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METHOD OF MAKING PROTEINACEOUS FIBERS

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This invention relates to the manufacture of synthetic protein fibers. More particularly, the invention relates to an improved process whereby synthetic fibers are produced from proteinaceous materials such as casein, which fibers have physical and chemical properties approximating those of natural animal fibers.

The production of synthetic fibers from regenerated cellulose and various cellulose esters and other derivatives has become a well developed art and industry. Such fibers are generally made in imitation of silk and for uses for which silk would otherwise be normally used. While such materials have a limited usefulness for many purposes for which silk is used, they are essentially of a cellulosic nature, i. e., a carbohydrate or derivative thereof; they are different, therefore, in chemical composition and properties from fibers of animal origin which are essentially proteinaceous in their nature. Such artificial silk fibers do not ordinarily have the physical properties, such as "spring" and ability to resume their shape after crushing in the hand, which is characterized by natural protein fibers, nor can they be treated by all of the washing, cleaning, dyeing and other operations to which natural fibers are subjected.

In accordance with my invention, the material from which the fibers are produced is essentially of a protein nature, and the fibers therefore approximate more closely the chemical and physical properties of fibers of animal origin.

It has been proposed heretofore in several isolated instances, and in fact over thirty years ago, to place a protein material, such as casein, into solution with an alkali, and spin the same into fibers which are coagulated in an acid-formaldehyde bath. By such a process an effort was made to obtain synthetic fibers of a protein nature, but the processes have been singularly unsuccessful from a commercial point of view and have been little more than paper prophecies. Such a state of the art is readily understandable when it is considered that the fibers so produced are not suitable for the production of fabrics which could be used for ordinary purposes such as covering materials, upholstery, and clothing. The fibers made by such proposed processes are usually of low tensile strength, are brittle and subject to shattering even if their strength is acceptable, and therefore inferior in flexibility and elasticity; they are deficient in their resistance to light, air, water, acids, alkali, and other conditions to which fibers are normally subjected in ordinary use.

Practically all fabrics today are a mixture of several kinds or species of fibers, for example and admixture of Australian, Argentine and domestic wool, or a mixture of mohair and wool. It is even common to blend cellulose acetate fiber with wool or mohair, or to blend wool and silk. It is important that a synthetic fiber should have qualities and characteristics with respect to acid, alkali, boiling, dyeing and the like which are similar or identical with the fibers with which they are to be blended. The fibers made by such prior proposed process do not have properties which render them suitable for blending or admixture with natural fibers.

In accordance with my invention I have overcome these difficulties and am able to produce a protein fiber having physical and chemical properties similar to those of natural protein fibers. The fibers made in accordance with my invention can be used for most of the purposes for which natural fibers are normally used, and for many purposes have properties uniquely their own.

It is an object of my invention to provide a protein fiber having increased tensile strength in both the wet and dry state, having a minimum of scroop and an improved softness of feel, and having greater elasticity, spring, and flexibility.

It is also an object of my invention to provide a protein fiber which is resistant to water, ordinary washing, and other cleaning solutions and operations, and which does not deteriorate rapidly when subjected to ordinary exposures of light, air, water, acids, alkalis, and other conditions to which fibers and fabrics are normally exposed.

It is a further object of my invention to produce fibers which have a chemical composition and chemical properties similar to those of natural fibers, whereby the fiber may be dyed in accordance with the technique now standardized for dyeing of natural fibers without deleteriously affecting the synthetic fibers, and thereby obtain a dyed product in which the fibers are blended with natural wool, and in which there is no observable difference in the dyeing characteristics of the natural and synthetic fibers.

Fibers having the characteristics above referred to may be made in continuous filaments or in staple lengths similar to natural fibers.

The process of making the fibers is described herein and differs materially in many respects from processes heretofore proposed or described in connection with the production of fibers from a proteinaceous material.

It is an additional object of my invention to disperse the protein under closely controlled and critical conditions as to the temperature, both with respect to the temperature to which the dispersion is heated and the length of time it is maintained at this temperature.

It is a further object of my invention, after the protein has been dispersed and maintained at any desired temperature for any desired length of time, to quickly cool the dispersion before it is modified by retention at the heating temperature. In particular, it is an object of my invention to accomplish this quick cooling by introducing the dispersion into a vacuum whereby the temperature of the dispersion is reduced to the boiling point of water at the absolute pressure existing under the vacuum.

It is also an object of my invention to deaerate the dispersion by means of the above vacuum treatment.

It is also an object of my invention in placing the proteinaceous raw material in solution to employ such dispersing agents and modifying ingredients and in such quantities as to produce a fiber having the described characteristics. More particularly it is an object of my invention to provide a spinning solution which is subjected to a predetermined heating and cooling treatment, and which has a pH value not appreciably above 7 and preferably below that value.

It is also an object of my invention to prepare the protein dispersion with a quantity of water such that with the heretofore mentioned amount of alkaline dispersing agent and under the conditions of temperature, the dispersion will have a high viscosity upon cooling to the temperature at which the dispersion is spun. More particularly, the viscosity is of not less than 40,000 centipoises when it is spun at a spinning temperature.

Still a further object of my invention is the provision of an acidic coagulating bath containing both a mineral and a vegetable tanning agent. More particularly the vegetable tanning agent may be "Goulac" which facilitates the coagulation of the fiber and imparts to it desirable properties such as permits additional processing operations.

A further object of my invention includes the hardening of the coagulating fibers by means of a formaldehyde bath followed by a continuation of the hardening action by means of formaldehyde vapor.

The objects above noted have been stated generally and it is apparent that my invention comprises numerous additional objects of a more specific nature; these will be readily apparent from the description of my process as hereinafter set forth, and in avoiding unnecessary duplication it is believed unessential to state them in detail at this time.

The protein to be used as the raw material in the practice of my invention may be any relatively pure acid coagulable protein which can be dissolved or dispersed with an alkaline material.

The casein referred to herein may be from either an animal or vegetable source, such as casein from milk or soya bean casein, and the word casein as used herein is intended to be generic to both types of material. The casein obtained from milk, either skimmed milk or buttermilk is an inexpensive and readily available raw material, and for this reason would probably be selected in the practice of my invention commercially. I will therefore describe my inven-

tion particularly with reference to casein from milk as a raw material. But it is to be understood that other alkali-dispersible acid-coagulable proteinaceous materials besides milk casein and soya bean casein may be used, particularly the alkali-dispersible acid-coagulable protein obtained from cottonseed meal, peanut meal, natural wool, and other vegetable and animal alkali-dispersible acid-coagulable proteins, may be used in practicing my invention.

The raw material need not be from a single source. For example, excellent results are obtained when 25 to 50% soya casein is admixed with casein from milk. Natural protein fiber, such as wool shoddy, also can be dissolved or dispersed and blended with a dispersion of casein.

While a wide variety of caseins may be used to produce fibers in accordance with my invention, it is often necessary to modify somewhat the steps to be used in processing different raw materials in order to obtain a fiber having at least the minimum desirable qualities, and in order to compensate in the processing for any deficiencies in the casein.

Inasmuch as it is desirable to standardize fiber manufacturing operations on a commercial scale, it is important that the casein should have uniform physical and chemical characteristics. If it does not, the process may have to be varied with a variance in the supply of raw material.

In accordance with my invention, the casein should be produced by a process operated on such a large scale and with such careful control as to produce a uniform product, or the casein should be produced by a process which because of its inherent nature is susceptible to producing a casein having uniform characteristics even when operated on a small scale.

In addition to being uniform, the ash content of the casein should be as low as possible.

In addition to uniformity and low ash, sugar, and acid content, the casein to be used as the raw material should also be soft and friable in nature with good plastic properties, and should have a minimum of hard, brittle characteristics.

The casein may be either acid precipitated or enzyme precipitated. Examples of a satisfactory acid precipitated casein may be made in accordance with a process disclosed in the U. S. patents to Sheffield, No. 1,716,799; Chappell, No. 1,992,002, and Clickner, No. 2,044,282, by which methods a relative uniform high grade casein of low ash content can be produced.

An enzyme precipitated low ash casein may be produced in accordance with the process disclosed in application Serial No. 260,334, filed March 7, 1939.

After having selected the casein to be used as a raw material, the next step in the process is that of dissolving or dispersing the casein. Water is preferably used as the solvent, and inasmuch as casein is not readily soluble in pure water, it is necessary to employ an agent to disperse the casein; this agent is generally and more conveniently of an alkaline nature, or a material with a pH value higher than the iso-electric point of casein.

The word solution is used in its generic sense to include both true and colloidal solutions or dispersions; the solutions may vary in viscosity to such an extent as to include a thick paste or gel.

The casein solution may be made, in general, in two different ways; (1) employing only an alkaline compound, such as caustic soda, caustic

potash, soda ash, ammonia, amines, hydroxyl amines, hydroxy amines, or amino alcohols, and alkylamines, as the dispersing agent; (2) employing modifying or plasticizing compounds, such as unctuous materials, i. e., fatty acids, fatty esters, fatty alcohols and the derivatives thereof; polyatomic alcohols; monoses; polyoses; soaps; lanolin or modified lanolin emulsions, and various resinous materials, with or without an alkaline material depending on the modifying agent.

In either of these two methods, if desired, various swelling agents may be employed, such as sodium fluoride, sodium formate, and sodium stannate, which may be incorporated to assist in the dispersion of the casein. If desired, various viscosity modifying and deaerating agents such as diethylene glycol and partly water-soluble alcohols, ethers, esters and ketones may be added to assist in deaerating the solution and bringing it to the proper viscosity and density, and to facilitate ripening and preparing the solution for spinning.

The particular ingredients to be employed in dispersing the casein will depend largely upon the properties desired in the finished fibers. From the economic standpoint a casein dispersed with caustic soda is the most desirable because of the small amount of caustic required and the inexpensive nature of such a dispersion. The fibers produced thereby are relatively strong in both the wet and dry state, but they do not have quite as soft a feel nor are they quite as flexible in most instances, unless modified by after treatments during washing operations, as fibers produced from a casein solution containing a modifying or plasticizing agent. However, fibers of the latter type do not have as great a tensile strength as those made from a caustic casein solution. The dispersing or modifying agent also must be such as to enable the casein solution to be spun, i. e., will yield a fiber of an initial wet strength which can be elongated during spinning as will be described later.

The dispersing and/or modifying agent will depend also upon the properties of the raw material. For example, fibers made from paracasein dispersed solely with caustic have a high tensile strength and are also sufficiently soft and flexible for most purposes as not to require a modifying agent. The choice of a dispersing or modifying agent will also depend somewhat upon the subsequent treatments to which the fiber is subjected during the spinning operation or during one of the subsequent treating stages. If the fiber is to be treated with an unctuous material at a subsequent stage after it is completely formed, it is not so essential that an unctuous or plasticizing material should be included in the initial composition.

Inasmuch as I have been able to obtain highly desirable fibers by dispersing casein solely with caustic, and in view of the tremendous economic advantage of this procedure, I will describe this first.

In preparing the casein dispersion, the water is placed in a steam jacketed kettle equipped with a stirring device and the casein is added slowly during the stirring. The casein is allowed to soften in the water for a short time and the solvent is then added slowly, first dissolved in a portion of the water. Heat is applied gradually by means of the steam jacket during the stirring and the temperature of the solution is raised. If desired, a controlled denaturation may be obtained by heating the swelled or puffed-up casein

with hot water prior to its dispersion or solution. In some instances, after the temperature reaches about 140° F., it is preferable to maintain the mixture under agitation at this temperature for a period of about five to twenty minutes before increasing the temperature. In other instances, no advantage is gained by this procedure, in which event it is preferable to continue the heating gradually until a temperature of about 170 to 190° F. is reached. If desired, the agitation may be continued at this temperature for one-half to one hour to insure complete dispersion. As soon as this condition is reached, the solution is cooled as quickly as possible after which it is filtered. The filtering removes any undissolved particles of casein or impurities that would cause weak places in the finished fiber. A very fine filter is preferably employed. If the casein solution is to be kept for any period longer than six to twelve hours, a preservative, such as phenol, may be required and may be added before filtering in order to prevent decomposition of the casein solution before spinning. The need for a preservative will depend to some extent on the denaturation of the casein, since a properly denatured casein does not require the use of a preservative.

The solution is ready to be spun immediately, but it may stand for 6 to 24 hours. The length of time between the preparation of the solution and the spinning of the same does not appear to affect the properties of the finished fiber.

The heating and cooling cycle and the temperature to which the casein is heated contribute materially to the desired characteristics in the final product, and it is known that the heating and cooling cycle, both as to the speed at which the temperature is raised, the ultimate temperature and the length of time at which this temperature is maintained, have an effect upon the solution. While these factors are by no means critical, it is preferable not to heat the mixture too rapidly as the casein is being dispersed, in order to permit the dispersion to be as gradual as possible. There also appears to be a procedure for effecting optimum results, and it may be stated generally that a temperature as high as 165-180° F. should be reached but that a temperature of the order of 180° to 190° F. should not be exceeded unless this temperature is reduced very quickly in a cooling operation. A higher temperature and a longer heating period may exert a desirable denaturing action on the casein, provided it is carefully controlled and terminated before the denaturation proceeds too far.

Casein solutions are difficult to cool uniformly because their viscosity makes it difficult to obtain uniform heat transfer. A vigorous stirring, while achieving more even cooling, is undesirable because it stirs air bubbles into the solution which result in points of weakness in the finished fiber.

I have discovered that the cooling operation may be carried out by a so-called flash cooling process, in which the hot casein solution, as it comes from the filter, is subjected to a vacuum boiling process. In this method, the hot solution is sprayed in a vacuum chamber maintained at a high vacuum, i. e., 29 inches or more, and recycled until a temperature drop to about 90° F. is obtained. This can be accomplished in a few minutes. Such a cooling method greatly expedites the manufacture of the fiber and at the same time deaerates the casein solution by eliminating small air bubbles. This method of

cooling also permits a quick and even cooling of the entire mixture, thereby terminating any denaturing or other process induced by the heat, and permitting a more careful control of the extent of the denaturation.

The relative proportions of the various ingredients and the manner of compounding the casein solution will also have some effect upon the viscosity; this is an important element in obtaining the proper spinning of the solution. For purposes of convenience, the viscosity is measured at 100° F. and a satisfactory casein solution for spinning at a room temperature of from 70 to 75° F. should have a viscosity of 8,000 to 18,000 centipoises (measured with a Hoeppler viscosimeter) at 100° F., preferably about 15,000 centipoises. The casein solution at the actual spinning temperature of 70 to 75° F. has a greater viscosity; this should be a minimum of 40,000 centipoises; good spinning results are obtained with a solution having a viscosity of 75,000 to 100,000 centipoises at the spinning temperature. Viscosities higher than this may be employed depending upon the type of fiber that is to be manufactured, and the type of pump and spinnerette employed in the spinning operation. In general, the viscosity at spinning temperature should not be less than 40,000 centipoises.

If the temperature of the casein solution at the time of spinning is to be above that of room temperature, it is necessary to compound the solution with a higher percentage of casein in order that the spinning viscosity at the higher spinning temperature may be above the preferred minimum of 40,000 centipoises, and preferably approach the optimum value of around 75,000 to 100,000 centipoises.

The relative amount of water and casein employed will depend to some extent upon the properties of the casein used as a raw material. For example, casein that is hard and brittle will produce a solution having a somewhat higher viscosity for a given proportion of casein to water. Paracasein made by the rennet-precipitation and acid treating processes described heretofore will produce a solution having a much lower viscosity than will acid precipitated casein when used in the same ratio to water. One part of paracasein to 3½ to 4 parts of water will produce a solution having the same viscosity as a solution otherwise identical but containing one part of acid precipitated casein to 5 parts of water. The increased amount of paracasein in the solution, however, does not render the process less economical because a given weight of finished fibers will require a given weight of casein, irrespective of the proportion of casein in the spinning solution. As mentioned heretofore, a controlled heat denatured casein will also produce solutions of greater viscosity.

The amount of caustic to be used also will depend on the casein and particularly its acidity or pH value. In general, the amount of caustic should be such that the pH value of the casein solution will be between 6 and 7. This amount will ordinarily be about 2% based on the weight of the casein. I have found that no advantageous result is secured by increasing the pH value of the casein solution, and optimum qualities in the fiber are obtained when the casein spinning solution has a pH value below 7.5, and preferably between 6 and 7. Fibers spun from solutions outside this range are inferior in strength and elongation. Too high a percentage of alkaline ma-

terial in the solution also may cause uncontrolled, haphazard or casual hydrolysis of the casein and other types of denaturing.

As illustrative of the preparation of casein spinning solutions the following specific examples are given:

About 95 pounds of water is introduced into a steam jacketed kettle and agitation begun. About 25 pounds of an acid precipitated low ash casein is slowly added and the stirring continued five minutes after the casein has been added. Seven and one-half ounces of sodium hydroxide is dissolved in 5 pounds of water and this is added very slowly to the casein water mixture during agitation. Heat is applied immediately after the solvent is added and the temperature raised to 180° F., holding it at this point for one hour. If desired, 8 ounces of phenol may be added dissolved in a portion of the water that is retained for this purpose. The solution is filtered and cooled to about 80 to 90° F. The above formulation should yield a solution that has a pH value of 6.0 to 6.5, and a viscosity of 10,000 to 15,000 centipoises at 100° F.

When employing rennet-precipitated acid treated casein described heretofore, which represents one of the preferred embodiments of my invention, the procedure is identical to that just described except that the proportions are 30 pounds of casein, 11.32 gallons of water, and 272 grams of sodium hydroxide; ½ pound of phenol may be added if desired.

In practicing my invention as applied to the production of casein dispersions containing modifying agents, the same general procedure is followed, except for the employment of modifying agents together with or in place of a part or all of the alkali, depending on the modifying agent. In my application Serial No. 142,574, filed May 14, 1937, I have disclosed numerous modified protein compositions and resinous casein mixtures, all of which are suitable for the production of casein fibers. These include various alkaline compounds, alkaline salts, soaps of alkali metals, amines, hydroxyl amines, hydroxy amines or amino alcohols, and alkylolamines. These may be used alone or with various high molecular weight esters, acids, oils, fats or resins, urea, aldehydes, or unsaturated acids. I may mention in particular as modifying agents triethanolamine and "Petrex" (a terpene and maleic acid combination), triethanolamine and a condensation of China-wood oil, fatty acids and maleic acid, and high molecular weight fatty amines.

In general, while compositions comprising glycerine, either introduced directly or liberated from glyceride fats, can be used, they do not produce superior fibers, and I prefer other modifications to those containing glycerine. This does not appear to be so in the case of the glycols and glycol esters.

It would be impossible to list all of these modifications of plasticized casein solutions included in my invention, and one example is given merely as illustrative: Commercial triethanolamine, which comprises a mixture of mono-, di-, and triethanolamine, is reacted with di-glycol oleate. The latter may be an available commercial product containing glycol di-oleate and glycol mono-oleate as well as some free oleic acid; alternatively it may be made from diethylene glycol and oleic acid, preferably from teaseed, or from a mixture of teaseed and castor oil fatty acids, the latter being primarily ricinoleic acids. The proportions may be varied from two to three parts

of the triethanolamine with two and three parts of di-glycol oleate. About two parts of the former to three parts of the latter represent the optimum quantities. It is believed that a portion of tri-ethanolamine reacts with the di-glycol oleate to form a soap, with an accompanying liberation of glycol. This mixture which may or may not contain free triethanolamine, depending upon the proportions employed, is used to disperse the casein in an aqueous solution. The amount employed should be such that the final pH value of the dispersion is preferably between 6.0 and 7.5. In the case of the modified dispersions, slightly higher pH values may be employed without disadvantage. No improvement is obtained with pH values above 8 and, in fact, fibers having the most desirable properties are obtained when the spinning solution has a pH value under this figure and preferably between 6.5 and 7.5. The proportion of triethanolamine to di-glycol oleate will determine largely the plasticizing and softening action upon the fiber, and an increase in the latter increases the softening action.

The various modifying agents employed exist in the mixture in a complete dispersion and are believed to be present in more than a mere emulsified form. In many instances they will exist chemically combined but the exact nature of the chemical combination is not known.

As an illustration of the preparation of a triethanolamine di-glycol oleate casein solution, 20 pounds of acid precipitated low ash casein is employed with 100 pounds of water, and 6 pounds of the soap formed by reacting two parts of triethanolamine with three parts of di-glycol oleate by weight. The procedure is the same as that previously described except that the heating cycle is slightly different in that the solution is heated to a temperature of 140° F. and held at this temperature for about ten minutes after which the temperature is raised to 180° F. and maintained for about thirty minutes.

If desired, various antioxidant agents may be introduced. These are well known and include amines such as diphenyl amine, and phenols such as hydroquinone. Metallic antioxidants such as tin salts and tin oleate may be employed. The inclusion of these ingredients prolongs or inhibits oxidation of the fiber and its deterioration during use.

Prior to the spinning of the solution into fibers, the solution may be mixed or admixed with various viscose or cellulose derivative solutions used in making the so-called rayon type of fibers. The incorporation of such modifying materials would produce fibers having properties of both cellulosic and proteinaceous nature. There may also be added a hardening agent, such as formaldehyde, but I prefer treating the fibers with such an agent after the spinning operation. If desired, a potential hardening agent, such as bichromate, may be included, which can be reduced to a chromium compound having a hardening action after the fibers are formed.

There may also be included in the casein solution a lanolin or sodium or sodamide treated lanolin emulsion in which the particles are less than five microns in size. When these particles are drawn out in the spinning process they will form elongated lubricating cells similar to the cells in natural wool.

The casein solution prepared as above described is next spun into fibers. In this operation, the casein solution is forced under pressure through small holes of a spinnerette into an acid coagu-

lating bath, and from which the fibers are continuously withdrawn. Merely for convenience, the entire spinning operation is carried out at room temperature and the casein solution to be spun is also conveniently used at room temperature.

As has been pointed out above, the viscosity of solution at the time of spinning should preferably be a minimum of 40,000 centipoises and should approach the optimum value of about 75,000 centipoises. A difference of one or two degrees in temperature makes a very considerable difference in the viscosity. It is preferred, therefore, to employ such spinning apparatus as permits a close control of the temperature of the casein solution. This may be accomplished by a jacketed pressure tank, or by permitting the solution to assume room temperature before the spinning operation is carried out. It is also desirable to have the temperature of the coagulation bath at about the same temperature as that of the casein solution to be spun.

Other than as described herein, the mechanical details of the spinning operation are not critical and in general any suitable arrangement may be employed. It is convenient to place the casein spinning solution in a large tank; dissolved air or air bubbles are removed or allowed to rise to the surface of the solution, and compressed air at 50 to 100 pounds per square inch is introduced. The casein solution is thereby forced from the tank through a pipe to a pump which forces the solution into the spinnerette and through the holes thereof. The pressure in the tank, the viscosity of the solution, as well as the speed of the pump determines the rate at which the casein solution is extruded from the spinnerette and this rate can be varied by adjusting the pump speed or the pressure in the tank or both. A gear type pump may be used, but I prefer a continuous flow pump of the "Moyno" type which gives a smoother delivery of the solution to the spinnerette.

The speed at which the fibers are withdrawn from the bath can also be varied, but the temperature of the casein solution as well as the temperature and pH value of the coagulating bath have a substantial effect upon the rate at which the fiber can be withdrawn from the spinnerette. The speed of withdrawal and the rate at which the solution is extruded from the spinnerette will determine to an appreciable extent the size of the filaments. By varying the speed of withdrawal and the rate of extrusion, the size of the final filaments can be varied over wide limits. It will be apparent that this variation is accomplished by an elongation or stretching of the fiber immediately after extrusion, and in the very early stages of coagulation of the casein composition before the fibers have coagulated sufficiently to resist this elongation. The strength of the final filaments also can be altered by varying the rate of withdrawal of the fiber from the spinnerette face and within the coagulating bath. The increase in strength is due, no doubt, to an orientation or stratification of the micelles during the chemical change involved in the coagulation. Other things being equal, fiber spun at slower speeds will have less strength and be more brittle. Higher speeds are desirable and are limited only by the properties of the casein being used and the rate of coagulation of the spun fiber. I prefer to use a speed of 50 to 300 feet per minute at the face of the spinnerette.

Inasmuch as it is generally desirable to have

filaments that have as small a diameter as possible, because such filaments have a much softer feel and have greater tensile strength per unit weight of fibers, it is preferably to make the filaments as small as possible, and I prefer to produce them having a diameter of from 15 microns to 50 microns.

The diameter of the fiber that is to be produced is determined to a large extent by the product for which the fiber is to be used. For example, a fiber for manufacturing upholstery should have a diameter of 25 to 35 microns; a carpet fiber would be slightly larger in diameter and would be about 35 to 50 microns; a fiber for clothing preferably should have diameters ranging from 20 to 30 microns; and very high grade products having an exceedingly soft feel require fibers of the diameter of the order of 15 to 20 microns. Fibers having all of these ranges of diameters may be made in accordance with my invention.

By means of the process above described, the filaments will be smaller in diameter than the actual diameter in the holes in the spinnerette. It is much easier to adjust the size of the filaments by elongation than it is by varying the size of the openings in the spinnerette. Obviously there is a practical limit to the reduction of the diameter of the fibers by elongation, but it is preferred to the use of spinnerettes having unusually small holes which would tend to become clogged more readily.

The coagulating bath comprises essentially sulfuric acid in aqueous solution. Other acids such as acetic, sulfamic, formic, etc. may be used. It may also contain advantageously a soluble salt, such as sodium sulfate or sodium chloride, which augments the action of the acid and possibly has a dehydrating action. The bath may also contain a metallic tanning agent, such as an aluminum or chrome alum, a zinc salt or other metallic compound, particularly of an amphoteric metal, which has a hardening or tanning action. One or more softening, wetting, plasticizing agents, or vegetable tanning agents, depending upon the final properties desired to be imparted, may also be contained in the coagulating liquid depending on the ingredients that are compounded in the casein spinning solution. A material found advantageous for this purpose is "Goulac," which is the lignin bearing waste matter obtained by the evaporation and drying of the liquid from the sulphite paper process either in a purified or unpurified form. In some instances, the unpurified form appears to be highly satisfactory. The "Goulac" is particularly desirable for a coagulating bath when the spinning solution is dispersed solely with caustic, inasmuch as the "Goulac" imparts a softening effect. The "Goulac" also tends to reduce the surface tension of the coagulating liquid so that the latter can contact the fibers more completely and uniformly; it also assists in keeping the individual fibers separated one from the other during the coagulation.

The combination of a mineral tan, such as alum, and a vegetable tan, such as contained in "Goulac," is particularly beneficial. It is probable that the alum hardens the surface of the fiber, and before it has a chance to shrink, the surface is more or less filled with the tannin bearing material such as "Goulac". The tanning action of alum by itself would be relatively harsh and the tanning action from the Goulac counteracts this action while at the same time

producing a filling and tanning action characteristic of vegetable tanning agents.

Other materials that may be used are tartaric acid and sugars. Corn syrup, which is a mixture of several sugars, is very useful in this connection. It is also possible to use hydrolyzed lactone, and mixtures of galactose and glucose as derived from milk sugar, which provide a beneficial action in the coagulating liquid. An aldehyde, such as formaldehyde or acetaldehyde, is often desirable in the coagulating bath.

The acidity of the solution will depend somewhat upon the rate of travel of the fibers through the coagulating liquid, but I have found that solutions having an acidity of 1.3 to 2.0 pH value, and preferably 1.5 are desirable.

During the coagulation, the acid in the coagulating bath is used up, so that the pH value of the acid bath is gradually increased. The casein in the spinning solution is no doubt in the form of a caseinate which is reconverted by the acid in the bath to a casein at a pH near its isoelectric point. In view of the exhaustion of the acid, I have found it desirable to continuously replace the acid, preferably by continuously running a supply of fresh coagulating liquid into the coagulating bath, and continuously withdrawing a corresponding portion, the acidity of which is adjusted to the desired pH value by the addition of sulfuric acid before being replaced in the bath. The alum is also exhausted from the bath and must be replaced.

It is probable that the initial coagulation is more or less of a skin formation on the fiber, and that further coagulation within the fiber proceeds relatively slowly. In order that the fibers may be completely and uniformly coagulated throughout their cross section, it is preferable that the fibers should remain in contact with the coagulating liquid for sufficient time to achieve this effect, and to establish an equilibrium of pH value throughout the cross section of the fiber. After the fibers are withdrawn from the bath, they are permitted to remain wet with the coagulating liquid that normally adheres to them and for a suitable length of time. This action is such as to completely coagulate the entire mass of the fiber.

As the fiber is removed from the coagulating bath, the fibers of two or more spinnerettes can be combined into a single strand, and this single strand or rope-like bundle of continuous fibers advanced through the remaining treatments.

Following the coagulation of the fibers, the process may be operated to subject the fibers successively to subsequent treating operations while in the form of a continuous strand. Alternatively, the fibers may be cut into staple lengths at any stage of the process after coagulation, and the staples subjected to similar subsequent treating operations.

After the fiber has been coagulated to the extent desired, it is placed in a hypertonic solution more conveniently referred to as a "pickling" bath. This bath comprises preferably a solution of sodium sulphate of rather high concentration.

After the fibers have been treated in a pickling bath, they are hardened preferably with an aldehyde such as crotonaldehyde, acrylaldehyde or acrolein, or formaldehyde. The latter is the most readily available and the process will be further described with reference to it. When a formaldehyde solution is employed, it is preferably of a concentration of 5% to 20%. In higher concen-

trations the hardening bath need not contain any element other than the formaldehyde. In the more dilute solutions it is desirable to include a salt such as sodium sulphate to assist in the dehydration and to prevent swelling of the fibers.

If desired, the pickling and hardening action can be carried out jointly, in which case a combined pickling and hardening bath may contain 10% sodium sulfate and 10% formaldehyde. Such a combined bath is more convenient and easier to work with than a more concentrated solution of formaldehyde.

The fibers may be treated to a formaldehyde solution or vapor for various lengths of time ranging from one-half hour to over night.

After being taken out of the formaldehyde solution, the fiber may be packed in a large air tight box while wet with the formaldehyde solution and the formaldehyde remaining either in the liquid or vapor phase is sufficient to impart the desired hardness to the fiber if permitted to stand from 1 to 10 hours. In the alternative processing of staple fiber, the staples may be treated in a similar manner.

A satisfactory fiber is produced when the bundle of fibers is wet uniformly and kept in motion in the formaldehyde solution for approximately an hour, and is then kept in motion while wet with formaldehyde but after removal from the formaldehyde bath. If the fiber is kept in motion and exposed in a warm cabinet after removal from the bath, it is possible to complete the necessary hardening action after removal from the bath in an hour. At any event, it is not necessary to hold the fibers in a concentrated formaldehyde solution for a long period of time as has been regarded as essential heretofore.

The temperature of the formaldehyde bath or vapor may be varied and convenience indicates a preference for room temperature. The rate of reaction of the fiber and the formaldehyde, however, is greatly accelerated by slight increases in the temperature of the bath, as well as the temperature of the vapor with which the fiber is permitted to remain in contact after being removed from the bath. Temperatures as high as 90 to 100° F. may be employed, and temperatures within this range are probably the optimum for imparting the most beneficial results in the shortest length of time. The use of an increased temperature also permits the employment of lower concentrations of formaldehyde.

If the formaldehyde treatment is more vigorous, such as that obtained at an elevated temperature and with the formaldehyde under pressure, especially in the gaseous form, the formaldehyde appears to be bound into the casein micelle more tightly. The reaction of the fiber with the formaldehyde is speeded up by an increase in temperature to such an extent that at 100° F. the reaction is two to four times as fast as at normal temperatures of 65 to 75° F.

After the hardening treatment, the fiber is washed with water to remove the formaldehyde or salt.

The fibers at this time may be treated with solutions of various types of mild alkalies, soaps, and softening or unctuous materials, described more particularly hereinafter. The treatment at this stage accomplishes at least two functions; the pH value of the fiber is raised and the fiber is placed in a condition to facilitate the subsequent water-resisting treatment. The treatment also renders the fiber more flexible and imparts a softer feel. This operation can be carried out

at a later stage, but is advantageously carried out before the fiber is dried, if the treating material is an aqueous solution or emulsion. If the treating material is in an organic solvent, or if it is applied to the fiber directly, the treatment may take place after the fiber is dried. Such treatment is also preferred if the casein spinning solution does not contain a modifying or plasticizing agent. In certain instances it may be desirable to soften or plasticize only the surface of the fiber to impart the desired feel and retain the center of the fiber unmodified for imparting greater strength.

If the fiber is to be dry or partially dry at the time it is subjected to the water resisting treatment, it is next subjected to a drying operation. The drying should be such that there is no coalescing of the individual filaments that would cause them to adhere to each other. Care should be taken to employ a temperature well below the melting or softening point and below a temperature that will discolor the product. This will depend somewhat on the casein used as the raw material and the modifying agents incorporated.

The fiber in a dry or partially dry condition is then ready to be treated to render it more water-resistant, to improve its dyeing properties and to improve its strength, particularly its wet strength.

For the purpose of rendering the fiber more water-resistant in accordance with my invention and improving its dyeing properties, a treatment with ketene as described in application Serial No. 291,616 is the most economical and therefore represents the preferred embodiment. Such a treatment is described in detail in said copending application Serial No. 291,616, filed August 23, 1939, which is in part a continuation of application Serial No. 242,279, filed November 25, 1938, and of which this application is a continuation-in-part.

After the fiber has been suitably hardened, such as by a treatment of the fiber with ketene, the pH value of fiber may be lower than that desired.

The pH value of the fiber may be raised to any desired value. The extent of the washing or the raising of the pH of the fiber is not an essential nor a critical operation, and the action in this regard will depend entirely upon the use and properties desired in the finished fiber.

The pH value of the fiber is measured by wetting the fiber with a minimum quantity of pure water and allowing it to stand for about 30 minutes, after which the glass electrodes of the pH meter are contacted directly with the mass of fiber and the pH value read from the meter. Although there are numerous methods of measuring pH values, the above described method was used in determining the values mentioned herein.

After drying, the fiber may be cut into the staple lengths desired depending upon the diameter of the fiber that is produced and the use for which it is desired.

My process may be carried out rapidly and from the time the raw material is placed in solution until the fiber is obtained, a lapse of only 8 to 10 hours is necessary. It is possible, for example, to place the casein in solution in the morning and spin it in the afternoon. It may be delivered as an article of commerce early the next day or within a total elapse of not over 24 hours. This is very important from the com-

mercial standpoint and is to be distinguished from known processes of making synthetic fibers, both of proteinaceous and cellulosic type, which require anywhere from 5 to 10 days to carry out the various steps resulting in the final fiber.

It will be apparent from the description heretofore that many slight variations in the method of making the fiber can be used, and that certain properties of the fiber may be made more pronounced or others less evident or both, depending on these variations in the method. This is desirable since different properties may be preferred in fiber to be used for various different purposes. But irrespective of such variations in the process, the fiber produced in accordance with my invention has the common property of being different from and superior to that produced by any process heretofore employed or proposed for the manufacture of synthetic fiber from casein or other proteinaceous material.

The fiber produced in accordance with the above process may be put to substantially any use for which natural fiber is now employed. It may be used in the formation of fabrics for upholstery purposes and for wearing apparel; it may be used as the pile for rugs and other piled fabrics, and it may be used in the formation of blankets and as a filling material where proteinaceous fibers are desired. The fiber produced in accordance with my invention may be admixed with natural protein fibers such as wool, silk and mohair, or it may be admixed with natural or synthetic fibers of cellulosic origin such as cotton and rayon.

One of the important properties of the finished fiber is its resistance to air, light, water and other cleaning solutions. It may be described as stable, and chemically resistant to mild chemicals with which it would normally come in contact. It does not take on a slimy and unpleasant feel in water, even when boiled in water. The fiber can be placed in solution only with great difficulty, and a relatively large amount of alkali is required to effect such a solution. For example, the fiber is capable of being boiled in solutions having pH values as high as 8 to 9 without any material alteration in its properties, whereas fiber made in accordance with the prior art would be rendered useless if boiled in solutions of such alkalinity. This will permit laundering with any mild soap normally used for wool and silk. After such a treatment the fiber does not become brittle upon drying. It can be subject to boiling dye solution, and after such treatment will retain its soft and flexible properties.

The fiber produced in accordance with my invention has substantially the same or superior dyeing properties as natural wool in that it is colored by the same dyes that color wool and is not colored by dyes that do not affect wool. This is not true of synthetic fibers heretofore known. The fiber is capable of being heated in a dye bath at the usual dyeing temperatures of 80° C. to 100° C. for at least an hour even though such solutions are quite acid. The fiber is fast to dyes, that is, the dyes remain fixed in the fiber, a property not possessed by synthetic protein fibers made heretofore.

Another important property of the fiber is its pH value. This controls to a large extent the texture or feel as well as the dyeing properties of the fiber. The softness of the fiber is often referred to as an absence of scroop, and a fabric with a high scroop has a characteristic rustle such as that associated with silk taffeta. Fibers having a lower pH value have a more harsh feel

and texture and they are referred to as having a predominance of scroop. Fibers having a higher pH value have a relatively smaller amount of scroop.

The fiber produced in accordance with my invention has a relatively high strength.

The fiber made in accordance with my invention also has a relatively high strength when wet.

Another significant property of the fiber produced in accordance with my invention is the roundness and the smoothness of its surface.

The fibers produced in accordance with my process are also characterized by their uniformity in diameter. Such a characteristic is particularly desirable when the fiber is to be used in worsted spinning.

Natural protein fibers, such as silk and wool, have a "springiness" and "live" feel, which is greatly desired in textile fabrics and enables cloths and materials made therefrom to retain their form and shape. Synthetic fibers made in accordance with my invention approach to a notable extent the properties of natural protein fibers in this respect.

The fiber made in accordance with my invention is quite elastic and resilient when subjected to longitudinal stresses as well as torsional and bending stresses. This elastic property I believe contributes as much as anything to the desirable live quality of the fiber. The elasticity and relatively low elongation also makes the fiber resistant to "plastic flow." This is an important property in textiles to be used in making clothes where it is desirable to prevent the clothes from losing their shape at portions such as the elbow and knee of the garments where stresses tend to produce "baginess."

The fiber produced in accordance with my invention also has a desirable moisture holding property which prevents the surface from becoming too dry or horny.

It will be apparent that my invention includes many variations depending upon the raw material and the processing that is to be followed in the various operations as well as the properties required in the finished fiber. Many equivalent chemical materials and operations will suggest themselves to persons skilled in the art to which my invention relates. I intend all such variations and equivalent materials to be included within the scope of my invention as defined in the following claims.

I claim:

1. In a process of producing a synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the step which comprises preparing the dispersion by mixing and heating an alkali-dispersible protein in an aqueous medium containing an alkaline compound in an amount to impart to the dispersion a pH value of not over 7.5 and continuing the heating to a temperature of at least 170° but below a temperature at which the dispersion would be rendered unsuitable for spinning into fibers.

2. In a process of producing a synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the step which comprises preparing the dispersion by heating to a temperature of 170° to 190° F. and mixing an alkali-dispersible protein in an aqueous medium containing an alkali in an amount to impart to the dispersion a pH value of not over 7.5, the alkali of said medium consisting essentially of an alkali metal hydroxide.

3. In a process of producing a synthetic proteinaceous fiber, in which process a casein dispersion is spun into an acidic coagulating bath, the steps which comprises preparing the dispersion by heating to a temperature of 170° to 190° F. and mixing casein in an aqueous medium containing an alkali in an amount to impart to the dispersion a pH value of 6 to 7, the alkali of said medium consisting essentially of an alkali metal hydroxide.

4. In a process of producing synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the steps which comprise preparing the dispersion by heating an alkali-dispersible protein to an elevated temperature of at least 170° F. but not over a temperature that would render the dispersion unsuitable for spinning into fibers and mixing in an aqueous medium containing an alkaline compound to disperse the protein, and introducing the dispersion at said temperature into a vacuum to uniformly flash-cool the dispersion to its boiling point at the reduced pressure and immediately terminate any denaturation and other action induced by said elevated temperature.

5. In a process of producing synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the steps which comprise preparing the dispersion by heating an alkali-dispersible protein to an elevated temperature of from 170° to 190° F. in an amount of water and with an amount of an alkaline compound to impart a relatively high viscosity to the dispersion and a pH value of not over 7.5, and introducing the dispersion at said temperature into a vacuum of the order of 29 inches to simultaneously deaerate and uniformly flash-cool the dispersion, whereby the dispersion may be spun at a reduced temperature in a deaerated form.

6. In a process of producing synthetic proteinaceous fiber, in which process a casein dispersion is spun into an acidic coagulating bath, the steps which comprise preparing the dispersion by mixing and heating casein to an elevated temperature of from 170° to 190° F. with an amount of water and with an amount of an alkali to impart a relatively high viscosity to the dispersion and a pH value of 6 to 7, said alkali consisting essentially of an alkali metal hydroxide, and introducing the dispersion at said temperature into a vacuum of the order of 29 inches to uniformly flash-cool the dispersion and simultaneously deaerate the same, whereby any denaturation and other action induced by the elevated temperature is immediately terminated and the dispersion may be spun at a reduced temperature in a deaerated form.

7. In a process of producing a synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the step which comprises preparing the dispersion by mixing and heating an alkali-dispersible protein in an aqueous medium containing an alkali in an amount to impart to the dispersion a pH value of not over 7.5, the alkali of said medium consisting essentially of an alkali metal hydroxide.

8. In a process of producing a synthetic proteinaceous fiber, in which process a casein dispersion is spun into an acidic coagulating bath, the step which comprises preparing the dispersion by mixing and heating casein in an aqueous medium containing an alkali in an amount to

impart to the dispersion a pH value of 6 to 7, the alkali of said medium consisting essentially of an alkali metal hydroxide.

9. In a process of producing synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the step which comprises spinning a dispersion of an alkali-dispersible protein, which has been dispersed in an aqueous medium with an alkaline compound in an amount to impart a pH value of not over 7.5, into a coagulating bath containing a mineral tanning agent and an amount of acid to impart a pH value of between 1.3 and 2.0.

10. In a process of producing synthetic proteinaceous fiber, in which process a casein dispersion is spun into an acidic coagulating bath, the step which comprises spinning a dispersion of casein, which has been dispersed in an aqueous medium at a temperature of 170° to 190° F. with an amount of sodium hydroxide to impart a pH value of not over 7.5, into a coagulating bath containing sodium sulfate, alum, and an amount of sulfuric acid to impart a pH value of between 1.3 and 2.0.

11. In a process of producing synthetic proteinaceous fiber, in which process a dispersion of an alkali-dispersible acid-coagulable protein is spun, the step which comprises spinning the dispersion and coagulating the spun fibers in an acidic coagulating bath having a vegetable tanning agent and a mineral tanning agent.

12. In a process of producing synthetic proteinaceous fiber, in which process a dispersion of an alkali-dispersible acid-coagulating protein is spun, the step which comprises spinning the dispersion and coagulating the spun fibers in an acidic coagulating bath having a mineral tanning agent and a vegetable tanning agent comprising Goulac, which is a lignin bearing waste material obtained by drying of the liquid from the sulfite paper process.

13. In a process of producing synthetic proteinaceous fiber, in which process a dispersion of casein is spun, the step which comprises spinning the dispersion and coagulating the spun fibers in an acidic coagulating bath having an alum as a mineral tanning agent and Goulac, which is a lignin bearing waste material obtained by drying of the liquid from the sulfite paper process, as a vegetable tanning agent.

14. In a process of producing synthetic proteinaceous fiber, in which process a protein dispersion is spun into an acidic coagulating bath, the steps which comprise preparing the dispersion by heating to a temperature of 170° to 190° F. and mixing an alkali-dispersible protein in an aqueous medium and with an alkaline material in an amount to impart to the dispersion a pH value of not over 7.5, cooling the dispersion by passing it into a vacuum, and spinning the cooled dispersion while having the above mentioned pH value into an acidic coagulating bath having a pH value of 1.3 to 2.0.

15. In a process of producing synthetic proteinaceous fiber, in which process a protein dispersion is spun into a coagulating bath, the steps which comprise preparing the dispersion by mixing and heating casein in an aqueous medium and with an alkali in an amount to impart to the dispersion a pH value of not over 7.5, the alkali of said medium consisting essentially of an alkali metal hydroxide, continuing the heating until the temperature of the mixture is 170° to 190° F., maintaining the mixture at this tem-

perature until the dispersion of the protein is substantially complete, cooling and deaerating the dispersion by passing it into a vacuum, and spinning the dispersion while having the above mentioned pH value into an acidic coagulating bath containing a mineral tanning agent and having a pH value of 1.3 to 2.0.

16. In a process of producing synthetic proteinaceous fiber, in which process a casein dispersion is spun into a coagulating bath, the step which comprises preparing the dispersion by heating casein in an aqueous solvent in an amount such that the dispersion has a viscosity of not less than 40,000 centipoises at the time the dispersion is spun and with an alkaline material in an amount to impart to the dispersion a pH value of 5.5 to 7.5, continuing the heating until the temperature of the mixture is not less than 170° F., maintaining the mixture at this temperature until the dispersion of the protein is complete, cooling the dispersion to about room temperature by spraying the dispersion into a vacuum, and spinning the dispersion while having the above mentioned viscosity and pH value into an acidic coagulating bath having a pH value of 1.3 to 2.0.

17. In a process of producing synthetic proteinaceous fiber, in which process a casein dispersion is spun into a coagulating bath, the step which comprises preparing the dispersion by heating casein in an aqueous solvent in an amount such that the dispersion has a viscosity of not less than 75,000 centipoises at the time the dispersion is spun and with an alkali metal caustic in an amount to impart to the dispersion a pH value of 6 to 7, continuing the heating until the temperature of the dispersion is 170° F. to 190° F., maintaining the mixture at this temperature until the dispersion of the protein is complete, cooling the dispersion to about room temperature by spraying the dispersion into a vacuum, and spinning the dispersion while having the above mentioned viscosity and pH value into an acidic coagulating bath containing a mineral tanning agent and a vegetable tanning agent and having a pH value of 1.3 to 2.0.

18. In a process of producing synthetic proteinaceous fiber, in which process a casein dispersion is spun into a coagulating bath, the steps which comprise preparing the dispersion by heat-

ing casein in an aqueous solvent in an amount such that the dispersion has a viscosity of not less than 8000 centipoises when measured with a Hoeppler viscosimeter at 100° F. and with an alkaline material in an amount to impart to the dispersion a pH value of 5.5 to 7.5, continuing the heating until the temperature of the mixture is at least 170° F. but below that at which the casein dispersion would be rendered unsuitable for spinning into fibers, maintaining the mixture at this temperature until the dispersion of the protein is complete, cooling the dispersion by spraying it into a vacuum, and spinning the dispersion while having the above mentioned pH value into an acidic coagulating bath having a pH value of 1.3 to 2.0.

19. In a process of producing synthetic proteinaceous fiber, in which process a casein dispersion is spun into an acidic coagulating bath, the steps which comprise preparing the dispersion by heating casein in an aqueous solvent in an amount such that the dispersion has a viscosity of not less than 8000 centipoises when measured with a Hoeppler viscosimeter at 100° F. and with an alkali metal hydroxide in an amount to impart to the dispersion a pH value of 6 to 7, continuing the heating until the temperature of the dispersion is 170° to 190° F., maintaining the mixture at this temperature until the dispersion of the casein is complete, cooling the dispersion by spraying it into a vacuum, and spinning the dispersion while having the above mentioned pH value in to an acidic coagulating bath containing a mineral tanning agent and having a pH value of 1.3 to 2.0.

20. In a process of producing synthetic fiber from an alkali-dispersible protein, the step which comprises treating the spun fiber in a solution containing formaldehyde, withdrawing the fiber from the formaldehyde containing solution and further treating the fiber with formaldehyde by placing it while still wet with the formaldehyde containing solution in a confined space, and without drying the fiber, maintaining the fiber wet with the formaldehyde solution and in contact with formaldehyde vapor present in the confined space not occupied by the wet fiber so that the fiber is wet at the time it is removed from the confined space.

FRANCIS CLARKE ATWOOD.

CERTIFICATE OF CORRECTION.

Patent No. 2,342,994.

February 29, 1944.

FRANCIS CLARKE ATWOOD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 3, for the word "and" before "admixture" read --an--; page 5, first column, line 61, before "bichromate" insert --a--; page 6, first column, line 4, for "preferably" read --preferable--; and second column, line 7, for "lactone" read --lactose--; page 10, second column, line 33, claim 19, for "in to" read --into--; line 37, claim 20, for "portein" read --protein--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of April, A. D. 1944.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.