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## TEXTILE SIZING COMPOSITIONS AND PROCESS OF MAKING THEM

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The present invention relates to textile size and the process of making same. It is an object of the invention to provide semi-permanent and temporary sizing compositions for use on textile materials, such sizes being capable of being removed readily if desired. Other objects will be apparent from the detailed discussion which follows.

In certain textile operations, for instance in the knitting and handling of sheer hose, it is necessary that the objects knitted or woven be suitably sized so as to render them relatively stiff or in a condition where loose ends or edges do not curl during finishing. Furthermore, such an amount of size which gives easy handling in certain operations is undesirable to leave in the article destined for retail, such as woman's hose. It is, therefore, necessary to provide a material which will size the textile fibers evenly from a relatively non-viscous aqueous solution; which may be partially cured to yield a tough, non-scaling, non-tacky stiff sizing effect; which lastly after performing the desired operations satisfactorily may be removed or reduced in amount so that the finished article is in a satisfactory condition to be sold.

In the field of stocking and hosiery made of silk, cotton, rayon, acetate or nylon it has been normal to employ such materials as glues, starches, gelatins, or synthetic materials such as polyvinyl alcohol. These materials possess several disadvantages, chief among them being their relatively high viscosity in solution which occasionally clogs machinery and moving parts which may be built up with a surplus of the sizing solution. Furthermore, the size in some cases scales badly after being dried on the fibers and consequently clogs the delicate parts of knitting machines or weaving looms, or on the other hand may impart undesirable brittleness to the fibers and threads.

I have found, however, that I may make sizing compositions which have hardly greater viscosity than water itself and which may be hardened on fibers, threads and textiles to give tough, uniform, non-tacky, non-scaling sizing of good stiffness from the reaction products of ethylenic alpha-beta polycarboxylic acids such as maleic acid or anhydride and the like and polyhydric alcohols, particularly hexahydric alcohols such as mannitol and sorbitol.

Such reaction products as, for instance, sorbitol maleate are not sufficiently soluble in water, but may be made to yield satisfactory solutions by adding small amounts of aqueous ammonia solutions to the materials. Furthermore, the aqueous ammonia solutions preferably have incorporated with them a curing agent of neutral reaction such as hydrogen peroxide, soluble organic peroxide or soluble inorganic persulfate such as ammonium persulfate and the like, although their use is not essential in some cases.

The aqueous sizing solutions which may vary in concentration between about 0.1% and 10% depending upon the use desired are non-viscous. When the resinous reaction product is deposited on the fiber or thread or textile and dried at room temperature or slightly above, the resinous material is converted into a hard tough material by polymerization, thereby obtaining the desired sizing effect.

The following examples are illustrative of the process of the present invention.

*Example 1.*—36 parts by weight of fumaric acid were thoroughly mixed with 36 parts by weight of crystalline sorbitol. The mixture was heated slowly up to 215° C. with agitation. At first the mixture become pasty, then fluid, then entirely clear. Owing to the rapidity with which the fluid increased in viscosity, it was cooled and poured into trays when a test bead remained clear on cooling to room temperature. The reaction product was slightly cloudy, very tough and hard. It was pulverized to a powder and 1 part by weight mixed with 2 parts by weight of warm water. No solution took place but on the addition of a small amount of ammonia water of 28% strength a clear, relatively non-viscous, light brown solution was obtained.

The above solution is useful as a textile size when diluted with more water to 0.1% to 10% strength and 5% ammonium persulfate based on the solids content added. Slower but satisfactory curing may be obtained by omitting the ammonium persulfate.

*Example 2.*—30 parts by weight of crystalline sorbitol and 30 parts by weight of maleic anhydride were thoroughly mixed and heated in a Monel metal reaction vessel to 150° C.–160° C. for 45–50 minutes. In this time a viscous resinous material was formed which on cooling solidified to a hard, tough, glassy mass. The material was put through a rotary grinder to pulverize and when powdered 29 parts by weight of the resin were mixed with 50 parts by weight of water at 70° C. Aqueous ammonia was added until the solution remained clear on indefinite dilution with water. The solution was then made up to 33% solids and filtered.

The above solution when properly diluted with

water was tested under commercial condition on rayon thread which was then knitted to form a stocking. It was found that the sized stocking possessed non-curling properties not given by any commercial size previously tested. It also was found to be of correct stiffness, did not scale and was outstanding because of its extremely low viscosity in solution.

*Example 3.*—66 parts by weight of mannitol and 66 parts by weight of maleic anhydride were mixed and heated at 180°–210° C. for 20 minutes. The mixture which rapidly became fluid thickened quickly and was poured into trays. It was pulverized and dissolved in water by the addition of a small amount of ammonia. The solution remained acid in reaction indicating that to secure solubility not all the free carboxyl groups need be neutralized.

It has also been found that cobalt salts may be employed in curing the sizings of the present invention and, if desired, used in conjunction with certain organic or inorganic per-salts, such as benzoyl peroxide, peracetic acid, ammonium persulfate and the like, to obtain greater speed of curing.

Although the hexahydric alcohols are preferred in the present invention, they may be replaced partially but not wholly by other polyhydric alcohols to secure special sizing effects. These polyhydric alcohols may be glycerol, pentaerythritol, ethylene glycol or polyethylene glycol and the like.

*Example 4.*—36.4 parts by weight of mannitol, 38.8 parts by weight of tetraethylene glycol, 78.4 parts by weight of maleic anhydride were mixed and heated at 200° C. for 1 hour. In this time test beads of the reaction product when cooled to room temperature indicated a hard, tough, glassy resinous product. The product was not soluble in water by itself but readily so when a small amount of ammonia was added to the solution. A good sizing solution may be made by diluting the ammoniacal water solution of the above product to 0.1% to 10%. (5% ammonium persulfate based on the reaction product may be added to the solution if desired.)

It may readily be seen that numerous variations may be made on the reaction products of the present invention to give satisfactory sizing solutions without departing from the spirit thereof. For instance, in place of maleic and fumaric acids, I may employ citraconic and itaconic acids. Acetylene dicarboxylic acid and the like may also be used. Some portion of the alpha-beta unsaturated acid may be replaced by other acids such as phthalic, succinic, adipic acids and the like. However, this replacement should not be to such an extent that the reaction products may not be cured properly. I prefer to employ ammonia as the solubilizing base of the present invention but I may also use amines which confer water-solubility or certain inorganic bases such as sodium and potassium hydroxide.

The proportions of the reactants may be varied between quite wide limits to yield satisfactory sizes. For instance, I have used equal parts by weight of hexahydric alcohol and maleic or fumaric acids; however, an equally effective size could be made of two parts of hexahydric alcohol and one part of unsaturated acid or conversely two parts of acid to one of alcohol. By varying these proportions one skilled in the art may produce textile sizing suited for a variety of uses without substantially departing from the scope of this invention. Furthermore, the amount of curing agent may be varied considerably to suit the particular processes involved in finishing the textile material. For instance, from 0.5% or somewhat less to 10% based on the reaction product of per-compound such as ammonium persulfate may be used. The curing agent may be entirely omitted, however, since on exposure to air the products of the present invention are cured by polymerization induced by atmospheric oxygen. Thus the sizes of this invention can be cured with or without added catalysts as desired. The relatively large areas of size exposed to the atmosphere when coated onto textiles and fibers renders the curing by air practicable. The curing temperature may also vary greatly. For instance, room temperature of 28° C. for about 10 hours is satisfactory or temperatures up to 100° C. or higher can be employed. The conditions in general will depend upon the degree of permanency and toughness and stiffness desired of the sizing material of this invention.

The reason that this size is of value particularly in rayon preparation for the hosiery industry, is that the filaments are held together by the size, the yarn is protected during the thread-making operation, and in knitting on a full-fashion or seamless hosiery machine, the fabric lies out flat. When a fabric such as rayon is unsized it rolls up on the machine, causing a great deal of difficulty in the final operation of hosiery preparation and manufacture.

The present practiced method by which rayon is prepared for the hosiery industry is to oil it in the cone or skein prior to thread-twisting. This is an inconvenient method as well as a rather expensive one. If the treatment is done in an inkless soaking solution where the yarn can be tinted to identify it, it can be lubricated and sized all in one operation and when the yarn finally dries, it can then be made into threads and knitted with the advantages heretofore stated.

The reason that a synthetic size like the one described herein is of interest is that it dries or cures into the yarn. By the old system where a substance such as gelatin, starch, dextrine and like materials was used, sizing is obtained because the solid gel is on the surface. This is all right for broad silk manufacture but, being used in the knitting of hosiery, this size scrapes or scales off from the surface and therefore fills up the working parts of the knitting machine.

Possibly the most important thing in the use of the synthetic size described herein is that after the size has been cured into the original yarn and has been given a thread-twisting operation, some excess amount of twist can be put into the yarn. When this yarn is then steamed at high temperatures (up to 190° F. for instance) and then later cooled to the running conditions of the mill, the resetting of the size on cooling retains a higher twist in the yarn. Thus, when the thread undergoes the intricate motion of the knitting machines to form it into perfect knitted loops, the yarn does not kink up into little pigtails like loops and thus cause poor knitting. The presence of this synthetic size seems to give a certain firmness or set to the yarn which allows it to be knitted cleanly into hose sections. Furthermore, in knitting the fabric lies out smooth and flat. This is beneficial to the yarn fabric because after the hose are made flat and then sewed up the backs to make the hose for encasing the leg, the selvage of the yarn lays out, which

assists in sewing together the two edges. Unsized soft yarn rolls up and complicates the sewing operation.

The size of the present invention may be applied to various kinds of yarns. It may be applied advantageously to rayon yarns like Bembergs, viscose yarns and other types of rayons (whether they are bright, dull or pigmented) by treating in skein form and in an inkless solution as follows:

To a half case of rayon yarn, for example 110 pounds, make up a bath containing 55 gallons of water to a temperature of 125° F. Dissolve in this water 3 to 4 pounds of a 33% aqueous ammonia solution as described in Example 2. When properly dissolved add 8 pounds of lubricant such as that sold under the name of Warco Rayon Oil 1105, which is in an emulsifiable mineral-vegetable oil system used to lubricate and plasticize the yarns and size in the bath. There may also be added a water-soluble tint to mark the yarns. The rayon skeins are immersed in this solution for a period of one to three hours and the oils, size and tint are allowed to lightly migrate into the yarns. After this soaking treatment, the yarn is centrifuged down to about 100% water content, then dried in a rayon drier and in dry skein form is ready for the winding department. Depending upon the ratio of plasticizing agents to size, a thread can be thus made of various natures which will result in a fabric to suit the requirements of almost any knitting operation.

The various advantages which I obtain in the use of this size, if properly applied to the yarn and if ultimately knitted into a hosiery fabric, may be listed as follows, these factors being noted particularly with respect to rayon:

(*a*) The filaments are bound together and thus a cleaner yarn is made.

(*b*) It allows the yarn to be twisted to a higher twist and to hold at that twist without kinking up.

(*c*) Due to the higher twist, a stronger yarn is obtained.

(*d*) This sizing bonds the yarn on the interior as well as the exterior covering and thus is beneficial in that it will not scrape off on the fine parts of the knitting machinery as happens in an encasement like gelatin, starch, dextrine or the like sizing materials.

(*e*) In allowing this yarn to be knitted on the hosiery knitting machine and as the fabric is thrown away from the needle bar, said fabric will lie flat for easel inspection. This is very necessary in full-fashioned hosiery to have the whole width of the yarn exposed and not rolled up in a shoestring-like thread.

(*f*) The normal process after hose is made and completed flat is then to seam it up the back and thus make a complete full-fashioned hose. This is a delicate mechanical operation and any undue rolling in the fabric which encumbers the selvage, makes it a very difficult and expensive operation.

(*g*) The presence of size of this nature in and on the yarn makes the yarn less receptive to atmospheric changes. It is well known that moisture has a very definite effect on the strength of rayon. That is, the more moisture in rayon, the weaker it is. Thus, during the knitting operation if the yarn contains a set moisture content but is indifferent to the outside atmosphere, the length of the whole sole made on the knitting machine will be generally of the same length. The yarn takes a higher twist and gives greater strength. It also holds this twist without kinking. As an example, consider a 100 denier viscose yarn. Twenty turns are about the highest twist that can be put in yarn of this type so that it can be handled in the thread-making plant and knitted satisfactorily without kinking. It is believed that, with the size described herein, a twist of possibly 30 to 35 turns can be obtained, thus increasing the twist of the yarn. Due to this higher twist, the yarn will show more beauty of sheerness on a woman's leg, it will have greater strength, and it will have greater wearability.

(*h*) Scouring for removal of the size is a simple operation.

I claim:

1. A textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, consisting essentially of a solution in dilute aqueous ammonia of the ammonia-soluble reaction product of one to two parts of a hexahydric alcohol selected from the group consisting of mannitol and sorbitol, and two to one parts of an unsaturated dicarboxylic acid selected from the group consisting of maleic acid, maleic anhydride and fumaric acid, the composition containing about 0.1 to 10% of the reaction product.

2. The textile sizing composition of claim 1 to which is added a water-soluble curing agent therefor.

3. A textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, consisting essentially of a solution in dilute aqueous ammonia of the ammonia soluble reaction product of equal parts of sorbitol and maleic anhydride, the composition containing about 0.1 to 10% of the reaction product.

4. A textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, consisting essentially of a solution in dilute aqueous ammonia of the ammonia soluble reaction product of equal parts of sorbitol and fumaric acid, the composition containing about 0.1 to 10% of the reaction product.

5. A textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, consisting essentially of a solution in dilute aqueous ammonia of the ammonia soluble reaction product of equal parts of mannitol and maleic anhydride, the composition containing about 0.1 to 10% of the reaction product.

6. Process of making a textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, comprising dissolving in dilute aqueous ammonia the ammonia soluble reaction product of one to two parts of a hexahydric alcohol selected from the group consisting of mannitol and sorbitol, and two to one parts of an unsaturated dicarboxylic acid selected from the group consisting of maleic acid, maleic anhydride and fumaric acid in amount to form a composition containing about 0.1 to 10% of the reaction product.

7. Process of making a textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, comprising dissolving in dilute aqueous ammonia the

ammonia soluble reaction product of one to two parts of a hexahydric alcohol selected from the group consisting of mannitol and sorbitol, and two to one parts of an unsaturated dicarboxylic acid selected from the group consisting of maleic acid, maleic anhydride and fumaric acid, and adding a water-soluble curing agent to said solution in amount to form a composition containing about 0.1 to 10% of the reaction product.

8. Process of making a textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, comprising dissolving in dilute aqueous ammonia the ammonia soluble reaction product of equal parts of sorbitol and maleic anhydride in amount to form a composition containing about 0.1 to 10% of the reaction product.

9. Process of making a textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, comprising dissolving in dilute aqueous ammonia the ammonia soluble reaction product of equal parts of sorbitol and fumaric acid in amount to form a composition containing about 0.1 to 10% of the reaction product.

10. Process of making a textile yarn sizing composition of low viscosity and capable of drying on textile yarn to produce non-curling thereof and removable therefrom by scouring, comprising dissolving in dilute aqueous ammonia the ammonia soluble reaction product of equal parts of mannitol and maleic anhydride in amount to form a composition containing about 0.1 to 10% of the reaction product.

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