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ASBESTOS PAPER CONTAINING VINYL ALKYL ETHER-MALEIC ANHYDRIDE COPOLYMER AND METHOD OF FORMING SAME

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This invention relates to new and improved asbestos papers and methods for preparing same, and in particular, to methods for the production of an improved bonded asbestos paper product and the resultant asbestos paper.

The outstanding properties of asbestos are of course well known, and render it particularly useable where problems of heat and flame stability are important. As an insulation material in the form of a textile product which is woven as a cloth or in the form of a paper laid web, asbestos has no peer. In the manufacture of asbestos cloth from asbestos yarns and threads, substantially regular textile equipment is employed and the fibers which are used are of the long fiber type such as the crudes and group 3 fibers (Quebec screen test of the Quebec Asbestos Producers Association). Many different types of asbestos fibers are known but the one in greatest product and of greatest value especially in the preparation of woven textile asbestos products, chrysotile asbestos, which is a simple magnesium silicate which is easily fibered and can be readily spun. It has great tensile strength and substantial heat stability. Even with such an outstanding fiber, it is usually necessary to add cotton or other fibrous materials to give added strength and to serve as a vehicle on the card. Such fibers are much too expensive and the processing to form cloth economically unfeasible for many applications of asbestos products. For such reasons there is a tremendous outlet for asbestos in the form of an asbestos paper product. In the production of such paper products from asbestos, substantially normal paper making techniques are employed wherein a slurry of the asbestos fiber in aqueous medium is laid upon a screen and then formed into a dry sheet in the usual manner. From the point of view of economics, it is desirable to use the cheapest asbestos raw materials available. These are, of course, the shorter fibers which are unsuitable for use in textile spinning operations. The shorter fibers are classified according to the Quebec screen test from groups 4 through 7, the increasing numbers indicating shorter fiber lengths. In spite of the tremendous advantages in the resin and plastic technologies to date, there has been found no satisfactory substitute for starch as a binder for asbestos products in the production of asbestos paper. This is true from all points of view, namely, economicswise as well as the properties attendant with the use of the different materials with asbestos.

It has now been discovered that an outstanding asbestos paper product can be prepared which is far superior to the product using starch as a bind, and additionally, is more economical to produce. It has been found that by replacing the heretofore employed starch with an alkyl vinyl ether-maleic anhydride copolymer of the type hereinafter to be described, vast improvements in the properties of the resultant asbestos paper have been obtained. In particular, outstanding improvements in tensile and bursting strengths of the resultant papers are achieved.

It is therefore an object of the present invention to provide an improved process for the preparation of asbestos paper.

It is still another object of the present invention to provide an improved process for the production of asbestos paper containing minor amounts of a vinyl alkyl ether-maleic anhydride copolymer as a binder.

It is still a further object of the present invention to provide a new and improved process for the preparation of asbestos papers having improved and outstanding tensile and bursting strengths.

It is still another further object of the present invention to provide new and improved asbestos papers.

It is still another further object of the present invention to provide new and improved asbestos papers which are bonded and using alkyl vinyl ether-maleic anhydride copolymers in minor amounts.

It is a still further object of the present invention to provide new and useful asbestos papers which have outstanding tensile and bursting strength characteristics.

It is still a further object of the present invention to provide new and useful asbestos papers which are readily prepared in an economical manner and which are far superior and cheaper than heretofore known bonded asbestos papers.

Other objects will appear hereinafter as the description proceeds.

As pointed out above, the objects of the present invention are achieved by employing as a binder for the asbestos fibers a minor amount of an alkyl vinyl ether-maleic anhydride copolymer. The alkyl vinyl ether monomers which are herein contemplated are those wherein the alkyl group contains from 1 to 4 carbon atoms, and thus include:

Methyl vinyl ether
Ethyl vinyl ether
n-Propyl vinyl ether
Isopropyl vinyl ether
n-Butyl vinyl ether
Isobutyl vinyl ether, and
Tertiary butyl vinyl ether

It has been found that the alkyl vinyl ethers copolymerize stoichiometrically with maleic anhydride in a 1:1 ratio even though one of the reactants may be present in excess during the copolymerization procedure. It is therefore understood that when reference is made to the copolymers by name of the monomeric ingredients, each of the recited comonomers is present in equimolar amounts. Depending upon conditions of copolymerization, copolymers of varying viscosity characteristics may be produced. Such different viscosities are manifestations of different average molecular weight distributions. The higher viscosities materials are those having the higher average molecular weights. Another indication of the average molecular weight of a polymeric material is the K value which may be calculated from viscosity data. The determination of the K value is fully described in "Modern Plastics," vol. 23, No. 3, pages 157–61, 212, 214, 216, and 218 (1945), and is defined as 1000 times K in the empirical relative viscosity equation:

$$\frac{\log_{10} \eta \text{ rel.}}{C} = \frac{75k^2}{1+1.5kC} + k$$

wherein C is the concentration in grams per 100 cc. polymer solution and η rel. is the ratio of viscosity of solution to that of pure solvent. The K values are reported as 1000 times the calculated viscosity coefficient in order to avoid the use of decimals. For the purpose of the present invention, there may be employed those polymeric substances having a K value of about 10 to 200, and preferably from about 15 to 100.

K values and specific viscosities (η sp.) are interconvertible and are related through relative viscosity (η rel.). Thus, when viscosity measurements are taken on solutions which have a concentration of 1.00 g. poly-

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mer per deciliter of solution at 25° C. ($C=1$), the relations are as follows:

(1) η rel.$=\eta$ sp.$+1$
(2) Relative viscosity=specific viscosity$+1$
(3) Relative viscosity$=10[0.001K$
$+0.000075K^2/(1+0.0015K)]$
(4) η sp.$=-1+10[0.001K$
$+0.000075K^2/(1+0.0015K)]$

Relative viscosity, specific viscosity, and K are dimensionless, whereas inherent viscosity ($\log_e \eta$ rel.$+C$) and intrinsic viscosity (the limit of inherent viscosity as C approaches 0) have the dimensions of dilution, that is, the reciprocal of concentration. Intrinsic viscosity and K are intended to be independent of concentration.

The copolymers which are herein contemplated are those characterized as having a specific viscosity range from 0.1 to 2.5. The corresponding K values of such copolymers range from about 10 to about 100. The concentration of copolymers to be employed with the asbestos may range from about 0.05% to about 5% by weight based upon the weight of the asbestos. It is preferred to employ from about 0.1% to about 1.0% copolymer by weight based upon the weight of the asbestos fibers. It is significant that as little as about 0.2% gives an asbestos product which is superior to that product obtained using over 5% starch, and on that basis the use of starch is about 2½ times as costly as the use of the instantly disclosed copolymers.

In addition to the aforementioned advantages and improvements derived from the use of the alkyl vinyl ether-maleic anhydride copolymers, it has further been found that in the paper making process a more efficient processing is achieved than when starch is used due to a far improved drainage of the aqueous medium when the product is sheeted in the conventional manner.

The following examples will serve to illustrate the present invention without being deemed limitative thereof, and in these examples, parts are by weight unless otherwise indicated.

Example 1

13 g. of chrysotile asbestos (fiber classification group 5—Quebec screen test) are dispersed in 2 liters of water. The pH is adjusted to about 3.5 using 10% hydrochloric acid. To the aqueous dispersion there is then added a 5% aqueous solution of a copolymer of vinyl methyl ether-maleic anhydride (specific viscosity 0.5 measured at 25° C. 1 g. per 100 ml. of benzene) until 0.19% based on the weight of the asbestos has been added (i.e., copolymer solids). The aqueous slurry is then beaten for 1 min. and hand sheets are then formed on a screen in the usual manner and where dried after removal from the screen the tensile strength of the resultant sheet is determined by ascertaining the weight required to break a strip 15 mm. wide. In this instance the weight is about 500 g.

Example 2

Example 1 is repeated except that 0.38% copolymer by weight based upon the weight of the asbestos is added to the asbestos dispersion. The tensile strength as measured in Example 1 is 1,160 g.

Example 3

Example 1 is once again repeated except that 5.5% of wheat starch by weight based upon the weight of the asbestos is added in lieu of the copolymer. The tensile strength of the resulting sheet is only 395 g. as measured in Example 1.

It is significant from the above examples that by the use of copolymer amounting to only 7% of the weight of starch used, a 300% improvement in tensile strength is forthcoming. In addition, it is noted that the sheets prepared in Examples 1 and 2 drain faster and better than the sheet of Example 3, and consequently a much faster process is achieved.

Examples 4 Through 6

Examples 1, 2 and 3 are repeated except that the pH of the asbestos dispersion is adjusted and maintaining at about 7.0. Similar improvements in tensile strength are obtained with the vinyl methyl ether-maleic anhydride copolymer.

Example 7

Example 2 is repeated employing vinyl ethyl ether-maleic anhydride copolymer having a specific viscosity of 0.35. Tensile strength as measured in Example 1 is 1000 g.

Example 8

Example 2 is again repeated employing the following copolymers.

Vinyl alkyl ether moiety:	Specific viscosity
(1) Vinyl methyl ether	0.2
(2) Vinyl ethyl ether	0.2
(3) Vinyl n-propyl ether	0.4
(4) Vinyl n-butyl ether	0.3
(5) Vinyl isobutyl ether	0.1
(6) Vinyl methyl ether	0.7
(7) Vinyl methyl ether	0.9
(8) Vinyl methyl ether	1.2
(9) Vinyl methyl ether	1.5
(10) Vinyl methyl ether	1.8
(11) Vinyl methyl ether	2.3
(12) Vinyl methyl ether	2.5

In each of the above examples there is a vast improvement in tensile strength, the values in each instance ranging from about 1000 to about 1200 g. as measured in Example 1.

Example 9

Example 8 is again repeated employing, however, concentrations of copolymer of 0.5%, 0.7%, 1.0%, 2.5%, and 5.0%. There is an increase in tensile strength as the amount of copolymer is increased but this increase tends to level off between 1% and 5% of copolymer, and due to the unfavorable economic picture at high copolymer concentrations, it is preferred, therefore, to employ in most instances no more than about 1% to 2% copolymer, although it is clearly understood that up to 5% is contemplated since there is some improvement in the resultant asbestos paper.

Example 10

Example 9 is repeated employing, however, a pH of 7 as used in Example 4. Outstanding results are obtained.

Example 11

Examples 1, 2 and 4 through 10 are again repeated using in place of chrysotile asbestos, crocidolite asbestos (fiber classification 4—Quebec screen test). Similar improvements with this asbestos are obtained as with the asbestos used in the previous examples.

Example 12

Each of Examples 1, 2 and 4 through 10 is again repeated using Type 6D chrysotile asbestos. As in the previous examples, excellent improvements in tensile strength are obtained.

Example 13

Example 10 is again repeated employing an asbestos mixture comprising 50% Johns-Manville Grade 4T04 and 50% Grade 7D15 in place of the chrysotile asbestos. Excellent tensile strengths are obtained.

Example 14

A dispersion of the asbestos mixture of Example 13 is made by adding 15 g. of asbestos to 2 liters of water. 0.25% of a vinyl methyl ether-maleic anhydride copoly-

mer, specific viscosity 1.8, is added to the dispersion. Sheets are formed as in Example 1 and tested for their burst strength (Mullen burst test). The values are in pounds per square inch per inch of thickness of sheet. The sheet prepared in this example has a Mullen burst strength of 211. A similar sheet using 5% wheat starch as a binder has a Mullen value of 180.

Example 15

Example 14 is repeated except that the copolymer employed is one having a specific viscosity of 0.31. The Mullen value is 147. This compares with a control sample using 5% wheat starch as the binder wherein the Mullen burst value is 133.

Example 16

Example 14 is a once again repeated employing a copolymer having a specific viscosity of 1.5. Again, the Mullen burst value is 147 as compared to the control sample having 5% wheat starch as a binder where the Mullen value is 133.

While in the above examples only certain specific asbestos products have been used, it is clear that the improvements which are forthcoming in the present invention are obtained with any asbestos fiber in a similar paper making process, and while longer fibered papers yield better papers in all instances, there is a vast improvement when the copolymers herein disclosed are used as binders, especially as compared to the heretofore employed wheat starch. In the absence of any binder, of course, the results are even more significant.

Other variations in and modifications of the described processes which will be obvious to those skilled in the art can be made in this invention without departing from the scope or spirit thereof.

I claim:

1. A process for preparing a sheet-like product from asbestos fibers comprising incorporating into an aqueous dispersion of asbestos fibers from about 0.05% to about 5% by weight based upon the weight of the asbestos fibers of a copolymer of an alkyl vinyl ether with maleic anhydride characterized by a K value of from about 10 to about 100, said alkyl vinyl ether moiety containing from 1 to 4 carbon atoms in the alkyl substituent and then forming a sheet from said dispersion.

2. A process for preparing a sheet-like product from asbestos fibers comprising incorporating into an aqueous dispersion of asbestos fibers from about 0.1% to about 1% by weight based upon the weight of the asbestos fibers of a copolymer of an alkyl vinyl ether with maleic anhydride characterized by a K value of from about 10 to about 100, said alkyl vinyl ether moiety containing from 1 to 4 carbon atoms in the alkyl substituent and then forming a sheet from said dispersion.

3. A process as defined in claim 2 wherein the copolymer is a vinyl ethyl ether-maleic anhydride copolymer.

4. A process as defined in claim 2 wherein the copolymer is a vinyl methyl ether-maleic anhydride copolymer.

5. A process as defined in claim 2 wherein the copolymer is a vinyl propyl ether-maleic anhydride copolymer.

6. A process as defined in claim 2 wherein the copolymer is a vinyl butyl ether-maleic anhydride copolymer.

7. A process as defined in claim 2 wherein the asbestos is chrysotile asbestos.

8. A process as defined in claim 3 wherein the asbestos is chrysotile asbestos.

9. A process for preparing an asbestos paper from asbestos fibers which comprises adding to an aqueous dispersion of said asbestos fibers from about 0.1% to about 1% by weight based upon the weight of the asbestos fibers of a vinyl methyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100 and then forming a sheet from said asbestos dispersion.

10. An asbestos paper containing from about 0.05% to about 5% by weight based upon the weight of the asbestos of a copolymer of an alkyl vinyl ether with maleic anhydride characterized by a K value of from about 10 to about 100, said alkyl vinyl ether containing from 1 to 4 carbon atoms in the alkyl substituent thereof.

11. An asbestos paper containing from about 0.05% to about 5% by weight based upon the weight of the asbestos of a vinyl methyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

12. An asbestos paper containing from about 0.05% to about 5% by weight based upon the weight of the asbestos of a vinyl ethyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

13. An asbestos paper containing from about 0.05% to about 5% by weight based upon the weight of the asbestos of a vinyl propyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

14. An asbestos paper containing from about 0.05% to about 5% by weight based upon the weight of the asbestos of a vinyl butyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

15. An asbestos paper containing from about 0.1% to about 1% by weight based upon the weight of the asbestos of a vinyl methyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

16. An asbestos paper containing from about 0.1% to about 1% by weight based upon the weight of the asbestos of a vinyl ethyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

17. An asbestos paper containing from about 0.1% to about 1% by weight based upon the weight of the asbestos of a vinyl propyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

18. An asbestos paper containing from about 0.1% to about 1% by weight based upon the weight of the asbestos of a vinyl butyl ether-maleic anhydride copolymer characterized by a K value of from about 10 to about 100.

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