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[54] **LAMINATED FELTED SHEETS AND ASBESTOS CONTAINING COATING COMPOSITION FOR USE THEREIN**
3 Claims, No Drawings

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[56] **References Cited**

UNITED STATES PATENTS

367,424	8/1887	Merrill	162/129
1,558,495	10/1925	Overbury	162/129
2,626,213	1/1953	Novak	161/205 X
2,881,072	4/1959	Clark	162/201 X
2,927,038	3/1960	Schulz	117/140 X
2,993,802	7/1961	Cascone	162/129 X
3,246,767	4/1966	Pall et al.	117/140 X

OTHER REFERENCES

Paper Trade Journal (Feb. 14, 1966) pg. 40–4, " New Type of Asbestos Shows Advantages in Papermaking" Ingalls et al.
" Pulp and Paper," Casey, James P., Interscience Publishers, N.Y. (1961), p. 1553–4 Vol. 3

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ABSTRACT: Disclosed is a process for forming laminated felted sheets wherein a wet base sheet of fibrous material is formed on a paper making screen and, before the wet base sheet is removed from the screen, a nonseparable, uniform asbestos-binder composition is applied thereto. The composition comprises an intimitate mixture containing (a) at least 50 percent by weight of chrysotile asbestos having a specific surface area from about 60–80 $m^2/g.$, a magnetite content of from about 0.04–0.5 percent, a reflectance of from about 72–78 percent, and a pulpability such that 0.2–1 percent of the asbestos is retained on a 65 mesh Tyler screen and (b) a binder therefore. The ratio of asbestos to binder, on a dry weight basis, ranges from about 3:1 to 9:1.

LAMINATED FELTED SHEETS AND ASBESTOS CONTAINING COATING COMPOSITION FOR USE THEREIN

The desirability of adding a binder to nonwoven felted sheets has been known for a long time, and numerous binders have been used for this purpose, for example, natural and synthetic resins, gums starches, waxes and various rubbery lattices. In accordance with prior art methods these binders have been incorporated into the felted fibrous materials in one of three ways. The most common way of incorporating the binder is to mix it with the fibrous furnish composition and then lay and dewater the mixture on a conventional Fourdrinier screen or cylinder machine. This type of process suffers from a variety of difficulties, the most important of which is improper coagulation and self-agglomeration of the binder causing weakness and lack of uniformity in the paper.

Another way of incorporating binders into felted fibrous sheets has been the practice, disclosed, for example, in U.S. Pat No. 2,022,687, of first forming a fibrous web upon a paper-making machine and thereafter impregnating the web, while supported on the paper-making screen, by passing it through a permeating bath containing the binder material. This practice suffers from the disadvantage of requiring a separate saturating machine, as well as difficulty in controlling the amount of binder added to the original sheet. Neither of the above-described methods serves to produce a laminated or coated structure, but rather produces a more or less imperfectly impregnated sheet.

A laminated sheet can, of course, be made by simply coating the surface of finished paper with a rubber, resinous or waxy binder. Such products, however, tend to have poor adhesion between the coating and the paper.

It has long been desirable to produce a paper product which contains on at least one side thereof a coating of a binder which is integrally bound to and substantially inseparable from its paper base sheet, i.e. to produce a laminated product wherein the lamina will not separate, and to be able to apply such coating to the base sheet simply, economically and without the need for additional complex machinery.

OBJECTS

It is an object of this invention to produce a coated nonwoven felted fibrous sheet containing on at least one surface thereof a substantially nonseparable uniform and smooth rubbery, resinous or waxy coating.

It is another object of this invention to provide a process for applying to at least one surface of a felted fibrous base sheet, a resinous, rubbery or waxy coating by use of conventional paper-making machinery.

It is yet another object of this invention to produce a composition suitable for coating nonwoven felted fibrous base sheets, such as paper and the like, which coating will be integrally bonded to said base sheet and form a uniform, smooth coating thereon.

DESCRIPTION OF INVENTION

The above mentioned and other objects which will become apparent from the detailed description to follow are achieved by a process comprising the steps of (1) providing a base sheet of felted fibrous material on a paper-making screen, and prior to removal of said base sheet from the screen, (2) applying on top of said base sheet a composition comprising an intimate mixture of chrysotile asbestos fibers having certain critical properties (hereafter defined) and a binder therefor.

Another aspect of this invention consists of a laminated product consisting essentially of a felted fibrous base sheet and integrally bonded thereto a coating or lamina; the latter comprising an intimate mixture of chrysotile asbestos having certain critical properties (hereafter defined) and a binder therefor.

A third aspect of this invention consists of a composition, suitable for coating nonwoven felted sheets, comprising an intimate mixture of chrysotile asbestos fibers having certain critical properties (hereafter defined) and a binder therefor. Said composition, which may also be used to form a self-supporting sheet, may if desired, include optional ingredients such as conventional paper-making fibers, fillers, pigments, dyes and the like.

To be suitable for purposes of this invention the asbestos used must have the following critical properties:

specific surface area	60–80 m.²/g.
Magnetite content	0.04–0.05%
Reflectance	72–78%
Pulpability	0.2–1.0%

Asbestos having the aforementioned properties is commercially available as high purity grade Calidria*

*Trademark of Union Carbide Corp.asbestos.

The properties of the asbestos material set forth above are critical in the sense that only by use thereof are the desired results of the invention obtained.

Specific surface area is calculated from adsorption data using the BET (Brunauer, Emmet, Teller) method as described in Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press (1945).

Magnetite content is measured by a permeametric device patterned after ASTM standard method D–1118–57. Since the lower limit of detection of the ASTM device is only about 0.20 percent magnetite, the ASTM method has been improved with respect to sensitivity to measure a limit of detection of 0.005 percent magnetite, and the range of measurements has been extended to measure 0.10 percent magnetite in the midscale of the instrument. In order to obtain this greater range and improved sensitivity, the ASTM method has been modified to detect the phase changes of the current generated when magnetic materials are placed in the transformer core rather than the voltage changes generated.

Reflectance is measured on a sample prepared according to TAPPI (Technical Association of the Pulp and Paper Industry) standard T–452–*m*–58 and is reported as percent of ultimate reflectance based on magnesium oxide as the standard of 100 percent reflectance.

The pulpability of the high purity asbestos must be such that less than 1.0 percent and preferably less than 0.5 percent is retained on a 65-mesh Tyler screen when measured in accordance with the procedure described below. The term "+65 —mesh" is used to mean the amount, expressed as the percent of the sample, which does not pass through but is retained on a 65-mesh Tyler screen. The measurements are made on a wet pulped sample rather than a dry sample, since the particle size under wet pulped conditions is significant for purposes of paper manufacture. The pulpability is determined by adding 40 g. of asbestos and 2 liters of water to a TAPPI Standard Disintegrator and agitating the mixture for 4 minutes. A 250 ml. aliquot sample is then taken from the disintegrator and diluted to 3 liters with water. The diluted slurry is then poured through a 65-mesh (Tyler standard) wire screen held at an angle of about 30° from the horizontal position. The oversize remaining on the screen is washed back into a 4 liter beaker diluted with water and poured through the screen again as before. The oversize remaining is then backwashed, diluted and poured over the screen a third time. The oversize remaining is then dried at about 105° **50** C. and weighed. The net weight of the oversize multiplied by 20 is the percent +65-mesh asbestos material contained in the original sample. This is the value referred to as the "Pulpability."

Table I below illustrates the differences in the properties of the closest chrysotile asbestos of the prior art and the chrysotile asbestos essential for use in the present invention. Although Coalinga chrysotile* asbestos is preferred as the source of the asbestos, any chrysotile asbestos is suitable

*Coalinga chrysotile asbestos is mined from a large deposit near Coalinga, California.

for use in this invention, provided it has the critical properties defined above.

TABLE I.—COMPARATIVE PHYSICAL PROPERTIES OF ASBESTOS FIBERS

Type of asbestos	Percent reflectance	Percent magnetite	Specific surface area, m.²/gm.	Pulpability percent +65 mesh
Canadian chrysotile	55–70	3.5–4.8	19–31	10–20
Conventional coalinga chrysotile	60–64	1.0–3.0	55–59	10–67
Required for invention	72–78	0.04–0.5	60–80	0.2–1.0

Binders which are useful in the preparation of the coating composition of this invention include all of the common sizing agents used in the paper industry, such as animal glues, starches, gelatin, rosin, rosin derivatives, waxes, bituminous materials such as asphalts, tars, pitches and bituminous as well as resinous and rubbery lattices.

Synthetic, resinous and rubbery lattices are the preferred binders. Illustrative suitable rubbery lattices are copolymers of butadiene and styrene (i.e. GR–S rubber containing 50–80 percent by weight butadiene), copolymers of butadiene and acrylonitrile (i.e. Buna—N—or Hycar rubber containing 50–80 percent butadiene), polychloroprenes (i.e. neoprenes), homopolymers of butadiene, butadiene-isoprene copolymers, and terpolymers of butadiene, styrene and acrylic acid or lower alkyl acrylites.

Illustrative resinous binders which are useful are thermosetting resins such as phenol aldehyde resins, and melamine formaldehyde resins. Suitable thermoplastic resin binders include, for example, vinyl and substituted vinyl resins such as polyvinylchloride, polyvinylacetate, polyvinylacetal, polyvinylalcohol, polystyrene, polyacrylates, polymethacrylates, polyacrylonitrile, polyacrylamide and copolymers of these materials. Any resinous binder is useful for depositing the asbestos of this invention onto a base sheet, as long as it is dispersible in an aqueous medium or suspendible therein in particulate form.

The coating composition is prepared by first dispersing the asbestos in an aqueous slurry by means of a high shear device; for example, a Reitz disintegrator, a Fitzmill or a waring blender. The binder, usually in an aqueous suspension, is then blended in with the asbestos using low shear mixing such as obtained with an ordinary mixer.

The concentrations of both the asbestos slurry and the binder suspension are ordinarily kept below about 3 percent solids by weight, since at higher concentrations the composition becomes too viscous for easy handling. The proportions of asbestos to binder are controlled to give optimum efficiency in terms of the retention of the solids on the paper-making screen. The asbestos content, however, must be sufficiently high to insure that its cationic charge will be adequate to coflocculate all the other solid components of the mixture. If the concentration of the binder is too high, the binder in excess of that which the asbestos can flocculate will in large part be lost by draining through the base sheet into the white water. The optimum proportions of asbestos to binder will vary depending upon the particular binder and other additives used. Preferably, the ratio of asbestos to binder (on a dry weight basis) is from 3:1 to 9:1. The same proportions are useful whether the composition is to be used for coating purposes or for making an extruded, self-supporting film. Self-supporting films of this composition have the properties of an asbestos filled plastic film, and can be used, for example, as packaging film or as wallpaper.

The asbestos-binder coating composition may contain additives such as fillers, pigments or fibrous materials. The use of TiO_2 and clay are illustrated below, however, any conventional paper making fillers and/or pigments may be used, as well as mixtures thereof. Furthermore, fibrous materials other than asbestos, both synthetic and natural, may also be included, if desired, in the coating composition. For example, one or more natural or synthetic mineral or vegetable fibers may be added to the composition. In all such cases, however, the weight of asbestos having the critical characteristics previously described must be at least 50 percent of the weight in the composition. The asbestos in such a coating composition is believed to act as a coupling agent between the binder and the other fiber or nonfibrous additives, since the cationic nature of the asbestos is believed to be attracted by the other fibers, the nonfibrous additives, as well as the latex binder, all of which are anionic in character. The binder is preferably added after the asbestos and additive have been adequately mixed, since the asbestos will cause the binder to coagulate.

The asbestos-binder composition of this invention is novel and unusual in that it can be applied directly on top of a wet base sheet before the sheet is taken off the paper-making screen. Such "on the wire coating" has not previously been feasible because coating formulations tried in the past have drained through the base sheet. Use of asbestos having the critical properties previously defined "holds out" the coating composition from the base sheet, and enables the binder composition to be applied directly onto the paper making screen containing the wet base sheet. Furthermore, there is no need for using organic surfactants, wetting agents, dispersing agents, or other flocculating agents required by prior art methods to obtain flocculation and deposition of a binder onto the fibers. The critical properties of the above described asbestos itself assure both proper coflocculation of the binder onto the asbestos and deposition of the asbestos-binder coating onto the base sheet.

Any felted product which can be prepared on a paper making screen can be used as the base sheet in the present invention. These felted products can be formed from organic, inorganic or mixed materials. Paper base sheets are preferred. As used throughout the specification and claims of this disclosure the term "paper" is used in its generic sense, i.e. to include any nonwoven, felted fibrous sheet, including but not restricted to bond, wrapping, tissue, printing, wall and backing paper as well as cardboard, wallboard, millboard, and the like.

Suitable inorganic fibrous materials for base sheets include glass wool, mineral wool, and silicate fibers. Useful organic fibers include, for example, cotton, silk, hemp, ramie, alpaca, hair, fur and animal bristles. Useful synthetic organic fibers are fibers made from polyamides, acrylates, polyesters, cellulose acetate, regenerated cellulose (rayon), polyvinyl chloride, polyethylene, polyurethane, polytetrafluoroethylene and the like.

Preferred base sheets are those made from conventional cellulosic pulp used for the manufacture of paper for example, mechanical, semichemical, sulfite, sulfate, or craft (soda) pulp. Mixtures of cellulosic pulp or mixtures of cellulosic and noncellulosic fibers may also be used.

The paper base sheet useful in this invention may have included in it conventional fillers such as, for example, clay, sodium silicoaluminate, diatomaceous silica, calcium silicate, talc, calcium carbonate, calcium sulfate, barium sulfate, zinc sulfate and titanium dioxide. Such fillers may be incorporated not only into the base sheet, but also into the asbestos coating composition of this invention, if desired.

In general, a base sheet is made by first preparing a dilute aqueous pulp of suspended fibers, incorporating into the pulp desired additives such as fillers or pigments to make a paper furnish composition, depositing the furnish composition from a head box onto a moving fine mesh screen, and then draining the excess water through the screen. The asbestos-binder coating composition of this invention is then applied directly onto the wet felted fibrous web or sheet while the latter is still moving on the paper making screen. The coating step is conveniently carried out by having a second head box from which the coating composition is applied onto the wet base-covered screen.

Laminated felted sheets and asbestos containing coating composition for use therein (US Patent 3,619,354, 1971) Published by AsbestosClaims.Law
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EXAMPLES 1–12

Two-ply laminated sheets consisting of a cellulosic base sheet with a coating of asbestos and binder were prepared on a laboratory Noble and Wood handsheet machine using the following procedure. A base sheet having a basis weight of 60 g./m² was first prepared by adding unbleached craft pulp to the deckle box of the handsheet machine and allowing it to drain almost completely. Then a second composition consisting of a mixture of binder and asbestos having the critical properties heretofore defined was poured on top of the base sheet which was still in the deckle box. The proportions (on a dry weight basis) of asbestos to binder used are given in table II below. In examples 1 through 7 the binder used was an aqueous dispersion of a synthetic late of a copolymer containing about 60 percent styrene and 40 percent butadiene. In examples 8 through 12 the binder used was an aqueous dispersion of a copolymer containing about 40 percent styrene, 5 percent acrylic acid and 55 percent ethylhexyl acrylate. The asbestos latex coating composition contained about 1 percent solids. It was added to the deckle box slowly in order to minimize the disturbance of the wet cellulosic base sheet. The deckle box was then allowed to drain completely. The laminated sheet was then removed from the deckle box, pressed with a felt press, and dried in a drum dryer operated at a temperature of about 105° C. The heat of the drier not only dried the laminated sheet but also cured the latex.

Twelve samples were prepared in the manner described above and tested to determine optimum retention of the coating, as well as the physical properties of the laminates produced.

The data from table II demonstrates that optimum retention of the coating is achieved when the ratio of asbestos to latex (on a dry weight basis) is from 80:20 to 90:10, in other words, when about 10–20 percent of the asbestos latex composition is latex and 80–90 percent is asbestos. The data above also demonstrates that in general the best physical properties are obtained when there is maximum retention of the coating.

EXAMPLES 13–22

The following examples demonstrate the method of making a two-ply laminated paper, in accordance with the invention, on a continuous paper-making machine by using a secondary head box on a conventional Fourdrinier machine. The base sheets were made from a furnish containing 50 percent wood and 50 percent bleached soft wood sulfate pulp. The sulfate pulp was refined to a freeness of 370 and the freeness of the mixture of ground wood and sulfate was 250. The only additive used in the base sheet furnish was alum, added in sufficient amount to give a pH of 4.5 at the first headbox. The first headbox contained the furnish composition for the base sheet, and the secondary headbox contained the coating composition for the cop laminate.

Three different furnishes were used in the secondary headbox for laying down the top ply of the two-ply paper. The first top ply coating composition, labeled composition A in table III below, consisted of 85 percent asbestos and 15 percent latex. The second top ply coating composition, labeled composition B in table III below, consisted of 40 percent asbestos, 40 percent clay and 20 percent latex. The third top ply coating composition, labeled composition C in table III below, consisted of 52.8 percent asbestos, 27.2 percent TiO_2 and 20 percent latex. All of the coating compositions were applied as 1 percent solids slurries directly onto the wet base sheet as it moved continuously along the Fourdrinier wire. The asbestos used had the critical properties set forth above. In all cases the latex used was an aqueous dispersion of a copolymer containing about 60 percent styrene and 40 percent butadiene.

One objective of this series of experimental runs was to make the top layer as heavy as possible, and to apply it onto a light base sheet as well as onto a heavy base sheet. Changes in the thickness of both the top ply and the bottom ply were made by setting the flow rate from a headbox at a steady rate and then adjusting the speed of the Fourdrinier wire. Once a base sheet had been run long enough to insure steady state conditions, the flow of top ply furnish was started from the second headbox and increased slowly until the wet web appeared to be just on the verge of breaking between the couch roll and the first press. Under these conditions the run was continued for 10 to 15 minutes. Thereafter the wire speed was changed, and the procedure repeated with a different top ply or coating furnish.

Samples of paper were taken from each set of runs and cut into sheets. Some of the sheets from each set were calendered at room temperature and some at approximately 230° F. After conditioning at a constant temperature and humidity room critical wax tests were made on the calendered sheets, as well as on uncalendered samples of sheet. The results of the critical wax tests are shown in table III below.

The critical wax tests were conducted in accordance with TAPPI standard test T–459 su–65. This test consists of taking a standard series of wax sticks, each having a different tackiness, heating them to their melting point and then applying each of the sticks to the paper sheet. The number of the

TABLE II

	Ratio of asbestos to latex	Top laminate retention (percent) [1]	Percent reflectance [2]	Tensile strength Dry (lbs.)	Tensile strength Wet (oz.)	H_2O adsorption [3] (minutes)	Oil adsorption [4] (minutes)
Example:							
1			21	16.0	12.3	0.7	16.8
2	50:50	67	41	11.3	23.6	6.6	51.0
3	60:40	81	42	14.7	24.5	10.8	77.0
4	70:30	88	43	14.2	29.0	13.0	100.0
5	80:20	95	52	16.4	28.7	27.0	64.0
6	90:10	95	57	15.3	20.4	6.8	56.0
7	100:	89	55	7.4	5.4	2.0	19.0
8	50:50	51	59	13.8	10.7	4.7	36.0
9	60:40	81	64	14.9	15.7	10.6	37.0
10	70:30	70	64	14.1	13.8	10.3	51.0
11	80:20	84	62	15.0	16.7	32.0	46.0
12	90:10	95	60	12.9	16.6	20.6	44.0

[1] Top laminate retention is the percent asbestos—latex retained based on the quantity applied to the base sheet.
[2] Percent reflectance was determined with a photovolt meter according to TAPPI standards.
[3] H_2O adsorption was determined by placing a drop of water on the surface of the sheet and recording the time in minutes for the water to be adsorbed.
[4] Oil adsorption was determined in the same manner as water adsorption, using one drop of oil.

TABLE III

Example:	Wire speed (f.p.m.)	Top ply	Basis weight, (gm./m.)	Weight ratio top ply: base ply	Critical wax number: Uncalendered	Critical wax number: Calendered room temperature	Critical wax number: Hot calendered 230° F.
13	40	A	117	.86	6	6	7
14	25	B	154	.81	7	10	11
15	30	B	100	.35	6	9	10
16	35	B	126	.91	6	8	11
17	40	B	88	.76	7	7	10
18	50	B	105	1.06	8	9	10
19	30	C	109	.36	10	10	11
20	35	C	88	.33	10	10	11
21	45	C	69	.35	8	9	10
22	75	C	79	.20	8	9	10

highest numbered stick that does not pull fibers from the surface is the critical wax value of the paper. It can be seen from table III that very good bonding between the plies was obtained as indicated by the critical wax numbers ranging from 6 to 11 Some increase in critical wax was obtained by calendering the sheet, with hot calendering giving the best results. The tests also indicate that an increase in the ratio of latex to asbestos and pigment increases ply bonding.

The laminated paper of the present invention has numerous advantages not possessed by prior art materials, such as improved ply bonding and low cost of manufacture due to the fact that separate equipment for coating is not required. The coated paper of the present invention is particularly useful for one side "hold out" items such as paper plates, drinking cups, flexible packaging and the like.

I claim:

1. A process for the manufacture of laminated sheets comprising the steps of:

1. forming on a paper making screen, a wet base sheet of felted fibrous material and prior to removal of said base sheet from said screen

2. providing a nonseparable, uniform, asbestos-binder coating on the surface of said base sheet by applying on top of said wet base sheet before said wet base sheet is removed from the paper-making screen a composition comprising an intimate mixture containing at least 50 percent by weight of chrysotile asbestos characterized by a specific surface area between about 60 to 80 $m^2/gm.$, a magnetite content of from about 0.04 to 0.5 percent, a reflectance of about 72 to 78 percent and a pulpability such that 0.2 to 1 percent of the asbestos is retained on a 65-mesh Tyler screen and a binder therefor, the ratio of asbestos to binder, on a dry weight basis, being from about 3:1 to 9:1.

2. The process of claim 1 wherein the coating composition applied on top of said base sheet contains an additive selected from the group consisting of fibrous materials, fillers, pigments and mixtures thereof.

3. The process of claim 1 wherein the base sheet is paper.

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