Cl 92

Published July 13, 1943 Serial No. 474,320

ALIEN PROPERTY CUSTODIAN

SUBSTITUTES FOR PAPER, CARDBOARDS AND ARTIFICIAL LEATHER AND PROCESSES FOR THE MANUFACTURE THEREOF

Maurice Désiré Emile Déribéré, Courbevoie-Beeon, France; vested in the Alien Property Custodian

No Drawing. Application filed February 1, 1943

The present invention relates to the production of continuous or discontinuous sheets intended to be printed by hand or by machine and for all known uses of paper, cardboards or artificial leathers, such as wrapping, folding, protection, presentation, printing, writing and publishing, as well as all transformations having papers, cardboards or artificial leathers for basis.

The invention resides in the discovery that certain mineral materials, having definite physico-chemical properties, can constitute, provided they are utilised in a suitable manner, a foundation raw material and a substitute for cellulose and all other fibres used in the manufacture of papers, cardboards and artificial leathers, as well as sheets already possessing, independently of any addition, an inherent cohesion and flexibility comparable to sheets obtained from cellulose materials or the like used in the manufacture of paper, cardboards and artificial leather.

One of the necessary conditions which the mineral material must satisfy is that it must have a fibrous molecular structure, said structure being moreover not necessarily revealed by the macroscopic aspect of the material. Precise details will be given hereinafter concerning what is meant by "fibrous molecular structure."

All mineral materials having such a structure are however not suitable. A second condition to be satisfied by said materials is that they must be capable of being put into relatively stable suspension in water, after being crushed to a sufficiently fine state, without however it being necessary to reach a gel or colloidal solution.

It is furthermore necessary that the mineral material should swell to a certain extent when it is put in suspension in water.

Finally, the particles of the materials must have an electric charge, so that an orientation or setting of the micellae takes place when the sheets are formed.

Experience shows that if mineral substances satisfying these four conditions, are crushed to a suitable degree of fineness and put in stable suspension in water, it is possible to obtain from such suspensions, by sedimentation, films which, after drying, have such a cohesion and flexibility that, in consideration of a sizing and other treatments or additions usual in paper-making, a substitute for paper, cardboard, and artificial leather can be obtained from these materials, which is capable of receiving the same applications as paper, cardboard and artificial leather themselves.

It seems that the cohesion of the films obtained from these suspensions is due to an arrangement or imbrication of the crypto-crystals of the material, which would explain:

1. The necessity of starting from a material in a state of fibrous cryptocrystallization.

2. The necessity of putting in suspension, of swelling and of the presence of an electric charge, so that each particle should have, upon drying, a freedom of movement sufficient for assuming, under the effect of the electric reactions between the adjacent particles, a well defined position of equilibrium or orientation, the cohesion appearing to be due to said orientation of the molecules or particles of material.

Whatever may be the value of this attempt to give a scientific explanation, the applicant has found that the result sought for was obtained every time that the material satisfied the above-mentioned conditions and that, on the contrary, the result was null, or very poor, when one of them was not satisfied, as will be seen from the examples given hereinafter.

The invention, which is based on the above-defined facts, consists in bringing to a state of suitable division, a mineral material having a fibrous molecular structure, capable of being put in relatively stable suspension in a liquid, of appreciably swelling in said liquid and the particles of which are electrically charged, putting the material thus divided in stable suspension in a liquid, forming a film of suitable thickness from said suspension, drying said film and incorporating with the material before, during, or after the formation of the film, all sizing substances, charges, plasticizers, supplying substances or the like as is usual in paper-making.

The invention has also for object, by way of new industrial product, a substitute for paper, the basis of which is constituted by a mineral material having a fibrous molecular structure, capable of being put in stable suspension in a liquid, of appreciably swelling in said liquid, and the particles of which are electrically charged.

Among the mineral materials having the above-indicated properties capable of forming, by deposition, homogeneous sheets, are included various minerals which exist in nature in a suitable form: tremolite, crocidolite, chrysotile, amosite, palygorskite, sepiolite and, in a general manner, minerals having a fibrous, cork-like, papyraceous structure, known under the denominations of mountain leathers, cardboards and papers, asbestos, etc., as well as analogous minerals having a structure of the same kind, but finer and which is not macroscopically apparent in such an obvious manner.

Thus, white, light Tyrol tremolite, having the appearance of cork (mountain cork) which is tough but does not present fibres macroscopically, has given, when crushed, a homogeneous suspension. Said suspension deposited on a glass plate, then dried, gave very homegeneous, strong and tough sheets. With medium crushing, a few irregular fibres in the final sheet obtained will be noticed under the microscope. When the crushing is very fine, said fibres are inexistent, but the sheet is quite as tough.

Asbestos materials have also given coherent sheets, but after fine crushing during which the apparent fibres are destroyed and are no longer visible, either in the suspension, or in the sheet obtained, at the greatest magnifications of the microscope. This crushing is necessary, however, for causing two further indispensable conditions to appear: the fineness and the swelling property both attached to colloidal or pseudo-colloidal forms.

In fact it appears very important that the elementary particles should be put in relatively stable and homogeneous suspensions and that the deposit leading to the formation of the sheets should be slow and more function of the drying than of a precipitation.

Indeed, in a suspension suitably prepared for obtaining satisfactory sheets, if the deposit is accelerated by a secondary action, for instance by modification of the pH, the sheets obtained are no longer coherent or the material cracks and is deposited without forming sheets.

Swelling is also a necessary secondary condition. Phyllites such as talc, kaolin, mica, do not form sheets, as these materials, even well crushed, do not swell.

Palygorskite from Nijni Novgorod (U. R. S. S.) right bank of the Oka (sample which is a specimen of No. 110,358 of the collection of the Natural History Museum in Paris) which has given stiff sheets, swells to about seven times its volume as the Table mineral (C. R., des séances de l'Académie des Sciences t. 198, p 1795, 1934) and Tyrol tremolite. Very coherent sheets have been obtained with crushed asbestos materials swelling only from two to three times their volume.

All the substances having given rise to the formation of sheets, are given negative electric charges and distinctly migrate towards the positive pole when they are subjected, in the form of a suspension, to the action of an electric field. A voltage of 10 to 20 volts is always sufficient for ensuring a deposit on the anode, the electrodes being constituted by a nickel or platinum plate for the cathode and by a nickel or platinum wire for the anode.

The action of the pH seems accessory. It is very marked for suspensions on which it has a responsive effect and not for the others. It therefore does not act directly, but by its action on the sedimentation and swelling.

The Table mineral is only very slightly influenced by the surrounding pH. Its suspensions have the same stability on all the pH values 3 to 12. In an alkaline medium there is only a slight thickening of the suspensions. The sheets obtained with suspensions having a pH value 3, 5, 7, 9 (value of natural aqueous suspensions) 10 and 12, are all coherent and approximately of the same strength.

These different results allow of drawing a few conclusions relating to the internal mechanism of the formation of coherent sheets from suspensions of various mineral substances.

This formation results from the fibrous structure of the minerals contemplated. But the particles having such structures must moreover be very fine and of colloidal or pseudo-colloidal dimensions and capable of swelling in the aqueous support.

The swollen and stable particles are gradually deposited near each other, in proportion as the liquid support is eliminated by drying. Owing to their form and to the electric charges they must necessarily possess, they set themselves, by falling into alignment and by overlapping. As the drying proceeds, their volume is affected, since they were swollen and this modification prevents the internal stresses which would upset the equilibrium of the electric actions.

Finally, the particles are set side by side in overlapping relation and on the whole they constitute a mechanically stable and coherent structure.

The work can be effected on various smooth or treated supports, for instance powdered with talc or other materials, or parafined or oiled. Said supports can be movable for allowing endless sheets to be produced.

The sheets can be sized or not. The sizing can be effected by means of suitable substances such as rosin with or without alum, natural resins, synthetic resins, latex, waxy or resin emulsions, etc. These products can be introduced in the liquid phase of formation or during a subsequent treatment, either by a liquid process (solution, emulsion, wetting, atomisation, coating) or by a dry process (melting in the mass of a resin for instance).

The sizing imparts to the paper a certain resistance to water. If it is necessary to improve the latter, the dressing desired will be obtained by a chemical, physical or heat treatment. Chemically, the sheets can be treated, in course of production, either subsequently by suitable chemicals, such as tannins, salts, and in particular, chlorides, sulphates, acetates and nitrates of heavy metals, such as copper, cobalt, manganese, lead, chromium. By a physical process the surface can be metallized or a coating or treatment can be obtained by means of an emulsion or of a molten bath of waxes, paraffin. Finally, by a heat treatment the sheet can be heated, without, or better, with pressure. For instance, heating will be effected, with compression between calenders at 150° C with a pressure of 10 to 60 kgs/cm^2.

Some substances can be incorporated with the sheets to render them more flexible. Use will be made of known plasticizers such as glycol, glycerine and their derivatives, solvents and acetone esters, organic acetates.

The charges can be mineral charges and in powder form as in cellulose papers, or, on the contrary, formed by materials of particular structure and in particular fibrous or phyllitic of mineral origin (asbestos, micas, colloidal clays for instance) or vegetable origin (cotton waste, rags, paper pulps) or again animal origin (wool, silk).

The dyestuffs may be organic dyes, black pigments (lamp-black for instance), white pigments (titanium dioxide for instance) or coloured pigments (ultramarine, chrome-yellow).

For obtaining white sheets, certain synthetic or natural materials claimed are naturally very suitable. In other cases, for instance with blue crocidolite, or with green chrysotile, the product is more or less highly coloured. Bleaching after crushing can be obtained by simply washing with a hot acid. Thus, for instance, the suspension will be boiled in a 25% solution of hydrochloric acid, then it will be rinsed by washing two or three times with water, each washing being followed by a decantation. The particles constituting the suspension will then be perfectly white.

The drying of the finished sheets will be effected by means known in the paper industry or by passage under lamps emitting infra-red rays near 12,000 A. The finishing of the sheets can comprise all the usual operations, in particular, coatings, glazings, calenderings, etc.

A few brief examples are given hereinafter:

I. 10 parts by weight of fibrous amosite, finely crushed, are mixed with five parts by weight of short and carded fibres of chrysotile asbestos, one part of latex, four parts of titanium white and eighty parts of water: by deposition, a dull white sheet is obtained.

II. 10 parts by weight of fibrous or cork-like termolite, finely crushed, are mixed with five parts by weight of paper pulp, two parts of paraffin in emulsion and 83 parts of water, a somewhat translucent white sheet is obtained.

III. 15 parts by weight of blue crocidolite, finely crushed, are mixed with 1 part by weight of chrome-yellow; four parts of finely dispersed vinylic resin and 80 parts of water; a blue-green sheet is obtained whieh must be heated to 50° C. when drying, so as to distribute the resin and to impregnate the sheet therewith.

IV. 15 parts by weight of Canary (Corsica) asbestos, finely crushed, are mixed with 5 parts of the same substance, coarsely crushed, five parts of lamp-black and 75 parts of water; a flexible dull black sheet is obtained.

V. 15 parts by weight of Canary (Corsica) asbestos, finely crushed, are mixed with five parts of a 10% acetone solution of vinyl chloro-acetate resin and 80 parts of water; after calendering, a flexible dull grey impervious sheet, having a strength of 50 kgs/cm^2 is obtained.

VI. 10 parts by weight of finely crushed tremolite mixed with 5 parts of titanium white, 5 parts of a solution of vinylic resin and 80 parts of water give, after calendering, a flexible smooth white sheet having a strength of 40 kgs/cm^2 satisfactorily receiving the impression (printing, with a pad or by hand).

VII. 10 parts by weight of finely crushed tremolite are mixed with 5 parts of rayon waste cut into short and well dispersed fibres, 3 parts of zinc white and 2 parts of latex or of a dispersion of synthetic rubber. A flexible dull white sheet is obtained, having a strength of 30 kgs/cm^2, satisfactorily receiving all kinds of impressions.

VIII. 10 parts by weight of papyraceous mineral from Table (Savoy), finely crushed, mixed with 90 parts of water gives by simple deposition, flexible yellowish sheets, having a strength of 20 kgs/cm^2 before any sizing. After calendering in the hot state, said sheets become stronger; they lose their porosity and become capable of receiving all kinds of impressions.

IX. 10 parts by weight of papyraceous mineral from Table (Savoy), finely crushed, mixed with 5 parts of bentonite, 5 parts of asbestos fibrils and 80 parts of water, give flexible and dull sheets.

X. 15 parts of finely erushed papyraceous mineral from Table (Savoy) are bleached by washing with hydrochloric acid, then mixed with 5 parts of a vinylic synthetic resin in solution and 80 parts of water; a perfectly white sheet is obtained having a strength of 40 kgs/cm^2 satisfactorily receiving the impression after calendering.

It is obvious that, in these few examples, which are not given in a limiting sense, the proportions and the nature of the constituents can vary within wide limits according to the result to be obtained. The only common point is the final obtainment of a coherent sheet.

MAURICE DÉSIRÉ EMILE DÉRIBÉRÉ.