially streak-free, multi-colored or colorable textured yarns, it has been found that improved composited-yarn structures may be obtained by simultaneously crimping a plurality of continuous synthetic filaments to a crimp level of 8 to 20 crimps per inch. These synthetic filaments must comprise at least two nylon filaments prepared from polyamides, each differing from the other by at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer. The composited or crimped synthetic filaments comprising an effective amount of the different colorable nylon filaments are then subjected to a mechanical operation including entangling to a level of at least 25 entanglements per meter and twisting to a level of about 0 to 2.0 turns per inch. The multi-color or colorable textured yarn structures prepared in accordance with this invention may be characterized as composited bulk yarns

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having 8 to 20 crimps per inch, at least 25 or more entanglements per meter and 0 to 2 turns per inch. These composited yarns are particularly useful in the preparation of textile structures, e.g., carpets, having a tweed-like character with improved uniformity with respect to chevroning, coring or streaking.

Accordingly, it is an object of this invention to provide a process for preparing streak-free, multi-colored or colorable composited-yarn or textile structures comprising at least two nylon filaments prepared from polyamides, each differing from the other by at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer.

It is another object of this invention to provide a process for preparing multi-colored or colorable bulk yarn structures particularly useful in the production of tweed-like textiles having improved heatherness and are substantially free of coring and chevroning.

It is another object of this invention to provide means of avoiding the disadvantages of prior processes which required dyeing the different yarns before forming the tweed, which added to the overall cost of producing the products.

It is still a further object of this invention to provide a process whereby improved composited-yarn structures are obtained which are particularly suitable for the preparation of tweed textiles of improved quality at reduced manufacturing costs.

It is still a further object of this invention to provide new multi-colorable textile structures useful for preparing tweed-like fabrics or carpets having improved uniformity with respect to coring, chevroning and the like.

These and other objects of the invention will become apparent from a further and more detailed description to follow.

More specifically, this invention relates to a process and the products obtained thereby for preparing texturized, streak-free, multi-color or colorable composited-yarn and textile structures comprising at least two nylon filaments obtained from polyamides, each differing from the other by at least 12, and preferably by at least 18, milliequivalents of terminal amine-end groups per kilogram of polymer. These yarn structures are particularly useful in preparing tweed-like textile structures having improved heatherness and are relatively free of coring and chevroning.

More particularly, these composited-yarn structures are prepared by simultaneously crimping a plurality of continuous-synthetic nylon filaments, which may include a minor amount of other synthetic filaments, to a crimp level of 8 to 20, and preferably 10 to 18, crimps per inch. Still more specifically, the synthetic filaments may comprise all or a major amount, i.e., 50–100% by weight, of at least two chemically different nylon filaments and a minor amount, i.e., less than about 50% by weight, of at least one other synthetic filament selected from the group consisting of polyesters, e.g., polyethylene terephthalate, polyblends comprising a blend of polyethylene terephthalate and a polyamide, polypropylene, polyacrylics, and other known synthetic or man-made fibers including, for example, rayon, rayon acetate, the polysynthetic and the like.

The relative proportions of the various polyamide filaments, which differ from each other by at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer, are such that the final composited-yarn structures are multi-colorable because of the difference in the chemical structure of the polyamides. In other words, if the synthetic filaments comprise at least two polyamide filaments which differ one from the other by at least 12 milliequivalents of terminal amine-end groups, the relative proportion of these two polyamide filaments may obviously cover a wide range limited only by the necessity

to have one of the polyamide filaments present with respect to the others in an amount sufficient to impart multi-colorability to the final yarn products. Thus, for example, where a plurality of two chemically different polyamide filaments are employed in preparing a particular yarn structure, one type of said filaments may be present in an amount, e.g., as low as 10% and preferably 20% by weight, with respect to the other type of polyamide filaments, sufficient to impart multi-colorability to the final yarn structure.

The plurality of synthetic filaments comprising the different polyamide filaments are first simultaneously crimped to a level of 8 to 20 crimps per inch and more preferably, to a level of 10 to 18 crimps per inch. The composited-crimped filament structures are then subjected to a mechanical operation including (2) entangling to a level of at least 25 entanglements and preferably, to a level of 30 to 100 and more preferably to 30 to 60 entanglements per meter, and (3) twisting to a level of 0 to 2.0 turns per inch, and preferably, to a level of 0.001 to 2.0 and more preferably 0.7 to 1½ turns per inch.

The individual untextured synthetic filaments are combined in a predetermined ratio as they enter the crimping device which imparts a saw-tooth crimp, e.g., stuffer box crimper, jet crimper, etc. The composited multi-colorable homogeneous yarn structures exiting from the crimping device are then entangled and twisted to the levels indicated. However, it should be noted that the degree of heather, etc., desired in the final products may be determined by the levels of entanglement and twist employed. These yarns may be tufted or woven into carpets or knitted fabrics and then dyed with selective dyestuffs particularly sensitive to the chemical differences of the synthetic filaments to produce multi-colorable, streak-free products.

One of the advantages in combining the various multi-colorable filaments during texturizing, i.e., crimping, is the production of a single-end yarn at any one location in addition to obtaining yarn having some degree of in-phase crimp in each of the different dyeable filaments. The in-phase crimp prevents the separation of the individual filaments from the yarn bundle in the subsequent commingling and twisting operations. Thus, the possibility of obtaining multi-colorable yarns with a different distribution of each of the individual filaments on the surface of the yarn bundle may be avoided.

The following examples are illustrations of the process and products obtained in accordance with this invention.

EXAMPLE 1

Multi-colorable three-component nylon (polyamide) composited-yarn structures were prepared by adding specific terminators to ε-caproamide. The light-dyeing component or filament was prepared by employing acetic

acid as the terminator. No terminator was employed in preparing the medium-dyeing component and metaxylidenediamine was employed in preparing the ultra-deep dyeing component. The polymers were used to prepare the different filaments and were dried to a moisture content of less than 0.15% and then processed through a melt-spinning extruder at the rate of about 32 pounds per hour to obtain 1050 drawn denier filamentary yarns. The yarns were subsequently drawn to a UTS of 4-6 grams/denier and to ultimate elongations of between 32% and 48%.

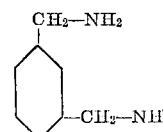
As shown in the following tables, Examples 1, 72 ends of feeder yarn or filaments A, B and C were guided in combination to a preheated chamber to produce 24 combined yarn ends with three multi-colorable ends. The ends were then passed to a stuffer box crimper at a lineal speed of 1460 feet/minute where the three components were crimped simultaneously. The yarn discharging from the crimper rolls entered a stuffer box of two inches in width where sufficient pressure, e.g., between 20 and 35 pounds/inch were supplied to obtain the level of crimp desired. (See the data in Tables I, II and III.)

After the yarns exited from the stuffer box, they were deposited on a belt. Here, the point of yarn pickup on the crimper belt was fixed to maintain the crimp at the desired level, as more particularly pointed out in copending application Ser. No. 510,591, filed on Nov. 30, 1965, now U.S. Pat. 3,406,436. The yarn was then passed through a shake-out ladder and separated into 24 composited yarn ends, each of which contained the individual 1050/70 denier yarn components A, B and C. These 24 composited ends were then guided through a crimp removal zone where 10 to 25% of the crimp level was removed and a 5% off-package creep-back was reduced to less than 2%.

The composited yarn had a total unbulked denier of 3150 and 210 filaments. The yarn was then passed through a commingling fluid-jet which is specifically described in copending application Ser. No. 535,480, filed Mar. 18, 1966, now U. S. Pat. 3,473,315. In the jet, the yarn obtained 42 entanglements/meter at air pressures of 40 p.s.i.g. The yarn was then passed through a continuous forwarding twisting device wherein a twist level of 0.001 to 1½ turns per inch may be applied. Subsequently, the yarn was carried to a traverse winder where the yarn was wound on a 3½ inch tube at a speed of about 1100 feet/minute to obtain the finished package.

This particular yarn was then tufted and woven into carpets by conventional methods, as shown in the data in Tables II and III. The yarns were subsequently dyed according to known procedures utilizing the di- and trisulfonate anionic dyes to obtain products having a contrast of greater than 16 Gardner units between the individual filaments of the yarn.

TABLE I

	Light dye colorable component filaments A	Intermediate dye colorable component filaments B	Ultra-deep dye colorable component filaments C
Formic acid viscosity.....	58±2	54±3	52±3
Amine end-groups.....	22±3	50±4	78±2
Carboxyl end-groups.....	70±5	48±4	16±5
Total end-groups.....	92	98	104
Terminators employed.....	(1)	(2)	Metaxylidenediamine
			
TiO ₂ , percent.....	0.3	0.2	0.2
Filament cross section.....	Round	Round	Round
Denier/filament count.....	1050/70	1050/70	1050/70
Drawn physicals: Ultimate tensile strength, g./d.....	5.0	5.0	5.1
Ultimate elongation, percent.....	47±2	46±2	47±2

¹ Acetic acid.

² No terminator employed.

TABLE II

Example 2				
Separate crimp properties of A', B', C' Filaments				
Crimped properties	Example 1 A,B,C, combined	Light dye colorable component A'	Intermediate dye colorable component B'	Ultradeep dye colorable component C'
Crimps per inch.....	15.8	17.2	15.1	15.1
Crimp elongation after boil.....	29.0	29.2	28.7	29.1

Example 1		Example 3	
Crimped properties	A,B,C, combined	A', B', C', Combined	
Commingle entanglements/meter.....	42.....	42.....	
Twist, turns/inch.....	1.5S.....	1.5S.....	
Tufted into a carpet.....	16 oz. yd. ² 7 stitches/in.....	16 oz. yd. ² 7 stitches/in.....	
Streak ratings.....	No apparent construction streaks.....	Variable with 50 streaks per 2.5 x 24' carpet.....	

TABLE III

Examples.....	4		5		6		7		8	
Feeder yarn.....	A, B, C		A, B, C		A, B, C		A, B, C		A, B, C	
Cross section.....	Round		Round		Round		Round		Round	
Crimps/in.....	13		13		13		13		13	
Crimp elongation, after boil.....	27.0		27		27		27		27	
Entanglements/meter.....	42		42		42		42		42	
Twists, turns/in.....	0		3/4S		1.0S		1.25S		1.5S	
Carpet construction.....	(1) Tufted	(2) Woven	(1) Tufted	(2) Woven	(1) Tufted	(2) Woven	(1) Tufted	(2) Woven	(1) Tufted	(2) Woven
Streakiness ³	0	8	0	6	0	4	0	4	0	4
Rating, streaking appearance ⁴	Excellent	Good	Excellent	Excellent	Outstand- ing	Outstand- ing	Outstand- ing	Outstand- ing	Outstand- ing	Outstand- ing
Heather, rating ⁵	HN	HL	HL	HL	HL	HL	HM	HM	HS	HS
Carpet utility ⁶	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Design characteristics.....	Z, SM	Z, SM	Max. C	Max. C	Med. C ⁷	Med. C ⁷	HM	HM	HS	HS

1 Tufted—16 oz. yd.² 7 stitches/in. .563 in. gage.
2 Woven—8 x 8 construction produced at 216 pitch.
3 Streakiness, panel jury rating, streaks per 2.5' x 24' of carpet evaluated.
4 0-0.5 outstanding, .5-1.0 excellent, 1-1.5 good, 15-25 fair.
5 Heatherness—HN, HL, HM, HS.
6 Carpet utility.
7 Contract commercial, improved product.
8 Quality residential.

Design characteristics:
A—massive design, space dye effect,
B—strong uniform tweed,
C—light heather,
D—medium heather,
E—strong heather,
HN=heather not noticeable.
HL=light heather,
HM=medium heather,
HS=strong heather.

Carpet utility:	Designation
Contract commercial—improved product	CC
Quality residential	QR
Design Characteristics—Zebrastripe & Marl	ZSM
Maximum contrast	Max. C
Medium contrast	Med. C

It was unexpected to find that streaks could be substantially or completely eliminated by first crimping the different filaments simultaneously, followed by an entanglement and twisting to the levels indicated. The homogeneity of the structures obtained by intermingling of the in-phase crimp after passing through the stuffer box crimper virtually excluded streaks from all of the textiles prepared from these yarns. It was found that by passing the yarn filaments side-by-side, for example, through a stuffer box crimper, to impart a saw-tooth crimp, separation of one or more of the multi-colored components along the strandular structure was prevented. Normally, separation of the filaments occurs during the subsequent operations including, for example, sizing, dyeing, tufting, weaving, etc.

By comparing the data in Table II, it is shown (Example 1), that where the filaments were first composited simultaneously in a crimper and then commingled and twisted, etc., there was a ten-fold reduction in streaks in comparison to Examples 2 and 3 where the filaments were crimped separately and then entangled and twisted. Examples 4 through 8 of Table III further illustrate the effect of increasing the twist level from 0 to 1½ turns per inch on carpets produced by both tufting and weaving procedures. Here, the woven carpets exhibited a significantly lower streak level in those instances where there was an increase in twist of 0 to 1.0 turn per inch. It should be noted also that both the tufted and woven structures had a significantly lower degree of streakiness in comparison to the structures prepared from filaments which were separately crimped and then entangled and twisted.

The data in the following table illustrates the adaptability of this invention to a variety of yarn modifications or cross sections. In Table IV, in Examples 9, 10 and 11, a Y-cross section was produced which, like the round cross

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section of Examples 1, 3, 4, 5, 6, 7 and 8, was free of streakiness.

TABLE IV

Examples	9	10	11
Different nylon filaments			
	D	E	F
Formic acid relative viscosity	60	50	53
Amines end-groups	22	50	78
Carboxyl end-groups	70	48	25
Total end-groups	92	98	103
TiO ₂ , percent	.3	.2	.2
Filament cross type	Y	Y	Y
Total denier/denier/filament	1125/70	1125/70	1125/70
Drawn physicals, UTS, g./d.	4.8	4.5	4.4
Ultimate elongation, percent	36	36	44
Composited Yarns:			
Feeder yarns	DEF	DEF	DEF
Examples	9	10	11
Crimps/inch	16.1	16.1	16.1
Crimp elongation after boil	29.1	29.1	29.1
Entanglements/meter	38	38	38
Turns/inch	0	1.0	1½
Carpet type	Tufted	Tufted	Tufted
Streakiness	0	0	0
Carpet appearance rating, freedom from streaks	Excellent	Excellent	Outstanding
Carpet utility	CC, QR	CC, QR	CC, QR

EXAMPLE 12

Yarn was prepared in accordance with the procedure of Example 1 except that polypropylene filaments were substituted for the light-dyeing nylon filament. During the crimping, the temperature was maintained throughout the operation below about 140° C. to avoid fusing the polypropylene filaments. After the yarn was passed through the crimping device wherein the polypropylene filaments were simultaneously intermingled with the medium and high-dyeing nylon filaments (filaments B and C), the yarn was tufted to carpeting in a manner similar to that employed in preparing the all-nylon carpet structures. The medium and deep-dyeing nylon filaments accepted the acid dyes wherein the polypropylene filaments remained white or undyed in the carpet structure. As a result, a higher degree of contrast and a more tweed-like carpet was obtained in comparison to structures prepared from all nylon. Similarly, to the nylon structures, however, the polypropylene containing carpet also was substantially free of streaks.

The above examples were repeated except that the polypropylene was replaced with polyester, i.e., polyethylene terephthalate, filaments as the light-dyeing component. A homogeneous yarn structure was prepared which, when tufted into carpet, exhibited the polyester as a white, colorless yarn. The nominally higher modulus polyester remained as part of the homogeneous structure throughout the various dyeing, tufting, and/or weaving operations, and similar to the polypropylene, resulted in a high contrast tweed-like carpet structure completely free of streaks.

Normally, the synthetic filaments, e.g., polypropylene and polyesters, because of their different stress-strain curves, compressional-resilient properties, and because of their different modulus characteristics which change with moisture level, have a tendency to separate along the strandular structure which inevitably results in a highly streaked carpet. However, it was found that the polyesters and polypropylene, for example, when combined with nylon in accordance with the procedure of this invention, resulted in structures which were essentially streak-free. Thus, it is obvious that other known synthetic or man-made filaments may be employed also as one of the colorable filaments in accordance with this invention to obtain improved structures.

To illustrate that the degree of color contrast is a function of the terminal-amine content of the nylon polymer employed, crimped filaments from polymers A, B and C above having 22, 50 and 78, respectively, millicivalents of terminal amine-end groups per kilogram of polymer

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were dyed by using a one-half percent by weight of the fabric of alizarine-milling blue (Acid Blue 80), Color Index No. 61585. The following color differences were obtained for the dyed structures:

TABLE V

Different colorable nylon filaments	A	B	C
Amines, meq./kilogr. polymer	22	50	78
"Rd" scale C4 meter reading 1	47.7	22.4	8.0
"A" scale C4 meter reading 1	-9.9	-7.6	-1.4
"B" scale C4 meter reading 1	-12.0	-38.7	-66

¹ Gardner Model C4.

The color contrast of the different yarns were measured by employing a Gardner Model-C4 colorimeter utilizing the techniques described by ASTM Method D-2244-64T (1964), entitled "Evaluation of Color Difference of Opaque Materials." The Gardner-C4 colorimeter has three scales which yield numerical color values suited for comparison with the Munsell U.S. Bureau of Standards Color Values. The scale readings of the Model-C4 meter are approximately lineal for the nylon products exemplified by this invention. If a color combination such as greenish-red is encountered which has both positive and negative values for the preferred "A" scale, then the "Rd" scale is preferentially employed. The Gardner scales are illustrated in the following table:

TABLE VI.—GARDNER SCALES

Color	Scale	Value	Depth of Color Increase towards
Black	"Rd"		100→0
White	"Rd"		0→100
Red	"A"	Plus	0→100
Green	"A"	Minus	0→100
Yellow	"B"	Plus	0→100
Blue	"B"	Minus	0→100

While various synthetic and man-made fibers, such as polyesters, polyacrylics and polypropylene, may be employed as one of the dyeing components or filaments, it is desirable to utilize those fibers having similar stress-strain properties. Thus, as a preferred embodiment, the composite-yarn structures of this invention may comprise several filaments of equivalent stress-strain character, such as the various polyamides. However, in addition to the polyamide filaments, polyblend filaments obtained from polymeric mixtures containing up to about 50% of a polyamide and a polyester, e.g., polyethylene terephthalate, have similar stress-strain characteristics suitable to be employed with nylon in preparing the composite structure of this invention. The polyblend filaments are more particularly described in copending application Ser. No. 368,028, filed May 18, 1964, now U.S. Pat. 3,369,057, and may be further characterized as generally having an amine-end group of less than 15 and thus can be employed as the low-dyeing filament of the multi-colorable composite structure.

As examples, for purposes of this invention, the low-dyeing filaments may have an amine-end group value ranging from 3 to 35. The medium-dyeing filaments may have an amine-end group value ranging, for example, from 40 to 55, while the high-dyeing filaments may have an amine-end group value ranging from 60 to 100. The formic acid relative viscosities of these materials may range from about 25 to 80 and more preferably, from 40 to 65.

The individual ends which are composited in accordance with this invention may have a denier of 1 to 25 per filament with a total denier of 20 to 5,000. For most end uses which include, for example, upholstery and carpeting, the total denier per end to be crimped, entangled and twisted is preferably between 100 and 3500. The preferred denier per filament for carpeting and upholstery ranges between 6 and 20 denier per filament.

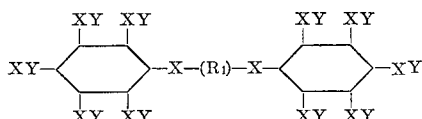
The differentially dyed polymers for purposes of this invention may be prepared by procedures described in

U.S. Pat. No. 3,090,773, using batch polymerization techniques and/or by techniques disclosed in U.S. Pat. No. 3,171,829, utilizing a continuous polymerization technique. The different low-dyeing filaments may be produced, for example, by procedures more specifically described in copending application Ser. No. 426,632, filed Jan. 19, 1965, wherein a dibasic acid is employed as the terminator as follows:

EXAMPLE A

About 400 parts of epsilon caprolactam and 0.45 part of sebacic acid (.24 mole percent) were charged to a vessel equipped with external heating means and a horse-shoe agitator. Polymerization was accomplished by applying steam pressure of 50 p.s.i.g. to the space above the fluid in the vessel, heating to 255° C. within 1 hour, and holding the temperature of the mixture at 255° C. for 1 hour under the 50 p.s.i.g. steam pressure. Steam pressure was then released and the vessel returned to atmospheric pressure, maintaining the temperature of the polymerization mixture at 255° C. The surface of the agitated polymer mass was swept with dry nitrogen gas at the rate of 10 liters per minute for approximately 10 hours. At this time, after essentially 12.8 hours at the 255° C. temperature, there was little further increase in viscosity. The polymer was extruded into a warm water bath and chopped into pellets $\frac{1}{10}$ by $\frac{1}{10}$ inch in size. The pellets were then washed, and dried to less than 0.1% moisture. The polycapromide thus produced was found to have a number average molecular weight of 30,800 and an amine-end group value of 7.

The ultradeep-dyeing polyamides may be obtained by employing various diamines as the terminators. The filaments prepared from these polymers may have a total amine-end group value ranging from about 60 to 100 milliequivalents per kilogram of polymer and a ratio of carboxyl to amine-end groups greater than 1 to 3.5. The preferred amines which may be employed in forming the deep-dyeing polyamide filaments may be characterized as alicyclic diamines as illustrated:



wherein:

X is selected from the group consisting of NH_2 , H and $(\text{CH}_2)_n\text{—NH}_2$;

Y is selected from the group consisting of CH_3 , H, OH, OCH_3 , $\text{H}_n\text{—}(\text{CH}_2)_n\text{—N—}(\text{CH}_2)_n\text{—H}$ and $(\text{CH}_2)_n\text{—CH}_3$; and

R_1 is a bond between the rings or alternatively, the substituent $(\text{CH}_2)_n$ where n is an integer of 1 to 10.

The medium-dyeing filaments may be prepared from polyamides containing equal acid and amine-end groups. To prepare the preferred polymers, the terminators should have a boiling point above 250° C., preferably saturated, and should have a basicity of between 1×10^{-3} and 1×10^{-7} . Of these terminators, the preferred may include, for example, 4-amino-1,2,3,5-tetramethyl benzene and other amino isomers of tetramethyl benzene, 4-amino-3-methyl-1-phenyl pyrazolone and other long-chain primary amines having 10 or more carbon atoms in the chain. In addition, similar saturated alicyclic compounds which were described useful for the deep-dyeing filaments may be employed here except that it is preferred that they contain a single amine group.

In a similar manner, the monocarboxylic acids may be employed to give the proper distribution between the monodiamine and the monocarboxylic acids for the desired number of amine-end groups. Any aliphatic monocarboxylic acid having a boiling point above 250° C. may be employed. In addition, alicyclic and aromatic carboxylic acids may be used in conjunction with the di-

amines to give the desired number of amine-end groups. In general, however, the terminators containing chlorine, nitro groups, carboxyl groups or hydrolyzable ester groups are undesirable substituents for preparing dyeable filaments for purposes of this invention. These groups interfere with the polymerization and/or impart undesirable color characteristics to the final polymer.

The method and apparatus which may be used for entangling or commingling the fine denier yarns for purposes of this invention are more particularly pointed out in copending application Ser. No. 388,592, filed on Aug. 10, 1964, now abandoned. Here, for example, an entangled yarn product is obtained by simultaneously treating a light, colorable drawn 230/32/0 Nylon-6 yarn and a darker contrasting drawn 70/32/0 nylon yarn; said yarns having different propensities toward shrinking and dyeing. The specific apparatus employed had the following dimensions:

Guides:

Distance between guides—20.0 mm.

Distance between tip of nozzle and mouth of chamber—10.0 mm.

Inside diameter of guides—1.5 mm.

Chamber:

Inside diameter of chamber mouth—4.3 mm.

Depth of chamber—15.0 mm.

Nozzle:

Diameter of nozzle orifice—1.5 mm.

The chamber member and the yarn guides are fabricated of AlSiMag ceramic material above identified.

In operation, the yarns follow a Z-shaped path in a plane perpendicular to the axis of the nozzle, each yarn passing through the uppermost guide in the same 135° angle and the yarns being withdrawn through the lower guide at a 135° angle to the line between the guides. By means of a constant speed driven take-up roll and upstream tension control means, the tension on the partially drawn yarn is maintained uniformly at 5.0 grams and the tension of the fully drawn yarn is maintained uniformly at 7.0 grams. The rate of yarn throughput for both yarns is 500 yd./min. Air at a pressure of 85 p.s.i.g. is employed as the entangling medium. In the course of yarn treatment the filaments are observed by high speed photography to separate and oscillate and the yarn as a whole to vibrate and contact the upper and lower portions of the mouth of the chamber at least 100 times per second. The entangled yarn obtained has a coherency factor of 312.

The yarns which are particularly suitable for entanglement or commingling in this gas jet apparatus include yarns having deniers ranging from about 10 to 4,000 denier with individual filament deniers ranging from about 0.5 to 16 denier.

For the heavy denier yarns, i.e., yarns having deniers ranging up to 10,000, the commingling jet apparatus may be used, which is particularly set forth in copending application Ser. No. 535,480, filed on Mar. 18, 1966, now U.S. Pat. 3,473,315. Here, the apparatus was employed to entangle untwisted 3600 denier, 210 filament nylon yarns having a zigzag stuffer box crimp, a packaged crimp index of 8.5% and a relaxed crimp index of 23.5%. The specific apparatus employed had the following characteristics:

Overall length of yarn passageway—3.5 in.

Length of large diameter segment of yarn passageway—2.3 in.

Diameter of large diameter segment of yarn passageway—0.25 in.

Diameter of small diameter segment of yarn passageway—0.125 in.

Length of small diameter segment of yarn passageway—1.5 in.

Diameter of gas passageway—0.20 in.

Ratio of area of gas passageway to area of yarn passageway—0.64

Percent of gas which exits from entrance end of yarn passageway—94%

Angle of gas passageway—45°

The yarn was fed into the apparatus on a straight line path at a rate of 265 yards/minute and a tension of 22 grams (.006 gram per denier). The yarn emerged from the device in a straight line, and a speed of 263 yards per minute. In order to properly center the air stream, the cylindrical air passageway was constructed to be slightly off center within the cylindrical walls of tube and this tube was adjusted by twisting it to achieve smooth operation forming yarn with alternating zones of commingling and no commingling. A deviation of as much as 6 mils in the position of the central axis of air passageway away from the plane which is parallel to said axis and also contains the central axis of yarn passage was found to make the yarn twist off the feed rolls, and failed to give the yarn product of the invention having alternating sites of commingling and no commingling; and even 3 mils deviation caused the device to run less smoothly.

The method employed to determine the level of entanglement is known as the Hook Drop Method described below.

HOOK DROP TEST

Meter lengths of yarn to be tested are clamped at the upper end and allowed to hang in the vertical position under the tension provided by a weight in grams which is 0.20 times the yarn denier (but not greater than 100 grams), inserting through the yarn bundle approximately midway within a region of no apparent commingling a weighted hook having a total weight in grams numerically equal to the mean denier per filament of the yarn (but not weighing more than 10 grams), and lowering the hook at a rate of one to two centimeters per second until the weight of the hook is supported by the yarn. The distance of hook travel is measured. Since the commingling is fairly random in nature, 100 separate meter lengths are tested to define a representative sample for a given package of yarn or for a multitude of presumably identical packages of yarn. Of the 100 separately obtained hook drop distances, the upper 20 and lower 20 values are discarded, and the remaining 60 are averaged to determine the average distance of hook travel. This value, D, measured in centimeters, is essentially one-half the average distance between sites of strong-enough commingling to stop the hook travel.

The method of texturizing or crimping the yarns in accordance with this invention may include the stuffer box methods, as particularly described in U.S. Pats. Nos. 3,037,260 and 3,031,734. Other crimping methods may include the jet process, as particularly described in U.S. Pat. No. 3,005,251, and the belt or gear crimping devices as shown in U.S. Pat. No. 2,751,661. Other apparatuses including the stuffer box crimper which may be used to produce the sawtooth, three-dimensional crimp are described in U.S. Pats. Nos. 2,862,279 and 2,933,771.

Of the various methods, a preferred method which may be used for purposes of this invention is particularly set forth in copending application Ser. No. 562,893, filed on July 5, 1966, now U.S. Pat. 3,409,956.

Here, for example, a 2400-denier, 70-filament drawn yarn in the form of a strand spun from polycapraamide polymer of formic acid, relative viscosity 52

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and a different polyamide strand of 40-denier, 12-filament was delivered simultaneously to the steam-jet texturizing apparatus at 3,000 feet per minute and at a tension of 50 to 100 grams. The angle A of the diverging cone measured 30°. There were 12 equally spaced holes in the rear exhaust which measured 0.0595". Steam at 120 p.s.i.g. and 470° C. temperature was directed from a 0.061

diameter steam nozzle, into a preheat tube 4" in length and having a diameter of 0.125 inch. The yarn strand in the preheat tube was heated to a temperature of about 125° C. and the steam and yarn strands were thereafter directed into the chamber where a yarn plug was formed. The steam forced the incoming yarn strand against a slower moving textured yarn plug in the texturizing chamber. The spent steam escaped to the rear through vent holes and provided a blanket of heat around the preheater tube. The temperature of the yarn was found to drop by about 20 to 30° C. as it moved in a compacted mass to the end of the texturizing chamber. After leaving the texturizing chamber, the textured yarn was pulled over several tension bars and wound on a package. The crimp definition of the crimped yarn was: crimp elongation before boil 10%; crimp elongation after boil 25%; and the free shrinkage 3.0%.

Another method of crimping multi-color yarns in accordance with this invention is described in copending application Ser. No. 510,591, filed on Nov. 30, 1965, now U.S. Pat. 3,406,436. Here, 20 ends of 1,050-denier, 70-filament, polycapraamide, along with 20 ends of a different yarn, were fed into a stuffer box at a feed rate of 1425 feet per minute and wound-up on a yarn package at 1160 feet per minute. The gas pressure was varied during the process to vary the resistance against the yarn, thereby maintaining substantially constant yarn volume in the stuffer box. The weights placed on the stuffer varied between 1.5 pounds and 5.0 pounds. The yarn received a uniform crimp having 14 crimps per inch controlled within ± 2.0 crimps per inch. Still other methods which may be employed for producing the crimp in accordance with this invention are more specifically described in copending applications Ser. No. 570,913, filed on Aug. 8, 1966, now U.S. Pat. 3,373,469, and Ser. No. 603,912, filed on Dec. 22, 1966, now U.S. Pat. 3,438,101.

In general, the mechanical operations may include ring and traveller twisting, false-twisting, jet-twisting, entanglement by sonic jet, standard jet entanglement, commingling jet entanglement, needling entanglement, hydraulic jet entanglement, etc.

The texturizing operation for compositing the filaments may include stuffer box crimping, jet crimping, i.e. to produce a saw-tooth, three-dimensional crimp, gear crimping, edge crimping, thermal-shock crimping a combination of chemical and jet crimping etc.

As a specific illustration, multi-colorable carpet yarns comprise three plies of yarn wherein each of the plies are prepared from polyamides having different amine-end group values. The yarn filaments prepared from these polyamides given three-tone dye effects when dyed with selective acid dyestuffs. The process of preparing these yarn structures comprises spinning, winding, texturizing or crimping, commingling, entangling, twisting and winding. Usually, the polyamide filaments are spun simultaneously on different spin units under identical extrusion conditions. Each of the three undrawn multi-colorable filaments are hot-drawn, under identical conditions, using heavy denier draw-winders. These packages of the drawn yarn of each of the three polymer types are placed in a texturizing creel so that one-end of each type of polymer is placed in each of the 24 end-feed guide slots. The three different filaments are composited into a three-dye level tow in the texturizing device. The textured yarn exits the texturizer, i.e., stuffer box crimper, and is separated into 24 three-ply textured yarns. The textured yarn is commingled or entangled to a level of at least 25 entanglements per meter and then down-twisted to $1\frac{1}{2}$ turns/inch S twist.

The three different polyamides used in preparing the filaments had amine end-group values of 21, 48 and 77, each differing from the other by more or less than at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer. The bulk yarns which were used to prepare carpets were tufted on a 9-ounce per square

yard jute backing. The carpeting was dyed with an anionic acid dye (Acid Blue 92), Sulfonine Acid Blue-R at concentrations of 0.25% by weight of the fiber, at a pH of about 7, with temperatures of 205° F. over a period of about one hour. Subsequently, the carpet samples were evaluated with respect to coring, chevroning and heather-ness.

Other dyes which were found to give excellent results were the Acid Yellow 38 (25135); Milling Yellow O; Acid Red 145 (23905); Acid Light Scarlet GL; Acid Blue 92 (13390); Fast Wool Blue R; and Acid Blue 80 (61585); Alizarine Milling Blue R, which is an anthraquinone substituted anionic diacid dyestuff. Improved heatheriness may be obtained by using, in combination with the above anionic dyes, various other dyes such as, Disperse Blue 3 (61505), Nacelan Blue FFRN, and Disperse Yellow 3 (11855), Nacelan Fast Yellow CG. Dyeing is usually carried out after bleaching the carpet with 3% by weight of the fabric of sodium perborate and 0.25% ammonia at 165° F. for about 30 minutes with a liquor ratio of approximately 50 to 1. The carpet structures are dyed with the appropriate color mixtures which usually contain a wetting agent such as Triton X-100. The dye baths are usually adjusted to the desired pH with known salts, such as, monobasic sodium phosphate, trisodium phosphate, etc.

As suggested, the yarns may contain also various additives to impart particular properties to the finished fabric.

These additives may be incorporated into the filaments either by adding the ingredients to the polymer prior to spinning or by after-treatment of the yarn and include, for example, flame-retardants, e.g., antimony, phosphorus and halogen compounds; delustrants, e.g., titanium dioxide; antistatic agents; adhesion promoting agents, i.e., isocyanates and epoxides; heat and light stabilizers, e.g., inorganic reducing ions, such as manganese, copper, tin, etc. Other additives include the amines, fluorescent agents and brighteners, crosslinking agents, bacteriostats, e.g., phenols and quaternary amines, etc. A more detailed description of the methods employed in incorporating the various additives into the synthetic filaments may be found in U.S. Pat. No. 3,279,974 and Canadian Pat. No. 882,293.

Various fabrics and other textile articles may be manufactured from the composited-yarn structures of this invention by utilizing well known methods including, for example, circular knit, e.g., Double-knit, Jersey knit, Jacquard-type knit, etc. Alternatively, warp knitting, e.g., tricot knits, Milanese, Simplex, Raschel, Jacquard, etc., may be employed. In addition, woven goods may be prepared from the composite structures and include the three basic weaves, i.e., plain weave, twill weave and satin weave. Other type weaves which may be considered as plain twill or satin-type include, for example, the Bedford cord, the Birdseye weave, the Waffle weave, the Swivel weave, Double cloth weave, Pile weave, etc.

While this invention has been described with respect to a number of specific embodiments, it is obvious that there are other variations and modifications which can be resorted to without departing from the scope of the invention, as particularly pointed out in the appended claims. What is claimed is:

1. A process for preparing multi-color or colorable composite-yarn structures which comprises (1) simultaneously crimping a plurality of continuous, synthetic filaments to a crimp level of 8 to 20 crimps per inch; said synthetic filaments comprising at least two nylon filaments obtained from polyamides, each differing from the other by at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer; (2) entangling said crimped filaments to a level of at least 25 entanglements per meter; and (3) twisting said filaments to a twist level of 0 to 2.0 turns per inch.

2. The process of claim 1 further characterized in that the relative proportions of the different polyamide fila-

ments are present in the composite-yarn structures in amounts sufficient to render said structures multi-color or colorable.

3. The process of claim 1 further characterized in that said plurality of filaments used in preparing the composite-yarn structures comprises a major amount of the nylon filaments obtained from the different polyamides and a minor amount of at least one synthetic filament prepared from polymers selected from the group consisting of polypropylene, polyesters and blends of polyesters and polyamides.

4. The process of claim 3 further characterized in that the synthetic filament is prepared from blends of polyethylene terephthalate and a polyamide.

5. The process of claim 1 further characterized in that at least one of the nylon filaments is obtained from a polyamide having 60 to 100 milliequivalents of terminal amine-end groups per kilogram of polymer.

6. The process of claim 5 further characterized in that at least one of the nylon filaments is obtained from a polyamide having 40 to 55 milliequivalents of terminal amine-end groups per kilogram of polymer.

7. The process of claim 6 further characterized in that at least one of the nylon filaments is obtained from a polyamide having 3 to 35 milliequivalents of terminal amine-end groups per kilogram of polymer.

8. The process of claim 7 further characterized in that said plurality of different polyamide filaments used in preparing the composite-yarn structures are present in relative proportions sufficient to render said yarn structures multi-color or colorable.

9. The process of claim 1 further characterized in that said plurality of synthetic filaments comprise at least three nylon filaments obtained from polyamides, each differing from the other by at least 18 milliequivalents of terminal amine-end groups per kilogram of polymer.

10. The process of claim 9 further characterized in that the plurality of continuous synthetic filaments are crimped to a level of 10 to 18 crimps per inch and subsequently entangled to a level of 30 to 60 entanglements per meter and twisted to a level of 0.7 to 1½ turns per inch.

11. The process of claim 1 further characterized in that the polyamides are selected from the group consisting of polycapromamide, polyhexamethylene adipamide and polypyrrolidone.

12. The process of claim 1 further characterized in that the plurality of synthetic filaments are crimped to a level of 10 to 18 crimps per inch in a stuffer box crimper.

13. A multi-color or colorable, composite-yarn structure comprising a plurality of continuous, synthetic filaments; said filaments comprising at least two nylon filaments obtained from polyamides, each differing from the other by at least 12 milliequivalents of terminal amine-end groups per kilogram of polymer; said yarn structure having 8 to 20 crimps per inch, an entanglement of at least 25 entanglements per meter and a twist of 0.001 to 2.0 turns per inch.

14. A multi-color or colorable composite-yarn structure comprising a plurality of continuous, synthetic filaments; said filaments comprising at least two nylon filaments obtained from polyamides, each differing from the other by at least 18 milliequivalents of terminal amine-end groups per kilogram of polymer; said yarn structure having 10 to 18 crimps per inch, an entanglement of 30 to 60 entanglements per meter and a twist of 0.7 to 2.0 turns per inch.

15. The multi-color or colorable composite-yarn structure of claim 14 further characterized in that said yarn structure comprises a major proportion of the polyamide filaments and a minor proportion of a man-made synthetic filament.

16. The multi-color or colorable composite-yarn structure of claim 14 further characterized in that a major proportion of the filaments comprises at least three nylon

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filaments obtained from polyamides, each differing from the other by at least 18 milliequivalents of terminal amine-end groups per kilogram of polymer, and a minor proportion of at least one synthetic filament prepared from polymers selected from the group consisting of polypropylene, polyesters, and blends of polyesters and polyamides.

17. A non-streaking, multi-colored textile prepared from the composite-yarn structures of claim 13.

18. The textile of claim 17 further characterized as being a tufted or woven non-streaking tweed carpet.

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JOHN PETRAKES, Primary Examiner

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