Patented Sept. 6, 1949 2,480,930

UNITED STATES PATENT OFFICE

2,480,930

PROCESS FOR MAKING SILVER PROTECTIVE CLOTH

Elwood C. Jackson and Tully H. Babb, Lyman, S. C., assignors to Pacific Mills, a corporation of Massachusetts

No Drawing. Application February 11, 1948, Serial No. 7,704

7 Claims. (Cl. 21—2.5)

1

This invention relates to cloth for covering silverware to prevent tarnishing and more particularly to an improved process of treatment of the cloth to impart to it the protective properties.

In the prior processes of this type the cloth has been treated with various silver compounds which have an affinity for and absorb the tarnishing gases and thereby protect the silverware wrapped in the treated cloth. One of the best of these prior processes is disclosed in Barnard Patent No. 2,003,333 issued June 4, 1935. In the process of that patent the silver protective cloth is prepared by a two-bath or two-step procedure. In the first bath or treating step the cloth is impregnated with aqueous silver nitrate solution and the excess solution squeezed out. In the second bath or step the cloth is impregnated with an aqueous solution of sodium ferrocyanide, and these two chemicals are then caused to react, in situ, on the cloth, so as to produce silver ferrocyanide which is the active chemical compound for preventing tarnishing. In this patented process locust bean gum is used as a protective colloid or dispersing agent for the sodium ferrocyanide solution.

In addition to the disadvantage of the two-bath or two-step feature required by this patented process, it is characterized by a tendency to produce dark streaks in the treated cloth. Also, it is subject to loss of silver salts caused by the silver dissolving out in the second bath and precipitating in the solution instead of on the fabric.

The process of the present invention constitutes a substantial improvement over the above prior process in that it requires only a one-bath or one-step procedure, substantially eliminates the loss of silver salts, and does not substantially discolor or streak the cloth. In accordance with this new process, the silver ferrocyanide is not formed, in situ, on the cloth but instead is produced prior to application to the cloth.

One of the important features of this new process is that the silver ferrocyanide is precipitated in extremely fine particle size and this finely divided precipitate is applied directly to the cloth, and adheres strongly thereto. There is no opportunity for the silver salts to be dissolved out in the second bath, in contrast to the above Barnard process, because the salts are precipitated preliminarily in the solution rather than on the fabric and the fabric is treated only once.

A commercially advantageous procedure for precipitating the silver ferrocyanide is to carry out the precipitation in an aqueous medium and use in this medium a dilute solution of locust bean gum that assures the formation of a very finely

2

divided precipitate, which is stable as to particle size. A typical but nonlimiting example of the constituents and procedure used for preparing this finely divided silver ferrocyanide precipitate is as follows:

A. Cooked and cooled 6 lbs. of locust bean gum per 120 gal. water.

B. In 60 gallons of solution A dissolved 59 lbs. of silver nitrate.

C. In 60 gallons of solution A dissolved 46 lbs. of sodium ferrocyanide.

In preparing the precipitated silver ferrocyanide from the above constituents it was found that a critical procedure was involved; that is, the solution produced in "C" above must be added to the solution produced in "B" above to obtain the fine particle precipitate. When the reverse order of mixing these two solutions was used, that is, when solution "B" was added to solution "C", undesirable large particles were obtained in the precipitate. Accordingly, in the preferred process, solution "B" was first poured into a wooden tub and agitated vigorously by means of a propellor-type mixer. Next, solution "C" was slowly poured into the tub. At first the mixture became very thick but toward the end of the addition it thinned out. After all of solution "C" had been added to solution "B" the final mixture was further agitated by means of an homogenizer, or other high speed mixer, or alternatively the mixture was passed several times through a colloid mill. After the completion of this homogenizing treatment the final mixture had a consistency of and looked like a thin cream. This cream was of a uniform finely dispersed nature and free of large particles. This final mixture contained the reaction products of silver ferrocyanide and sodium nitrate.

Although it is not considered essential, we may use in the above composition a small amount of alkali, e. g. sodium carbonate, to keep the solution on the alkaline side and thereby prevent the possibility of free hydrogen cyanide gas being liberated in the after-use of the treated cloth. The amount of alkali, such as sodium carbonate, which may be added may be the theoretical amount (or slight excess) needed to react with any such liberated gas to convert it to the sodium salt. The procedure for preparing the composition utilizing the alkali is substantially the same as described above but the amounts of the respective constituents vary slightly because of the addition of the alkali, as shown by the following illustration:

A. Cooked and cooled 5–6 lbs. locust bean gum per 120 gal. water.

B. In 49 gal. of solution A dissolved 59 lbs. of

silver nitrate. Added 4 gal. of ammonia (25%) to this.

C. In 60 gal. of solution A dissolved 43–45 lbs. of sodium ferrocyanide.

D. In 7 gal. of water disssolved 18½ lbs. of sodium carbonate.

Here again it was important that the solutions be mixed in the order given to obtain the fine particle precipitate of silver ferrocyanide.

The ammonia used in the modified composition described just about serves the purpose of preventing any increase in particle size of the preciptate caused by the presence of the sodium carbonate. It was found that sodium carbonate produced some increase in the particle size of the precipitate and caused the precipitate to settle out too quickly. By adding ammonia to the silver nitrate before precipitation it was found that this settling-out tendency was eliminated entirely and the resulting suspension would stand for several days with only very slight settling. This function of the ammonia in producing a better dispersion appears to be quite unique, and although it causes some small amount of the silver to precipitate as brownish silver oxide when the sodium ferrocyanide was added, this brown color disappeared and the white silver ferrocyanide was formed. In the drying of the cloth on which this composition is used the ammonia is liberated by the heat.

For application of either of the above compositions to cloth to impart to it silver protective properties, any suitable type of textile treating equipment which is commonly used for applying treating solutions to cloth may be employed. For example, the composition may be padded onto the cloth in a conventional pad using either one or two dips of the cloth in the composition and either single or double squeezing operations on the padded cloth. After the composition is padded on the cloth the treated cloth is passed to a suitable type of drying equipment such as a conventional tenter frame equipped with hot air drying where the cloth is air dried while being stretched to the desired width.

Cloth treated in this manner has excellent silver protective properties and may be used for silver-wrap and like purposes. The finely precipitated silver ferrocyanide which remains in this treated cloth will absorb or take up tarnishing gases to which the cloth is subjected, and in that way these gases are prevented from penetrating the cloth and tarnishing the silver wrapped within the cloth. When using the above typical formulations and assuming approximately 90% pick-up of the treating solution on the cloth in the padding operation, the amount of silver introduced into the cloth is approximately 3.4% based on the weight of the cloth. While these amounts are representative of good commercial practice it is to be understood that they can be lowered or raised as desired.

The amount of sodium ferrocyanide specified above is slightly greater than the theoretical amount, i. e. 42 pounds, required to react with the silver nitrate. This excess is used for the purpose of assuring complete reaction but the amount may be varied, as desired, from the theoretical amount to any suitable excess. An excess of some proportion is usually desirable to make sure that all the silver is precipitated as silver ferrocyanide and thereby eliminate any opportunity of black streaks developing in the cloth upon drying due to any unreacted silver nitrate.

Although we have found the above mentioned locust bean gum to be commercially advantageous and we have obtained very good results with this gum, it is to be understood that this invention contemplates the use of other suitable gums, such as for example gum karaya, gum tragacanth and gum arabic, which will function satisfactorily. The locust bean gum serves initially as a precipitating medium for the silver nitrate and sodium ferrocyanide reactants and assures the formation of an extremely fine precipitate when these two chemicals are reacted in the aqueous locust bean gum solution. This gum also functions to some extent to bind the reaction product, i. e., silver ferrocyanide, in the fabric; although the very fine particles of this product are probably partially held by entrapping action of the fibers.

Various modifications and changes may be made in the above-described products and procedures for carrying out the process of this invention so long as the characteristic extremely fine precipitate of silver ferrocyanide is produced and the composition does not have any discoloring or other adverse effects on the cloth.

What is claimed is:

1. In a process of preparing silver protective cloth in which silver nitrate is reacted with sodium ferrocyanide to produce silver ferrocyanide, the improvement of carrying out this reaction in aqueous solution preliminarily to application of the composition to the cloth so as to form the silver ferrocyanide beforehand and thereby enable deposit of the silver ferrocyanide in the cloth in a one-bath procedure and without staining or discoloring the cloth.

2. In a process of preparing silver protective cloth in which silver nitrate is reacted with sodium ferrocyanide to produce silver ferrocyanide, the improvement of dissolving the silver nitrate in an aqueous solution of locust bean gum, separately dissolving the sodium ferrocyanide in an aqueous solution of locust bean gum, mixing the two separately prepared solutions to effect reaction therebetween with the production of silver ferrocyanide in finely dispersed particle-size form, and applying this fine precipitate of silver ferrocyanide to the cloth to impart silver protective properties thereto.

3. In the production of silver ferrocyanide composition for treatment of cloth to impart silver protective properties thereto, the improvement of precipitating the silver ferrocyanide in an extremely fine particle size which is especially adapted for uniform application to the cloth and without substantial discoloration of the cloth, said precipitation being carried out by reacting an aqueous solution of silver nitrate and a separately prepared aqueous solution of sodium ferrocyanide in the presence of locust bean gum which effects formation of minimum size particles in the precipitated silver ferrocyanide.

4. The process of preparing a composition suitable for treatment of cloth to impart silver protective properties thereto comprising preparing separate aqueous solutions of silver nitrate and sodium ferrocyanide each dissolved in locust bean gum solution, and reacting said solutions together so as to produce an extremely finely divided precipitate of silver ferrocyanide.

5. The process of preparing a composition suitable for treatment of cloth to impart silver protective properties thereto comprising preparing an aqueous cooked solution of locust bean gum, adding to an amount of this solution an amount

of silver nitrate, adding to another substantially equal amount of the locust bean gum solution an amount of sodium ferrocyanide, adding to this silver nitrate solution the sodium ferrocyanide solution and producing by this order of addition a finely divided precipitate of silver ferrocyanide which is suitable for application to cloth by padding.

6. The process of preparing a composition for treating cloth to impart silver protective properties thereto comprising preparing first an aqueous cooked solution of locust bean gum, dissolving in a portion of this aqueous solution an amount of silver nitrate and adding ammonia to this solution, then dissolving in another portion of said aqueous cooked solution of locust bean gum a suitable amount of sodium ferrocyanide, next slowly adding to the locust bean gum solution of silver nitrate and ammonia the said solution of sodium ferrocyanide dissolved in locust bean gum, agitating the resulting mixture and

finally adding thereto an amount of sodium carbonate sufficient to neutralize any free hydrogen cyanide which might be liberated from the composition or in its after-use on cloth.

7. A process of preparing a composition suitable for application to cloth to impart silver protective properties thereto comprising dissolving silver nitrate in an aqueous solution of locust bean gum, dissolving in another portion of aqueous solution of locust bean gum, sodium ferrocyanide in sufficient amount to react completely with the silver nitrate, mixing these two solutions so as to precipitate in a finely divided form silver ferrocyanide, and subjecting this mixture to an homogenizing treatment which effects a fine uniform dispersion of all of the constituents.

ELWOOD C. JACKSON.
TULLY H. BABB.

No references cited.