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3,076,740
ASBESTOS PAPER MANUFACTURE

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5 Claims. (Cl. 162—155)

This is a continuation-in-part of our copending application Serial No. 765,320, filed on October 6, 1958, now Patent No. 3,019,157.

The present invention relates to the manufacture of asbestos paper, board and other water-laid asbestos products (hereinafter termed "paper"), and is particularly directed to the manufacture of asbestos paper by a method disclosed therein wherein an ultra-high molecular weight polymer is added to asbestos papermaking pulp to increase the freeness of the pulp (i.e., the rate at which water drains therefrom during sheeting).

Asbestos paper is currently manufactured by a process wherein mineral asbestos is mechanically defibered to form a crude fibrous batt, after which the batt is slurried in water to form a papermaking fibrous suspension by means analogous to those employed in the manufacture of cellulose paper. This suspension is then flowed on a moving papermaking screen in such manner as to form a water-laid web of the desired thickness.

The bulk of the water in the web is removed from this web by gravity, pressure, and suction. The remainder of the water, often a substantial amount, is tenaciously held and is removed by passage over steam-heated rolls.

The discovery has now been made that a substantial improvement in the manufacture of asbestos paper can be effected by complexing an ultra-high molecular weight, anionic polymer on the surface of the papermaking fibers while they are in aqueous suspension, and that this may be done by simply adding the polymer preferably in aqueous solution to the fibrous suspension.

We have found that in preferred embodiments formation of the polymer-fiber complex more than trebles the freeness of the pulp without significantly changing the dry tensile strength of the paper produced. By this means the amount of water which is removed by gravity and by suction is greatly increased, with corresponding decrease in the amount of water which must be removed by the use of heat.

The manner in which the adsorbed polymer acts to permit this increase in freeness is not known and we do not wish to be bound by any theory. Comparative laboratory experiments based on the preparation of a series of pulps containing increasing amounts of the polymer have indicated that the effect of the polymer is to cause selective agglomeration of the asbestos fines, i.e., agglomeration or coalescence of the fines without corresponding agglomeration or coalescence of the larger fibers. These conclusions are based on the observation that the polymer, when present in amounts called for by the present invention, causes a major improvement in the rate at which free water drains through the wet web during the papermaking operation without objectionably changing the formation of the sheets obtained. The process thus has substantially no adverse effect upon the dry tensile strength of the sheet.

The invention has the following additional advantages.

(1) The process is very effective. In preferred embodiments we have found it possible to increase machine speeds by more than 20%. Since papermaking machines are customarily run at the maximum speed of which they are capable in any instance, the present invention permits a substantial increase in machine output.

(2) The process is economical. To date we have not found it necessary to use more than about 0.1% of polymer, based on the dry weight of the fibers, and usually far less is required.

(3) The process resides essentially in the addition of the polymer, and it is not necessary to add any agents which assist the operation of the polymer or to modify the conditions normally employed in the manufacture of asbestos paper. The process may be employed in conjunction with currently employed sizes and strengthening agents for asbestos.

The polymer may be added at any convenient point in the papermaking operation. However, the speed at which it complexes with the asbestos is nearly instantaneous and, therefore, it can be added immediately before the wire, for example at the fan pump, and best results are generally obtained when it is added at this point. The polymer is compatible with wax sizes, starches and pigments customarily used in the manufacture of asbestos paper and is most advantageously added subsequent to the addition of these materials.

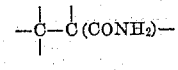
Asbestos pulps are normally alkaline in the range of about pH 8–10 and the polymer is effective when the pH of the aqueous suspension of the asbestos fibers is in that range.

The amount of polymer added in any one instance according to the present invention depends on a number of variables of which the composition of the polymer itself, its molecular weight, the particular asbestos or asbestos mixture used (and proportion of fines therein) are perhaps the most important.

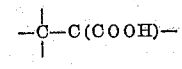
At least sufficient polymer is added to increase the speed at which free water drains through the web. The amount of polymer added is insufficient to decrease substantially the dry tensile strength of the asbestos paper formed.

In general, more polymer is needed to produce a given increase in machine speed when the proportion of carboxyl groups is outside the preferred range and when the molecular weight is low as compared with high. Moreover, pulps which are high in fines are particularly responsive to the polymer complex. As a result, the optimum amount of polymer to be added in any one instance is generally most conveniently determined by actual trial, employing the methods illustrated in the examples below as guides.

The polymer employed in the process of the present invention is substantially composed of carbamoylalkylene



and carboxyalkylene



linkages containing not more than 4 carbon atoms each having a molecular weight in excess of 5 million (determined from its intrinsic viscosity by modified Staudinger equation shown below), the number of carboxyalkylene linkages in the polymer being between about 2% and 20% and preferably between 2% and 10% of the total number of carbamoylalkylene and carboxyalkylene groups therein.

The molecular weight of the polymer is obtained by determining its intrinsic viscosity at 30° C. as a 0.1% to 0.01% solution in 0.1 N aqueous NaCl. The determination is made by standard method in a capillary viscosimeter of the Ubbelohde or suspended level type, preferably using the No. 50 instrument made by Cannon Instrument Co., State College, Pa., in which the rate of shear varies between 600 and 1500 reciprocal seconds at the solids concentrations used. The values obtained are plotted to infinite dilution, which gives the intrinsic viscosity of the polymer in deciliters per gram.

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The molecular weight is calculated from modified Staudinger formula

$$(1) \qquad M=1.4\times10^5[\eta]^{3/2}$$

wherein M is the weight average molecular weight, and $[\eta]$ is the intrinsic viscosity determined as shown above.

Suitable polymers may be prepared by partially hydrolyzing a polyacrylamide of ultra-high molecular weight or by copolymerizing acrylamide and acrylic acid in suitable ratio to suitable molecular weight.

The polymerization reaction is advantageously performed by polymerizing a suitable monomer or mixture of monomers in the presence of particular classes of redox catalyst systems. These are mixtures of water-soluble tertiary amines with oxidizing agents such as the water-soluble persulfates, for example an alkali metal or ammonium persulfate, or with peroxides such as hydrogen peroxide and the like and, as a second class, mixtures of water-soluble bromates such as an alkali metal bromate with water-soluble sulfite reducing agents such as sodium sulfite or sodium bisulfite. When these catalysts systems are used it is possible to obtain polymers within the molecular weight ranges discussed herein by controlling the polymerization temperature and the molar ratios of the two ingredients of the redox catalyst system.

When the tertiary amine-chemical oxidant redox system is used, polyacryiamides having molecular weights of 10–11 million and higher are obtained by employing a substantial molar excess of tertiary amine over the persulfate or peroxide, and in most cases quantities of from 2 to about 6 mols of tertiary amine for each mol of persulfate or peroxide should be used. Polymers having molecular weights from about 6 to 10–11 million are also obtainable with molar ratios of the catalyst ingredients within this range when polymerization temperatures in excess of about 30° C. are used, particularly when the weight ratio of the catalyst system to the acrylamide monomer in solution is increased. When the second type of redox system is used the preferred new polyacrylamides having molecular weights of at least 10–11 million are produced by operating at temperatures below 20° C. and preferably below 10° C. with a system containing from about 0.1 to 0.8 mol of the sulfite for each mol of the bromate. The intrinsic viscosity of the polymer decreases as the molar ratio of the sulfite to the bromate approaches 1:1, and also as the weight ratio of bromate to acrylamide monomer is increased. A molecular weight of 5 million is about the least that makes the present invention economically worth-while, and much better results without offsetting difficulties are obtained from polymers having a molecular weight in excess of 10 million, and particularly in the range of 15–25 million, which are therefore preferred. The polymers larger than about 25 million molecular weight yield still better results, but because of their high viscosity even at great dilutions are not as convenient to use and thus fall outside of the preferred range.

The polymeric linkages specified above result from the presence of combined acrylamide, methacrylamide, acrylic acid, methacrylic acid, etc. The polymers may contain minor amounts of other active linkages, for example those derived from maleamide, maleimide, maleamic acid and maleic acid. The polymers may further contain minor amounts of inert (diluent) linkages, for example those derived from acrylonitrile, vinyl acetate (which on hydrolysis subsequent to polymerization yields alcoholic groups), styrene and the lower acrylate and methacrylate esters. It is within the scope of the invention to employ mixtures of polymers of the above description.

In practice we have found that at least about 0.02% of the polymer based on the dry weight of the fibers is usually needed to produce a significant improvement and that no more than 0.2% is needed to achieve about maximum improvement in freeness. We have further found

that as a practical matter the advantage between about 0.05% and 0.1% of the polymer based on the weight of the fibers provides a very substantial increase in freeness while minimizing consumption of this agent.

The invention will be further illustrated by reference to the examples. These examples constitute embodiments of the invention and are not to be regarded as limitations thereon.

Example 1

The following illustrates the preparation of an ultra-high molecular weight linear carbon chain polymer suitable for use in the process of the present invention by homopolymerizing acrylamide followed by hydrolysis of a portion of the amide groups.

Distilled water was freed from oxygen by boiling for 15 minutes under a blanket of nitrogen and cooled to 20° C. (also under nitrogen). A solution was made by dissolving 70 parts by weight (1 mol) of acrylamide in 630 parts of this water and charged into a jacketed reactor having a bottom inlet for the injection of nitrogen. Ammonium persulfate and 3,3',3''-nitrilotrispropionamide were added in amounts of 0.04% and 0.16%, respectively, on the weight of the acrylamide and mixed by vigorous injection of nitrogen. Active polymerization began within a few minutes and was continued under a nitrogen blanket for about 8 hours when it was about 98% complete.

During the reaction the temperature was maintained at 20° C. by admission of cooling fluid into the jacket.

The material was dissolved in 6,400 parts of hot water containing 2 parts (1/20 mol) of sodium hydroxide causing hydrolysis of about 5% of the carbamoyl linkages. The product was thus composed of carbamoylethylene and carboxyethylene linkages having the respective theoretical formulae of



and —CH_2—CH(COOH)—. It had an intrinsic velocity of 18 dl./gm. and hence a calculated molecular weight of about 10.5 million.

Example 2

The following illustrates the preparation of a similar ultra-high molecular weight polymer by direct copolymertization of acrylamide and a rylic acid.

A 10% by weight solution of a 95:5 molar ratio acrylamide:acrylic acid mixture was prepared in distilled oxygen-free water containing sufficient of a 1:0.3 molar ratio sodium bromate:sodium sulfite mixture to provide 0.02% by weight of sodium bromate based on the weight of the monomer mixture. The mixture was reacted by the method of Example 1 at 0°–5° C. to about 98% completion. During the reaction a small proportion of the amide groups present underwent hydrolysis to carboxyl groups.

The intrinsic viscosity of the polymer as determined by the method of Example 1 was 20 dl./gm. and the calculated molecular weight was therefore 12.5 million.

Example 3

There is a substantial market for water-laid asbestos webs which (with or without subsequent treatment) are used as fire barriers, gasket paper and pipe wrappings. One difficulty in the manufacture of water-laid asbestos webs for such purposes is that the asbestos pulps are excessively slow to drain, so that slow machine speeds are the rule. The present invention permits the drainage rate of aqueous asbestos fiber suspensions to be greatly increased without significant alteration in the physical properties of the webs produced. The following illustrates a preferred method for the purpose, showing the effect of increasing amounts of the treating agent. Asbestos pulps have an alkaline pH which was not adjusted during the tests.

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Canadian chrysotile asbestos fibers were slurried in a 1½ lb. Niagara-type laboratory beater and lightly beaten at a consistency of 4.5% for 10 minutes, until the fibers developed web-forming properties. The suspension was diluted to 0.3% consistency with water and 1,000-ml. aliquots of this were placed in liter graduates. The suspension in one of the graduates was reserved as control and to this nothing was added. To the other suspensions were added amounts of ultra-high molecular weight partially hydrolyzed polyacrylamide, as shown in the table below. The polymer had a molecular weight (calculated by the modified Staudinger method as described above) of about 6 million and was 4% hydrolyzed as determined by titration. The polymer was added as a 0.05% solution in water. After addition of the polymer, the graduates were inverted a few times to mix the polymer with the pulp, and the freeness of the suspensions then determined by the Canadian standard method. Results were as follows.

Run No.	Percent Polymer Added [1]	Pulp pH [2]	Pulp Freeness Sec.[3]	Remarks
Control	None	9.7	120	White water opaque with suspended fibers.
1	0.017		140	White water much clearer.
2	0.033		200	Do.
3	0.067		260	Do.
4	0.100		410	White water practically clear.

[1] Based on dry weight of fibers.
[2] Not adjusted.
[3] By Canadian standard method.

In subsequent trials no improvement was obtained by adding alum or caustic to the pulp.

Example 4

Asbestos paper is normally hydrophilic and weak, and it is accordingly common to add strengthening agents to the papermaking suspension. The benefits of the present invention are obtained with two commonly-used agents as follows:

The procedure of Example 1 is repeated to the point where the suspension is diluted and divided into aliquots.

To one aliquot is added 2% (based on the dry weight of the fibers) of a wax size prepared by emulsifying molten paraffin wax in hot water containing an anionic dispersing agent and a natural gum such as common arabic as colloid protector and homogenizing the mixture, after there is added 0.1% (based on the weight of the fibers) of the ultra-high molecular weight polymer of Example 1.

To another aliquot is added 5% (based on the dry weight of the fibers) of cooked starch as strengthening agent, followed by 0.1% of the polymer as described above.

The presence of the ultra-high molecular weight polymer in the suspension renders the freeness of the pulp substantially higher than would otherwise be the case.

Example 5

The procedure of Example 3 was repeated using a polyacrylamide which was 5% hydrolyzed as determined by titration and which had a molecular weight of 15 million determined as described above, the amount of polymer added being 0.017% of the weight of the fibers. The pulp had a freeness of 240 ml.

This indicates that the efficiency of the polymer is roughly proportional to its molecular weight.

We claim:

1. A process of increasing the rate at which water drains from the fibers during the manufacture of asbestos paper which comprises adding to an aqueous papermaking asbestos fiber suspension a water-soluble anionic linear carbon chain polymer having a molecular weight in excess of 5 million as calculated from its intrinsic viscosity by modified Staudinger equation and substantially composed of carbamoylalkylene and carboxyalkylene linkages containing not more than 4 carbon atoms each, the number of said carboxyalkylene linkages being between about 2% and 20% of the total number of carbamoylalkylene and carboxyalkylene linkages, sheeting said suspension on a papermaking screen to form a water-laid web, draining free water from said web, and drying said web to form paper, the amount of said complex being sufficient to increase the rate at which free water drains through said web and being insufficient to decrease substantially the dry tensile strength of the paper.

2. A process according to claim 1 wherein the molecular weight of the polymer is in excess of 10 million.

3. A process according to claim 1 wherein the number of carboxyalkylene linkages is between about 2% and 10% of the total number of carbamoylalkylene and carboxyalkylene linkages.

4. A process according to claim 1 wherein the pH of the fibrous suspension is between 8 and 10.

5. A process according to claim 1 wherein the weight of polymer added is between about 0.02% and 0.1% of the dry weight of the fibers.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,076,740 February 5, 1963

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 1, for "advantage" read -- addition --.

Signed and sealed this 31st day of March 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents

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