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## METHOD OF COAGULATING RUBBER UPON FIBERS

Harold W. Greider, Wyoming, and Marion F. Smith, Cincinnati, Ohio, assignors to The Philip Carey Manufacturing Company, a corporation of Ohio

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This invention relates to the deposition of rubber or rubberlike material alone or with other materials upon fibrous materials and relates especially to the manufacture of asbestos paper, millboard, or other waterlaid asbestos fiber sheet containing rubber, or rubber and other materials, and the product of said process.

It is one purpose of this invention to improve upon the deposition of rubber upon fibrous materials such as mineral fiber in a process wherein rubber latex contained in an aqueous pulp is coagulated about and among fibers contained in the pulp. Purposes of this invention relate not only to improving the process but also to improvements in pulps containing rubber latex and in paper made from such pulps. A further purpose of this invention lies in the manufacture of paper containing rubber and/or waterproofing material.

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 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. 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.

Rubber latex has heretofore been suggested as a binder for asbestos paper. However, serious difficulties have been encountered heretofore in successfully and economically incorporating the latex with asbestos fiber.

Rubber latex according to present knowledge is believed to contain rubber suspended in an aqueous vehicle as microscopic globules. In the usual commercial product, the rubber content of the liquid is between about thirty-five per cent. and forty per cent., although concentrated latices containing about sixty-five per cent. of rubber are also sold to some extent. The liquid is of a milky white color, and is stabilized and preserved for shipment usually by the addition of a small amount of ammonia. The microscopic rubber particles are believed to carry a negative electric charge and are free to move about. The rubber particles coalesce or coagulate so as to form rubber clots upon the addition of acids, certain metallic ions, removal of water, neutralization of electric charge, or the removal of naturally-occurring stabilizing proteins.

Asbestos fiber when mixed with latex causes immediate coagulation of the rubber in the latex with precipitation of the rubber in large irregular clots. Thus, if asbestos fiber is added to the latex, a plurality of large clots of rubber becomes mixed with the pulp of asbestos fiber and the rubber does not uniformly cover the asbestos fibers. If attempt is made to make a felted paper on a paper machine with the rubber in the clotted condition referred to, an unsatisfactory product is obtained which cannot be sold commercially due to its low strength and due to the uneven distribution of the rubber in the form of clots or lumps in the paper with portions of asbestos fiber between the lumps carrying little or no rubber.

While this invention is not limited by the theories which are advanced herein as to the reason for the precipitation of the rubber latex

by the asbestos fiber, it is believed that the precipitation of the latex may be due to the fact that the asbestos carries a positive electric charge which neutralizes the negatively-charged rubber latex suspension, destroying its stability. The asbestos fiber is soluble in water to some extent and, due to the adsorbed moisture content of the fiber, there is a surface water film on the fibers carrying dissolved salts. The ions of these dissolved salts may disturb the equilibrium condition of the latex emulsions by reason of their electric charge or by precipitating certain stabilizing substances in the latex. Moreover, the finely-divided talc or rock always associated with the asbestos fiber or the very fine asbestos fibers themselves, may also contribute to the coagulation effect, since certain finely-divided substances have this effect on latex, probably due to adsorption of stabilizing substances from the latex suspension, on the great surface area of such finely-divided substances.

Attempts have been made heretofore to overcome the tendency of asbestos paper to cause the latex to precipitate in clots which result in a lumpy paper that is commercially unsatisfactory because of lack of uniformity. Thus it has been proposed to extract the asbestos fiber with acid as by subjecting the asbestos fiber to treatment with boiling dilute mineral acid. After the acid treatment, the fiber is washed and then treated with rubber latex. This treatment is disadvantageous because of the time and expense required for washing the asbestos with acid and then washing the asbestos to free it from the acid. Moreover, the structure of the asbestos fiber is changed and weakened so as to reduce the strength of the paper made therefrom. The expense for equipment and reagents used in the extracting step is also disadvantageous. Also, if the latex is to be deposited on the asbestos fiber after the fibers have been washed with acid, chemical coagulants must be employed. The addition of chemical coagulants to the rubber latex is extremely disadvantageous due to the extreme care and excessively long time required to prevent local over-concentrations of the added reagent and formation of clots in the pulp. Moreover, the coagulant acts not only to coagulate the rubber on the fiber, but also to form coagula of rubber in the aqueous vehicle which are not firmly bonded to or intimately mixed with the fiber, and this is also disadvantageous.

It has also been proposed to incorporate in the latex or in the asbestos pulp certain protectives such as alkali and the like which prevent the asbestos fiber from causing the latex to coagulate and then coagulate the latex by the addition of chemical coagulating agents such as acids, alum, zinc sulphate and the like. The disadvantages of using chemical coagulants has been mentioned above. In this method of coagulating in the latex, that is by means of chemical coagulants, the coagulating agent has to be added very slowly over long periods of time such as about one and one-half hours to prevent the formation of clots of coagulated latex. In the last stages of coagulation of the latex, the coagulating agents may have to be added practically drop by drop. The handling of acids and similar materials likewise is disadvantageous and even dangerous in ordinary plant operation. Moreover, substances such as alum are believed by rubber technologists to exercise an injurious effect on the rubber. Furthermore, mineral salts, acids and the like decrease the electrical insulation value of the resulting material and involves an additional uneconomical step.

Instead of adding all of the chemical coagulating agent after the latex is added to the asbestos pulp, it has also been proposed to add some of the coagulating agent, such as alum, to the latex prior to the addition of the latex to the asbestos fiber, but this procedure does not eliminate the disadvantages of using chemical coagulants which have been referred to above.

It has also been proposed heretofore to mix with latex a protective such as hemoglobin which acts as a protective when cold, but does not act as a protective when heated, and then heating the pulp so that the heat will coagulate the latex. It is apparent, however, that this procedure is likewise disadvantageous, as considerable time and excessive expense are required to heat the large volumes of aqueous mixture that are used in the manufacture of asbestos paper.

As distinguished from methods of coagulation which have heretofore been proposed, our invention provides a method whereby rubberized asbestos paper can be manufactured without excessive handling of the latex or of the asbestos pulp and without the use of chemical coagulating agents which are disadvantageous for the reasons above mentioned. Moreover, according to our invention, the coagulation of the rubber is conducted in such a manner that even unskilled laborers can successfully produce rubberized products of high quality. Furthermore, the time for performing the coagulation step is much shorter than in the operations which have been proposed heretofore. It is a still further advantage of our invention that it lends itself admirably to the formation of a felted asbestos sheet on a paper machine and 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 coagulation of rubber latex 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, rubber latex and a protective such as bone glue, which protective, at concentrations of the materials comprised in the pulp, is effective to prevent the formation of clots of rubber 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 substantial quantities of water, the effectiveness of the protective is decreased and that the coagulation of the rubber then takes place more rapidly. However, notwithstanding the increased rate of coagulation, caused by dilution, the coagulation of rubber in the mixture is uniform about and among the asbestos fibers. Since the asbestos fiber itself exercises a coagulating effect upon the rubber latex, the rubber latex is coagulated on the fibers so as to be deposited about and among the fibers in firmly bonded relation thereto. When the coagulation is caused by dilution of the pulp, the deposition of the rubber is apparently more uniform and bonded better to the fibers as the resulting product has greater strength and decreased water absorption as compared with asbestos papers prepared by coagulation of latex by chemical coagulants. 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 protective and cause the latex to be precipitated in the pulp.

For example, we have found that when rubber latex and asbestos fiber are mixed in proportion to produce a paper containing about 7.0 per cent. rubber, the coagulation of the rubber latex can be substantially prevented by the incorporation of about 2.0 per cent. of bone glue and about 3.0 per cent. of soda ash 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 latex remains substantially uncoagulated for a considerable period of time. Upon diluting the mixture to about five per cent., for example, we have found that the rate of coagulation of the rubber increases considerably and that rubber coagula are deposited on the asbestos fibers. Upon further diluting the mixture to about one per cent., the coagulation proceeds still more rapidly and the latex rubber is completely deposited as rubber coagula upon the asbestos fiber. While the accomplishment of uniform and substantially complete coagulation of rubber latex upon diluting an aqueous pulp containing asbestos fiber, rubber latex, and a protective 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 actual manufacture of latex-bonded asbestos paper.

The method of coagulation of rubber latex according to our invention by diluting a mixture of asbestos fiber, rubber latex and a protective requires no special care to be exercised by the operator. The latex can be added to the aqueous asbestos pulp containing a protective just as it is commercially sold on the market. The pulp merely has to be mixed to the extent that is required for making a 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 coagulated rubber on the asbestos fibers. No excessive or expensive manipulation of the latex, either before or after the addition of the same to the asbestos fiber pulp, is required. Moreover, no time-taking and expensive step wherein chemical coagulating reagents are used is necessary nor are deleterious chemicals carried into the coagulated rubber. No time and expense for heating the mix has to be expended.

As an illustration of one method of carrying out our invention, 1,600 pounds of 2X asbestos fiber and 1,000 pounds of 3X asbestos fiber are dumped into a beater containing 26,000 pounds of water. The beater is operated so that the fibers are merely separated and distributed but not cut up. About sixty pounds of bone glue and about ninety pounds of soda ash are added to the asbestos fiber aqueous pulp. The latex is then added, the quantity of latex of any commercial concentration being added so that about 195 pounds of rubber is incorporated in the mixture. The mixture can be made in any beater of usual type, and mixing for only about ten minutes is all that is necessary to secure a substantially uniform distribution of the various materials in the pulp. The mixture as then made up will have about ten per cent. of insoluble materials in proportion to the water which is present, and at this time and concentration there is very little coagulation of the rubber latex and no formation of clots in the mass. Preferably the amount of protective 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 coagulating tendency of other substances in the pulp including the natural coagulating effect of the asbestos.

The beater 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 chests for the paper-making machines where it is slowly stirred and diluted to about five per cent. In the storage chests, substantially uniform and gradual coagulation takes place so that the rubber becomes uniformly deposited upon the asbestos fibers without formation of clots. Thus instead of attempting to destroy the natural coagulating effect of the asbestos fiber, this coagulating effect is utilized by first counteracting it with a protective and then reducing the effectiveness of the protective by diluting the pulp. When the pulp is diluted, the protective probably exercises a decelerating effect which insures better and more uniform deposition of the rubber 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 one per cent. at which dilution all of the remaining uncoagulated rubber latex becomes coagulated 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 coagulation of the rubber latex is thus secured. The fibers bearing rubber deposited thereon are then 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 is sometimes desirable to age the paper or dry it in a drying oven to complete the removal of the 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 is effective to prevent coagulation of the rubber latex with the formation of clots in the pulp, but which upon being diluted causes the protective to become less effective with the result that the rubber latex is coagulated and deposited uniformly on the asbestos fibers. In general, the more concentrated the pulp the less protective has to be used in proportion to the asbestos fiber to prevent the asbestos fiber from coagulating the latex. The relative proportions of asbestos fiber and latex may also be varied depending on the proportion of rubber to asbestos desired in the finished product, the protective being used in sufficient amount to prevent the formation of clots of coagulated rubber 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 paper-making grade of asbestos

fiber may be used. The mixture above mentioned is advantageous as being economical and as providing a combination of long fibers for giving strength to the finished paper and shorter fibers for filling the interstices in the felted fabric. This is advantageous in the production of a paper which has 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 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 albumen, 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.

While this invention has been described in connection with the coagulation of rubber about and among asbestos fibers, it is apparent that this invention may be also practiced in connection with the coagulation of rubber upon other fibers than asbestos fiber, e. g., vegetable and animal fiber. If such fibers do not have a natural coagulating effect upon rubber latex analogous to that caused by asbestos fiber, then there can be mixed with the fiber pulp a coagulant which tends to coagulate the rubber latex such as certain mineral salts, metallic oxides, hydroxides, or acids, together with a protective which at the concentration of the materials in the pulp is effective to counteract the tendency of the coagulant to coagulate the rubber latex and deposit the latex on the fiber. When asbestos fiber is used, the fiber or material carried by the fiber acts as a coagulant for the rubber latex. This coagulant furnished by the asbestos fiber is ordinarily sufficient to coagulate the latex and, according to our invention, the coagulant is first counteracted by a protective and then permitted to become operative to uniformly coagulate the rubber on the asbestos fibers by dilution of the aqueous pulp. It is apparent that added coagulant in addition to the coagulant 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 coagulant for the rubber latex, coagulating material can be included in the pulp from other sources. For example, to a pulp containing fiber which is substantially free of coagulant, an amount of coagulant such as zinc sulphate, magnesium oxide, or acetic acid may be added so that the pulp will have a tendency to coagulate rubber latex which is about the equivalent of that which a pulp would have if made up using asbestos fiber. The tendency of the coagulant to coagulate rubber latex is then counteracted and retarded by a protective such as bone glue and an alkali so that when latex is added to the pulp, the latex will not coagulate in lumps in the pulp. The pulp with added latex is then diluted so that the protective becomes less effective; and so that the latex coagulates more rapidly. But the coagulation is uniform and the rubber is deposited uniformly about and among the fibers in the pulp. The fiber carrying the rubber can then be made into paper in the usual way.

Above we have illustrated the practice of our invention whereby rubber latex alone is precipitated or coagulated by diluting a pulp containing asbestos or other fibers, rubber latex and a protective which prior to dilution of the pulp prevents the coagulation of the latex in clots in the pulp. In many cases it is advantageous to practice our invention in the manufacture of paper containing a waterproofing material as well as the rubber latex. We have found that the waterproofing material can be deposited on the fiber in a manner similar to that employed in the coagulation of the latex and preferably in conjunction with the coagulation of the latex.

In the manufacture of asbestos paper containing waterproofing material, an aqueous pulp can be made up as above described containing asbestos fiber, a protective and rubber latex and in addition containing emulsified waterproofing material together with an emulsifying agent to keep the waterproofing material in an emulsified state. 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 counteracted 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° Be. 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 158° 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 precipitation 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 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 rubber may vary from about 3% to 50% and the asbestos fiber may vary from about 50% to 97%. As above described, no paraffin or equivalent waterproofing material may be used at all or the percentage of this material may be increased from 0% to about 20% in the manufacture of desirable waterproofed asbestos papers. 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 or 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 waterproof and water-repellent characteristics 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, coumarone resin, stearin, rosin, linseed oil, tung oil and the like may also be used, but at the present time these waterproofing materials are somewhat more expensive than paraffin. Preferably the wax or other waterproofing material should have a melting point which is relatively high, that is, about 100° F. The paraffin used in the foregoing illustration has a melting point of about 120° F. to about 130° F. Synthetic wax like materials may also be used such as chlorinated naphthalene, chlorinated diphenyl, 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 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.

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 coagulating rubber alone, this modification of our invention can be practiced in connection with other fibers than asbestos fiber by employing a coagulant or coagulants for the latex and emulsified material which is first counteracted by 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 containing chlorine (referred to herein for purposes of brevity as chlorinated rubber) may be used, such synthetic rubber containing chlorine as incorporated in the new paper being insoluble in gasoline and oil as well as in water. A substance such as poly-

merized chloro-2-butadiene-1,3 (chloroprene) is regarded as the equivalent for such purpose as chlorinated natural rubber. Other halogenated (e. g. brominated) rubbers may also be used. 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 purposes of illustration and that this invention is to be limited only by the scope of the following claims.

We claim:

1. A method of coagulating rubber upon mineral fibers which comprises preparing an aqueous pulp containing rubber latex, mineral fibers which tend to coagulate said rubber latex, and a protective in effective amount at the concentration of materials comprised in said pulp of preventing the coagulation of said rubber latex at a rate which results in the formation of clots in said pulp, and then adding sufficient water to said pulp to substantially increase the rate of coagulation of said rubber latex thereby effecting substantially uniform coagulation and deposition of the rubber latex about and among the mineral fibers by said dilution of said pulp with water.

2. A method of coagulating rubber upon asbestos fibers which comprises preparing an aqueous pulp containing asbestos fibers, rubber latex, and a protective which inhibits the coagulation of said latex, the concentrations of the materials in said pulp being such that said latex does not coagulate with the substantial formation of clots in said pulp, and then substantially diluting said protective therein by substantially increasing the total amount of said pulp without proportionally increasing the total amount of said protective therein and thereby cause coagulation of said rubber about and among said asbestos fibers.

3. A method of coagulating rubber upon asbestos fibers which comprises preparing an aqueous pulp containing asbestos fibers, rubber latex, and a protective effective at the concentrations of the materials comprised in said mix of preventing substantial formation of clots of coagulated rubber in said pulp, and then adding sufficient water to said pulp to cause substantially complete and substantially uniform coagulation of the rubber latex about and among the asbestos fibers by said dilution of the pulp with water.

4. A method of coagulating rubber latex upon fibers which comprises preparing an aqueous pulp containing a major proportion of fiber, rubber latex, a coagulant tending to coagulate said latex and a protective effective at the concentrations of the substances comprised in said pulp of substantially counteracting the tendency of said coagulant to coagulate said latex in the form of clots of coagulated rubber in said pulp, and then diluting said pulp with water to a point at which said protective is substantially less effective in counteracting the tendency of said coagulant to coagulate said latex, thereby causing said latex to coagulate substantially uniformly about and among said fibers.

5. A method of coagulating rubber latex upon fibers which comprises preparing an aqueous pulp containing fiber, rubber latex, a coagulant tending to coagulate said rubber latex, and a protective effective at the concentrations of the substances comprised in said pulp of preventing the formation of clots of coagulated rubber in said pulp, and then diluting said pulp with water to a point at which the effectiveness of said protective is substantially decreased and the rubber latex in said pulp is substantially completely coagulated about and among said fibers.

6. In a method of coagulating rubber on asbestos fibers, the steps comprising preparing a non-acid aqueous pulp containing asbestos fibers, rubber latex, and a protective effective at the concentrations of the materials comprised in said pulp of preventing substantial formation of clots of coagulated rubber in said pulp and then adding water to said pulp until said pulp contains less than about 2½% of undissolved materials in proportion to water thereby causing gradual, uniform coagulation and deposition of rubber about and among said asbestos fibers.

7. In a method of making asbestos paper wherein an aqueous pulp of asbestos fibers is formed into a waterlaid felted paper on a paper-making cylinder, screen or felt, the steps which comprise making a non-acid aqueous pulp containing asbestos fibers, rubber latex and a protective in effective amount at the concentrations of the materials comprised in said pulp of preventing the substantial formation of rubber clots in the pulp and then decreasing the concentration of said non-acid pulp by at least about half by adding water thereto so as to substantially decrease the effectiveness of said protective thereby causing said rubber to be coagulated in said non-acid pulp uniformly about and among said asbestos fibers prior to forming said pulp into waterlaid felted paper.

8. A method of treating mineral fibers which comprises preparing a pulp containing mineral fibers, rubber latex, emulsified waterproofing material, and protective material effective at the concentrations of the materials comprised in said pulp of preventing the coagulation of said latex and the precipitation of said waterproofing material as clots in said pulp, and then causing the uniform coagulation of said latex and precipitation of said waterproofing material about and among said fibers by diluting said pulp with water to a concentration at which said protective ma-

terial is substantially less effective in preventing coagulation of said latex and precipitation of said waterproofing material than at said original concentration.

9. A method of treating mineral fibers which comprises preparing a pulp containing mineral fibers, rubber latex, emulsified waterproofing material, and protective material effective at the concentrations of the materials comprised in said pulp of preventing the coagulation of the rubber latex and precipitation of the waterproofing material as clots in said pulp, and then diluting the pulp with water to cause substantially all of said rubber latex and said waterproofing material to become coagulated and precipitated about and among said mineral fibers.

10. A method of treating fibers which comprises preparing a pulp containing fibers, rubber latex and emulsified waterproofing material, coagulant adapted to tend to coagulate said rubber latex and to precipitate said waterproofing material, and protective material effective to substantially counteract the tendency of said coagulant to coagulate said rubber latex and precipitate said waterproofing material at the concentrations of the materials comprised in said pulp, and then adding sufficient water to said pulp to cause coagulation of said rubber latex and precipitation of said waterproofing material by said dilution of said pulp with water, said protective being rendered substantially less effective by said dilution of said pulp to counteract the tendency of said coagulant to coagulate said rubber latex and to precipitate said waterproofing about and among said fibers.

11. A method of treating fibers which comprises preparing a pulp containing fibers, rubber latex, emulsified waterproofing material, coagulant adapted to tend to coagulate said rubber latex and to precipitate said waterproofing material, and protective material effective to counteract the tendency of said coagulant material to coagulate said rubber latex and to precipitate said waterproofing material at the concentrations of the materials comprised in said pulp as clots in said pulp, and then diluting said pulp with water to cause substantially all of said rubber latex to become coagulated and substantially all of said waterproofing material to become uniformly precipitated about and among said fibers.

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

13. In a method of making asbestos paper from an aqueous pulp, the steps comprising preparing an aqueous pulp containing asbestos fiber, rubber latex, dispersed paraffin and protective material, said protective material at the concentrations of materials comprised in said pulp being effective to prevent the coagulation of the rubber latex and the precipitation of said paraffin in clots on the pulp, and then diluting the pulp with water so as to increase the rate of coagulation of said latex and the rate of precipitation of said paraffin about and among the asbestos fibers of said pulp.

14. In a method of making rubberized waterproofed asbestos fiber from an aqueous pulp containing emulsified rubber latex, the steps comprising making an aqueous pulp of asbestos fiber, making an emulsion of waterproofing material at a temperature above the melting point of said waterproofing material and then adding 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, the said rubber latex being included in said pulp in emulsified condition, and thereafter diluting said pulp with water to coagulate said rubber latex and to precipitate said waterproofing material about and among the asbestos fibers in the pulp.

15. In a method of making waterlaid asbestos fiber from an aqueous pulp, the steps comprising preparing a heated solution of bone glue and alkali in water, mixing wax with the water and agitating the mixture, then adding soap and soluble silicate to the mixture to produce an emulsion of wax in water, mixing asbestos fiber with water to form a pulp, mixing said emulsion with said pulp, then adding rubber latex to the pulp, and finally coagulating the latex and precipitating the wax about and among the asbestos fibers in the pulp by diluting the pulp with water.

HAROLD W. GREIDER.
MARION F. SMITH.