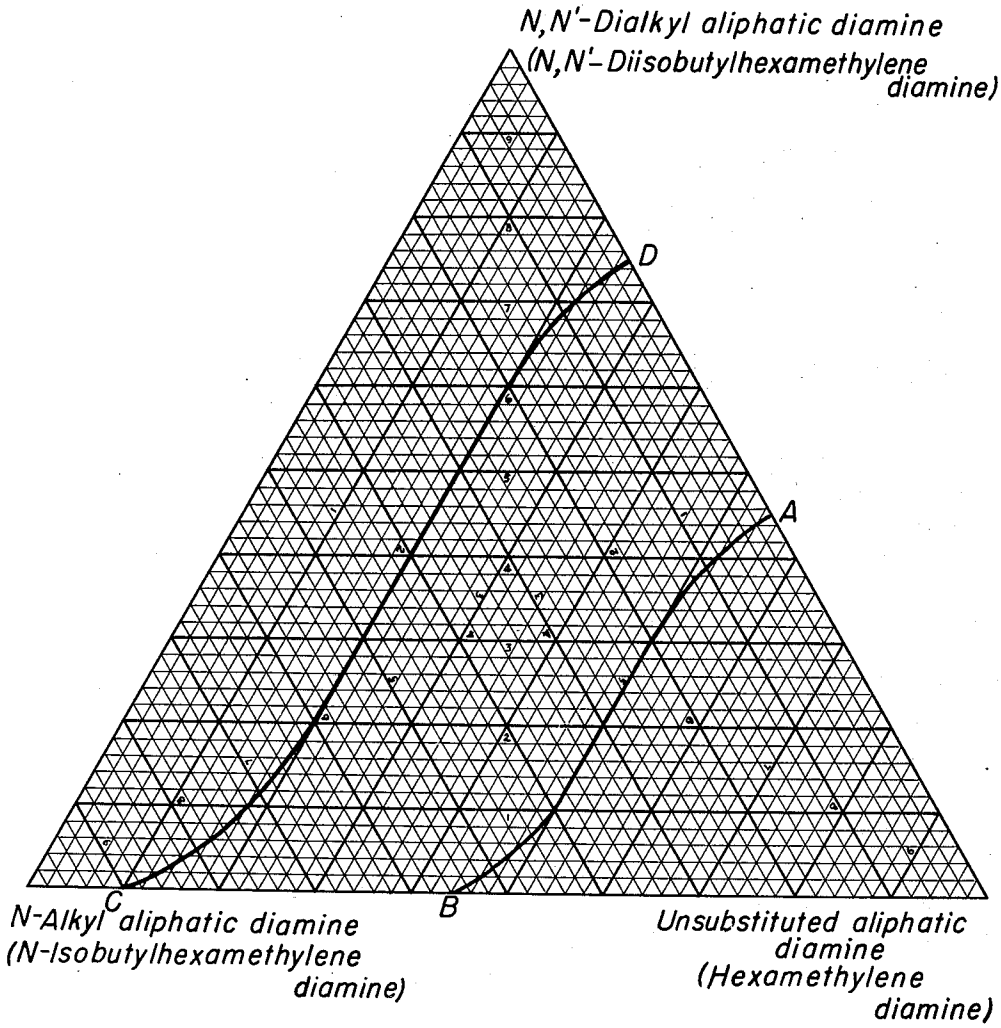
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HEAT-TREATMENT OF N-ALKYL POLYAMIDES

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HEAT-TREATMENT OF N-ALKYL POLYAMIDES

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This invention relates to highly elastic synthetic structures such as filaments, fibers, yarns, threads, etc., and more particularly to a novel method for heat-treating filamentary structures comprised of certain N-alkyl substituted polyamides.

Copolyamides formed from various mixtures (within limits hereinafter defined) of salts of a straight chain dibasic carboxylic aliphatic acid containing at least six carbon atoms in the chain and an unsubstituted aliphatic diamine containing at least five carbon atoms in the chain and a mono- and/or a di- N-alkyl substituted aliphatic secondary diamine containing at least five carbon atoms in the chain, can be readily spun into filaments and yarns having in addition to high tenacity, high heat stability, and high water-insensitivity, a considerable degree of stretch and an elastic recovery comparable to vulcanized rubber which gives them a place of considerable importance in the field of textiles and the like.

These highly elastic N-alkyl substituted copolyamides when formed into yarn by the melt-spinning process commonly used in the nylon art are drawn or stretched by a hot or cold drawing process up to 500% to improve both the tenacity and recovery properties. This may be followed, if desired, by a relaxation step which gives a lower net draw ratio. This drawing operation, even after relaxation, does not stabilize the yarn to shrinkage under boil-off conditions or, indeed, under conditions less than those observed at the boil. This is unsatisfactory since the usefulness of knit or woven fabrics containing such a yarn would be seriously reduced for many textile purposes if under normal conditions of its use or washing, it were to shrink 25–50%.

In the past when such an unstable nature has been noted in yarns made from various polymeric materials, a solution has been to heat-set the yarn or fabric, in a single stage, under critical temperature and tension conditions so that a stable configuration results, which configuration is normally resistant to shrinkage during finishing operations or under washing and ironing conditions of the final garment. It was found, however, that when such a heat-setting process in the vicinity of 90–100° C. was tried upon cakes of N-alkyl (e. g., N-isobutyl) substituted copolyamide yarns, the yarn properties from inside to outside of the cake were not uniform. The yarn in the outer sections of the cake had tenacity lower than that in the interior portion of the cake, and, in fact, in some cases the tenacity of the outer yarn was only half that of the inner yarn. The reason for this non-uniformity was at first thought to be caused by non-uniform heat transfer through the cake. This, however, proved to be erroneous when it was found that even single strands of yarn so heat-treated had tenacity considerably inferior to that of the starting material. Since it had

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been earlier noted that heat-setting at any temperature below this range gave yarns less stable and of higher shrinkage under boil-off, it seemed obvious that a new process of heat-setting would have to be evolved.

An object of this invention therefore is, without damaging the yarn properties, to uniformly heat-set the highly extensible, highly elastic filamentary structures formed from polyamides comprising N-alkyl substituted polyamides.

Another object is to provide a method for heat-treating filaments, fibers, yarns, threads and like structures of copolyamides of sebacic acid with hexamethylenediamine and with mono- and/or di-N-isobutyl-hexamethylenediamine, whereby to uniformly heat-set said structures and effectively reduce the shrinkage thereof under boil-off conditions.

The above and other objects will more clearly appear hereinafter.

These objects are accomplished by this invention, which, briefly stated, comprises subjecting oriented filaments, yarns, etc., prepared from N-alkyl sustituted copolyamides wherein the alkyl group(s) contains at least two carbon atoms, to a two-stage heat treatment. This heat-treatment consists of an initial exposure of the yarn at substantially constant length to a suitable inert heating medium such as heated water or air at high relative humidity until the yarn is heated to a temperature of from 60°–80° C., followed by a second exposure to the medium until the yarn is heated to a temperature of from 90–100° C. When using the process of this invention, it is possible to reduce the shrinkage under boil-off conditions to acceptable levels, i. e., 2–5%, rather than the 25–50% shrinkage characteristics of the non-heat-set material, uniformly throughout the yarns or filaments being treated in various types of yarn packages without damage to yarn tenacity.

The particular copolyamides with which this invention is concerned are those obtained by reacting under linear polyamide-forming conditions a mixture of unsubstituted aliphatic diamine containing a straight chain of at least five carbon atoms separating the nitrogen atoms of the amine groups, and mono- and/or di- N-alkyl substituted aliphatic secondary diamine containing a straight chain of at least five carbon atoms separating the amine groups and wherein the alkyl group contains at least two carbon atoms, with dibasic aliphatic carboxylic acid containing a straight chain of at least six carbon atoms, in the proportions of about one mol of combined diamines to one mol of dibasic acid.

In all cases, in forming the reaction product from diamine and dibasic acid, the amine components must be a mixture of unsubstituted diamine and an N-alkyl substituted secondary diamine. Thus, the polyamide made only from N-isobutylhexamethylene diamine and sebacic acid is not an elastic yarn although it contains

exactly 50% N-alkyl substitution in the diamine. Also, a polymer produced by reacting the dibasic acid with a mixture of N,N'-diisobutylhexamethylene diamine and N-monoisobutylhexamethylene diamine will not result in the production of an elastic yarn. The accompanying drawing illustrates a triangular graph based on the use of mixtures of N,N'-di- and N-monoisobutylhexamethylene and unsubstituted hexamethylene diamine expressed in mol per cent of each amine in the mixture, the mol per cent of each amine increasing from 0% at the base to 100% at the apex which bears the name of the particular amine. The area ABCD, shown as representing an irregular section of the diagram, defines the area which, for practical purposes, includes the mixtures of diamines on a mol per cent basis which may be used as the amine reactant for producing the polymers and products of this invention. It will be understood that while the area may be shifted somewhat when other diamines and when other dibasic acids are used, the diagram, for practical purposes, represents the proportions of all of the N,N'-di- and N-mono-substituted diamines and the unsubstituted diamine which may be used. Generally speaking, the diamine mixtures will vary from 75–0–25 to 45–0–55 to 0–55–45 to 0–90–10 within the limits of said area, these numbers representing the mol per cent successively of the di-mono- and unsubstituted amines. Thus, 40–20–40 represents a 50% substitution wherein 40% is the di- and 20% the mono-substituted diamine and 40% is unsubstituted diamine, the degree of substitution, e. g., 50%, representing the mol per cent of the theoretical maximum substitution possible. Since the limits are based on mol per cent, the specific constitution and molecular weight of the amines will not cause any great change in the limits of the field covered by the invention. Likewise, the diagram may be applied in general regardless of the dibasic acid used so long as the dibasic acid contains at least six carbon atoms in a straight chain.

N,N'-dialkyl and N-alkyl substituted diamines which may be used in place of those specifically mentioned above are N,N'-dilauryl and N-laurylhexamethylene diamine, etc. and in place of hexamethylene diamine, there may be used decamethylene diamine, et seq. As is so common in homologous series, the first member of the series is abnormal. Thus, in the present case, the use of methyl-substituted diamine, whether di- or mon- in combination with unsubstituted diamine will not yield an elastic yarn. From N-ethyl substitution up, within the conditions described herein, the yarns will be elastic. Thus, a polyamide from N-methyl-substituted hexamethylene diammonium sebacate (60–0–40 amine mixture used) elongated only about 25% in the elastic recovery test, whereas the corresponding N-ethyl substituted polyamide had an elongation of more than 100% under similar testing conditions. X-ray diagrams also show the N-methyl-substituted polyamide to be different from other N-alkyl substituted polyamides. It is not necessary that the N-substitution be completely aliphatic; thus, in addition to the strictly alkyl substituents, the aralkyl group, exemplified by benzyl, may also be used for the N-substitution. The N-substitution in the case of the di-substituted diamine need not be the same for each substituent. Furthermore, various mixtures of diamines, whether substituted or unsubstituted, may be used; thus, the N-substituent need not be the same for both the di- and mono-substituted amines and a different number of carbon atoms may comprise the different amines in the mixture, e. g., N-alkyl substituted hexamethylene diamines may be admixed with unsubstituted decamethylene diamine, etc.

Likewise, more than one dibasic acid may be used in the mixture of polyamide-forming reactants to produce different types of interpolyamides. The dibasic acid, however, should contain at least six carbon atoms in the straight chain. Sebacic acid is illustrative. Alternative representative acids include azelaic, pimelic, adipic, suberic and bis-4-carboxybutyl sulfide. Acids containing an even number of carbon atoms in the chain are preferred from the viewpoint of melting point.

It will be understood that the area ABCD may shift somewhat depending on specific factors, including the particular diamine or dibasic acid, the presence or absence of carbon substitution in either, the particular alkyl substituent and the use of interpolyamides containing two or more of the diamines or dibasic acids or both. In general, the area ABCD will cover the useful range.

It is to be understood too, that these illustrative examples, reversing as they do previously conceived opinions, will make it possible for experts to synthesize related elastomers not specifically discussed and this invention contemplates such related polyamides. For example, one can have interpolymers of different polyamides and less substitution will be required as the unsubstituted interpolymer tends to have elastic properties itself. Thus, an interpolyamide made from hexamethylene diamine and adipic acid, hexamethylene diamine and sebacic acid, and caprolactam in the proportions of 40–30–30 described in Brubaker U. S. Patent No. 2,285,009 is already soluble and of a low degree of elasticity. When in such an interpolyamide, the sebacic acid is reacted with a mixture of N,N'-diisobutylhexamethylene diamine and N-isobutylhexamethylene diamine to produce a final interpolyamide having 21% of its nitrogen substituted, the polymer is substantially more rubbery than that of the simple system previously described. The polymer has a low melting point and a high water sensitivity, probably due to its complexity, but it can be quite interesting for certain uses.

The copolyamides hereinabove defined, may be prepared from a mixture of separately prepared diamine-dibasic acid salts as generally described e. g., in Carothers U. S. Patents Nos. 2,071,250, 2,071,251, 2,071,253 and 2,130,948.

These copolyamides, as described previously, have good recovery from high extensions. Thus an undrawn unstretched yarn possesses an elongation in excess of 100% and elastic recovery in excess of 90%. such undrawn yarns, however, remain tacky for a considerable period of time immediately after spinning. The yarn gradually becomes non-tacky. Such reduction in tackiness is promoted, however, by imparting a considerable degree of stretch to the yarn after it has been extruded from the spinneret. Thus, if a yarn made by this invention is stretched 100–500% by passing it between stretching rollers, it loses tack, may be easily handled and may be directly wound thereafter on a bobbin and may subsequently be unwound therefrom. In connection with the matter of tackiness, it is preferred that immediately after the yarns have been solidified and anti-tack agent (e. g., talc or other

inert solid, in finely divided form) be applied to the yarn to prevent initial adherence of the filaments as it passes over the first guide or roll. It is also preferred to relax the yarn as it passes beyond the draw roll to a considerable extent in order to obtain a balance of the desired properties of tenacity, elongation and the like. Thus, if a yarn is drawn 400% to the draw roll, it may advantageously be wound up at lower tension, accomplishing the desired degree of relaxation and giving an over-all draw ratio of 2.0–2.5 or an elongation of 150%. The reason for this lies in the fact that with a greater degree of draw, tenacity and elastic recovery increase, elongation decreases and the amount of force (modulus of elasticity) required to extend the yarn a given percentage also increases. Thus, the stretching and winding conditions are preferably so chosen in accordance with well understood principles as to obtain the optimum relationship of yarn properties for a particular use.

The temperature of spinning varies depending upon the spinning viscosity of the polymer, that temperature being used at which the viscosity of the polymer is suitable for spinning under the conditions used. Generally speaking, the temperature of spinning varies from 200–285° C. Melt-spinning is preferred, although solvent-spinning may be used if desired.

The annealing temperature of the process of this invention is between 60° and 80° C. when a liquid bath medium is used. The starting temperature, of course, may be lower as long as the yarn being treated does not pass through the annealing range faster than a minimum heating time of the order of ½ minute if the yarn is in a package such as a cone, or 3 seconds if the yarn is in single strands. When air, nitrogen, or some other heated gas is used as the heating medium, the temperature of annealing may be higher, 70°–100° C. dry bulb and at least 5° C. lower wet bulb temperature, since the rate of heat transfer from a gas to the yarn is such that the heating rate is diminished so that the conditions of the process as stated herein are substantially met.

The actual heat-setting temperature in the case of a liquid-bath is preferably in the range of 90°–100° C. At this temperature the desired degree of heat-setting occurs, depending upon the size of the package, in a reasonable length of time of the order of 15 minutes to an hour (but, preferably, not less than 5 minutes). Again, as in the case of the annealing treatment if a gas is used as the heating medium, a higher temperature, 95°–105° C. dry bulb and about 5° C. lower wet bulb temperature, may be tolerated because of the reduced rate of heat transfer.

The following specific representative examples further illustrate the principles and practice of this invention:

A 45% aqueous solution of a 40:20:40 salt mixture consisting of 40 mol per cent N,N'-diisobutylhexamethylenediammoniumsebacate, 20 mol per cent N-isobutylhexamethylenediammoniumsebacate and 40 mol per cent hexamethylenediammoniumsebacate is placed in an autoclave and evaporated at atmospheric pressure until a temperature of 132° C. is obtained. The autoclave is then sealed and heated to 225° C. for 3 hours, during which time a steam pressure of 225–275 p. s. i. develops. The pressure developed will vary with the free board in the autoclave above the polymer. The temperature of the batch is raised to 260° C. over a period of about one hour during which the pressure is maintained at about 250 p. s. i. by venting steam. After reaching a batch temperature of 260° C. the rest of the steam is released in ½ to 1 hour. The batch is then held at the same temperature and atmospheric pressure for half an hour. A vacuum is then gradually applied with agitation until a pressure of 1–25 mm. Hg is reached. Agitation is continued under the reduced pressure until the desired degree of polymerization is reached, as indicated by the melt viscosity. Relative viscosity at this point is 35. The molten polymer is then melt-spun by the conventional process through a spinneret into a cooling atmosphere where solidification of the filaments occurs. After this solidification of the yarn occurs and before wind-up, talc is applied to prevent the sticking of the individual filaments. The yarn as spun has 15 filaments and a 430 total denier. This yarn is then drawn by the conventional cold-drawing process (U. S. 2,290,232—Babcock) about 200% so that the final denier is in the vicinity of 200. This yarn has a tenacity of .85 gram per denier (g. p. d.) and a break elongation of 300%. When a sample of this drawn yarn is boiled off for a period of 10 minutes it is observed to shrink 40%. Several samples of this drawn but not boiled off yarn are then given an annealing treatment as indicated below, followed by a final heat-setting operation in water at 90° C.–100° C. to give a residual shrinkage of the order of 2–3%. The yarn is on cones during the annealing treatment and the heat-setting treatment. It is thus held at fixed length and is not free to shrink. To demonstrate the improvement of this invention, there is shown in Table I the differences from the inside to the outside of the yarn package when the yarn package is exposed to the final heat-setting temperature without a prior annealing treatment as compared to the uniformity of the product when this process is used. No data are shown for yarn from the inside of the yarn package in the case of the annealed yarn, since there is no substantial difference from the outside yarn.

Table I

Example	Location of yarn in package	First Yarn Heat Treatment	Elastic Recovery[1] Percent Unexercised/Exercised	Tenacity (g. p. d.)	Stress at 10% Elongation (g. p. d.)	Break Elongation, Percent	Boil-Off Shrinkage, Percent
Control	Outside	90° C. water	91.8/97.1	0.55	.077	261	0–1½
	Inside	90° C. water	96.5/98.9	0.91	.083	272	3
1	Outside	5 minutes, 60° C. water	93.4/97.8	0.81	.085	334	3
2	Outside	5 minutes, 70° C. water	93.0/98.0	0.85	.085	322	3
3	Outside	5 minutes, 80° C. water	93.2/97.9	0.83	.082	322	3

[1] Elastic recovery, unexercised—The yarn is stretched 100% and held for 60 sec., then released for 60 sec. and measured again. Percent recovery $= \frac{2\times\text{original length}-\text{final length}}{\text{original length}}\times 100$

[2] "Elastic recovery, exercised—The sample used above is used again, measuring a new original length."

As an alternative procdure the yarn either on a cone or bobbin or as single ends may be entered into a liquid bath maintained in the vicinity of 50–80° C. and the temperature raised as rapidly as desired up (minimum time of the order of 30 seconds for yarn on cones, spools, bobbins, and the like or about 3 seconds for yarn as single ends) to the final heat-setting temperature in the vicinity of 100° C. in the case of Table II and 90° C. in the case of Table III. The following tables show examples of a yarn so treated, the yarn being the same as that described in Table I. The properties of the yarn at various locations in the package are determined to show the uniformity throughout the cake.

Table II

Example	Location of yarn in package	First Yarn Heat Treatment	Elastic Recovery [1] Percent Unexercised/Exercised	Tenacity (g. p. d.)	Stress at 50% Elongation (g. p. d.)	Break Elongation, Percent	Boil Off Shrinkage, Percent
4	Outside	50° C. water [2]	93.3/98.2	0.75	.091	312	3
	Middle	50° C. water [2]	94.0/98.3	0.75	.090	302	3
	Inside	50° C. water [2]	94.3/98.5	0.77	.093	322	3

[1] Same as Table I.
[2] Initial water temperature.

Table III

Example	Location of yarn in package	First Yarn Heat Treatment	Elastic Recovery [1] Percent Unexercised/Exercised	Tenacity (g. p. d.)	Stress at 50% Elongation (g. p. d.)	Break Elongation, Percent	Boil Off Shrinkage, Percent
5	Outside	50° C. water [2]	93.0/98.2	0.88	.084	289	3
	Middle	50° C. water [2]	93.3/98.5	0.90	.085	296	3
	Inside	50° C. water [2]	93.0/98.2	0.91	.089	301	3

[1] Same as Table I.
[2] Initial water temperature.

As many widely different embodiments may be made without departing from the spirit and scope of this invention, it is to be understood that said invention is not to be restricted in any way except as set forth in the appended claims.

I claim:

1. The process which comprises heating yarns of oriented filaments of a copolyamide produced by reacting (1) at least one unsubstituted aliphatic diamine containing a straight chain of at least five carbon atoms separating the amine groups, (2) at least one member of the group consisting of N-alkyl substituted aliphatic diamines and N,N'-dialkyl substituted aliphatic diamines each containing a straight chain of at least five carbon atoms separating the amine groups and each alkyl group containing at least two carbon atoms, and (3) at least one straight chain aliphatic dibasic carboxylic acid containing at least six carbon atoms in the chain, the relative proportions of said unsubstituted diamines, alkyl substituted diamines, and acids being such as to come within the area ABCD of Fig. 1 of the accompanying drawing, in a medium from the group consisting of water, and air at a high relative humidity, to a temperature of from 60° to 80° C., at substantially constant length for at least 3 seconds and thereafter heating said yarn at substantially constant length and at a temperature of from 90° to 100° C., for from about 5 minutes to about one hour.

2. The process which comprises heating yarns of oriented filaments of a copolyamide produced by reacting (1) an unsubstituted aliphatic diamine containing a straight chain of at least five carbon atoms separating the amine groups, (2) at least one member of the group consisting of an N-alkyl substituted aliphatic diamine and an N,N'-dialkyl substituted aliphatic diamine each containing a straight chain of at least five carbon atoms and each alkyl group containing at least two carbon atoms, and (3) a straight chain aliphatic dibasic carboxylic acid containing at least six carbon atoms in the chain, the relative proportions of said unsubstituted diamine, said alkyl substituted diamines, and said acid being such as to come within the area ABCD of Fig. 1 of the accompanying drawing, in a medium from the group consisting of water, and air at a high relative humidity to a temperature of from 60° to 80° C., at substantially constant length for at least 3 seconds and thereafter heating said yarn at substantially constant length and at a temperature of from 90° to 100° C., for from about 5 minutes to about one hour.

3. The process of claim 2 wherein the unsubstituted diamine is examethylene diamine, the N-alkyl substituted diamine is N-isobutylhexamethylene diamine, the N,N'-dialkyl substituted diamine is N,N'-diisobutylhexamethylene diamine, and the acid is sebacic acid.

4. The process which comprises heating a yarn of oriented filaments of a copolyamide produced by reacting (1) an unsubstituted aliphatic diamine containing a straight chain of at least five carbon atoms separating the amine groups and each alkyl group containing at least two carbon atoms, (2) at least one member of the group consisting of an N-alkyl substituted aliphatic diamine and an N-N'-dialkyl substituted aliphatic diamine each containing a straight chain of at least five carbon atoms, and (3) a straight chain aliphatic dibasic carboxylic acid containing at least six carbon atoms in the chain, the relative proportions of said unsubstituted diamine, said alkyl substituted diamines, and said acid being such as to come within the area ABCD of Fig. 1 of the accompanying drawing in a medium from the group consisting of water, and air at a high relative humidity while maintaining said filaments at substantially constant length, the said heating procedure proceeding gradually from an annealing temperature within the range of from about 60° C. to 80° C. within which limits the said yarn is maintained for a period of at least about three seconds to a heat-setting temperature within the range of from about 90° C. to 100° C. at

which said yarn is held for a period of at least about five minutes.

5. The process of claim 4 wherein the unsubstituted diamine is hexamethylene diamine, the N-alkyl substituted diamine is N-isobutylhexamethylene diamine, the N,N'-dialkyl substituted diamine is N,N'-diisobutylhexamethylene diamine, and the acid is sebacic acid.

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