

UNITED STATES PATENT OFFICE

2,160,375

WATER-REPELLENT TEXTILE MATERIAL AND PROCESS OF MANUFACTURING IT

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10 Claims. (Cl. 91-68)

This invention relates to water-repellent tex-
tile material and to a process of manufacturing
the material and is a continuation in part of our
application Ser. No. 94,482, filed August 5, 1936
and entitled "Water-repellent material and a
process of manufacturing the material".

We have found that textile materials can be
made water-repellent in an advantageous manner
by treating them with solutions or emulsions of
mixed polymerizates which are prepared from
maleic anhydride the free acid or a functional
derivative thereof and vinyl-esters of higher fatty
acids (having at least 12 carbon atoms), for in-
stance, according to the process described in
U. S. Patent 2,047,398 for manufacturing mixed
polymerisation products from maleic acid an-
hydrides and vinyl esters (see Example 4 of the
U. S. Patent 2,047,398). These mixed polymeri-
zates yield stable solutions or emulsions which,
when applied to textile fibers, especially fibers of
vegetable origin, such as, for instance, cotton,
have a very good waterproofing action, the treated
material being repellent to water to a very high
extent. The material has this property directly
after the treatment and does not require an after-
treatment, as is the case in most similar processes.

With the same good result there may also be
used the mixed polymerisate from maleic anhy-
dride and the vinyl ether of an aliphatic alcohol
of high molecular weight with at least 12 carbon
atoms in the molecule, as free acid or a functional
derivative thereof. These mixed polymerisates
which as previously stated are obtainable ac-
cording to the process described in U. S. Patent
2,047,398 (see Example 6 for the manufacture of
mixed polymers from maleic acid anhydride and
vinyl ethers) or which may be obtained by mutual
polymerisation of a functional derivative of maleic
acid and of a vinyl ester or vinyl ether of high
molecular weight are composed of compounds of
the formula:



wherein R_1 and R_2 stand for a member of the
group consisting of COOH , COO , alkyl, CN ,
 CONH_2 . R_1 and R_2 together represent



and compounds of the formula



wherein X stands for R, OR or O.OCR, R repre-
senting an aliphatic hydrocarbon radical with at
least 12 carbon atoms.

The reaction upon the textile materials is ex-
ecuted in the following way: The textile ma-
terial is introduced into the solution or emulsion
of the mixed polymerisate and, after drying in
the air, dried for a short time at a higher tem-
perature (at about 100°C.).

The above described process is distinguished
by the fact that the fiber is not only made water-
proof when treated in this manner but that it
retains its waterproofness even after repeated
washing to an extent which could hitherto not
be attained by any process, that is to say, the
mixed polymerizates above characterized are so
intimately combined with the fiber that similar
to fast-dyestuffs, they irreversibly adhere to the
fiber.

The following examples serve to illustrate the
invention but they are not intended to limit it
thereto:

(1) A web of cotton or artificial silk is im-
pregnated with a solution of 0.5 per cent strength
of the mixed polymerisate from vinyl-octodecyl-
ether and maleic-acid-dimethylester in carbon
tetrachloride or a mixture thereof with alcohol,
and is dried at ordinary temperature. The web
thus treated has a very good water-repellent
effect and does not lose this property even when
repeatedly washed or boiled with water.

(2) Loose wool is impregnated as indicated in
Example 1 with a solution of the mixed polymeri-
sate from vinyl-octodecyl-ether and maleic acid
in a mixture consisting of methylene chloride and
ethyl-alcohol. After drying, the wool thus treat-
ed shows an enhanced water-repelling effect
which it does not lose by washing.

(3) A web of cotton or artificial silk is im-
pregnated with a solution in methylene chloride
of the mixed polymerisate from vinyl-stearate
and the semi-ester of maleic acid with methyl
alcohol, and is dried at ordinary temperature.
The fabric thus treated has a very good water-
repellent effect and does not lose this property
even after repeated washing or boiling with
water.

(4) A web of viscose artificial silk is treated
with a solution of 0.5% strength in alcohol and
carbon tetrachloride of the mixed polymerisate
from maleic acid and vinyl-octodecyl-ether ob-
tained by treating with steam the anhydride
mixed polymerisate and dried for a short time.
The fabric thus treated has a very good water-

repellent effect and does not lose this property even by washing or boiling.

(5) Loose spun rayon is impregnated with a solution of 2% strength in carbon tetrachloride of the mixed polymerisate from vinyl-stearate and maleic acid monomethyl ester, squeezed and dried. The spun rayon thus treated is very hydrophobe and does not lose this property by subsequent fulling.

(6) Piece goods consisting of a mixture of wool and spun rayon are impregnated with an aqueous solution of 1% strength of the pyridine salt of a mixed polymerisate from maleic acid and vinyl-hexadecyl ether and subjected for a short time to a heat treatment at 90° C.-100° C. The material thus treated has a very good water-repellent effect and does not lose this property even by washing.

(7) Loose cotton is impregnated with an aqueous solution of 0.8% strength of the amide-ammonium salt of the mixed polymerisate from maleic acid and vinyl stearate, obtainable by the treatment of the anhydride with dry ammonia, and dried. Cotton thus treated has the same properties as those of the material obtained according to Example 6.

(8) A cotton fabric is impregnated by passage through a solution of a mixed polymerizate from vinyl stearate and maleic anhydride in methylene chloride, dried by exposure to air and heated for half-an-hour to about 100° C. The fabric thus treated is highly repellent to water and does not lose the property even after repeated washing with water and soap.

(9) A cotton or artificial silk fabric is impregnated with an aqueous emulsion of a mixed polymerizate from vinyl palmitate and maleic anhydride and worked up as indicated in Example 8. If desired the heat-treatment may be followed by a further treatment with aluminium formate, whereby the water-repelling effect is further increased. This fabric also retains its water-repellent property after repeated washing.

(10) Loose wool is immersed into a solution of 5 per cent strength of a mixed polymerizate from vinyl stearate and maleic anhydride, pressed and dried at 90-100° C. The material thus treated has an increased resistance to water.

(11) A fabric of cotton or artificial silk is impregnated with a solution of a mixed polymerizate from vinyl octo-decyl ether and maleic anhydride in ethylene chloride, dried and then heated for a short time at about 100° C., whereby the mixed polymerizate is intimately combined with the fibre. The fabric thus treated is highly repellent to water and does not lose this property even when washed with water and soap.

Instead of the aforesaid mixed polymerizate from maleic anhydride and vinyl octodecyl ether, the mixed polymerizate from maleic anhydride and the vinyl ether of the alcohol mixture obtainable by reduction of the coconut oil fatty acid and which contains chiefly carbon chains with 12 to 14 carbon atoms, may be applied in a similar manner for rendering the textile fiber highly waterproof.

(12) A cotton fabric is impregnated with a solution of 0.5% strength of a mixed polymerizate of maleic anhydride and vinyl dodecyl ether in carbon tetrachloride and dried subsequently, finally for a short time at a temperature of 100° C. The fabric treated in this manner is highly repellent to water and does not lose this property even when washed with water and soap.

(13) A fabric of viscose artificial silk is im-

pregnated with a solution of 0.2 per cent strength of a mixed polymerizate of maleic anhydride and the vinyl-ether of the montan wax alcohol of the formula $C_{27}H_{55}C(C_2H_5)_2OH$ in methylene-chloride. After drying which is finally performed for a short time at a temperature of 100° C., this artificial silk shows an extraordinarily good water-repellent effect, and does not lose this property when extracted with organic solvents or boiled or washed with water.

(14) Loose wool is impregnated with a solution of 0.5 per cent strength of a mixed polymerizate of maleic anhydride and hexa-decylene in carbon tetrachloride. The material thus treated shows after drying which is finally performed for a short time at a temperature of 100° C., an excellent water-repellent effect and a great stability to water.

We claim:

1. A process for waterproofing textile materials which comprises treating the textile materials with baths containing mixed polymerisates being composed of compounds of the formula:



R₁ and R₂ standing for a member of the group consisting of COOH, COO, alkyl, CN and CONH₂ and R₁ and R₂ together stand for



and compounds of the formula:



wherein X stands for a member of the group consisting of R, OR, O.O.C.R, R standing for an aliphatic hydrocarbon radical with at least 12 carbon atoms.

2. A process for waterproofing textile materials which comprises treating the textile materials with baths containing mixed polymerisates being composed of maleic acid of the formula:



and compounds of the formula:



wherein X stands for a member of the group consisting of R, OR, O.O.C.R, R standing for an aliphatic hydrocarbon radical with at least 12 carbon atoms.

3. A process for waterproofing textile materials which comprises treating the textile materials with baths containing mixed polymerisates being composed of maleic acid of the formula:



and vinyl octodecylether.

4. A process for waterproofing textile materials which comprises treating the textile materials with baths containing mixed polymerisates being composed of maleic acid of the formula:



and vinylhexadecylether.

5. Textile materials impregnated with mixed polymerisates being composed of compounds of the formula:



R₁ and R₂ standing for a member of the group

consisting of COOH, COO, alkyl, CN, and CONH₂ and R₁ and R₂ together stand for



and compounds of the formula:



wherein X stands for a member of the group consisting of R, OR, O.CO.R, R standing for an aliphatic hydrocarbon radical with at least 12 carbon atoms.

6. Textile materials impregnated with mixed polymerisates being composed of maleic acid of the formula

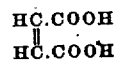


and compounds of the formula:



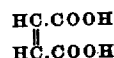
wherein X stands for a member of the group consisting of R, OR, O.O.C.R, R standing for an aliphatic hydrocarbon radical with at least 12 carbon atoms.

7. Textile materials impregnated with mixed polymerisates being composed of maleic acid of the formula:



and vinyloctadecylether.

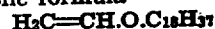
8. Textile materials impregnated with mixed polymerisates being composed of maleic acid of the formula:



and vinylhexadecylether.

9. A process of waterproofing textile materials which comprises treating the textile materials with baths containing mixed polymerizates from maleic anhydride and the compound of the formula $\text{H}_2\text{C}=\text{CH.O.C}_{12}\text{H}_{25}$.

10. Textile materials impregnated with mixed polymerizates from maleic anhydride and the compound of the formula



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CERTIFICATE OF CORRECTION.

Patent No. 2,160,375.

May 30, 1939.

ARTHUR VOSS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 46, and page 3, first column, line 1, claim 5, strike out the comma after "COO" and insert instead a period; page 1, first column, line 47, strike out the period after "CONH₂" and insert instead a comma; page 2, second column, line 27, claim 1, strike out the comma after "COO"; 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 19th day of September, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

consisting of COOH, COO, alkyl, CN, and CONH₂ and R₁ and R₂ together stand for



and compounds of the formula:



wherein X stands for a member of the group consisting of R, OR, O.CO.R, R standing for an aliphatic hydrocarbon radical with at least 12 carbon atoms.

6. Textile materials impregnated with mixed polymerisates being composed of maleic acid of the formula

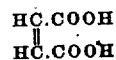


and compounds of the formula:



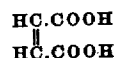
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7. Textile materials impregnated with mixed polymerisates being composed of maleic acid of the formula:



and vinyloctadecylether.

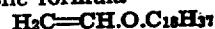
8. Textile materials impregnated with mixed polymerisates being composed of maleic acid of the formula:



and vinylhexadecylether.

9. A process of waterproofing textile materials which comprises treating the textile materials with baths containing mixed polymerizates from maleic anhydride and the compound of the formula $\text{H}_2\text{C}=\text{CH.O.C}_{12}\text{H}_{25}$.

10. Textile materials impregnated with mixed polymerizates from maleic anhydride and the compound of the formula



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