Patented Aug. 12, 1941

2,252,386

UNITED STATES PATENT OFFICE

2,252,386

MANUFACTURE OF SURFACE COVERING MATERIALS

Richard O. Roblin, Jr., Old Greenwich, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application October 28, 1939, Serial No. 301,794

7 Claims. (Cl. 106—264)

This invention relates to the acceleration of the rate of curing or "seasoning" of surface covering compositions such as floor compositions containing siccative binders, as well as to the improvement in the alkali resistance of such compositions.

An object of this invention is to provide accelerators for surface covering compositions containing siccative binders which will cause such compositions to cure more rapidly. Another object of this invention is to improve the alkali resistance of surface covering compositions containing siccative binders.

These and other objects are attained by incorporating in a siccative composition which is to be used in a floor covering composition or other surface covering composition a di-substituted cyanamide, the substituents containing a total of not more than 14 carbon atoms. The substituents may be aliphatic, cycloaliphatic, aralkyl or aryl groups of the benzene series.

The following examples are given by way of illustration and not in limitation.

Example 1

	Parts by weight
Binder	30
Wood flour	30
Whiting	20
Lithopone	20
Diethyl cyanamide	0.3

These substances with or without a small proportion of drier, e. g. 0.1% cobalt naphthenate, are mixed together, e. g. in an internal mixer. The compacted mass which is delivered from the mixer may be disintegrated, as by a set of "scratch rolls" which comprises a plurality of rolls having intermeshing teeth projecting from their surfaces. The resulting material is sheeted on calender rolls or optionally it may be further mixed and disintegrated and then calendered. The material may be calendered on to burlap or other fibrous backing if desired. The sheeted material is placed in a stoving oven through which a current of air heated from about 70° C. to about 90° C. is circulated until the material is completely "seasoned," i. e. until the sheet acquires the necessary degree of hardness.

The hardness may be measured by any of the methods generally employed in the manufacture of linoleum. See the Federal Stock Catalogue (U. S. Government Printing Office), section 4, part 5, pages LLL-L-351 et seq. and pages LLL-L 361 et seq., for the method employed herein. The time required for "seasoning" a 2 mm. sheet of the above composition is about eight to nine days. The resulting "seasoned" floor covering shows improved alkali resistance. One method of determining alkali resistance is to measure the depth in millimeters to which a 5% solution of sodium hydroxide in water penetrates in one hour at a temperature of 70° F. By this method the alkali resistance of the "seasoned sheets" is about 0.20 mm. penetration.

The "seasoning speed" of a 2 mm. sheet of the same mixture which does not contain diethyl cyanamide is about twelve to fourteen days and the alkali resistance of such a composition is about 0.28 mm. The marked improvement obtained with my composition is outstanding inasmuch as I have found it to be very difficult to improve the alkali resistance by even as little as 0.01 mm.

Example 2

	Parts by weight
Binder	35
Wood flour	30
Whiting	20
Lithopone	20
Diethyl cyanamide	3

These substances may be mixed and sheeted in the same general manner as the procedure set forth in Example 1. The resulting floor covering sheets "season" or "mature" in about five to six days and the "seasoned" sheets have an alkali resistance of about 0.24 as compared with a seasoning speed of twelve to fourteen days and an alkali resistance of about 0.28 characteristic of similar compositions which omit the diethyl cyanamide.

Example 3

	Parts by weight
Binder	35
Wood flour	30
Whiting	20
Lithopone	20
Diamyl cyanamide	0.3

This composition may be mixed and sheeted according to the procedure of Example 1. The sheeted composition "seasons" in about eleven days and has an alkali resistance of about 0.19.

Example 4

	Parts by weight
Binder	30
Wood flour	30
Whiting	20
Lithopone	20
Dibenzyl cyanamide	3

If these substances be mixed and sheeted according to the method described in Example 1, the resulting floor covering sheets "season" in about eleven days and have an alkali resistance of about 0.11.

The binders may be derived from the drying

oils and may be made in any convenient well-known manner, such as the methods described in British Patent 305,656 or the binders may comprise any of the various alkyd resins having siccative properties. For drying oil binders, linseed oil is preferable for economic reasons but other siccative oils may be used such as, for example, menhaden or fish oil, tung oil, soy bean oil, perilla oil, oiticica oil, Scheiber oil, sunflower seed oil, etc. The term "siccative oil" as used herein is intended to include not only the so-called drying oils but also the so-called semi-drying oils. Furthermore it is possible to use mixtures of siccative oils with other fatty oils of the non-drying type.

It may be preferable in the manufacture of linoleum to make use of so-called "scrim-oil" or "shed oil" either alone or fluxed with rosin or other gums or resins and/or mixed with a proportion of the so-called "mechanical oil." Either of these types of oils may be used singly if desired.

In the preparation of the siccative oil binders it is customary to use rosin in admixture with the oil although other substances of the same type may be used, e. g. Kauri gum, Congo gum, ester gum, abietic acid and its esters, pimaric acid, etc.

Other siccative binders which may be used in the examples are the alkyd resins which have siccative properties. Among these, the drying oil modified reaction products of maleic or fumaric acid with terpenes and polyhydric alcohols are particularly suitable. Other alkyd resins which are modified with drying oils or drying oil acids may be used such as the phthalic-glyceride resins, the glycol-maleic resins, and mixed resins such as the phthalic-fumaric-glycol-glyceride resins.

Instead of wood flour and/or the whiting and lithopone used in the examples, other fillers or pigments may be used. Examples of such fillers are: cork, cellulose pulp, asbestos, cottonwood tree pulp, walnut shell meal, glass fibers, foliated glass, etc. Among the pigments which may be used are included: lithopone, barytes, zinc oxide, titanium oxide, chromates, red lead, white lead, malachite green, chrome green, chrome yellow, Prussian blue, iron oxide, etc. Similarly dyes and lakes may be used if desirable.

It is generally preferable to use driers in the preparation of the binders. The drier is usually added to the binder during the oxidation process and if desirable additional drier may be added when the binder, fillers, etc., are mixed together. Suitable driers include the oil soluble salts such as the naphthenates, resinates and linoleates of cobalt, lead, manganese, zinc, chromium. Only a small proportion of these driers based on the siccative oil content, is generally sufficient, e. g. about 0.005–1%, although larger proportions may be used as expedient. Obviously various mixtures of driers may be used.

The term "seasoning" as applied to linoleum compositions indicates the process of curing by heating or equivalent treatment to polymerize and/or oxidize the composition to a stage wherein the floor covering is sufficiently hard and resistant to abrasion to be suitable for its intended purpose and yet is still sufficiently flexible to permit the usual bending and rolling required of linoleum. The term "maturing" is similarly used.

Other accelerators which may be used include dimethyl cyanamide, dipropyl cyanamide, dibutyl cyanamide, dihexyl cyanamide, dicyclohexyl cyanamide and diphenyl cyanamide.

Only a small proportion of these accelerators is generally sufficient, e. g. 0.1–5% of the siccative composition but obviously smaller or larger proportions may be used if desirable.

The accelerators described herein are preferably added during the mixing of the binder with the fillers, etc., although they may be added before or during the oxidation of the binder. If the accelerators are added before or during the oxidation they appear to inhibit somewhat the gelation of the siccative binder. It is to be noted, however, that after gelation the accelerators speed up the curing of the siccative composition.

Obviously many modifications in the processes and compositions described above may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. In a process of curing a surface covering composition including a siccative material selected from the group consisting of drying oils and drying oil modified polyhydric alcohol-polybasic acid resins, the step which comprises adding to such a composition a dihydrocarbon-substituted cyanamide containing not more than 14 carbon atoms in the substituent groups.

2. In a process of curing a surface covering composition including a siccative material selected from the group consisting of drying oils and drying oil modified polyhydric alcohol-polybasic acid resins, the step which comprises adding to such a composition a di-aliphatic substituted cyanamide, the substituent groups of which contain not more than 14 carbon atoms.

3. In a process of curing a surface covering composition containing a siccative oil binder, the step which comprises adding to such a composition a dihydrocarbon-substituted cyanamide, the substituent groups of which contain not more than 14 carbon atoms.

4. In a process of curing a surface covering composition containing a siccative alkyd resin binder, the step which comprises adding to such a composition a dihydrocarbon-substituted cyanamide, the substituent groups of which contain not more than 14 carbon atoms.

5. In a process of curing a surface covering composition including a siccative material selected from the group consisting of drying oils and drying oil modified polyhydric alcohol-polybasic acid resins, the step which comprises adding to such a composition a small proportion of diethyl cyanamide.

6. In a process of curing a surface covering composition including a siccative material selected from the group consisting of drying oils and drying oil modified polyhydric alcohol-polybasic acid resins, the step which comprises adding to such a composition a small proportion of diamyl cyanamide.

7. A surface covering composition including a siccative material selected from the group consisting of drying oils and drying oil modified polyhydric alcohol-polybasic acid resins and a dihydrocarbon-substituted cyanamide containing not more than 14 carbon atoms in the substituent groups.

RICHARD O. ROBLIN, JR.