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TREATMENT OF TEXTILE MATERIALS

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This invention relates to the treatment of textile materials and more particularly to the sizing, finishing, dyeing and printing of textiles by a treatment wherein the laundry resistance, permanency of finish and other properties of textile materials are enhanced.

As is well known, synthetic resins are being used in increasing amounts in the textile industry in the sizing, finishing, dyeing and printing of textiles to improve the laundry resistance, dyeing qualities and other characteristics. For example, in the case of finishes, synthetic resins have been used to produce goods which do not become limp on repeated washing. In the dyeing and printing field they have been used to give clearer, sharper prints which in many cases do not require the regular aging treatment. In some cases it has been possible to use cheaper dyestuffs. Apparently the principal characteristic which the resins impart to the fabric or fiber is that of resistance against disintegration of the finish by water. The resins also seem to be of value in retaining dyes on the textile fiber or fabric, probably due to the fact that the resin imprisons the dye in a water resistant coating, and hence, prevents the access of water which would ordinarily tend to remove a small amount of dye when the fiber or fabric is washed. Among the disadvantages of the use of resins are their relatively high cost, fire hazards, odors, and high temperatures required in drying the fabrics.

The present invention has for one of its objects the provision of a new and improved method for the treatment of textile fibers which imparts greater permanency to films on fibers or fabrics without the necessity of employing a synthetic resin, although such a resin may be employed if desired.

Another object of the invention is to provide a method of imparting water resistance to films on textile fibers and fabrics by employing compositions wherein the major proportion of the compositions is relatively inexpensive materials, as, for example, amylaceous materials such as starches, dextrines or other starch degeneration products, including modified starches, and natural gums, as locust bean gum.

Still another object of the invention is to produce new and improved textile sizing and finishing compositions.

An additional object is to produce new and improved textile treating compositions which are especially useful in conjunction with the dyeing and printing of textiles.

Other objects will appear as the description proceeds.

In accomplishing these objects in accordance with this invention it has been found that new and improved results can be obtained in the treatment of textile fibers or fabrics by applying thereto a water dispersible, or hydrophilic, film forming binding agent, preferably an amylaceous substance, a natural gum or a polyvinyl alcohol in conjunction with a fixing agent, preferably potassium pyroantimonate. In accordance with the invention, increased permanency of the films on textile fabrics or fibers is obtained.

The treatment may be carried out in a number of different ways, of which the following may be mentioned:

The fixing agent, for example, potassium pyroantimonate may be mixed directly with the binding agent, as, for example, an amylaceous substance, a natural gum, or a polyvinyl alcohol, to form a dry blend which may be dispersed in water, or the two components may be mixed directly together in the water. The dispersion thus obtained may then be applied to a textile fiber or fabric in a sizing or finishing operation. However, it has been found that in some instances there is a tendency for the composition to gel or become rubbery before it is applied, particularly if the composition is allowed to stand any length of time. In making such compositions, moreover, if an amylaceous substance such as a starch or a modified starch is employed, it is often desirable to cook the starch in order to disperse it, and cooking the stareh in the presence of the fixing agent sometimes causes it to gel during cooking.

The concentration of starchy material influences the amount of jelling. Likewise the temperature and time of cooking influence the extent of the jelling. For this reason the cooking should preferably be carried out under controlled conditions. One preferred method of operation is to bring the temperature of the dispersion containing a starch, water and the fixing agent, for example, potassium pyroantimonate, to a temperature of about 170° F. to 175° F. and shut off the heat as soon as this temperature is reached. If the heating is prolonged at this temperature, or a higher temperature, the paste is more likely to gel. Jelling is more pronounced in the case of thick starches. For this reason it is sometimes desirable to employ a mixture of starches or starch degeneration products. Thus, an undegenerated starch may be mixed with a modified or degenerated starch.

In some instances a gel is obtained when the binding agent is cooked with the fixing agent in the manner above described, but these gels are for the most part "thixotropic," that is to say, the gels are broken by mechanical action such as mixing or stirring.

In certain instances the fixing agent has the advantage of producing an increased body or viscosity of the dispersion and thereby reduces the amount of binding agent necessary to obtain the desired result. For example, potassium pyro-

antimonate has this effect on amylaceous substances. Thus, the presence of the potassium pyroantimonate may make it possible to reduce the amount of amylaceous substance to, say, 5 to 8 ounces per gallon instead of 12 to 16 ounces per gallon if no potassium pyroantimonate were used. Added amounts of potassium pyroantimonate may always be added later.

In practicing the invention the binding agent such as an amylaceous material, a natural gum, or a polyvinyl alcohol, may be applied to the fabric or fiber in a separate phase from the fixing agent. Thus, the fixing agent may be applied to the textile fiber or fabric either before or after the binding agent. The reaction between the two components then takes place in situ, that is to say, either on or within the textile fiber or fabric, and hence, the difficulty often encountered due to premature jelling or setting up is avoided.

The invention is particularly valuable in finishing treatments for textile fabrics. The expresion "finishing treatments" is employed to describe treatments which are given to the fabric in the last or finishing stage of manufacture. These treatments may be applied to either undyed or dyed materials.

The invention may also be applied to the sizing of textile fibers, for example, by warp sizing or by skein sizing, particularly where it is desired to produce a sized material which will resist the mechanical action of the loom and from which it is not necessary to remove the sizing after weaving and before dyeing. The term "sizing" as used in the trade normally refers to the treatment of the yarn or fiber prior to weaving.

The invention may also be employed for weighting textile materials to replace losses in weight incurred through soap scouring, kier boiling, mercerizing and bleaching prior to dyeing or printing. The weighting operation is normally applied to the cloth.

The practice of the invention when applied to previously dyed materials has substantial advantages in that the reaction product formed by the reaction between the fixing agent and the binding agent tends to fix the dye and produce a fabric or cloth in which the color is faster than would otherwise be the case.

The invention is of further importance particularly in the printing of dyes on textile fabrics because in the printing operation special problems are involved and it is often difficult to obtain prints of satisfactory brilliance, clarity and fastness except with the most expensive of dyes. The present invention makes possible the employment of cheaper dyes and at the same time is relatively less expensive than methods heretofore proposed to accomplish this object.

The invention will be further illustrated but is not limited by the following examples in which the quantities are stated in parts by weight unless otherwise indicated:

Example I

A finishing composition was prepared by cooking 8 ounces of modified starch with .04 ounce of potassium pyroantimonate in one gallon of water to a temperature of 170° F. to 175° F. and shutting off the heat as soon as this temperature was reached. The resultant finishing composition was then applied directly to textile materials, including cotton cloth and other textile fabrics at temperatures within the range varying from about room temperature (75° F.) to about 175° F. The finishing treatment was applied to the fabric by immersion, dipping, coating and other similar methods. The fabric was then dried at a temperature from about 240° F. to 300° F. to a moisture content of preferably 2% or less. An excellent permanent finish was obtained.

Example II

A finishing composition was prepared by cooking 16 ounces of a modified starch known as thin boiling #40 with .08 ounce of potassium pyroantimonate in a gallon of water to a temperature of 170° F. to 175° F. and then shutting off the heat.

Cotton cloth and other textile fabrics were finished with this composition by giving them a finishing treatment at temperatures from about room temperature to 175° F. by immersion, dipping and other known methods. The fabric was then dried to a moisture content of preferably 2% or less. An excellent finish was obtained.

Example III

The procedure was carried out as in Examples I and II except that the fabric, after being treated with the finishing composition and before drying, was passed through a bath consisting of an aqueous 0.25% solution of potassium pyroantimonate. The fabric was then dried to a moisture content of preferably about 2% or less. Excellent results with regard to the permanency of the finish were obtained.

Example IV

The procedure was carried out as in Examples I and II except that the fabric, after being finished and dried, was passed through an aqueous bath containing about 0.25% of potassium pyroantimonate and was then redried to a moisture content of preferably 2% or less. Again excellent results with regard to the permanency of the finish were obtained.

Example V

A denim yarn was warp sized with corn starch and then woven into cloth. After weaving the cloth was passed directly through a 4% aqueous solution of potassium pyroantimonate and dried at a temperature within the range of 240° F. to 300° F. to a moisture content of preferably 2% or less, whereby the size was fixed on the goods. The material was then finished with a finishing composition made by cooking 8 ounces of a modified starch with .32 ounce (4% based on the weight of the starch) of potassium pyroantimonate and .16 ounce (2% based on the weight of the starch) of antimony trifluoride to a temperature of about 190° F. The finishing treatment was carried out at a temperature of about 190° F. and the material was then dried at a temperature within the range of about 240° F. to 300° F. Thereafter the material was after-treated with a 4% solution of potassium pyroantimonate in water and again dried to a moisture content of preferably 2% or less.

After washing for one hour at the boil with 0.5% soap and 0.2% soda ash, the goods lost 30% of the size as compared to about 90% for the untreated material.

Example VI

A size composition was made by cooking 180 lbs. of tapioca flour and 8 lbs. of tallow in 250 gallons of water. This composition was then applied to a cotton material in the first box of

a slasher at a temperature of about 200° F. The warps were given a treatment with potassium pyroantimonate in the second box of the slasher. The treating composition employed in the second box consisted of 5 lbs. of potassium pyroantimonate dissolved in 30 gallons of water and the treatment was carried out at a temperature of 200° F. The goods were then finished with a composition made from 25 lbs. of modified starch, 2 lbs. of potassium pyroantimonate, .75 lb. of sodium silico fluoride and 8½ lbs. of Twitchell oil dispersed in 75 gallons of water. The finishing treatment was carried out at a temperature of 160° F., although lower temperatures may be employed. The relative permanency of the finish was evidenced by the fact that denims processed in this manner lost only 41.8% of their size on washing for one hour at the boil with 0.5% soap and 0.2% soda ash, while the same denims untreated lost 82.2% of their size. It may be observed that this is relatively stringent washing treatment as compared with ordinary household laundry practice.

Example VII

A piece of 80/80 cotton bleach print cloth was finished with a composition having the following formula: 12 ounces of modified starch, .6 ounce of ammonium oxalate (5% based on the weight of the starch), .36 ounce of potassium pyroantimonate (3% based on the weight of the starch). After finishing, the material was dried to a moisture content of preferably 2% or less. The material was then tested by washing it in three separate 15 minute washings at the boil with 0.5% soap and 0.2 soda ash. The results obtained were as follows:

	Per cent
Size in cloth after finish	6.83
Size left after one wash	5.80
Size left after second wash	5.64
Size left after third wash	5.62

Where the finishing composition did not contain the potassium pyroantimonate the loss of size was substantially complete.

Example VIII

A finishing composition was prepared by cooking 16 ounces of a modified starch, 0.8 ounce of sodium silico fluoride and 0.32 ounce of potassium pyroantimonate in one gallon of water at a temperature of 200° F. for 15 minutes. This composition was then employed as a finishing composition for finishing 80/80 cotton print cloth at a temperature of 160° F. The finished cloth was given three 15 minute washes at the boil with 0.5% soap and 0.2% soda ash. The results were as follows:

	Per cent
Size put into cloth	8.90
Size left after two washings	7.50
Size left after three washings	7.44

Example IX

The following tests illustrate the relative permanency obtained by first starching a patch of cotton cloth in the regular manner and then after-treating it with a solution of potassium pyroantimonate:

(*a*) The patch was sized with 1 lb. of a modified starch per gallon and while still wet was padded through a 1% aqueous solution of potassium pyroantimonate. The material was dried at a temperature within the range of about 240° F. to 300° F. to a moisture content of preferably 2% or less. On being washed for 15 minutes it lost 3% of the size.

(*b*) The method of treatment was the same as in (*a*) except that the sizing composition was prepared by cooking 8 ounces of thin boiling #40 corn starch with 0.5% potassium pyroantimonate and 0.25% antimony trifluoride based on the weight of the starch in one gallon of water for 30 minutes at 200° F. After two 1 hour washes the material showed very little loss of size.

(*c*) A finishing composition was prepared by cooking 16 ounces of thin boiling corn starch #40 with 0.5% potassium pyroantimonate based on the weight of the starch in one gallon of water at a temperature of 200° F. for 30 minutes and was applied to the cloth by immersion. While the cloth was still wet it was padded through 0.25% aqueous solution of potassium pyroantimonate and dried to a moisture content below about 2% at a temperature from about 240° F. to 300° F. It was then finished with a finishing composition made by cooking 8 ounces of the thin boiling starch with 0.5% of potassium pyroantimonate based on the weight of the starch in one gallon of water at 200° F. for 30 minutes. The finished cloth lost only 1% of its size after washing for 1 hour.

(*d*) The same procedure was employed as in (*c*) except that the sizing composition consisted of 12 ounces of Superior tapioca cooked in a gallon of water for 1 hour at 200° F. The sized material, while wet, was padded with a 0.25% aqueous solution of potassium pyroantimonate, dried to preferably less than 2% moisture, and finished with the same type of finishing composition described in (*c*). After one hour's washing, the fabric exhibited substantially no loss of size.

When the sizing composition was made alkaline to a pH of about 10, it was observed that there was a much greater final loss. In practically all instances the final loss was at least doubled with the higher alkalinity.

Example X

Antimonic oxide (Sb_2O_5) may be substituted for potassium pyroantimonate either wholly or in part in the preceding examples. However, because of its greater insolubility, the use of Sb_2O_5 is less desirable, particularly in the after-treatment.

Example XI

A precipitate was made by mixing together 10 parts of potassium pyroantimonate and 3 parts of antimony trifluoride in the presence of water at room temperature and this precipitate was employed in whole or in part in place of potassium pyroantimonate in the procedures described in the previous examples with good results.

Example XII

A precipitate was made by mixing 10 parts potassium pyroantimonate with 3 parts of antimony lactate in the presence of water at room temperature and this precipitate was employed in whole or in part to replace potassium pyroantimonate in the procedures described in the previous examples with good results.

Example XIII

Antimony metal was dissolved by an excess of nitric acid at room temperature and the resultant product was then employed in whole or in part to replace potassium pyroantimonate in accordance with the preceding examples with good results.

Example XIV

The following compositions were padded on bleached 80/80 cotton print cloth: 12 ounces of Superior tapioca cooked with a gallon of water for 1 hour at 200° F. was applied to the cloth which was then treated while still wet with 0.25% aqueous solution of potassium pyroantimonate at room temperature. The cloth was dried to a moisture content of preferably 2% or less, at a temperature from about 240° F. to 300° F. and was then treated with a finishing composition made by cooking 8 ounces of thin boiling #40 corn starch in one gallon of water with 0.5% potassium pyroantimonate based on the weight of the starch at a temperature of 200° F. for 30 minutes. The cloth was then redried, preferably to less than 2% moisture content at about 300° F. and tested by washing for 1½ hours in a washing machine at the boil with 0.5% soap and 0.25% soda ash. The amount of loss was only about 12%.

In practicing the invention it is preferable to employ a starch or a starch degeneration product as the binding agent. By a starch degeneration product is meant a derivative of starch such as may be obtained by the various processes of making thin boiling and so-called modified starches and dextrines. In general, especially good results have been obtained with specially modified starches. If desired, mixtures of undegenerated and degenerated starches may be used. Starch degeneration products of a predominantly starchy nature are preferable to the more highly dextrinized starches, because after a certain degree of disorganization of the starch it usually requires a much larger percentage of the fixing agent, e. g., a water soluble pyroantimonate, to bring about fixation, water insolubilization, or a hydrophobic state of the starch. Among the suitable starchy materials may be mentioned wheat, rye, barley, oat, rice, corn and potato starches, sago and cassava flours and colloidal modifications thereof, and other starches and flours and derivatives thereof. Among the natural gums which may be employed may be mentioned particularly locust bean gum, gum tragacanth and other water dispersible, film forming natural gums. Of the water dispersible synthetic film forming substances, special mention may be made of polyvinyl alcohols.

The fixing agents which have been found to be preferable for the purpose of the present invention are antimony compounds capable of converting water dispersible, polyhydroxylated, film forming substances from a hydrophilic to a hydrophobic state. The antimony compounds which have been found to be especially suitable are those in which antimony is present in its pentavalent state. Certain antimony compounds are of less value for the purpose of the present invention, as, for example, antimonous oxide (Sb_2O_3) and sodium antimonate. These two compounds are better when freshly precipitated. Tartar emetic has some effect when employed under alkaline conditions. Larger amounts of the trivalent antimony compounds are normally required.

Of the fixing agents, potassium pyroantimonate is of principal importance. It occurs in two modifications; namely, the acid salt ($K_2H_2Sb_2O_7$) and the neutral salt ($K_4Sb_2O_7$). Up to the present time the material which is available commercially is what is called "re-agent material" which is largely acid salt, although it contains some neutral salt. Antimonic oxide (Sb_2O_5) may also be employed as the fixing agent. A product obtained by dissolving antimony metal in excess concentrated nitric acid which was apparently the acid H_3SbO_4 also acted as a fixing agent. It was further observed that when potassium pyroantimonate and antimony tri-fluoride were mixed together or when potassium pyroantimonate and antimony lactate were mixed together, the resultant precipitate could be employed as a fixing agent for the water soluble film forming component of the composition.

In all cases the binding agents found to be suitable for the purpose of the invention have been polyhydroxylated compounds which form colloidal dispersions in water and are capable of forming continuous films. For the most part these materials are carbohydrates or polysaccharides hydrolyzable by acids to simpler molecular compounds.

In practicing the invention it has been found that as previously indicated the addition of an auxiliary agent, particularly an agent capable of thinning starches, that is, of decreasing their viscosity in aqueous dispersions, may be advantageous in order to prevent jelling or too rapid reaction by the fixing agent on the starch. The same considerations apply to other water dispersible film forming substances which may be employed in accordance with the invention. The addition of the auxiliary agents is especially desirable in finishing compositions. Generally speaking, the auxiliary agent is preferably any compound or salt having a thinning action on the binding agent which has a pH or develops a pH within the range of about 2.5 to about 10.0. Among the salts or other compounds which may be employed are, for example, sodium silico fluoride, antimony trifluoride, ammonium oxalate, sodium perborate, sodium persulphate, citric acid, lactic acid and acetic acid. Enzymes may also be added to produce a thinning action. Some of these salts such as, for example, antimony trifluoride, have some fixing value of their own when used as auxiliary agents, and it is, therefore, more advantageous to use these as thinning agents. Others, such as ammonium oxalate, are illustrative of salts which become acidic on heating. Other salts, such as sodium perborate and sodium persulphate, derive their thinning action from their oxidizing properties. The free acids, such as citric acid, lactic acid and acetic acid are capable of thinning starches without breaking them down too much. If the pH is too low, the starch may be broken down so much as to require a relatively large amount of the fixing agent. Likewise, the strongly acidic condition may adversely affect the cloth on which the mix is being applied. If the pH is too high, the desired fixing action either does not occur or is greatly reduced, particularly as to the pentavalent antimony compounds. The latter are more reactive on the acid side while some of the trivalent antimony compounds, such as tartar emetic, seem to have only a relatively small amount of fixing action as compared with the pentavalent antimony compounds and this only on the alkaline side.

The proportions and concentrations of the various materials may vary rather widely, depending upon the type of treatment and upon the type of material being treated as well as upon other related factors. In sizing and finishing compositions of the invention the weight ratio of solids to water is preferably within the range of 1% to 15%.

The amount of the composition retained by the material treated will depend largely upon the method of treatment. Good results in sizing and finishing may be obtained if the amount of sizing or finishing composition on the material is within the range of about 1% to about 15% by weight of the material. Ordinarily, the treating bath may be either hot or cold.

The amount of fixing agent, as, for example, potassium pyroantimonate, is preferably within the range of about 0.25% to about 25%, based upon the weight of the binder or binding agent. Thus, with locust bean gum good results can be obtained with say 1% potassium pyroantimonate on the weight of the gum while with a dextrine it may be desirable to employ 25%. If the potassium pyroantimonate is applied in a separate phase in solution form, the amount thereof is preferably within the range of about 0.01% to about 2%, based upon the total weight of the solution.

In practicing the invention it is very important to thoroughly dry the fabric or cloth which has been impregnated or treated with the fixing agent. It has been found that the fastness of the reaction product formed by reaction between the binding agent and the fixing agent is more nearly perfect after complete drying of the cloth or impregnated material. As an example, when 10% moisture is left in a piece of fabric that has been starched with a composition containing a starchy material and potassium pyroantimonate, there may be a loss on the first wash test of about 75% of the starch added to the fabric. With 5% moisture left in the fabric, the loss may be around 40% to 50%. Below 2% moisture left in the fabric and down as low as 1%, the loss may be reduced to little or nothing. In connection with the drying of textile fabrics and fibers containing a binding agent and a fixing agent of the character herein described, as, for example, amylaceous substances and locust bean gum solutions containing potassium pyroantimonate, it is preferable to dry the fabric at a temperature of 180° F. or higher prior to the time that the moisture contained in the treating composition is lost or reduced materially. Otherwise, the fixation, permanency or insolubility of the finish is apparently lessened.

It will be recognized that a wide variety of auxiliary agents may be added to the compositions herein described. Among such addition agents may be mentioned fuller's earth, bentonite, and related substances. The compositions may also contain natural or synthetic resins, as, for example, urea formaldehyde resins, vinyl resins, methyl methacrylate resins and other suitable types of resins such as are normally employed in the treatment of textile materials. The proportions of these materials may also vary depending upon the type of treatment and the material treated. The use of fulling or softening agents in the treating composition such as glycerine, sulfonated oils, higher alcohol sulfates (e. g. dodecyl sulfate or cetyl sulfate) is not always desirable because such agents sometimes decrease the amount of fixation of the binding agent on the cloth or fabric, but they may be applied later.

In preparing the various compositions, a dry blend of the binding agent and fixing agent may be prepared. This blend is marketed in dry or powdered form and requires only the addition of water and mixing, preferably with heating, to produce the composition in dispersed form. Auxiliary materials such as those previously mentioned may also be included in the dry base.

The type of material which may be treated in accordance with the invention is subject to variation but ordinarily any textile material, and particularly woven and knit materials, may be treated. Among the materials which may be given a finishing treatment as herein described, are cloth, fabrics or flexible sheet materials made from cotton, linen, wool, asbestos, glass, cellulose esters and ethers and regenerated cellulose, and other synthetic fibres. Paper may also be sized or given a finish in accordance with the invention.

The invention may also be practiced by incorporating compositions of the character herein described containing a binding agent, for example, starch, and a fixing agent, for example, potassium pyroantimonate, into laundry compositions in order to give the laundered product a better finish. The composition may be cooked and used in the same way as starch is being used for laundry purposes now. The heat from the laundering operations such as ironing assists the reaction between the binding agent and the fixing agent and produces a more permanent finish.

The generic aspects of the present invention are claimed in our copending application Serial No. 430,412, filed February 11, 1942, which matured into United States Patent No. 2,343,898 on March 14, 1944.

We claim:

1. A textile sizing and finishing composition comprising a major proportion of a water dispersible film forming amylaceous substance, a minor proportion of a potassium pyroantimonate and a substantial quantity of antimony trifluoride.

2. A textile sizing and finishing composition comprising a major proportion of a starchy material, a minor proportion of potassium pyroantimonate and a minor proportion of sodium silico fluoride.

3. A textile sizing and finishing composition comprising a water dispersible film forming carbohydrate material of the type hydrolyzable by acids to simpler molecular compounds, a fixing agent comprising an antimony compound reactive with said carbohydrate material to render said carbohydrate material water insoluble upon dehydration and a fluoride selected from the group consisting of antimony tri-fluoride and sodium silico fluoride.

4. The method of imparting a substantially permanent finish to a textile material which comprises applying to the textile material in the presence of water a water dispersible film forming binder and a fixing agent comprising an antimony compound reactive with said binder to render said binder water insoluble upon dehydration, together with a fluoride selected from the group consisting of antimony tri-fluoride and sodium silico fluoride, and then drying said material to a moisture content less than about 2%.

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