Patented Oct. 18, 1938 2,133,694

UNITED STATES PATENT OFFICE

2,133,694

METHOD OF MAKING FIBROUS MATERIAL

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No Drawing. Application August 8, 1935, Serial No. 35,302

19 Claims. (Cl. 92—21)

This invention relates to the deposition of waterproofing material either alone or with other materials upon fibrous materials and relates especially to the manufacture of asbestos paper, millboard or other waterlaid asbestos fiber sheets containing waterproofing material or waterproofing material together with other materials preferably rubber and the product of the process.

This application is continuation in part of our application Ser. No. 733,984, filed July 6, 1934 for Fibrous materials and method of making the same. Said application Ser. No. 733,984 is directed primarily to the deposition upon fibrous material such as mineral fiber of rubber or rubber together with other material, e. g., a waterproofing material. This application is directed primarily to the deposition of a waterproofing material, either in the absence or in the presence of some other material such as rubber, on fibrous material such as mineral fiber from an aqueous pulp. Purposes of this invention relate not only to improvements in the process but also to improvements in pulps containing waterproofing material and in the product.

As an example of one use to which paper embodying our invention may be put, reference is made to the utilization of asbestos paper in the automobile industry as heat-resistant gasket material. Until comparatively recently, the automobile industry has used gaskets made from starch-bound asbestos paper encased in thin copper sheets. In addition to the copper-sheathed type of gasket, a gasket has been used having a pronged sheet steel core upon each side of which is a sheet of asbestos paper. The prongs on the steel core are pressed into the paper and are clinched to the paper by pressure, making a composite steel-reinforced asbestos gasket having no external sheet copper casing. Heretofore, such gaskets have been made by impregnating asbestos paper with a material which hardens and renders the asbestos paper as water-, gasoline- and oil-resisting as possible and then usually by giving the impregnated asbestos paper a surface coating of graphite.

It is one of the advantages of this invention that asbestos paper may be made on a paper machine in the usual way which is capable of resisting disintegration by water, gasoline and oil and which, without more treatment, can be used as gasket material as by securing it to a steel core sheet to give a finished gasket, either with or without surfacing with graphite. Thus, by using asbestos paper made according to our invention, gaskets, such as the steel cored type, can be made without the usual operations of handling, dipping, drying, baking and the like.

Asbestos fiber without a binder does not form a strong sheet when felted and requires some sort of binder to make it sufficiently strong for use in gaskets and the like. Heretofore starch has been commonly used as a binder. Starch gives the asbestos paper sufficient strength for many purposes, so long as the paper is kept dry. However, when the paper is dampened with water, the starch binder is softened so that there is pronounced loss of strength in the paper, or even complete disintegration. This type of paper, even when dry, has very low fold endurance and tear resistance. Attempts to improve asbestos paper employing starch as a binder by the addition of insoluble soaps, resins, sizes, etc., to make it waterproof, have not been successful, as these substances for some reason affect the starch binder and result in a paper that is too weak for ordinary handling.

The uniform deposition of an emulsified waterproofing material such as paraffin, for example, on mineral fiber involves certain difficulties which have been obviated according to this invention. Mineral fiber such as asbestos fiber has the property of tending to cause rapid coagulation of emulsions of waterproofing materials of the type referred to herein. This may be due to the fact that the mineral fiber carries a positive electric charge which tends to neutralize the electric charge carried by the dispersed particles of waterproofing material and/or carries salts which react with the stabilizing substances contained in the dispersion and/or finely-divided talc or rock which acts as a precipitating agent. If a waterproofing agent is distributed in a pulp in the absence of a protecting emulsifying agent, the waterproofing material tends to form coarse coagula in the pulp which result in a very unsatisfactory product. If an emulsifying agent is used and neutralized by chemical precipitating reagents such as acids, salts or the like, the process of neutralization is tedious if local overconcentrations of precipitating agent are to be avoided. In the last stages of precipitation, the precipitating agent has to be added practically drop by drop. Moreover, such neutralization involves added expense for materials and the inclusion of a certain amount of the precipitating agent in the final product, which inclusion is frequently undesirable especially where electrical conductivity is to be avoided.

It is a feature of the present invention that a water-proofing material such as paraffin may be readily deposited from an emulsion on fibrous materials, uniformly and without the formation of coarse clots, and without using expensive and inconvenient precipitating agents for the waterproofing material. The deposition of the waterproofing material may be performed successfully even by unskilled laborers in a relatively short time. This invention has the further advantage that it lends itself admirably to the formation of a felted asbestos sheet on a paper machine

without requiring special equipment. Any standard types of known apparatus may be used in the practice of this invention.

Illustrating our invention first in connection with the precipitation of a waterproofing material from an aqueous vehicle upon asbestos fibers, we have found that this can be successfully accomplished by first producing an aqueous pulp containing asbestos fiber, a dispersed waterproofing material and an emulsifying agent such as soap chips and/or sodium silicate, which emulsifying agent at concentrations of the materials comprised in the pulp is effective to prevent the formation of clots of waterproofing material in the pulp. Any coagulation that takes place in the pulp is retarded and controlled so that it does not result in undesirable formation of clots in the pulp. We have found that when such a pulp is diluted as by the addition of a substantial quantity of water, the effectiveness of the emulsifying agent is decreased and that the precipitation of the waterproofing material then takes place more rapidly. However, notwithstanding the increased rate of coagulation, caused by dilution, the precipitation of waterproofing material in the mixture is uniform about and among the asbestos fibers. Since the asbestos fiber itself exercises a precipitating effect upon the dispersed waterproofing material, the waterproofing material is precipitated on the fibers so as to be deposited about and among the fibers in firmly bonded relation thereto. When the precipitation is caused by dilution of the pulp, the deposition of the waterproofing material is apparently more uniform and bonded better to the fibers. While the pulp is normally diluted with water, it is within the scope of this invention to dilute the pulp with other materials so as to decrease the effectiveness of the emulsifying agent and cause the waterproofing material to be precipitated in the pulp.

For example, we have found that when waterproofing material and asbestos fiber are mixed in proportion to produce a paper containing about five per cent. waterproofing material, the precipitation of the waterproofing material can be substantially inhibited by the incorporation of about 0.5 per cent, of soap chips and about 1.5 per cent. of sodium silicate on the weight of insoluble material in the pulp when the proportion of insoluble material in the mixture to water is in the neighborhood of ten per cent. The water in the mixture will appear cloudy, indicating that all or most of the waterproofing material remains substantially unprecipitated for a considerable period of time. Upon diluting the mixture to about five per cent., for example, we have found that the rate of precipitation of the waterproofing material increases considerably and that fine particles of waterproofing material are deposited on the asbestos fibers. Upon further diluting the mixture to about one per cent., the precipitation proceeds still more rapidly and the waterproofing material is substantially completely deposited upon the asbestos fibers. While the accomplishment of uniform and substantially complete precipitation of waterproofing material upon diluting an aqueous pulp containing asbestos fiber, waterproofing material and an emulsifying agent which at the initial concentration of the pulp is effective to prevent the formation of clots in the pulp is unexpected, it is nevertheless an actual fact which has been demonstrated repeatedly in experimental operation and in actual manufacture of asbestos paper.

The method of precipitation of emulsified waterproofing material according to our invention by diluting a mixture of asbestos fiber, waterproofing material and an emulsifying agent requires no special care to be exercised by the operator. The pulp merely has to be mixed to the extent that is required for making the relatively homogeneous mixture of the materials comprised in the pulp. The dilution can be carried out immediately after uniform mixing is accomplished and results in a gradual and uniform deposition of the waterproofing material on the asbestos fibers.

As an illustration of one method of carrying out our invention, 1,600 pounds of 2X asbestos fiber (Quebec Asbestos Producers Assn. grade 5R, screen test about 0—0—10—6) and 1,000 pounds of 3X asbestos fiber (Quebec Asbestos Producers Assn. grade 7D, screen test about 0—0—5—11) are dumped into a beater containing 30,000 pounds of water. The beater is operated so that the fibers are merely separated and distributed but not cut up. An emulsion of waterproofing material is preferably made up separately. The emulsion of waterproofing material may be made up so as to contain, for example, 150 lbs. of paraffin emulsified with water by means of an emulsifying agent such as 15 lbs. of soap chips and 40 lbs. of silicate of soda of 42° Bé. Any commercial sodium silicate may be used such as the commercial 42° Bé. product having a ratio of Na_2O to SiO_2 of 1 to 3.25. In making up the emulsion of waterproofing agent, enough water is first heated, as with steam jets, to produce with the amount of paraffin used a 20% to 50% paraffin emulsion. In other words, for 150 pounds of paraffin, the amount of water that is used may be about 150 lbs. to about 600 lbs. When the water reaches about 200° F. the heating is discontinued and the paraffin, which may be in the form of small pieces or melted, is added to the hot water while the water is agitated as with a high speed propeller type agitator. The heat of the water tends to melt the paraffin if the paraffin is added in a solid state. The paraffin cools the mixture to about 140° to 160° F. The agitation of the mixture is continued and thereafter the silicate of soda and soap chips are incorporated in the emulsion tank. Stirring for ten to fifteen minutes produces an emulsion of desired characteristics.

The emulsion of waterproofing material, preferably while still warm, is added to the pulp of asbestos fiber, containing a small proportion of a binder, such as about 1% to 2% of starch. No particular care has to be exercised at this step of the procedure. All that is necessary is that the paraffin emulsion be mixed substantially uniformly through the pulp of asbestos fiber. The mixture can be made in any beater of usual type. The mixture as thus made up will have about 10 per cent of insoluble materials in proportion to the water which is present, and at this time and concentration there is very little precipitation of paraffin and no formation of lumps and clots in the mass. Preferably the amount of emulsifying agent that is used is equal to or slightly in excess of the amount required at the concentration of the materials in the pulp to overcome the precipitating tendency of other substances in the pulp including the natural precipitating effect of the asbestos.

The particular mixture made up as above described is now ready to be diluted and formed, for example, into a felted sheet on a paper-making machine of usual type. The mixture from the beater is taken to the storage chest for the

paper-making machine where it is slowly stirred and diluted to about 5%. In the storage chest substantially uniform and gradual precipitation takes place so that the paraffin becomes uniformly deposited upon the asbestos fibers without formation of clots. Thus instead of attempting to destroy the natural precipitating effect of the asbestos fiber, this precipitating effect is utilized by first counteracting it with a protective (emulsifying) agent and then reducing the effectiveness of the protective agent by diluting the pulp. When the pulp is diluted, the protective agent probably exercises a decelerating effect which insures better and more uniform deposition of the paraffin on the asbestos fibers. When the thin pulp in the storage chest is taken to the head box of the paper-making machine, it is still further diluted to about 1% at which dilution virtually all of the remaining unprecipitated paraffin becomes precipitated and deposited on the asbestos fibers. We have found it advantageous to dilute the pulp so that the concentration of undissolved substances in the mix is less than about 2½%, as more uniform and complete precipitation of the paraffin or other waterproofing material is thus secured. The fibers bearing paraffin thereon are taken up on the paper-making cylinders, screens or felts according to usual paper-making operations and made into a water-laid felted web or paper. When the paper is formed and dried on the drying cylinders of the paper-making machine, it is completed and no further operations are necessary except that in the case of thick sheets, it sometimes is desirable to age the paper or dry it in the drying oven to complete the removal of water therefrom.

While specific dilutions have been mentioned above, it is to be understood that these dilutions or concentrations of the aqueous pulp are given by way of illustration. It is apparent that other dilutions or concentrations of the pulp can be employed which as originally made up are such that the protective agent is effective to prevent precipitation of the paraffin or other waterproofing material with the formation of clots in the pulp but which upon being diluted causes the protective agent to become less effective with the result that the waterproofing material is deposited uniformly on the asbestos fibers. In general, the more concentrated the pulp the less protective agent has to be used in proportion to the asbestos fiber to prevent the asbestos fiber from precipitating the waterproofing material. The relative proportions of asbestos fiber and waterproofing material may also be varied depending on the proportion of waterproofing material to asbestos desired in the finished product, the emulsifying agent being used in sufficient amount to prevent the formation of clots of waterproofing material in the pulp. Other materials may also be included in the pulp when their presence is desired in the finished paper.

While a mixture of 2X and 3X asbestos fiber has been mentioned above, it is, of course, apparent that any suitable paper-making grade of asbestos fiber may be used. The mixture above mentioned is advantageous as being economical and as providing a combination of relatively long fibers for giving strength to the finished paper and shorter fibers for filling the interstices of the paper, thus securing the combined properties of strength and low porosity. Instead of ordinary asbestos fiber, other mineral fibers may also be used such as crocidolite, actinolite, mineral wool and the like.

A mixture of soap flakes and sodium silicate has been found to be particularly effective as an emulsifying agent for the waterproofing material. It is to be understood, however, that each of these substances may be used alone and that other emulsifying agents for the waterproofing material may also be used as pointed out in greater detail below.

While mention has been made above of preparing separately an emulsion containing emulsified waterproofing material and an emulsifying agent, and adding the emulsion to an aqueous pulp containing mineral fiber, such procedure, while preferable, is not essential. Thus a mixture of mineral fiber (or other fiber as mentioned below), water-proofing material, and emulsifying agent can be made in other ways as, for example, by making an aqueous pulp containing fiber and an emulsifying agent and then distributing a waterproofing material throughout the mixture in a highly dispersed state.

While this invention has been described in connection with the precipitation of waterproofing material, such as paraffin, about and among asbestos fibers, it is apparent that this invention may be also practiced in connection with the coagulation of waterproofing material upon other fibers than asbestos fiber, e. g., vegetable and animal fibers. If such fibers do not have a natural precipitating effect upon waterproofing material analogous to that caused by asbestos fiber, then there can be mixed with the fibrous pulp a precipitating agent which tends to precipitate the waterproofing material such as fine asbestos powder, certain mineral salts, metallic oxides, or hydraulic oxides, together with a protective (emulsifying) agent which is compatible with the added precipitating agent and which at the concentration of the materials in the pulp is effective to inhibit the tendency of the precipitating agent to precipitate the waterproofing material and deposit it on the fiber. When asbestos fiber is used, the fiber or material carried by the fiber acts as a precipitant for the waterproofing material. This precipitant associated with the asbestos fiber is ordinarily sufficient to precipitate the waterproofing material and according to our invention the precipitant agent is first counteracted or inhibited by a protective agent and then permitted to become operative to uniformly precipitate the waterproofing material on the asbestos fibers by dilution of the aqueous pulp. It is apparent that added precipitating agent in addition to the precipitant agent normally afforded by the asbestos may be included in the pulp in practicing our invention but usually this is not necessary or desirable. In the case of fibers other than asbestos fibers which do not naturally carry a precipitant for the waterproofing material, a precipitating agent can be included in the pulp from other sources. For example, to a rag or paper pulp containing fiber which is substantially free of a precipitating agent, an amount of precipitating agent such as fine asbestos fiber, asbestos "floats", Portland cement, magnesium oxide, or fibrous talc ("Asbestine") may be added so that the pulp will have a tendency to precipitate water-proofing material, which tendency is about the equivalent of that which a pulp would have if made up using asbestos fiber. The tendency of the precipitating agent to precipitate the waterproofing material is then counteracted and retarded by a protective such as soap flakes and sodium silicate so that when waterproofing material is added to the pulp

the water-proofing material will not precipitate in lumps in the pulp. The pulp with added waterproofing material is then diluted so that the emulsifying agent becomes less effective and so that the waterproofing material deposits more rapidly but the precipitation is uniform and the waterproofing material is deposited uniformly about and among the fibers in the pulp. The fiber carrying the waterproofing material can then be made into paper in the usual way.

Above we have illustrated the practice of our invention whereby a waterproofing material alone is precipitated by diluting a pulp containing asbestos or other fibers, waterproofing material and a protective agent which prior to dilution of the pulp inhibits the precipitation of the waterproofing material in clots in the pulp. In many cases, it is advantageous to practice our invention in the manufacture of paper containing materials other than waterproofing material, for example, rubber latex. The rubber latex can be deposited in the fiber in a manner similar to that employed in the precipitation of the waterproofing material and preferably in conjunction with the precipitation of the waterproofing material. The problems involved in coagulating rubber latex upon fibers, and the effect of mineral fibers in tending to cause coagulation of rubber latex are set forth in greater detail in our application Ser. No. 733,984 above referred to.

In the manufacture of asbestos paper, for example, containing both a waterproofing material and rubber latex, an aqueous pulp can be made up as above described containing asbestos fiber, an emulsified waterproofing material together with an emulsifying agent to keep the waterproofing material in an emulsified state, and rubber latex together with a protective agent adapted to prevent the rubber latex from coagulating. At the concentration of the materials in the pulp, the asbestos fiber exerts a tendency to coagulate the rubber latex and to precipitate the emulsion of the waterproofing material, but this tendency is inhibited or retarded in its action by the presence of the protective and the emulsifying agent so that neither the rubber nor the waterproofing material is thrown down in the form of clots in the pulp. Upon dilution of the pulp by the addition of a material thereto which dilutes the pulp, the rubber latex is coagulated and the waterproofing material is precipitated uniformly throughout the pulp. Prior to the dilution of the pulp, the protective for the rubber latex and the emulsifying agent for the emulsion of waterproofing material are believed to exert in the pulp a conjoint protective effect in inhibiting the coagulation of the rubber latex and the precipitation of the waterproofing material. It is within the scope of this invention, however, to utilize protective material which is specific to preventing the coagulation of the rubber latex together with an emulsifying agent which is specific to the prevention of the precipitation of the waterproofing material or a single material which exercises both of these effects. In any such event, such materials or mixture thereof may be referred to as protective material in the pulp.

While it is preferable to coagulate the rubber latex and to precipitate the waterproofing material substantially simultaneously, this is not essential, as these operations may be performed separately upon diluting prepared pulps containing protective material within the principles of this invention.

By way of illustrating the manufacture of asbestos paper containing a waterproofing agent, reference may be had to the following example wherein an aqueous asbestos pulp is prepared containing 1,600 lbs. of 2X asbestos fiber, 1,000 lbs. 3X asbestos fiber, and 30,000 lbs. of water (3,600 gals.). Prior to the addition of protective agents and latex to the asbestos fiber, an emulsion is preferably separately made up containing emulsified waterproofing material. The emulsion of waterproofing material may be made up so as to contain, for example, 150 lbs. of paraffin emulsified with water by means of an emulsifying agent such as 15 lbs. of soap chips and 40 lbs. of silicate of soda of 42° Bé. Any commercial sodium silicate may be used such as the commercial 42° Bé. product having a ratio of Na_2O to SiO_2 of 1 to 3.25. The protective agent for the rubber latex may be added either to the emulsion of waterproofing agent or to the asbestos pulp. We have found it convenient when an emulsion of waterproofing agent is produced to add the protective for the rubber latex to this emulsion. In making up the emulsion of waterproofing agent, enough water is first heated, as with steam jets, to produce with the amount of paraffin that is used a 20% to 50% paraffin emulsion. In other words, for 150 lbs. of paraffin, the amount of water that is used may be about 150 lbs. to about 600 lbs. To the heated water, the bone glue and soda ash which later are employed as protective agents for the latex are first added while stirring the water as with a high speed propeller type agitator. The heating is meanwhile continued until the temperature reaches about 200° F. The heating is then discontinued and the paraffin which may be in the form of small pieces or melted is added to the hot solution. The heat of the water tends to melt the paraffin if the paraffin is added in a solid state. The paraffin cools the mixture to about 140° to 160° F. The agitation of the mixture is continued and thereafter the silicate of soda and soap chips are incorporated in the emulsion tank. Stirring for about ten to fifteen minutes produces an emulsion of desired characteristics. We have found that an emulsion of particularly desirable characteristics is produced when a portion that adheres to a stick inserted into the emulsion tank upon being allowed to cool cannot be worked into a ball of paraffin by rubbing and rolling between the fingers.

The emulsion while preferably still warm enough to be above the melting point of the paraffin is added to the pulp of the asbestos fiber. No particular care has to be exercised at this step of the procedure. All that is required is that the paraffin emulsion be mixed substantially uniformly through the pulp of asbestos fiber. 500 lbs. of latex, containing about 195 lbs. rubber, is then added to the pulp of asbestos fiber and mixed through the fiber for about five to ten minutes until the latex is also uniformly distributed with the asbestos fiber.

The precipitattion of both the latex and the emulsion at this stage of the operation is retarded due to the presence of protective material in the mixture. Any precipitation that does take place is very gradual and uniform without the formation of objectionable clots of either rubber latex or paraffin and the pulp remains cloudy, indicating the presence of the uncoagulated latex and/or waterproofing material in the pulp. Upon passing the pulp to the storage chests for a paper machine, the pulp is diluted to about five per cent., for example, and both the latex and the

paraffin are to a considerable extent precipitated, but the precipitation is uniform and the minute particles of paraffin and rubber tend to strongly adhere to the asbestos fibers. Before the pulp is run on the paper machine, the mixture is finally diluted to about one per cent. or less, at which dilution the precipitation of both the paraffin and the rubber latex is substantially complete.

While in the above example it was stated that the emulsion of waterproofing material was added to the asbestos pulp prior to the latex, this is not essential, as the asbestos pulp can likewise be prepared by adding the protective for the latex to the asbestos pulp, then adding the latex, and finally adding the emulsified waterproofing agent. Moreover, by successive diluting operations, the latex can be deposited on the fibers separately from the waterproofing agent and either before or after the deposition of the waterproofing agent on the fiber, depending on the properties desired in the product.

The finished paper made according to our invention as described in the foregoing specific example will contain about 88.5% asbestos fiber, about 5% paraffin, and about 6½% rubber, together with traces of soluble ingredients which are present in the pulp. While this is an illustration of a desirable type paper, it is apparent that the percentages of the various ingredients can be changed considerably. Thus the amount of paraffin or other waterproofing material may vary considerably and may be employed with or without other materials such as rubber. Usually up to 20% of waterproofing material is all that is desirable and preferably the waterproofing material is used in conjunction with rubber. Preferably the rubber content varies from about 5% to about 30%, the paraffin content varies from about 3% to about 12%, and the asbestos varies from about 70% to 92%. The proportion of protective agent used is also adjusted according to the amounts of latex and paraffin in the product.

The finished paper containing coagulated rubber and paraffin is tough and flexible and does not crack when folded as ordinary asbestos paper does. It has high strength and is not greatly affected by water, either cold or hot. In fact, the paper may even be boiled in water for considerable periods of time and after removal from the boiling water and drying will be found to retain its characteristics only slightly impaired. The paper will not quickly disintegrate when boiled in water as does ordinary asbestos paper. Specimens of paper produced as above described have been subjected to various tests, the results being indicated in the following table:

	Specimen A	Specimen B	
	Tested immediately	Tested immediately	Aged 2 months
Weight, pounds per 100 sq. ft.	23.4	18.2	18.2
Caliper, inches	.047	.040	.040
Tensile strength, pounds per inch width, with	44	35	40
Across	25	14.5	20
Tear strength (Elmendorf), with grams	224	----------	208
Across	336	----------	256
Mullen strength, pounds	47	----------	32
Water absorption, percent	30	31	16

A specimen of paper produced as above described has also been tested for water, gasoline and oil absorption when applied to a steel core in the manufacture of steel core gaskets. The results of these tests are as follows:

24 hour water absorption	24 hour gasoline absorption	24 hour oil absorption
Percent 9.9	*Percent* 8.7	*Percent* 8.3

In the foregoing tables, attention is called to the fact that allowing the paper to become thoroughly dried by standing thirty to sixty days decreases the water absorption to about 16–20%. The same results may be obtained by thoroughly drying the paper on the paper-making machine so that thin paper run over the machine and thoroughly dried is immediately very water-resistant, while thicker paper which still contains a small amount of moisture when removed from the paper-making machine has a water-absorption that decreases on exposure to air on further drying in an oven. The asbestos sheet as it comes from a paper-making machine of usual type usually contains about 3.5% moisture. When this residual moisture is removed, water-absorbing characteristics of the paper are decreased.

The water-, gasoline- and oil-absorption of the new paper is relatively low. This is a very desirable characteristic of the new paper. In this respect, the new paper is even superior to other gasket materials made by impregnation and the application of coatings of various types. The absorption tests were made by soaking samples of gaskets in either water, gasoline or motor oil for twenty-four hours, wiping off the excess surface liquid, weighing and then calculating the per cent. of liquid absorbed. It is to be understood that the above given results of tests are in connection with only one embodiment of our invention and are not to be regarded as limiting the scope of this invention.

The inclusion of paraffin or other waterproofing agent in the paper is regarded as of advantage so as to impart both water-repellent characteristics and resistance to disintegration by water to the finished paper. Also the presence of the paraffin or other waterproofing material during the deposition of the rubber latex on the asbestos fiber is believed to retard the coagulation of the rubber and result in a more uniform deposition of the rubber on the asbestos fiber. Paraffin has been mentioned as a specific example of a waterproofing material which may be used, as this material gives satisfactory results and at the present time may be obtained at a relatively low price on the market. Other waxes or waxy, oily, or resinous materials such as Montan wax, cumarone resin, stearin, rosin, bitumens, linseed oil, tung oil and the like may also be used, but at the present time these waterproofing materials are either more expensive than paraffin or have been found somewhat less effective. Preferably the wax or other waterproofing material should have a melting point which is relatively high, that is, above 100° F. The paraffin used in the foregoing illustration has a melting point of about 120° F. to about 130° F. Synthetic waxlike materials may also be used such as chlorinated naphthalene, chlorinated di-phenyl, and the like. The chlorinated wax-like materials or halogenated waxes

or wax-like materials, e. g., brominated, have the advantage of being fireproof, that is, they are not combustible under ordinary conditions. According to this invention, any suitable wax-like, resinous, oily, or fatty material, natural or artificial, may be employed as a waterproofing material by producing an emulsion of the material in the pulp in the presence of an emulsifying agent and then precipitating the waterproofing material by diluting the pulp to decrease the effectiveness of the emulsifying agent. In general, waterproofing material, as the term is used in this application, is to be understood as meaning a material which if deposited among the fibers of a waterlaid felted sheet formed from a water pulp, will impart to the waterlaid fibrous sheet water repellency and resistance to absorption of liquid water. Such materials are referred to herein as waterproofing materials.

In making the emulsion of waterproofing material, mention has been made of the use of a mixture of sodium silicate and soap. Either one of these substances will make an emulsion of the waterproofing agent but the specific mixture of soap and sodium silicate has been found to make a better emulsion than either soap or sodium silicate alone. Other emulsifying agents may be used such as sulphonated oils, and their soaps, but such materials have to be used in greater quantities than the materials above mentioned and are also more expensive. Other soluble silicates than sodium silicate, e. g., potassium silicate, may also be used, but the other soluble silicates are somewhat more expensive than sodium silicate. Any ordinary commercial soluble soap may be used, such as white and yellow flake soaps. Preferably, starch is not used as an emulsifying agent for the waterproofing material, as starch is softened in water and is not desirable in a paper that is liable to become moistened.

A mixture of bone glue and soda ash has been found to be particularly effective as a protective for the rubber latex. Other animal glues such as flake glue, gelatine, hide glue, casein, etc., may also be used instead of bone glue, but bone glue is inexpensive and has been found to be at least as effective as the other equivalent substances just mentioned. Other protectives such as blood albumin, egg albumen and the like and synthetic protective colloids such as sulphonated oils and their soaps, sulphonated higher fatty alcohols and the like, as well as saponin, may also be used but these substances are more expensive than bone glue and have been found to be somewhat less effective. The soda ash mentioned above is of the commercial grade which is about ninety-five per cent. pure. Other alkalis, such as ammonia and the caustic alkalis, may also be used but are somewhat more expensive, and less safe and less convenient to handle than soda ash. Such substances as the above are referred to herein as protectives for inhibiting the coagulation of rubber latex.

Glue may be used by itself without the presence of alkali, but alkali has been found to render the glue more effective as a protective for rubber latex. Alkalis could be used without the presence of other protectives, but with asbestos fiber relatively large amounts of alkali would have to be used, so it is normally advantageous to use an alkali such as soda ash with colloidal protective agents such as bone glue and the like.

In preparing the emulsion, the temperature of the mixture is preferably kept above the melting point of the waterproofing agent that is used, although this is not absolutely essential after emulsification, if proper agitation is maintained to prevent the formation of clots of agglomerated paraffin. In the beater which contains the asbestos pulp, however, the temperature is preferably kept below the melting point of the waterproofing agent. This is advantageous in that it has been found that the keeping of the temperature below the melting point of the waterproofing agent prevents the waterproofing agent, if its density is less than that of water, from rising to the surface and becoming separated from the fibers in the beater.

The modification of our invention wherein rubber and a waterproofing material are deposited on asbestos fiber, has been illustrated above. As with the case of precipitating waterproofing material alone, this modification of our invention can be practiced in connection with other fibers than asbestos fiber by employing a coagulant or precipitating agent for the waterproofing material and rubber latex which is first counteracted by the protective material and then, upon diluting the pulp, is permitted to become effective to coagulate the latex and precipitate the waterproofing material uniformly upon the fiber.

In referring to latex herein, it is to be understood that this term includes not only naturally occurring rubber latices but also artificial dispersions of rubber in aqueous vehicles. It is also to be understood that this invention may be practiced with the inclusion of vulcanized rubber dispersed in aqueous vehicles or with the use of vulcanizing compounds together with the rubber latex that is also used so as to produce an asbestos fiber sheet containing vulcanized rubber. For certain purposes, we have found that dispersions of synthetic rubber such as chlorinated rubber may be used and that these substances as incorporated in the new paper are insoluble in gasoline and oil as well as insoluble in water. Where gasket material is liable to become contacted with gasoline and oil as well as with water, the synthetic rubbers which are insoluble in gasoline and in oil are advantageous in the practice of our invention. Other materials than those above mentioned such as fillers and reinforcing pigments may, of course, also be incorporated in the aqueous pulps.

The paper produced according to this invention has been found to be stronger and more waterproof than paper made by the utilization of coagulating agents such as alum, acetic and hydrochloric acids and the like for the purpose of producing coagulation of rubber and rubber latex mixed with the asbestos fiber. It is advantageous that the finished product produced according to our invention is substantially free of chemical coagulants such as acids, alum, heavy metal salts and the like, as these materials are disadvantageous because of being injurious to the rubber, impairing the electrical insulating properties of the paper and the like. The complete deposition of the rubber latex as well as the waterproofing material, where waterproofing material is used, can be readily accomplished so that there is no loss of rubber latex or waterproofing material according to our invention.

By our invention, a product which is superior to the products produced heretofore is produced by a process which requires less skilled labor, less total labor, less danger, less expense, and less time than processes utilized heretofore. While this invention has been described in connection with

specific illustrations shown herein, it is understood that this has been done merely for the purpose of illustration and that this invention is to be limited only by the scope of the following claims.

We claim:

1. A method of precipitating a waterproofing material upon mineral fibers which comprises preparing an aqueous pulp containing said waterproofing material in a highly dispersed state, mineral fibers which tend to precipitate said waterproofing material, and an emulsifying agent in effective amount at the concentrations of the materials comprised in said pulp of preventing the precipitation of said waterproofing material at a rate which results in the formation of clots in said pulp, and increasing the rate of precipitation of said waterproofing material while effecting substantially uniform precipitation and deposition of said waterproofing material about and among said mineral fibers by diluting said pulp with water.

2. A method of precipitating a waterproofing material upon mineral fibers which comprises preparing an aqueous pulp containing mineral fibers, emulsified waterproofing material and an emulsifying agent which inhibits the precipitation of the waterproofing material, the concentrations of the materials in the pulp being such that said waterproofing material does not precipitate with the substantial formation of clots in said pulp and then substantially diluting said emulsifying agent therein by substantially increasing the total amount of said pulp without proportionally increasing the total amount of said emulsifying agent therein and thereby cause precipitation of said waterproofing material about and among said mineral fibers.

3. A method of precipitating waterproofing material upon asbestos fibers which comprises preparing an aqueous pulp containing asbestos fibers, said waterproofing material in a highly dispersed state and an emulsifying agent effective at the concentrations of the materials comprised in said pulp to prevent substantial formation of clots of precipitated waterproofing material in said pulp and then causing substantially complete and substantially uniform precipitation of the waterproofing material about and among the asbestos fibers by diluting the pulp with water.

4. A method of precipitating waterproofing material upon fibers which comprises preparing an aqueous pulp containing fiber, emulsified waterproofing material, a precipitating agent tending to precipitate said waterproofing material and an emulsifying agent effective at the concentrations of the substances comprised in said pulp of substantially counteracting the tendency of said precipitating agent to precipitate said waterproofing material in said pulp and then diluting said pulp with water to a point at which said emulsifying agent is substantially less effective in counteracting the tendency of said precipitating agent to precipitate said waterproofing material, thereby causing said waterproofing material to precipitate substantially uniformly about and among said fibers.

5. A method of precipitating emulsified waterproofing material upon fibers, which comprises preparing an aqueous pulp containing fiber, emulsified waterproofing material, a precipitating agent tending to precipitate said waterproofing material and an emulsifying agent effective at the concentrations of the substances comprised in said pulp of preventing the formation of clots of precipitated waterproofing material in said pulp and then diluting said pulp with water to a point at which the effectiveness of said emulsifying agent is substantially decreased and at which the waterproofing material in said pulp is substantially completely precipitated about and among said fibers.

6. In a method of precipitating emulsified waterproofing material on asbestos fibers, the steps comprising preparing an aqueous pulp containing asbestos fibers, emulsified waterproofing material, and an emulsifying agent in effective amount at the concentrations of the materials comprised in said pulp of preventing the formation of clots of said waterproofing material in said pulp and then gradually precipitating said emulsified waterproofing material upon asbestos fibers in said aqueous pulp by adding water to said pulp until said pulp contains less than about 2½% of undissolved solid materials in proportion to water in the presence of said emulsifying agent which at the concentrations of the materials in said pulp after the addition of water to said pulp as aforesaid retards but nevertheless permits gradual uniform precipitation and deposition of waterproofing material about and among said asbestos fibers.

7. A method of precipitating waterproofing material on mineral fibers which comprises making an aqueous pulp containing mineral fibers, making an emulsion containing emulsified waterproofing material and an emulsifying agent for the waterproofing material, mixing said pulp with said emulsion to form a mixture wherein the emulsifying agent at the concentrations of the materials in the mixture is effective to prevent formation of clots of waterproofing material in said mixture, and then diluting said mixture with water thereby causing said waterproofing material to be substantially uniformly precipitated and deposited about and among said mineral fibers.

8. The method of precipitating waterproofing material on mineral fibers which comprises preparing an aqueous pulp containing substantially distributed through the pulp mineral fibers and an emulsifying agent adapted to inhibit the precipitation of waterproofing material, adding waterproofing material to the pulp and distributing it in a highly dispersed state substantially uniformly through the pulp, the emulsifying agent at the concentrations of the materials in the pulp being effective to prevent formation of clots of waterproofing material in the pulp and then adding water to the pulp to substantially dilute the pulp so as to reduce the effectiveness of said emulsifying agent, thereby causing said waterproofing material to be uniformly precipitated about and among said mineral fibers.

9. In a method of making asbestos paper from an aqueous pulp, the steps comprising preparing an aqueous pulp containing asbestos fibers, an emulsified waxy waterproofing material and an emulsifying agent comprising soap, said emulsifying agent being effective at the concentrations of the materials in said pulp of preventing the formation of clots of precipitated waterproofing material in said pulp and then diluting said pulp with water, thereby causing said waterproofing material to be substantially uniformly precipitated and deposited about and among said asbestos fibers.

10. In a method of making asbestos paper from an aqueous pulp, the steps comprising preparing an aqueous pulp containing asbestos fiber, an emulsified waxy waterproofing material, and an

emulsifying agent comprising soluble silicate, said emulsifying agent being effective at the concentrations of the materials in said pulp of preventing the precipitation of said waterproofing material in the form of clots in said pulp, and then diluting the pulp with water, thereby causing uniform precipitation of said waterproofing material about and among said asbestos fibers.

11. In a method of making asbestos paper wherein an aqueous pulp of asbestos fibers is formed into a water laid felted paper on a paper-making cylinder, screen or felt, the steps which comprise making an aqueous pulp containing asbestos fibers, emulsified waterproofing material and an emulsifying agent in effective amount at the concentrations of the materials comprised in said pulp of preventing the substantial formation of clots of waterproofing material in the pulp and then diluting the pulp with water thereby decreasing the concentration in said pulp by at least about half so as to substantially decrease the effectiveness of said emulsifying agent, and thereby causing said waterproofing material to be precipitated uniformly about and among said asbestos fibers prior to forming said pulp into water laid felted paper.

12. In a method of making water laid asbestos paper from an aqueous pulp of a concentration suitable for a paper making operation, the steps comprising preparing an aqueous pulp containing asbestos fiber, preparing an emulsion of a waterproofing material stabilized by an emulsifying agent, and then adding the emulsion to the pulp, said pulp being non-acid and the concentration of the pulp being higher than that desired for said paper making operation and said emulsifying agent at said concentration of said pulp being effective to prevent the formation of clots of precipitated waterproofing material in said pulp, and then diluting said non-acid pulp with water to desired concentration for said paper making operation, said emulsifying agent being rendered less effective by said dilution of said pulp so that substantially all of said waterproofing material is substantially uniformly precipitated about and among said asbestos fibers prior to the paper making operation.

13. In a method of making fibrous paper containing a waterproofing material, the steps comprising making an aqueous pulp containing asbestos fiber, making an emulsion of waterproofing material at a temperature above the melting point of said waterproofing material and then adding the emulsified waterproofing material to said pulp, said pulp being at a temperature below the melting point of said waterproofing material, to form an aqueous pulp containing the waterproofing material in emulsified condition, and thereafter diluting said pulp with water to precipitate said waterproofing material about and among the asbestos fibers in the pulp.

14. A method according to claim 2 wherein the waterproofing material is a waxy waterproofing material.

15. A method according to claim 2 wherein the waterproofing material is an oily waterproofing material.

16. A method according to claim 2 wherein the waterproofing material is a resinous waterproofing material.

17. A method according to claim 4 wherein the waterproofing material is a waxy waterproofing material.

18. A method according to claim 4 wherein the waterproofing material is an oily waterproofing material.

19. A method according to claim 4 wherein the waterproofing material is a resinous waterproofing material.

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