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2,707,689

ALLYL STARCH COATING COMPOSITION, METHOD OF MAKING SAME, METHOD OF APPLYING SAME TO KERATINOUS MATERIAL, AND ARTICLE PRODUCED THEREBY

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This invention relates to coating compositions of the type employed in the treatment of fabrics and fibrous materials. More particularly, the invention relates to a resinous coating composition and to a manner of treating fabrics and fibrous materials therewith for depositing on fibers a coating of polymerized allyl starch resin either alone or in conjunction with other materials for insect proofing or otherwise pre-treating fabrics and fibrous materials.

In the finishing of fabrics and other bodies of fibrous material and particularly in the finishing of articles comprising keratinous fibers, it is customary to employ coating agents such as waxes or resins to impart desirable properties and characteristics to the fibers such, for example, as softness and flexibility imparting a desired hand or feel to fabric, increased tensile strength improving the durability of spun fibers and fabrics, and improved sheen or lustre often desirable in felts and yarn of keratinous fiber, and the like. Keratinous fabrics and fibrous bodies, i. e., those comprising wool, hair, alpaca, cashmere, camel hair, vicuna and the like are subject to insect attack, and it is desirable, therefore, to coat or impregnate such fabrics or fibrous bodies with an insecticidal material to provide protection against such insect attack. Such insect proofing can be applied to fabrics and fibrous bodies after treatment with a wax or resin as above described, but in such instances the insecticide is generally loosely bonded and is readily removed from the fabric or fibrous body by either washing or dry cleaning.

Attempts to provide a more permanent insect proofing of keratinous materials involving the use of a wax, resin or other fixing agent in the past have not been entirely satisfactory. Many of the agents which have been tried if present in an amount to effectively bind the insecticide to the fabric or fibrous body detracted from the desirable softness thereof, rendering them unsatisfactory for many uses such as clothing, blankets, and the like. On the other hand, more sparing use of the fixing agents to preserve the desired hand or feel of treated fabrics generally results in a rather loose bonding of the insecticide so that protection against insect attack is lost after a very few washings or dry cleanings.

I have now discovered a new coating composition which is particularly suited for the treatment of keratinous material, i. e., keratinous fabrics and fibrous bodies. This new coating composition which is applied to keratinous material from an aqueous emulsion, and polymerizes on the keratinous material to form on individual fibers thereof a film which provides desirable softness and improved tensile strength and at the same time serves to bond a previously applied insecticide to the fibers in a manner to render the same surprisingly resistant to both washing and dry cleaning. While various insecticides can effectively be bound to keratinous material by means of my new coating composition, best results have been obtained with triethanolamine silicofluoride insecticides.

Regarded in certain of its broader aspects, my invention comprises a new coating composition in the form of a con-

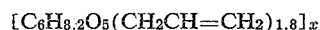
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centrated aqueous emulsion containing sodium lauryl sulfate as an emulsifying agent and having a dispersed phase comprising allyl starch dissolved in an organic solvent medium essentially comprising toluene, procedures for applying said composition to keratinous material and insecticidally treated keratinous material from an aqueous bath to deposit and polymerize allyl starch thereon, and the improved keratinous materials thus obtained wherein individual fibers are coated with polymerized allyl starch in an amount equivalent to about 0.4 to 1.0% of the weight of said material.

Allyl starch as employed in my new coating composition can be prepared according to the procedure disclosed in Ind. & Eng. Chem., 37, 201 (1945) or may be obtained from commercial sources. In either event, allyl starch is initially obtained in organic solvent solution, and in order to provide satisfactory concentrated emulsions, I prefer to employ an allyl starch solution wherein the organic solvent consists essentially of toluene and contains 0-10% and preferably about 5%, based upon the total weight of solvent, of a 1-4 carbon alcohol, i. e., methanol, ethanol, propanol, isopropanol, and the butanols. The presence of a 1-4 carbon alcohol serves to clarify the allyl starch-toluene solution.

The starting allyl starch solution defines or controls the composition of the dispersed phase in my concentrated or stock emulsions as well as in the dilute emulsions or treating baths used for applying the coating composition to keratinous material. While the composition of the starting organic solvent solution of allyl starch can be somewhat varied, I prefer to employ a solution containing about 40% by weight of allyl starch and 60% by weight of solvent. The allyl starch can, if desired, be increased to about 45% (and the solvent reduced to about 55%). At concentrations above about 45% allyl starch, the organic solvent solution becomes quite viscous and hence is not suited for use in my coating composition. Concentrations lower than 40% allyl starch can be employed but the relatively greater amounts of organic solvent serve no useful purpose. Such weaker concentrations of allyl starch are, therefore, considered to be impractical from the economic standpoint.

The allyl starch itself can vary considerably in composition based upon the number of allyl groups present per glucose unit in the starch. The number of allyl groups per glucose unit is called the "substitution factor" and is used to characterize any particular allyl starch. Thus, for example, an allyl starch having a substitution factor of 1.8 may be represented by the empirical formula



The allyl substitution factor or the degree of substitution is calculated from the Iodine number determined by the Wijs method, as described by Hoffman and Green in Oil and Soap, 16, 236 (1939).

I prefer to use an allyl starch having a substitution factor within the range of 1.80 to 1.85, although starches having a somewhat lower substitution factor can also be employed. I find, however, that allyl starch having a substitution factor of 1.80 to 1.85 has properties and characteristics including solubility, rate of polymerization, and ability to impart a desired soft hand or feel to fabric which particularly adapts the same for use in my coating composition and process.

In preparing my new coating composition or concentrated allyl starch emulsion, an organic solvent solution of allyl starch is added with constant agitation to approximately an equivalent weight of water containing a small amount, i. e., about 1% on a weight basis, of sodium lauryl sulfate. After formation of the emulsion, it should be filtered to remove any impurities such as rosin-like particles as these impurities occasionally have

a tendency to split the emulsion. The stable emulsion thus obtained contains as the dispersed phase allyl starch solids dissolved in organic solvent. The preferred form of concentrated emulsion, i. e., emulsion prepared from allyl starch solution of about 40% concentration will have the following composition:

	Per cent
Allyl starch (substitution factor 1.80-1.85)-----	20
Toluene -----	27-30
Isobutanol (or other 1-4 carbon alcohol)-----	0-3
Water -----	49.5
Sodium lauryl sulfate-----	0.5

Sodium lauryl sulfate appears to be unique in its ability to give a stable and even flowing emulsion. A number of other surface active agents including sorbitan monolaurate, sorbitan monopalmitate, polyoxyalkylene derivatives of the foregoing, sulfonated ethers and fatty alcohol sulfates other than sodium lauryl sulfate have been tried but fail to give emulsions. It is significant also to note that even when the concentrated emulsion is diluted with water in ratios of about 5 parts by weight of emulsion concentrate to 2000 parts by weight of water in forming a bath for treating keratinous materials, the remarkable stability of the allyl starch emulsion (in the presence of sodium lauryl sulfate) is maintained.

Fibrous keratinous material such as woolen fabrics and the like are effectively treated with my new coating composition from a dilute aqueous bath, and I preferably employ a relatively large amount of the bath per weight of fabric, i. e., about 20 lbs. of solution per lb. of fabric. An amount of the concentrated or stock emulsion (20% allyl starch) equivalent to about 2-5% of the weight of fabric to be treated is added to the bath thus providing a dilute emulsion containing an amount of allyl starch equal to about 0.4-1.0% of the weight of the fabric. The fabric is agitated in the bath for about 5 minutes while maintaining a temperature of about 75-80° F. and for an additional 10 minutes during which time the temperature is raised slowly to about 90° F. The fabric is then extracted or centrifuged to remove most of the liquid and dried by ordinary procedures such as are commonly employed in the drying of textile fabrics. This drying effects a simultaneous removal of water and organic solvent from the fabric and polymerization of the allyl starch on the fabric. The effectiveness of the coating operation appears to depend largely upon the control of the bath temperature. For example, temperatures below about 75° F. even when the treatment is continued for an extended period, result in a low emulsion exhaustion, whereas maintaining a temperature of 75-80° F., then increasing the temperatures to about 90° F. as above described, removes 75% or more of the allyl starch emulsion from the bath. At temperatures above about 90° F., on the other hand, the exhaustion of the emulsion on to the fabric may be too rapid with the result that after drying, the fabric may have a somewhat harsh feel. A similar effect is obtained if more than about 5% of the stock emulsion based upon the weight of the fabric is used in the treating bath, i. e., an allyl starch concentration in the bath greater than about 1% allyl starch solids based upon the weight of the fabric.

It should be noted that the amount of allyl starch polymerized on the dried fabric when treated as above described depends upon the percent of allyl starch emulsion removed from the treating bath. Thus if 75% of the emulsion is removed, the amount of polymerized allyl starch on the finished fabric is about 0.3-0.75% of the weight of the fabric, whereas if emulsion is completely removed from the bath, the finished fabric will contain about 0.4-1.0% of polymerized allyl starch. Thus the treated fabrics may contain from as little as about 0.3% to as much as about 1.0% of polymerized allyl starch.

When the allyl starch is applied to fabrics according to the preferred procedure above mentioned, the allyl starch resins which polymerize on the fabric provide a desirable softness in the fabric, as well as enhancing the tensile strength and wearability. In addition, however, when fabric previously impregnated with an insecticide is treated according to the same procedure a coating of allyl starch resin on the fabric acts to bind the insecticide in a manner to render it resistant to repeated washing and dry cleaning.

Insecticides which are most effectively bound to fabric by my allyl starch coating composition are the fluoride type insecticides, particularly those containing triethanolamine silicofluoride. Insecticides of this type are disclosed in U. S. Patent No. 2,176,894; however, the insecticides there described contain a somewhat higher concentration of aluminum sulfate than is necessary or advantageous when the insecticide is bound to the fabric with my allyl starch resin. Some types of insecticides, i. e., particularly those containing higher metals such as copper and zinc should be avoided as these metals have a tendency to split the emulsion causing the formation of a curd. Aluminum and sodium fluorides and other salts of these metals appear to have a gradual effect, if any, on the emulsion, and these materials do not interfere with the application of the allyl starch emulsion to keratinous fabrics.

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The following insecticide composition will serve to illustrate the type of insecticide which is very effectively bound to wool by subjecting the insecticide impregnated wool to treatment with my allyl starch emulsion:

	Per cent
Hydrofluosilic acid-----	111.5
Triethanolamine -----	24.0
Hydrofluoric acid-----	1.0
Aluminum sulfate -----	0.5
Sodium lauryl sulfate-----	0.5
Water -----	62.5

¹ All percentages are on a weight basis.

In applying insecticides to a keratinous material such as wool, the fabric is immersed in a water solution containing an amount of the insecticide equal to about 1-6% of the weight of the fabric to be treated, and the quantity of bath employed is preferably about 20 lbs. of solution per lb. of fabric. With an insecticide having the composition above described, the fabric is treated in the bath for about 15 minutes at 75° F. during which time substantially all of the insecticide is taken up by the fabric. In order to apply allyl starch coating, it is merely necessary to add the required amount, i. e., 2-5% based upon the weight of the fabric, of concentrated allyl starch emulsion, i. e., the 20% emulsion above described to the insecticide exhausted solution, and run the fabric at about 75-80° F. for about five minutes and then for an additional ten minutes, raising the temperature to about 90° F., followed by extraction and drying of the fabric as above described.

The following example will show how procedures for treating keratinous material according to my invention can be carried out and how the results of such treatment can be evaluated. It is to be understood, however, that this example is given by way of illustration and not of limitation.

EXAMPLE

A number of practical mill runs of woolen blanket fabric were made using the following procedure. The woolen fabric was first impregnated with insecticide by treating the fabric with 20 lbs. per pound of fabric of an aqueous solution containing about .06 lb. per pound of fabric of a triethanolamine silico-fluoride insecticide having the following composition: 11.5% hydrofluosilic acid, 24.0% triethanolamine, 1.0% hydrofluoric acid, 0.5%

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aluminum sulfate, 0.5% sodium lauryl sulfate, and 62.5% water. The fabric was treated for about 15 minutes at 75–80° F. in this insecticide bath during which time substantially all of the insecticide was taken up by the fabric. At this point samples of fabric were treated according to three different procedures, i. e.:

(a) One group of samples was removed from the machine, extracted by centrifuging and dried at approximately 220° F. The fabric was then finished by the processes ordinarily used in finishing woolen blanket fabrics.

(b) A second group of samples was further treated with allyl starch emulsion by adding to the insecticide exhausted bath about .025 lbs. per pound of fabric of a 20% allyl starch emulsion having the composition: 20% allyl starch having a substitution factor of 1.80–1.85, 28.5% toluene, 1.5% isobutanol, 49.5% water and 0.5% sodium lauryl sulfate. The fabric was run in the resulting dilute emulsion for about 5 minutes at a temperature of 75–80° F. and for an additional 10 minutes while the temperature was raised slowly to about 90° F. The fabric was then extracted by centrifuging, air dried at about 220° F., and finished in the regular manner.

(c) The third group of samples was treated with allyl starch emulsion by adding to the insecticide exhausted bath about .05 lb. per pound of fabric of a 20% allyl starch emulsion having the composition described in (b) above. The fabric was run in the resulting dilute emulsion and then extracted by centrifuging as described in (b) above. After drying, however, the fabric was scoured with a 5% (based on weight of fabric) soap and alkali solution (formed by diluting a mixture containing 4 ounces of solid chip soap and 6 ounces of sodium carbonate per gal. of water) for one-half hour at 90° F., rinsed with water for two hours and again extracted before drying and finishing in the regular manner.

The various samples of fabric thus obtained were subjected to the following tests:

(1) Overall shrinkage was determined by measuring the width of fabric after drying and after napping, and the results of these measurements as tabulated below clearly demonstrate that the fabric treated with allyl starch emulsion shrinks less and can be finished off at a greater width than fabric which is not subjected to the allyl starch emulsion treatment.

Overall shrinkage in finishing

	Width as dried, in.	Width after napping, in.	Percent Shrinkage
No Allyl starch treatment.....	77	70	9.1
Treated with 2½% of allyl starch emulsion.....	77	71½	7.15
Treated with 5% of allyl starch emulsion.....	75	72	4

(2) The various samples were subjected to a number of hand washings (washing for 5 minutes at 100° F. in a 0.5% soap solution, rinsed twice at 95° F., extracted and dried) and machine washings (in a General Electric washer with a 0.5% soap solution at 100° F., rinsed at 95° F., extracted and dried). Before the first of these washes and following each wash, fabric samples were analyzed for fluorine content and the results of these tests as tabulated below show that initial insecticide impregnation is about the same with and without the allyl starch emulsion treatment. (In considering the initial retention of insecticide with samples treated with 5% of the allyl starch emulsion, it is to be noted that the added step of scouring with soap and alkali for one-half hour at 90° F. represents a treatment equivalent to about 8–10 hand washings or 4–5 machine washings of the fabric.) The tabulated data also shows that there is a much higher retention of insecticide in the allyl starch treated fabric after repeated hand or machine washings.

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Hand washing

Fabric Treated With—	Percent Fluorine Content by Chemical Analysis					
	Wash No. 0	1st	2nd	3rd	4th	5th
Insecticide alone.....	.30	.19	.09	.07	.06	.04
Insecticide plus 2½% allyl starch emulsion.....	.35	.26	.12	.10	.10	.09
Insecticide plus 5% allyl starch emulsion and scouring.....	.09	.09	.08	.07	.07	.07

Machine washing

Fabric Treated With—	Percent Fluorine Content by Chemical Analysis			
	Wash No. 0	1st	2nd	3rd
Insecticide alone.....	.30	.08	.03	.02
Insecticide plus 2½% allyl starch emulsion.....	.35	.12	.09	.09
Insecticide plus 5% allyl starch emulsion and scouring.....	.09	.09	.08	.08

(3) In connection with the experimental washes referred to in paragraph (2) above, the samples after the 1st, 2nd, 3rd and 4th hand washings and after the first machine washing were further examined for shrinkage in the warp and filling. The percent shrinkage was calculated from the distance between two predetermined marks on the fabric prior to the first washing and the distance between the marks after each successive washing. The results of these measurements as tabulated below show that the percent shrinkage in fabric which has not been treated with allyl starch emulsion is 2 to 3 times as great as shrinkage in fabric treated with allyl starch emulsion.

Percent shrinkage

	No Treatment With Allyl Starch Emulsion		Treatment With 2½% Allyl Starch Emulsion		Treatment With 5% Allyl Starch Emulsion	
	Warp	Filling	Warp	Filling	Warp	Filling
1st hand wash.....	0	5	0	2.5	0	1.25
2nd hand wash.....	2.5	5	0	2.5	0	2.5
3rd hand wash.....	2.5	6.25	0	3.7	0	1.25
4th hand wash.....	1.25	11.25	0	2.5	1.25	1.25
1 machine wash.....	5.0	16.25	1.25	2.5	2.5	5.0

(4) Samples of the fabric after finishing were subjected to tests for determining tensile strength in the warp and filling according to standard procedures, i. e., 6" x 1" strips of fabric were subjected to tension in a Scott tester and the tearing point recorded in pounds of tension. The results of these tests as tabulated below clearly indicate that there is a substantial increase in tensile strength of the warp and a still greater increase in the tensile strength of the filling after treatment with allyl starch emulsion.

Tensile strength

	Warp		Filling	
	lbs.	Percent Increase	lbs.	Percent Increase
No Emulsion.....	29.1	-----	15.2	-----
2½% of Allyl Starch Emulsion.....	31.5	8.5	23.8	57
5% of Allyl Starch Emulsion.....	40.1	38	29.4	94

In addition to the foregoing tests, it was also observed that the fiber loss in washing and in napping was substantially greater with fabrics which had not been subjected to the allyl starch emulsion treatment, an effect

which is apparently due to a binding together of the fibers by polymerized resin in the allyl starch treatment of fabrics. It was further found that the allyl starch treated fabrics showed a much greater resistance to wear when given a one minute run in a high speed wear tester.

Various changes and modifications may be made in carrying out the present invention without departing from the spirit and scope thereof and insofar as these changes are within the purview of the annexed claims, they are to be considered as part of my invention.

I claim:

1. A coating composition comprising an aqueous emulsion having a dispersed phase consisting of allyl starch, having a substitute factor of about 1.80-1.85, dissolved in an organic solvent comprising toluene, and containing as an emulsifying agent an amount of sodium lauryl sulfate equal on a weight basis to about 1% of the dispersed phase.

2. A coating composition comprising an aqueous emulsion having as a dispersed phase a solution of about 40-45 parts by weight of allyl starch having a substitution factor of about 1.80-1.85 in about 55-60 parts by weight of toluene containing 0-10% of a 1 to 4 carbon alcohol, and containing as an emulsifying agent an amount of sodium lauryl sulfate equal on a weight basis to about 1% of the dispersed phase.

3. A coating composition comprising a concentrated aqueous emulsion adapted for dilution with water, said emulsion having a dispersed phase comprising a solution of about 40-45 parts by weight of allyl starch having a substitution factor of about 1.80-1.85 in about 55-60 parts by weight of toluene containing 0-10% of isobutanol, and a continuous phase comprising water in an amount to provide an allyl starch concentration of about 20% based upon the total weight of the emulsion, and said emulsion containing as an emulsifying agent an amount of sodium lauryl sulfate equal on a weight basis to about 1% of the dispersed phase.

4. As a treating bath for keratinous materials, a dilute aqueous emulsion having a dispersed phase comprising a solution of about 40-45 parts by weight of allyl starch having a substitution factor of about 1.80-1.85 in about 55-60 parts by weight of toluene containing 0-10% of a 1 to 4 carbon alcohol, said emulsion containing as an emulsifying agent an amount of sodium lauryl sulfate equal on a weight basis to about 1% of said dispersed phase, and the amount of said dispersed phase being sufficient to provide in the dilute emulsion a concentration of allyl starch equal to about 0.4 to 1.0% of the weight of keratinous material to be treated.

5. The process that comprises adding a quantity of allyl starch, having a substitute factor of about 1.80-1.85, dissolved in an organic solvent comprising toluene with constant agitation to a substantially equivalent quantity of water containing an amount of sodium lauryl sulfate equal on a weight basis to about 1% of said allyl starch solution, thereby forming a stable emulsion wherein the dispersed phase has the composition of said allyl starch solution.

6. The process that comprises adding a quantity of an allyl starch-organic solvent solution, containing about 40-45 parts by weight of allyl starch having a substitution factor of about 1.80-1.85 in about 55-60 parts by weight of toluene containing 0-10% of a 1 to 4 carbon alcohol to a substantially equivalent quantity of water containing an amount of sodium lauryl sulfate equal on a weight basis to about 1% of said allyl starch solution, thereby forming a stable emulsion wherein the dispersed phase has the composition of said allyl starch solution.

7. The process for treating a fibrous keratinous material that comprises immersing said keratinous material in a bath of dilute aqueous emulsion having a dispersed phase comprising allyl starch dissolved in toluene containing 0-10% of a 1 to 4 carbon alcohol, said emulsion containing as an emulsifying agent an amount of sodium

lauryl sulfate equivalent on a weight basis to about 1% of said dispersed phase, and said dispersed phase being present in an amount to provide an allyl starch concentration equivalent on a weight basis to about 0.4 to 1.0% of said keratinous material, moderately heating the bath and keratinous material immersed therein to effect a deposition of said dispersed phase on said keratinous material then removing and drying the keratinous material to simultaneously eliminate water and organic solvent therefrom and polymerize the allyl starch on said fibrous keratinous material.

8. The process as defined in claim 7 wherein the bath of dilute emulsion is prepared by adding to a bath, from which an insecticide has been exhausted on the keratinous material, a quantity of 20% allyl starch emulsion equivalent on a weight basis to about 2 to 5% of the weight of keratinous material.

9. The process for treating a fibrous keratinous material that comprises immersing said keratinous material in a bath of dilute aqueous emulsion having a dispersed phase comprising about 40-45 parts by weight of allyl starch having a substitution coefficient of about 1.80-1.85 dissolved in about 55-60 parts by weight of toluene containing 0-10% of a 1 to 4 carbon alcohol, said emulsion containing as an emulsifying agent an amount of sodium lauryl sulfate equivalent on a weight basis to about 1% of said dispersed phase, and said dispersed phase being present in an amount to provide an allyl starch concentration equivalent on a weight basis to about 0.4 to 1.0% of said keratinous material, heating the bath and keratinous material immersed therein for about 5 minutes at a temperature of 75-80° F., and for an additional 10 minutes while raising the temperature to about 90° F. to effect a deposition of said dispersed phase on said keratinous material then removing and drying the keratinous material to simultaneously eliminate water and organic solvent therefrom and polymerize the allyl starch on said fibrous keratinous material.

10. The process as defined in claim 9 wherein a keratinous material is employed which has impregnated on the fibers thereof a triethanolamine silicofluoride insecticide.

11. The process for insect proofing fibrous keratinous material that comprises immersing keratinous material in a solution containing an insecticide under conditions to exhaust the insecticide on said keratinous material, adding to the insecticide exhausted solution an allyl starch emulsion having a dispersed phase comprising allyl starch dissolved in toluene containing 0-10% of a 1 to 4 carbon alcohol and containing as an emulsifying agent an amount of sodium lauryl sulfate equivalent on a weight basis to about 1% of said dispersed phase, the quantity of said emulsion being sufficient to provide an amount of allyl starch equivalent to about 0.4 to 1.0% of the weight of said keratinous material, moderately heating the resulting bath and keratinous material immersed therein to deposit said dispersed phase on said keratinous material, then removing and drying the keratinous material to simultaneously eliminate water and organic solvent therefrom and polymerize the allyl starch on said keratinous material.

12. The process for insect proofing fibrous keratinous material that comprises immersing keratinous material in an aqueous bath containing a triethanolamine silicofluoride insecticide in an amount equivalent on a weight basis to about 6% of said keratinous material, moderately heating said aqueous bath to exhaust the insecticide on said keratinous material, adding to the bath an allyl starch emulsion having a dispersed phase comprising allyl starch with a substitution factor of about 1.80-1.85 dissolved in toluene containing 0-10% of a 1 to 4 carbon alcohol, and containing as an emulsifying agent an amount of sodium lauryl sulfate equivalent on a weight basis to about 1% of said dispersed phase, the quantity of said emulsion being sufficient to provide an amount of allyl starch equivalent to about 0.4-1.0% of the weight

of said keratinous material, heating the resulting bath for about 5 minutes at 75-80° F. and for an additional 10 minutes while raising the temperature to about 90° F. to deposit said dispersed phase on said keratinous material, then removing and drying the keratinous material to simultaneously eliminate water and organic solvent therefrom and polymerize the allyl starch on said keratinous material.

13. An insect proof fibrous keratinous material having on individual fibers thereof a triethanolamine silicofluoride insecticide and an enveloping film of polymerized allyl starch, said film being equivalent on a weight basis to about 0.3 to 1.0% of the weight of said keratinous material.

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