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2,709,694

REACTION OF POLYUREAS AND FORMALDEHYDE AND HYDROLYSIS, AND THE PRODUCTS

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This invention relates to synthetic linear polyureas and more particularly to a new process for preparing fibers therefrom.

This application is a continuation-in-part of our co-pending application Serial No. 197,501, filed November 24, 1950, now abandoned.

Linear condensation polyureas have been prepared from dibasic diamines and carbonic acid or amide-forming derivatives thereof, e. g., the anhydride, i. e., carbon dioxide; however, certain of these polyureas, although readily preparable by the polyamide forming reactions taught in U. S. Patents 2,071,250, 2,071,251, 2,071,253, 2,130,948, have been of little utility because of the extreme difficulty experienced in forming shaped objects from them. For instance, no convenient or readily feasible method for preparing fibers therefrom by wet spinning procedures is known. Similarly, the very high softening points of these polyureas have militated against melt spinning them by the standard procedures used with the other linear fiber-forming polyamides, e. g., polyhexamethylenedipamide and the like. These difficulties are particularly apparent in the case of the polyureas containing polymethylene chains separating the urea units and most particularly with polyureas of this type wherein the polymethylene chains are relatively short. For instance, polyethylene, polytrimethylene, polytetramethylene, and polyhexamethylene polyureas show no tendency to melt but rather decompose at extremely high temperatures. It has proven possible to plasticize polyhexamethylene urea with certain polyhydroxy aromatic hydrocarbons, e. g., m-cresol, and in such a plasticized condition to melt-spin the polyurea. However, such a procedure is obviously not readily amenable to standard commercial procedures.

This invention has as an object a method for preparing shaped objects, particularly fibers, from these polyureas. A particular object is a method for preparing shaped objects, and particularly fibers, from polyureas from the short chain polymethylenediamines, e. g., tetramethylene- and hexamethylenediamines, the relatively high thermal resistivity of which polyureas would suggest their use in many high quality outlets demanding the utmost in fiber properties, particularly as regards insensitivity to heat as is desired, for instance, in tire cords. Another object is the preparation of tough, strong, markedly heat resistant shaped objects from high molecular weight polyureas, i. e., high molecular weight condensation polyamides from diamines and carbonic acid or the amide-forming derivatives thereof. Other objects will appear hereinafter.

These objects are accomplished by the present invention wherein a high molecular weight linear polyurea condensation product, of inherent viscosity of at least 0.7 in solution in 98% sulfuric acid at a concentration

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of 0.5 gm. per 100 cc. of solution wherein at least 50% on a molar basis of the combined urea units carry hydrogen on both urea nitrogens, i. e., are —NHCONH— units, is reacted in solution in a solvent predominately, i. e., in major proportion, a strong oxygen-containing acid whose dissociation content is greater than 1×10^{-4} , with from 0.2 to 1.0 mole of formaldehyde for each mole weight of said combined urea unit carrying hydrogen on both urea nitrogens, i. e., for each said —NHCONH— unit, forming the reaction mixture thus obtained into the desired shaped objects, e. g., films or fibers, by wet spinning or wet casting into an aqueous coagulating medium, and finally hydrolyzing the thus formed formaldehyde modified polyurea in dilute aqueous mineral acid, preferably at elevated temperatures, until the combined formaldehyde is substantially removed, i. e., until the starting polyurea is substantially completely regenerated in the desired shaped form. Because of the greater ease of handleability in the formation of shaped objects therefrom, it is preferred to use from 0.2 to 0.6, and most preferably from 0.3 to 0.5, mole of formaldehyde for each mole weight of combined —NHCONH— unit when the polyurea has no more than four chain atoms between each —NHCONH— unit and with from 0.2 to 1.0, and most preferably from 0.5 to 1.0, mole of formaldehyde for each mole weight of combined —NHCONH— unit when the polyurea has more than four chain atoms between each —NHCONH— unit. The process of this invention is especially useful in the formation of fibers. The following examples, in which the parts given are by weight, are submitted to further illustrate and not to limit this invention. As used therein, inherent viscosity ($\eta_{inh.}$) is defined by the following equation:

$$\eta_{inh.} = \frac{\ln \eta_{rel.}}{C}$$

wherein $\ln$ is the natural logarithm,

$$\eta_{rel.} = \frac{\eta_{solution}}{\eta_{solvent}}$$

η being viscosity, C is the concentration of the solute in grams per 100 cc. of solution. Unless otherwise noted all inherent viscosity results are obtained with the polyurea involved dissolved in concentrated sulfuric acid at a concentration of 0.5 gram of polymer per 100 cc. of solution at 25° C.

EXAMPLE I

A solution is prepared by dissolving 64.5 parts of N,N'-polyhexamethyleneurea (prepared from hexamethylenediamine and diethyl hexamethylenediurethane in the manner given in U. S. Patent 2,181,663 and of inherent viscosity 0.99) in 605 parts of 98% formic acid and 54.5 parts of sulfuric acid (95.5% minimum concentration) and 29.5 parts of 37% formaldehyde (10.9 parts of formaldehyde on a 100% basis, corresponding to 0.8 mole of formaldehyde per urea unit, i. e., per —NHCONH— unit). The clear, viscous solution thus obtained is pressure spun at the rate of 2.9 ml. of spinning solution per minute through a 30 hole (0.005 inch hole diameter) stainless steel spinneret into water at 50° C. The yarn travel in the coagulating bath is 38 inches and the yarn windup on a Godet wheel is at 20 feet per minute. The yarn is then drawn 4.6:1 through water at 100° C. immediately after coming off the Godet wheel and taken up on a windup bobbin. The yarn is then boiled taut on the windup bobbin in 2% aqueous sulfuric acid for two hours and finally water washed to remove traces of acid, dried, sized, and twisted two turns

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per inch. The resulting yarn, after boil-off for 45 minutes in skein form, exhibited the following properties:

Denier	96.0
Dry tenacity/elongation (g. p. d./per cent) ¹	1.7/18
Wet tenacity/elongation (g. p. d./per cent) ¹	1.4/18
Modulus dry (g. p. d./100%)	31
Modulus wet (g. p. d./100%)	19
Sticking point	230° C.
Per cent shrinkage in 100° C. water before boil-off	3

¹ As measured on the Instron tensile tester.

EXAMPLE II

Part A.—In a stainless steel bomb of internal capacity corresponding to 1,000 parts of water is placed 40 parts of purified, freshly distilled tetramethylenediamine in an open end glass vessel—the latter being used to prevent contact of the diamine with the internal surface of the metal bomb. The bomb is closed, purged of air by pressuring to the top pressure of a standard commercial fifty pound cylinder of carbon dioxide and then bleeding to a pressure of 25 lbs./sq. in. and repeating the pressuring and bleeding cycle for three times at room temperature. [This top pressure will vary from 600 to 1,000 lbs./sq. in. depending on the ambient temperature and the amount of carbon dioxide in the cylinder.] The bomb is then pressured to 500 lbs./sq. in. with carbon dioxide and then heated to 190° C. The pressure is then adjusted to the maximum cylinder pressure available, approximately 1,000 lbs./sq. in., and heating is continued at 190° C. for a total of two hours. The temperature is then raised to 200° C. and subsequently to 210° C. and held at each of these temperatures for two hours. The temperature is then raised to 235° C. and the vessel then bled to a pressure of 225 lbs./sq. in. and then repressured to full carbon dioxide cylinder pressure. This procedure is repeated every 30 minutes for a total period of two hours. The temperature is then raised to 250° C. and the vessel bled and repressured as at 235° C. for a period of two more hours, followed by the same bleeding and repressuring schedule at a temperature of 265° C. for a period of two more hours. The temperature is finally raised to 280° C. and maintained at this level for a period of four hours while bleeding and repressuring as before. The bomb is then cooled, bled to atmospheric pressure, opened and the solid N,N-polytetramethyleneurea cake removed from the glass liner, cut into pieces weighing approximately 0.5 gram each and then heated at 306° C. under a pressure corresponding to approximately that of 2 mm. of mercury for four hours. There is thus obtained 36 parts of N,N'-polytetramethyleneurea as a white, hard polymer, which exhibits at 25° C. an inherent viscosity in sulfuric acid of 1.07 at a concentration of 0.5 g. of polymer per 100 cc. of solution.

Part B.—A solution is prepared by dissolving 13.9 parts of the polyurea from tetramethylenediamine and carbon dioxide (prepared in general as described previously and of inherent viscosity 1.2) in 100 parts of a mixture of 80.4% formic acid and 19.6% sulfuric acid (6:1 by volume). To the resulting solution is added 1.46 parts of formaldehyde, introduced as 37% formalin (sufficient to furnish 0.4 mole of CH₂O per



unit of the polyamide). The clear, viscous solution is spun in general as described previously in Example I into a 20% aqueous sodium sulfate bath at 50° C. and the yarn drawn 5.8:1 through hot 5% aqueous sulfuric acid solution between the Godet wheel and the windup bobbin. The yarn on the windup bobbin is then boiled taut for two hours in 2% or 5% aqueous sulfuric acid and subsequently washed free of acid with water, dried

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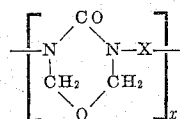
and treated as before. Samples of this yarn exhibited the following properties:

Acid strength in aftertreatment boil	percent	5	2
Denier		128.0	124.0
Dry tenacity/elongation (g. p. d./percent, Incline Plane)		3.6/27	3.4/24
Sticking point	°C	315	320
Percent Shrinkage 100° C. water		1	1

Part C.—Another solution prepared in a similar fashion to that previously described is spun under the same conditions except that the bath travel distance is 100 inches. The yarn is drawn 1.4:1 through air in being taken off the Godet wheel to a windup bobbin. This air-drawn yarn is washed and dried and then drawn through hot oil at 210–220° C. at draw ratios of 5.0:1 and 5.7:1. These hot drawn yarns are boiled off taut on the bobbin in 3% aqueous sulfuric acid for two hours, then skined and boiled off in water. These yarns exhibit the following properties:

Hot-draw ratio	5.0:1	5.0:1	5.7:1
Denier	73.3	94.0	82.3
Dry tenacity/elongation (g. p. d./percent, Incline Plane)	4.5/18	5.0/32	4.3/19
Percent Shrinkage at 100° C	2.0	4.1	1.8
Modulus (g. p. d./100 percent)	47		
Sticking point	°C	300	

The process of the present invention depends for its successful operation on the intermediate formation of uron rings, more particularly, through the formation of 3,5-di-substituted-tetrahydro-1,3,5-4H-oxadiazines, by reaction between the two moles of formaldehyde with each —NHCONH— unit which is reacted. The nitrogens in ring positions 3 and 5 are thus integral members of the polyurea chain and further are the two nitrogens of a single —NHCONH— unit in the polyurea. The structure of these uron intermediates is as follows:



wherein X is the divalent radical joining the urea nitrogens in the starting polyurea. In the final acid hydrolysis step such ring structures are hydrolyzed with the regeneration of the original linear polyurea.

Solutions of these uron intermediates, i. e., the formaldehyde/polyurea reaction products, in strong acids, preferably oxygen-containing strong acids, are surprisingly stable for as long as 24 hours or more at 30° C. in contrast to the formation of insoluble, infusible crosslinked polyamides from such reaction mixtures prepared from the long-chain, dibasic acid/diamine condensation polyamides. Fibers and films may be formed from these solutions at room or elevated temperatures as high as 40° C. without any evidence of deposition of insoluble crosslinked products. Higher solution temperatures are generally avoided because of excessive bubbling, particularly when formic acid is used.

The polyureas to which the film- and fiber-forming process of this invention can be applied, as has been stated before, are the linear condensation polymers resulting from the interaction under amide-forming conditions of essentially equimolar portions of carbonic acid or any of its amide-forming reactants with dibasic amines, i. e., diamines. Carbonic acid or any of its amide-forming reactants such as the acid halides, the anhydride, the esters, for instance with phenols or the lower alkanols, the half amide, i. e., carbamic acid, the half amide esters, i. e., the urethanes, and diisocyanates (see U. S. Patent 2,292,243) can be used in conjunction with the desired diamine in preparing the polyureas. However, for reasons of readier availability, lower cost and easier handling in the polymerization reaction, it is

preferred to use carbonic acid anhydride, i. e., carbon dioxide.

The diamines, which are used in conjunction with carbonic acid or its amide-forming derivatives to form the polyureas which are usable in the process of this invention, are those which contain two hydrogen containing amino groups and are free from nuclear hydrogen, i. e., hydrogen on nuclear (aromatic) carbon, activated by strong ortho-, para-directing groups. Such groups may be defined as those possessing a polarizing force of less than about 0.40×10^{-4} dynes as discussed in some detail at pages 13 through 31 of Mechanisms of Reactions at Carbon-Carbon Double Bonds, Price, Interscience, 1946. Included among such groups as indicated in the table on page 25, *ibid.*, are the amino, methoxy, dimethylamino, chloro, methyl, and chloromethyl radicals but not aminomethyl. Expressed another way, since the amino group is so strongly ortho-, para-directing, this means that those amines wherein one or both of the amino groups is or are directly bonded to nuclear carbon must have substituents on the carbons ortho- and para- to said amino groups, i. e., carrying no hydrogens on said carbons. To illustrate specifically, diaminodurene or p-xylylenediamine can be used in preparing polyureas usable in the process of this invention, although the latter are not as acid resistant as is desired. On the other hand the diaminobenzenes or even the aminomethylanilines cannot be used in preparing operable polyureas. The reason for this, of course, resides in the well-known aniline/formaldehyde resin forming reaction. Polyureas containing these activated hydrogens would obviously react through such hydrogens with the formaldehyde used in the process of this invention to form cross-linked, unhandleable, and probably unregenerable products.

Since the process of this invention depends upon the reaction of the polyureas with formaldehyde and the concomitant formation thereby of polyurons, the polyureas used must contain combined urea chain units carrying hydrogen on each urea nitrogen, i. e., must contain —NHCONH— units as obtained from diprimary diamines. In this connection, it should be pointed out that polyureas prepared from mixtures of diprimary diamines and dissecondary diamines containing less than 50% dissecondary diamine are usable in the process of this invention. Such mixed polyureas contain a preponderance of hydrogen-bearing urea nitrogens, i. e., are prepared from mixtures of diprimary diamines and dissecondary diamines which are predominantly primary. Examples of the preferred primary diamines include, linear, saturated, aliphatic primary diamines, e. g., tetra-, penta-, hexa-, hepta-, octa-, and decamethylenediamines; branched chain, saturated, aliphatic primary diamines, e. g., 3-methylhexamethylenediamine; aromatic primary diamines, wherein the amino groups are directly bonded to an aromatic nucleus and the remaining hydrogens of the annular aromatic carbons are replaced by lower aliphatic hydrocarbon radicals, e. g., diaminodurene, i. e., 1,4-diamino-2,3,5,6-tetramethylbenzene; aromatic/aliphatic primary diamines, wherein the amino groups are separated from the aromatic nucleus by a chain of at least one and preferably two aliphatic carbons, e. g., 1,4-di-(beta-aminoethyl)benzene; cycloaliphatic primary diamines, e. g., 1,4-diaminocyclohexane; aliphatic cycloaliphatic primary diamines, e. g., 1,4-diaminomethylcyclohexane, bis-(4-aminocyclohexyl)methane; primary diamines containing a heteroatom, e. g., oxygen, nitrogen, or sulfur, in the chain or radical separating the two amine groups, e. g., 1,7-diamino-4-oxaheptane, 1,7-diamino-4-thiaheptane, 1,7-diamino-4-methyl-4-azaheptane, and bis-(3-aminopropoxy)ethane.

Because of the greater ease of formation of the polyureas therefrom in higher molecular weights, it is preferred to use those diamines wherein the amino nitrogens are directly bonded to aliphatic carbons. Particularly preferred among this group are those diamines which other

than the amino nitrogens are solely non-aromatic, i. e., aliphatic, including cycloaliphatic, hydrocarbon, i. e., diamines which apart from amino nitrogen and hydrogen thereon are saturated hydrocarbon, i. e., saturated aliphatic and cycloaliphatic hydrocarbon. Due to the decreased formation of colored by-products and the greater ease of polymerization to higher molecular weight polymers, as well as their greater availability at lower cost, the primary diamines wherein the two primary amino groups are separated by a straight chain hydrocarbon radical, i. e., the polymethylenediamines, are especially preferred.

In carrying out the process of this invention, formaldehyde from any source can be used. For instance, the formaldehyde can be added as such in its anhydrous form, usually as the solid cyclic trimer, alpha-trioxymethylene or meta-formaldehyde, or it can be added in its normal commercial form as a 37 to 40% aqueous solution, i. e., the so-called formalin. Alternatively, the formaldehyde can be formed in situ, e. g., through reaction between cyclic formals and aqueous acid. The amount of formaldehyde used in carrying out the process of this invention varies with the polyurea. It is within the scope of this invention to react from 10% to 50% of the urea groups bearing hydrogen on each urea nitrogen in the polyureas with formaldehyde and to carry out the spinning process on the intermediate polyurons therefrom resulting. For most efficient formation of fibers by the process of this invention, it has been found that at least 15% of the —NHCONH— groups in the starting polyurea must be reacted with formaldehyde to form the polyurons. The most effective level of formaldehyde reaction is a direct function of the nature of the polyurea being used. For instance, tough, strong, heat resistant fibers can be most readily prepared from an N,N'-polytetramethylenurea by reacting from 15 to 25% of the urea groups with formaldehyde, wet spinning into fibers, and subsequently drawing and regenerating the polyurea. On the other hand, the best fibers are prepared from an N,N'-polyhexamethylenurea by reacting from 25 to 50% of the urea groups with formaldehyde, wet spinning, acid regenerating, etc. In general, the best products are obtained from the various polyureas by reacting from 15 to 50% of the —NHCONH— groups in the polyurea with formaldehyde.

The polyurea at a concentration of 10–20% in the strong acid, e. g., sulfuric, formic, perchloric, benzene-sulfonic, p-toluenesulfonic, methanesulfonic, ethanesulfonic, chlorosulfonic, methylsulfuric, etc. acids, is reacted with the formaldehyde until the viscosity which at first increases due to the addition of the formaldehyde returns to substantially the initial value. It is to be noted that the formaldehyde in the desired amount is normally added at once to the solution of the polyurea and that the viscosity of the solution increases markedly upon the addition but as the reaction proceeds returns to substantially the initial value.

The aqueous coagulating medium used in preparing films and fibers from these formaldehyde/polyurea reaction products can contain the water soluble salts of ammonia and alkali metal or alkaline earth metals, preferably with the strong mineral acids, and in any case the aqueous coagulating medium is preferably at slightly elevated temperature, e. g., 30–70° C. In some instances, water alone serves sufficiently well as a coagulating medium; whereas in others, relatively high concentrations as high as 50% by weight of the alkali metal or alkaline earth metal salts are needed. The necessity of using these salts in the coagulating baths and the concentration found most efficient are both functions of the density of the polyureas being spun. Preferably the density of the coagulating bath is maintained at that point at which the yarn being spun will move easily through the coagulating bath to the take-up wheel without adhering to itself or falling to the bottom of the coagulating bath. The density of

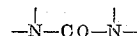
the polyurea yarn being spun varies with the degree of polymerization, i. e., the molecular weight of the polyurea, and also to an appreciable extent on the carbon content of the diamine used in preparing the polyurea. The controlling factor appears to be the number of carbons contained in the diamine for each of the amino nitrogens. For instance as illustrated in the examples, the polyurea from hexamethylenediamine can be readily and easily spun into a warm water coagulating bath; whereas, for greatest ease in handling as well as the quality of yarn therefrom obtained, the polyurea from tetramethylenediamine is preferably spun into an aqueous coagulating bath containing approximately 20% of one of these alkali metal or alkaline earth metal mineral acid salts, e. g., sodium sulfate.

The polyurea fibers of this invention can be prepared in oriented, i. e., drawn, fashion. This can be accomplished by carrying out the drawing at either or both of two stages in the process. For instance, the fibers can be drawn at that stage in the process where they are first formed, i. e., as first removed from the coagulating bath. At this stage the fibers are presumably those of the intermediate polyuron. Drawing at this stage may be in the range from 1.4:1 to 10:1 and may be done in either one step or in several steps, for example, one draw of 3:1 followed by a second draw of 2:1. Drawing may also be carried out on the formaldehyde modified yarns after they have been washed substantially free of acid (and any residual salts from the coagulating bath, if any are used) and dried. It is usually desirable and in many instances even necessary that drawing of the washed and dried formaldehyde modified polyurea yarns be carried out at elevated temperatures, for instance, in the range 150 to 250° C., usually using an inert heat transfer medium, e. g., mineral oil, to more readily effect the heating of the yarn. Drawing may also be accomplished in a hydrolyzing medium, e. g., hot 5% sulfuric acid, as shown in the examples. In any event, no matter how the draw is applied, whether in two stages or in one, whether as first formed or after being washed free of acid and dried, whether in a heat transfer medium or a hydrolyzing medium at elevated temperatures, it is advisable that a total draw of from 2:1 to 8:1 and preferably from 4 to 6:1 be effected. Yarns drawn to the intermediate ratios generally exhibit tenacity-elongation characteristics more desirable for most purposes than those drawn to lower or higher ratios.

The regeneration of the drawn formaldehyde modified polyurea yarns is carried out by simply immersing the yarn, usually in packages or, more conveniently, on bobbins, i. e., as obtained directly from the spinning process, in an aqueous mineral acid solution at 25 to 100° C. for from one to six hours or even longer at temperatures near room temperature. If desired, of course, the regeneration process can be accomplished in a continuous fashion by passing the yarn, drawn or not, as obtained from the spinning process directly through an aqueous mineral acid bath. In this latter instance, it is usually preferred to use high temperatures and thereby cut down the operating time necessary to complete the regeneration. For the most desirable strength properties in the regenerated polyurea yarn, it is preferred that at least 80% of the combined formaldehyde be removed by the hydrolysis procedure. Expressed another way, this means that the preferred yarns will have less than 10% of the original —NHCONH— linkages in the previously described uron rings.

In carrying out the last stage of the process of this invention, i. e., the regeneration of the starting polyurea by dilute aqueous acid hydrolysis of the intermediate polyuron fibers, it is necessary to hydrolyze a major proportion of the uron rings, i. e., to remove a major proportion of the combined formaldehyde. As the degree of hydrolysis increases, i. e., as the percentage of removal of the combined formaldehyde increases, the fibers be-

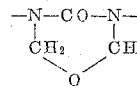
come stronger, tougher, more water-insensitive, more heat-resistant, and less elastic. When the combined formaldehyde is removed, until but about 0.15% of the urea groups are in the form of uron groups, i. e., when the starting polyurea has all but about 0.15% of its urea groups regenerated, the fibers of this invention are outstandingly stronger, tougher, and more thermally resistant. These preferred products have all but about 0.3% of the combined —NHCONH— groups regenerated, i. e., have but about 0.3% of the combined —NHCONH— units in the form of uron rings, i. e., those fibers containing but about 0.6 mole percent formaldehyde calculated on a molar basis of the —NHCONH— units present, which can be no less than 50% of the



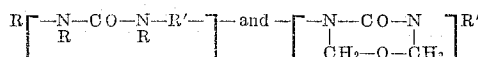
units in the polymer. It is to be noted that because of the extremely high levels of water insensitivity exhibited by the polyurea/polyuron copolymers when this low level of uron content, i. e., this high level of —NHCONH— regeneration, is attained, it is extremely difficult to carry the hydrolysis further, i. e., to remove more of the combined formaldehyde and complete the regeneration of the —NHCONH— units.

This regeneration step, i. e., hydrolysis of the intermediate uron rings, i. e., removal of the combined formaldehyde, can be carried out in any aqueous acidic medium at temperatures in the range 25 to 100° C. for from one to six hours or more, depending on the temperature employed. Because of their greater hydrolytic efficiency, readier availability and low cost, the dilute, e. g., 0.25% to 10%, preferably 1–10%, aqueous mineral acids, e. g., hydrochloric, sulfuric, nitric, phosphoric and the like, are preferred. Since the hydrolysis reaction is essentially complete with no polymer degradation and because of the convenience of such conditions, it is preferred to carry out the hydrolysis in the dilute aqueous mineral acids, e. g., 2–5% sulfuric acid for from one to three hours at the boil.

As stated previously, the first spinning stage of the process of this invention involves wet spinning a strong acid solution of the formaldehyde-modified polyurea into an aqueous coagulating bath, preferably at slightly elevated temperatures, usually in the range 30° to 70° C. Thus, the fibers are, at least for a short time, subjected to the action of an aqueous strong acid. Despite this fact, the percentage of combined formaldehyde in the fibers obtained at this stage of the process is, within analytical errors, the same as that in the spinning solution. At the end of this stage, the fibers are still those of the formaldehyde modified polyurea, i. e., the polyurea/polyuron. Similarly with films, these new polymeric shaped objects have recurring urea groups, separated by aliphatic hydrocarbon chains, in which polymers from 0.10 to 50% of the urea groups are in the form of uron,

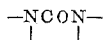


groups. The polymers may be formulated as having the recurring units

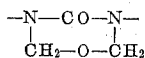


wherein R' is a divalent saturated aliphatic hydrocarbon radical and R is hydrogen or a monovalent hydrocarbon

radical. The polyuron polymers having from 0.15 to 10%, or better, 0.15 to 2.5%, of the recurring urea



groups in the form of uron,



groups are preferred because of the strength, toughness, etc., of the shaped objects therefrom.

Thus, to prepare the desired polyurea fibers, the final stage of the process is necessary, i. e., the dilute aqueous acidic hydrolysis at elevated temperatures in the neighborhood of 100° C. This final regeneration stage of the starting polyurea in fiber form can apparently only be carried out by this dilute aqueous acidic hydrolysis at elevated temperatures. It cannot be carried out by merely boiling with water for the same amount of time nor by heating the formaldehyde treated yarn at the same temperature under vacuum for the same amount of time.

Thus, 100 parts of polytetramethyleneurea ($\eta_{inh.}=1.2$) is dissolved in 700 parts of a 14.3/85.7% by volume concentration of sulfuric/100% formic acid solution, 28.5 parts of 37% formaldehyde, corresponding to 10.5 parts of formaldehyde (20% of the theoretical amount needed to react with all the urea links in the polyurea) is added, and the resultant modified polyurea formed into fibers by wet spinning into an aqueous coagulating bath containing 20% of sodium sulfate at 50° C. The yarn so formed is stretched 1.4:1 in air after being taken up from the Godet wheel. Samples of the yarn so formed are (a) washed with cold water and air dried, (b) taken directly from the take-up bobbin while still wet with aqueous coagulating bath (which, of course, becomes more acid as the spinning proceeds) and placed in boiling water for two hours and subsequently air dried, (c) taken directly from the take-up bobbin while still wet and placed in an oven at 100° C. for two hours under a vacuum corresponding to 2 mm. of mercury, (d) washed in water and dried in an oven for two hours at 100° C. under the same vacuum as above, and (e) washed in water and dried. These various samples were analyzed for combined formaldehyde by a colorimetric procedure involving chromotropic acid. The samples indicated the following formaldehyde contents, respectively, 10.0%, 9.92%, 9.48%, 9.59%, 9.62%.

The theoretical value for the combined formaldehyde in the starting formaldehyde modified polyurea, i. e., a polytetramethyleneurea having 20% of the urea links reacted with formaldehyde, is 9.8%. Thus, it can be seen that the formaldehyde modified polyurea contains the required amount of combined formaldehyde after the spinning process (a) when it has been merely washed with cold water, (b) when it has been boiled with water for two hours (said water containing the residual strong acid adsorbed on the fibers from the spinning process), (c) when it has been heated at 100° C. for two hours under vacuum in the presence of the adsorbed acid, and (d) when it has been washed free of the adsorbed acid and again heated at 100° C. for two hours under vacuum. These results demonstrate the necessity of the dilute aqueous acidic hydrolysis step in preparing, i. e., regenerating, the desired polyureas.

The polyurea shaped objects, as prepared by the process of this invention, are useful in the regular fields of use for such objects. For instance, the polyurea fibers are useful in preparing fabrics for use per se or for reinforcing rubber articles such as tires and the like. The polyurea films are useful as wrapping materials, fabric replacement items and the like. The polyurea films and fibers are particularly outstanding in their various fields of use because of their relatively greater thermal re-

sistivity. This makes the polyurea fibers of particular interest in such uses as tire cord.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

What is claimed is:

1. A process for the preparation of shaped objects having at least one dimension large with respect to another which comprises reacting, in solution in a strong, oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear polyurea having at least 50% combined intrachain —NHCONH— units, of inherent viscosity of at least 0.7 in 98% sulfuric acid at a concentration of 0.5 gm. per 100 cc. of solution, and free of hydrogen on aromatic carbon activated by a strong ortho-, para-directing group, with, as essentially the sole reactant for the polyurea, from 0.2 to 1.0 mole of formaldehyde for each mole weight of combined —NHCONH— group, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified polymer by bringing the same in contact with dilute aqueous mineral acid until at least 80% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

2. A process for the preparation of shaped objects which comprises reacting, in solution in strong, oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear condensation polymer of carbonic acid and a saturated acyclic aliphatic diprimary diamine of up to four carbons, said polymer being of inherent viscosity, in solution in 98% sulfuric acid at a concentration of 0.5 gm. per 100 cc. of solution, of at least 0.7, with from 0.2 to 0.6 mole of formaldehyde for each mole weight of combined —NHCONH— in the polyurea, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified polymer by bringing the same in contact with dilute aqueous mineral acid until at least 95% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

3. A process for the preparation of shaped objects which comprises reacting, in solution in strong, oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear condensation polymer of carbonic acid and a saturated acyclic aliphatic diprimary diamine of up to four carbons, said polymer being of inherent viscosity, in solution in 98% sulfuric acid at a concentration of 0.5 gm. per 100 cc. of solution, of at least 0.7, with from 0.3 to 0.5 mole of formaldehyde for each mole weight of combined —NHCONH— in the polyurea, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified polymer by bringing the same in contact with dilute aqueous mineral acid until at least 95% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

4. A process for the preparation of shaped objects which comprises reacting, in solution in strong, oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear condensation polymer of carbonic acid and tetramethylene diamine, said polymer being of inherent viscosity, in solution in 98% sulfuric acid at a concentration of 0.5 gm. per 100 cc. of solution, of at least 0.7, with from 0.3 to 0.5 mole of formaldehyde for each mole weight of combined —NHCONH— in the polyurea, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified

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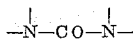
polymer by bringing the same in contact with dilute aqueous mineral acid until at least 95% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

5. A process for the preparation of shaped objects which comprises reacting, in solution in strong, oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear condensation polymer of carbonic acid and a diamine composition consisting essentially of diamines free from hydrogen on nuclear (aromatic) carbon, of more than four chain carbons, and having hydrogen on amino nitrogen which composition contains a major proportion of diprimary diamines, said polymer being of inherent viscosity, in solution in 98% sulfuric acid at a concentration of 0.5 gm. per 100 cc. of solution, of at least 0.7, with, as essentially the sole reactant for the polyurea, from 0.2 to 1.0 mole of formaldehyde for each mole weight of combined —NHCONH— in the polyurea, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified polymer by bringing the same in contact with dilute aqueous mineral acid until at least 95% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

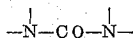
6. A process for the preparation of shaped objects which comprises reacting, in solution in a strong, oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear polyurea, of inherent viscosity, in solution in 98% sulfuric acid at a concentration of 0.5 gm. per 100 cc. of solution, of at least 0.7, having hydrogen on at least 50% of the urea nitrogens and free of hydrogen on aromatic carbon activated by a strong ortho- para-directing group and having at least four chain carbons between the urea groups with, as essentially the sole reactant for the polyurea, from 0.5 to 1.0 mole of formaldehyde for each mole weight of combined —NHCONH— in the polyurea, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified polymer by bringing the same in contact with dilute aqueous mineral acid until at least 95% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

7. A process for the preparation of shaped objects which comprises reacting, in solution in a strong oxygen-containing acid of ionization constant of at least 1×10^{-4} , a high molecular weight linear condensation polymer of carbonic acid and an aliphatic diprimary diamine of more than four chain carbons saturated hydrocarbon but for the two —NH_2 groups, said polymer being of inherent viscosity, in solution in 98% sulfuric acid at a concentration of 0.5 gm. per 1000 cc. of solution, of at least 0.7, with from 0.5 to 1.0 mole of formaldehyde for each mole weight of combined —NHCONH— in the polyurea, forming the reaction mixture thus obtained into the desired shape, coagulating the same, and finally hydrolyzing the thus formed formaldehyde modified polymer by bringing the same in contact with dilute aqueous mineral acid until at least 95% of the combined formaldehyde is eliminated but at least 0.15% of the urea groups remain in the form of uron groups.

8. A shaped object of a high molecular weight linear condensation polymer having recurring

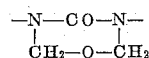


groups separated by saturated aliphatic hydrocarbon chains wherein from about 0.10% to 50% of said

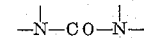


groups are in the form of uron,

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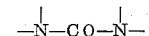


groups, the extra chain valences of the remaining

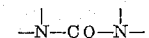


groups not satisfied by hydrogen being satisfied by monovalent hydrocarbon radicals.

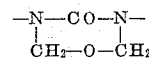
9. A shaped object of a high molecular weight linear condensation polymer having recurring



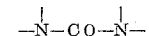
groups separated by saturated aliphatic hydrocarbon chains wherein from about 0.15% to 10% of said



groups are in the form of uron,

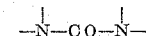


groups, the extra chain valences of the remaining

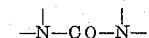


groups not satisfied by hydrogen being satisfied by monovalent hydrocarbon radicals.

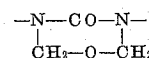
10. A shaped object of a high molecular weight linear condensation polymer having recurring



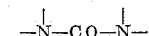
groups separated by saturated aliphatic hydrocarbon chains wherein from about 0.15% to 2.5% of said



groups are in the form of uron,

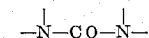


groups, the extra chain valences of the remaining

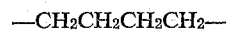


groups not satisfied by hydrogen being satisfied by monovalent hydrocarbon radicals.

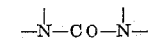
11. A shaped object of a high molecular weight linear condensation polymer having recurring



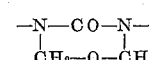
groups separated by tetramethylene,



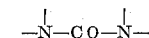
radicals wherein from about 0.15% to 10% of said



groups are in the form of uron,

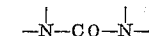


groups, the extra chain valences of the remaining



groups not satisfied by hydrogen being satisfied by monovalent hydrocarbon radicals.

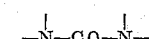
12. A shaped object of a high molecular weight linear condensation polymer having recurring



groups separated by tetramethylene,



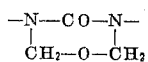
radicals wherein from about 0.15% to 2.5% of said



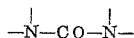
75 groups are in the form of uron,

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groups and the extra chain valences of the remain



groups are satisfied by hydrogen.

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2,430,860
2,441,057
2,550,767

574,739
582,518

14

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