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3,542,743

## BASIC DYEABLE ACID DYE RESISTIVE POLY-AMIDES CONTAINING TERMINAL ARYL DISULFONATED GROUPS

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3 Claims

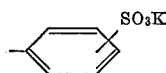
### ABSTRACT OF THE DISCLOSURE

Fiber-forming linear polycarbonamides modified to contain as an integral part of their polymer chain certain terminal aryl disulfonated groups resist yellowing and possess excellent acid dye-resistant and basic dyeable properties. Fibers formed from the polycarbonamides may, for example, be combined with standard polycarbonamide fibers to provide fabrics which are dyeable in a single dye bath to multiple color effects, i.e., patterns and designs.

This application is a continuation-in-part of applicant's copending application, Ser. No. 500,232, filed Oct. 21, 1965, now abandoned.

### BACKGROUND OF THE INVENTION

Unmodified nylon is dyeable to a single color only and is almost exclusively dyed with acid dyes that are absorbed by amine groups of the nylon molecules. The application of basic dyes which are absorbed by carboxyl groups of the nylon molecules, results in colored nylon having unacceptable wash and light fastness properties. Nylon has been modified, however, to improve its dyeability by forming the nylon in the presence of a monofunctional, monosulfonated compound to provide nylon comprising molecules having at least one terminal group of the structure



Modified nylons of this type are described in U.S. Pat. 3,142,662. The modified molecules serve a dual role. First, they provide sulfonate groups which can be activated to absorb basic dye under acid conditions without activation of carboxyl groups, thereby providing color of acceptable wash and light fastness secondly, they impart acid dye-resistant properties to the nylon by forming salt with amine end groups of unmodified molecules, thereby rendering these amine groups no longer available to absorb acid dyes.

Recently, modified nylons of the type just described have found utility in preparing textile fabrics which are dyeable in a single dye bath to multiple color effects. These fabrics, hereinafter referred to as "multi-yarn fabrics," are prepared by weaving or knitting a plurality of nylon yarns, each having different dyeing characteristics, into a single fabric. For example, the fabric may be prepared by combining yarns spun from the modified nylon with yarns spun from unmodified (standard) nylon in such a manner that, when the fabric is immersed in a dye bath containing selected acid dyes or selected basic dyes or a combination of selected acid and basic dyes, the fabric is dyed to a plurality of different colors or color tones defining a pattern or design. Also, since the modified yarns tend to resist acid dyes and retain their natural white color when subjected thereto, a fabric prepared from modified and standard nylon yarns can be dyed with

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acid dyes to obtain a fabric, the pattern of which is defined by white yarn and one or more colored yarns.

Nylon manufactured for textile applications to be of practical value in commercial operations must have a relative viscosity of at least 25 (as determined by ASTM Method D-789-53T), otherwise the nylon cannot be economically processed into yarn because the spinnability of the nylon and draw-twist performance of the filaments are unsatisfactory. Also, modified nylon yarn which is combined with standard nylon yarn in the manufacture of multi-yarn fabrics must have the following additional characteristics:

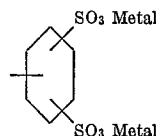
- (1) dyeable with basic dyes to deep, brilliant colors;
- (2) dyeable with basic dyes to colors of acceptable wash and light fastness;
- (3) resistant to acid dyes; and
- (4) resistant to yellowing when exposed to light and heat.

Modified nylon yarns of the prior art do not possess sufficient basic dyeability and acid dye-resistant properties or sufficient resistance to yellowing to be of practical value in manufacturing multi-yarn fabrics.

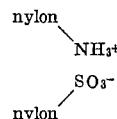
It is therefore an object of the present invention to provide modified nylon possessing all of the characteristics essential for use in manufacturing multi-yarn fabrics.

### SUMMARY OF THE INVENTION

This and other objects are accomplished by the polycarbonamides of the present invention which comprise modified polycarbonamides having a sulfonate to amine end group ratio of at least 1:1, and preferably, from 1.5 to 3.0 to 1 formed by heating polyamide-forming reactants in the presence of a disulfonated aromatic compound having an amide-forming functional group. Preferably, the functional group is a carboxyl group or an amide-forming derivative thereof. The modified polycarbonamides therefore comprise molecules having at least one terminal group of the structure



Yarns spun from the modified nylons embodied herein have enhanced dyeing properties and are particularly useful in fabricating multi-yarn fabrics, previously described, which are dyeable in one-bath dyeing procedures to multiple color effects. The enhanced dyeing properties of the subject nylons, when compared to the related nylons of the prior art, result from the presence of two sulfonate groups in the modified molecules of the subject nylon. The prior art sulfonate modified nylons are inherently limited to a maximum sulfonate content that is insufficient for certain applications, for example, in manufacturing multi-yarn fabrics. The difficulty with the prior art nylons arises from the fact that basic dyes must be applied to the multi-yarn fabrics under acid conditions to prevent activation of carboxyl groups. Under acid conditions sulfonate groups of modified molecules form a salt with amine end groups of unmodified molecules:



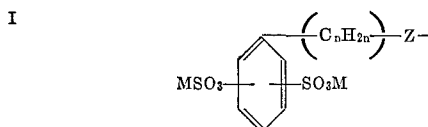
Thus, only the sulfonate groups in excess of the amount forming salt are available for basic dyeing. Also, it is apparent that sulfonate groups in forming salt with amine

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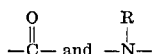
groups impart acid dye-resistive properties to the modified nylon. However, the amount of monofunctional-amide-forming compound, and therefore sulfonate groups, which can be incorporated into nylon fibers is inherently limited, since these compounds function as chain terminators tending to reduce the molecular weight and relative viscosity of nylon when added to the nylon-forming reactants. Nylon modified with monofunctional monosulfonate compounds simply does not contain sufficient sulfonate groups (at the minimum required relative viscosity) to provide a yarn which has requisite dyeing characteristics for use in manufacturing commercially attractive multi-yarn fabrics of multiple color effects. The modified nylon embodied herein not only provides such a yarn, but also provides a yarn which unexpectedly resists yellowing.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polycarbonamides of the present invention are fiber-forming linear polycarbonamides, wherein recurring carbonamide linkages are an integral part of the polymer chain, which contain, in an amount sufficient to resist yellowing and impart acid dye-resistant and basic dyeability characteristics to the fiber, molecules containing terminal groups of the structure:



wherein  $n$  is an integer having a value from 0 to 8, wherein  $M$  is an alkali metal and wherein  $Z$  is a divalent radical selected from the class consisting of



wherein  $R$  is hydrogen or lower alkyl containing from 1 to 6 carbon atoms, with the proviso that when  $Z$  is



$n$  has a value of at least 1. Accordingly it is pointed out that the  $Z$  radical may be linked to the benzene nucleus directly or through a straight or branched chain alkylene group.

The monofunctional disulfonated compound acts as a chain terminator of the linear polycarbonamide polymer and, therefore, the maximum amount of disulfonated compound is inherently limited if fiber-forming properties are required in the polymer. Generally an amount from about .05 to about 1.0 mole percent of disulfonated compound based upon the moles of amide linkages in the nylon polymer is suitable. Preferably sufficient disulfonate compound is employed to provide a modified nylon having a ratio of sulfonate groups to amine end groups of from 1:1 to 3:1, and most preferably, from 1.5:1 to 2.6:1. Of course, in keeping with standard practices in the art an additional chain terminating compound, such as acetic acid, can be added to the fiber-forming polymer in addition to the disulfonated compound to regulate molecular weight.

In a typical preparation, the novel polycarbonamides of this invention are formed by interpolymerizing a polycarbonamide selected from the group consisting of those prepared by interpolymerizing from (A) a mixture comprising substantially equimolar proportions of a dibasic carboxylic acid having the formula:

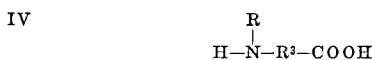


wherein  $\text{R}^1$  is a divalent hydrocarbon radical, and a diamine having the formula:

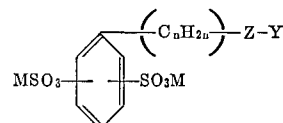


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wherein  $\text{R}^2$  is a divalent hydrocarbon radical and  $\text{R}$  is as defined above, or (B) a monoaminocarboxylic acid of the formula:



wherein  $\text{R}^3$  is a divalent hydrocarbon radical and  $\text{R}$  is as defined above; in the presence of a monofunctional amide-forming disulfonated compound having the general formula:



wherein  $n$ ,  $Z$  and  $M$  are as defined above and wherein  $Z-Y$  represents an amide-forming group. Accordingly when  $Z$  is carboxyl, e.g.,



$Y$  represents a monovalent radical selected from the group consisting of  $-\text{OH}$ , halogen, and  $-\text{OR}^4$  wherein  $\text{R}^4$  represents a monovalent hydrocarbon group, preferably an alkyl group such that the alcohol  $\text{R}^4-\text{OH}$  is volatile below the decomposition point of the polycarbonamide prepared according to (A) or (B) above, and when  $Z$  represents



$Y$  represents hydrogen. It is further pointed out that, consistent with Formula I above, when  $Z$  is



$n$  has a value of at least 1, which indicates that the nitrogen atom is separated from the aromatic nucleus by at least one methylene group.

The disulfonated compounds of this invention include the alkali metal salts of disulfonated benzoic acid, disulfonated phenylalkanoic acid, and of disulfonated phenylalkylamines. The suitable metals include the alkali metals, sodium and potassium. The compounds may be prepared by reacting the precursor monofunctional compound with fuming sulfuric acid followed by treatment with a metal bicarbonate, e.g., potassium bicarbonate, to precipitate the salt. It is to be understood that the  $-\text{SO}_3\text{M}$  groups of the salt may be placed at any position on the benzene ring nucleus, although preferably the two metal salt groups are in positions which are relative to one another and to the amide-forming reactive group  $Z-Y$ , are meta.

The useful disulfonated compounds which may be employed in the practice of the invention include the disulfobenzoic acid bis-metal salts such as 3,5-di(potassium sulfonate) benzoic acid, 3,5-di(sodium sulfonate) benzoic acid and the like; the disulfophenylalkanoic acid bis-metal salts such as 3,5-di(potassium sulfonate)phenylacetic acid, 3,5-di(sodium sulfonate)phenylpropionic acid, 3,5-di(potassium sulfonate)-phenyl(2-methylpropionic) acid, 3,5-di(sodium sulfonate)phenyl(2-ethylhexanoic) acid, and the like; and the disulfophenylalkylamine bis-metal salts such as 3,5-di(potassium sulfonate)phenylmethanamine, 3,5-di(sodium sulfonate)phenylethylamine, 3,5-di(sodium sulfonate)phenylpropyl-N-methanamine, 3,5-di(potassium sulfonate)phenylhexylamine and the like. Also useful are the disulfobenzoic acid halide bis-metal salts, the disulfophenylalkanoic acid halide bis-metal salts, the disulfobenzoic acid ester bis-metal salts and the disulfophenylalkanoic acid ester bis-alkali salts, the said esters being derived from alcohols volatile at a temperature below the decomposition temperature of said polycarbonamides, such that upon being heated with the polycarbonamide the ester will produce amide-forming groups. Illustrative of these compounds are 3,5-di(potassium sulfonate)benzoyl

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chloride, 3,5-di(sodium sulfonate)benzoyl bromide, 3,5-di(potassium sulfonate)phenylacetyl chloride, methyl[3,5-di(potassium sulfonate)]benzoate, isopropyl[3,5-di(potassium sulfonate)phenyl]acetate and the like. Highly preferred are the 3,5-disulfo benzoic acid bis-alkali salts such as the sodium and potassium salts. In the above-listed sub-generic designations the term "metal salt" is deemed to include salts of alkali metals.

In the preparation of the polycarbonamide itself, the nature of the divalent hydrocarbon groups of the dicarboxylic acids, the diamines, and the amino acids of Formula II, III, and IV, respectively, is not critical. Preferably these divalent hydrocarbon radicals contain at least two and no more than about 20 carbon atoms. Typical acids of the class illustrated by Formula II above are oxalic, adipic, suberic, pimelic, azelaic, sebacic, brassylic, octadecanedioic, undecanedioic, glutaric, tetradecanedioic, p-phenylene diacetic, isophthalic, terephthalic, hexahydroterephthalic, and the like, and mixtures thereof.

Typical suitable diamines of the class illustrated above by Formula III are ethylenediamine, propylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, p-xylylenediamine, p-phenylenediamine, hexahydro-p-phenylenediamine, bis(4-aminocyclohexyl)methane, piperazine, dimethylpiperazine, tetramethylpiperazine, the N,N'-dimethyl, the N,N'-diethyl and the N,N'-diisopropyl derivatives of the above, and the like, as well as mixtures thereof. Preferably the useful diamines contain from 2 to about 20 carbon atoms.

Suitable amino acids of the class represented by the Formula IV above are 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid and 17-aminoheptadecanoic acid, as well as the cyclic compounds such as  $\epsilon$ -caprolactam and the like.

In place of the above dibasic carboxylic acids, diamines, and amino acids, the amide-forming derivatives thereof can be employed to produce fiber-forming polymers in which the disulfonated compounds of this invention may be employed. Amide-forming derivatives of the dibasic carboxylic acids comprise the mono- and di-ester, the anhydride, the mono- and di-amide, and the acid halide. Amide-forming derivatives of the diamines include the carbamate and the N-formyl derivatives. Amide-forming derivatives of the amino acids include the ester, the anhydride, amide, lactam, acid halide, N-formyl derivative, carbamate, and, in the presence of water, the nitrile.

Particularly preferred polycarbonamides for use with the disulfonated compounds of this invention are the "66" nylon polycarbonamides, or polyhexamethylene adipamides, derived from the copolymerization of a 6 carbon diamine, i.e., hexamethylene diamine, and a 6 carbon diacid, i.e., adipic acid; the "6, 10" nylon polycarbonamides, or the polyhexamethylene sebacamides, derived from the copolymerization of a 6 carbon diamine, i.e., hexamethylene diamine and a 10 carbon acid, i.e., sebacic acid; and the "6" nylon polyamides or poly-epsilon-caproamides derived from 6-aminocaproic acid or epsilon-caprolactam.

The polycarbonamides of this invention are prepared by procedures well known in the art and commonly employed in the manufacture of simple polyamides. That is, the reactants are heated at a temperature of from 180° C. to 300° C. and preferably from 200° C. to 295° C. until the product has a sufficiently high molecular weight to possess fiber-forming properties, which properties are reached when the polycarbonamide has an intrinsic viscosity of at least 0.4. The reaction can be conducted at super-atmospheric, atmospheric, or sub-atmospheric pressure. Often it is desirable, especially in the last stage of the reaction, to employ conditions, e.g., reduced pressure, which will aid in the removal of the reaction by-products. Preferably the reaction is carried out in the absence of oxygen, for example, in an atmosphere of nitrogen.

The amount of disulfonated additive which may be present as a component part of the polymer chain of the

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polycarbonamides of this invention may vary depending upon the type of polymer desired and the particular shaped article in which it is to find its end use. To obtain satisfactory basic dyeable and acid dye-resist properties when dyeing at pH's of less than 7, it has been found necessary to employ between about 0.5 and 2.0 mole percentage as defined above. At least 0.5 mole percentage of additive is required in order that a significant level of basic dyeable and acid dye-resist properties be obtained. It has been found that the best results are obtained when between 0.5 and 1.0 mole percent of additive is employed, e.g., 0.87 mole percent which provides a sulfonate to amine ratio of 2:1. Amounts greater than 2.0 mole percentage have an adverse effect on the viscosity of the polycarbonamide produced. Since the additives employed in this invention contain only one functional group, i.e., one carboxyl or one amino group, it can be seen that they react in such a manner as to terminate the polymer chain of the polycarbonamide. This type of reaction is similar to the reaction which occurs upon the addition of additives, such as acetic acid, which are termed chain terminators in the art. Thus, it is obvious, that the greater amount of additive which is employed in the present invention, the shorter will be the polymer chain of the polycarbonamide and the lower will be the viscosity of the polycarbonamide. When employing preferred such amounts of disulfonated compound the polycarbonamide produced has been found to possess excellent basic dyeability and acid dye-resist properties and to have a viscosity in the fiber-forming range.

The following examples are illustrative:

#### EXAMPLE I

This example illustrates the preparation of a conventional polycarbonamide, namely, polyhexamethylene adipamide. The polymer and fiber produced therefrom was used as a control and as a standard of comparison with polycarbonamides modified with acid dye resist additives.

To a stainless steel evaporator there was added 8.47 moles of water containing 0.562 mole of hexamethylene diammonium adipate salt dissolved therein. The unit was purged with nitrogen and then pressurized to 13 pounds per square inch gauge. The salt solution was then concentrated to 75% by weight of salt by heating to 137° C. with continuous removal of steam condensate. At this point the salt concentrate was piped under pressure to a stainless steel high pressure autoclave which had been purged previously with nitrogen. In this reactor, which contained a stirrer for agitation, the pressure was immediately raised to 250 pounds per square inch gauge and the temperature was rapidly raised to 220° C. The steam was removed until the polymer melt temperature reached 243° C. At this point the reactor pressure was gradually reduced to atmospheric pressure and the polymer melt allowed to equilibrate for 30 minutes at 278° C.

The finished polymer so produced was melt spun at 280° C. through a 13-hole spinneret yielding white multifilament yarns. These yarns were drawn over hot pins at 90° C. under a maximum draw ratio of 5.65 times their original length.

Dyeing of these yarns was carried out by immersing in an acid dye bath containing 3 percent, based on the weight of the yarn of Scarlet 4RA Conc. CF (C.I. Acid Red 18) and 1.2 percent formic acid. The weight ratio of dye bath to fiber was maintained at 40:1 and dyeing was conducted for 2 hours at 100° C. and at a pH of 3.1. These yarns absorbed .86 percent dyestuff.

#### EXAMPLES II-V

The procedure of Example I was repeated with the exception that various acid dye resist additives were added with the salt to the autoclave in amounts to provide finished polyhexamethylene adipamides having the mole percent indicated below. The modified nylon polymers so produced were spun as in Example I to produce white multifilament yarns which were drawn over hot pins at 90° C. under a maximum draw ratio of 4.60 times their

original length. Under a dyeing procedure as above the following results were obtained. Note the additive of Example II is potassium-3,5-dicarboxy benzene sulfonate which is described in U.S. Pat. 3,039,990. Inasmuch as this additive is difunctional while the additives of the instant invention are monofunctional, a small amount of hexamethylene diamine was added to the batch of Example II so as to adjust the viscosity of the polymer to be approximately the same as the viscosity for the batches of Examples III, IV and V.

TABLE A

| Example | Additive                                  | Mole percent in polymer | Percent dye absorbed |        | Color after 2 hrs. |
|---------|-------------------------------------------|-------------------------|----------------------|--------|--------------------|
|         |                                           |                         | 30 min.              | 2 hrs. |                    |
| II      | Potassium-3,5-dicarboxy benzene sulfonate | 1.0                     | 0.15                 | 0.38   | Light red.         |
| III     | 3,5-di(potassium sulfonate) benzoic acid  | 1.0                     | 0.00                 | 0.32   | White.             |
| IV      | do                                        | 0.39                    | 0.10                 | 0.31   | Do.                |
| V       | do                                        | 0.0695                  | 0.35                 | 0.45   | Light red.         |

<sup>1</sup> By weight.

## EXAMPLES VI AND VII

To compare again the acid dye resistivity imparted by the novel disulfonated compounds of this invention with known acid dye resist compounds, two batches of nylon salt were prepared as follows.

To a 250 pound capacity stainless steel autoclave adapted for batch polycondensation of nylon-66 was charged an aqueous solution containing 49 percent by weight of the adipic acid salt of hexamethylene diamine (nylon 66 salt). The temperature of the charge was 150° C. and the pressure of the autoclave approximately 150 pounds per square inch gauge. To Batch 1 there were added 500 grams of a 25 percent by weight aqueous solution of acetic acid, 3.26 pounds of 5-sulfoisophthalic acid potassium salt which is a monosulfonated acid dye resist additive, and 1.45 pounds of an 85 percent by weight aqueous solution of hexamethylene diamine. The resulting polymer had a relative viscosity of 27.8.

A second batch was prepared in a similar manner adding only 2.20 pounds of 3,5-disulfobenzoic acid bis-potassium salt. The polymer resulting had a relative viscosity of 29.1.

The sulfur content of Batch 1 was 1661 p.p.m. while there was 1702 p.p.m. sulfur in Batch 2 as determined by X-ray analysis.

In addition both batches contained small amounts of an anti-foam additive, and of titanium dioxide.

The contents in each batch autoclave were heated quickly to a temperature of 220° C. and the pressure raised to 250 pounds per square inch gauge. Heating of the contents was continued until the nylon-forming material in the autoclave reached a temperature of 240° C. At this stage water vapor was bled off the autoclave and the pressure in the autoclave reduced to atmospheric pressure. During this pressure reduction the polymer temperature was gradually increased to about 270° C. Upon completion of the polycondensation reactions of each batch the polymers were extruded in the form of a resin on a casting wheel where they were quenched with water. Thereafter the resin was cut in chips suitable for forming into filaments by the use of heated grid spinning apparatus.

The nylon chips comprising each batch were then separately melted in a steam atmosphere in a grid spinning apparatus and spun by conventional melt spinning into a 40 total denier 13 filament yarn. Draw-twist performance, internal quality, physical properties, and dyeing data for the yarn produced from each batch are set forth below. The dye employed was Anthraquinone Blue SWF, an acid type dye.

|                       | Example VI,<br>Batch 1 | Example VII,<br>Batch 2 |
|-----------------------|------------------------|-------------------------|
| Breaks/pound          | 0.61                   | 0.62                    |
| Tenacity (g.p.d.)     | 4.2                    | 4.5                     |
| Acid dye depth rating | Control                | -3.8                    |

Acid dye depth was determined qualitatively by preparing circular knit test fabric-containing control panels knitted from a single bobbin of yarn spun from Batch 1 each next to test panels knitted from different bobbins

of yarn produced from Batch 2. One layer of test fabric is stretched just taut and is viewed against a white background under the light from a Macbeth Daylight Lamp. The test sections are rated for dye depth on a scale ranging from -5 to +5, with plus values indicating the test panel is darker than the control and minus values indicating that test panels were lighter than control. A rating difference of 1 unit indicates the least discernible difference in dye depth. The above rating is the average of six panels of fabric made from yarn of Batch 2 compared with test panels knitted from the same bobbin of yarn produced in Batch 1. Ratings are made visually and hence are qualitative.

A knitted tricot fabric containing panels knitted from Batches 1 and 2 was also prepared and graded with a Colormaster Differential Colorimeter, according to the Modified Adams Chromatic Value System developed by the National Bureau of Standards and recommended for use with this instrument. The following reflectance values were obtained.

| Filter                                     | Percent reflectance |         |
|--------------------------------------------|---------------------|---------|
|                                            | Batch 1             | Batch 2 |
| Green                                      | 29.20               | 30.91   |
| Red                                        | 20.25               | 21.94   |
| Blue                                       | 70.70               | 72.36   |
| Total color value (NBS units) <sup>1</sup> | 0                   | 1.49    |

<sup>1</sup> Control.

According to definitions set forth by the National Bureau of Standards this total color value difference represents a "noticeable" difference. Simultaneously in this reflectance test the hue and saturation of the fabrics knitted from Batches 1 and 2 showed substantially no difference.

## EXAMPLE VIII

In this example the performance of nylon 66 modified with the disulfonate additive described herein (indicated in Table B as "Additive A") was compared with that of nylon 66 modified with the corresponding monosulfonated additive described in U.S. Pat. 3,142,662 (indicated in Table B as "Additive B").

Six yarns were prepared, each containing an additive at the concentration level indicated in Table B. The yarns were all prepared on commercial equipment according to the following procedure: Aqueous nylon 66 salt solution (49% concentration) was charged to an evaporator and concentrated to 75% by weight salt by heating under 13 p.s.i.g. to a batch temperature of 137° C. The concentrated salt (2400 pounds) and an amount of additive (specified in Table B) were charged to an autoclave and heated to 220° C. while the autoclave pressure was

increased to 250 p.s.i.g. to boil off the remaining water of solution. To effect polymerization the temperature was first increased over a period of about 40 minutes to about 243° C. while maintaining the pressure at 250 p.s.i.g.; then increased over a period of about 90 minutes to about 280° C. while the pressure was decreased from 250 to 0 p.s.i.g. The molten nylon after equilibrating under 1 atmosphere steam pressure for 30 minutes was extruded under 25 p.s.i.g. into a ribbon which was quenched with water and air, and cut into ½ inch flake. The nylon flake was charged to a spinning unit where it was melted and, after passing through a sand pack consisting of screen and sand layers and then a distribution plate, was extruded from a 68-hole spinneret; the pressure above the pack was maintained at about 4,000 p.s.i.g. The molten nylon in passing through the sand pack was subjected to a high rate of shear to assure a uniform product. The molten filaments were quenched by cross-current flow of air and gathered into two filament bundles each consisting of 34 filaments. Each bundle was wound onto a bobbin and subsequently drawn the

equivalent sulfonate groups per 10<sup>6</sup> grams of polymer (Batch 2) results in a polymer which, when processed with commercial equipment into drawn yarn, possesses unsatisfactory draw-twist performance as evidenced from the number of breaks per pound of yarn drawn, whereas nylon modified with an amount of Additive A to provide the same equivalent of sulfonate groups possesses acceptable draw-twist performance. Additionally, the filaments of Batch 2 exhibited erratic filament action during quenching caused by its low relative viscosity which resulted in a low quality yarn as evidenced by the breaking strength and tenacity thereof.

In Table C data are given which indicate the basic dyeability of each yarn. The data was obtained by immersing each yarn in a dye bath containing 20 percent, based on the weight of the yarn, Sevron Blue 2G, and determining the amount of dye absorbed. The weight ratio of dye bath to fiber was maintained at 40:1 and dyeing was carried out for 4 hours at 85° C. and at a pH of 6.5.

TABLE C

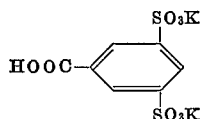
| Batch | Additive | Equivalents per 10 <sup>6</sup> grams |                 | Relative viscosity | Processability <sup>1</sup> | Dye absorbed percent |
|-------|----------|---------------------------------------|-----------------|--------------------|-----------------------------|----------------------|
|       |          | SO <sub>3</sub>                       | NH <sub>2</sub> |                    |                             |                      |
| 1     | A        | 76                                    | 38              | 27.6               | S                           | 10.28                |
| 2     | B        | 76                                    | 30              | 18.6               | U                           | 12.02                |
| 3     | A        | 38                                    | 43              | 34.6               | S                           | 2.97                 |
| 4     | B        | 38                                    | 38              | 26.7               | S                           | 3.54                 |
| 5     | A        | 19                                    | 46              | 38.3               | S                           | 1.01                 |
| 6     | B        | 19                                    | 43              | 34.4               | S                           | 1.02                 |

<sup>1</sup> S=satisfactory, U=unacceptable.

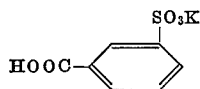
amount indicated in Table B. Physical properties of each yarn were determined and are given in Table B.

TABLE B

Nylon 66 fiber containing the indicated additive where additive "A" is



and additive "B" is



|                                                       | Batch |      |       |       |       |       |
|-------------------------------------------------------|-------|------|-------|-------|-------|-------|
|                                                       | 1     | 2    | 3     | 4     | 5     | 6     |
| Additive                                              | A     | B    | A     | B     | A     | B     |
| SO <sub>3</sub> equivalents per 10 <sup>6</sup> grams | 76    | 76   | 38    | 38    | 19    | 19    |
| NH <sub>2</sub> equivalents per 10 <sup>6</sup> grams | 38    | 30   | 43    | 38    | 46    | 43    |
| Mole percent                                          | 0.87  | 1.74 | 0.43  | 0.87  | 0.22  | 0.43  |
| Relative viscosity                                    | 27.6  | 18.6 | 34.6  | 26.7  | 38.3  | 34.4  |
| Draw ratio                                            | 3.51  | 3.82 | 3.31  | 3.51  | 3.13  | 3.27  |
| Breaks and wraps per lb.                              | 0.028 | 7.00 | 0.065 | 0.013 | 0.053 | 0.024 |
| Drawn denier                                          | 70.5  | 70.0 | 69.9  | 69.7  | 70.1  | 70.6  |
| Tenacity (g.p.d.)                                     | 4.56  | 3.54 | 5.08  | 4.87  | 5.18  | 4.99  |

The data in Table B indicate that nylon 66 modified with Additive B in amounts sufficient to provide 76

The data show that the dye absorbed by the yarns is not a linear function of sulfonate groups present in the nylon and that about 76 sulfonate equivalents are necessary before substantial amounts of dye are absorbed. The data indicate therefore that only the sulfonate groups in excess of the number used in forming salt with amine end groups of unmodified nylon molecules are available for absorbing dye. The nylon of Batch 2 absorbs slightly more dye than the nylon of Batch 1 since twice as many moles of the additive is present to react with amine end groups which reduces the number of amine end groups available to form salt with the sulfonate groups. However, the data further show that to provide 76 sulfonate equivalents with the monosulfonated additive, the molar amount of additive which must be employed adversely affects the relative viscosity of the resulting nylon. Yet, if less of the monosulfonated additive is employed in an effort to provide a nylon having acceptable relative viscosity for spinning and processing, e.g. 0.87 mole percent, the amount of dye absorbed by the resulting nylon is insufficient to attain deep, brilliant colors.

In Table D data are given which show the acid dye-resistant characteristic of each yarn. The data was obtained by immersing each yarn in a dye bath containing 2 percent, based on the weight of the yarn, Kiton Red 2G, and determining the amount of dye absorbed. The weight ratio of dye bath to fiber was maintained at 40:1 and dyeing was carried out for 1 hour at 100° C. and at a pH of 3.5.

TABLE D

| Batch | Additive | Equivalents per 10 <sup>6</sup> grams |                 | Relative viscosity | Processability <sup>1</sup> | Dye absorbed percent |
|-------|----------|---------------------------------------|-----------------|--------------------|-----------------------------|----------------------|
|       |          | SO <sub>3</sub>                       | NH <sub>2</sub> |                    |                             |                      |
| 1     | A        | 76                                    | 38              | 27.6               | S                           | 0.026                |
| 2     | B        | 76                                    | 30              | 18.6               | U                           | 0.021                |
| 3     | A        | 38                                    | 43              | 34.6               | S                           | 0.350                |
| 4     | B        | 38                                    | 38              | 26.6               | S                           | 0.173                |
| 5     | A        | 19                                    | 46              | 38.3               | S                           | 0.940                |
| 6     | B        | 19                                    | 43              | 34.4               | S                           | 0.850                |

<sup>1</sup> S=satisfactory, U=unacceptable.

The data show that the yarn of Batch 1 provides a commercially acceptable nylon having exceptional acid dye resistant properties. The acid dye resistant properties of the nylon of Batch 2 is slightly better than the nylon of Batch 1 which is to be expected since twice the molar amount of Additive B has been used. However, the nylon of Batch 2 does not have acceptable commercial spinability and draw-twist performance.

In Table E data are given which indicate the resistance of each yarn against yellowing when subjected to heat. The data was obtained by successively subjecting the yarns to dry heat for 45 seconds, first at 200° C. and then at 204° C., and measuring the percent whiteness retained.

TABLE E

| Batch | Additive | Initial | Whiteness, percent |         | Equivalents per 10 <sup>6</sup> grams |                 | Mole percent additive |
|-------|----------|---------|--------------------|---------|---------------------------------------|-----------------|-----------------------|
|       |          |         | 200° C.            | 204° C. | SO <sub>3</sub>                       | NH <sub>2</sub> |                       |
| 1     | A        | 92.3    | 74.5               | 67.2    | 76                                    | 38              | 0.870                 |
| 2     | B        | 89.5    | 67.8               | 56.8    | 76                                    | 30              | 1.74                  |
| 3     | A        | 89.8    | 78.8               | 70.2    | 38                                    | 43              | 0.435                 |
| 4     | B        | 91.4    | 83.4               | 80.8    | 38                                    | 38              | 0.870                 |
| 5     | A        | 88.8    | 77.5               | 75.0    | 19                                    | 46              | 0.218                 |
| 6     | B        | 90.4    | 78.1               | 77.6    | 19                                    | 43              | 0.435                 |

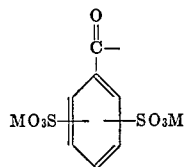
The data in Table E show that the yarn of Batch 1 containing 76 sulfonate equivalents is initially whiter than the yarns of Batches 2-6 and further retains its whiteness to a greater extent than does the yarn of Batch 2 which also contains 76 sulfonate equivalents.

The data in the tables of this example show that nylon modified with the disulfonated compounds described herein provide a nylon which is easily spinnable into fibers having commercially acceptable draw-twist performance. The drawn fibers resist yellowing and when dyed with basic dyes, are dyeable to deep, brilliant colors, and, when subjected to acid dyes, resist dyeing.

In addition to their utility in textile fibers, the polycarbonamides embodied herein are useful in the production of other shaped articles by molding, casting or the like, to produce pellicles, bearings, ornaments and the like.

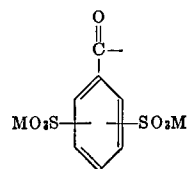
What is claimed is:

1. A linear, fiber-forming polycarbonamide having improved acid dye-resistant and basic dyeability properties wherein recurring polycarbonamide linkages are an integral part of the polymer chain and are formed by condensation of substantially equimolar portions of a dicarboxylic acid of the formula HOOC—R—COOH and a diamine of the formula H<sub>2</sub>N—R—NH<sub>2</sub>, wherein R is a divalent saturated aliphatic hydrocarbon, said polycarbonamide containing as an integral part of the polymer chain disulfonated units of the structure



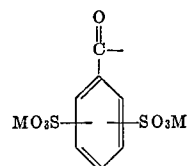
wherein M is an alkali metal, said disulfonate units being present in an amount sufficient to provide a polycarbonamide having a sulfonate group to amine end group ratio of from 1.5:1 to 3.0:1.

2. Fiber-forming polyhexamethylene adipamide containing as an integral part of the polymer disulfonated units of the structure



wherein M is an alkali metal, said disulfonate units being present in an amount sufficient to provide a polymer having a sulfonate group to amine end group ratio of from 1.5:1 to 3.0:1.

3. Fiber-forming polyhexamethylene sebacamide containing as an integral part of the polymer disulfonated units of the structure



wherein M is an alkali metal, said disulfonate units being present in an amount sufficient to provide a polymer having a sulfonate group to amine end group ratio of from 1.5:1 to 3.0:1.

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HAROLD D. ANDERSON, Primary Examiner

U.S. Cl. X.R.

8—55; 57—140; 161—227