Patented Jan. 4, 1938 2,104,081

UNITED STATES PATENT OFFICE

2,104,081

LAMINATED SHEET AND PROCESS OF MAKING SAME

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No Drawing. Application January 20, 1934, Serial No. 707,530

11 Claims. (Cl. 92—21)

My invention relates to fibrous products, such as paper, wall board, laminated articles and similar materials containing resin of the coumarone-indene type, and to methods of producing the same.

It is well known that materials such as rosin and similar natural resins, as well as glue and similar adhesive materials, are employed as sizing agents and in the manufacture of wall board and laminated products. Ordinarily the resins used are saponified by treatment with an alkaline material and the resulting resin soaps are dissolved in water and applied to the materials to be treated in the form of a solution. Glue and similar adhesives are also employed in the form of a solution as sizing and adhesive materials. Numerous attempts have been made to employ resins of the coumarone-indene type as sizing and binding agents in the manufacture of paper and in the production of wall board, etc. These resins are excellent adhesives and are inexpensive. They are also resistant to action of water and alkali and are valuable as electrical insulators. However, resins of the coumarone-indene type cannot be saponified, and therefore, it is impossible to introduce these resins into a pulp of fibrous material in the form of a paracoumarone soap.

Resins of the coumarone-indene type have been pulverized and added to a fibrous pulp in pulverized form, but this method of procedure has certain disadvantages. The pulverized resin tends to collect or segregate in the paper or fibrous pulp so that some portions of the product contain insufficient resin to bind the fibers together, whereas other portions of the product contain too much resin so that the paper or material treated sticks to the calender rolls over which it is passed.

It has been suggested that resins of the coumarone-indene type may be prepared for use in the sizing of paper by dissolving the resin in a solvent and applying the solution of resin to paper or fabric or introducing the resin solution into a pulp of fibrous material. However, this procedure involves the use of organic solvents that are expensive and may be inflammable. Furthermore, this procedure usually also requires the use of costly solvent-recovery apparatus.

I have discovered that resins of the coumarone-indene type having relatively high melting points, e. g., melting points of about 80° C. or higher and particularly the varnish grades of these resins which melt at temperatures of about 100° C. or higher, can be dispersed or suspended in an aqueous medium in a form particularly adapted for use in the sizing of paper and in the production of fibrous and laminated material, such as panels for radio construction, table tops, wall boards, and similar products.

In my co-pending application Serial No. 707,527 filed January 20, 1934 (now Patent No. 2,051,409 issued August 18, 1936) and application Serial No. 707,528 filed January 20, 1934 (now Patent No. 2,051,410 issued August 18, 1936), I have described various methods of producing dispersions of resins of the coumarone-indene type substantially free from saponifiable material and the products obtained by such methods. In accordance with the present invention, dispersions of resins, preferably substantially free from saponifiable material such as those described in my co-pending applications, are employed as sizing or binding agents for fibrous materials and as adhesives for the laminae of laminated products.

In a preferred method of carrying out my invention, I employ an aqueous dispersion of resin of the coumarone-indene type that has a melting point in the neighborhood of 100° C. or higher. The dispersion may contain any suitable amount of resin but I prefer to employ dispersions containing an amount of resin equal to about 50 per cent of the weight of the water used in producing the dispersion. The resin dispersion is added to a pulp of fibrous material such as paper stock in sufficient proportions to introduce an amount of resin equal to from 5 to 25 per cent or more of the dry weight of the fiber in the pulp. The pulp is then agitated until the dispersion has been uniformly distributed throughout the pulp. I then add a precipitant such as alum to the mixture until the pH value of the mass has been reduced to about 4.0 to 5.0, and preferably about 4.6, thereby precipitating the resin uniformly onto the fibers of the pulp and decomposing the silicate of soda to form colloidal or finely divided silica (SiO_2). The addition of the alum causes the breaking down of the dispersion, the dispersed particles being deposited on the fiber. In the case of higher melting point paracoumarone resins, e. g., resins melting above 80° C., the dispersed particles will be deposited in solid, non-adhesive condition onto the fibers. Hence, the mixture of fibrous material and paracoumarone resin particles can be sheeted on a paper-making machine without adherence of the binder particles to the paper-making instrumentalities. The binder particles are coalesced and substantially homogeneously distributed throughout the paper upon the drying and calendering of the paper. The

pulp in the beater is then passed through the Jordan engines to the paper machine where the pulp is formed into sheets or boards of the desired thickness. As above indicated, due to the presence of the resin particles in solid non-adhesive condition, the particles will not adhere to the machine parts and can readily and efficiently be sheeted. Water is extracted from the sheets of material thus produced, leaving the fibrous material with the resin and silica adhering thereto. The pulp onto which the resin and silica are precipitated may also be used in the production of molded products, in which case, it is not essential that the material be passed through a paper machine or formed into sheets.

The character of the resulting product depends upon the nature of the pulp being treated and upon the amount and character of the resin employed in treating the pulp. When the resin dispersions are used for sizing paper, I ordinarily add a relatively small amount of resin dispersion to the pulp; for example, I may add sufficient dispersion to introduce an amount of resin equal to about 5 per cent or less of the dry weight of the fiber in the pulp. The sheet of material produced is dried and passed between heated calender rolls to soften or fuse the resin and cause coalescence of the resin particles.

When producing wall boards or sheets of material that are to be used in producing laminated products, I ordinarily introduce a larger amount of resin into the pulp, the amount of resin used depending upon the hardness desired in the product. For example, I may add sufficient dispersion to introduce an amount of resin equal to about 25 to 35 per cent or more of the dry weight of the fiber in the pulp. The sheets of material thus formed, after being dried, are subjected to heat and pressure to fuse the resin and cause it to flow throughout the sheet. In producing molded products, the pulp from the beater or Jordan engine is dried and subjected to heat and pressure in molds of the desired shape and construction. The temperature to which the material is heated in producing wall board, etc., will ordinarily vary with the melting point of the resin employed, and when I use a resin having a melting point of about 110° to 140° C., the temperature to which the sheets are heated will ordinarily be about 125° to 165° C. By thus heating the resin to a temperature above the melting point thereof, the resin particles may flow together to form a continuous bond of resin throughout the mass. The amount of pressure employed in producing the article will depend upon the nature of the final product desired. When producing wall board or laminated products, such as insulating sheets of material, or in producing molded articles, I prefer to subject the material to a pressure of about 2000 pounds per square inch. In a typical example of my process when producing a laminated product, a plurality of sheets of material from a paper machine, each containing about 25 per cent or more by weight of resin having a melting point of about 110° to 140° C. are placed one upon the other and subjected to a pressure of about 2000 pounds per square inch at a temperature of about 140° to 175° C. for a period of about 15 to 30 minutes. When the article is removed from the press, it is found that the sheets of material are firmly bonded together with the resin distributed uniformly throughout the product. Upon examination, it is found that the resin of adjacent sheets has flowed together to form a continuous body of resin throughout which the fibers of the product are distributed.

Laminated products have also been produced according to my invention by applying a sheet of paper or other material containing little or no resin to one or both sides of a sheet of material produced as described above, containing about 25 per cent or more by weight of resin, and pressing the sheets together while heating the same. In a similar way, laminated products have been produced by impregnating sheets of material with the resin dispersions or applying the dispersions to the surfaces of a sheet and heating and pressing the sheet into intimate contact with coated and uncoated sheets of material. The products obtained may be used in various ways for wall board, panels of insulating material, in the production of furniture, boxes and similar products.

In my copending application, Serial No. 707,528, now Patent No. 2,051,410, I have pointed out that in removing water from pulp that has been treated with a dispersion of resins of the coumarone-indene type, a portion of the resin in the dispersion is sometimes removed from the pulp. In order to avoid this loss, I have suggested that a material, such as clay, be added to the dispersions in order to increase the retention of the resins on the fibers. In carrying out the present invention, I may use dispersions which contain clay or similar material, or I may use dispersions which do not contain any material of this type. I may also vary the proportions of the material employed in producing the product as well as the method of procedure for introducing the resins into the final produce. In lieu of resins of the paracoumarone type, stable emulsions or dispersions of other substantially non-saponifiable resinous materials may be used. For example, dispersions of hard resins made from cracked petroleum, glyptal resins, Bakelite, pitch resins, and the substantially non-saponifiable ester gum may be used in the sizing of paper and in the production of fibrous and laminated material as hereinabove described in the case of the dispersions of the resins of the coumarone-indene type. Therefore, I do not wish my invention to be limited to the specific examples cited except as defined by the claims. Resins made by the polymerization of cracked distillates obtained from petroleum and/or natural gas have properties similar to the properties of paracoumarone resins and for many purposes may be used interchangeably with paracoumarone resins. The term "paracoumarone resin-like material" as used in the claims herein is intended to be a generic term to include both paracoumarone resin and resin obtained by the polymerization of such cracked distillates.

I claim:

1. The process which comprises forming an aqueous dispersion of a resin of the coumarone-indene type that has a melting point of at least about 100° C., forming a pulp of fibrous material in water, adding said resin dispersion to said pulp in sufficient proportions to introduce an amount of the resin not substantially less than about 5 per cent of the dry weight of the fibers of said pulp, precipitating the resin onto said fibers, forming the pulp into a sheet, withdrawing water from the sheet of material thus formed, and heating the sheet to a temperature above the melting point of the resin.

2. The method of producing a waterproof sheet, which comprises mixing fibrous material and a

dispersion of high melting point paracoumarone resin in an aqueous medium containing a stabilizing agent, adding a precipitating agent to the resultant mixture to decompose the emulsion and to cause the adherence of the high melting point paracoumarone resin particles to the fibrous material, sheeting the resultant mixture, and drying and pressing the same to coalesce the binder particles homogeneously throughout the resultant sheet.

3. A laminated product at least one of the laminae of which contains at least about 25 per cent by weight of resin of the coumarone-indene type, the resin in said lamina being coalesced and substantially homogeneously and continuously distributed throughout the lamina.

4. A fibrous product containing not less than about 5 per cent by weight of resin of the coumarone-indene type that has a melting point above about 80° C.

5. A fibrous product containing at least about 25 per cent by weight of resin of the coumarone-indene type having a melting point of at least about 125° C.

6. The process which comprises forming a dispersion of a resin of the coumarone-indene type, adding said dispersion to a pulp of fibrous material in proportion sufficient to introduce an amount of resin equal to substantially 24 per cent to 35 per cent of the dry weight of the fibers, mixing said dispersion with the pulp, forming the pulp into a sheet and compressing the sheet with other sheets to form a laminated product.

7. The process of forming a fibrous product which comprises dispersing hard resin of the coumarone-indene type in an aqueous solution of sodium silicate, adding the dispersion to a pulp of fibres, mixing the resin dispersion into the pulp, precipitating the resin from the dispersion onto the fibres in solid substantially non-adhesive form, forming the pulp into a sheet, and subjecting the sheet to pressure and to a temperature considerably above the melting point of the resin thereby resulting in coalescence of the resin particles and the formation of a sheet in which the resin is dispersed substantially continuously and homogeneously throughout the same.

8. The process of producing a fibrous product which comprises dispersing hard resin of the coumarone-indene type in an aqueous solution of silicate of soda, adding the dispersion to a pulp of fibres in proportion sufficient to introduce an amount of resin equal to substantially from 24% to 35% of the dry weight of the fibres, mixing said dispersion with the pulp, forming the pulp into a sheet, subjecting the sheet to pressure at a temperature considerably above the melting point of the resin thereby resulting in coalescence of the resin particles and the formation of a sheet in which the resin is substantially continuously and homogeneously distributed throughout the same.

9. The process of forming a fibrous product which comprises producing a dispersion of resin of the coumarone-indene type in an aqueous medium, which dispersion is substantially free of saponifiable material, adding the dispersion to a pulp of fibres, precipitating the resin from the dispersion onto the fibres and forming the pulp into a sheet.

10. The process of forming a fibrous product which comprises producing a dispersion of hard resin of the coumarone-indene type in an aqueous solution of sodium silicate, which dispersion is substantially free of saponifiable material, adding the dispersion to a pulp of fibres, precipitating the resin from the dispersion onto the fibres in solid, substantially non-adhesive condition, forming the pulp into a sheet, and subjecting the sheet to pressure and to a temperature considerably above the melting point of the resin, thereby resulting in coalescence of the resin particles and the formation of a sheet in which the resin is dispersed substantially homogeneously throughout the same.

11. The process of forming a fibrous product which comprises producing a dispersion of hard resin of the coumarone-indene type in an aqueous solution, adding the dispersion to a pulp of fibers and substantially uniformly distributing the dispersion throughout the pulp, precipitating the resin from the dispersion onto the fibers in solid, substantially non-adhesive condition, forming the pulp containing the solid, non-adhesive resin into a sheet, and subjecting the sheet to pressure and to a temperature above the melting point of the resin thereby resulting in coalescence of the resin particles and the formation of a sheet in which the resin is dispersed substantially homogeneously throughout the same.

JOHN A. KENNEY.

CERTIFICATE OF CORRECTION.

Patent No. 2,104,081. January 4, 1938.

JOHN A. KENNEY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 20, after the word and period "products." insert the following paragraphs:

> Among the objects of my invention are to produce fibrous products containing resins of the coumarone-indene type, and to provide methods whereby these resins may be uniformly distributed over the fibers of a pulp as sizing or binding agents, and the pulp so treated, molded or formed into a sheet. A further object of my invention is to provide a method of utilizing resins of the coumarone-indene type in the production of laminated products and as adhesive or binding agents for materials of this type.
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> In practicing my invention in the sizing of paper or production of a product having resin distributed throughout the same in a substantially uniform manner, I produce an aqueous dispersion of resins of the coumarone-indene type in any suitable manner, for instance by the use of silicate of soda as described in my copending applications referred to above, and mix the resin dispersion with a pulp of fibrous material. The resin is then precipitated onto the fibers of the pulp and the pulp formed into sheets from which the water of the pulp is removed. The sheets of material thus produced are dried and may be subjected to heat or to heat and pressure to cause the resin to flow throughout the sheet to produce a substantially continuous body of resin throughout which the fibers of the material are distributed. I may also utilize the dispersions in the production of laminated products by applying the resins in dispersed form to a sheet of material by distributing the resin throughout a fibrous pulp or I may apply the dispersions to sheets of material by immersion or by spraying or painting the dispersion onto the material. Additional layers of material are then applied to the sheet of material containing the resin or to which the resin has been applied, and the sheets of material are subjected to heat and pressure to bind the sheets together.;

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 8th day of February, A.D. 1938.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.