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COATED ARTICLES AND METHOD OF
MAKING SAME

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This invention relates to coated films and it
pertains particularly to moistureproof, coated,
non-fibrous sheets or films having a surface coat-
ing which tenaciously adheres to or is anchored
to the base film.

Ordinary sheets or films of regenerated cellu-
lose have been rendered moistureproof by coat-
ing with a moistureproofing composition compris-
ing in its preferred form a flowable solution of a
cellulose derivative, a wax or wax-like material,
a resin or blending agent and a plasticizer. These
coated sheets or films are very effective as a
wrapping material for such products as bread,
cake, candy, or the like, which it is desired to
maintain in substantially their original fresh
condition without any change in moisture content.
Such coated sheets, however, are frequently
unsuited for use as a wrapping material directly
in contact with products having an exceedingly
high water or moisture content, such as butter,
cheese, wet or frozen fish, ice cream or the like,
when such articles are kept over long periods of
time in storage. In direct contact with products
of high moisture content, such as these, the surface
moistureproof coating loosens and/or flakes off
from the sheet of regenerated cellulose and thereby
effectively destroys the moistureproof property of
the wrapping material and gives an unsightly appearance.

Various methods have been suggested for the
anchoring of moistureproof coatings to cellulosic
base sheets, but the present invention embraces a
method which overcomes disadvantages arising
from prior art methods.

One object of the invention comprises a process
of anchoring coatings to base materials.

A further object of the invention relates to the
production of coated films in which the coating
is permanently secured to the base film.

A further object of the invention relates to the
moistureproofing of non-fibrous, transparent,
cellulosic films suitable for use as a wrapping
tissue, in which a moistureproofing coating applied
to the base film remains securely anchored there-
to even when in direct contact with water over
substantial periods of time.

It has now been discovered that by a simple
process easily applicable to conventional equip-
ment such, for example, as that used for pro-
ducing sheets or films of regenerated cellulose,
cellulosic sheets can be produced with a surface
coating having a cellulose derivative base, prefer-
ably a moistureproof surface coating, which coat-
ing remains firmly anchored to the cellulosic
sheet for substantial periods of time even when

in direct contact with water or moisture, by
forming on the cellulosic sheet an extremely thin
deposit of an insoluble, inorganic substance. This
is accomplished, in general, by leading the cellu-
losic sheet or film through an aqueous solution
of a salt or ester capable of hydrolyzing or de-
composing at elevated temperatures to form a
volatile compound and an insoluble, inorganic
compound, and subsequently drying the sheet at
elevated temperatures, during which drying the
inorganic compound is formed on the sheet, pro-
ducing an extremely thin film or coating over
the surface of the sheet without interfering sub-
stantially with the transparency thereof, after
which said sheet is ready for the application of
the surface coating, usually a moistureproofing
surface coating.

The process of this invention is simple, work-
able and directly applicable to existing equipment
for the manufacture of moistureproofed, regen-
erated cellulose sheets.

As a base this invention contemplates any
smooth, dense, non-fibrous, preferably trans-
parent, cellulosic sheet or film precipitated from
an aqueous cellulosic solution or dispersion.
While the invention, in its preferred form, per-
tains to sheets or films of regenerated cellulose
whether precipitated from viscose or cupram-
monium cellulose solution, the invention may also
be applied to sheets or films of other cellulosic
materials, for example, such cellulose esters or
ethers as are precipitated from aqueous solutions
or dispersions such as glycol cellulose, cellulose
glycolic acid, methyl cellulose, ethyl cellulose, cellu-
lose phthalic acid and similar cellulosic products.
When any given coating composition is applied
to such cellulosic sheets or films, the coating com-
position will not penetrate therethrough and will
normally result in a surface coating.

As a surface coating this invention contem-
plates any film-forming composition with a cel-
lulose derivative base, such as nitrocellulose, cel-
lulose acetate, ethyl cellulose, benzyl cellulose or
other suitable ester or ether of cellulose, which
base may be modified as desired by the addition
of resins or blending agents, waxes or wax-like
materials, plasticizers, et cetera. In its preferred
form, this invention contemplates as a surface
coating a moistureproof coating comprising a cel-
lulose derivative and a wax or wax-like material
or other moistureproofing agent and preferably
a resin or blending agent and a plasticizer. The
invention also contemplates non-cellulosic coat-
ings, for example, resin-wax and rubber-wax

coatings which may be applied from a solution or from a melt.

As an anchoring medium the instant invention contemplates any inorganic oxide which is insoluble in water and in organic solvents of the type employed in coating compositions for use in coating regenerated cellulose and other non-fibrous cellulosic sheets, the said oxide being present on the surface of the cellulosic sheet in an extremely thin film or coating. This very thin film or coating of oxide, which may be so thin as to be substantially invisible and to have no apparent effect on the transparency of the sheet, is present on the surface of the cellulosic sheet as the result of applying to said sheet an aqueous solution of a salt or ester capable of dissociating readily at an elevated temperature to form an insoluble oxide and a volatile product, such as a volatile acid or alcohol, and subsequently drying the sheet at an elevated temperature sufficient to effect the desired dissociation and the removal of the volatile product formed. Obviously, if the transparency of the oxide coating is not essential, the same may be somewhat heavier without affecting the operativeness thereof as an anchoring medium. Since the cellulosic sheet is usually immersed in the aqueous salt or ester solution used, the salt or ester in question probably penetrates into the cellulosic sheet as well as being present on the surface, and consequently the resulting oxide is probably formed both in the sheet and on its surface. In connection with the anchoring to the cellulosic sheet of surface coatings, however, it is believed that it is the very thin surface film or coating of oxide, rather than the presence of the oxide within the film which is responsible for the good anchorage obtained.

As suitable insoluble oxides which may be formed on the non-fibrous cellulosic sheet from aqueous solutions of their salts or esters may be mentioned such oxides as aluminum oxide, iron oxide, silicon dioxide or the like, and as compounds suitable for use in preparing aqueous solutions designed for treating the cellulosic sheet in order to produce on the sheet the insoluble oxide may be mentioned aluminum chloride, ferric chloride, ethyl-ortho-silicate or the like. Aqueous solutions of such suitable salts or esters may be employed in any suitable concentration. We prefer to use dilute solutions ranging in concentration from 0.1 to 5 per cent of salt or ester by weight.

The aqueous solution of the salt or ester capable of producing an insoluble oxide may be applied to the cellulosic sheet when the sheet is either in the finished, dried form or while it is in the gel condition, i. e., after having been coagulated and at least partially regenerated, but before being dried. The solution may be applied to the base sheet by spraying or brushing the solution on the sheet or by applying the solution to the sheet with rollers or in any other suitable manner. If desired, a softener for the cellulosic sheet may be incorporated in the solution of the salt or ester used to obtain anchorage of the surface coating. After the cellulosic sheet has been thoroughly wet with the oxide-forming, anchoring solution, the excess solution is removed from the sheet by squeeze rolls or other suitable means so that the sheet then contains preferably three to four times its weight of solution. The sheet is then dried at elevated temperatures, preferably at temperatures between 50° and 110° C. During this drying not only is

the excess water removed from the sheet but the salt or ester present in and on the sheet is converted to an insoluble oxide and a volatile product which latter is removed from the sheet by means of the elevated drying temperature. Thus, where aluminum chloride is used, a deposit of aluminum oxide is formed on the cellulosic sheet, together with hydrochloric acid which is removed during the drying of the sheet. In the case of ferric chloride, a deposit of iron oxide is formed in place of aluminum oxide and if ethyl-o-silicate is used in the aqueous solution, silicon dioxide is formed on the sheet and ethyl alcohol is volatilized from the sheet at the elevated drying temperatures.

In cases where an acid like hydrochloric acid is formed along with the insoluble oxide, as in the case of the heating and hydrolysis of aluminum or ferric chloride, for example, it may be desirable to subject the cellulosic sheet during the drying to the action of dilute ammonia gas, or to pass the cellulosic sheet through a dilute basic solution of ammonium hydroxide or an amine, for example, either prior to the drying operation or when the sheet has been partially dried. This treatment with a basic substance facilitates the oxide formation and removes the acid formed.

In its preferred form this invention contemplates incorporating the salt or ester capable of forming an insoluble oxide readily at elevated temperatures directly in the aqueous softening bath, such as the glycerine bath, on the casting machine for producing regenerated cellulose sheets, and thus applying the solution to the gel sheet as it passes through the glycerine bath, subsequently forming the insoluble oxide on the cellulosic sheet as the sheet is dried on the heated dryer rolls, with or without causing dilute ammonia gas to act on the film during the drying. The finished, dry cellulosic sheet is then ready for the application of the surface coating, preferably a moistureproof surface coating, without any further treatment and will be found to anchor said surface coating even when in direct contact with water for substantial periods of time.

From the foregoing, it will be apparent that this invention constitutes a marked departure from and improvement over previous processes for the production of moistureproof, non-fibrous cellulosic sheets in which the moistureproof surface coating firmly adheres to the cellulosic sheet even in direct contact with water or moisture. This process is much simpler since it requires no additional equipment over that used to produce, for example, regular regenerated cellulose sheets and eliminates the inconvenience and expense of two coating operations. Moreover, the materials used in the aqueous solutions employed to obtain anchorage according to this invention are very cheap and easily obtainable and the cellulosic sheets produced by their use are always completely odorless. Furthermore, cellulosic sheets prepared according to this invention are capable of satisfactorily anchoring a surface coating having a cellulose derivative base, preferably a moisture-proof coating, for a substantial period of time even when in direct contact with water or when used as a wrapping directly in contact with products having a high water or moisture content such as butter, cheese, wet or frozen fish, ice cream or the like.

In order more clearly to illustrate this invention, the following examples are given. It is, of course, to be understood that the invention is

not limited to these precise examples which are merely illustrative of the invention. Obviously various other modifications will occur to those skilled in the art, which, however, do not depart from the nature or spirit of the instant invention.

Example I.—A sheet of regenerated cellulose in the gel condition which has been desulfured, bleached and washed free of impurities is passed through an aqueous solution containing 4 per cent by weight of ethyl-o-silicate so that the sheet is in contact with the solution for a brief period of 10 to 60 seconds, for example. The excess solution is removed from the sheet by squeeze rolls or in any desired manner so that the solution remaining in the sheet is equal to 3 to 4 times the weight of the cellulose and the sheet is then dried at a temperature of 95° C. After being cooled and humidified, it is coated with a moistureproofing lacquer of the following composition:

	Per cent
Nitrocellulose.....	6.75
Gum damar.....	1.64
Dibutyl phthalate.....	2.80
Paraffin (tem. 60-61° C.).....	0.48
Zinc stearate.....	0.15
Ethyl acetate.....	56.34
Toluene.....	28.53
Ethanol.....	3.20
Acetone.....	0.11

The sheet is passed through the moistureproofing lacquer, the excess lacquer removed by scraping or by any suitable means, and the sheet dried at temperatures above the melting point of the wax used in the lacquer. The sheet is then cooled and rehumidified, after which it will be found to retain the moistureproof surface coating even in direct contact with water or moisture for appreciable and substantial periods of time.

Example II.—A sheet of regenerated cellulose in the gel condition which has been desulfured, bleached and washed free of impurities is passed through an aqueous solution of aluminum chloride containing 0.5 per cent by weight of aluminum chloride and is then partially dried at a temperature of 80°-95° C., after which it is passed briefly through a 15 per cent ammonium hydroxide solution and dried at 80°-95° C. The dry film, after humidification, is passed through a moistureproofing composition consisting of a solution of ethyl cellulose, a wax, a blending agent and a plasticizer, the excess coating composition removed by suitable means and the sheet dried at a temperature above the melting point of the wax.

Example III.—A finished dry sheet of regenerated cellulose is immersed in a 0.2 per cent by weight aqueous solution of ferric chloride, the excess solution removed from the sheet and the sheet dried in an atmosphere of ammonia at a temperature between 50° and 100° C. The dry sheet after being cooled and humidified is coated with a moistureproofing composition comprising a solution of nitrocellulose, paraffin, gum damar and a plasticizer.

For the purposes of this specification and claims, I define "moistureproof" materials as those which, in the form of continuous, unbroken sheets or films, permit the passage of not more than 690 grams of water vapor per 100 square meters per hour, over a period of 24 hours, at approximately 39.5° C.±0.5° C., the relative hu-

midity of the atmosphere at one side of the film being maintained at least at 98% and the relative humidity of the atmosphere at the other side being maintained at such a value as to give a humidity differential of at least 95%.

Moistureproofing coating compositions are defined as those which, when laid down in the form of a thin, continuous, unbroken film applied uniformly as a coating with a total coating thickness not exceeding 0.0005" to both sides of a sheet of regenerated cellulose of thickness approximately 0.0009", will produce a coated product which is moistureproof.

For the purposes of experimental tests especially for those materials adaptable as coating compositions, moistureproof materials include those substances, compounds or compositions which, when laid down in the form of a continuous, unbroken film applied uniformly as a coating with a total coating thickness not exceeding 0.0005" to both sides of a sheet of regenerated cellulose of thickness approximately 0.0009", will produce a coated sheet which will permit the passage therethrough of not more than 690 grams of water vapor per 100 square meters per hour over a period of approximately 24 hours, at a temperature of 39.5° C.±0.5° C. (preferably 39.5° C.±0.25° C.), with a water vapor pressure differential of 50-55 mm. (preferably 53.4±0.7 mm.) of mercury. For convenience, the number of grams of water vapor passed under these conditions may be referred to as "the permeability value". An uncoated sheet of regenerated cellulose having a thickness of approximately 0.0009" will show a permeability value of the order of 6900.

From the foregoing, it is apparent that under the conditions set forth, a moistureproofed regenerated cellulose sheet is capable of resisting the passage of moisture or water vapor there-through at least ten times as effectively as the uncoated regenerated cellulose sheet.

By the expression "anchor" or its equivalent, as used herein, is meant the securing of the surface coating imposed on the base, so that the product will withstand the deleterious effect of water or moisture to a degree substantially greater than a product in which the surface coating is not secured by special treatment.

Any variation or modification of the invention described above, which conforms to the spirit of the invention, is intended to be included within the scope of the claims.

I claim:

1. In a process for producing a product suitable for use as a wrapping tissue and comprising a cellulosic sheet base and surface coating which exhibit a greatly improved adhesion of such a character as to remain tenacious when subjected to contact with water over a long period of time, the steps which comprise applying to said sheet an aqueous solution of a member of the class consisting of salts and esters capable of yielding an insoluble, inorganic oxide, effecting the conversion of said member to said oxide and precipitating said oxide from said solution, then applying over said oxide a surface coating which normally does not adhere strongly to said sheet.

2. In a process for producing a product suitable for use as a wrapping tissue, the steps which comprise applying to a sheet of regenerated cellulose an aqueous solution of a member of the class consisting of salts and esters capable of yielding an insoluble, inorganic oxide, effecting the conversion of said member to said oxide and

precipitating said oxide from said solution, and applying over said oxide a surface coating including a cellulose derivative.

3. In a process for producing an anchored, moistureproof product, suitable for use as a wrapping tissue, the steps which comprise applying to a sheet of regenerated cellulose an aqueous solution of a member of the class consisting of salts and esters capable of being readily hydrolyzed or dissociated to an insoluble, inorganic oxide and a volatile product, drying the sheet at an elevated temperature whereby the insoluble oxide is deposited from said aqueous solution onto the sheet and the volatile product is removed from the sheet along with the excess water, then applying over said oxide a moistureproofing surface coating.

4. In a process for producing an anchored, moistureproof product, suitable for use as a wrapping tissue, the steps which comprise applying to a sheet of regenerated cellulose an aqueous solution of a member of the class consisting of salts and esters capable of being readily hydrolyzed or dissociated to an insoluble, inorganic oxide and a volatile product, drying the sheet at an elevated temperature in the presence of ammonia gas whereby the insoluble oxide is deposited from said aqueous solution onto the sheet and the volatile product is removed, or in the case of acids is neutralized by the ammonia, then applying over said oxide a moistureproofing surface coating.

5. In a process for producing an anchored, moistureproof product, suitable for use as a wrapping tissue, the steps which comprise applying to a sheet of regenerated cellulose an aqueous solution of a member of the class consisting of salts and esters capable of being readily hydrolyzed or dissociated to an insoluble, inorganic oxide and a volatile product, drying the sheet at an elevated temperature, said sheet having been treated with an alkaline solution either prior to the drying or after partial drying, whereby the insoluble oxide is deposited from said aqueous solution onto the sheet and the volatile product is either removed or in the case of an acid neutralized by the alkaline treatment, then applying over said oxide a moistureproofing surface coating.

6. In a process for producing a product suitable for use as a wrapping tissue and comprising a cellulosic sheet base and surface coating which exhibit a greatly improved adhesion of such a character as to remain tenacious when subjected to contact with water over a long period of time, the steps which comprise applying to said sheet an aqueous solution of aluminum chloride, drying the sheet at an elevated temperature, then applying to said dried sheet a surface coating which normally does not adhere strongly to said sheet.

7. In a process for producing a product suitable for use as a wrapping tissue and comprising a cellulosic sheet base and surface coating which exhibit a greatly improved adhesion of such a character as to remain tenacious when subjected to contact with water over a long period of time, the steps which comprise applying to said sheet an aqueous solution of ferric chloride, drying the sheet at an elevated temperature, then applying to said dried sheet a surface coating which normally does not adhere strongly to said sheet.

8. In a process for producing a product suitable for use as a wrapping tissue and comprising a cellulosic sheet base and surface coating which exhibit a greatly improved adhesion of such a

character as to remain tenacious when subjected to contact with water over a long period of time, the steps which comprise applying to said sheet an aqueous solution of ethyl-o-silicate, drying the sheet at an elevated temperature, then applying to said dried sheet a surface coating which normally does not adhere strongly to said sheet.

9. A product suitable for use as a wrapping tissue comprising a composite sheet produced by treating a nonfibrous cellulosic sheet with an aqueous solution of a compound capable of yielding an insoluble inorganic oxide by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide from said aqueous solution, and applying a surface coating comprising a cellulose derivative over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

10. A moistureproof product suitable for use as a wrapping tissue comprising a composite sheet produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound capable of yielding an insoluble inorganic oxide by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide from said aqueous solution, and applying a moistureproof surface coating over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

11. A moistureproof product suitable for use as a wrapping tissue comprising a composite sheet produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound capable of yielding an insoluble inorganic oxide by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide from said aqueous solution, and applying a moistureproof surface coating comprising a cellulose derivative over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

12. A product suitable for use as a wrapping tissue comprising a composite sheet produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound of aluminum capable of yielding an aluminum oxide by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide from said aqueous solution, and applying a surface coating comprising a cellulose derivative over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to

contact with water over a long period of time.

13. A product suitable for use as a wrapping tissue comprising a composite sheet produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound of iron capable of yielding ferric oxide by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide from said aqueous solution, and applying a surface coating comprising a cellulose derivative over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

14. A product suitable for use as a wrapping tissue comprising a composite sheet produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound of silicon capable of yielding silicon dioxide by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide from said aqueous solution, and applying a surface coating comprising a cellulose derivative over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

15. A product suitable for use as a wrapping

tissue comprising a composite sheet substantially identical with that produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound capable of yielding an insoluble inorganic material by precipitation at a temperature which does not substantially impair the sheet, depositing said material in an aqueous solution, and applying a surface coating comprising a cellulose derivative over said material, the material film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and coating surface when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

16. A product suitable for use as a wrapping tissue comprising a composite sheet substantially identical with that produced by treating a non-fibrous cellulosic sheet with an aqueous solution of a compound capable of yielding an insoluble inorganic oxide on decomposition by precipitation at a temperature which does not substantially impair the sheet, depositing said oxide in an aqueous solution, and applying a surface coating comprising a cellulose derivative over said oxide, the oxide film being substantially invisible to the naked eye, the said sheet and said coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and coating surface when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

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