June 10, 1969 G. F. HERON ET AL 3,449,227

MANUFACTURE OF ASBESTOS

Filed Nov. 8, 1966 Sheet 1 of 2

Fig. 1.

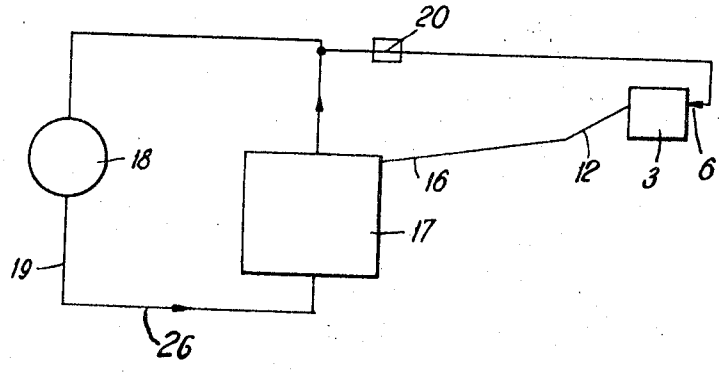
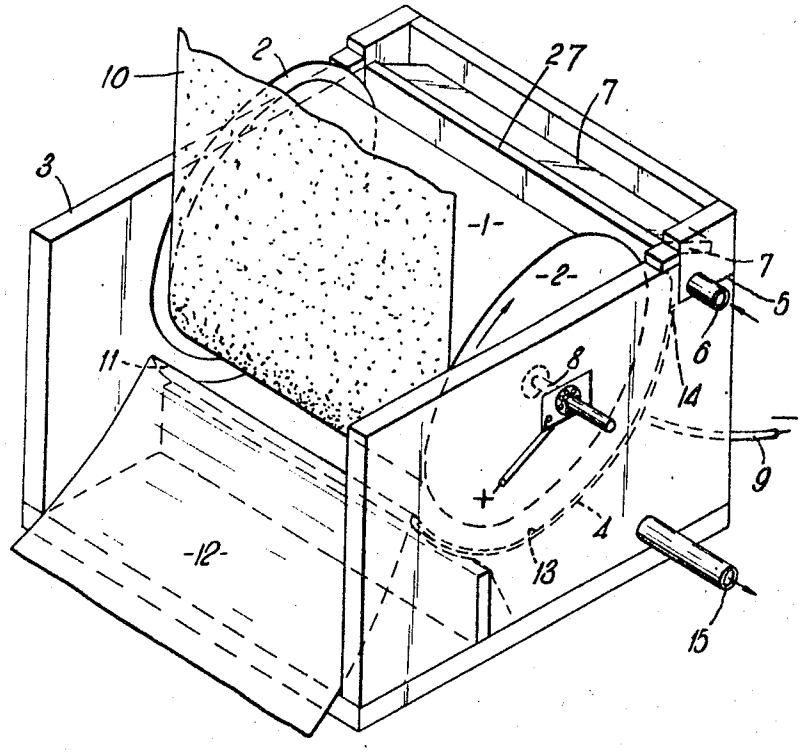
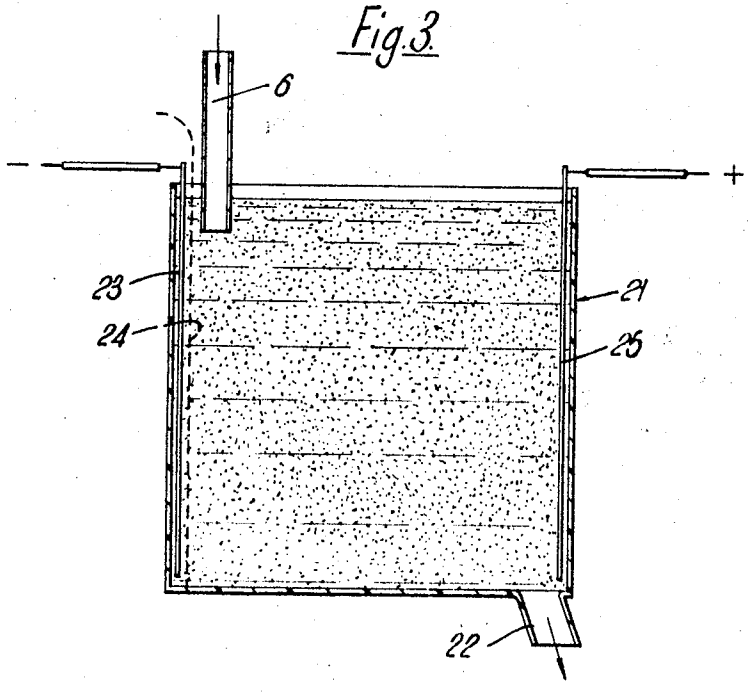


Fig. 2.



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Fig. 3.



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MANUFACTURE OF ASBESTOS

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U.S. Cl. 204—180 9 Claims

This invention relates to the manufacture of asbestos articles, that is to say, articles composed essentially of or containing asbestos. The invention is based on the phenomenon of electrophoresis, which involves the passage of a direct current through a dispersion of electrically charged particles between two electrodes, the particles being electrically attracted towards the oppositely charged electrode so that they move towards it and deposit on it.

It is known that if a dispersion is to be subjected to electrophoresis it must contain very highly dispersed particles. These particles are said to be colloidally dispersed, since one of the properties of colloidally dispersed particles is that they are charged and that, accordingly, they may undergo electrophoresis. It is also known that of the three most common types of asbestos, namely chrysotile, amosite and crocidolite, chrysotile can readily be dispersed colloidally in water with an anionic dispersing agent. In the invention anionic dispersions of asbestos are used and they may contain some noncolloidally dispersed asbestos fibres and they may even contain other constituents, either colloidally dispersed or merely intimately mixed, which are not asbestos. The necessary property a dispersion must possess to be usable in the invention in response to electrophoresis is that asbestos fibres in it will be electrically attracted to an electrode when a current is passed through the dispersion. Whether any given dispersion has this property is readily ascertainable by test.

Chrysotile asbestos is sold in various grades and all grades can be colloidally dispersed. Fibres of dry chrysotile asbestos are positively charged but when the fibres are opened and dispersed in water by means of anionic dispersing agents (e.g., soaps) their surfaces become negatively charged (due to adsorption of a layer of negative soap anions). Under the influence of a direct current, therefore, the fibres then move towards the anode.

In an application by two of us (G. F. Heron and J. O. Halstead) filed simultaneously herewith, a process is described in which the dispersion is passed between two electrodes across which an electric potential difference is applied, whereby constituents are caused to migrate towards the anode, the migrating constituents are collected as a deposit on the anode or on an ion-permeable membrane interposed in their path to the anode, and the deposit is removed from the remainder of the dispersion. Products which may be produced in this way include sheets, tapes and yarns, membranes, such as glass cloth, coated or impregnated with asbestos, and wire and other electrically conducting surfaces coated with asbestos.

It is necessary to pass the dispersion between the electrodes while the process is carried out since if this is not done localised electrolytic effects occurring around the electrodes will interfere with satisfactory deposition of asbestos.

Now if the same dispersion is repeatedly passed between the electrodes, or is passed very slowly between the electrodes, the process must clearly come to a stop at the stage when all the asbestos in the dispersion between the electrodes has been deposited but, in practice, we have found that satisfactory deposition ceases before this point is reached, inferior products then being obtained. For instance, satisfactory deposition may cease when only about 60% of the fibres of the initial dispersion have been deposited, and thus there can be a serious wastage of asbestos.

The primary object in this invention is to avoid this wastage.

Another object is to provide an electrophoretic process which can be carried on substantially indefinitely.

In the present invention we circulate the dispersion continuously through a reservoir and replenish it periodically or continuously. Replenishment asbestos is made at substantially the rate at which asbestos is deposited, so that, except for dispersion remaining in the apparatus when the process is stopped, there is complete deposition of asbestos and there is no wastage.

The provision of the reservoir gives proper opportunity for determining the contents of the dispersion and making the necessary replenishment. In practice, the need for replenishment can often be judged merely by eye. Asbestos is, of course, the most important constituent of the dispersion which has to be replenished, but other constituents are also consumed during the electrophoretic process and the replenishment must replace these as well. During electrophoresis the pH of the dispersion rises because hydrogen evolution at the cathode and removal of acid in the deposit result in a rise in hydroxyl ion concentration in the dispersion. The replenishment of the asbestos dispersion should therefore involve the addition of acid to maintain the pH of the dispersion substantially constant. If no acid is added, satisfactory deposition will eventually stop.

The process of electrodeposition may be carried out in numerous ways. Particularly advantageously the deposit is continuously stripped off the anode as a coherent body. We have surprisingly found that it is possible to produce deposits of such high wet strength that the deposit can be stripped off the anode while it is still immersed in the dispersion. However, the deposit may be carried out of the dispersion on the anode or membrane and then either left in position to form a permanent coating on the electrode or membrane or stripped off.

When the deposit is drawn off the anode or membrane while wet, high wet strength is an extremely important property. For highest wet strength, long fibres should be used. Moreover, we have found that to impart high wet strength it is necessary to deposit a binder with the asbestos. This binder is not required for dry strength in the final product, as is shown by the fact that a product made with it maintains its strength on removal by solvent extraction or by heating to 450° C. of the organic matter in it. This suggests that the very fine, highly opened asbestos fibrils may be giving dry strength to the product by random arrangement and entanglement, a theory which is supported by electron microscopic examination of the deposits.

We find that the fibres are oriented in the direction in which the dispersion flows, and in particular any incompletely opened bundles are deposited parallel to one another. This fact accounts for an observed large difference in strength of electrodeposited asbestos products in directions at right angles to one another. Strengths are much higher in the direction of drawing of continuously deposited materials and the coarse fibres are seen to be aligned in this direction. Alignment is apparently not merely a result of the drawing or flowing motions since alignment occurs in static deposition.

To produce the binder required for high wet strength, we use a water-soluble soap as an anionic dispersing

agent. During the electrophoresis process, electrolysis and electroosmosis occur, the electrolysis resulting in the release of cations at the anode and a build-up of acidity there. If the anode does not corrode during the process free fatty acids are formed by reaction of the resultant acid with the water-soluble soap, and these improve the wet strength. Much better wet strength is obtained by the use as the anode of a metal which will corrode during the process as a result of electrolytic action. Ions dissolved from such an anode react with the water-soluble soap to yield a water-insoluble soap which acts as a binder. The preferred metals for use as the anode are aluminum and zinc, but copper, lead or iron may also be used.

When high wet strength is not important the electrode can satisfactorily be of materials, for example platinum or carbon, which do not corrode to give ions that form insoluble soaps.

Although the water-soluble soaps serve both as dispersing agents and binder-formers, they do not give wholly satisfactory dispersions when used as the sole dispersing agents. To form the best dispersion and get the highest west strength, we prefer to use a mixture of soap and another anionic surface-active dispersing agent, for example an alkyl-aryl sulphonate, an alkyl sulphosuccinate or a sulphated higher alcohol. We find a very suitable mixture to be one of 6 parts soap to 1 part of the other anionic dispersing agent. Unless otherwise specified, all parts and percentages quoted in this specification are by weight. Two examples of dispersions which are responsive to electrophoresis are as follows:

EXAMPLE 1

	Parts
Tap water of hardness of about 100 p.p.m. expressed as calcium carbonate (at 60° C.)	1,000
Chrysotile asbestos (Canadian Cassiar A35, length approximately 0.30")	20
Sodium dodecyl benzene sulphonate	1.2
Soap (sodium salts of mixed long-chain fatty acids)	7

If this dispersion is used with an anode of aluminum, zinc or copper the wet strength is good. Equal dry strength may be obtained if the anode is of carbon or platinum.

EXAMPLE 2

The dispersion contains 2% chrysotile asbestos fibre (South African C and G3, length aproximately 0.18") and 0.3% sodium dioctyl sulphosuccinate. This dispersion can be deposited on a corrodible or noncorrodible anode, and it requires support until it is dry. It presents the advantage that it yields a deposit containing only about 5% organic matter.

The proportion of the fibre in the dispersion is small, though it may advantageously depend on the fibre length. With long fibres such as Canadian Cassiar A35 the proportion in the dispersion may be from 0.5 to 5%. With very short fibres such as Canadian Bells F7M (length approximately 0.02") the proportion may be as high as 15% and preferably is at least 1%.

There is an optimum pH of the dispersion for each anode material, so it may be necessary to adjust the pH of the dispersions of Examples 1 and 2 to obtain satisfactory deposition with some anodes.

The dispersion need not consist solely of asbestos fibres, but rather one or more constituents having the same electric charge as the dispersed fibres may also be present in the dispersion, these materials thus undergoing electrophoresis with the asbestos fibres. In particular, the dispersion may contain both chrysotile asbestos fibres and particles of a polymeric material. The proportion of the polymer particles may vary from a very small to a substantial figure.

Particularly useful products, e.g., gaskets, may be made by the codeposition of asbestos and a styrenebutadiene rubber or polytetrafluorethylene. Other useful reinforced

polymer compositions may be made by the codeposition of asbestos and a thermoplastic, thermosetting or rubber polymer, examples of suitable polymers being styrene rubbers, copolymers of acrylonitrile and butadiene, copolymers of carboxylic butadiene and acrylonitrile, polyvinyl chloride, polyethylene, polystyrene, polyester resins and various mixtures of these.

Some examples of dispersions which contain polymer particles and are responsive to electrophoresis are as follows:

EXAMPLE 3

The dispersion contains by weight:

2% chrysotile asbestos fibre (Canadian Cassiar A35),
2½% polyvinyl chloride added as latex,
0.8% soap,
0.12% sodium dodecyl benzene sulphonate.

This dispersion will give a deposit containing about 34% asbestos, 57% polyvinyl chloride and 9% soap products.

EXAMPLE 4

An equivalent amount of polyeterafluorethylene is substituted for the polyvinyl chloride in Example 3, and a product of low wet strength but good dry strength is obtained. This deposit must therefore be carried out of the dispersion on a continuous anode or other support.

EXAMPLE 5

The dispersion contains by weight:

5% chrysotile asbestos fibre (Canadian Bells C5R, length approximately 0.06"),
20% polytetrafluorethylene (added as a dispersion),
0.5% sodium dioctyl sulphosuccinate.

The dispersion gives deposits containing about 35% asbestos, 63% polyetetrafluorethylene and 2% other organic matter. These deposits are useful as gasket materials. From this dispersion a deposit of good dry strength but low wet strength is obtained, and the deposit must therefore be carried out of the dispersion on a continuous anode or other support.

The dispersions have a surprisingly high tolerance for charged or uncharged particles and fibres, which may themselves be able to undergo electrophoresis or which may be deposited simply by being mechanically entrained by the deposited fibres. Examples of colloidally dispersible particles which can be added are bentonite, clay, colloidal silica and graphite. Bentonite will also act as a dispersing agent, though it does not produce a satisfactory colloidal dispersion without another dispersing agent. One example is as follows:

EXAMPLE 6

The dispersion contains by weight:

4% bentonite,
3% chrysotile asbestos fibre,
0.15% sodium diotcyl sulphosuccinate.

This dispersion gives a deposit having a low wet strength.

When graphite is colloidally dispersed with the asbestos the product is graphitised asbestos. Such products are known, but when they are made by impregnation the graphite is largely concentrated at the surface, whereas in the product made by the invention it is uniformly dispersed throughout the product. As an example, 20 parts of graphite by weight in the form of a colloidal dispersion may be added to the dispersion of Example 1.

The mechanical entrainment of uncharged constituents is surprising. For example, 20 parts by weight of glass fibres as chopped roving ¼ inch long may be added to the dispersion of Example 1. Broadly, examples of constituents which may be entrained by colloidally dispersed fibres that migrate under electrophoresis are glass fibres

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(as chopped roving), slag wool and noncolloidally dispersed asbestos fibres, such as fibres of amosite or crocidolite or even of chrysotile.

In order to prevent contamination of the dispersion by bubbles of gas evolved at the cathode it is often preferable to cover the cathode by a membrane, for example a nylon cloth, which is permeable to ions but not to gas bubbles. This cathode membrane separates the liquid around the cathode from the rest of the dispersion between the electrodes, and when the dispersion is being circulated it is advantageous to prevent this cathode liquid from reentering the dispersion since removal of the cathode liquid, which is alkaline, considerably reduces the rise in pH of the liquid.

Dispersing agent is carried out of the dispersion by the deposit during the electrophoretic process, especially when the anode is of a metal which dissolves during the process and the dispersion includes a soap, since the soap then reacts with the dissolved metal to form an organic binder. Dispersing agent is also carried out of the dispersion in any cathode liquid which is removed. It is thus necessary to replenish the dispersion with dispersing agent also. If a mixed dispersing agent is used the individual components of the mixture are replenished as necessary. If there is any excess alkali, providing an excess of alkali metal ions, in the dispersion, then the soap can be replenished by merely adding a soap-forming fatty acid since this acid will react to form soap. This method has the advantage that the pH of the dispersion is reduced by the single addition. A mixture of soap-forming fatty acids may be used. If the dispersion contains dispersed constituents other than asbestos, for example polymer, these are replenished as necessary; it is sometimes found that replenishment of, say, polymer, needs to be made at a greater rate than would be expected from the relative proportions of asbestos and polymer in the initial dispersion.

Replenishment may be effected with a dispersion, but it will be appreciated that if this dispersion has the same composition as the desired composition of the dispersion in the reservoir it will be necessary to add some additional quantities of some of the constituents, since they are not consumed at the same proportional rate during the electrophoretic process. We prefer to replenish the dispersion with undispersed constituents, and to disperse them by circulating the dispersion through a circuit that contains one or more pumps. The pump or pumps should be effective to disperse the added asbestos fibres quickly, but, since dispersions used in the invention can contain noncolloidally dispersed asbestos fibres, substantially complete colloidal dispersion of the added asbestos before any of it passes between the electrodes is not necessary. Provided good dispersion of the added fibres is achieved quickly, the quality of the product will not be seriously impaired, probably because the amount of asbestos added at any one time is small compared with the amount of asbestos in the existing dispersion, so that there will only be a small proportion of freshly added asbestos fibres in the dispersion subjected to electrophoresis at any particular time and most of these fibres will at least be sufficiently highly dispersed to be entrained by colloidally dispersed fibres. Sufficient dispersion of undispersed constituents added as replenishment can normally be obtained by passage through a single dispersing pump, for example a centrifugal pump, but if more complete dispersion is required a number of dispersing pumps may be put in series in the circuit.

The circuit in which the added replenishing constituents is dispersed may include the passage between the electrodes, but it is usually better to make the rate of flow through the dispersing pump or pumps higher than that between the electrodes. Accordingly, in order to avoid the need for duplicating pumps, part of the circulating dispersion may be tapped off from the dispersing circuit downstream of the pump or pumps and passed between the electrodes.

The shape of the anode on which the deposit is formed depends on the required product. It may be a plate of the width desired for a sheet or tape of asbestos. In order to facilitate drawing of the product off the electrode it is desirable that deposition should occur only on the electrode surface having the shape of the desired product and in order to prevent extraneous deposition the other surfaces are generally shielded. For example, an electrode for the production of sheet or tape may be sunk in a recess in the surface of a larger nonconducting sheet, and the whole then machined to present a flat surface. Alternatively a backing of nonconducting material may be provided on a very thin electrode, a suitable nonconducting material being polymethyl methacrylate. However, if the plate has two conducting flat surfaces and is located between two cathodes or within an encircling cathode, sheet or tape can be produced on both surfaces simultaneously.

A particularly suitable anode is a rotary cylinder.

If the deposit has not got sufficient wet strength to be drawn off without breaking, it may be formed on a flexible band, which may be a membrane that moves over the face of the anode, for instance round a rotary anode, or which may be of metal and thus constitutes the anode.

The invention is useful in the production of yarn. This may easily be made by twisting tape made either in tape form or by slitting wider sheets.

Once the wet deposit has been removed from the dispersion it is not generally necessary to subject it to any special treatment if it has a high wet strength, since strength will be maintained on drying. The drying may occur naturally in air, even when the deposit is rolled up, or it may be forced by heating. Similarly no special treatment is necessary if the deposit is to form a permanent coating on an electrode or membrane. If, however, it has low wet strength it is preferably heated to dry it on leaving the dispersion.

In the annexed drawings, FIGURE 1 is a flow diagram and FIGURE 2 shows one form of container in which the electrodeposition may be carried out; and FIGURE 3 shows another form of container.

In the apparatus diagrammatically shown in FIGURE 1, there is a main reservoir **17** containing a large volume of dispersion, a centrifugal pump **18** for pumping the dispersion around a circuit **26** and a metering pump **20** for tapping off part of the dispersion downstream of the pump **18** and passing it through an inlet **6** into and through a container **3** containing two electrodes. After passing between the electrodes dispersion flows out down a chute **12**, which is of fairly steep gradient close to the container but which has an extension **16** of very slight gradient leading to the top of the reservoir **17**. The entrainment of air into the dispersion should be kept to a minimum throughout by avoiding turbulent flow where possible, and it is because of this that the extension has only very slight gradient.

The preferred construction of the container **3** is shown in FIGURE 2. In this a cylindrical anode **1** having end discs **2** of insulating material is rotatably mounted within the container **3** (which is an open box) above a trough formed by a curved cathode **4**. An inlet trough **5** extends across the top of the box immediately above one edge **14** of the cathode, and contains an inclined baffle **7** above an inlet **6**. Dispersion supplied to the inlet **6** by the pump **20** at a uniform rate flows round the lower edge of the baffle **7** and then over the baffle and a weir **27** formed by the edge of this baffle through the gap between the anode and the cathode. Current is supplied to the anode through bearings **8** having electrical connections, and to the cathode by a contact **9**, and some of the asbestos present in dispersion between the anode and cathode is deposited as a sheet **10** on the anode while excess dispersion flows over a weir **11** formed by the edge of the cathode and down a chute **12**. Once an appreciable deposit has

formed on the anode its end can be picked off and the deposit drawn slowly upwards. Thereafter the sheet deposit is continuously slowly drawn upwards, this movement causing the anode to rotate and so to present continuously fresh surface to the dispersion. Acid forming in the V-shaped space between the upwardly moving deposit and the anode is permitted to flow around the edges of the deposit into the excess dispersion flowing over the weir **11**. This acid causes some coagulation of the dispersion, but the clots so formed are broken up and the fibres in them redispersed on passage through the pump **18**.

Any clots adhering to the deposit should be broken off, and it may be desirable to trim off the edges and feed them back into the reservoir of dispersion.

It is advantageous to cover the cathode by a membrane **13** of nylon cloth which is permeable to ions but not to gas bubbles. This prevents contamination of the dispersion by evolved gas. Cathode liquid, formed between the membrane and the cathode and containing bubbles of the gas, flows axially off each end of the cathode into the container **3** and leaves through an outlet **15**. This cathode liquid is alkaline and advantageously should not reenter the dispersion.

As an example, in an apparatus as shown in FIGURE 2 the anode **1** was approximately 7 inches wides and there was a half-inch space between the anode and the cathode membrane **13**. The total initial volume of a dispersion of Example 1 in the reservoir and in circulation was approximately 30 litres, the dispersion also containing a sufficient amount, approximately 55 grams, of a mixture of 65 parts oleic acid and 35 parts stearic acid to give the dispersion a pH in the range of 8.5 to 8.7, this pH being the most suitable for the anode, which was of zinc. A current of 5 amps at between 15 and 20 volts DC was applied between the anode and cathode and dispersion was continuously pumped in through the inlet **6** and excess dispersion flowed over the weir **11** back into the reservoir **17**. A deposit of wet asbestos paper was formed on the anode and was drawn off, squeezed to remove excess acidic liquor and then dried. This liquor was returned to the dispersion in the reservoir tank to assist in pH control. After about 20 minutes it was seen by eye that the appearance of the dispersion in the reservoir was changing, and replenishment was started. This replenishment was effected by adding undispersed asbestos fibres, oleic acid and stearic acid, soap, and sodium dodecyl benzene sulphonate as necessary. The process was run continuously for 42 hours, during which time approximately 125 litres of dispersion were added to maintain the level of dispersion in the reservoir tank (i.e., 125 litres of dispersion were actually used for deposition). Approximately 65 litres of cathode liquid were collected and 16 litres of acidic liquid were squeezed from the paper during winding, 3,500 grams of dry paper (0.004" thick) were produced, containing (when dried to 1% moisture content) from 20 to 25% organic matter. This represents 100% deposition of the asbestos in the dispersion.

If the deposit has not got adequate wet strength, then a carrier, which may be an ion-permeable membrane, for example of fine-mesh nylon cloth, may be run round the rotary anode and the deposit forms on it and can either be left on it or stripped from it after drying as desired.

Products may be made batch-wise, examples being gaskets made by the co-deposition of asbestos and a styrene-butadiene rubber or polytetrafluorethylene. FIGURE 3 shows a container suitable for use in the manufacture of such a gasket. This container is an open pot having an outlet pipe **22**. A cathode **23** is immersed in one side of the pot, which is electrically insulated and a membrane **24** which is permeable to ions but impermeable to gas bubbles separates the cathode from the dispersion. Dispersion is fed into the pot through the inlet **6** by the pump **20** and leaves through the outlet **22**. An anode **25** is dipped into the dispersion and a current passed until a deposit has formed on the anode, which is then withdrawn, carrying the deposit with it. While the current is passed dispersion continuously passes between the electrodes, being returned to the reservoir **17** where replenishment is effected when necessary.

We claim:

1. A process for the production of an asbestos product comprising the steps of drawing from a reservoir an anionic aqueous disperson of asbestos fibres that is responsive to electrophoresis, passing the withdrawn dispersion between a cathode and an anode, applying an electric potential difference across said cathode and anode, whereby solid constituents are caused to migrate towards the anode, collecting the migrating constituents as a deposit, removing the deposit from the remainder of the dispersion, returning the remainder of the dispersion to the reservoir, and replenishing the dispersion.

2. A process according to claim **1** in which the replenishment is effected in the reservoir with undispersed constituents which are dispersed in a circuit in which the dispersion is circulated to and from the reservoir.

3. A process according to claim **2** in which the dispersion circulated between the electrodes is tapped off from the said circuit at a point downstream of that at which the undispersed constituents are dispersed.

4. A process according to claim **1** in which the pH of the dispersion is maintained substantially constant by the replenishment.

5. A process as claimed in claim **1** in which the asbestos dispersion contains other dispersed particles carrying electric charges such that they undergo electrophoresis and are deposited with the asbestos fibres, and the dispersion is replenished in the said other particles as well as in asbestos fibres.

6. A process as claimed in claim **1** in which the dispersion contains additional fibres which are entrained by and codeposited with the dispersed asbestos, and the dispersion is replenished in these fibres as well as in asbestos fibres.

7. A process for the production of an asbestos product comprising the steps of establishing a reservoir of an anionic aqueous dispersion of asbestos fibres that is responsive to electrophoresis and contains a water-soluble soap as a dispersing agent, continuously circulating said dispersion through a reservoir and between a cathode and an anode, the anode being of electrolytically corrodible metal, applying a potential difference across said cathode and anode whereby solid constituents are caused to migrate towards the anode and metal ions are dissolved from the anode and combine with the soap to form a water-insoluble soap, collecting the migrating constituents and water-insoluble soap as a deposit on the anode, continuously stripping the deposit while wet off the anode as a coherent body, and replenishing the circulated dispersion.

8. A process according to claim **7** in which the anode is of aluminium.

9. A process according to claim **7** in which the anode is of zinc.

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