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PROCESS FOR IMPARTING WATER REPELLENCY TO CELLULOSIC MATERIAL
COMPRISING CELLULOSIC FIBERS BY REACTION WITH
AN AEROSOL CONTAINING ORGANO SILICON HALIDES
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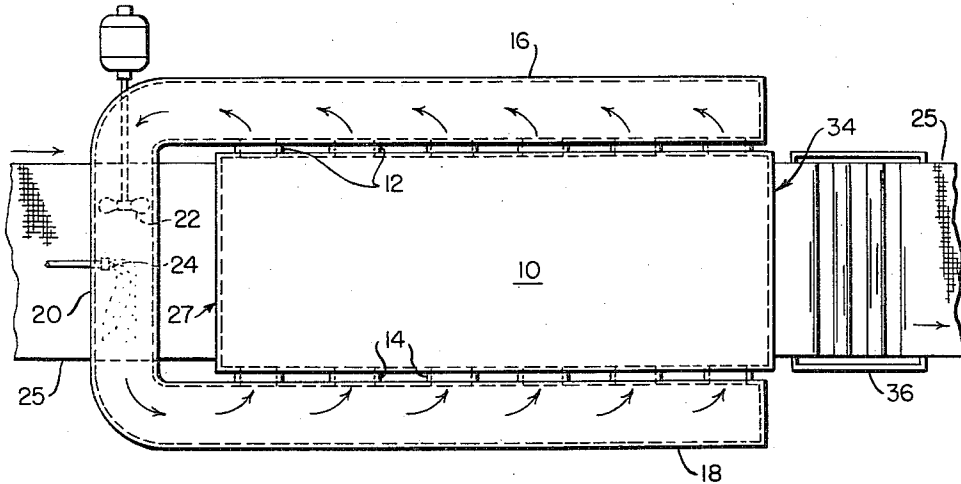


Fig. 1

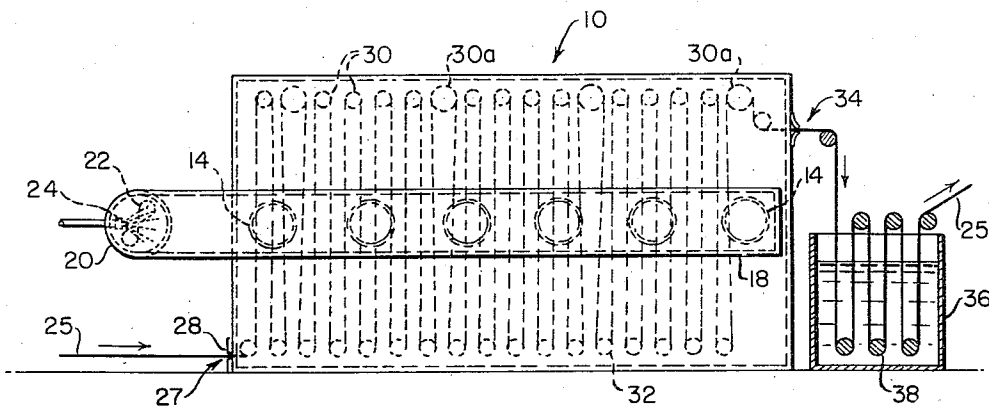


Fig. 2

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PROCESS FOR IMPARTING WATER REPELLENCY TO CELLULOSIC MATERIAL COMPRISING CELLULOSIC FIBERS BY REACTION WITH AN AEROSOL CONTAINING ORGANO SILICON HALIDE

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10 Claims. (Cl. 8—116)

This invention relates to the treatment of cellulosic materials, particularly materials comprising cellulosic fibers, such as cotton fabrics, paper, fabrics containing fibers of regenerated cellulose (rayon) or cellulose esters (cellulose acetate or cellulose nitrate), and similar materials, and consists in a novel process of treating such materials with organo halogeno silanes (also known as organo silicon halides) to render them water repellent without seriously impairing the strength of the material or degrading its cellulosic constituents. In the treatment of fabrics, the invention is moreover, useful in stabilizing them against shrinkage and in imparting size.

Prior attempts to treat cellulosic fibers, such as paper, cotton goods and fabrics of regenerated cellulose or cellulose esters, with organo halogeno silanes have met with only limited success. Although there has been little difficulty in rendering the fabrics water repellent, no process has heretofore been developed which does not result in serious degradation and loss of strength of the fabric, and none of the processes yet developed have, for this reason, met with commercial acceptance.

The present invention not only avoids the difficulties previously encountered in efforts to utilize organo halogeno silanes in treating cellulosic materials, but in addition, provides a process which may be carried out continuously with the treatment being completely uniform over the entire area of the material treated. To assure uniformity, in any case, it is desirable that every bit of material be treated under identical conditions, and that the silane be presented to the material at the rate it is used up in the treatment and at constant concentration, and this invention provides a sure and simple feature for accomplishing this result even though the rate of adding the silane to the treating apparatus be non-uniform.

In general, the process of this invention is practiced by exposing the cellulosic material to a gaseous mixture of the silane and an inert gas under time and temperature conditions found suitable for permitting the desired reaction between the material and the silane while avoiding the side reactions causing degradation, and immediately or very shortly thereafter neutralizing the acidic reaction by-products by immersing the material in a mild alkaline solution. The material is thereafter preferably rinsed in water to remove excess alkali and salts and dried.

Preferably, the silane is present in the gaseous mixture as an aerosol to assure constant saturation of the gaseous phase with silane vapors. The liquid aerosol particles serve as a reservoir supplying silane vapors to and throughout the gaseous phase as these vapors are removed by reaction with the material being treated. This is particularly advantageous in the continuous treatment of materials, since it assures constant and uniform silane vapor concentration throughout the reaction cham-

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ber while avoiding the necessity of carefully correlating the rate of adding silane with the rate the material is fed.

The time and temperature of the treatment are interdependent in accordance with well known principles of chemical kinetics. At high temperatures, shorter exposures are required, since increased temperature not only increases the rate of reaction, but also increases the concentration of silane in the vapor phase, and at lower temperatures, the time of exposure may be considerably longer. Thus, if the treatment is carried out at about 100° F., the time of exposure should be less than about 10–15 seconds, and preferably only a second or two, whereas at 75° F. exposures as long as 2–6 minutes are generally satisfactory, but an exposure of from 1–60 seconds is preferred. At 85° F. the exposure may be as long as from 1–5 minutes, with exposures of from 1–30 seconds being preferred. Thus, within the normal room temperature range of about 70–100° F. the maximum exposure time will vary generally between about 10 seconds and 6 minutes, and best results can generally be attained with exposure times of between about 1 second and 1 minute.

In any treatment, it will be appreciated, the time of exposure will depend not only on the temperature, but also on the degree of water repellency desired, and, in the case of fabrics at least, also on the degree of size to be imparted and on the nature of the fiber, type of weave, etc. Another factor entering the selection of the proper exposure time is the composition of the silane used in the process. Methyl chloro silanes, which are preferred, are commercially available as mixtures including such compounds as dimethyl dichloro silane $(CH_3)_2SiCl_2$, methyl tri chlorosilane CH_3SiCl_3 , trimethyl chlorosilane $(CH_3)_3SiCl$, silicon tetrachloride $SiCl_4$, and methyl dichlorosilane CH_3SiHCl_2 . As the components vary in volatility and in their reactivity toward the material treated, mixtures having higher concentration of the more volatile and/or more reactive components demand shorter exposure time than mixtures less reactive or less volatile. The time and temperatures described above have been found suitable for treatments with the commercially available methyl chloro silanes, such as Dri-Film sold by the General Electric Company.

In general, organo halogeno silanes suitable for use in this invention include the methyl chloro silanes listed above, preferably those having two or more chlorine atoms, since they form polymeric chains of silicones when hydrolyzed. Cross-linked silicones are preferred to linear polymers and for this reason it is desirable that the silane include some having three or four chlorine atoms, e. g. methyl trichlorosilane, silicon tetrachloride, or trichlorosilane $(HSiCl_3)$, or some methyl dichloro silane, which cross links through the valence bond of the hydrogen atom which is readily removed, apparently by oxidation or hydrolysis. In addition to the methyl chloro silanes, it is believed apparent that the corresponding ethyl and propyl compounds are also suitable, and that the bromo and fluoro compounds could also be used except for their expense and the dangerous nature of the latter. They are, however, known to react similarly to the chlorosilanes. This invention accordingly contemplates that other organo halogeno silanes may be used, particularly the lower alkyl silicon halides (e. g. methyl, ethyl, and propyl silicon halides).

Generally, the process is carried out using silane vapor mixed with air, as by vaporizing silane in a chamber and placing the material after equilibrating in an atmosphere of between about 30 and 100% relative humidity, in the chamber for the desired period of time, then removing it and further treating it to neutralize the reaction by-

products. Other inert gases are, however, entirely satisfactory, for instance, nitrogen and carbon dioxide which have the advantage of eliminating any explosion hazard. Also, in this connection, it has been found that by adding the vapors of carbon tetrachloride, to an air-silane mixture, the explosion hazard is also reduced.

In forming the gaseous mixture of the silane and inert gas, the former may be incorporated in air or other inert gas, but is preferably atomized to produce an aerosol mixture in the form of a noticeable fog, or condensed to produce the same result as by cooling a saturated silane vapor and gas mixture.

After exposure to the silane the material is neutralized, preferably immediately after exposure since acidic reaction byproducts cause continued degradation, particularly at high temperatures. At low temperatures neutralization may be delayed, for instance, up to about 5 minutes at 75° F., since degradation appears to proceed slowly, but nothing is gained by such a delay. Neutralization is conveniently carried out by immersing the material in a mildly basic aqueous solution, preferably one buffered at a pH of between 7 and 11. Alkaline neutralizing agents particularly suitable include sodium carbonate, sodium bicarbonate, calcium hydroxide, disodium phosphate, trisodium phosphate, sodium acetate and similar water-soluble basic compounds which form slightly basic aqueous solutions of high neutralizing capacity. Strongly basic solutions, e. g., of pH higher than 11.0, are preferably avoided since they tend to remove the silicone formed by the silane treatment. Dilute solutions of such strongly basic materials as sodium hydroxide having a pH below 11 could be used, but the neutralizing capacity is quite low because of the extreme dilution necessary for such low alkalinity. Ammonia and amines are also preferably avoided as neutralizing agents since their salts, formed during neutralization, tend to be retained on the cellulosic material and cause gradual degradation. The neutralizing bath preferably also includes a wetting agent effective to aid the wetting of the treated cellulose such as a nonionic or cationic wetting agent or others well known to the art.

After neutralization the material may then be rinsed in water to remove residual salts and alkaline solution, and dried.

The following examples describe in detail representative examples of methods for treating materials according to this invention, as it relates to the treatment of fabrics.

A suitable container, for instance a larger beaker, is supplied with an atmosphere of an aerosol of a mixture of methyl chloro silanes consisting chiefly of methyl trichloro silane and dimethyl dichloro silane (GE Dri-Film,¹ sold by the General Electric Company, Schenectady, New York), by atomizing the silane in the container to produce a noticeable fog. The fabric, after equilibration in an atmosphere of about 50% relative humidity is exposed to the silane aerosol atmosphere in the beaker, and is then removed and immersed in a warm (e. g. 100° F.) concentrated aqueous solution of sodium bicarbonate, containing a small amount of a wetting agent (e. g. 0.02% by weight of an ordinary nonionic wetting agent such as Triton X100, sold by Rohm & Haas Co., Philadelphia, Pa., and described as an alkyl aryl poly ether alcohol) and is agitated therein. The fabric is then removed, rinsed in water and dried.

Samples of cotton muslin were treated by the procedure outlined above at various times and temperatures, and the tensile strengths of them were then measured to determine the degree of degradation. Untreated samples exhibited a tensile strength warpwise of about 65 lbs./inch. The results of the various treatments are shown in Table I.

¹ Actual analysis: (CH₃)₂SiCl₂—38.1% ; CH₃SiCl₃—48.3% ; SiCl₄—0.3% . By weight (CH₃)₂SiCl₂—2.9% ; CH₃SiHCl₂—0.7% ; miscellaneous high boiling point inert resinous material—9.7%.

Table I

Example	Temp. of Treatment, ° F.	Time of Exposure	Tensile Strength, lbs./inch
1	75	1 sec.	67
2	75	8 sec.	65
3	75	20 sec.	61
4	85	2 sec.	64
5	85	8 sec.	59
6	85	30 sec.	57
7	85	2 min.	51
8	85	5 min.	46
9	104	2 sec.	58
10	104	8 sec.	62
11	104	15 sec.	45

Each of the treated samples was found to be water repellent by the fact that water showered on them formed droplets which were readily shed, and from Table I it will be seen that under the preferred condition, the treated fabric has retained upwards of 90% of its tensile strength.

Similar results may also be attained with fabrics of rayon, acetate and mixtures of these with other fibers such as wool or nylon.

Paper may also be treated in this manner with equally advantageous results in being made water repellent without serious loss of strength. Moreover, the wet strength of the paper is greatly increased.

A typical procedure for continuously treating fabrics or paper by the process of this invention consists in advancing the material through a chamber in which is circulated an aerosol mixture of air and the silane. A preferred apparatus for continuously carrying out the process of this invention is described in detail below with reference to the drawings in which:

Fig. 1 is a plan view of the apparatus, and
Fig. 2 is a side elevation of the apparatus.

The apparatus consists of an elongated chamber 10 having a row of ports 12 and 14 in each side wall, and a U-shaped duct having a leg 16 and 18 extending along each side wall and connecting with the row of ports therein, and a section 20 connecting the legs and extending around an end of the chamber. The connecting section 20 houses a fan 22 in front of which is a spray injector 24 through which the silane is introduced under pressure and atomized into aerosol-size particles.

The fabric 25 enters the chamber 10, through a slit 27 glanded by a rubber strip 28 and passes up and down through the chamber around overhead rollers 30 (some of which are driven rollers 30a for advancing the fabric) and lower rollers 32, then out through a second glanded slit 34. From the chamber the fabric is passed through a neutralizing tank 36 under one or more dunking rollers 38, then through a similar rinsing tank (not shown), and finally through a drier, for instance, a standard tenter drier, (not shown).

In operation, the atmosphere in the chamber 10 is circulated by the fan 22 while the silane is introduced and atomized in the air stream to provide an aerosol atmosphere within the chamber. The fabric 25 is then run through the chamber at a rate to provide the desired exposure time, while additional silane is supplied from the spray injector 24, to maintain the aerosol atmosphere.

As has been pointed out above, constant precise correlation of the rate of introduction of silane with the rate of fabric passage is not necessary, since the presence of aerosol particles assures constant and uniform concentration of the silane vapor content of the atmosphere at saturation value, and thus assure uniform treatment of the fabric. The rate of supplying silane in a typical operation is 2% by weight of the weight rate of fabric passage.

After the fabric leaves the chamber, it is run through the neutralizing bath 36, conveniently, a warm saturated aqueous solution of sodium bicarbonate containing a wetting agent, and is then rinsed and dried in the rinsing tank and drier.

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It is not completely understood why fabrics treated in accordance with this invention are not impaired by degradation or loss of strength. It is believed, however, that the silane reacts with surface moisture in the fabric and with free hydroxyl groups in the cellulosic fibers to form a water repellent surface coating accompanied by the liberation of a hydrogen halide, and that degradation is avoided by maintaining careful control over the time-temperature conditions during the exposure to the silane and by complete and immediate neutralization and removal of the acid reaction by-products.

A woven fabric consisting of about 30% animal fibers and of about 70% of an approximately 50-50 mixture of viscose and acetate rayons was treated according to the process of this invention. Subsequent tests showed no loss of tensile strength, an increase of about 15% in resistance to crease and wrinkle, and an abrasion resistance three times as great as that of the same fabric conventionally finished, as well as high water repellency which was no more than slightly reduced by five washings.

This application is a continuation-in-part of applicant's copending application, Serial No. 318,734, filed November 4, 1952, now U. S. Patent 2,782,090.

Having thus disclosed my invention and described in detail as representative thereof the best manner I have yet found of practicing it, I claim and desire to secure by Letters Patent:

1. In the method of reacting organo silicon halides having as organo substituents alkyl groups with between one and three carbon atoms, with cellulosic material comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating by contacting said material with said organo silicon halide in vapor form, the improvement of advancing said material continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said material by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said material in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, and continuously removing said material from said atmosphere.

2. In the method of reacting organo silicon halides having as organo substituents alkyl groups with between one and three carbon atoms, with cellulosic material comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating with the liberation of free hydrogen halide by contacting said material with said organo silicon halide in vapor form, the improvement of advancing said material continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas, and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said material by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said material in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, continuously removing said material from said atmosphere, and removing the liberated hydrogen halide from the material.

3. In the method of reacting organo silicon halides having as organo substituents alkyl groups with between one and three carbon atoms, with cellulosic fibrous sheet material reactive with said organo silicon halides to form a water repellent surface coating with the liberation of free hydrogen halide by contacting said material with said organo silicon halide in vapor form, the improvement of advancing said material continuously into contact with an atmosphere comprising an aerosol mixture

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of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said material by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said material in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, continuously removing said material from said atmosphere, and finally neutralizing and removing hydrogen halide by contacting the material with a basic aqueous solution having a pH between 7 and 11.

4. In the method of reacting organo silicon halides selected from the group consisting of: methyl trichlorosilane; dimethyl dichlorosilane; methyl dichlorosilane; trimethyl chlorosilane; and mixtures of the foregoing silanes, with cellulosic material comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating by contacting said material with said organo silicon halide in vapor form, the improvement of advancing said material continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said material by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said material in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, and continuously removing said material from said atmosphere.

5. In the method of reacting organo silicon halides selected from the group consisting of: methyl trichlorosilane; dimethyl dichlorosilane; methyl dichlorosilane; trimethyl chlorosilane; and mixtures of the foregoing silanes, with cellulosic fibrous sheet material reactive with said organo silicon halides to form a water repellent surface coating with the liberation of free hydrogen chloride by contacting said material with said organo silicon halide in vapor form, the improvement of advancing said material continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said material by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said material in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, continuously removing said material from said atmosphere, and finally neutralizing and removing hydrogen chloride by contacting the material with a basic aqueous solution having a pH between 7 and 11.

6. The process defined by claim 5 wherein the material is exposed to the atmosphere at a temperature of less than about 100° F. and for a time of not more than about six minutes.

7. In the method of reacting organo silicon halides having as organo substituents alkyl groups with between one and three carbon atoms, with a fabric comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating with the liberation of free hydrogen halide by contacting said fabric with said organo silicon halide in vapor form, the improvement of advancing said fabric continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said fabric by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said fabric in contact with said atmosphere until the

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organo silicon halide vapor reacts therewith and renders it water repellent, continuously removing said fabric from said atmosphere, and removing the liberated hydrogen halide from said fabric.

8. In the method of reacting organo silicon halides selected from the group consisting of: methyl trichlorosilane; dimethyl dichlorosilane; methyl dichlorosilane; trimethyl chlorosilane; and mixtures of the foregoing silanes, with a fabric comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating with the liberation of free hydrogen chloride by contacting said fabric with said organo silicon halide in vapor form, the improvement of advancing said fabric continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said fabric by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said fabric in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, continuously removing said fabric from said atmosphere, neutralizing and removing hydrogen chloride by contacting the fabric with a basic aqueous solution having a pH between 7 and 11.

9. In the method of reacting organo silicon halides having as organo substituents alkyl groups with between one and three carbon atoms, with paper comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating by contacting said paper with said organo silicon halide in vapor form, the improvement of advancing said paper continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon

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halide vapor adjacent to the surface of said paper by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said paper in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, and continuously removing said paper from said atmosphere.

10. In the method of reacting organo silicon halides having as organo substituents alkyl groups with between one and three carbon atoms, with paper comprising cellulosic fibers reactive with said organo silicon halides to form a water repellent surface coating with the liberation of free hydrogen halide by contacting said paper with said organo silicon halide in vapor form, the improvement of advancing said paper continuously into contact with an atmosphere comprising an aerosol mixture of liquid particles of said organo silicon halide dispersed in an inert gas and maintaining a constantly substantially saturated vapor phase of said organo silicon halide vapor adjacent to the surface of said paper by supplying and maintaining dispersed liquid particles of said organo silicon halide in said atmosphere, maintaining said paper in contact with said atmosphere until the organo silicon halide vapor reacts therewith and renders it water repellent, continuously removing said paper from said atmosphere, and removing the liberated hydrogen halide from the paper.

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