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Description

This invention relates to a novel structure of paper and to a method of making paper. Within the term "paper" we include all hydraulically deposited webs of fibres of all kinds including for example fibres made from cellulose, glass, asbestos, carbon fibre and mineral wool or other synthetic materials.

The conventional wisdom in the paper-making art is that it is possible to form a properly coherent paper from a slurry of cellulosic fibres such as wood, cotton or flax fibres which have been subjected to an appropriate treatment, for example by beating or refining. Binders or other materials may be added. The inter-action between the fibres is partly due to such friction as is caused by mechanical intermeshing but is primarily by hydrogen bonding between the hydroxyl groups existing on the fibres and on fibrils formed by the treatment to which the fibres have been subjected. Binders if present will act to adhere the surfaces of the fibres together, or to form a self bonding matrix in and around the fibrous web.

There are many fibres, particularly synthetic polymer fibres and inorganic fibres, for which inherent interengagement is weak and there are some applications for which such adherence without binders is inadequate. It is impossible, for example, to achieve high strength without binders when the fibres in question are glass, mineral wool fibres, quartz, alumina and so on, or when non-fibrous materials, such as ion exchange resins or silica gels or activated carbon, are incorporated. Furthermore, although cellulosic fibres on the one hand can be interengaged with adequate strength and, on the other hand, inorganic fibres such as glass fibres can, by special treatments, form a paper of some strength, it has been impossible in the past to make a material where layers made from certain sorts of fibres form a strong interface except by using large amounts of binder or, of course, by adhesive lamination of pre-prepared webs.

It appears that the interengagement between fibres of one type in one layer is taking place by one mechanism and of another type in a separate layer by a different one, even when the fibres in each layer are different types only to the extent that they are fibres of the same material but have been differently treated or are of different length or of different thickness. One layer is usually stronger than the other. The problem of forming an interface is particularly difficult when the fibres are different in each layer. This is especially so when the fibres in each layer are of different materials.

Where great thickness was not required, papers have generally been made of a single slurry and any special surfaces were achieved by surface treatment of the web as for example in the application of coatings or sizes.

For a lot of applications however it is the properties of the surface of the paper which matter, the remainder of its bulk giving only mechanical strength or the like. Alternatively, one property may be desired on one surface and a different one within the thickness of the paper or at the other surface.

In these cases therefore it would be economic to make such papers in a single process by selecting the material of a surface layer of the paper itself with a view to its having a desired property and making the body of the paper or its other surface of some other material.

For example, in some chemical treatment/filtration applications we wish to have a paper having inert surface characteristics but a reactive material such as an ion exchange compound incorporated in the body of the paper between the two surface layers. Alternatively, for filter papers a layer of glass fibres having desirable filtration properties may be supported by a layer of cellulosic or different glass fibres giving mechanical strength. We would also wish to have the facility for building up a comparatively thick paper from thin layers of fibres which of their nature could not practicably be applied in the full thickness—for example because of slow water removal due to their extreme fineness.

It has previously been proposed to build up a relatively thick paper board having the same type of fibre across it by a continous "wet-on wet" process in which a first slurry of the fibres is deposited onto the wire of a Fourdrinier papermaking machine and, while the first slurry is still wet, a second slurry of the fibres is deposited on the first so as to allow interlaminar mixing of the fibres. In such processes it is known to introduce the second slurry to the first at a speed slower than that at which the first slurry is moving.

A theoretical discussion of the "wet-on wet" process is given by B. Radvan and A. J. Willis, in "Paper Industry Conference Papers", available at Royal Hall, Exhibition Centre, Harrogate 26—28th October 1982. Though not specifically stated, it appears that the article relates to conventional cellulosic paper board the fibres of which are of the same physical and chemical characteristics throughout the thickness of the paper. Radvan and Willis address themselves to the problem of forming the second layer on the first without disturbing the first so that the number of fibres at the interface which lie across the board is reduced so that the board appears homogeneous. To this end they employ the "Coanda effect" to introduce the respective stocks at zero angle and zero speed relative to a moving wire in which the stocks are deposited. The success of such a process relies upon the hydrogen bonding between the cellulosic fibres and the presence in the slurries of a binder which is conventionally present. The possibility of radically affecting the fibrous structure of the web, e.g. through repeated application of "micro-turbulence" throughout the process of formation, is also suggested by Radvan and Willis as something which may be discerned in the future, though this suggestion is clearly within the same general principle of keeping disturbance of the respective layers to a minimum.

US—A—2098733 discloses a practical method of forming a thick paper board by depositing a second slurry on a first slurry while the first is still wet so as to allow interlaminar mixing of the fibres. The fibres in the first may be longer than those in the second slurry. Again the process is controlled so as to minimize the number of fibres oriented generally across the paper so that the paper appears homogeneous. A size binder is included in both slurries to achieve adequate bond strength, and it appears that a silicate adhesive is also employed.

A process in which a second slurry is deposited on a partially dehydrated first slurry has also been employed to produce papers which are at least primarily of asbestos fibre. The fibres through the width of the paper are of the same chemical and physical characteristics, but those in one layer are more densely packed than those in the other. In this process the degree of flocculation of the fibres was controlled so as to provide some fibres lying generally in the Z-direction in an attempt to improve bonding (US—A—3353682).

Paper made by the abovementioned known processes is weakest at the interface between adjacent layers.

Even though the fibres throughout the width of the paper made by such known processes were generally of the same chemical and often physical nature, it was still considered necessary to include a binder, often in large amounts (see particularly US—A—3353682) to achieve adequate strength. The presence of such a binder is, however, highly undesirable in certain applications, such as in scientific laboratory papers and battery separators (see US—A—4216280 which employs a single layer containing glass fibres, some coarse, some fine and no binder). In other applications, such as filters for cleansing gases, e.g. air filters, especially so-called "HEPA" (high efficiency particulate air) filters, the presence of more than small amounts of binder is highly undesirable though such small amounts have sometimes, in the past, been included to give the paper sufficient strength.

For a battery separator or HEPA filter, it is known to be desirable to have one layer of relatively coarse fibres and another of finer ones. To date, because it was believed to that too much binder would be required to form a unitary structure, the two layers were separately preformed and then laminated either with an adhesive or mechanically (see, for example, US—A—4262068). It would be particularly advantageous to be able to provide a battery separator or HEPA filter comprising a single unitary sheet which contained no binder, and which could be made by a single process.

CH—A—461253 discloses a wet-on-wet process where fibres of different slurries intermingle. Different fibres may be used from the different headboxes. A binder can be employed in the slurries to ensure sufficient bonding where the material of the slurries does not have an inherent high binding strength.

US—A—4274915 (Munari) describes a method of manufacturing heat sealed proof paper from two slurries, one slurry containing only conventional cellulose pulp and the other consisting of a mixture of 60% olefin fibres and 40% pulp. It is suggested that interpenetration of the fibres can be achieved with the use of a Fourdrinier machine with one wire and two feed tanks. For more efficient bonding, Munari relies upon a hot calendering operation after the paper is formed, which operation brings the polyolefin fibres in a condition close to their melting point.

US—A—4220500 describes a non woven glass fibre-containing multi-layer sheet, in which respective layers additionally contain other fibres. The sheet is made by a paper-making process but the conditions of operation of the process are not disclosed. Binding is achieved by the use of a polyvinyl chloride sol and the resultant product is used for flooring, walling, roofing etc.

The present invention permits the manufacture in a single process of a paper having at least two material layers which are inherently bonded together during the papermaking operation from distinct slurries which will usually be of different fibres (i.e. different chemically, physically or both), and which layers are joined at an interface which comprises a region where the fibres of the two distinct slurries are intermingled. If the first slurry has fibres A and the second has fibres B then the structure of the finished paper is layer A followed by interface A+B followed by layer B and then optionally B+C. C and so on. This is achieved in the present invention without the necessary use of a binder.

The present invention provides a papermaking process in which a plurality of layers of distinct slurries are laid down one upon the other in the papermaking machine such that a composite is built up in the wet state, a second layer being applied to the first in a determinate relationship of the composition of the two slurries at the time of application and of the physical relationship between the slurries at that time, whereby disturbance is caused only in a surface region of the two layers to cause penetration of the fibres of the second slurry among the fibres of the first in that region but to leave substantially undisturbed the fibres in the majority of the thickness of each of the respective layers. It is found that by such control we have an adherence strength at the interface which is equal to or, frequently, greater than the strength of at least one and possibly each of the respective layers, even in the case where the fibres of the two layers are widely dissimilar, and all this without necessarily using a binder material.

This is because the fibres are by the controlled disturbance intermingled at the interface between adjacent layers. This allows the fibres to become interlinked. Thus, on attempting to tear the adjacent layers apart from one another the fibres interengage so as to resist the tearing. Hence the paper has a tendency to tear along a plane in the weakest of the two adjacent layers rather than at the interface. On attempting delamination, a high percentage of the top ply fibres are still physically attached to the bottom ply via the interface.

By enabling adjacent layers to be bonded to one another in this manner, a binderless unitary structure having characteristics which vary through its width, including variations in the chemical nature of the fibres, variation in their physical characteristics (especially fineness) and variations in the loading of other additives which paper, for certain uses, desirably includes, e.g. silica gel or particles of ion exchange resin in laboratory filter paper, or perlite in battery separators, may be obtained.

The physical relationships which are of primary importance in a process of the invention are the relative velocities of the two slurries at the time of application, the height of the flow box nozzle of the second above the first layer and the angle of that nozzle to the first layer. By these variables we can control the degree and extent of intermingling of fibres at the interface and the degree and extent to which fibres are reorientated in the interface from the plane in which they are predominantly deposited in either layer. The liquid content of the respective layers may also play a part in determining the characteristics of the final paper.

It is particularly preferred that the second slurry is introduced to the first at a speed greater than that at which the first slurry is moving.

In certain fields, the use of a binder material is highly undesirable. This is so in the field of scientific laboratory papers such as filter papers. etc. where the object of using fibres such as glass fibres is to provide a paper which is chemically highly inert and pure. The presence of binders in such papers may be deleterious to the results obtained, since they may introduce chemical impurity and do reduce filtration efficiency. Binders are also highly undesirable in battery separators; the binder would not be chemically compatible with the electrolytic cell and would also restrict absorption of electrolyte into the separator.

In another aspect of the invention we provide a paper made integrally of different fibres in respective layers with an interface between the layers comprising fibres of both layers and causing a cohesion between the layers, and in particular such a paper when free of binder. The fibres may be different either chemically or physically or both. Furthermore, one or other or each of the layers may have incorporated into it in the slurry stage or deposited onto it non-fibrous materials appropriate to the use of the paper and this in the laboratory context may include particles of ion exchange resin or in the ordinary context incorporating in a surface layer (which may be of lesser thickness than the other layer or layers), furnishes for achieving a desired surface characteristic. It is also possible to affect the properties of the paper as a whole by controlling the properties of the interface. For example, desirable properties of, for example, a filter paper, battery, separator or gas-cleansing filter, such as an air filter, especially a so-called "HEPA" filter, can be affected or even determined by control of the amount of disturbance and hence of disorientation and intermingling which is induced at the time of application of the second or other subsequent slurries.

The preferred parameters for the relative consistencies and relationships of adjacent layers at the time that a subsequent layer is applied to an earlier layer are determined by the respective properties of the two fibres involved.

It can be generally said that the greater the dissimilarity between the fibres of the layers and especially when one (or both) havw a low bond strength with the layer, the greater should be the angle of incidence and the height from which the subsequent layer is applied. In dependence upon the nature of the paper required, each of the relative velocities, angle and height may be chosen independently of one another. Suitable angles of incidence may be between 1.5° and 20°, preferably between 2.5° and 12°. For many papers a particularly suitable angle is about 4°—6°. The height may lie between 1 and 50 mm, preferably between 1 and 20 mm, more preferably between 1 and 10 mm. The velocity difference between the two slurries may be 2 to 15%, preferably between 2 and 12%, and, for many papers, more preferably about 5—7, (the second travelling faster than the first). For example to apply a glass layer (e.g. Johns Manville 106 glass microfibres having an average diameter of 0.49—0.58 micrometers) to a cellulosic layer (e.g. cotton) the glass slurry is most effectively applied from a height of 8 mm at an angle of incidence of 7.0° to the cellulosic layer: if the lower layer ware a glass layer (e.g. Johns Manville 104 glass microfibres having an average diameter of 0.34—0.48 micrometers) it would require 6.0 mm and 4.0° respectively.

In all cases, control of the consistency of the layers at the time of application is critical. A second layer should be applied to a first when the first slurry is still highly liquid and, in dependence upon the nature of the paper to be made, preferably contains between 80—95%, more preferably between 86.5 and 93.5%, more particularly 87.5—92.5%, especially 89—91% by weight water, and when the second contains between 98 and 99.9% water, more particularly 99.0 to 99.8%, especially 99.5—99.7% by weight water (the rest in each case being solid content). A third slurry if used may be applied at a consistency of 85 to 95% water, more particularly 90%, at which time the consistency of these first two layers, taken together overall, may be between 89 and 91% of water: in this case, where the first two layers have already consolidated to a certain extent, the formation of an interface may be aided by mechanical disruption of the face of the third layer by subjecting this layer to a change of direction by passing it over a roll immediately prior to its being deposited upon the first two (or more) layers.

In each case an interface is formed of mixed fibres which is about 5 to 15% of the total thickness of the two layers, more usually about 10%. The extent of thickness of the interface layer depends primarily, though not solely, on the nature of the first layer rather than on the consistencies and the variables mentioned above.

Processes embodying the invention may be carried out so as to produce novel materials for two fields of use which present particular difficulty, battery separators and gas-cleansing filters such as air filters, especially HEPA filters. Thus, a multilayer structure can be produced for use as a gas-cleansing filter or battery separator which structure will consist of two or more layers of cellulose, synthetic organic or inorganic fibres.

In particular, such processes allow the preparation of a paper suitable for use, inter alia, as a battery separator or gas-cleansing filter comprising a paper having a density gradient across it, the fibres at the interface between adjacent respective layers being sufficiently intermingled and interlinked to provide sufficient bond strength between the layers without the necessity for binder to be present. Such binderless graded density paper does not appear to have been previously disclosed in the literature.

A battery separator embodying the invention is particularly suitable for use in gas recombination batteries which require separator integrity. The separator, in a single unitary structure, provides sufficient bulk to absorb and hold the electrolyte and efficiently prevents passage therethrough of bodies such as small crystals harmful to the battery, while allowing the gases to pass through it. The process of the invention allows particularly efficient use of the fibres when producing such battery separators.

In a process in accordance with the invention, the fibres in respective slurries may be different from one another in either their physical or chemical characteristics, or both. Furthermore each respective slurry may contain in that slurry a mixture of fibres different from each other in their physical and/or chemical characteristics.

The fibre may be natural or synthetic, inorganic or organic, for example, cellulosic (either natural or regenerated) fibres such as wood pulp, cotton and cellulose acetate, inorganic fibres such as glass, asbestos and alumina, natural organic fibres such as mineral wool and synthetic organic fibres such as polyesters (e.g. polyethylene terephthalate), polyolefins (e.g. polyethylene, polypropylene), acrylics (e.g. polyacrylonitrile), carbon fibre and polyamides (e.g. nylon), especially aromatic polyamides (e.g. Kevlar^R-Kevlar is commercially available from Du Pont). Kevlar is particularly suitable for HEPA filters for use in the nuclear industry because it is not attacked by the hydrofluoric acid emitted by reactors.

Papers made by processes embodying the invention are those in which at least one of the fibres is non-cellulosic and these may be selected from inorganic and synthetic organic fibres, e.g. glass, polyester, polyamide or polyolefin.

Other preferred papers have one layer comprising cellulosic fibres and another comprising non-cellulosic fibres, e.g. cellulose on glass, especially fine cellulosic fibres on relatively coarse glass fibres.

The process is particularly applicable to forming papers having two adjacent layers each of which comprises non-cellulosic fibres. For example filters having respective layers of polyester and glass are useful in gas masks.

The fibres in the respective layers may be the same as one another chemically but differ in their respective thicknesses. Such papers, when made entirely out of glass, provide especially suitable battery separators or HEPA filters.

Where glass fibres are employed these may be of a thickness within a range wider than for many other fibres. Thus, the glass in the fine layer may be as fine as a Johns Manville 100 microfibre (having an average diameter of from 0.2 to 0.29 micrometers), while the glass in the coarse layer may be as coarse as Johns Manville "Chop Pak" fibres, which are either about 12.7 or 6.3 mm in length and 15 micrometers in thickness.

Typically, a battery separator may have an average weight/unit area of from 60—240 g/m^2 and comprise two layers, viz a coarse layer of e.g. a mixture of Johns Manville 112 and 110 microfibres (average diameters 2.6—3.8 and 2.17—3.10 micrometers respectively) and a fine layer of either Johns Manville 108 or 106 microfibres (average diameter 0.59—0.88 or 0.49—0.58 respectively). The glass may be a borosilicate glass with or without zinc oxide (e.g. Johns Manville type 475 or 753 respectively).

A two-layer battery separator embodying the invention may have:—

Layer (1)—a furnish of acid resistant glass micro-fibre having a nominal fibre diameter of 3.5 microns and a grammage between 50 and 250 g/m^2.

Layer (2)—(and layer (3) if used)—a furnish of acid resistant glass microfibre having a nominal value of 0.65 microns and a grammage between 5 and 100 g/m^2.

In the case of a three ply structure layer (1) would form the centre ply with layers (2) and (3) forming the outer surfaces of the structure.

The qualities which make such unitary glass microfibre separators embodying the invention successful are as follows:

1. Their stability in sulphuric acid.

2. They are binder free multiple structures which provide the ability to make more efficient use of the different grades of glass fibres by

(a) using a thin continuous layer of fine fibres to give a fine pore structure and so reduce the possibility of unwanted transfer between the electrodes, and

(b) increasing the bulk of the material by use of continuous layers of coarse fibres, capable of absorbing comparatively large amounts of electrolyte per unit weight of separator.

3. Their improved strength as compared with the thin, flimsy, single, mixed fibre, layer. In the

unitary strucutre embodying the invention, the thin layer of fine fibres is strongly bonded without binder or mechanical aids to the bulk layer of coarse fibres by which it is supported.

A typical HEPA filter may have an average weight/unit area of from 60—110 g/m^2 and comprise two layers, viz. a coarse layer of e.g. Johns Manville 112 microfibres (average diameter 2.6—3.8 μm), and fine layer of Johns Manville 100 microfibres (average diameter 0.2—0.29 micrometres). The glass may be a borosilicate glass containing a small amount of zinc oxide (e.g. Johns Manville type 475).

A two-layer HEPA filter embodying the invention may have:—

(A) Layer (1)—a furnish of between 50%→100% glass microfibre having a nominal fibre diameter of 0.3 microns, 0—50%, preferably 5%→50%, synthetic organic fibre and 0→10% acrylic binder with a grammage between 20→200 g/m^2.

Layer (2)—a furnish of 90%→100% glass microfibre having a nominal fibre diameter of 0.65 microns or less and 0→10% additive, with a weight of between 5 and 100 g/m^2.

(b) Layer (1)—a furnish of 50%→100% cellulose, 50%→100% synthetic organic fibre with a grammage between 10→100 g/m^2.

Layer (2)—a furnish of 90%→100% glass microfibre having a nominal fibre diameter of 0.65 microns or less and 0→10% additive with a grammage between 5 and 100 g/m^2.

A multi-density HEPA filter embodying the invention thus produced has the following advantages over a conventional filter, which is a homogeneous mixture of glass fibres.

1. Substitution of relatively fine fibres by coarser fibres in part of the thickness gives a reduction in pressure drop without loss of strength and may also mean that lower-cost materials can be used.

2. The material has a gradation of pore sizes from the relatively large pores in the continuous coarse fibre structure of the layer we call a "pre-filter" layer through a range of medium sized pores in the central (mixed fibre) area, to the relatively small pores of the continuous fine fibre structure of the filter layer.

3. The structure allows for more efficient depth filtration to take place. Particles are in effect more evenly distributed throughout the structure.

4. Loading capacity can be greatly increased by the careful design of a filter/pre-filter material for specific applications.

5. For a given loading, i.e. similar weights of particulate matter, the pressure drop would be lower for the multi-density filter than for a single ply filter.

6. The layer of fine fibres would be protected by the pre-filter layer and hence the effective life of the filter could be increased.

7. The amount and diameter of the fine fibres used would be determined by the required filtration performance. This would lead to a more efficient use of the expensive fine fibres.

In the accompanying drawings:

Figure 1 is a highly diagrammatic view of a Fourdrinier type machine modified to operate the invention;

Figure 2 is a detailed scheme of the region of the flow-box nozzle applying a second slurry;

Figures 3 to 7 are photomicrographs of partial sections through various papers according to the invention, at various enlargements, showing the region of the interface.

A Fourdrinier machine 1 has the conventional flow-box nozzle 3 to deposit a slurry onto a moving web (or "wires") 4 to form a layer 5′ of wet fibre. Water drains conventionally from this into a sump 6 for recycling/treatment. At a selected position along the wire is provided a second flow box 7, fed with a different slurry from a second header. The second head box nozzle 8 issues a stream 9′ of the second slurry directly onto the upper surface of the layer 5′ which at that time is of a known consistency dependent on the constitution of the first slurry, the speed of the wires, the speed of drainage and the distance of the second box 8 from the first. The nozzle is set at a height h above the surface of the layer 5′ and has a flow angle a to that layer. The velocity of the layer 5′ is V_1 and the velocity of the stream 9′ as it leaves the nozzle is V_2. The effect of this and of making the consistency of this layer 5′ be about 90% water while the slurry stream 9′ is about 99.5% water, is to cause a disturbance of the upper surface only of the layer 5′ and an intermingling of the fibres of the two layers in the interface between them, indicated at 10′.

Fibres of the second slurry if finer than those of the first may be drawn down between them by gravity, drainage or suction so as to enhance the effect of the disturbance in the interface region; if the fibres of the second layer are coarser than those of the first they may be thought of as stakes penetrating into the first layer and anchoring the layers together.

The composite layer then passes to a suction belt 11 and to drying rollers 12 in the conventional way.

If desired a third layer may be applied from a third flow box 13 via an auxiliary wire 14 to be pressed onto the composite layer at a time when that, as a whole, has a water content of 89 to 91% and when the third slurry has a water content of approximately 90%.

Examples of the manufacture of various specific papers, using in each case the apparatus of Figures 1 and 2, follow.

Example 1: wood on cotton

A first slurry was made of cotton fibres and a second of wood pulp. The first slurry was run onto the wire and at a position where its water content was 90% the second slurry was projected onto it with the second nozzle being at a height h 3 mm from the surface of the layer formed by the first slurry at an angle of about 3°, and at a velocity V_2 5% or 6% greater than that, V_1, of the layer formed by the first slurry. The consistency of the second slurry was at the time of contact 99.5%

water.

A coherent two-layer paper was formed after the conventional drying and pressing stages the two layers of which were separated only with difficulty and which showed under the microscope an interface layer, extending to about 10% of the thickness of the paper, where there was great intermingling and disorientation of the wood and cotton fibres.

Example 2: glass on cotton

A first slurry was made of cotton fibres and a second of Johns Manville 104 glass microfibres. The first slurry was run onto the wire and at a position where its water content was 90% the second slurry was projected onto it with the second nozzle being at a height h, 10 mm from the surface of the layer formed by the first slurry at an angle of about 6°, and at a velocity V_2 about 5% greater than that, V_1, of the first slurry. The consistency of the second slurry was at the time of contact 99.6% water.

A coherent two-layer paper was formed after the conventional drying and pressing stages the two layers of which were not separable, in the sense that the bond strength between the layers was greater than the fibre-fibre bonding in the glass layer.

Examination of the structure of the paper showed an intermediate layer 10 in which fibre from the two layers 5, 9 were intermingled and disorientated. The thickness of the layer 10 was about 10% of that of the paper. Photomicrographs of sections through this sample are seen in Figures 3, 4 and 5 which are respectively at ×500, ×1800 and ×5500 magnifications. Figure 5 is also of interest showing at 15 a glass fibre penetrating a cotton fibre. This product provides a particularly efficient strong, flexible liquid filtration medium.

Example 3: glass on cotton

Example 2 was repeated except that the glass fibres were Johns Manville 106 microfibres, the nozzle was spaced at 13 mm from the surface of the layer and at an angle of 9°. A photomicrograph at ×550 of the paper thus prepared is Figure 6.

Example 4: glass on glass

A first slurry was made of Johns Manville 108B glass microfibre and a second of Johns Manville 104 glass microfibre. 108B is coarser than 104. The first slurry was run onto the wire and at a position where its water content was 91.5%. The second slurry was projected onto it with the second nozzle being at a height h 4 mm from the surface of the layer formed by the first slurry at an angle of about 3°, and at a velocity V_2 5 or 6% greater than that V_1, of the layer formed by the first slurry. The consistency of the second slurry was at the time of contact 99.7% water.

A coherent two-layer paper was formed after the conventional drying and pressing stages, the two layers of which were not separable, in the sense that the bond strength between the layers was greater than the fibre-fibre bonding in the glass layer.

Examination of the structure of the paper showed an intermediate layer 10 on which fibre from the two layers 5, 9 were intermingled and disorientated, a photomicrograph at ×550 of the paper produced being seen at Figure 7.

This structure provides a particularly efficient pre-filter (or depth) filter, especially a HEPA filter, or battery separator.

Example 5: glass on glass/polyethylene

Example 4 was repeated except that a first slurry was made of 90% Johns Manville 108B glass microfibre and 10% Solvay Pulpex polyethylene fibres, and a second of Johns Manville 104 glass microfibre.

A coherent two-layer paper was formed after the conventional drying and pressing stages the two layers of which were not separable, in the sense that the bond strength between the layers was greater than the fibre-fibre bonding in the glass layer.

Examination of structure of the paper showed an intermediate layer 10 on which fibres from the two layers 5, 9 were intermingled and disorientated.

Similarly, a quantity of granules of ion-exchange material or other non-fibrous material may be incorporated in one of the slurries.

A strong, flexible laboratory liquid filter with high wet strength is obtained.

Example 6: glass on polyester

In a manner similar to Examples 4 and 5 a slurry of glass microfibres was laid down on a slurry of polyester fibres, with the same satisfactory results.

This is useful as a highly efficient gas face mask medium.

Examples 7—11

Papers particularly suitable for HEPA filters and battery separators were made as follows.

Equipment

1. Black Clawson 8′ HCVT Tile Hydrapulper, (60 cm (24″) Diameter Vokes Rotor and Drive Assembly—75 KW (100 hp.) 1800 r.p.m. Westinghouse Motor.

2. Semtile Chests, (13 500 l (3000-gal.) and 32 000 l (7000-gal.) capacities with side-entering lightning mixers.

3. Black Clawson Secondary Flow Box—installed on a 90 cm (36-inch) Fourdrinier.

4. Fourdrinier Paper Machine 90 cm (36″), described in detail as follows:

Sandy Hill Corporation Fourdrinier Paper machine with a wire width of 90 cm (36″) and designed to operate at speeds from 1,5 m/min (5 f.p.m.) to 90 m/min (300 f.p.m.). Headbox with multiple-type operation—static, pressure or vacuum—equipped with manifold-type inlet and various specially designed homogenizer and distributor rolls and Neilson slice. Fourdrinier table adjustable for inclined operation of 7,5 cm (3″) in 4,5 m (15′) table length. The press section consists of two main presses, the first one being a straight through plain press and the second press a plain reversing press. The rolls are cast iron with various special rubber and stonite covers. One smoothing press has a straight through run. The drier sections consist of seven and five driers with integrally cast journals and two felt driers on the bottom and top first section felts. A combination horizontal and vertical size press is provided and equipped with various composition coverings. It was not used in this series of runs. The calender stack consists of eight rolls with the intermediate rolls bored for steam. Each roll is constructed of chilled iron and is precision ground and carried in anti-friction bearings. Also included is a 90 cm (36″) diameter Pope type reel with a 90 cm (36″) face and capable of winding rolls up to 1 m (40″) in diameter.

Stock preparation

Each furnish was dispersed in the Hydrapulper at 3.0 pH for designated periods of time. The furnish was then pumped to either the 32 000 l(7,000-gal.). Secondary stock chest or the two 16 000 l (3,500-gal.). Primary Stock Chests and adjusted to the required consistency and pH.

Papermaking

Primary system

The Fourdrinier wet-end was used for the primary layer. Each Furnish was pumped from the machine chests and metered with a Foxboro Flow Controller to the suction of the fan pump where white water from the wire was added to give the required papermaking consistency. From the fan pump, the diluted furnish was metered with a Foxboro Flow Controller (total flo) through a five-pipe manifold into the headbox.

Secondary system

The Black Clawson Secondary Flow Box was installed over the fourth foil box and used to form the secondary layer. The furnish was pumped from a 32 000 l (7,000-gal.) stock chest and metered with a Foxboro Flow controller into the flow box.

The edges of the first press were taped to prevent any pressure being applied to the sheet.

All dryer cans were felted during the trial.

In all Examples, the secondary slurry was deposited on the primary slurry at an angle of 4° 4,5 m (15′) from a height of 10 mm. The second slurry issued at a speed of around 8% faster than the primary.

Example 7 (HEPA filter)

Furnish—Primary slurry:—

90% Johns Manville glass 112 microfibre (average thickness 2.6—3.8 micrometres), type 475 (borosilicate glass containing a small quantity of zinc oxide).

10% Johns Manville Chop Pak A20 BC 1,27 cm (½″) glass fibre (average thickness 15 micrometres).

Water content when second slurry impinges—93.32%.

Weight basis of primary layer—54 g/m^2.

Second slurry:

100% Johns Manville glass 104 microfibre (average thickness 0.34—0.48 micrometres) type 475.

Water content—99.765%.

Weight basis of secondary layer—26 g/m^2.

Example 8 (HEPA filter) (Best method)

Furnish—Primary slurry:—

90% Johns Manville glass 110 microfibre (average thickness 2.17—3.10 micrometres) type 475.

10% Johns Manville Chop Pak A20 BC 1,27 cm (½″) glass fibre.

Water content when second slurry impinges—94.37%.

Weight basis of primary layer—52 g/m^2.

Second slurry:—

100% Johns Manville glass 100 microfibre (average thickness 0.2—0.29 micrometres), type 475.

Water content—99.765%.

Weight basis of secondary layer—26 g/m^2.

This gave a particularly efficient HEPA filter, there being a substantial density gradient from the coarse primary to the fine secondary layer.

Example 9 (HEPA filter)

Furnish—Primary slurry:—

90% Johns Manville glass 110 microfibre (average thickness 2.17—3.10 micrometres), type 475.

10% Johns Manville Chop Pak A20 BC 1.27 cm (½″) glass fibre (average thickness 15 micrometres).

Water content when second slurry impinges—93.72%.

Weight basis of primary layer—55 g/m^2.

Seconary slurry:—

100% Johns Manville glass 106 microfibre (average thickness 0.49—0.58 micrometres).

Water content—99.769%.

Weight basis of secondary layer—29 g/m^2.

Example 10 (Battery separator)

Furnish—Primary Slurry:—

90% Johns Manville glass 110 microfibre, type 475.

10% Johns Manville Chop Pak A20 BC 1,27 cm (½″> glass fibre.

Water content when second slurry impinges—94.41%.

Weight basis of primary layer—75 g/m^2.

Second slurry:—

100% Johns Manville glass 108A microfibre (average thickness 0.59—0.88 micrometres), type 753 (a zinc oxide free borosilicate glass).

Water content—99.755%.

Weight basis of secondary layer —30 g/m^2.

Example 11 (Battery separator)
Furnish—Primary slurry:—

90% Johns Manville glass 110 microfibres, type 475.

10% Johns Manville Chop Pak A20 BC 1,27 cm (½'') glass fibre.

Water content when second slurry impinges—91,60%.

Weight basis of primary layer—155 g/m^2.

Secondary slurry:—

100% Johns Manville glass 108A microfibre, type 475.

Water content—99.752%.

Weight basis of secondary layer—40 g/m^2.

Delamination tests were conducted on papers embodying the invention by adhering double sided tape to both faces of the paper and a pulling member to the other face of the two sided tape. The pulling members were then pulled apart from one another and the paper examined to determine where tearing occurred.

With papers such as those of Examples 7—11, tearing occurred in either the primary layer or the secondary layer, the interface remaining intact.

Claims

1. A paper having a first layer (5) comprising a first fibre and a second layer comprising a second fibre (9) different from the first, the fibres of at least one of the first and second layers being non-cellulosic, the paper additionally having an interface layer (10) bonding the first and second layers together and in which both the first and second fibres are intermingled and interlinked in orientations more disordered than the fibres in the first and second layers, the interface layer (10) bonding together the first and second layers with a bond strength at least as great as the bond strength of at least one of the first (5) and second (9) layers.

2. A paper according to claim 1, wherein the non-cellulosic fibres are glass, polyester, polyamide or polyolefin fibres.

3. A paper accorbing to claim 1 or claim 2, wherein the first and second fibres are the same as each other chemically but differ in at least one of their physical characteristics.

4. A paper according to claim 3, wherein the fibres in one of the said first and second layers are finer than the fibres of the other of the said first and second layers, whereby the paper has a density change across it.

5. A paper according to any preceding claim, wherein the first and second fibres are glass fibres.

6. A paper according to any preceding claim, which is essentially free of binder.

7. A paper according to any preceding claim, wherein the thickness of the interface layer (10) is about 5 to 15% of the total thickness of the three layers (5, 10, 9).

8. A paper according to any preceding claim, wherein the interface layer (10) has a bond strength greater than the bond strength of at least one of the first (5) and second (9) layers.

9. A method of making paper which involves applying a secbnd slurry (9') of fibres to a surface of a travelling layer of a first slurry (5'0 of fibres to form a second layer thereon with intermingling and interlinking of the first and second fibres, fibres of the respective slurries being different from one another, the applying being done at a time when the fibres of the first slurry (5') are mobile at the upper surface region of the first slurry by virtue of its being in the wet state and when the second slurry (9') has a higher water content than that of the first, characterised in that the fibres of at least one said slurry are non-cellulosic and in that at the time of application the velocity (V_2) of the second slurry is precontrolled in relation to the velocity (V_1) of travel of the first slurry and the said applying is also done under precontrolled conditions of angle (α) and height (h) relative to the first slurry to control the thickness of an interface layer (10)

Formed by the application of the second slurry, between the first and second layers the precontrol being such as to cause a disturbance to an extent sufficient to ensure bonding together of the first and second layers irrespective of the nature of the first and second fibres with a bond strength of the interface layer (10) at least as great as the bond strength in at least one of the first and second layers.

10. A method according to claim 9, wherein the velocity (V_2) of the second slurry is greater than that (V_1) of the first.

11. A method as claimed in claim 10, wherein the velocity (V_2) of the second slurry is from 102 to 115% of that (V_1) of the first.

12. A method according to claim 9, claim 10 or claim 11 wherein the first slurry (5') has a consistency at the said time which is 87.5 to 92.5% water and the second slurry (9') has one which is 98 to 99.9% water.

13. A method according to any one of claims 9 to 12 wherein the angle of application of the second slurry (9') relative to the first (5') is between 2.5° and 12°.

14. A method according to any one of claims 9 to 13, wherein the height (h) above the upper surface of the first slurry from which the second is applied is between 1 mm and 20 mm.

15. A method according to any one of claims 9 to 14, wherein the interface layer (10) is 5% to 15% of the total thickness of the paper produced from the two slurries.

16. A method according to any one of claims 9 to 15, wherein both the slurries are essentially free of binder.

17. A method according to any one of claims 9 to 16, wherein the interface layer of the paper has a bond strength greater than that of at least one of the first and second layers.

18. A method according to any one of claims 9 to 17, wherein both the first and second fibres are glass fibres.

19. A method according to any one of claims 9 to

18, wherein the fibres of the second slurry are finer than those of the first, whereby the paper formed has a density change across it.

Patentansprüche

1. Papier mit einer ersten Schicht (5) aus ersten Fasern und einer zweiten Schicht (9) aus zweiten Fasern, die von den ersten Fasern verschieden sind, wobei die Fasern mindestens einer der beiden Schichten keine Zellulosefasern sind, wobei das Papier zusätzlich eine Trennschicht (10) aufweist, die die erste und die zweite Schicht miteinander verbindet und in der die ersten und zweiten Fasern unter Orientierungen miteinander vermengt und verkettet sind, die stärker fehlgeordnet sind als die Fasern in der ersten und der zweiten Schicht, wobei die Trennschicht (10) die erste und die zweite Schicht mit einer Haftkraft miteinander verbindet, die mindestens so groß ist wie die Haftkraft von mindestens einer der beiden Schichter (5, 9).

2. Papier nach Anspruch 1, wobei die Fasern, die keine Zellulosefasern sind, Glas-, Polyester-, Polyamid- oder Polyolefin- fasern sind.

3. Papier nach Anspruch 1 oder 2, wobei die ersten und zweiten Fasern in chemischer Hinsicht gleich sind, aber hinsichtlich mindestens einer ihrer physikalischen Eigenschaften verschieden sind.

4. Papier nach Anspruch 3, wobei die Fasern der ersten und der zweiten Schicht eine unterschiedliche Feinheit haben, weshalb sich die Dichte des Papiers in Querrichtung ändert.

5. Papier nach einem der vorhergehenden Ansprüche, wobei die ersten und die zweiten Fasern Glasfasern sind.

6. Papier nach einem der vorhergehenden Ansprüche, das im wesentlichen frei von einem Bindemittel ist.

7. Papier nach einem der vorhergehenden Ansprüche, wobei die Dicke der Trennschicht (10) ungefähr 5 bis 15% der Gesamtdicke der drei Schichten (5, 10, 9) beträgt.

8. Papier nach einem der vorhergehenden Ansprüche, wobei die Trennschicht (10) eine Haftkraft hat, die größer ist als die Haftkraft mindestens einer der beiden Schichten (5, 9).

9. Verfahren zur Herstellung von Papier, bei dem ein zweiter Faserbrei (9') auf ein Oberfläche einer bewegten Schicht aus einem ersten Faserbrei (5') aufgebracht wird, um auf diesem unter Vermengung und Verkettung der ersten und zweiten Fasern eine zweite Schicht zu bilden, wobei die Fasern des ersten und zweiten Faserbreis voneinander verschieden sind, wobei das Aufbringen zu einem Zeitpunkt erfolgt, wo die Fasern des ersten Breis (5') im Oberflächenbereich des ersten Breis beweglich sind, weil sich dieser im nassen Zustand befindet, und wo der zweite Brei (9') einen höheren Wassergehalt hat als der erste Brei, dadurch gekennzeichnet, daß die Fasern mindestens eines Breis keine Zellulosefasern sind und daß zum Zeitpunkt der Aufbringung die Geschwindigkeit (V_2) des zweiten Breis im Verhältnis zur Bewegungsgeschwindigkeit (V_1) des ersten Breis gesteuert wird und daß die Aufbringung unter einer bestimmten Winkel (α) und einer bestimmten Höhe (h) in Bezug auf den ersten Brei durchgeführt wird, um die Dicke einer Trennschicht zu steuern, die durch die Aufbringung des zweiten Breis zwischen der ersten und der Schicht gebildet wird, wobei die Steuerung derart ist, um eine Störung zu bewirken, die ausreichend ist, um die erste und die zweite Schicht unabhängig von der Art der ersten und zweiten Fasern miteinander zu verbinden, wobei die Haftkraft der Trennschicht (10) mindestens so groß ist wie die Haftkraft mindestens einer der beiden Schichten.

10. Verfahren nach Anspruch 9, wobei die Geschwindigkeit (V_2) des zweiten Breis größer ist als die Geschwindigkeit (V_1) der ersten Breis.

11. Verfahren nach Anspruch 10, wobei die Geschwindigkeit (V_2) des zweiten Breis 102 bis 115% der Geschwindigkiet (V_1) des ersten Breis beträgt.

12. Verfahren nach Anspruch 9, 10 oder 11, wobei der erste Brei (5') zu dem besagten Zeitpunkt einen Wassergehalt von 87,5 bis 92,5% und der zweite Brei (9') einen Wassergehalt von 98 bis 99,9% hat.

13. Verfahren nach einem der Ansprüche 9 bis 12, wobei der zweite Brei (9') unter einem Winkel von 2,5° bis 12° auf den ersten Brei (5') aufgebracht wird.

14. Verfahren nach einem der Ansprüche 9 bis 13, wobei der zweite Brei aus einer Höhe (h) von 1 bis 20 mm über der Oberseite des ersten Breis aufgebracht wird.

15. Verfahren nach einem der Ansprüche 9 bis 14, wobei die Dicke der Trennschicht (10) 5 bis 15% der Gesamtdicke des aus dem ersten und zweiten Brei hergestellten Papiers beträgt.

16. Verfahren nach einem der Ansprüche 9 bis 15, wobei so wohl der erste als auch der zweite Brei im wesentlichen frei von Bindemittel sind.

17. Verfahren nach einem der Ansprüche 9 bis 16, wobei die Trennschicht des Papiers eine Haftkraft hat, die größer ist als die Haftkraft mindestens einer der beiden Schichten.

18. Verfahren nach einem der Ansprüche 9 bis 17, wobei die ersten und zweiten Fasern Glasfasern sind.

19. Verfahren nach einem der Ansprüche 9 bis 18, wobei die Fasern des zweiten Breis feiner sind als diejenigen des ersten Breis, weshalb sich die Dichte des Papiers in Querrichtung ändert.

Revendications

1. Papier ayant une première couche (5) comprenant une première fibre et une seconde couche comprenant une seconde fibre (9) différente de la première, la fibre d'au moins une des deux couches étant non cellulosique, le papier ayant en plus une couche d'interface (10) liant ensemble les première et deuxième couches et dans laquelle les première et deuxième fibres sont entremêlées et interconnectées dans des orientations plus désordonnées que les fibres

dans les première et deuxième couches, la couche d'interface (10) liant ensemble la première et la deuxième couches avec une résistance de liaison au moins aussi grande que la résistance de liaison d'au moins l'une des première (5) et deuxième couches (9).

2. Papier selon la revendication 1, dans lequel les fibres non cellulosiques sont des fibres de verre, de polyester, de polyamide ou de polyoléfine.

3. Papier selon la revendication 1 ou la revendication 2, dans lequel les première et seconde fibres sont les mêmes chimiquement mais diffèrent au moins par l'une de leurs caractéristiques physiques.

4. Papier selon la revendication 3, dans lequel les fibres dans l'une desdites première et seconde couches sont plus fines que les fibres dans l'autre desdites première et seconde couches, la densité du papier variant dans sont épaisseur.

5. Papier selon l'une quelconque des revendications précédentes, dans lequel les première et deuxième fibres sont des fibres de verre.

6. Papier selon l'une quelconque des revendications précédentes, qui est essentiellement exempt de liant.

7. Papier selon l'une quelconque des revendications précédentes, dans lequel l'épaisseur de la couche interface (10) représente environ 5 à 15% de l'épaisseur totale des trois couches (5, 10, 9).

8. Papier selon l'une quelconque des revendications précédentes, dans lequel la couche d'interface (10) a une résistance de liaison supérieure à la résistance de liaison d'au moins l'une des première (5) et seconde (9) couches.

9. Procédé de fabrication du papier qui comprend l'application d'une deuxième suspension (9') de fibres sur la surface d'une couche mobile d'une première suspension (5') de fibres pour former une deuxième couche sur la première avec entremêlage et interconnexion des première et seconde fibres, les fibres des suspensions respectives étant différentes les unes des autres, l'application étant faite à un moment où les fibres de la première suspension (5') sont mobiles à la surface supérieure de la première suspension du fait qui celle-ci est à l'état humide et lorsque la deuxième suspension (9') a une teneur en eau supérieure à celle de la première, caractérisé en ce que les fibres d'au moins l'une desdites suspensions sont non cellulosiques et en ce que au moment de l'application, la vitesse (V_2) de la seconde suspension est précontrôlée en relation avec la vitesse (V_1) de déplacement de la première suspension et en ce que ladite application est réalisée également dans des conditions précontrôlées d'angle (α) et de hauteur (h) par rapport à la première suspension pour contrôler l'épaisseur d'une couche d'interface (10) formée par l'application de la deuxième suspension entre la première et la seconde couches, le précontrôle étant tel qu'il cause une perturbation d'étendue suffisante pour assurer la liaison mutuelle des première et deuxième couches sans tenir compte de la nature des première et deuxième fibres avec une résistance de liaison de la couche d'interface (10) au moins aussi grande que la résistance de liaison dans l'une ou l'autre des première et deuxième couches.

10. Procédé selon la revendication 9, dans lequel la vitesse (V_2) de la deuxième suspension est supérieure à la vitesse (V_1) de la première suspension.

11. Procédé selon la revendication 10, dans lequel la vitesse (V_2) de la deuxième suspension est 102 à 115% celle (V_1) de la première suspension.

12. Procédé selon la revendication 9, la revendication 10 ou la revendication 11, selon lequel la première suspension (5') a une consistance audit moment qui est de 87,5 à 92,5% d'eau et la deuxième suspension (9') a une consistance de 98 à 99,9% d'eau.

13. Procédé selon l'une des revendications 9 à 12, selon lequel l'angle d'application de la second suspension (9') par rapport à la premìre (5') est compris entre 2,5° et 12°.

14. Procédé selon l'une des revendications 9 à 13, selon lequel la hauteur (h) au-dessus de la surface supérieure de la première suspension depuis laquelle est appliquée la seconde suspension est comprise entre 1 mm et 20 mm.

15. Procédé selon l'une des revendications 9 à 14, selon lequel la couche d'interface (10) représente 5 à 15% de l'épaisseur totale du papier produit à partir des deux suspensions.

16. Procédé selon l'une des revendications 9 à 15, selon lequel les deux suspensions sont essentiellement dépourvues de liant.

17. Procédé selon l'une des revendications 9 à 16, selon lequel la couche d'interface du papier a une résistance de liaison supérieure à celle d'au moins l'une des première et deuxième couches.

18. Procédé selon l'une des revendications 9 à 17, selon lequel les première et deuxième fibres sont toutes deux des fibres de verre.

19. Procédé selon l'une des revendications 9 à 18, dans lequel les fibres de la deuxième suspension sont plus fines que celles de la premìere, la densité du papier formé variant dans l'épaisseur de celui-ci.

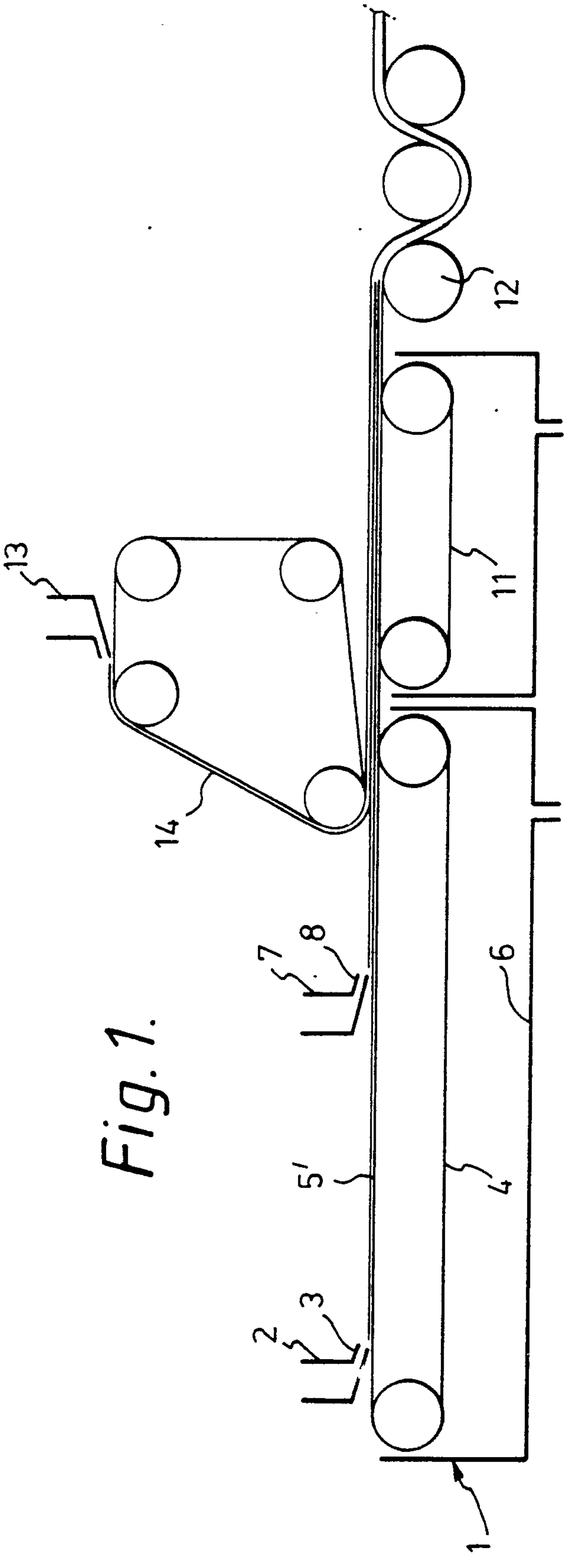
Fig. 1.

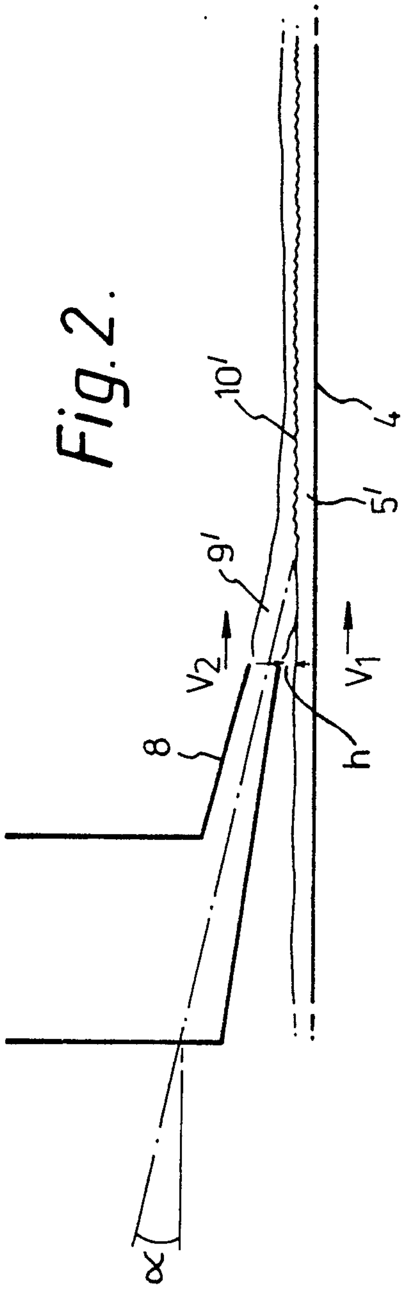
Fig. 2.

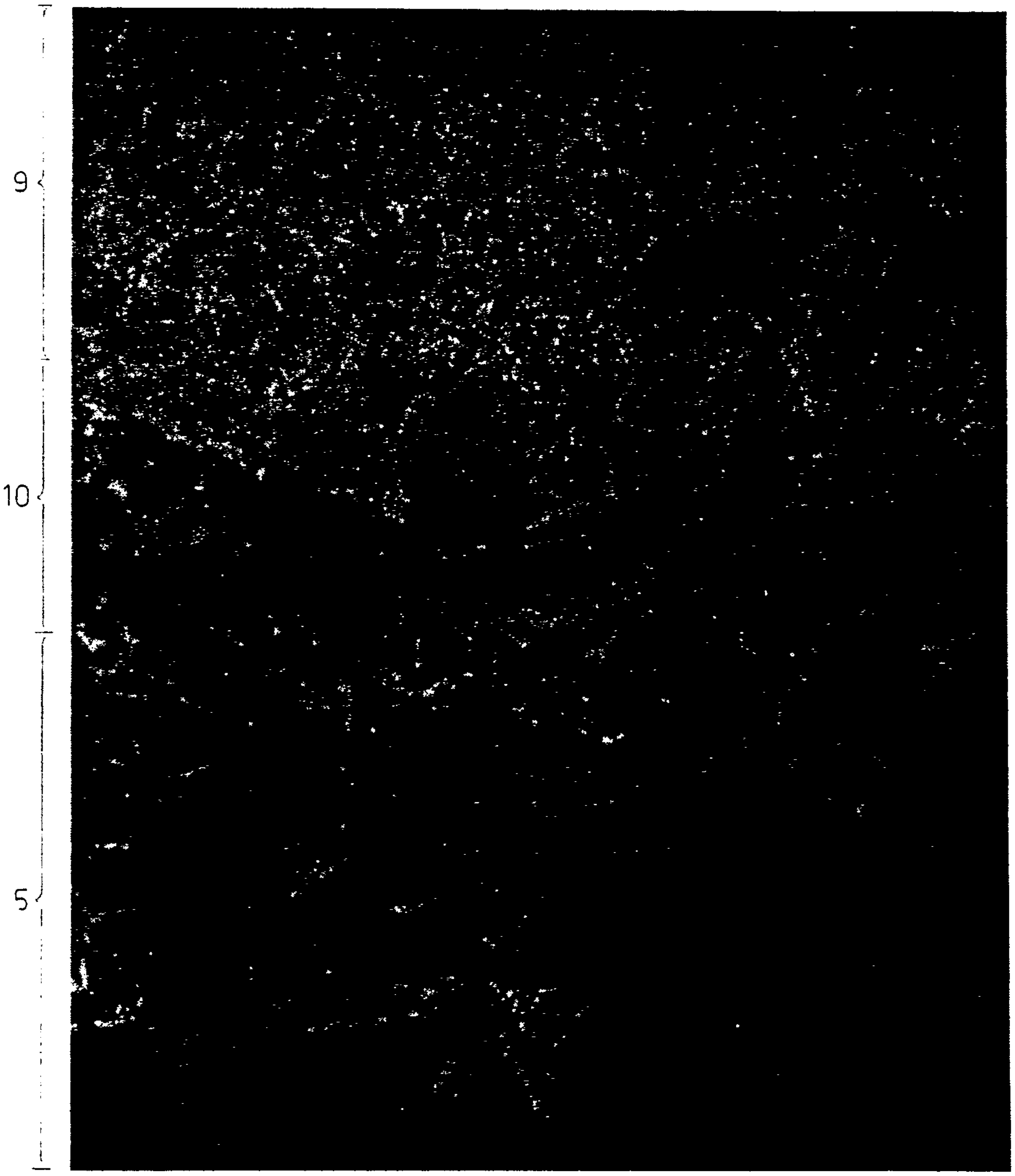

Fig.3.

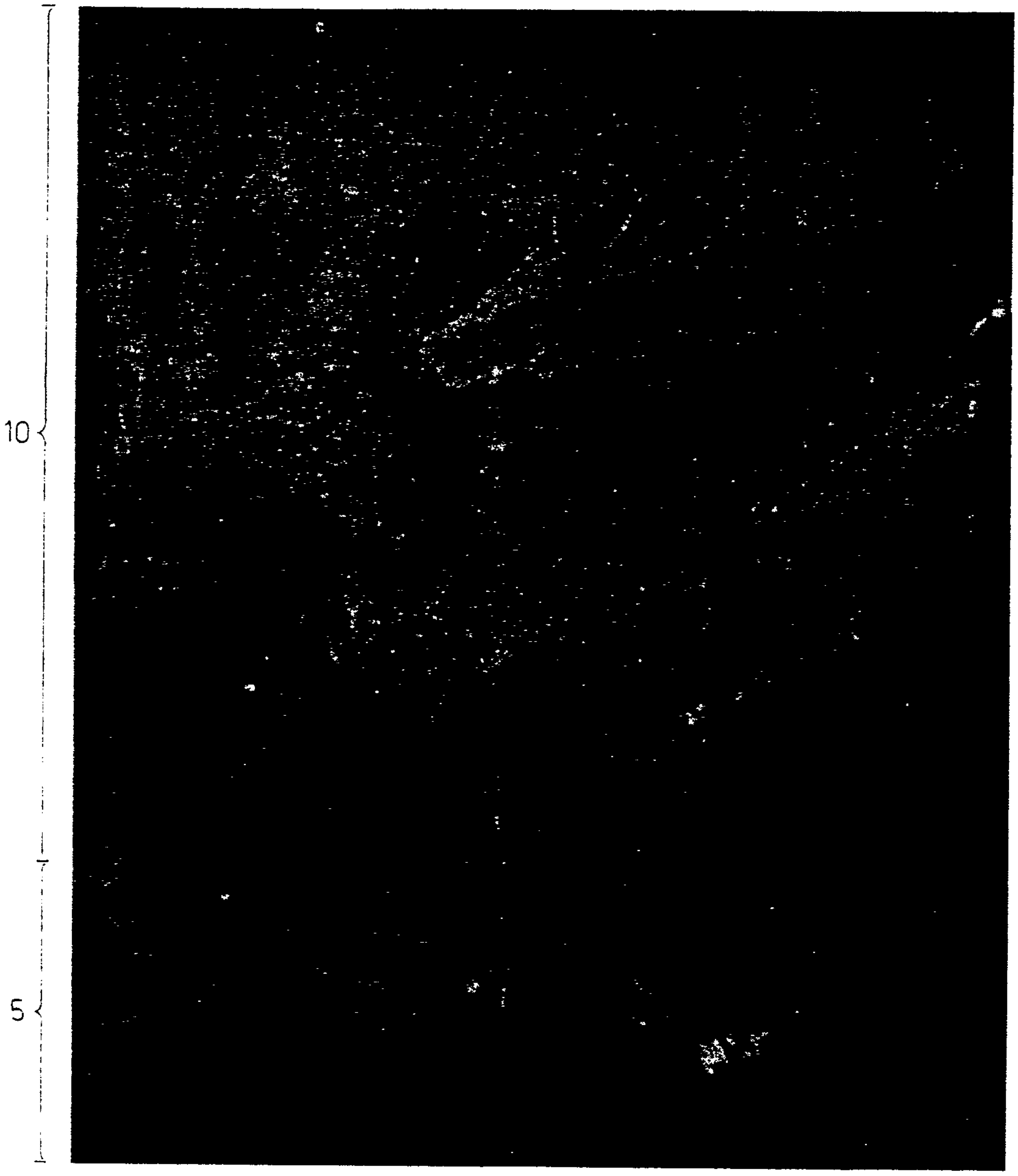

Fig.4.

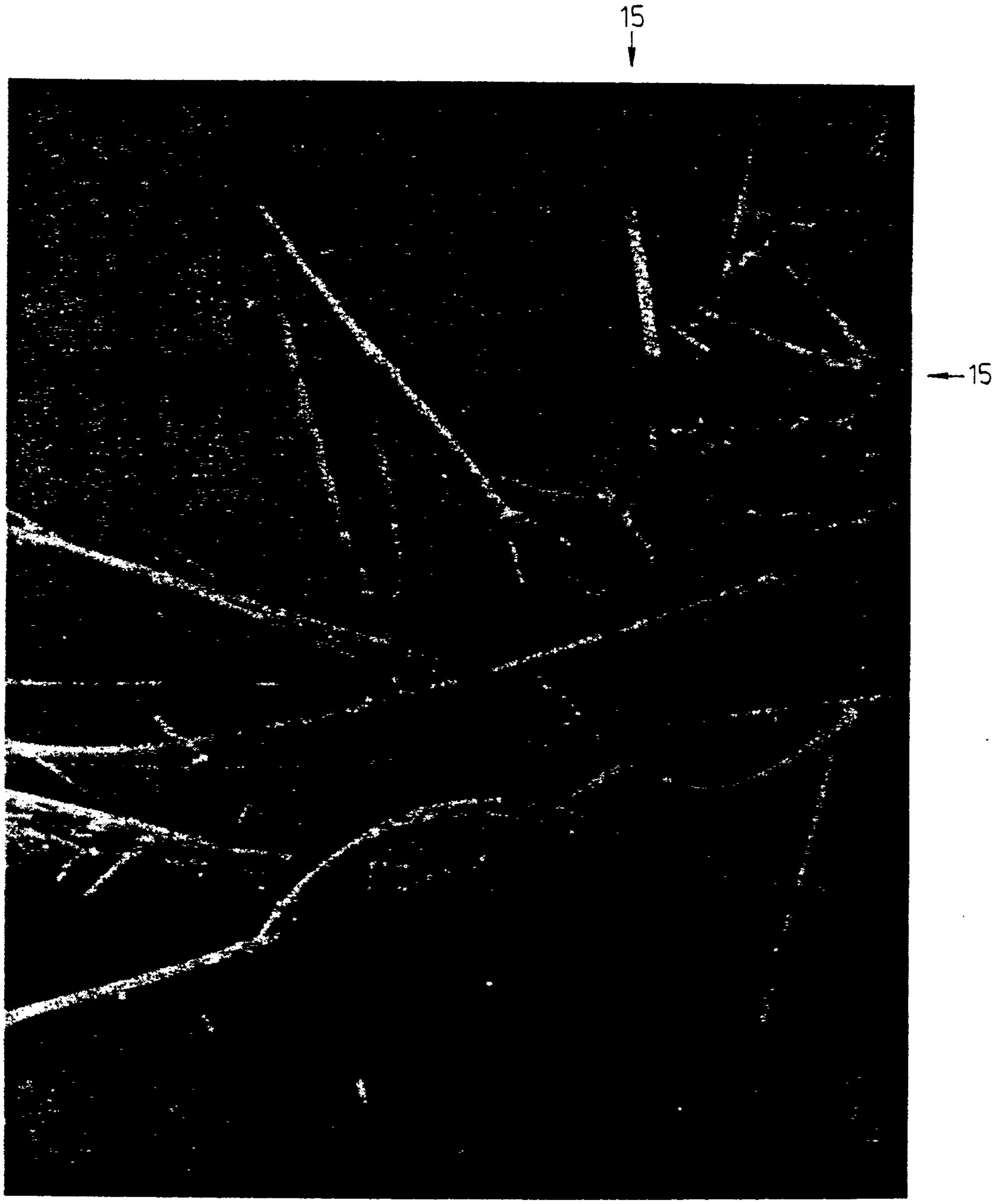

Fig. 5.

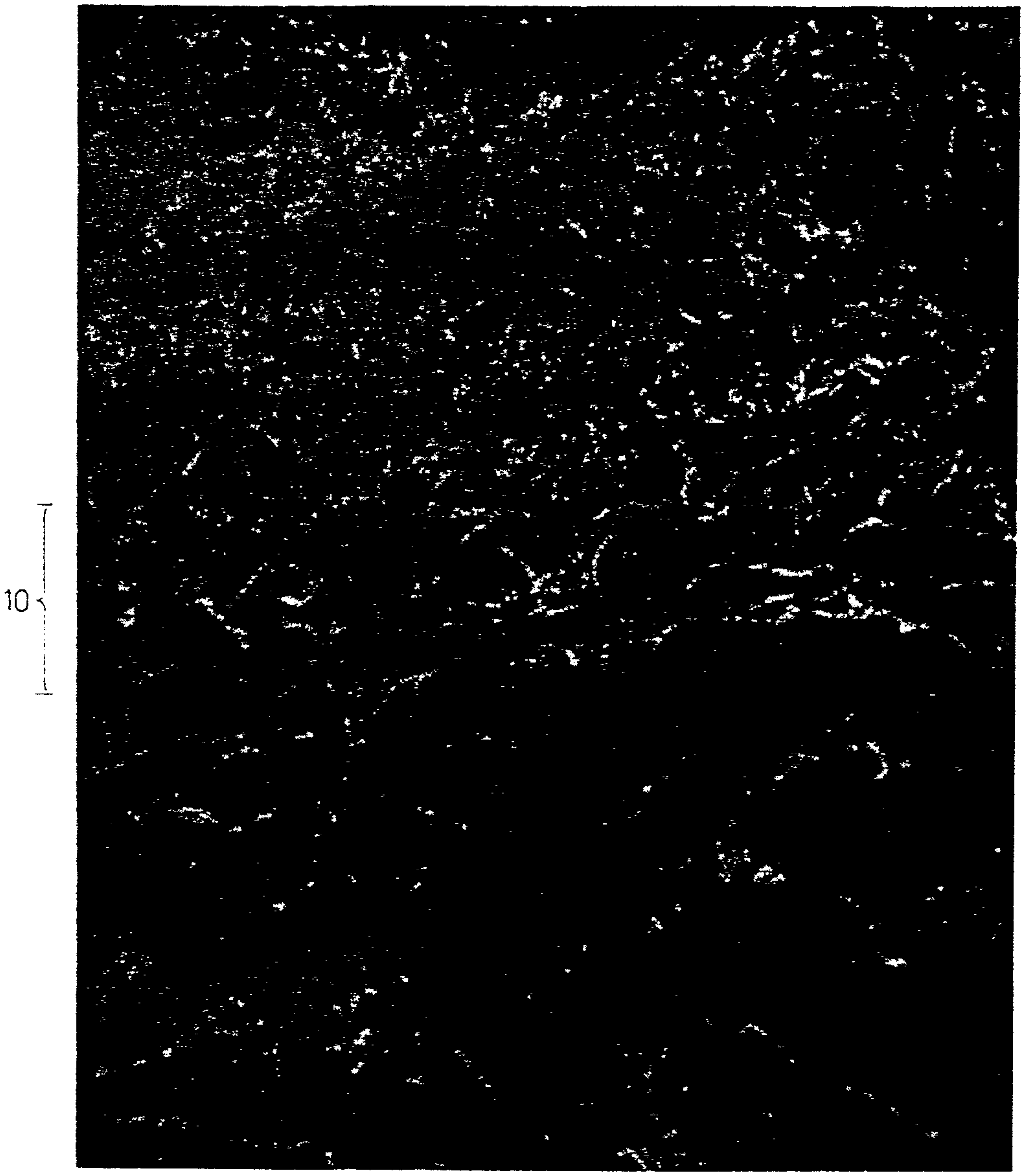

Fig.6.

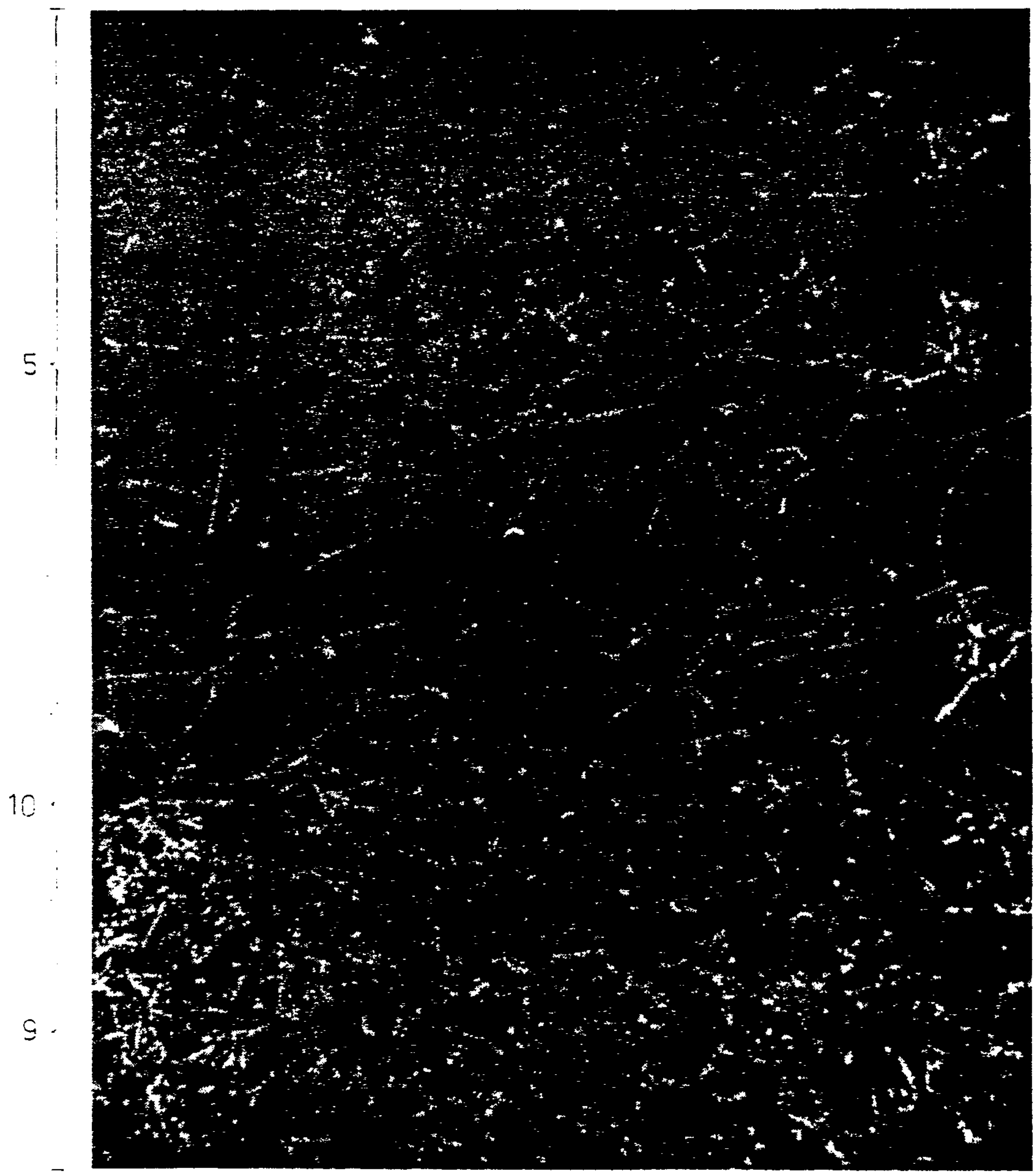

Fig.7.