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METHOD OF PROTECTING GOODS CONTAINING PROTEINS AGAINST INSECTS

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This invention relates to protecting goods consisting of or containing protein material or conversion products thereof from the attack of small organisms.

One of its objects is a process of protecting goods of the aforesaid kind from the attack of small organisms. Another object are the goods treated according to this process. Further objects will be seen from the detailed specification following hereafter.

According to this invention it has been found that natural or artificial products from proteins or conversion products of protein, such as wool, natural silk, skins, leather or feathers may be protected to a large degree from being eaten by small organisms or may be completely protected from being eaten by such organisms if they are subjected to the action of an alkylene oxide or a derivative or an analogue thereof under such conditions that a permanent chemical change (substitution) is produced.

The product may be treated in an aqueous bath, if desired in conjunction with a washing or a dyeing process, particularly dyeing with dyestuffs in a neutral bath, or by impregnation and subsequent steaming or heating under predetermined conditions of hygrometric state of the surrounding atmosphere or by action of the reagent in gaseous or gasified condition, this mode being of particular advantage. The fundamentally new treatment with the gaseous or gasified reagent is also applicable for protecting effectively objects which cannot, at all events without further precautions, be subjected to a treatment with solutions of the known agents for protecting goods against damages by moths; such objects are pieces of furniture, carpets, skins, confectioner's wares, military equipments, valuable museum specimens, any of these containing in one part or another a protein substance liable to attack or already attacked by the small organism. Objects which have already suffered from moth, for instance furniture upholstered with wool or hair, down quilts or cushions, may be very simply both ridden of moth and rendered permanently resistant to moth.

Suitable reagents are propylene-oxide, cyclohexene-oxide, butadiene-dioxide, epichlorhydrin, epifluorhydrin, 1-chlor-2.3-propylensulphide halogenphenoxypropene-oxide, alkylethyleneimine, such as butylethyleneimine, diethylalkyleneiminium halide, 3-hydroxy-1-dialkyltrimethyleneiminium salts; also products which have in their composition capillary active radicals which are specifically protective groups of an effect in itself known and/or groups lending solubility in water other than basic groups are useful for the invention, for example propene-oxide derivatives of halogen-hydroxy-triphenylmethane sulfonic acids.

For the gaseous treatment all substances of the said kind are useful which at normal or diminished pressure have a substantial vapour pressure at temperatures up to 100° C.

The action is the more rapid and deep seated the higher the degree of swollenness of the material to be treated. On the other hand, by increasing the swelling the temperature of treatment may be reduced. The simplest method of controlling the swollen condition in the gaseous treatment is by adjusting the relative moisture in the atmosphere. This may vary between, for instance, 60 and 95%. It is also possible to use saturated vapour insofar as the nature of the material to be treated permits. The choice of a certain hygrometric state, therefore, is not only an expedient for obtaining the desired effect, but also always depends on the kind of goods to be treated and their resistance to treatment. In the case of pieces of furniture, for example, operating in a highly moist atmosphere requires caution. Above all things condensation of the moisture during the cooling of the piece must be avoided. It is therefore advantageous before opening the treating chamber to expel the moist air by warm dry air, or to remove the main quantity of the moist air by evacuation. The swollen condition of the material can be enhanced for the gaseous treatment by the presence of volatile substances having a swelling effect, for example an amine such as pyridine or trimethylamine or formamide.

A thorough penetration of the gases in the treatment of goods in large quantity and particularly tightly packed goods, such as bales of cloth or cops of yarn, is much facilitated if the gases are not only continuously circulated but at the same time are subjected to frequent rhythmical alternating pressure as described in my copending application Ser. No. 46,445 filed October 23, 1935, for example from 40–200 mm. water column.

In a wet treatment a volatile or non-volatile swelling agent, such as formamide, acetamide, phenol, sodium cresolsulfonate, a sulfocyanide or another substance accelerating the reaction, may be added to the treating bath or padding solutions.

A particularly powerful effect is exerted by

the epihalogenhydrins, for instance epichlorhydrin or epifluorhydrin. The epihalogenhydrins are of the first importance in the gaseous treatment. If the treatment, for instance with epichlorhydrin, is to be combined with a dyeing or washing operation, for example with the washing of raw wool, it is to be recommended that, so far as the reacting substances are comparatively easily hydrolysed, the operation should be conducted at the lowest possible temperature to begin with, for example 40–50° C. and with as little treating liquid as possible, closed apparatus (dyeing apparatus, washing drum) being used in the case of relatively easily volatile substances.

The reagents used according to the invention may also be added to organic solvents used in the extraction of raw wool; preferably in this case also care is taken that there is a somewhat increased percentage of moisture in the goods, so that a sufficient effect may be obtained. This effect can be increased by heating or steaming after the organic solvent has been separated, particularly when non-volatile agents, namely such as have affinity to the goods under treatment, are used. The capacity of the solvent to take up moisture may be increased by the addition of an alcohol or a benzine soap.

In order to counteract any yellowing of the material under treatment the treatment may be conducted in the presence of an oxidizing or reducing bleaching agent or of an anti-oxidizing agent. The process may also be conducted with exclusion of atmospheric oxygen. Uncolored raw or finished products may be bleached with the usual bleaching agents in known manner after the treatment. When properly carried out the treatment is without influence on the final degree of bleaching.

In the case of very sensitive materials it is recommended that an agent adapted to protect fiber or a buffer substance, for example an alkali phosphate, magnesium sulfate, a hydroxy-alkylated water-soluble protein substance, a tertiary amino-acid, a condensation product of phenol-sulfonic acid and formaldehyde may be added. The presence of formaldehyde is sometimes also of advantage. The goods may also be treated beforehand with agents that prevent yellowing and are protective to the fiber.

In the treatment of colored material it must be remembered that not all dyestuffs are stable to the action of the agent used for the treatment. The most generally used and especially the valuable fast dyestuffs remain practically unaffected; a few, for instance azo-fuchsine, are gradually altered by treatment with alkylene-oxides, for example epichlorhydrin.

It is known that small organisms can be killed by gaseous alkylene-oxides. It is also known that the action of epichlorhydrin is similar to that of the halogen-free alkylene-oxides, particularly ethylene-oxide. However, it has not been known that an intensified action of these agents, particularly in the presence of moisture, leads to a change of protein substances which makes these substances distasteful to animal pests, particularly moth, nor could this effect be foretold, since, under the conditions which fully suffice to kill with certainty the said organisms no chemical effect occurs which remains capable of detection.

This effect, which obviously consists in a substantial alkylization of the amino-groups, probably partly as far as the quaternary stage, may be controlled, apart from analytical methods, by a color test, for instance. With increasing alkylization, so far as acid-groups do not enter into the molecule, the power of absorbing acid dyestuffs, particularly in a neutral bath, increases more and more, whereas the affinity to basic dyestuffs diminishes. The treatment of materials which have been dyed with dyestuffs of little fastness to water and washing increases the fastness quite considerably. In the case of Orange II (Schultz Farbstofftabellen, 7th edition, Vol. I, No. 189) or Alizarine Direct Blue A (Schultz Farbstofftabellen, 7th edition, suppl. vol., page 62), for example, this increase is such that in the washing test prescribed by the Rules of the Fastness Commission of the Association of German Chemists (5th edition, 1931), the washing liquors are only feebly colored, and white goods remain practically uncolored. Wool which exhibits this effect is no longer attacked by moth.

Although the process is associated with an essential chemical action the treatment may be so conducted that a practically perceptible weakening of the material is avoided. Wool treated with epichlorhydrin at 50° C. and with a 75 per cent relative moisture content retains its dry and wet tenacity and also shows by the scouring test no appreciable impoverishment as compared with untreated wool.

The following examples illustrate the invention:

Example 1.—500 grams of wool material, dyed with 3 per cent of Alizarine Direct Blue A, are heated at 50° C. for 8 hours in a container of 50 litres capacity in which there is an atmosphere of 75 per cent saturation with aqueous vapour and carrying 50 grams of epichlorhydrin. The color remains practically unchanged in this treatment, but the goods will no longer be attacked by moth.

With greater density of packing the quantity of epichlorhydrin in proportion to the weight of the goods may be diminished if it is not preferred to shorten correspondingly the duration of the treatment. The unconsumed epichlorhydrin may be recovered in known manner, for example, by absorption in active carbon or by evacuation and compression while cooling.

If instead of epichlorhydrin an alkylene-oxide, for instance propylene oxide, is used the unconsumed gas may be recovered by washing with ammonia and in the form of a hydroxy-alkylamine be used for other purposes.

Example 2.—A piece of furniture upholstered with wool which has been attacked by moth is treated for 14 hours at 50° C. in an atmosphere of 75 per cent of relative moisture and containing epichlorhydrin, under a rhythmically alternating pressure. The moth in the furniture is killed and the wool is protected against attack by moth.

Example 3.—Raw wool is washed in a closed drum for 8 hours with a liquor at 30–50° C. containing per litre 3 grams of sodium oleyl-hydroxy-ethane-sulfonate and 10 grams of epichlorhydrin. The treated wool is much less liable to the attack of moth than is the untreated wool. In like manner slivers can be treated with epichlorhydrin solution in a dyeing apparatus. The epichlorhydrin is more profitably utilized when there is added to the liquor a salt, for instance sodium sulfate.

Example 4.—Woolen piece goods are impregnated on the foulard apparatus with a solution of 5 per cent strength of diethyl-ethyleneiminium

chloride, then wrung out, lightly dried, rolled up and heated for 8 hours in an atmosphere of 75 per cent saturation with water-vapour. The fabric is thus protected against the attack of moth.

What I claim is:

1. The method of permanently protecting goods containing proteins against insects, which comprises treating the goods at a temperature above 40° C. with a compound selected from the group consisting of alkylene oxides, alkylene imines, and alkylene sulfides until the amino groups of the protein material are substantially alkylized.

2. The method of permanently protecting goods containing proteins against insects, which comprises treating the goods at a temperature above 40° C. with the vapor of a compound selected from the group consisting of alkylene oxides, alkylene imines, and alkylene sulfides until the amino groups of the protein material are substantially alkylized.

3. The method of permanently protecting goods containing proteins against insects, which comprises treating the goods at a temperature above 40° C. with an epihalogenhydrin until the amino groups of the protein material are substantially substituted with hydroxyhalogen alkyl groups.

4. The method of permanently protecting goods containing proteins against insects, which comprises treating the goods at a temperature above 40° C. with a compound selected from the group consisting of alkylated ethylene imines and the quaternary salts thereof, until the amino groups of the protein material are substantially alkylized.

5. The method of permanently protecting goods containing proteins against insects, which comprises treating the goods with a swelling agent and at a temperature above 40° C. with a compound selected from the group consisting of alkylene oxides, alkylene imines and alkylene sulfides until the amino groups of the protein material are substantially alkylized.

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