Patented Sept. 27, 1949 2,483,008

UNITED STATES PATENT OFFICE

2,483,008

PROOFING PROTEINACEOUS FIBERS AGAINST BIOLOGICAL ATTACK

Eric Berkeley Higgins, Welwyn, England, assignor to Tewin Industries, Inc., New York, N. Y.

No Drawing. Application December 21, 1944, Serial No. 569,279. In Great Britain January 29, 1944

9 Claims. (Cl. 8—128)

1

It is known that pentachlorphenol in quite low concentrations has to a very high degree the property of preventing the development of and of killing moulds and fungi. The lethal and inhibitory actions are exerted respectively by the substance in concentrations of the order of 0.2 per cent and 0.02 per cent while in higher concentrations it can act as an insecticide in respect of biting insects and has an especially good effect, if not a unique effect, in the protection of wood against the attack of termites and can be used for protecting both raw and worked timber. As a consequence, pentachlorphenol both in the form of the free phenol, separated from non-aqueous solution, in particular as a solution in crude petroleum, and in the form of its sodium salt separated from aqueous solution, has been used extensively for the preservation of timber.

Attempts to obtain similar effects with textile materials, however, have had only poor success owing to the difference in the conditions of use of the treated materials. In particular, the extreme tendency of pentachlorphenol to crystallise and its tendency to facile sublimation which is probably ultimately due to the same phenomena, have acted against its use in the textile field despite its extremely low vapour pressure at ordinary atmospheric temperatures, which is of the order of 0.00017 mm. of mercury at 20° C. Furthermore, the problem is not solved by the obvious alternative of employing its salts, for example, the alkali salts instead of the free phenol, because these salts are excessively soluble in water and would therefore not be permanent, there being no reservoir of material in the case of textiles as is furnished by the mere bulk of timber; again, there is not only the possibility but the extreme probability of injury to the user, which is quite fatal for textile use, the reason being that solutions of the alkali salts of pentachlorphenol have a caustic action on the skin. The free phenol is practically insoluble in water, being soluble only to the extent of 0.0001 per cent at 15° C.

Its copper and lead salts are stable and soluble in water only to such a minute extent as may be regarded negligible for the purposes in question, and in view of the increased toxicity of the cation, would seem to be advantageous from the toxic point of view. Indeed in particular cases, they might be employed but the copper salt has an intense chocolate colour and the lead salt colours easily with hydrogen sulphide due to the formation of lead sulphide. This prevents their use except in cases where colour is of no importance which in the textile trade is practically never the case. Other common metals either do not yield stable salts, or they yield salts which are highly coloured or both unstable and highly coloured.

2

There are two practical effects of the two points already mentioned in respect of the free pentachlorphenol. The first is that any deposition of the phenol upon cloth, for example, by impregnating the cloth with the soluble sodium salt and subsequently precipitating the free phenol in situ by means of an acid bath is not permanent; on storage, the phenol, though colliodal and adherent when formed, crystallises and the fine needle crystals have no attachment to the fibre and come away in the form of dust, thus not only depriving the cloth of its protection but attacking the nose and throat of the wearer, and when worn, causing painful skin rashes which, though they heal by first intention and have no enduring dermititic effect, are an effectual bar to the use of the expedient. The second is the ready sublimation of the phenol which is specially marked at high temperatures, such as 60° C. up to 105° C., which are used in drying cloth and highly marked in the presence of steam, and may in fact lead to the total loss of the phenol during the normal drying of the treated cloth on "tins."

The present invention is based on the important discovery that in solutions having a pH value of between 7 and 4, pentachlorphenol can form loose addition compounds with proteins—possibly of the nature of chloramines or chloryl compounds involving the nitrogen group of the protein. The complex is formed in general with any protein most readily and is most stable at the so-called iso-electric point of the protein. Thus, the present invention consists in the production of these complexes and the application of pentachlorphenol to the textile fibres by means of them. Where the textile fabric is itself of a protein nature, as is the case, for example, with wool and silk, it is not necessary to supply an external protein and the new reaction can be produced direct on the fabric provided always that the pentachlorphenol be presented for reaction in a sufficiently finely-divided state. Such complexes formed in accordance with the invention show no tendency to crystallise, remain colloidal, and when formed separately and attached to the fibre, are firmly adherent and the sublimation of pentachlorphenol from them does not take place at temperatures below 120° C. even in the presence of steam. They are colourless and odourless and relatively insoluble in water.

The formation of the compounds by reaction with the protein of the fibre itself may be accomplished, for example, by grinding the pentachlorphenol to micron size, but it is most readily accomplished by precipitating the free phenol from its sodium salt by means of a large excess of volatile acid in the presence of a protective colloid. The latter is not necesarily of a protein nature or origin, although a highly demerised pro-

tein such as lysalbic acid is very suitable for the purpose, and so is the water-soluble product obtained by profound alkaline degration of wool, hair, or silk waste. In such conditions, a dispersion of the free phenol of micron size is easily obtained without employing mechanical grinding.

It is only necessary to work the goods in such a suspension and to dry the impregnated goods to expel the excess of volatile acid and thus cause the complex or addition compound to be formed. However, improved effects may be obtained by adding salts of polyvalent metals to the impregnating bath, such as aluminium formate; no doubt the anionic charging of the suspended particles ensures a more intimate initial contact between the fibres and the particles. This mode of carrying out the invention is particularly of advantage in the wool industry, in which resistance to moth attack is of special importance since it may be conveniently applied at various stages of the usual woollen treatment. Thus, the suspension may be added to the mill during acid milling or to the dolly during the finishing operation or to the dye bath when an acid dye bath is used, as is almost always the case.

The complex compound finally formed is extremely stable and the objectionable volatility of the toxic product is completely suppressed, and in fact no measurable loss of that product occurs, if a woollen cloth so treated is exposed to a current of dry or wet air at 100° C. for 24 hours.

It is obvious that the process can be combined with the application of water-repellent protein emulsions, that is to say, emulsions of wax or other water-repellent bodies in protein solutions in the presence of aluminium salts, such as described in British Patent Specification No. 380,076, can be substituted for or added to the acid baths or additions used in the methods already described provided only that the acid or acid salts in them are volatile, preferably being formic acid or formates. It is thus possible by one treatment to confer water-repellent properties simultaneously with the biological protection which is an advantageous procedure since the protection afforded by the pentachlorphenol is much enhanced if the textile is also rendered less likely to be wetted.

It has been found that an amount of the complex corresponding to 0.2 per cent of pentachlorphenol on the weight of the cloth is sufficient to protect any textile from moth in storage or transit; that a concentration equivalent to 0.5 per cent of pentachlorphenol renders the cloth rot-proof even when exposed to the greatest variations in atmospheric conditions, and also renders woollens proof against moth; while a treatment by an amount of the material equivalent to 1 per cent of pentachlorphenol on the weight of the textile renders it immune to insect attack, in particular to the attack of termites.

In order that the invention may be clearly understood and readily carried into effect, some examples of methods of carrying out the invention will now be described in greater detail.

Example 1

10 lbs. of skin glue or gelatine are allowed to swell in 64 lbs. of water and then brought into solution by heating to 80 to 90° C. with continuous stirring. Then, 22½ lbs. of neutral sodium pentachlorphenolate is added with thorough stirring part at a time, the stirring being effected until a homogeneous mass is formed. The glue employed is merely a convenient protective colloid for the dispersion, but it is not demerised and is not in sufficient quantity to deal with the pentachlorphenol present, and it is removed later during the final water wash while, moreover, the complex between the pentachlorphenol and the protein is not formed to any extent until the mass is dried and the excess of acid thus expelled. To the homogeneous mass 6 lbs. of 85 per cent formic acid is added and the mass is cooled with continuous stirring until the increase in viscosity indicates the approach of gelation. The stirring is then stopped and the mass allowed to set to a soft jelly, which itself is a form in which the product can be handled in commerce. As already indicated, this fine suspension of pentachlorphenol may then be employed in accordance with the invention to produce the new complex in situ upon protein textiles in a number of ways:

(*a*) In adding the suspension to the mill during acid milling, the woollen piece to be treated is scoured as usual, washed on the dolly to remove soap and grease, soured, and transferred to the mill. 3 lbs. of the jelly described above is dissolved in 30 lbs. of water at 70–80° C. and uniformly distributed on the running piece from a watering can. If additional acid to that carried forward from the pre-milling sour is required, this is added to the solution of the jelly previously made. During the milling, the toxic compound is taken up so that no departure from normal milling practice is necessary. When the goods are correctly milled, the piece is removed and finished as usual with or without a water wash after the milling. During the subsequent drying a pH within the range 4 to 7 is established by expulsion of the volatile acid.

(*b*) If the suspension is added to the dolly during the finishing operation, a woollen piece in the dolly after being freed from alkali if necessary by souring in the usual way, preferably with formic or acetic acid, is run in cold water using the customary ratio of about 50 gallons of water to 100 lbs. of cloth. Then 3 lbs. of the jelly described above is dissolved in 2 to 3 gallons of hot water at 70 to 90° C. and poured into the dolly when the cloth is run until the original cloudy liquor has become clear, indicating the attachment of the pentachlorphenol to the wool. The latter is finished in the usual way. During the drying the excess volatile acid is expelled and a pH value between 4 and 7 established, whereby the pentachlorphenol becomes permanently fixed to the fibre.

(*c*) If the suspension is added to the acid dye bath, the jelly previously dissolved in hot water is run into the dye bath and the toxic compound and the dyestuff are affixed to the fibre at the same time. The subsequent drying ensures expulsion of excess acid and establishment of a pH value between 4 and 7.

A suitable dye bath for 100 lbs. of wool may contain:

2 lbs. of an after-chrome dyestuff such as Fastchrome cyanine 2B
10 lbs. of Glauber salts
3 lbs. of 30 per cent acetic acid, and
3 lbs. of the jelly described above dissolved in 2 to 3 gallons of hot water.

The dyeing is carried out as usual, as is the subsequent treatment with 2 lbs. of sodium bichromate.

An alternative dye bath may contain:

2 lbs. of neutral dyeing dyestuff such as Coumassie Blue N or cyanine navy blue 2RNX

10 lbs. of Glauber salts
0.5 lb. of sodium bichromate
3 lbs. of jelly dissolved in 2 to 3 gallons of hot water.

The dyeing and subsequent treatment is as above.

Yet another dye bath contains:

2 lbs. of acid dyestuff such as Elite Fast Red G
15 lbs. of Glauber salts
3 lbs. of 85 per cent formic acid, and
3 lbs. of jelly dissolved in 2 to 3 gallons of hot water.

Such application ensures the uniform formation of the new complex on the piece which, as a result, is made permanently moth-proof, or at least moth-proof with normal and customary use for a very long period compared with the life of the cloth.

The treatment in accordance with the invention may be carried out simultaneously with waterproofing treatment by any of the methods described above if a suitable waterproofing agent be employed. The agents described in British Patent Specification No. 380,076 and commercially available under the trade-mark "Impregnol" are suitable for this purpose. The combined treatment may then, for example, be carried out in the following ways:

(*a*) If the treatment is carried out on the mill, the woollen cloth after scouring is washed off and soured on the dolly as usual and transferred to the mill. For every 100 lbs. of cloth, 3 lbs. of jelly as described above are employed, dissolved in 30 lbs. of water at 70 to 80° C., and to the mixture 2 to 3 lbs. of the waterproofing agent sold under the trade-mark "Impregnol" are added. The resulting solution is distributed uniformly over the cloth whilst running, for example, from a watering can, and the milling is continued until the piece attains the desired length and width. The piece is now moth-proof and waterproof and may go straight to the stenter for drying, but better results are obtained if it is washed for 5 to 10 minutes in the dolly in a bath containing 50 gallons of water and 2 lbs. of aluminium triformate, a commercial product at 48° Twad. being approximately 10 normal with respect to aluminium and 5 normal to formic acid, after milling and before drying. During drying a pH value between 4.2 and 5 is established.

(*b*) If the process is operated in the dolly, the procedure is exactly as before, but in addition to the jelly, 2 to 3 lbs. of the waterproofing agent mentioned above is dissolved in 2 to 3 gallons of hot water and added to the dolly liquor. The pieces are rotated in the cold until the liquors become clear and free from cloudiness. This operation normally occupies 10 to 15 minutes. A solution of 2 lbs. of aluminium triformate in 1 gallon of water is then thrown into the dolly and the goods are rotated for 3 to 5 minutes sufficiently in the judgment of the operator to saturate the piece uniformly. The piece is then run off, hydro-extracted, and finished as usual, drying at a temperature above 60° C., whereby a pH value between 4.2 and 5 is established.

(*c*) If waterproofing is also effected in the dye bath, the waterproofing agent mentioned above in an amount of 2 to 3 lbs. for each 100 lbs. of wool, for example, is added to the dyeing formula which may be one of those given above, and the dyeing conducted as usual. When the pieces are approaching full shade, for example, 1 hour after the bath has reached the boiling temperature,

2 lbs. of aluminium triformate of 48° Twad. dissolved in 1 gallon of hot water, is added to the dye bath and boiling is continued until the pieces are on shade. The finished goods are then moth-proof and waterproof, when dried since excess acid is expelled during drying and a pH between 4.2 and 5 is established.

Example 2

64 lbs. of gelatine or hide glue are soaked overnight in 256 lbs. of water so that they are well swollen. Next day the swollen mass is brought into solution while warming to 45° C. and when it is dissolved, 1¼ lbs. of ammonium sulphate and 400 cc. of ammonium solution of specific gravity 0.9 are added together with half an ounce of commercial pancreatin. To effect demerisation by this solution, the temperature is maintained at 45° C., and the mass very thoroughly agitated for 15 minutes. The temperature is then raised very rapidly to 80° C. to kill the ferment, for which purpose the apparatus should be provided with ample heating surface and a large steam supply. The mass is then cooled as rapidly as possible with continuous stirring. When the temperature has fallen to 60° C., 85 lbs. of neutral sodium pentachlorphenolate is added in stages with continuous stirring until the mass is homogeneous and has cooled to 20° C. or thereabouts. This solution is permanent and is diluted for use. This resulting solution can be utilized as an alternative to that described above.

Cloth may be padded through the solution dried on the tins or stenter, and then padded again through a 1% solution of formic acid and again dried. The treatment with acid causes the pentachlorphenol to be set free in finely dispersed form from its sodium salt and during the final drying, excess formic acid is expelled and a pH between 4 and 7 established.

I claim:

1. Process for the treatment of a proteinaceous textile fiber to render same proofed against biological attack by the combination of pentachlorphenol with a protein at the surface of the fiber, which comprises treating the said textile fiber with an aqueous liquid containing dispersed pentachlorphenol, a protective colloid and an acid substance and whilst maintaining the pH of the mass below 7 evaporating to dryness the resulting reaction product to render the same irreversibly stable.

2. Process as claimed in claim 1 in which the acid substance is a volatile acid which is vaporized during the drying.

3. Process as claimed in claim 1 in which the acid substance is a heat decomposable acid reacting polyvalent metal salt of a volatile acid which decomposes during the drying liberating volatile acid which vaporizes during the drying.

4. Process as claimed in claim 1 in which the acid substance includes a volatile acid and a heat-decomposable polyvalent metal salt of a volatile acid which later decomposes during the drying liberating volatile acid and polyvalent metal cations which are fixed to the fiber.

5. Process as claimed in claim 1 in which the fiber is mixed with a solution of an alkali metal salt of pentachlorphenol and a protective colloid and the mixture is acidified with a volatile acid to produce an acid dispersion of pentachlorphenol in contact with the fiber.

6. Process as claimed in claim 1 in which the fiber is mixed with the aqueous liquid containing

the dispersed pentachlorphenol and the acid substance.

7. Process as defined in claim 1 in which the dispersion of the pentachlorphenol contains a dispersed protein.

8. Process as defined in claim 1 in which the drying operation is carried out at a temperature above 60° C.

9. Process as defined in claim 1 in which the pH of the mass is maintained in the neighborhood of 4.

ERIC BERKELEY HIGGINS.

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