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AQUEOUS SIZING COMPOSITIONS

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This invention relates to sizing compositions and more particularly to sizing compositions especially adapted for use with yarns derived from synthetic fiber forming polymeric amides.

One object of the present invention is to provide a sizing composition for yarns derived from synthetic fiber forming polymeric amides which effectively improves the working properties of such yarns in the manufacture of sheer full fashioned hosiery.

Another object of the present invention is to provide a sizing composition for yarns derived from synthetic fiber forming polymeric amides which eliminates the difficulties ordinarily inherent in the use of such yarns in the manufacture of sheer full fashioned hosiery.

Another object of the present invention is to provide a sizing composition for yarns derived from synthetic fiber forming polymeric amides which substantially reduces the percentage of imperfect and defective stockings ordinarily formed when such yarns are utilized in the manufacture of sheer full fashioned hosiery.

Other objects of the present invention will be apparent from the description and appended claims.

There has been developed in fairly recent years a class of synthetic fiber forming materials which, due to their superior physical properties as compared to hitherto available fibrous materials, have largely supplanted in many textile applications those materials which were formerly used, yielding products of superior texture, appearance, durability and wearing comfort. The particular class of synthetic fiber forming materials referred to above comprise that group of compounds comprising any long-chain synthetic polymeric amide which has recurring amide groups as an integral part of the main polymer chain, and which is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis. These synthetic polyamides, as these materials will hereinafter be designated in the present invention, are usually prepared either by self-condensation of various amino acids or by amidation of dibasic acids with diamines. A description of the preparation of such synthetic polyamides and the production of fibers and textile yarns therefrom is set forth in U. S. Patent Nos. 2,071,250, 2,130,523, and 2,130,948.

Fibers and yarns derived from the synthetic polyamides possess the appearance and lustre of silk while exhibiting a uniformity, tensile strength, degree of elasticity and toughness unapproached by any of the commonly utilized tex-

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tile fibers. Furthermore, the moisture absorbency of synthetic polyamide yarns is very low as compared to other fibrous materials, therefore imparting a very high degree of wet strength to fabrics composed of such yarns. Another desirable feature of these materials is the ability of textile products fabricated with synthetic polyamide yarns to assume a permanent set upon the application thereto of a sufficient degree of heat. Because of the specific qualities and properties characteristic of synthetic fiber-forming polyamides, yarns derived from these materials have been found to be of particular interest for hosiery and especially as a replacement for silk in the manufacture of sheer full fashioned stockings.

The term "full fashioned" as applied to hosiery, is descriptive of that particular method of knitting whereby stockings are knitted on a single flat bed of spring needles, the fabric being knitted flat and shaped to conform to the circumference of that part of the leg which it fits by narrowing, that is, by reducing the number of needles knitting. As contrasted to those knitting methods in which the loop formation takes place progressively as completed individual loops, in the full fashioned knitting process the yarn is laid across the width of the needle bed, the loops are measured off all at one time and the needles simultaneously knit the loops through the previous course; that is, the row of loops extending from the edge of the fabric in a line across the width of the fabric. Thus each series of loops enters the fabric structure simultaneously. Due to the successive steps occurring in the knitting cycle, the full fashioned knitting machine requires a highly flexible and pliable yarn which will remain on the needles in loops as formed until the whole course enters the fabric structure.

However the very properties which seem to make synthetic polyamide yarns ideal for use in hosiery and which are so desirable in the finished stocking provide serious difficulties during the knitting operation in the manufacture of sheer full fashioned hosiery. The high resiliency of synthetic polyamide yarn causes the yarn, after knitting and release of tension to tend to straighten out, causing curling at the edges of the fabric and shrinkage along the length of the stocking. Then too the loops as formed during the knitting operation have a tendency to slip off the needles resulting in uneven stitch formation and a great number of dropped stitches. Furthermore when multi-filament, twisted yarns

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are bent into loops for knitting, the yarn does not bend into the plane of the fabric, thus tending to produce poor stitch formation along with an uneven fabric surface. This is very unattractive in appearance and the raised loops increase the chances of snagging the fabric upon subsequent handling operations.

The reasons why such difficulties are encountered in the manufacture of sheer full fashioned stockings using synthetic polyamide yarns are easily understood when it is considered that the full fashioned knitting method was designed primarily to process natural silk. Fibers and yarns of natural silk possess a natural coating of a gummy material called "Sericin" which controls the resiliency of the yarns during the knitting operation thus providing better working properties to the yarns, and which cements the loops together as formed and positions them in the plane of the fabric, thereby providing a firmer fabric which reduces the danger of damage to the stocking during subsequent handling operations. Since synthetic polyamide fibers are derived from a plastic, resinous material by extruding the fibers from the molten material or from solutions of such material, the fibers themselves, and yarns composed of such fibers, contain no such coating. Therefor in order to adapt synthetic polyamide yarns to the requirements of the full fashioned knitting process, it has been found necessary to apply to such yarns a coating of such properties and characteristics as to approximate the functions of sericin in the fabrication of full fashioned natural silk hosiery.

The size, as such coatings are known, has several important functions both during the knitting operation and in the operations which necessarily follow in order to produce the finished article. The size binds the twisted filaments together, reducing the chances of snagging or tearing of the individual filaments. The size also overcomes the high resiliency of the yarn and holds it in place during knitting operations to provide good stitch formation. A further purpose of the size is to eliminate the tendency of the loops of the twisted yarn to come up out of the plane of the fabric, thereby reducing picking of the yarn during operations subsequent to knitting. The size also prevents curling of the edges of the fabric and excessive shrinkage along its length allowing the formation of a straight seam during the seaming operation, and consequently, the production of a finished product of greatly increased beauty. Another function of the size is to provide a firmer fabric after knitting which allows the stocking to be handled more easily without danger of damage to the stitch formation during the operations subsequent to knitting, such as looping, seaming, boarding, etc.

However, ever since the first attempt to substitute synthetic polyamide yarns for natural silk in the manufacture of sheer full fashioned hosiery, there has been present the very real problem of finding a sizing material suitable for use with such synthetic polyamide yarns in the full fashioned knitting process, which would satisfactorily perform the necessary functions required of such a material to produce a finished product equal or superior to that obtained with natural silk, and which would also eliminate or reduce to a minimum the proportion of imperfect and defective stockings ordinarily formed. Ordinary sizing materials, such as the gums and glues which are utilized to size cottons, rayons,

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etc., are useless when applied to synthetic polyamide yarns or fibers because of the lack of adhesion of these materials to such fibers and yarns, the lack of sufficient adhesion resulting in the flaking off of the size during the knitting operation. Nor have the difficulties inherent in providing a suitable sizing material for synthetic polyamide yarns in the manufacture of sheer full fashioned hosiery been completely overcome by the sizing materials utilized for this purpose at the present time. One of the reasons for this arises from the fact that in order to improve the working properties of the sized yarn, the yarn is wetted either by immersion in water or by passing over wicks immersed in water immediately prior to the knitting operation. This has purpose of eliminating the stiffness of the yarn due to the size coating and of imparting sufficient flexibility to the sized yarn for satisfactory knitting. The moisture absorbed by the size in the wetting operation is eliminated from the fabric immediately thereafter by evaporation providing a firm stable, knitted structure. After the fabric has passed through all the operations necessary to produce the finished stocking, the size is removed by immersion in a hot water bath. Therefor if the particular sizing material utilized has too high a degree of water solubility, the wetted size becomes too soft for satisfactory knitting and has a tendency to clog the knitting needles, resulting in uneven stitching, torn threads, and the formation of holes in the fabric. Such a condition usually necessitates cleaning of the knitting needles, the required stoppage of the knitting operation resulting in the costly loss of much time and material. If the size is not sufficiently water soluble, it will remain too stiff and brittle for successful knitting, have a tendency to flake off during the knitting operation and will not be easily removable in the desizing bath. Furthermore, the very high resiliency of synthetic polyamide fibers and yarns demand a greater deposit of solids for adequate stitch control and other above-mentioned factors than do the less resilient textile materials. Therefor the sizing composition should be of such solubility in the particular liquid component utilized to prepare the sizing solution as to furnish a concentration of solids high enough to satisfactorily accomplish this at the viscosities ordinarily required for optimum results in the commonly utilized sizing processes.

We have found that a sizing composition which satisfactorily reduces to a minimum the difficulties involved in the manufacture of sheer full fashioned hosiery using synthetic polyamide fibers and yarns, and which enables the production of a finished product equal or superior to that obtained with natural silk, and which substantially reduces the proportion of imperfect and defective stockings ordinarily formed may be prepared with a solubilized casein and a compound selected from the group comprising the polyvinyl alcohols and water soluble derivatives of polyvinyl alcohols.

The term "solubilized casein," as utilized in the present invention, refers to that group of substances or compounds, the preparation, properties and compositions of which are described in U. S. Patents Nos. 2,005,730; 2,103,153; and 2,108,582. The process by which these compounds are prepared consists essentially in mixing an acid precipitated casein in the presence of a small amount of water, or other suitable plasticizing agent, with the desired amount of a

solubilizing agent, and thereafter subjecting the admixture to further mixing, preferably by kneading, under conditions of high pressures and controlled temperature. The products thus formed are water soluble homogeneous mixtures or chemical combinations, or both, having properties distinctive from those of the starting materials, or of simple mixtures of these materials, the properties varying according to the particular modifying or solubilizing materials utilized, the proportions in which such materials are used, and the processing conditions. The modifying or solubilizing agents which are generally used to prepare the solubilized caseins include borax, ammonium hydroxide, caustic soda, triethanolamine, alkaline earth hydroxides and various other alkaline substances.

The particular polyvinyl alcohol which we prefer to utilize in combination with the solubilized caseins to obtain sizing compositions exhibiting the desirable characteristics of the present invention is a highly water soluble, partially hydrolyzed derivative of polyvinyl acetate, the extent of hydrolysis being approximately 86-89 per cent, which exhibits a relatively low solution viscosity, the viscosity of a 4% water solution at 20° C. as determined by means of the Hoesppler falling ball method being approximately 4-6 centipoises.

As an example of a sizing composition exhibiting the desirable characteristics of the present invention we utilize about 87.25 parts of water, about 2.0 parts of the above specified polyvinyl alcohol, about 0.25 part of sodium orthophenyl phenate, and about 10.50 parts of a solubilized casein, which upon solution in the specified amount of water together with the other materials in the proportions as set forth, forms a homogeneous composition possessing a viscosity at 78° F. within the range of 60-140 seconds, the viscosity being determined by means of the Saybolt Universal viscosimeter.

In preparing the sizing composition comprising the components set forth above, the solubilized casein is slowly stirred into about 33 parts water and the mixture is thereafter slowly heated, with continuous agitation, to approximately 81±2° C. and held at that temperature till complete solution of the casein has been obtained. The polyvinyl alcohol is slowly sifted into about 30 parts of water under agitation conditions and stirred till any lumps which may have been formed during this operation are eliminated. This mixture is then heated to about 50° C. and agitation is continued till the polyvinyl alcohol has completely dissolved. The two solutions thus obtained are allowed to cool to about 30° C. whereupon the polyvinyl alcohol solution is added to the solubilized casein solution with agitation, and stirring is continued till a smooth homogeneous composition is obtained. The sodium orthophenyl phenate, which has been dissolved in about 5 parts of water, and the remainder of the water are then stirred into the polyvinyl alcohol-solubilized casein solution.

The above outlined procedure is merely demonstrative of a manner in which the various components may satisfactorily be combined to form a homogeneous sizing composition having the desirable properties and characteristics of the present invention, and this particular method therefor is not to be considered as essential for the preparation of our sizing compositions. The manner and the means by which the various components are combined may be varied or

changed without departing from the scope of the present invention, it being merely required that the resultant composition be homogeneous, not a gel, and possess a relatively low viscosity, preferably within the range as set forth in the above illustrative example.

Other water soluble polyvinyl alcohols of relatively low solution viscosities may be utilized in carrying out the present invention. By "other water soluble polyvinyl alcohols of relatively low solution viscosities," we mean those compounds resulting from the hydrolysis of polyvinyl esters which have been hydrolyzed to such an extent as to render them completely water soluble, and in which the degree of polymerization is such that the viscosity of a 4% water solution at 20° C. is preferably no more than approximately 20 centipoises, the viscosity being determined by means of the Hoesppler falling ball method. Water soluble polyvinyl alcohol derivatives which may also be utilized in combination with the solubilized caseins to provide the sizing compositions of the present invention include the water soluble polyvinyl alcohol esters such as those obtained by the esterification of polyvinyl alcohol with various acids, such as lactic, tartaric, citric, malic, oxalic, and maleic acids; mixed esters of polyvinyl alcohol; and the water soluble polyvinyl acetals resulting from the condensation of an aldehyde and polyvinyl alcohol. Water soluble alkyl and hydroxyalkyl polyvinyl ethers, formed by the interaction of an alkylene oxide with polyvinyl alcohol, may also be employed, as well as the water soluble products obtained by the partial or complete saponification of the mixed polymerization products obtained by the copolymerization of vinyl halide, styrene, butadiene, or acrylic ester, with vinyl acetate.

The particular solubilized caseins and the polyvinyl alcohols, or water soluble polyvinyl alcohol derivatives, which may be utilized in combination with each other, and the ratios in which they may be employed, depends primarily upon the compatibility of these materials for each other in aqueous solution at a solids concentration within the range required to yield the advantageous results of the compositions of the present invention. The proportion of solids in aqueous solution, that is, the percentage of combined solubilized casein and polyvinyl alcohol, or water soluble polyvinyl alcohol derivative, which should be employed in preparing aqueous solutions of these materials is dependent mainly upon the aqueous solution viscosities of the particular materials employed. Therefore it will be understood that the percentage of solids to solvent utilized in preparing the sizing compositions of the present invention necessarily will vary with the solution viscosities characteristic of the materials employed. For example, solutions containing the solubilized caseins which exhibit a fairly high solution viscosity will require a lower percentage of solids than will solutions prepared with solubilized caseins of low solution viscosity. Similarly, the percentage of polyvinyl alcohol, or water soluble polyvinyl alcohol derivative which may be used to prepare the sizing compositions of the present invention will necessarily decrease as the solution viscosities of those materials increase. We have found that a solids concentration of about 8-22 per cent in aqueous solution of the materials above set forth is most satisfactory to produce the desirable results of the present invention. We have also found that an amount of polyvinyl alcohol, or water soluble polyvinyl al-

cohol derivative, within the range of about 5-25 per cent by weight based upon the weight of the solubilized casein provides sizing compositions suitable for use with synthetic polyamide fibers and yarns employed in the manufacture of sheer full fashioned hosiery.

Casein solutions are ordinarily subject to the deteriorating influences of bacterial decomposition and hydrolysis, the resultant effects being a splitting of the protein molecule into smaller molecules, accompanied by a reduction in the strength of films deposited. Such reactions in the sizing compositions of the present invention would have a tendency to destroy the very properties which make these compositions so effective as sizes for synthetic polyamide yarns. However, this danger can be effectively prevented by incorporating into the sizing compositions a suitable preservative, such as sodium orthophenyl phenate sodium pentachlorophenate, sodium salicylate, alkaline salts of para meta cresol, or any one of the many phenolic compounds usually utilized for this purpose which is compatible with the various components of our sizing compositions. In utilizing such preservatives, we have found that an amount between approximately 0.10 per cent and 1.5 per cent based upon the weight of the size solution will satisfactorily protect such solutions from decomposition over relatively long periods of time.

Excellent sizing properties may also be obtained by incorporating plasticizers in the sizing compositions of the present invention. Thus, for example, 4 parts by weight of the water contained in the above illustrative example may be replaced by an equal amount of acetamide to provide a sizing composition exhibiting the improved properties and characteristics of the products of the present invention when utilized with synthetic polyamide fibers and yarns in the manufacture of sheer full fashioned hosiery. The addition of a plasticizing material to the sizing compositions of the present invention has the effect when applied to synthetic polyamide fibers and yarns, of providing a sized yarn of greater flexibility and of softer finish than is had without the presence of such an agent. Such qualities are particularly desired of sized polyamide fibers and yarns utilized in textile weaving operations and thereby increase the usefulness and scope of the products of the present invention. Other plasticizing materials which may similarly be utilized with our compositions include urea thiourea, dicyandiamide, formamide, ethanol formamide, glycerol, acetanilid, ethylene glycol, and generally the lower polyethylene glycols, sorbitol and the higher alcohols such as undecanol and dodecanol.

The highly advantageous sizing properties obtained by the utilization of the sizing compositions of the present invention with synthetic polyamide fibers and yarns in the manufacture of sheer full fashioned hosiery is rather surprising due to the fact that neither of the materials comprising the film forming component of our compositions is satisfactory for this particular purpose when utilized alone. Polyvinyl alcohol forms a film which is too highly water soluble and tends to become so soft when the sized yarn is wetted prior to the knitting operation as to accumulate on the knitting needles, causing many serious knitting problems. Moreover, due to the low coherence of polyvinyl alcohol size films and poor adherence to synthetic polyamide yarn, such films cannot be applied to synthetic polyamide yarns in an amount exceeding approximately 3-4

per cent by weight based upon the weight of the yarn, inasmuch as any amount of polyvinyl alcohol in excess of these quantities flakes off badly, causing needle clogging and poor stitch formation. Solubilized casein presents the problem of insufficient pliability and brittleness of film resulting in angular rather than circular stitch formation during the knitting operation. However, when solubilized casein and polyvinyl alcohol or the water soluble derivatives of polyvinyl alcohol are utilized in conjunction with each other, the combination behaves in such a manner as to provide a film, when utilized as a size for synthetic polyamide yarn, of increased flexibility, and adhesion, and of sufficiently decreased water solubility as to avoid excess softening of the size film when wetted.

A further advantage of the sizing compositions of the present invention lies in the fact that a size film in an amount up to approximately 15 per cent by weight based upon the weight of the yarn may be applied to synthetic polyamide yarns without impairing the running properties of the yarn and without danger of flaking off of the size film during the knitting operation. Such an amount of size upon the yarn provides a firmer, more stable knitted fabric which allows for easier handling.

The application of the sizing compositions of the present invention to synthetic polyamide yarns by such means as are commonly employed in the textile industry provides sized yarns especially suited for use in the manufacture of sheer full fashioned stockings. Due to the affinity of these sizes for synthetic polyamide yarns, the film deposited on the yarn adheres more firmly than those provided by the hitherto available sizes, and consequently improves the knitting properties of the yarn. Such yarns may be wetted prior to knitting without danger of the size film becoming tacky or so soft as to clog the knitting needles, thereby eliminating one of the most serious difficulties involved in the manufacture of full fashioned hosiery. Our sizes also impart improved stability to the hosiery fabric by increasing the firmness of the knitted structure, thereby preventing edge rolling and shrinkage of the fabric on the knitting machine and facilitating handling of the hose in the operations subsequent to knitting. By improving the working properties of synthetic polyamide yarns utilized in the manufacture of sheer full fashioned hosiery, and by imparting such properties to the fabric as to reduce to a minimum the possibility of damage to the knitted structure in the operations subsequent to knitting, the sizing compositions of the present invention substantially decrease the percentage of imperfect and defective stockings ordinarily formed, and insure the formation of more uniform and more nearly perfect stockings of greatly enhanced appearance.

Naturally, the use of the sizing compositions of the present invention with synthetic polyamide yarn to achieve the advantageous results of the present invention is not to be considered as being limited merely to the full fashioned method of knitting hosiery. These sizes will also be found to be especially effective in other knitting methods employing synthetic polyamide yarns such as tricot knitting and circular knitting of fabrics, as well as in weaving operations employing such yarns.

While the sizing compositions of the present invention are especially useful with synthetic

fibers and yarns which are relatively smooth surfaced and water repellent, they also adhere well to the more hydrophilic fibers and may easily be adapted by anyone skilled in the art to meet the various sizing requirements of other fibrous materials such as cotton, linen, rayon, cellulose acetate, etc. in such textile operations where a sized fiber or yarn is necessary for successful fabric formation. Our sizes are particularly advantageous for use with such materials because of the ease with which the desizing operation may be accomplished, the size being readily removed by soaking the finished fabric in a hot water bath. This eliminates the danger of damage to the fabric which is present when strong solvents are used to remove the size or when the particular size used requires long immersion in the desizing bath under high temperature conditions for complete removal.

While the products herein described and the processes of making the same constitute preferred embodiments of the present invention, changes may be made therein without departing from the scope of the present invention as defined in the appended claims.

What is claimed is:

1. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based on the weight of the said casein of a material selected from the group consisting of polyvinyl alcohol, water-soluble esters of polyvinyl alcohol, and water-soluble ethers of polyvinyl alcohol.

2. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22-8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of polyvinyl alcohol.

3. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of polyvinyl alcohol, said solu-

tion exhibiting a Saybolt viscosity at 78° F. within the range of 60 to 140 seconds.

4. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a partially hydroxylated polyvinyl acetate in which the extent of hydrolysis is approximately 86 to 89% and in which the degree of polymerization is such that the viscosity of a 4% aqueous solution at 20° C. is approximately 4 to 6 centipoises.

5. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a water-soluble partial acetal of polyvinyl alcohol.

6. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a water-soluble partial acetal of polyvinyl alcohol, said solution exhibiting a Saybolt viscosity of 78° F. within the range of 60 to 140 seconds.

7. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a water-soluble ester of polyvinyl alcohol.

8. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid

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and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a water-soluble ester of polyvinyl alcohol, said solution exhibiting a Saybolt viscosity of 78° C. within the range of 60 to 140 seconds.

9. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a water-soluble ether of polyvinyl alcohol.

10. As a size for yarn derived from synthetic fiber-forming polymeric amides of the type obtained by reaction of a dibasic carboxylic acid and

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an aliphatic diamine, an aqueous solution consisting essentially of from 78 to 92% by weight of water and from 22 to 8% by weight of a composition consisting essentially of solubilized casein, obtained by mixing acid precipitated casein and an alkaline material in an amount of water sufficient only to plasticize the admixture and subjecting said admixture to further mixing under high pressure conditions to obtain the same in a dry comminuted form, and of approximately 5 to 25% by weight based upon the weight of the said casein of a water-soluble ether of polyvinyl alcohol, said solution exhibiting a Saybolt viscosity of 78° F. within the range of 60 to 140 seconds.

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