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FIBROUS PRODUCT

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4 Claims. (Cl. 91—68)

This invention relates to a new type of paper and more particularly to a noiseless, water-proof paper.

This invention has as an object the preparation of a paper which is relatively noiseless and water-proof. A further object is the preparation of such paper containing waxes and other agents used for softening and water-proofing. A still further object is the preparation of such a paper on which the waxes and other softening and water-proofing agents are so fixed as not to penetrate from the paper into adjacent absorbent material even at temperatures above the melting points of the water-proofing and softening materials. A further object of the invention is the preparation of agents for use in the manufacture and treatment of paper to attain these particular properties. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a fibrous organic sheet material such as paper or cloth is impregnated with suitable softening and thereafter with water-proofing agents. these agents being fixed by means of an anchoring agent to the fibers of the paper or cloth.

It has been found that softening agents which have been applied to paper to soften it and thereby reduce the resulting noise produced on handling and to make it water-proof, can be so anchored to the fibers by certain agents that these agents will not bleed from the paper at temperatures even above their melting points. Cloth, as softened according to the present art, is treated with water soluble softening agents which are removed almost entirely in the first wash, leaving the cloth with an undesirable harsh finish. In the process of the present invention, the desirable soft finish obtained by treatment with the softening agents is made to survive laundering, by means of aftertreatment with deacteylated chitin. In the preferred mode of operation of the present invention, the paper or cloth in sheet form is impregnated with a softening agent in one bath and then with the water-proofing and anchoring agents in the second bath. The preferred softening agent is a mixture of aliphatic alcohols and salts of sulfated aliphatic alcohols containing twelve to twenty carbon atoms. The water-proofing agent and anchoring agent are preferably applied by means of an aqueous emulsion containing deacetylated chitin, a water-proofing material, and an acid-stable wetting agent with or without a fixing agent.

The preferred process is illustrated by the first of the following examples:

Example 1

The paper in a continuous sheet was passed through a bath at 170–180° F. containing:

3.0% octadecyl alcohol which has been 50% sulfated as the sodium salt
3.6% octadecyl alcohol (Techn.)
0.4% sodium 9, 10-octadecenylsulfate
1.5% propylene glycol
92.5% water

The paper was then passed between squeeze rolls and dried to 5–15% moisture. Then it was passed through a second bath at 140–150° F. containing:

30% of an emulsion, prepared mechanically and at a temperature such that the waxes were liquid, of:
16.7 parts Asiatic wax
1.3 parts partially deacetylated chitin
0.7 part diethylcyclohexylamine salt of dodecyl acid sulfate
1.3 parts glacial acetic acid
1.9 parts aluminum acetate
78.1 parts water
6% of a solution containing 3% partially deacetylated chitin in 0.9% acetic acid.
64% water

The paper was again passed between squeeze rolls and was thoroughly dried to less than 5% moisture.

Crepe paper of 10% shrinkage weighing 20 pounds per 24" x 36" ream and treated by this process, was highly water-resistant and produced very little noise or rustle on handling. When the paper was pressed against a layer of absorbent paper for several minutes at 250–300° F., the absorbent paper showed no loss of absorbency by absorption of waxes from the treated paper. All waxes used in the above process melt below 210° F.

Example 2

Paper in a continuous sheet was passed through a bath at 110–130° F. prepared by adding;

4.4 parts refined mineral oil of 85–100 Saybolt units viscosity at 100° F.
0.7 part 9, 10-octadecenyl alcohol
2.9 parts diethylcyclohexylamine salt of hexadecyl acid sulfate
To 1.5 parts propylene glycol
And 90.5 parts water

The paper was then passed between squeeze rolls and dried to 5–15% moisture. Then it was passed through a second bath at 140–150° F. containing:

25% of the methanically prepared emulsion used in the second operation of Example 1
5% of a solution containing 3% of partially deacetylated chitin in 0.9% acetic acid
70% water

The paper was again passed between squeeze rolls and was thoroughly dried to less than 5% moisture.

Crepe paper similar to that treated in Example 1 was treated by this process. It was found highly water resistant but more noisy than paper treated by the process of Example 1. The oils and waxes were equally as firmly fixed to the paper as those of Example 1 as determined by the test of Example 1.

Example 3

The paper in a continuous sheet was passed through a bath at 140–150° F. prepared by—

Adding 1.0 parts diethylcyclohexlamine salt of dodecyl acid sulfate
4.0 parts refined paraffin wax melting from 120–125° F.
0.1 part octadecyl alcohol
To 1.4 parts ethylene glycol
And 92.5 parts water

The bath was best prepared by melting together the first three ingredients and adding the molten mixture to the water and ethylene glycol at a temperature of 180–200° F.

The paper was then passed between squeeze rolls and dried to 5–15% moisture. Then it was passed through a second bath identical to the second bath used in Example 2, passed between squeeze rolls and was thoroughly dried to less than 5% moisture.

Crepe paper of 15% shrinkage weighing 15 pounds per 24" x 36" ream and treated by this process was equal to paper treated by Example 2 with respect to water-resistance, freedom from noise and the permanency with which the waxes were fixed to it.

Example 4

The paper in a continuous sheet was passed through a bath at 140–150° F. containing

20% commercial 50% sulfonated beef tallow
2% glycerine
78% water

The paper was then passed between squeeze rolls and dried to 5–15% moisture. Then it was passed through a second bath identical to the second bath used in Example 1.

Example 5

The paper in a continuous sheet was passed through a bath at 120–130° F. prepared by adding:

10 parts commercial 75% sulfonated castor oil
4 parts refined mineral oil 80–100 Saybolt units viscosity at 100° F.
To 2 parts glycerine
And 84 parts water

The paper was then passed between squeeze rolls and dried 5–15% moisture. Then it was passed through a second bath identical to that used in the second bath of Example 1. The paper was then again passed between squeeze rolls and was thoroughly dried to less than 5% moisture.

Crepe paper of 10% shrinkage and weighing 20 pounds per 24" x 36" ream and treated by the processes of Examples 4 and 5 was highly water-resistant and produced very little noise on handling. Further the waxes and oils were found to be very firmly anchored to the paper when the paper was subjected to the test described under Example 1. However, paper treated by Examples 4 and 5 was less satisfactory in all respects than that treated by Examples 1, 2 and 3.

Example 6

The paper was passed in a continuous sheet through a bath at 120–150° F. containing:

0.8% trimethyloctadecylammonium bromide
2% propylene glycol
97.2% water

The paper was passed between squeeze rolls and dried to 5–15% moisture. Then it was passed through a second bath identical to the second bath used in Example 1, and dried to less than 5% moisture.

Example 7

The paper was passed in a continuous sheet through a bath at 120–150° F. containing:

0.5% hexadecylpyridinium bromide
2.0% glycerine
97.5% water

The paper was passed between squeeze rolls and dried to 5–15% moisture. Then it was passed through a second bath identical to the second bath used in Example 1 and dried to less than 5% moisture.

As alternatives for the trimethyloctadecylammonium bromide and hexadecylpyridinium bromide of Examples 6 and 7, the following may be mentioned:

Dimethylhexadecyloctadecylammonium bromide
Dimethylhexadecyloctadecylammonium chloride
Dimethyloctadecyl-B-hydroxyethylammonium chloride
Dimethyloctadecyl-B-chloroethylammonium chloride
Dimethyldioctadecylammonium chloride
Trimethylhexadecylammonium bromide

Softening agents of the type used in Examples 6 and 7 (with the long carbon chain in the positive ion only) require a larger portion of the water-repellent bath to be applied to the paper than the softening agents of the earlier examples (with the long chain in the negative ion only) require. This is because, unlike the softening agents of the earlier examples, the softening agents of Examples 6 and 7 are not acted upon by the deacetylated chitin of the water-repellent bath to lose a portion of their surface active properties, which tend to counteract the action of the water-repellent agent. Accordingly the proportions of softening agents in the first baths of Examples 6 and 7 and the water-repellent agents of the second baths have been selected to give the maximum softening action compatible with satisfactory water repellency.

Cloth, such as viscose rayon taffeta, is softened and rendered wash fast by treating by a two step process.

The first bath contained 1–20 pts. softener (based on active ingredient) per 1000 pts. of water. One parts by weight of fabric was immersed in 20 pts. by weight of a treating liquor or was passed thru a pad mangle at such a temperature that the softening agent was dispersed or dissolved. This temperature will usually be above 90° F. and preferably 150–180° F. The treated fabric was wrung or extracted so that it contained 80–125% by weight of solution based on the weight of the dry fabric, dried preferably at 210–230° F., and immersed in a second bath containing deacetylated chitin of such concentration that a wash fast finish was imparted.

Example 8

Viscose rayon taffeta was immersed for 30 seconds in a bath containing one gram per liter of a softening agent consisting of a mixture of sulfated and unsulfated octadecyl alcohol. One portion A) of the taffeta was dried directly while another portion (B) was immersed for 30 seconds in a bath at 120° F. containing 10 grams per liter of 3% deacetylated chitin (30 g deacetylated chitin, 9 g acetic acid per liter) and dried. Another portion (C) was immersed for 30 seconds in a bath at 120° F. containing 25 grams per liter of 3% deacetylated chitin solution and dried. Samples A and B were approximately equally softer than the untreated taffeta while C was somewhat harsher and stiffer than the untreated materials. Samples A and B were submitted to a washing test at 120° F. in 0.5% neutral oleate soap and dried. Sample B retained all of its softness while A was approximately the same as the untreated taffeta.

Example 9

The cloth was passed through a bath at 120–180° F. containing:

0.1% partially sulfated octadecyl alcohol as the sodium salt
99.9% water

The cloth was then passed between squeeze rolls, dried and passed through a bath containing:

2.0% of the emulsion used in the second bath of Example 1
98.0% water

The cloth was then passed between squeeze rolls.

Example 10

The cloth was passed through a bath at 120–180° F. containing:

1.0% sodium hexadecylsulfate
0.2% propylene glycol
98.8% water

The cloth was passed between squeeze rolls, dried and then passed through a second bath containing:

15% of the emulsion used in the second bath of Example 1
85% of water

The cloth was passed between squeeze rolls and dried as above.

Example 11

The cloth was passed through a bath at 120–180° F. containing:

2% commercial sulfonated olive oil
98% water

It was then passed between squeeze rolls, dried and passed through a bath containing:

20% of the emulsion used in the second bath of Example 1
80% water

The cloth was passed between squeeze rolls and dried.

The proportions of the softening bath (first bath) and the water-repellent bath second bath) of Examples 8, 9, 10, and 11 may be adjusted to give the maximum degrees of softening in the cloth and water-repellency, while maintaining the wash-fastness of the finish.

In the above examples, the anchoring agent is partially deacetylated chitin. This is a material only recently available to the arts. In copending application of George W. Rigby, Serial No. 716,300, filed June 25, 1934, there are disclosed methods for the preparation of this material and suitable salts thereof. The method is briefly purification of chitin bearing materials, such as crab, shrimp or lobster shells by boiling with one per cent sodium carbonate solution, washing with five per cent hydrochloric acid solution and again boiling with one per cent sodium carbonate solution, the purified chitin being then deacetylated by treatment with alkali, for example, forty per cent sodium hydroxide for such a time at such a temperature, i. e. 4 hours at 110° C., that the material becomes soluble in dilute acetic acid, forming viscous solutions from which coherent films may be obtained upon evaporation. The above described copending application discloses a large number of salts which are suitable for the process of the present invention, discloses how the conditions of deacetylation may be varied and how the viscosity of the material may be altered, being decreased by controlled oxidation and increased by suitable heating of the solid material.

In addition to the deacetylated chitin from crab, shrimp or lobster shells which as prepared by the process above described, contains from twenty to ninety per cent and preferably seventy to ninety per cent of its nitrogen in the form of free amino groups, the acid soluble film forming materials obtained by the regulated deacetylation of the outer integuments of insects such as locusts, beetles and grasshoppers, and those from vegetable sources, such as mycelium from fungi, such as aspergillus niger, may be employed.

Anchoring agents of the deacetylated chitin type are much preferred to lacquers such as those of Ensminger U. S. Patent 1,915,301 as anchoring agents since, being applied from aqueous solutions, they are less hazardous from the fire and health standpoint and also waste no expensive volatile solvents. A further, and the more important, advantage lies in the markedly superior properties of the product.

In the process of the present invention, paper is softened by means of a softening agent in a first step. The softening agent is any material which when applied to paper softens it in such a manner as to reduce materially or to eliminate the rustling or cracking noisy characteristics of paper which are apparent when it is bent or flexed. The degree to which softening in this sense is accomplished depends on the amount and nature of the agent. Paper softening agents in general may be used, and the invention includes in its scope the use of all paper softening agents. The following classes of softening agents are listed in the order of their effectiveness in the present application:

(1) Metallic and organic base salts of the sulfate esters of aliphatic alcohols containing 10 to 20 carbon atoms, e. g., sodium hexadecylsulfate or diethylcyclohexlamine salt of dodecyl acid sulfate.

(2) Sulfonated vegetable and animal oils, fats

and waxes, e. g. sulfonated castor oil, sulfonated olive oil, sulfonated beef tallow, etc.

(3) Sulfonated mineral oil.

(4) Free fatty acids with 12 to 20 carbon atoms, e. g., palmitic, oleic, and stearic acids and the salts thereof.

(5) Positively charged agents containing a long carbon chain e. g. hexadecyltrimethylammonium bromide, octadecyldimethylsulfonium methylsulfate.

(6) Animal, vegetable and mineral oils, fats and waxes, e. g., beef tallow, olive oil, mineral oil ranging from 50–400 Saybolt units viscosity at 100° F., petrolatum and paraffin waxes.

(7) Synthetic oils, fats and waxes, e. g., aliphatic alcohol with 10–20 carbon atoms, halogenated aliphatic hydrocarbons with 10–20 carbon atoms and halogenated aromatic hydrocarbon waxes.

The preferred paper softening agents contains a long chain hydrocarbon radical together with a highly polar group. The particularly preferred agents are those wherein the long chain hydrocarbon radical is contained in the negative ion, as for example, in the case of the sodium hexadecylsulfate.

The softening agents need not be applied by means of an aqueous emulsion, although this is preferable because of the reduced fire and health hazard and the greater economy as compared with application from solution in a volatile organic solvent. In the preferred process of the present invention, a water-proofing agent is applied to the paper; this is any agent which when applied to paper resists the absorption of moisture into the paper and the penetration of the moisture through the paper. The degree to which moisture is repelled by the paper depends on the nature and amount of the water-proofing agent present and the presence or absence of surface active agents which are capable of resisting the penetration of moisture in the paper. The fat alcohol sulfate derivative and similar water-soluble softening agents which are applied to paper by the processes of this invention tend to counteract the actions of the water-proofing agents, and their presence requires the use of additional quantities of water-proofing agents to obtain a given degree of water-proofing. The proper choice and softening agents used to obtain a suitably water-proofed and softened paper is a contribution to the art made only by this invention.

Water-proofing agents comprising an emulsion of a wax in a solution of deacetylated chitin as disclosed in the co-pending application of David McQueen and Warner J. Merrill, Serial No. 11,273, filed March 15, 1935, are the preferred water-proofing agents in the process of the present invention. However, paraffin waxes, Japan wax, carnauba wax, higher aliphatic alcohols, and synthetic waxes, applied from a bath of molten wax or from solution in an organic solvent, mineral oils, natural and synthetic resins and waterproof lacquers also serve as water-proofing agents.

The purposes of the present invention are best served by a high melting wax. Animal oils may be employed, although these do not give as satisfactory a result as do the waxes. The addition of an emulsifying agent to the mixture of wax in the aqueous solution of the deacetylated chitin is highly desirable and the fat alcohol acid sulfates are particularly preferred in this connection.

In the process of the present invention, the water-proofing agent is fixed to the paper or other fibrous organic sheet material such as cloth by means of deacetylated chitin. This so attaches water-proofing agents to the fibers of the paper that when heated above its melting point and present in sufficient quantity to make the paper water-proofed, the molten water-proofing agent will not be absorbed from the paper into a layer of absorbent paper in contact with the water-proofed sheet.

A test for determining whether the water-proofing agents are sufficiently fixed or anchored to the paper and will not bleed therefrom is performed as follows:—The water-proofed sheet of paper is placed on several thicknesses of water leaf or absorbent paper and the sheets are pressed together to establish contact at essentially all points. The packet is then placed in an oven and heated to 300° C. for thirty minutes. The water-proofed sheet is then removed from the packet. The absorbency of the packet of water leaf paper is determined by observing the number of layers through which colored water will penetrate from the side of the packet which has not been in contact with the water-proofed sheet as compared with an equally thick packet of water-leaf paper. The packet must be thin enough to penetrate through it before the test. When the water-proofing agents are fixed or anchored to the paper satisfactorily, water leaf paper will not lose any absorbency as determined by this test.

In Example 1 and certain of the other examples, the use of aluminum acetate in the use of wax emulsion is disclosed. This material improves the stability of the water-proofing agent and gives better fixing action of the water-proofing agent on the paper. As disclosed in the above-identified McQueen and Merrill application, other polyvalent metal salts soluble in the aqueous solution of deacetylated chitin without reacting therewith may be employed, e. g., the chlorides, nitrates, acetates, and formates of aluminum, thorium, calcium, lead and zinc. The process of the present invention is preferably applied to an unsized, or very lightly sized, thin paper, preferably uncreped, with sufficient wet strength so that it may be run through two operations of the process. The process can be applied to thick paper such as blotting paper, to some advantage. The uses, however, of a softened, water-proofed paper are in general such that a thin unsized paper is desirable.

While the above examples disclose a second treatment with an emulsion of a water-proofing agent in a solution of a salt of deacetylated chitin, softened paper may be greatly improved by treatment with a solution of the anchoring agent alone or with pigments, delusterants, etc. added as shown in the following example:

The paper was passed through a bath at 120–180° F. containing:

1% sodium hexadecylsulfate
99% water

The paper was passed between squeeze rolls, dried, and then passed through a second bath, containing:

1% of 3% deacetylated chitin in 0.9% acetic acid
99% water

Other known softening agents for paper, such as sulfonated olive oil, beef tallow, emulsions of paraffin waxes prepared with sulfonated higher alcohols, soaps, and the like, may be substituted for the sodium hexadecylsulfate in this example.

The concentrations of the softening agent in the first bath and the fixing agent in the second bath may be varied to suit the requirements of the particular application for which the paper may be intended.

Paper treated in this manner is of use as soft, absorbent, non-linting paper toweling, provided the deacetylated chitin is not used in sufficient quantities to make the paper non-absorbent. Such paper may also be used as noiseless wind-proof lining for clothing.

Paper treated as in Example 12 is not water-proofed to a high degree and for many important purposes is insufficiently water-proof.

Fabrics treated with softeners which are incompatible in solution with Daktose may be treated in a second bath with a dispersion of a delustering pigment in deacetylated chitin salt solutions. This treatment makes the softening effect wash-fast in addition to delustering the fabric. Such a process is similar to the above examples of aftertreating softened fabrics with water-proofing emulsions, or with deacetylated chitin salt solutions alone, which fixes the softener to the fibers through the action of the deacetylated chitin salt solutions. This is illustrated by the following examples:

Example 13

Cloth was passed through a bath at 120–180° F., containing:

1% sodium hexadecylsulfate
99% water

The cloth was passed between squeeze rolls, dried, and then passed through a second bath, containing:

5% of a dispersion of 25 parts of lithopone in 1.25 parts partially deacetylated chitin, 0.4 parts glacial acetic acid and 73.35 parts water
95% water

The cloth was passed between squeeze rolls and dried.

Example 14

The cloth was passed through a bath at 120–180° F. containing:

2% of 75% commercial sulfonated olive oil
98% water

The cloth was passed between squeeze rolls, dried and then passed through a second bath, containing:

5% of a dispersion of 25 parts of titanium dioxide in 1.25 parts partially deacetylated chitin, 0.4 parts glacial acetic acid, and 73.35 parts water
95% water

The cloth was passed between squeeze rolls and dried.

Other known commercial softening agents, such as fatty alcohol sulfate derivatives, sulfonated oils, fatty acid salts, and emulsions of oils and waxes prepared with emulsifying agents known to the art, may be used in the first bath of this process. Other pigments than lithopone and titanium dioxide which have a delustering effect may be used. Other such pigments are bentonite, barium sulfate and zinc sulfide, alone as well as combined to form lithopone, and similar pigments. The processes are to be particularly applicable to viscose fabrics which particularly require softening and delustering in finishing.

Paper having the property of relative noiselessness and water-proofness combined with a fixing of the water-proof agent to the paper to such an extent that these waxes do not penetrate into adjacent absorbent material even on exposure to relatively elevated temperatures, has a wide variety of applications and fulfills a long felt want. The following specific applications indicate the utility of this paper:

1. Sanitary napkins, diapers, and surgical dressings:

The water-proof, noiseless paper may be used as a water-proof layer on absorbent pads to prevent penetration of absorbed liquids through the pad. The resistance of the waxes to heating allows the sanitary napkins, diapers, or surgical dressings to be subjected to sterilization temperatures of 250–300° F. without reduction of the absorbent properties of the absorbent pad through penetration of the waxes and oils into the absorbent paper. In this application noiselessness is a very important property of the paper, to such an extent as to preclude the use in this application of otherwise extremely satisfactory materials.

2. Water-proof lining for clothing:

The water-proof noiseless paper may be used as a water-proof inner lining for clothing which is noiseless and prevents moisture from penetrating through the clothing but without penetration of the waxes in the paper onto the clothing during pressing or ironing.

3. Water-proof wrapping paper:

The treated paper may be used as a water-proof wrapping for those cases where loss or easy removal of the waxes from the paper is objectionable. The finish on the treated paper, thus treated, does not crack or break on bending and thereby lose its water-proof properties as is the case with wax finishes applied from a bath of molten wax.

4. Water-proof paper articles:

The above method of treating paper to produce a soft, water-proof finish may be used for water-proofing paper articles such as cups, envelopes, decorations, etc. The water-proof finish produced by this method leaves the paper much more pliable and freer from the waxy feeling of the usual waxed water-proof finishes on paper. The method of water-proofing and softening has the advantage that it can be applied from an aqueous bath rather than from a bath of molten waxes as is the usual practice.

5. Paper garments.

All-paper garments which are soft, noiseless, pliable and free from an undesirable waxy feeling, but sufficiently water-proof to retain their tensile strength when subjected to moisture such as showers can be made from this noiseless, water-proof paper.

The above description and examples are intended to be illustrative only and any modifications and variations therefrom which conform to the spirit of the invention are to be included in the scope of the claims.

I claim:

1. A process for the preparation of water-resistant fibrous organic sheet material and of reduced noisiness which comprises impregnating fibrous organic sheet material with an aqueous mixture of an aliphatic alcohol of 12–20 carbon atoms and a water soluble salt of a sulfated aliphatic alcohol of 12–20 carbon atoms and thereafter with an aqueous emulsion of a wax in an aqueous solution of deacetylated chitin, said paper being then re-

sistant to flow of the wax at temperatures above the melting point of the wax.

2. A process for the preparation of water-resistant fibrous sheet paper of reduced noisiness which comprises impregnating fibrous sheet paper with an aqueous mixture of an aliphatic alcohol 12–20 carbon atoms and a water soluble salt of sulfated aliphatic alcohol of 12–20 carbon atoms and thereafter with an aqueous emulsion of a wax in an aqueous solution of deacetylated chitin, said paper being then resistant to flow of the wax at temperatures above the melting point of the wax.

3. Water-resistant fibrous organic sheet material impregnated with a mixture of an aliphatic alcohol of 12–20 carbon atoms and a water soluble salt of a sulfated aliphatic alcohol of 12–20 carbon atoms and thereafter with an emulsion of a wax in aqueous deacetylated chitin, said fibrous organic sheet material being resistant to flow of the wax at temperatures above the melting point of the wax.

4. Water-resistant fibrous sheet paper impregnated with a mixture of an aliphatic alcohol 12–20 carbon atoms and a water soluble salt of a sulfated aliphatic alcohol of 12–20 carbon atoms and thereafter with an emulsion of a wax in aqueous deacetylated chitin, said fibrous sheet paper being resistant to flow of the wax at temperatures above the melting point of the wax.

LUTHER B. ARNOLD, JR.

CERTIFICATE OF CORRECTION.

Patent No. 2,142,986. January 10, 1939.

LUTHER BISHOP ARNOLD, JR.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 73, for the word "parts" read part; page 3, second column, line 2, before "second" insert a parenthesis; page 5, second column, line 68, claim 1, strike out "and"; page 6, first column, line 6, and second column, line 7, claims 2 and 4 respectively, after "alcohol" insert of; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of April, A. D. 1939.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.