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SUPERSTRETCHING POLYESTER
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This invention relates to the manufacture of shaped structures comprised of linear super-polymers. More particularly, it relates to a new and improved method for manufacturing filament and film structures comprised of synthetic, linear polyesters.

The primary object of this invention is to provide an improved and economical method for manufacturing filaments, film and like structures of synthetic, linear polyesters.

Another object is to provide an economical method for manufacturing yarns, films and the like of linear polymethylene terephthalates.

A more specific object is to provide a method for producing low denier, textile filaments from molten linear polyethylene terephthalates with a minimum of melt-spinning equipment.

These and other objects will more clearly appear hereinafter.

With respect to the general procedure used for spinning melt-spinnable materials, such as synthetic linear polyamides and polyesters, a very large percentage of the total cost of production of textile yarns therefrom resides in the melt-spinning phase of the process. The orienting or cold-drawing operation is considerably cheaper and represents a much lower investment figure than the rather complex and expensive melt-spinning machines. Obviously, a much cheaper spinning process could be realized if it were possible to spin multi-filament yarns having large denier filaments and then by a relatively cheap drawing process to achieve the desired yardage of material of a given denier. In the case of almost all melt-spinnable polymeric materials, however, there appears to be an upper limit somewhere in the range of 300-900% insofar as extension of a given polymer is concerned. At this point orientation and/or crystallization has proceeded to such a point that the drawing cannot be accomplished further without actually rupturing or breaking the individual filaments and ultimately the yarn itself. Maximum extensions of this order will generally not justify the process as being commercially advantageous.

Unexpectedly I have found that under critical temperature conditions, a freshly melt-extruded, amorphous, polymethylene terephthalate structure such as an as-spun yarn, film etc., can be super-stretched up to 75 times its original length (75X) without appreciable orientation or crystallization, and that the stretched structure can be subsequently drawn or otherwise treated in known fashion to improve its tenacity, elongation, etc.

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Accordingly, the objects hereinabove stated are accomplished by this invention which comprises super-stretching freshly-formed (by the melt-extrusion process) yarns, films and like structures of substantially amorphous polymethylene terephthalate from 10-75 times their original length (10X-75X) at a temperature between 20° and 60° C. above the apparent minimum crystallization temperature (T_i) of the amorphous polyester, during which step no appreciable orientation or crystallization occurs, and thereafter orienting the structures to a useful degree by drawing them an additional 1.5-4X at a temperature between the second order transition temperature (T_g) of the amorphous polyester, and T_g+30° C. If a high degree of crystallinity is desired for a more stable configuration, the orientation step may be followed by another drawing operation of 1-2X at a temperature at least 50° C. above T_i . The same result may be obtained by heating the yarn or film in this temperature range at constant length. If desired, the drawing operation may be followed by a hot relaxing step to secure increased elongation. Thus, by the process of this invention, a polyethylene terephthalate structure, for example, may be permanently extended 50-200 or more times its original length.

To facilitate an understanding of the invention reference should be had to the following definitions and explanations of terms, it being understood that these terms whenever employed in the following description and claims are to be construed in accordance with such definitions and explanations.

The expression "intrinsic viscosity," denoted by the symbol η_0 , is used herein as a measure of the degree of polymerization of the polyester and may be defined as:

$$\text{Limit } \frac{\ln(\eta_r)}{C} \text{ as } C \text{ approaches } 0$$

wherein η_r is the viscosity of a dilute, phenol-tetrachloroethane (60:40) solution of the polyester divided by the viscosity of the phenol-tetrachloroethane mixture per se measured in the same units at the same temperature, and C is the concentration in grams of the polyester per 100 cc. of solution.

The expression "second order transition temperature" (T_g) is defined as the temperature at which a discontinuity occurs in the curve of a first derivative thermodynamic quantity with temperature. It is correlated with yield temperature and polymer fluidity and can be observed from a plot of density, specific volume, specific heat,

sonic modulus or index of refraction against temperature.

For the purpose of this invention, a satisfactory method for measuring the second order transition temperature is as follows:

A plug of the polymer to be tested is formed. The plug should preferably be formed from the melt and rapidly cooled so that it is obtained in the amorphous form. It is then weighed in air and fitted for hanging from a balance. The plug is so suspended from the balance that it hangs centrally in a bath of silicone oil and 1" below the surface. The temperature of the bath is thermostatically controlled. A silicone oil is especially desirable because of the excellent stability and low probability of attack on polymer specimens. A thermometer calibrated in 0.1° C. is placed in the bath with the polymer plug to measure the temperature. The bath is held at a given temperature until the polymer plug in the silicone oil has reached a constant weight. The plug normally reaches the value within 15 minutes. After the balance reading is made, the temperature is raised 10° C. and the process repeated. Usually a temperature range of approximately 0°-160° C. gives enough points to allow calculation of T_g . This range is obviously determined by polymer type.

From the weight of the polymer plug in air and in silicone oil, it is possible to calculate density and specific volume at a given temperature. Corrections are made for the buoyant effect of air on the polymer plug. The equation used in calculation is:

$$V_p = \frac{W_v - W_s}{W_v \times \rho_s - \rho_p}$$

where V_p =specific volume of polymer, ρ_p =density of polymer, ρ_s =density of silicone oil, W_v =weight of polymer in vacuo, W_s =weight of polymer in silicone oil.

The portions of the curve of specific volume vs. temperature above and below T_g are linear. The coefficients of expansion are calculated from the slopes of the curve.

$$\beta = \frac{\text{slope}}{V_0}$$

where β =volume expansion coefficient and V_0 =specific volume at 0° C. The second order transition temperature is the point at which the extensions of the two linear portions of the curve intersect.

The expression "apparent minimum crystallization temperature" (T_i) is defined as the lowest temperature at which a marked rate of density change, which is known to occur simultaneously with crystallization, takes place within six hours. For every temperature below the apparent minimum crystallization temperature a sample of polyester maintained constant at said temperature below T_i will not vary substantially in density over a long period e. g., six hours. However, as soon as the polyester is subjected to the temperature T_i there occurs a rapid change in density. Actually the rate changes quite abruptly from no change in six hours to a change within minutes for only a few degrees temperature difference. The value of T_i is conveniently assigned from density determinations done in air or silicone oil and is based on crystallization by heat only.

Since a change in density accompanies the mechanism of crystallization, it is only necessary to determine the temperature at which a

significant change in density occurs. Thus, the temperature at which the density of the polymeric material starts to rapidly increase may be taken as the apparent minimum crystallization temperature. A suitable apparatus with which to measure the density of polymeric materials is that of a density gradient tube. Briefly, one embodiment may consist of a long tube filled with partially mixed carbon tetrachloride and toluene, so that a density gradient of 0.86-1.59 grams per milliliter is maintained from top to bottom of the tube. After proper calibration of density vs. position, the tube can be used to measure densities of polymeric materials by determining the position of small samples in the tube. The method is especially applicable to heavy denier monofilaments, since with multi-filament yarns, there is always the possibility of small bubbles of air being entrapped, which will tend to give inaccurate density readings.

To measure T_i several small pieces of monofilament (approximately 10 grams) of the amorphous synthetic, linear polyester to be tested are suspended in silicone oil or air in such a manner that the temperature can be thermostatically controlled. A convenient starting temperature is the second order transition temperature, since no appreciable crystallization occurs below this limit. At the end of 5 minutes, the time necessary for the polymer sample to come to the temperature desired, a density measurement is taken by dropping a piece of the monofilament into the density gradient tube and allowing it to reach an equilibrium height. This occurs within about 15 minutes and does not allow enough time for swelling by the CCl₄-toluene mixture. At various time intervals up to 6 hours, density measurements are made and the density is plotted against time to show the rate of crystallization. Below the apparent minimum crystallization temperature, this graph will normally show a straight line with no apparent increase in density of the polymeric material over this period of time. Simultaneously, other samples may be run at increasing temperatures say in steps of 2, 5, or 10°. The plot of density vs. time will, in nearly all cases, be substantially a straight line until the apparent minimum crystallization temperature is exceeded, at which time the density will increase over a period of time until a maximum order of crystallinity is reached and the curve will again flatten out. This procedure will give a temperature range as an approximation of T_i . Further density determinations are carried out in the vicinity of this approximate temperature using smaller temperature increments of the order of 0.5-1.0° to determine accurately the apparent minimum crystallization temperature. Depending upon the accuracy of the apparatus used and the care with which the procedure is followed, T_i is ordinarily reliable to within 1 or 2°.

The term "drawing" as used herein is defined as the non-recoverable elongation of a preformed body, accompanied by a permanent change in molecular orientation of the body, while the term "stretching" is defined as the non-recoverable elongation of a preformed body, which elongation, however, does not result in any appreciable change in the molecular orientation of the body.

It is necessary in the process of this invention to carry out the super-stretching operation on totally amorphous or almost totally amorphous

polymer. This is essential because, otherwise, the stretch ratios of the type described herein as being obtainable at the super-stretching temperature, and the advantages resulting therefrom, will not be realized, since as the degree of crystallization increases the limit of maximum stretch ratio decreases until finally it is in the more or less conventional range of 3-7X. Further, any considerable degree of initial crystallization will prevent the attainment of maximum orientation, in the secondary draw carried out between T_g and $T_i+30^\circ\text{C}$. Obviously, if a partially crystalline material is super-stretched and then subjected to the secondary draw, it will have an even higher degree of crystallization and, thus, it will be very difficult to secure the alignment desired in orientation, since the free movement of the molecules in the polymeric structure will be restricted by crystal formation. The amorphous state of the polymer is readily achieved in known manner by forming the desired structure from a melt of the polymer and rapidly chilling or cooling the structure as it is formed.

When an amorphous material that is potentially crystalline, such as the synthetic linear polyesters with which this invention is concerned, is subjected to heating, two opposed forces are set in motion. First, with an increase in temperature the amorphous polymer, which obviously has no sharp melting point tends to get softer and softer and hence more fluid. Secondly, as the degree of mobility of the polymer molecule increases with an increase in polymer fluidity there is a tendency for the molecules to align themselves in the regular and orderly pattern of crystalline structure which, of course, tends to the solid state and a decrease in fluidity and stretchability. Obviously maximum fluidity and hence stretchability of the preformed structure of polymeric material is just below the temperature at which the rate of crystallization of the polymer overcomes the tendency of the polymer to soften. I have determined that for the synthetic linear polyesters herein concerned this critical temperature is $T_i+60^\circ\text{C}$. At temperatures below $T_i+20^\circ\text{C}$ the polyester structures are generally not sufficiently fluid to permit of a commercially useful degree of primary stretch. The useful temperature range in which the primary super-stretching of the preformed structure of amorphous polymeric material should be accomplished is therefore from $T_i+20^\circ\text{C}$ to $T_i+60^\circ\text{C}$.

The primary super-stretching operation, since neither appreciable orientation nor crystallization occurs, obviously does not result in a commercially useful structure except for very specialized uses. For example, super-stretched polyester yarns have tenacities in the range of 0.4-0.8 g. p. d., which tenacities are too low for most textile requirements. Therefore, the super-stretched filaments, films, etc., herein must be subjected to a drawing operation in which orientation, together with some crystallization, is obtained. This drawing operation should be carried out at a temperature between T_g and $T_i+30^\circ\text{C}$. It consists in subjecting the yarn to drawing tension at these temperatures so that an extension of the order of 1.5-4 times the original length is obtained (1.5-4X).

This drawing operation may in turn be followed, if maximum crystallization and maximum tenacity of polyester structure are desired, by a second drawing operation carried out prefer-

ably at a temperature at least 50° above T_i . Thus, with maximum orientation obtained by the secondary draw between T_g and $T_i+30^\circ\text{C}$, a high degree of crystallinity is obtained by giving it a final draw at a temperature above T_i . For the sake of efficiency and to secure maximum crystallinity with contact times commensurate with present-day high speed drawing operations, e. g., 0.1 of a second or less for yarn, it is necessary to raise the temperature of the polymer structure to a value at least 50° higher than its apparent minimum crystallization temperature for the final draw. If maximum crystallinity is not desired, the final draw may be imposed at lower temperatures above the apparent minimum crystallization temperature.

As an alternative procedure for obtaining a high degree of crystallinity, the yarn or film may be heat-treated without being subjected to drawing tensions. This may be done continuously or batchwise, as multiple ends, or on a suitable package. Whether or not the structure is allowed to shrink obviously depends on the end use for which it is intended. By the proper choice of tension conditions, the final elongation in the material can be varied considerably while the increased crystallinity insures a stable structure.

The initial super-stretching operation should preferably be carried out under the influence of dry heat, since a plasticizing medium will induce crystallization and lower the maximum stretch ratios obtainable. Suitable media might be: air, glycol, silicone oils, mineral oil or other media of like nature that are capable of being heated to the high temperatures needed without plasticizing the polyester. Of course, it will be realized that a preferred processing medium should not add unusual difficulties of removal from the finished product. Secondary and tertiary drawing operations may be carried out by any of the many means known in the art. For example in treating yarns, hot rolls, hot plates, heated draw pins, heated chambers or heated baths of inert liquids may be employed. The yarn may be packaged between the various drawing operations or preferably may be run in a continuous manner, from one draw to the other. It may also be desired to hot relax the yarn continuously after the final drawing operation. In this manner a completely continuous process may be obtained.

A convenient method for the super-stretching and drawing of film is by the extrusion of a large diameter tube of molten polyethylene terephthalate from a disk which contains an orifice through which air or other gases are blown to quench and expand the tube. The blown-out tube is nipped and squashed into a double sheet between rollers and super-stretched over a heated, suitably-shaped former, e. g., torpedo or horseshoe shaped, and so stretched simultaneously in two directions. To orient the film, a larger, suitably-shaped former may be used so that a drawing operation is obtained with accompanying orientation. Another method is to extrude the film from a slot orifice. Then the film may be stretched longitudinally by means of a pinch roll system and at the same time stretching laterally by means of clamps which are fastened at both edges of the film and move apart as the film is drawn longitudinally by the action of the pinch roll. This stretching may be followed by a drawing process in the same manner to secure orientation with con-

sequent improved properties of the film. This film, during a two-dimensional drawing operation, may be heated during the stretching or drawing operation by means of hot, inert gases or liquids or by induction heating. While it is preferred that the two-dimensional stretching and orientation of the films of this invention take place in two directions at once, it is not essential. A film may be stretched or drawn, for example, between two sets of rolls, first in one direction, then in another.

Continuous filaments of yarns of the high polymeric, linear esters of this invention are best prepared by melt-spinning the polyester, e. g., melting chips of synthetic, linear polyesters on a heated grid, passing the melt through a filter bed made up of a number of small particles, such as sand, forcing it through a spinneret and cooling the filaments so formed. When melt-spinning these polymeric esters, it is necessary for the ester to be substantially water-free, if hydrolysis of the polyester in this process is to be avoided. Filaments may also be formed from solutions of these polymeric esters using any of the solution spinning processes known in the art. Suitable solvents for these polymeric esters are cresol, nitrobenzene, chlorinated compounds such as tetrachloroethane, etc.

While this invention will be hereinafter described with particular reference to polyethylene terephthalate, it is understood that the invention comprehends the treatment of all fiber-forming synthetic linear polyesters including the inclusion therein of minor amounts of modifying materials. Polyethylene terephthalate itself is the poly-condensation product, preferably under melt polymerization conditions, of ethylene glycol and terephthalic acid or an ester-forming derivative thereof. It will be obvious, of course, that during the preparation of this polyester minor amounts of a modifying material may be added, for example, another glycol or another dicarboxylic acid. Thus, a suitable funicular structure comprised essentially of polyethylene terephthalate may have in the polymer molecule up to 10% of another glycol such as diethylene glycol; tetramethylene glycol, hexamethylene glycol, etc., or again, may contain up to 20% of another acid. As suitable examples of modifying acids, we may mention hexahydroterephthalic acid, bibenzoic acid, adipic acid, sebacic acid, azelaic acid, the naphthalic acids, 2,5-dimethyl terephthalic acid, bis-p-carboxyphenoxyethane, etc.

These modifiers may be added to the polymer molecule by inclusion as one of the initial reactants during the polymerization process, or again, the modifying materials may be polymerized separately and then melt-blended with the polyethylene terephthalate provided that the over-all amount of modifier in the final polymeric material does not exceed the limits stated above.

While I have spoken of the polymerization process by which the polyesters of this invention may be formed as being preferably carried out in the melt, it is, of course, to be understood that polymerizing in the solid phase, as well as in solution (e. g., in a solution of Fomal (a eutectic mixture of phenol and 2, 4, 6-trichlorophenol in a mol ratio of 3:1)) or emulsion by more or less conventional procedures is also comprehended. A more detailed explanation of a suitable polymerization process for the type of

polyesters comprehended here is contained in Whinfield and Dickson, U. S. Patent No. 2,465,319.

Fiber-forming, synthetic, linear polyesters should possess an intrinsic viscosity of at least 0.3 and preferably should have an intrinsic viscosity of from 0.3-1.5. Synthetic linear polyesters having intrinsic viscosities of less than 0.3 do not form commercially acceptable fibers. The transition temperatures and degradation temperatures are too low to be useful and, furthermore, the physical and chemical properties of fibers made from such low molecular weight materials are not in the useful range insofar as textile purposes are concerned.

The following examples wherein are set forth certain preferred embodiments further illustrate the principles and practice of this invention.

Example I

A 300-denier, 34-filament amorphous polyethylene terephthalate yarn (as-spun) ($T_g=67^\circ\text{C.}$; $T_i=99^\circ\text{C.}$) is run by a suitable system of guides through a mineral oil bath heated to a temperature of 127°C. at a speed of 2 ft. per min. As the yarn emerges from the bath, it is passed around a roll (3 wraps to prevent slippage), which roll rotates to give a yarn take-up speed of 28 ft. per min. or an effective stretch ratio of the order of $13\times$. From this roll, the yarn is passed around a pin (2 wraps) heated to a temperature of 94°C. This in turn passes to another (final) draw roll, around which the yarn passes (3 wraps) and then to a suitable take-up device. The final draw roll has a surface speed 4 times that of the first draw roll to give an effective draw ratio in the second stage of $4\times$, with an over-all total draw ratio of $52\times$. This final draw induces orientation and a small degree of crystallization in the polyethylene terephthalate yarn. The yarn drawn by this process exhibits a tenacity of 2.2 at an elongation of 30%.

Example II

Another sample of polyethylene terephthalate yarn of Example I having 70 filaments and a total denier of 1200 is passed in the as-spun or amorphous condition by a suitable system of guides into a mineral oil bath heated to a temperature of 128°C. This is taken up on an intermediate draw roll after passing through the bath in the manner described in Example I at a speed such that a stretch ratio of $52\times$ is obtained. This is in turn passed through another mineral oil bath heated to a temperature of 95°C. to another draw roll operating at a peripheral speed of twice that of the intermediate draw roll, to give a $2\times$ draw for a total of $104\times$. The yarn is then taken up in a suitable manner and, after washing to remove the mineral oil, followed by drying, the yarn exhibits a tenacity of 2 g. p. d. at 27% elongation.

Example III

50 ends of as-spun polyethylene terephthalate ($T_g=67^\circ\text{C.}$, $T_i=99^\circ\text{C.}$) 300-denier monofil in the form of a warp sheet are fed at a speed of 10 yards per minute into a mineral oil bath heated to 154°C. The monofilaments then pass around an intermediate draw roll several wraps to prevent slippage. This roll rotates at a peripheral speed of 300 yards per minute to give a primary super-stretch ratio of $30\times$. The ends then pass continuously into another oil bath heated to 120°C. , from which they pass to the final draw

roll and take-up mechanism at a speed of 620 yards per minute. This gives a secondary draw of $2.06\times$ or a total draw ratio of $62\times$. The individual monofilaments drawn by this process have a tenacity of 1.81 g. p. d., an elongation of 107% and a denier of 4.0-4.5.

Example IV

This example shows that the drawing process of this invention is not restricted to any one super-drawing medium.

A 2700-denier, 9-filament as-spun polyethylene terephthalate yarn ($T_g=67^\circ\text{C.}$, $T_i=99^\circ\text{C.}$) is fed at a rate of 2.67 yards per minute into a bath of a polyalkylene glycol heated to a temperature of 127°C. As in the previous examples, it is passed several wraps about an intermediate draw roll so that the stretch ratio originating in the primary bath is $26\times$. The yarn then goes to a suitable yarn take-up device. This yarn is next passed several wraps about a roll (85°C.) and then to another draw roll operating at a speed of 2.2 times that of the first draw roll, from which the yarn passes to a suitable take-up mechanism. The final yarn has a denier of 47 and a tenacity of 1.70 g. p. d. at an elongation of 81%. The overall draw ratio is $57\times$.

Example V

This example illustrates the use of hot air for the initial super-stretching. A vertical 9' heated tube (6" in diameter) with a cell wall temperature of about 200°C. , together with updraft recirculated air preheated to a temperature of about 105°C. , is used so that an air temperature of 160°C. is obtained. A 3450-denier, 10-filament polyethylene terephthalate yarn ($T_g=67^\circ\text{C.}$, $T_i=99^\circ\text{C.}$) is fed into this cell at the top at 8.3 yards per minute and passes down the cell to a primary draw roll having a peripheral speed of 172 yards per minute, to give a stretch ratio of $21\times$. The yarn from this operation is then passed with several wraps around a roll (100°C.) to insure uniform heating, and then to a final draw roll which is operated at such a speed as to give an over-all draw ratio of $40\times$. The yarn is taken up on a suitable cone or bobbin and is then baked in an oven (180°C.) for 1 hour. This yarn exhibits a tenacity of 2.4 g. p. d. at an elongation of 177%.

Example VI

Using the same type of starting yarn as described in the previous example and a similar cell, the yarn is fed into the cell at 8.3 yards per minute, and super-stretched in the cell $18\times$. The yarn then passes over a 16" hot plate heated to 95°C. where an additional draw of $2.5\times$ is imposed. This gives an over-all draw ratio of $46\times$ with the yarn being taken up at a wind-up speed of 390 yards per minute. This yarn has a tenacity of 1.9 g. p. d. at an elongation of 16%.

Example VII

A polyethylene terephthalate yarn as described in the previous example is fed at the rate of 10 yards per minute into a silicone oil bath heated to a temperature of 130°C. As the yarn emerges from the bath, it passes several wraps around the primary draw roll, which operates at a peripheral speed of 300 yards per minute for a super-stretch ratio of $30\times$. The yarn passes

continuously into a second silicone oil bath heated to 85°C. and then to the second draw roll, which operates at a peripheral speed twice that of the first to give a total draw to this point of $60\times$. Next, the yarn is fed across a 30" hot plate (190°C.) to the final draw roll, which operates at a speed to give a draw ratio for the third stage of $1.3\times$ or an over-all draw ratio of $78\times$. The yarn processed in this manner has a tenacity of 2.2 g. p. d. at an elongation of 16%.

It will be obvious from the foregoing description and examples that this invention provides a simple, convenient and economical process for preparing filaments, yarns, films and like structures of synthetic linear polyester wherein the ultimate productivity of melt-spinning and melt casting equipment is realized.

As many widely different embodiments can be made without departing from the spirit and scope of my invention it is to be understood that said invention is in no wise restricted save as set forth in the appended claims.

I claim:

1. The process which comprises forming filaments, yarns, films and like structures of substantially amorphous synthetic linear polyester and thereafter stretching said structures while in the amorphous state in at least one dimension from 10 to 75 times the original dimension at a temperature within the range of from 20° to 60°C. above the apparent minimum crystallization temperature for said amorphous polyester whereby to obtain a stretched structure substantially free of molecular orientation.

2. The process which comprises forming continuous filaments of substantially amorphous synthetic linear polyester having an intrinsic viscosity of at least 0.3 and thereafter stretching said filaments while in the amorphous state from 10 to 75 times their original length at a temperature within the range of from 20° to 60°C. above the apparent minimum crystallization temperature for said amorphous polyester.

3. The process of claim 2 wherein the amorphous synthetic linear polyester is polyethylene terephthalate.

4. The process which comprises first stretching continuous filaments, of substantially amorphous synthetic linear polyester having an intrinsic viscosity of at least 0.3 from 10 to 75 times their original length at a temperature in the range of from 20° to 60°C. above the apparent minimum crystallization temperature for said polyester and thereafter drawing the stretched filaments at a lower temperature between the second order transition temperature for said polyester and 30°C. above the apparent minimum crystallization temperature to impart to said filaments the desired degree of molecular orientation.

5. The process of claim 4 wherein the polyester is polyethylene terephthalate.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,465,319	Whinfield et al.	Mar. 22, 1949