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PRODUCTION OF RESINOUS FELTED FIBROUS COMPOSITION

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2 Claims. (Cl. 92—55)

This invention relates to the production of resinous felted fibrous compositions from a combination of fibrous pulp and a resin derived from the extraction of pine wood pitch, which composition is susceptible to consolidation under heat and pressure to produce a homogeneous product having physical properties particularly suitable for structural uses and other purposes.

This application is a division of our co-pending application Serial No. 354,628 filed August 29, 1940, now Patent No. 2,264,189.

The felted fibrous material of our invention is capable of being consolidated to produce products having a relatively wide range of thickness, of the order of one-eighth inch to one inch, more or less, by uniting a plurality of thin component layers to form a truly homogeneous structure capable of being machined, handled and used, distinguished in character and properties from the component materials or intermediate products, although in its broader aspects our invention contemplates the production of such a homogeneous product by consolidating a thick single layer of our composition.

The intermediate and final products of our invention are of the thermoplastic rather than the thermo-setting or thermo-curing type. The consolidated product is highly resistant to water and moisture and resistant to petroleum solvents in general; is highly non-brittle even though the resin is per se extremely frangible and brittle. Other characteristics and properties of the final consolidated product will be brought out later in this specification.

Felted fibrous compositions utilizing synthetic and natural resins, treated or modified, or untreated or unmodified, have been proposed. However, the employment of such resins involves a cost factor which is of commercial significance, and other well recognized shortcomings.

In our invention there is employed, in conjunction with the fibrous pulp, a plastic resinous material which is inexpensive and available in large quantities and which, when properly combined with the fibers and consolidated in accordance with our invention results in a product of relatively considerable resistance to the absorption of moisture and to warping, and which, together with a pleasing appearance, has desirable structural properties particularly in respect to rigidity and resistance to cracking, shattering, breakage or separation.

Felted fibrous products made with bitumens, such as asphalts and coal tar pitches, or with resins, such as cumar, are characterized by inferior resistance to deformation under moderately elevated temperatures, by surface instability, by inferior resistance to hydrocarbon oils, and in some instances by inferior resistance to water and moisture; and such products do not have satisfactory properties after being composited or consolidated under heat and pressure.

Our consolidated product possesses a desirable range of elastic resistance to deformation which renders it durable in normal use; has desirable resistance to deformation under moderately elevated temperatures such as would be encountered in many uses, and has exceptionally desirable surface stability.

The invention more particularly comprehends a series of related steps in which the resinous material is incorporated by suitable beater treatment with fibrous stock in such a manner as to permit formation into a continuous web by conventional paper machine equipment, without gumming the instrumentalities thereof; the subsequent drying of such web by conventional means and the uniting or consolidation under heat and pressure of the web or webs thereby formed to produce a homogeneous and rigid structure. Accordingly, it is an object of the invention to provide an improved process wherein the fibre and resin are caused to intermix and combine readily and to obtain and retain their homogeneous admixture in the final article.

In accordance with the invention, the resin is combined with any desired or conventional fibrous stock or pulp in a beater or some equivalent device in such a manner as to distribute the resin throughout the mass of pulp. The admixture, having been brought to the proper pulp consistency, is then passed over a conventional board forming or paper forming machine to deposit the solid constituents and remove the water, and the resulting product, after drying, is consolidated under heat and pressure.

Extracted pine wood pitch constituting the resin employed in accordance with our invention is a complex resinous material whose exact composition is unknown, and comprises the residue, solid at normal temperatures, left after the separation of rosin, turpentine and other valuable constituents of pine wood. It has heretofore been considered substantially commercially valueless and has ordinarily been discarded.

The extracted pine wood pitch comprises a residue low in abietic acid remaining after the separation of refined rosin high in abietic acid

from the resinous material obtained by extraction of pine wood with a solvent. It is characterized by substantial insolubility in cold petroleum hydrocarbons, but will differ somewhat in its specific characteristics, such as acid number, melting point, extract petroleum ether solubility and content of naphtha- and toluol-soluble matter, depending upon the method for the recovery of rosin from pine wood used in its production.

As is well known, rosin may be extracted from pine wood by the use of a suitable solvent, such as hot gasoline, benzol, et cetera, after steaming of the wood with live steam to remove volatile oils, such as turpentine and pine oil. Again, volatile oils, as turpentine, and pine oil, may be extracted with the resin without first steaming for their removal.

Following extraction, the extract is distilled for the removal of solvent in those cases where the wood was subjected to steaming before extraction; or for the removal of solvent and volatile oils, as turpentine and pine oil, in those cases where the wood was extracted directly without steaming. As the result of distillation a resinous material containing abietic acid and admixed impurities is obtained. This resinous material may be treated in any one of a number of ways, all known to the art, for the removal of refined rosin high in abietic acid. The residue remaining after the removal of refined rosin and comprising a dark colored, hard, resinous mass low in abietic acid constitute the extracted pine wood pitch employed in our invention. A commercial variety of such a resin is known by the trade name of "Vinsol". The resin is soluble in alcohol and has a melting point of approximately 225–235° F., ball and ring method, and a penetration of zero at 160° F., five at 180° F., and seventy at 210° F., (200 grams, 5 seconds). It is peculiarly characterized by absence of cold flow to the extent that, when powdered, the particles show substantially no tendency to cohere, even under summer heat or when subjected to considerable pressure. These properties are associated with extreme inertness to temperature changes as may be determined by penetration-temperature tests made in accordance with conventional methods, as reflected by the penetration-temperature tests above referred to. These properties distinguish this resin from the well known pitches and bituminous materials of which we have knowledge. It is preferred to use a resin having a penetration of less than fifteen hundredths of a centimeter at 180° F.

By virtue of these properties, the resin becomes peculiarly adapted to the fulfillment of the objectives contemplated by this invention. It can be powdered, stored in bags and shipped during hot weather without sintering together of the particles. Likewise, the absence of cold flow and the ability to resist press roll pressures on a paper machine without developing adhesiveness renders it capable of use on a paper or board machine without the presence of protective materials which are ordinarily necessary to prevent gumming of the instrumentalities thereof. These properties carry through into the finished product and impart to the finished product the structural stability and resistance to deformation heretofore noted.

We have found that the resin employed in accordance with our invention can be directly compounded or admixed in powdered form with the pulp in the beater. As an aid thereto, use may be made of so-called wetting agents, such as any of the well known higher fatty acid sulfonates and their sodium salts, Turkey red oil, various soaps, and alkyl aryl sulfonates. Among other so-called wetting agents which may be employed are the sodium salts of naphthalene sulfonic acid derivatives sold under the name of Alkanol B, as well as the free naphthalene sulfonic acid known as Neomerpin. By the term "wetting agent," as employed in the present specification and claims, it will be understood that reference is had to all agents of this class which are capable of permitting rapid intermixing of the resin with the aqueous contents of the beater, while retaining the resin in such form as to permit it to attach itself about the fibers. When use is made of a wetting agent, the charge is introduced into the pulp in the beater by first kneading or mixing the resin together with the wetting agent and a small amount of water to form a uniform slurry, which may be piped or otherwise carried into the beater.

In accordance with the invention, the fibrous pulp or paper stock may be of any conventional type, comprising vegetable fibers capable of being formed into sheets or layers, such as rag, sulphite or kraft pulps, or the pulps formed from waste papers, it being understood by anyone skilled in the art that the characteristics of the final product will depend in some degree upon the stock employed. The invention in its broadest aspect, however, contemplates the use of pulps of the type employed in making such materials as so-called asbestos paper or board and the like. The fibers of this broad class comprise asbestos, mineral wool and even glass fibers. In short, it may be stated that as used broadly the terms "paper pulp" or "fibrous pulp or stock" are intended to cover any fibrous material capable of being formed into sheets or layers, particularly where the fibers are matted or felted. The stock may be defibered in any conventional beater, such as the well-known Hollander beater, preferably in the conventional aqueous medium.

Our invention contemplates the addition of a substantial proportion of the resin. Products having good structural properties have been formed from pulp mixtures containing a quantity of resin substantially equal in weight to the weight of the admixed fibers, as well as from mixtures containing from forty to sixty percent, of the resin with respect to the total resin fiber mixture. On the other hand, results satisfactory for certain purposes have been obtained employing from 10% to 70% of resin by weight of the resin-fiber mixture.

The hydrogen ion concentration of the beater stock should be adjusted, preferably by the use of alum, to a condition favorable to the maximum retention of the resin upon the fibers.

The aqueous charge of the beater is next run onto any suitable paper or board forming machinery to form paper or board. The deposition of the solids occurs in accordance with conventional practice.

Subsequent to formation, the sheet or board is dried by any conventional drying procedure. It is important to note that in spite of relatively low fiber content, when high percentages of resin are employed, board or sheets have ample strength in the wet condition so that they may be freely handled during the drying steps. Drying may take place at conventional paper or

board drying temperatures since no detrimental effect upon the resinous material is caused at such temperatures because the resin is thermoplastic, in contrast with many of the known synthetic resins which tend to cure or react at the desirable drying temperatures so that drying must necessarily be carried out at low temperatures and over long periods of time.

After drying, the board or sheet product is consolidated under heat and pressure conditions correlated to bring about the desired degree of consolidation and flow of the resin to produce the homogeneity desired. We believe that, as a result of such consolidation, the fibers per se are compressed to such an extent that their natural tendency to absorb moisture is reduced and it appears that such fibers are locked or anchored in such compressed condition as a result of the solidification of the fused resin on cooling. The consolidated product retains its density without unmolding at moderately elevated temperatures. To effect the consolidation, the sheet or board may be pressed in a mold or between flat platens for example under a pressure of from about 100 to about 2,000 pounds or more per square inch at a temperature at which the desired plasticization of the resin occurs. It will be apparent that the applied pressure and temperature may be varied within considerable limits depending upon the result desired.

Following are illustrative examples of the formation of resinous-fibrous products in accordance with our invention. A beater furnish of the following composition is prepared:

	Pounds
Kraft pulp	40
Resin (e. g. Vinsol)	50

The beater is charged in a conventional manner with the pulp and water, the consistency of the aqueous pulp suspension being adjusted to about 4%. After defiberization of the pulp, the resin is added in the form of a finely divided powder and thoroughly admixed with the stock in the beater. Sufficient alum is added to adjust the beater stock to a condition favorable to a maximum association of the resin particles with the fibers, for instance, to a pH value of 4.5, and the consistency of the pulp suspension is adjusted by the addition of water to about ½ of 1%. The stock is then run onto a conventional wet machine and a sheet having a thickness of ½" is built up, after which it is stripped from the make-up roll. The board is dried in a heated atmosphere at conventional drying temperatures which ordinarily do not exceed 180° F. The dried board may be rolled or calendered prior to consolidation although the rolling or calendering step may be omitted. The sheet is now ready for consolidation and after being dusted with an anti-stick preparation, such as zinc stearate or calcium stearate, is subjected to compacting between flat platens at a temperature of approximately 220–250° F. and under a pressure of approximately 825 pounds per square inch, for a period of approximately five minutes. The temperature is then rapidly reduced, by passing a cooling medium through the press platens, to approximately 100° F. or slightly lower. The pressure is then released and the board removed from the press. The product is a hard, tough, dense material having excellent structural properties and having no tendency to separate. The sheet prior to pressing is preferably conditioned to a moisture content of approximately 4–6%.

In some instances it may be desirable to utilize a so-called wetting agent. In those cases the powdered resin and the wetting agent, which may be an alkyl aryl sulphonate such as Nacconol NR (56 grams) are made up into a thin slurry with sufficient water (48 pounds) to thoroughly wet out the powdered resin. In this procedure the thin slurry of the powdered resin and wetting agent are added to the stock in the beater in the same manner as the powdered resin itself was added in the example.

Where it is desired to produce a black product, a black pigment may be used such as any of the conventional carbon blacks. When a carbon black pigment is used, the carbon black (about 2 pounds) may be advantageously incorporated in the aqueous slurry of the wetting agent and the powdered resin, or when a wetting agent is not used, the carbon black and powdered resin may be incorporated directly into the fibrous stock in the beater.

Instead of sneeting the stock on a wet machine, it may be formed on a cylinder board machine having one or more cylinders. Like the product made by consolidating a single thick layer made on a wet machine, the product of the multi-cylinder board machine after consolidation under heat and pressure is a homogeneous unitary product having no tendency to separate. The sheet or board may likewise be formed on a Fourdrinier machine, as well as on any of the machines commercially used in the formation of paper or board for such uses as insulating board, wall board, and the like.

As a feature of this invention, a plurality of dried sheets may be composited under heat and pressure to produce a homogeneous unitary product. Thus, in the fabrication of angular and curvilinear products from the sheets or boards made in accordance with our invention a plurality of plies of our product may be composited under heat and pressure and the resulting product has an integral homogeneous structure resistant to delamination of the plies.

Our consolidated product has the distinctive property of reproducing the surface of the pressing means and permanently retaining at normal temperature the surface imparted thereto by the pressing means. We refer to this as surface stability, i. e. the surface will not be damaged on contact at normal temperatures with warm moist objects such as the fingers, as distinguished from thermo-plastic-fibrous compositions made with bitumen-pitch type materials, cumar resin and the like. The surface is non-sticky and is glossy when the surface of the pressing means is polished. The product is reasonably resistant to relatively dilute mineral and organic acids, and is extremely tough and stiff.

In view of the rapidity with which the sheets or boards may be pressed or consolidated various types of presses may be used. If the boards or sheets are preheated, the period of "dwell" in the press may be substantially reduced. Accordingly, the present invention permits the use of relatively slow-moving press rolls. It is possible to pass the board over a series of heated rolls or through a drying tunnel for drying and preheating purposes and thence directly to forming rolls adapted to compact the material at pressures within the range previously given. It will be obvious from the foregoing that the present product lends itself to rapid economical production while many hitherto known resins neces-

sitate excessively long curing or reacting steps, thus tying up expensive pressing equipment.

In accordance with the invention the entire process, including drying and consolidating, may be carried out continuously. As is pointed out above, the board may be continuously dried as rapidly as desired by any conventional means and may emerge from the drying step at just the temperature for proper pressing. From this point the preheated material may be delivered directly to the pressing equipment and compacted quickly. Proceeding in accordance with this process, the pressing means may or may not be heated. Satisfactory results have been obtained when employing pressing means which were unheated, the residual heat from the pre-heating operation being sufficient to permit the desired compacting of the mass in the press. For better results, however, it is preferred that the pressing means be heated somewhat to prevent too rapid chilling, but nevertheless, to a temperature below the proper consolidating temperature so that the product may be removed from the pressing means immediately after the pressure is released in hard, stiff condition.

Where desired, of course, the invention may be also carried out in such a manner that the board is supplied in the ordinary cold or slightly warm condition to the pressing machine which in this case must be heated above the temperature at which the resin becomes sufficiently plastic. Proceeding in this manner, however, a considerably longer pressing time is necessary to permit the heat to penetrate throughout the mass and the press platens must be cooled after the pressing operation below the softening point of the resin. Thus, the pressing time may vary within a range of the order of 10 seconds to 10 or more minutes, depending on the thickness of the board or sheet; the extent to which the sheet or board is preheated, if at all, and other factors.

We have found that it is desirable to have a certain amount of moisture in the sheets or boards being pressed during the pressing operation, one of the advantages being that it permits the use of lower temperatures to obtain the homogeneous product desired. Particularly where a plurality of sheets are to be consolidated, the moisture content of the sheets must be carefully controlled. Moisture in excess of approximately 7% appears to cause sticking of the fibrous structure to the surfaces of the pressing means or blistering, or both. Below approximately 4% moisture, it appears that materially higher temperatures are required during pressing.

While we have described our invention in connection with the production of sheets or boards, it is to be noted that the invention in its broad aspects is applicable to the production of any felted fibrous structure utilizing the resin of our invention, including felted fibrous products formed by the accretion of the fibre-resin mixture on foraminated forms of irregular contour.

It will be apparent that the optimum temperature and pressure for satisfactory consolidation to produce the desired homogeneous final product will vary depending on a number of factors. The temperature and pressure of course must be so correlated as to bring about the desired amount of consolidation at the most efficient temperature and pressure. Depending on the pressure, it may be stated as a general rule that consolidation should take place at a maximum temperature beyond which so much resin would be extruded or pressed from the sheet that the final product would be deficient in its properties.

It is an advantage of the invention that lower proportions of the resin may, within certain limits, be made interchangeable with higher proportions thereof, by increasing to a sufficient degree the temperatures and pressures employed in the step of consolidating the dried sheet, so as to insure a complete fusion of the resin particles uniformly throughout the sheet. Thus the required densification may be obtained within a relatively wide range of resin content, so that the production of satisfactory board is not dependent upon too exacting a control of the amount of the resin employed.

While the preferred embodiment of our invention comprises the use of heat and pressure during consolidation to produce the desired homogeneous final product, it is to be understood that for certain purposes, the intermediate product containing the particles of resin distributed throughout the mass of felted fibers may be subjected to temperature alone sufficiently high to cause the resin particles to fuse and coalesce with each other to form films surrounding the fibers.

By the use of the expression "substantially chemically unaltered" in certain of the claims, we intend to distinguish the properties of the resin when employed as herein described from the properties resulting when it is employed as a size, i. e., in the form of an alkali soap of the resin, from which an insoluble soap of the resin is precipitated by chemical reaction with alum or the like, as described, for example, in patent to Dreshfield 2,168,399, dated August 8, 1939.

We claim as our invention:

1. The process of producing consolidated sheet material which comprises providing a fibrous stock of pulp fibres in uniform mixture with a substantial proportion of a powdered thermoplastic resin, said resin consisting essentially of a residue low in abietic acid remaining after separation of refined rosin high in abietic acid from the resinous material obtained by extraction of pine wood with a solvent, subjecting the mixture to a sheet forming operation, adjusting the moisture content of the sheet to from about 4 to about 7%, consolidating the resulting product by heating it to a temperature of from about 220 to about 250° F., to plasticize the resin and subjecting it to a pressure of from about 100 to about 2,000 pounds per square inch to cause the plasticized resin to flow and permeate the fibrous structure and to substantially completely surround the individual fibres thereof and substantially fill the interstices between them, cooling the sheet to solidify the resin in blended state and to anchor the fibres in compressed condition, releasing the pressure, and recovering the cooled product as a hard, stiff, tough sheet material having the property of remaining consolidated and rigidified and of retaining its density without unmolding.

2. In a process of producing a hard, dense board-like homogeneous fibrous structure wherein a mixture of pulp fibres and a substantial proportion of a powdered thermoplastic resin is sheeted, said resin consisting essentially of a substantially chemically unaltered residue low in abietic acid remaining after the separation of refined rosin high in abietic acid from the rosinous material obtained by the extraction of pine wood with a solvent, the improvement which comprises conditioning the sheet material to a

moisture content of approximately 4 to 6%, consolidating a plurality of such sheets at a temperature of from about 220 to about 250° F., and a pressure of from about 100 to about 2,000 pounds per square inch for a period of from about 10 seconds to about 10 minutes to cause the resin to flow and to substantially uniformly permeate the fibrous structure, cooling the consolidated product to solidify the resin in blended state, and to anchor the fibres in compressed condition, releasing the pressure and recovering the cooled product as a homogeneous hard, dense, board-like product substantially free of tendency to delaminate at normal temperatures.

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