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(54) Titre : METHODE DE TRAITEMENT DE DECHETS DE FIBRE DE VERRE
(54) Title: METHOD FOR PROCESSING GLASS FIBER WASTE

(57) Abrégé/Abstract:
The present invention relates to a process for comminuting glass fibers from waste glass-based fibrous materials, comprising the process steps of

a) coarsely comminuting the glass fibers to obtain coarsely comminuted glass fibers; and

b) finely comminuting said coarsely comminuted glass fibers with a granular additive having a d50 value within a range of from 0.1 to 5.0 mm as an aggregate to obtain finely comminuted glass fibers, the mixing ratio of glass fibers to additive being from 25/75 to 95/05 by weight.

Abstract

The present invention relates to a process for comminuting glass fibers from waste glass-based fibrous materials, comprising the process steps of

a) coarsely comminuting the glass fibers to obtain coarsely comminuted glass fibers; and

b) finely comminuting said coarsely comminuted glass fibers with a granular additive having a d50 value within a range of from 0.1 to 5.0 mm as an aggregate to obtain finely comminuted glass fibers, the mixing ratio of glass fibers to additive being from 25/75 to 95/05 by weight.

METHOD FOR PROCESSING GLASS FIBER WASTE

The present invention relates to a process for comminuting glass fibers from waste glass-based fibrous materials, and to the use of an additive as an aggregate in a media mill for comminuting glass fibers.

In a typical production process of glass fibers, significant amounts of waste glass-based fibrous materials are formed in all production steps performed. These waste glass-based fibrous materials mainly consist of long fibers, usually having lengths within a range of 5 to 10 m. In order to be able to recycle these waste glass-based fibrous materials to the production process and thus to improve the economic efficiency of the process, it is desirable to comminute the fibers to a target length suitable for the production process.

US 2007/0042890 describes a process in which fibers are coarsely cut at first and then ground in a ball mill.

US 6,032,883 describes a process for processing glass fibers in which glass fibers are mixed with small amounts of glass powder, broken glass or water.

In preliminary experiments for the processing of such glass fibers, it was found that direct comminution to the desired target length using suitable cutting tools has a highly wearing effect on such tools. In addition, the glass fibers are contaminated with the particles abraded from the tools thereby.

Further, grinding experiments with the fibers have shown that the fibers basically tend to clot together. This produces woolly aggregates of the glass fibers, which significantly reduce the grinding performance of a mill, so that an efficient comminution of the material to be ground or of the glass fibers is no longer possible.

Therefore, it is the object of the invention to provide a process that enables waste glass-based fibrous materials to be reused.

According to the invention, this object is achieved by a process for comminuting glass fibers from waste glass-based fibrous materials, comprising the process steps of

a) coarsely comminuting the glass fibers to obtain coarsely comminuted glass fibers; and

b) finely comminuting said coarsely comminuted glass fibers with a granular additive having a d50 value within a range of from 0.1 to 5.0 mm as an aggregate to obtain finely comminuted glass fibers, the mixing ratio of glass fibers to additive being from 25/75 to 95/05 by weight.

The process yields a mixture containing glass fibers.

In contrast to the above mentioned US 2007/0042890, an additive is used that remains in the material, whereas US 2007/0042890 A1 uses grinding balls having diameters of from 3 to 9 mm, which are returned to the grinding process. Typically, a mill as described in that document contains 50% grinding balls and 50% material to be ground. With a density of alumina of 3.96 g/cm^3 and a glass fiber density of 0.7 to 0.9 g/cm^3, mass ratios of about 20:80 (glass fibers to Al_2O_3 grinding balls) are obtained.

The above mentioned US 6,032,883 uses glass powder among others as carrier materials. The proportions of glass powder are from 1:10 to 1:40 (glass powder to glass fibers).

The glass fibers employed according to the invention can be both coated and uncoated glass fibers. For example, coated glass fibers are glass fibers having an aminosilane coating.

If the waste glass-based fibrous materials have a high residual moisture content of, for example, ≥ 6% by weight, a drying step may be performed, preferably after said coarsely comminuting of the glass fibers and before the process step of finely comminuting said coarsely comminuted glass fibers. Suitable drying devices are known to the skilled person from the prior art. Thus, for example, the coarsely comminuted glass fibers can be dried with a temperature-controlled air blower.

The waste glass-based fibrous materials, which are obtained during glass fiber production, are coarsely comminuted by means of suitable cutting devices in a first step, step a). Typically, a loose bulk of the waste glass-based fibrous materials is loaded onto the suitable cutting device in an uncontrolled way, for example, from a container with waste glass-based fibrous materials. Alternatively, the waste glass-based fibrous materials may also be unwound from a bobbin or directly drawn from the glass melt and supplied to the cutting device.

The present process is particularly suitable for so-called random fibers, i.e., balls of glass fibers without a specific orientation.

According to a preferred embodiment, the step of coarsely comminuting is performed by means of a cutting mill, a guillotine cutter, an attrition wheel, a toothed roller mill, a hammermill, a pinned disk mill or an impact mill. Such devices are known to the skilled person from the prior art. Attrition wheels are also known under the designation of friction or frictional wheels. In some cases, it is useful to perform two or more coarse comminution steps successively.

In embodiments in which two coarse comminution steps are used, it may be useful to comminute only down to fiber lengths of 10 to 100 cm in the first step, followed by one or more runs for the further coarse comminution.

Preferably, coarsely comminuted glass fibers having an average length of 5 to 50 mm, preferably 5 to 35 mm, more preferably 10 to 20 mm, are obtained in process step a). The exact length depends on the type of coarse comminution device employed. A guillotine cutter yields rather uniform lengths, while attrition

wheels or toothed roller mills yield less uniform lengths. The coarse comminution reduces clotting in the subsequent process step of finely comminuting.

Preferably, the coarsely comminuted glass fibers have a residual moisture content of < 5% by weight, preferably < 2.5% by weight, more preferably < 1.5% by weight. Thus, it was found that a mixture of coarsely comminuted glass fibers and additive in the media mill, wherein the glass fibers still have a residual moisture content of more than 5% by weight, results in clotting and thus to a reduction of the fine comminution rate. The moisture content that results in a reduction of the fine comminution rate depends on the type of device.

In a second process step, step b), the coarsely comminuted glass fibers are mixed with a suitable granular additive having a d50 value within a range of from 0.1 to 5.0 mm as an aggregate. A d50 value within a range of from 0.1 to 2.0 mm is particularly preferred. The thus obtained mixture of glass fibers/additive is then exposed to the action of a mechanical force for some time. A mixture of finely comminuted glass fibers and additive is thereby obtained, which may again be supplied to a melt.

Thus, according to the invention, the added additive remains in the finely comminuted glass fibers, which are commonly introduced in a production process. As a rule, the additive is also comminuted thereby.

Granular additives according to the invention are those which are in a solid state of matter under normal conditions and preferably consist of generally spherical particles.

Preferably, the surface of the granular additive has sharp edges, i.e., at least two legs of the granular additive intersect in an acute angle in a cross-sectional view.

According to a preferred embodiment, the additive is selected from the group of quartz sand, lime, burnt lime, dolomite, burnt dolomite, blast furnace slag, Al_2O_3, aluminum hydroxide, albite, orthoclase, anorthite, boric acid, boron oxide, alkali and alkaline earth borates, and mixtures thereof. Thus, depending on the melt for

which the glass fiber is processed according to the invention, the suitable additive can be used as an aggregate for finely comminuting the coarsely comminuted glass fibers.

Alternatively or as a complement, other ingredients known to the skilled person that are employed in glass production may also be employed as additives. Sodium carbonate, potash, feldspar or used glass, preferably so-called cullet from production, are known to the skilled person. These additives too must be granular.

The use of Al_2O_3 and used glass is less preferred. In particular, the use of used glasses can lead to undesirably high sodium contents because of the high sodium content of the usual cullet.

In a particularly preferred embodiment, additives having a d50 value within a range of from 0.1 to 2 mm or from 0.1 to 1.5 mm, preferably within a range of from 0.3 to 1.0 mm, are used. It has been found that an additive having a higher d50 value (see Example 2) is better in comminuting the coarsely comminuted glass fibers into pieces of appropriate size. It is believed that an additive having a higher d50 value will pulverize the material to be ground by the pressure exerted by the grinding media in the mill, for example.

d50 means the particle size for which 50% by weight of the particles have a particle size smaller than the d50 value, and 50% by weight have a particle size greater than the d50 value. Such values are typically derived from grading curves.

Generally, it was found that the smallest possible d50 value of the additive depends on the hardness of the additive. Experiments demonstrate that the lower the Mohs hardness of the additive, the higher the d50 value of the additive must be to optimally comminute the coarsely comminuted glass fiber. Thus, the higher the d50 value of the additive, the longer is the duration of grinding in the second process step, i.e., step b).

According to another preferred embodiment, the fine comminution is performed in a mill. The mixture of glass fiber/additive loaded into the mill is finely comminuted over a defined grinding time.

In principle, all mills known to the skilled person are suitable.

Preferably, the fine comminution is performed in a media mill. Preferably, suitable media mills include a ball mill, a tumbling mill, a drum mill, or a tube mill. Unlike the additive, the grinding media are removed after grinding.

Suitable mixing ratios of glass fibers to the additive are preferably 30/70 by weight or more, or 40/60 or more, or 45/55 by weight or more. The upper limit is 95/05 or 80/20 by weight, preferably 70/30, 60/40 or 55/45. From 30/70 to 80/20 by weight is particularly preferred.

Different mixing ratios have an effect on the duration of grinding and on the product produced by the process.

Preferably, finely comminuted glass fibers having a length of < 2 mm, preferably < 1 mm, are obtained in step b). Fine comminution to below 0.1 mm is usually not necessary.

In a particular embodiment, the mixture of finely comminuted glass fibers and additive is subjected to sifting. Suitable sifters are known to the skilled person from the prior art.

If sifting is performed, the separated oversize can be recycled to increase the yield of the fine grain.

Basically, a product flow equilibrium is established because of the recycling into the process. The supply rate, at which coarsely comminuted fibers and additives are introduced into the process, determines the dwelling times. If too much material is directed into the process, the product becomes coarser grained, and the selectivity of the sifter deteriorates. In extreme cases, obstructions may occur.

If a media mill is used, the filling level of the mill with grinding balls is another variable; the more grinding balls there are, the higher is the grinding intensity.

The separation in an air separator can be determined by the number of revolutions of the fans employed. Typically, the separation is effected by two countercurrent or orthogonally flowing air streams. The numbers of revolutions determine the separating grain size.

Alternatively, the mixture of finely comminuted glass fibers and additive can be screened through a screen having a mesh within a range of from < 2.5 to 0.5 mm, more preferably within a range of from < 2 to 1 mm, before sifting in order to remove larger fragments.

The present invention also relates to the use of an additive selected from the group of quartz sand, lime, burnt lime, dolomite, burnt dolomite, blast furnace slag, Al_2O_3, aluminum hydroxide, albite, orthoclase, anorthite, boric acid, boron oxide, alkali and alkaline earth borates, and mixtures thereof as an aggregate at a ratio of 25/75 to 95/05 (glass fibers to additive) for comminuting glass fibers.

The present invention further relates to the glass fibers obtainable by the process according to the invention, and to a mixture containing glass fibers, containing:

- finely comminuted glass fibers having a length of < 2 mm;

- an additive having a d50 value within a range of from 5.0 µm to 5.0 mm, the mixing ratio of glass fibers to additive being from 25/75 to 95/05 by weight.

Since the additive may also be comminuted in the fine comminution step, the additive has a smaller grain size in the product as compared to the starting materials of the process.

Figure 1 shows glass fiber balls as obtained as a waste material.

Figure 2 shows a photograph of fibers having been subjected to a first coarse comminution step. These have lengths within a range of about from 20 to 100 cm.

Figure 3 shows fibers having been subjected to a second coarse comminution step. The fiber length is about from 0.5 to 10 cm.

Figure 4 shows a micrograph taken after fine comminution. In addition to the glass fibers, the ground additive is also a component of the material.

Example 1

Coarse comminution:

Waste glass-based fibrous materials having a length within a range of from 5 to 10 m was coarsely comminuted by means of a high performance guillotine cutting machine to a length of from 10 to 20 mm. The Fe_2O_3 content remained unchanged.

Fine comminution:

The coarsely comminuted glass fibers were finely comminuted in a 20 kg batch ball mill with quartz sand (Provodin foundry sand).

Experiment	Glass fiber content [%]	Grinding time [min]	Loading amount [kg]	Fiber length [mm]
1	50	45	20	0.3
2	50	20	12	0.3
3	60	10	12	< 1.5
4	70	10	12	< 2

Sifting:

The finely comminuted glass fibers and the additive were sifted with a separator. An air flow rate of 165 l/min and a rotation of the classifying wheel of 2000 rpm

were set. The mass ratio of undersize to oversize in the first separator run was 1:7.5. The fiber length obtained in the undersize was < 1 mm.

Example 2

Two grinding attempts with a 20 kg batch ball mill were performed, the present grinding attempt being set forth with china clay as a comparative example.

	Lime	China clay
Proportion of additive [%]	50	50
Proportion of glass fiber [%]	50	50
Additive - d50	1.8 mm	2.4 µm
Grain size	1.4 to 2.5 mm	35% < 2 µm
Loading of mill [kg]	12	12
Grinding time [min]	10	10

When china clay was added as an additive to the glass fiber grinding batch, the comminution of the glass fibers was completely suppressed. A mixing of the two components could not be achieved. The glass fibers assembled to clots over the grinding time, which were externally dusted with china clay dust, but internally contained exclusively glass fibers.

With granular lime, a grinding success was obtained over the grinding time. In this case, no fiber balls could be identified in the ground material. The fiber length was < 2 mm; the mixture obtained was highly suitable as a starting material for glass production.

Example 3

A continuous grinding attempt was made with a ball mill having a throughput of 100 kg/h.

The glass fiber and additive (quartz sand according to Example 1) were employed at a ratio of 50/50. The grain size of the additive was 0.18 to 1.4 mm, and the d50 value was 0.55 mm; the grinding ball filling level was 40% of the mill volume. The subsequent sifting was effected with a rotor at 900 rpm and a fan at 800 rpm. The oversize was recycled.

The continuously removed grain had a fiber length of < 500 µm, and the product had a d50 value of 14.5 µm. The following oversize proportions were obtained:

Screen size [µm]	Oversize proportion [%]
160	0.25
125	0.8
100	2.0
63	9.2
40	20

CLAIMS:

1. A process for comminuting glass fibers from waste glass-based fibrous materials, comprising the process steps of

   a) coarsely comminuting the glass fibers to obtain coarsely comminuted glass fibers; and

   b) finely comminuting said coarsely comminuted glass fibers with a granular additive having a d50 value within a range of from 0.1 to 5.0 mm as an aggregate to obtain finely comminuted glass fibers, the mixing ratio of glass fibers to additive being from 25/75 to 95/05 by weight;

   wherein said additive is selected from the group of quartz sand, lime, burnt lime, dolomite, burnt dolomite, blast furnace slag, Al_2O_3, aluminum hydroxide, albite, orthoclase, anorthite, boric acid, boron oxide, alkali and alkaline earth borates, and mixtures thereof.

2. The process according to claim 1, wherein said coarsely grinding includes 1, 2, 3 or more steps.

3. The process according to claim 1 or 2, wherein said coarsely grinding is performed by means of a cutting mill, a guillotine cutter, an attrition wheel, a toothed roller mill, a hammermill, a pinned disk mill, an impact mill, or a combination of the above.

4. The process according to any one of claims 1 to 3, wherein said finely grinding is performed in a mill, wherein the grinding media are subsequently separated out.

5. The process according to claim 4, wherein said mill is a media mill.

6. The process according to claim 5, wherein said media mill is a ball mill.

7. The process according to claim 5, wherein said media mill is a tumbling mill.

8. The process according to claim 5, wherein said media mill is a drum mill.

9. The process according to claim 5, wherein said media mill is a tube mill.

10. The process according to any one of claims 1 to 9, wherein coarsely comminuted glass fibers having a length of 5 to 50 mm are obtained in process step a).

11. The process according to any one of claims 1 to 9, wherein coarsely comminuted glass fibers having a length of 10 to 20 mm are obtained in process step a).

12. The process according to any one of claims 1 to 11, wherein said coarsely comminuted glass fibers have a residual moisture content of < 5% by weight.

13. The process according to any one of claims 1 to 11, wherein said coarsely comminuted glass fibers have a residual moisture content of < 2.5% by weight.

14. The process according to any one of claims 1 to 13, wherein finely comminuted glass fibers having a length of < 2 mm are obtained in step b).

15. The process according to any one of claims 1 to 13, wherein finely comminuted glass fibers having a length of < 1 mm are obtained in step b).

16. The process according to any one of claims 1 to 15, wherein the mixture of finely comminuted glass fibers and additive is subjected to sifting.

17. The process according to any one of claims 1 to 16, wherein the mixing ratio of glass fibers to the additive is 30/70 to 80/20 by weight.

18. The process according to any one of claims 1 to 16, wherein the mixing ratio of glass fibers to the additive is 40/60 to 70/30 by weight.

19. The process according to any one of claims 1 to 16, wherein the mixing ratio of glass fibers to the additive is 40/60 to 60/40 by weight.

20. The process according to any one of claims 1 to 16, wherein the mixing ratio of glass fibers to the additive is 45/55 to 55/45 by weight.

21. The process according to any one of claims 1 to 20, wherein additives having a d50 value within a range of from 0.1 to 1.5 mm are used.

22. The process according to any one of claims 1 to 20, wherein additives having a d50 value within a range of from 0.3 to 1.0 mm are used.

23. Use of an additive selected from the group of quartz sand, lime, burnt lime, dolomite, burnt dolomite, blast furnace slag, Al2O3, aluminum hydroxide, albite, orthoclase, anorthite, boric acid, boron oxide, alkali and alkaline earth borates, and mixtures thereof as an aggregate at a ratio of glass fibers to additive of 25/75 to 95/05 by weight, for comminuting glass fibers.

24. Use of an additive according to claim 23 at a ratio of glass fibers to additive of 30/70 to 80/20 by weight.

25. A mixture containing glass fibers, obtainable by a process according to any one of claims 1 to 22.

26. A mixture containing glass fibers, containing:

- finely comminuted glass fibers having a length of < 2 mm;
- an additive having a d50 value within a range of from 5.0 µm to 5.0 mm, the mixing ratio of glass fibers to additive being from 25/75 to 95/05 by weight, or from 30/70 to 80/20 by weight;

wherein said additive is selected from the group of quartz sand, lime, burnt lime, dolomite, burnt dolomite, blast furnace slag, Al_2O_3, aluminum hydroxide, albite, orthoclase, anorthite, boric acid, boron oxide, alkali and alkaline earth borates, and mixtures thereof.

27. The mixture containing glass fibers according to claim 26, wherein said additive has a d50 value of from 5.0 µm to 2 mm.

Fig.1

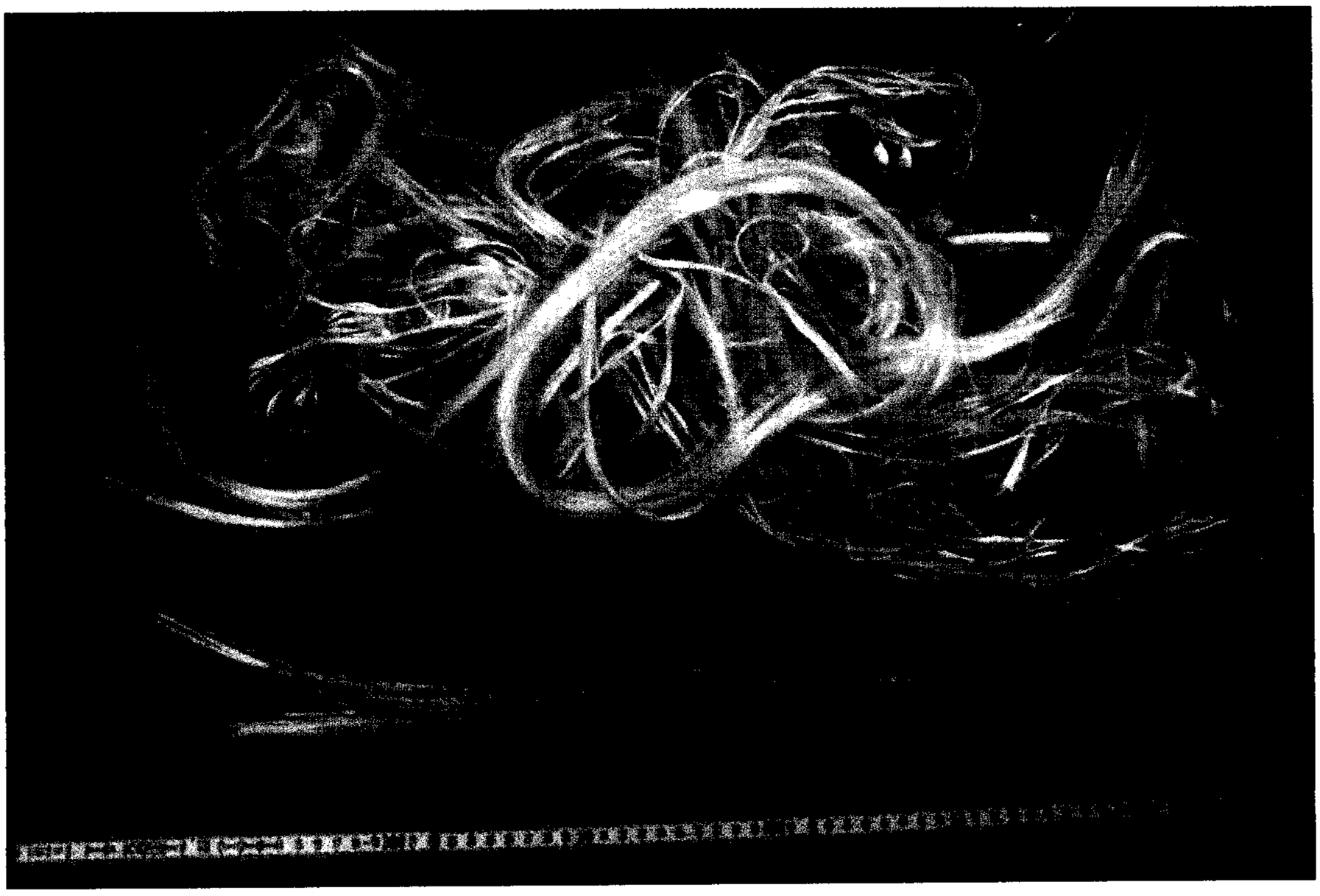

Fig.2

Fig.3

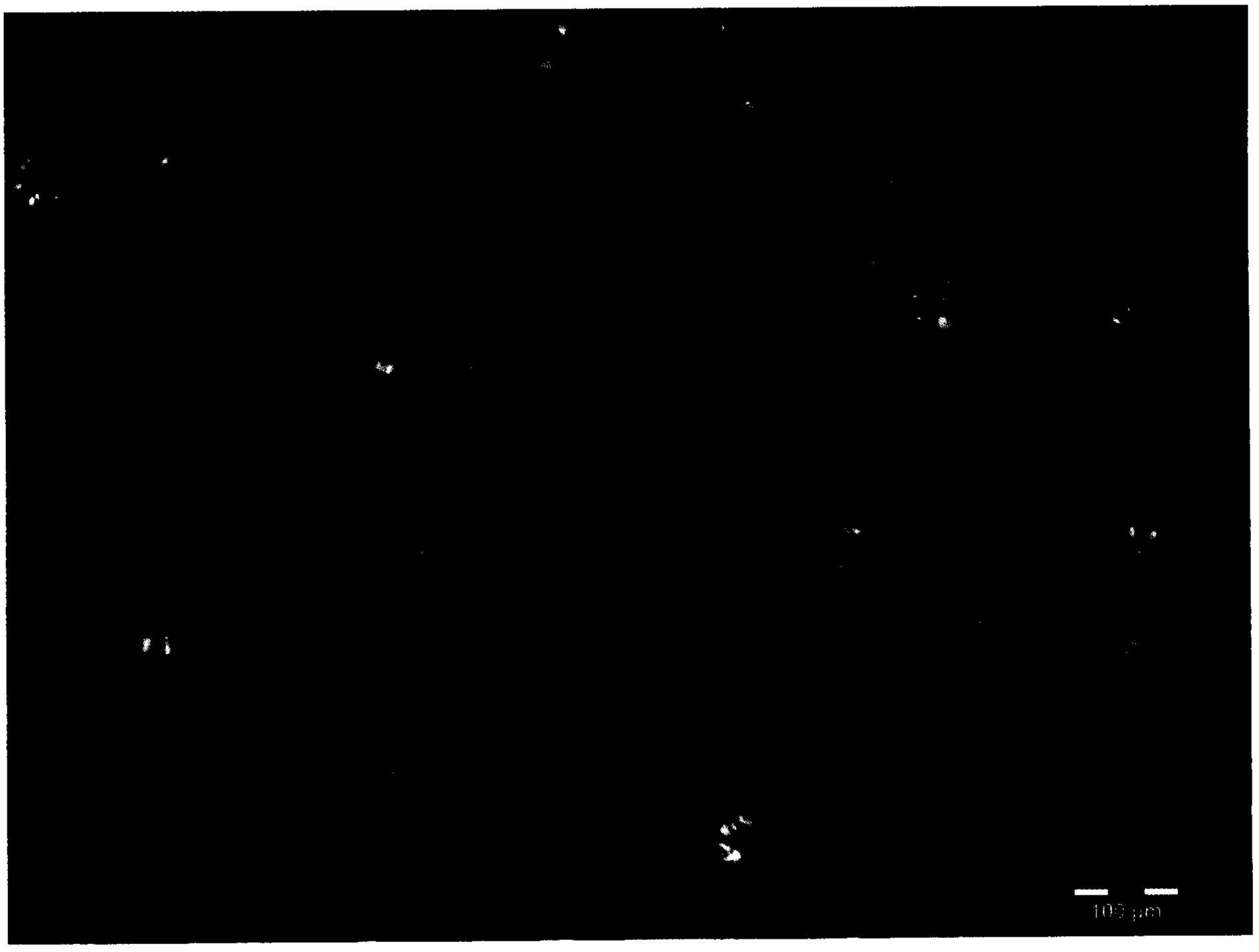

Fig.4