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MOLD INHIBITIVE CELLULOSIC STRUCTURE

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This invention relates to non-fibrous, trans-
parent, cellulosic wrapping tissue which is coated
with a moisture-proofing coating composition
having mold inhibitive properties.

In recent years films and foils of regenerated
cellulose which have been coated with a lacquer
to impart moistureproofness, which foils are ex-
tremely transparent and possess a surface of high
luster and agreeable appearance, have found
favor for wrapping a large variety of materials
and articles in order to protect them from con-
tamination, and in certain instances, to main-
tain the moisture content of the article or ma-
terial at some optimum value. These wrapping
tissues, being transparent, afford a view of the
object which aids greatly in its appeal and sales
value.

It has been observed, however, that this wrap-
ping material is often subject to unsightly mold
growth which greatly detracts from the appeal
of the package. This is particularly evident in
certain instances where the article wrapped is of
high moisture content and is apt to be infected
with mold spores. This, for instance, has been
observed in the case of cigars wrapped in regen-
erated cellulose film which is provided with the
usual moistureproofing coating composition of
the type disclosed in the Charch and Prindle U. S.
Patent No. 1,737,187.

It is an object of this invention to produce
a non-fibrous, transparent, moistureproof, cellu-
losic pellicle which is not subject to mold growth.

It is another object of this invention to pro-
duce a non-fibrous, transparent, moistureproof,
cellulosic pellicle containing a mold inhibiting
substance in the moistureproofing coating.

It is a further object of this invention to pro-
vide a moistureproofing composition which can
be used for the production of a transparent pel-
licle and which contains a material capable of
inhibiting mold growth on the pellicle.

Other objects of the invention will appear here-
inafter.

Attempts have been made, heretofore, to pro-
duce a non-fibrous, transparent, cellulosic wrap-
ping tissue, coated with a moistureproofing com-
position, which will be free from mold growth.
The criteria for materials which will prevent
mold on such cellulosic material are so precise
that as a general rule, previously known fungi-
cides and microbicides could not be satisfactorily
used for this purpose. A mold inhibiting ma-
terial to be satisfactory for preventing mold on
cellulosic materials of the type mentioned, must
have the following characteristics:

(1) It must not be toxic, even when in long
direct contact with foodstuffs.

(2) It must have no odor.

(3) It must be capable of functioning in such
very small amounts as will not interfere with the
transparency of the wrapping tissue.

(4) It must not interfere with the moisture-
proofness of the coating.

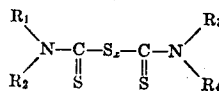
(5) It must not interfere with the heat seal-
ability of the coated tissue.

In view of these very exacting conditions the
incorporation in a non-fibrous, transparent, cel-
lulosic wrapping tissue of a material which will
satisfactorily inhibit mold growth presents a
special problem.

It has now been found that the objects of the
invention may be accomplished by coating a non-
fibrous, transparent, cellulosic pellicle with a
moistureproofing lacquer comprising a small
amount of an alkyl, aryl or alkyl-aryl derivative
of thiuram mono-sulfide or thiuram di-sulfide.

Smooth, transparent films of regenerated cel-
lulose or similar water-sensitive, non-fibrous,
transparent, cellulosic films, containing from 10%
to 20% of glycerol as a softener, or any one of a
number of materials well known to provide flexi-
bility and durability in such cellulosic structures,
is coated by any one of the means well known in
the art such as by dipping and smoothing with
doctor knives, spraying or brushing with a solu-
tion which comprises, in general, a moisture-
proofing agent (such as a wax), a film-forming
agent, such as a cellulose derivative, a resin serv-
ing as a blending agent for the wax and the
cellulose derivative, and a plasticizer to render
the coating flexible, together with a small propor-
tion of the sulfide agent hereinafter described.
These coating compositions may be applied from
a solvent or a mixture of solvents as described in
the Charch and Prindle patent referred to above.

The materials which have been found useful to
inhibit mold growth upon transparent pellicles
coated with moistureproofing compositions of the
kind referred to have the following structural
formula:



in which R_1 , R_2 , R_3 , and R_4 , may be hydrogen,
alkyl or aryl groups, and x may be either 1 or 2.
For example, R_1 , R_2 , R_3 , and R_4 , may be methyl
radicals, x may be equal to 1, giving the sub-
stance tetramethyl thiuram mono-sulfide. If x
is equal to 2, one will obtain the material tetra-

methyl thiuram di-sulfide. Since these materials are soluble in the solvents used in the moistureproofing coating compositions, they may be added directly to these compositions before application of the latter to the film surface. It has been found that only small amounts need be added to the coating composition, for example, from 0.1% to 1.0% of the lacquer solids and preferably from 0.3% to 0.5%. When it is considered that the coating on a pellicle is of the order of about 0.0001" in thickness, it is truly remarkable that the presence of the minute amount of the sulfide will very materially inhibit mold growth.

The following examples will aid in an understanding of the invention, although they are to be taken as illustrative and not limitative thereof:

Example I

A transparent sheet of regenerated cellulose of a thickness suitable for wrapping tissue and containing 15% of glycerol and 6% of water, based upon the weight of the cellulose, is passed through a bath with the following composition:

	Per cent
12.5% N ₂ 10 sec. nitrocellulose.....	6.70
Damar resin.....	1.77
Paraffin.....	0.50
Dibutyl phthalate.....	2.80
Tetramethyl thiuram di-sulfide.....	0.03
Alcohol.....	3.00
Ethyl acetate.....	51.00
Toluene.....	34.20

After passing through the bath, excess liquid is scraped from the surface of the sheet, smoothed, and the solvents evaporated. The film so obtained is found to show excellent transparency and moistureproofness, and to give a very tight seal when subjected to heat and pressure, entirely suitable for use in wrapping cigars and to be extremely resistant to the growth of mold. Furthermore, such film has no undesirable toxic effect nor undesirable odor and, hence, is suitable for use as wrapping tissue for cigars, foodstuffs, toilet articles, etc.

Example II

Regenerated cellulose film as in Example I is coated with the following composition:

	Per cent
12.0% N ₂ 15 sec. nitrocellulose.....	6.50
Ester gum.....	2.93
Dibutyl phthalate.....	4.30
Paraffin.....	0.40
Tetraethyl thiuram di-sulfide.....	0.07
Alcohol.....	2.10
Ethyl acetate.....	47.00
Toluene.....	36.70

Example III

Regenerated cellulose film was coated with the following formula:

	Per cent
12.5% N ₂ 10 sec. nitrocellulose.....	6.70
Damar resin.....	1.75
Paraffin.....	0.50
Dibutyl phthalate.....	2.80
Tetramethyl thiuram mono-sulfide.....	0.05
Alcohol.....	3.00
Ethyl acetate.....	51.00
Toluene.....	34.20

Example IV

Regenerated cellulose film as in Example I was coated with the following composition:

	Per cent
12.0% N ₂ 15 sec. nitrocellulose.....	6.50
Ester gum.....	2.88
Dibutyl phthalate.....	4.30
Paraffin.....	0.40
Tetrabutyl thiuram di-sulfide.....	0.12
Alcohol.....	2.10
Ethyl acetate.....	47.00
Toluene.....	36.70

After smoothing and drying, the films coated with the compositions of Examples II, III and IV were found to have the desirable properties of Example I.

Films prepared according to the above examples are found to exhibit either none or a negligible amount of mold even after storage for three months at a temperature of 104° F. and at a relative humidity of 95%.

Although the tetramethyl and tetraethyl derivatives of mono- and di-sulfides have been found to be particularly useful in accordance with the present invention, other alkyl, aryl, and alkyl-aryl derivatives of thiuram sulfides have been found to be operative. As further examples of such other derivatives of thiuram mono- and di-sulfide which may be used in accordance with the present invention, the following may be mentioned: tetrabutyl thiuram di-sulfide, tetraethyl thiuram di-sulfide, diethyl dimethyl thiuram di-sulfide, dicyclopentyl methylene thiuram di-sulfide, dicyclopentyl methylene thiuram mono-sulfide, ferric dimethyl dithiocarbamate. The thiuram sulfides may in fact contain, as substituent groups, methyl, ethyl, ethanol, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, benzyl, allyl, crotyl, *n*-amino ethyl; cyclohexyl and cyclic amino groups such as piperidine and methyl piperidine; aromatic groups such as methyl aniline, ethyl aniline, ethyl toluidene and propyl xyldine.

As non-fibrous, transparent, cellulosic pellicles which may be coated in accordance with the present invention any smooth, dense, non-fibrous, water-sensitive, transparent pellicle such as may be obtained by the coagulation and/or regeneration of an aqueous cellulosic dispersion is contemplated. Such pellicles include those of regenerated cellulose, glycol cellulose, cellulose glycolic acid, lowly esterified or lowly etherified cellulose derivatives in which one ester group or one ether group is associated with several cellulose units.

Any moistureproofing coating composition of the general type disclosed in the patent to Charch and Prindle Patent No. 1,737,187 or of the type disclosed in U. S. A. Patent No. 2,147,629 (Charch) may be used in accordance with the present invention. Such coatings contain a moistureproofing agent, such as wax, and a film-forming agent such as a cellulose derivative or a resin together with known modifying agents for said coatings, such as blending agents and plasticizers.

The mold inhibiting compounds of this invention being non-toxic and non-odorous in the proportions used, may be safely applied to coating compositions used in connection with the wrapping tissue for foodstuffs, cigars, toilet articles, perfume bottles, etc., where either toxicity or odor would be objectionable. Furthermore, since

these materials are effective in very low concentrations, the addition of small amounts will not adversely affect the properties and characteristics of the coating composition to which they are added. Since, in general, the balance of constituents of a coating composition is very critical in order to combine a large number of properties such as surface characteristics, moistureproofness, temperature resistance, transparency, etc., it becomes of considerable importance that the addition of an agent to inhibit mold growth will not change any of the large number of factors governing the characteristics of the coating composition. The compositions of this invention are found eminently satisfactory for this purpose.

Since it is obvious that many changes and modifications can be made in the above-described details, it is to be understood that the invention is not to be limited thereto except as set forth in the following claims.

I claim:

1. A non-fibrous, transparent, moistureproof, cellulosic pellicle suitable for use as wrapping tissue containing incorporated therein, as a mold inhibiting agent, a thiuram sulfide.
2. A non-fibrous, transparent, moistureproof, cellulosic pellicle suitable for use as wrapping tissue containing incorporated therein, as a mold inhibiting agent, 0.1% to 1.0% of an alkyl derivative of a thiuram sulfide.
3. A non-fibrous, transparent, moistureproof cellulosic pellicle suitable for use as wrapping tissue containing incorporated therein, as a mold inhibiting agent, 0.1% to 1.0% of a tetra-alkyl derivative of a thiuram sulfide.
4. A non-fibrous, transparent, moistureproof, cellulosic pellicle suitable for use as wrapping tissue containing incorporated therein, as a mold inhibiting agent, 0.1% to 1.0% of a tetramethyl thiuram sulfide.
5. A non-fibrous, transparent, cellulosic wrapping tissue coated with a moistureproofing composition, said moistureproofing composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing incorporated therein, as mold-inhibiting agent, alkyl thiuram sulfide.
6. A non-fibrous, transparent, cellulosic wrapping tissue coated with a moistureproofing composition, said moistureproofing composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing incorporated therein, as a mold inhibiting agent, an alkyl derivative of a thiuram sulfide.
7. A non-fibrous, transparent, cellulosic wrapping tissue coated with a moistureproofing composition, said moistureproofing composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing incorporated therein, as a mold inhibiting agent, a tetra-alkyl derivative of a thiuram sulfide.
8. A non-fibrous, transparent, cellulosic wrapping tissue coated with a moistureproofing composition, said moistureproofing composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing incorporated therein, as a mold inhibiting agent, a tetraethyl thiuram sulfide.
9. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising

a regenerated cellulose sheet coated with a composition consisting of:

	Parts
5 Nitrocellulose (12.5% N) -----	6.70
Damar resin -----	1.77
Paraffin -----	0.50
Dibutyl phthalate -----	2.80
Tetramethyl thiuram di-sulfide -----	0.03

10. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising a regenerated cellulose sheet coated with a composition consisting of:

	Parts
15 Nitrocellulose (12% N) -----	6.50
Ester gum -----	2.93
Dibutyl phthalate -----	4.30
Paraffin -----	0.40
Tetraethyl thiuram di-sulfide -----	0.07

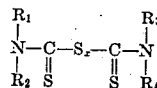
20. 11. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising a regenerated cellulose sheet coated with a composition consisting of:

	Parts
25 Nitrocellulose (12.5% N) -----	6.70
Damar resin -----	1.75
Paraffin -----	0.50
Dibutyl phthalate -----	2.80
30 Tetramethyl thiuram mono-sulfide -----	0.05

30. 12. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising a cellulosic pellicle coated with a moistureproofing coating composition, said moistureproofing coating composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing 0.1% to 1.0% (based on the solids thereof) tetra alkyl thiuram di-sulfide.

40. 13. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising a cellulosic pellicle coated with a moistureproofing coating composition, said moistureproofing coating composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing 0.3% to 0.5% (based on the solids thereof) tetra methyl thiuram di-sulfide.

45. 14. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising a cellulosic pellicle coated with a moistureproofing coating composition, said moistureproofing coating composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing 0.1% to 0.1% (based on the solids thereof) thiuram sulfide of the formula:



in which x represents a positive integer less than 3 and R_1 , R_2 , R_3 and R_4 represent radicals from the group consisting of hydrogen, alkyl and aryl.

50. 15. A mold resistant, moistureproof, transparent, flexible sheet wrapping material comprising a regenerated cellulose sheet coated with a moistureproofing coating composition, said moistureproofing coating composition being from the group consisting of cellulose substitution derivative film forming agent-wax and resin film forming agent-wax, and containing 0.1% to 1.0% (based on the solids thereof) thiuram sulfide

from the group consisting of tetra methyl thiuram mono-sulfide, tetra methyl thiuram di-sulfide, tetrabutyl thiuram di-sulfide, tetraethyl thiuram di-sulfide, diethyl dimethyl thiuram di-sulfide, dicyclopentyl methylene thiuram di-sulfide, and dicyclopentyl methylene thiuram mono-sulfide.

16. A non-fibrous, transparent cellulosic wrap-

ping tissue comprising a cellulosic pellicle base with a moistureproofing coating of the cellulose substitution derivative-wax type thereon, the said moistureproofing coating containing incorporated therein, as a mold inhibiting agent, an alkyl derivative of a thiuram sulfide.

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