Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2569772 A1 2006/01/19

(21) 2 569 772

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2005/07/07
(87) Date publication PCT/PCT Publication Date: 2006/01/19
(85) Entrée phase nationale/National Entry: 2006/12/06
(86) N° demande PCT/PCT Application No.: IB 2005/001972
(87) N° publication PCT/PCT Publication No.: 2006/006064
(30) Priorité/Priority: 2004/07/08 (CH01143/04)

(51) Cl.Int./Int.Cl. *C08G 63/91* (2006.01),
C08G 63/695 (2006.01)

(71) Demandeur/Applicant:
OFER, ZEEV, IL

(72) Inventeur/Inventor:
OFER, ZEEV, IL

(74) Agent: ROBIC

(54) Titre : POLYETHYLENE TEREPHTALATE CRISTALLISE CONTENANT DU SILICONE ET PROCEDE DE PREPARATION

(54) Title: CRYSTALLIZED POLYETHYLENE TEREPHTHALATE, WHICH CONTAINS SILICONE, AND PROCESS FOR ITS PREPARATION

(57) Abrégé/Abstract:
The present invention is directed to crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form. The crystallized form preferably has been ob-' tained by a temperature treatment of amorphous PET, which contains silicon in a bounded and integrated into the molecular structure of PET form. There is also described a process for the preparation of crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 January 2006 (19.01.2006)

PCT

(10) International Publication Number
WO 2006/006064 A1

(51) International Patent Classification[7]: C08G 63/91, 63/695

(21) International Application Number: PCT/IB2005/001972

(22) International Filing Date: 7 July 2005 (07.07.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01143/04 8 July 2004 (08.07.2004) CH

(71) Applicant and
(72) Inventor: **OFER, Zeev** [IL/IL]; Hatsmaut Str. 20/B/5, Bat Jam, 59378 (IL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/006064 A1

(54) Title: CRYSTALLIZED POLYETHYLENE TEREPHTHALATE, WHICH CONTAINS SILICONE, AND PROCESS FOR ITS PREPARATION

(57) Abstract: The present invention is directed to crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form. The crystallized form preferably has been ob-' tained by a temperature treatment of amorphous PET, which contains silicon in a bounded and integrated into the molecular structure of PET form. There is also described a process for the preparation of crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form.

Crystallized polyethylene terephthalate, which contains silicon, and process for its preparation

The present invention is directed to crystallized polyethylene terephthalate, PET, which contains silicon, and to a process for its preparation.

It is well known that some polymeric materials, for example PET, may only be used once in their original form.

There is not yet known an ecological save and economical effective process with which waste-PET, post consumer PET waste, may be regenerated and/or modified for a further use in the food industry (food contact substance).

It is a fact that all over the world a lot of waste-PET (post consumer PET waste) is collected and is just disposed. Therewith is created an environmental problem.

It is further known that waste-PET may not be burned in an environmental friendly way, because among others carcinogenic benzopyrenes are formed.

It has been proposed to incorporate waste-PET into new, fresh PET, so-called "virgin"-PET. Thereby in maximum 5 parts by weight of waste-PET may be incorporated into 95 parts by weight of "virgin"-PET, in order to not affect the quality of the respective product.

In this technology a very high vacuum must be applied in order to remove the volatile, toxic contami-

nations; see the VACUREMA technology of the company Erema in A-4052 Ansfelden/Linz in Austria.

It has also been proposed to cleave waste-PET into the components terephthalic acid and ethylene glycol. These components may be used again for the synthesis of PET. This process needs technical complicate devices and is correspondingly expensive.

In WO 03/104314 A1 is described a process for processing of polyester wastes, for example waste-PET. In this process neither a vacuum technology nor a cleavage into partial components is used.

In this process crushed, washed and dried waste-polyester flakes are heated to a temperature of 130°C ± 5°C. At this temperature is added a defined modifying agent in an amount from 4 % by weight to 6 % by weight, referred to the total mass.

Then the obtained mixture is stirred during about 60 minutes at this temperature.

Then this mixture is given into an extruder, heated to a temperature from 240°C to 250°C, and is extruded. The extrudate is pelletized.

The obtained pellets are amorphous. These amorphous pellets may not be further processed by means of standard injection moulding technology, because they stick together during the preheating.

In WO 95/01471 is described a process for producing soil-repellant and abrasion-resistant monofilaments for screen cloth having a diameter from 0.1 to

1.0 mm from a linear silicon modified polyethylene terephthalate. In this process are incorporated from 0.15 to 5.0 % by weight of polydialkylsiloxane by co-condensation into the chain of the polymer.

According to the example of WO 95/01471 the silicon containing polymer is prepared by polycondensation of the monomers dimethyl terephthalate and ethylene glycol with addition of 3.9 % by weight of polydimethyl siloxane and manganese acetate by using an antimony catalyst as an essential component of said polycondensation process.

The process of co-condensation takes place in an autoclave at elevated temperatures and by using different pressures.

In US 5 643 998 is described a recyclable polymer which comprises a plurality of oligomer units. This polymer is obtained by a polymerization process.

It is an object of the present invention to reduce the year-to-year increasing amount of waste-PET in that waste-PET is transformed into a convertible and demanded product.

It is a further object of the present invention to provide a simple and cost advantageous process for the preparation of this new product.

This new product shall be used as substitution in all industrial preparation processes where up to now "virgin"-PET is used.

With the present invention these objects are met.

The present invention is directed to crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form.

The inventive process for the preparation of crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, is characterized in that

- in a first step is added to melted PET not more than 4 % by weight, referred to the total of the mass, of at least one modifying agent, which contains silicon and which is able to connect together low molecular fragments of PET, is then mixed and allowed to react,

- in a second step the obtained product is extruded in the respective desired form, the extruded amorphous product, which contains silicon in a bounded and integrated into the molecular structure of PET form, is cooled for maintaining the amorphous form,

- in a third step the amorphous product is subjected for a controlled transformation into the crystallized form to a temperature treatment, and

- in a fourth step the formed crystallized product is obtained.

The inventive crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, may be used as a substitute of polyethylene terephthalate, which contains no silicon, for example as

- row material for the preparation of a preform,

- row material for the preparation of fibers, wires, sheets.

Preferred embodiments of this invention are defined in the dependent claims.

In the following part are described possible embodiments of the present invention.

Thereby also reference is made to the figures.

Figure 1 shows the microscopic analysis of amorphous PET; obtained according to the example 1 as mentioned further below.

Figure 2 shows the microscopic analysis of crystallized PET; obtained according to the example 1 as mentioned further below.

From the inventive crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, may be prepared by means of known injection moulding technology any preform. When before the injection a suitable colorant is added to the melt, then a correspondingly coloured preform is obtained.

From such a preform may be prepared by means of known blowing technology any commodity: for example closable containers of any shape. Such containers may be used for the uptake of food, for example mineral water,

soft drinks, vinegar, oil, or of cosmetic articles, for example creams, shampoos, gels.

It is preferred to prepare from a preform by means of the blowing technology bottles for the uptake of mineral water or of soft drinks with or without carbon dioxide (CO_2).

These commodities may be recycled after their use.

Without a further treatment the amorphous pellets as obtained at the end of the second step of the inventive process may not be further processed by means of standard injection moulding technology, because they stick together during the preheating.

The following examples illustrated the present invention.

Example 1

300 kg of crushed, washed and dried flakes from waste-PET bottles were given into the hopper of a twin screw extruder.

The flakes had a size from 2 mm to 10 mm.

The velocity of the extruder was adjusted such that 5 kg of PET flakes could be processed in one minute.

In the 12 zones of the extruder the temperature was from 230°C to 280°C.

The temperature within the melting zone was 260°C.

At the melting zone of the extruder was installed a dosing device.

The dosing device comprised a rotation pump by which the velocity of the addition of the modifying agent was adjusted. With the dosing device were dropped onto the PET-melt 50 ml of hexamethyldisilazane per minute.

For the processing of 300 kg of flakes were used 3 l of hexamethyldisilazane.

In the following zones of the extruder the reaction took place between the melted PET and the modifying agent.

The gaseous side products were drawn off in the degassing zone by means of a pump.

At the outlet opening of the extruder was installed an underwater pelletizing system (Master 1000) of BKG Bruckmann & Kreyenborg Granuliertechnik GmbH in D-48157 Münster / Germany.

The diameter of the obtained amorphous, transparent and clear pellets was from about 1 mm to about 3 mm.

These amorphous pellets may not be further processed by means of standard injection moulding technology, because they stick together during the preheating.

On a vibration transporting table of BKG Bruckmann & Kreyenborg Granuliertechnik GmbH were converted the amorphous pellets into crystallized pellets.

The crystallized pellets were mat and white.

From the amorphous pellets was made a microscopic analysis which is shown in figure 1.

From the crystallized pellets was also made a microscopic analysis which is shown in figure 2.

It is obvious from figure 1 that the molecules of PET are free and that the material is transparent and clear.

It is obvious from figure 2 that the structure of the molecules of PET is fixed and that the material is mat and white.

Both the amorphous and the crystallized pellets had a silicon content of 222 µg/g of pellets.

From the crystallized pellets may be prepared by means of known injection moulding technology any preform.

Example 2

In analogy to example 1 were used 3 l of tetraethoxysilane instead of hexamethyldisilazane.

There were obtained analogous results.

Example 3

In analogy to example 1 were used 3 l of polyethylhydrosiloxane instead of hexamethyldisilazane.

There were obtained analogous results, but the colour of the amorphous and of the crystallized pellets was grey.

Example 4

In analogy to example 1 were used 1.5 kg of diphenylsilandiol instead of hexamethyldisilazane and were added in finely powdered form by means of a feeding screw. There were added 25 g per minute.

There were obtained analogous results as described in the examples 1 and 2.

Patent Claims

1. Crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form.

2. Crystallized polyethylene terephthalate according to claim 1, characterized in that the crystallized form has been obtained by a temperature treatment of amorphous PET, which contains silicon in a bounded and integrated into the molecular structure of PET form.

3. Crystallized polyethylene terephthalate according to one of claims 1 to 2, characterized in that it has an average molecular weight of not less than about 40'000.

4. Crystallized polyethylene terephthalate according to one of claims 1 to 3, characterized in that it has a silicon content from 120 µg to 700 µg per gram of the total of the mass.

5. Crystallized polyethylene terephthalate according to one of claims 1 to 4, characterized in that the crystallized polyethylene terephthalate is mixed in any mixing ratio with any polymeric material, for example with polypropylene, PP, polycarbonate, PC, or polyethylene terephthalate, which contains no silicon.

6. A process for the preparation of crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, characterized in that

- in a first step is added to melted PET not more than 4 % by weight, referred to the total of the mass, of at least one modifying agent, which contains silicon and which is able to connect together low molecular fragments of PET, is then mixed and allowed to react,

- in a second step the obtained product is extruded in the respective desired form, the extruded amorphous product, which contains silicon in a bounded and integrated into the molecular structure of PET form, is cooled for maintaining the amorphous form,

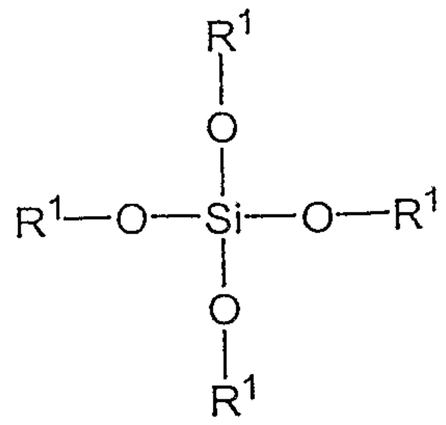
- in a third step the amorphous product is subjected for a controlled transformation into the crystallized form to a temperature treatment, and

- in a fourth step the formed crystallized product is obtained.

7. The process according to claim 6, characterized in that in the first step the modifying agent, which contains silicon and which is able to connect together low molecular fragments of PET, is added in an amount of not more than 3 % by weight, preferably in an amount of not more than 2 % by weight, for example in an amount of not more than 1 % by weight and not less than 0.5 % by weight.

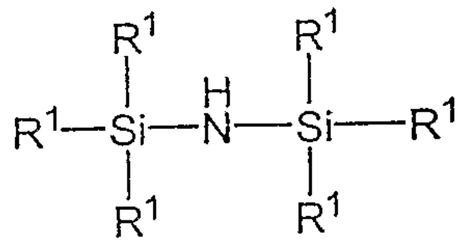
8. The process according to one of claims 6 to 7, characterized in that in the first step the modifying agent, which contains silicon and which is able to connect together low molecular fragments of PET, is added in the form of a powder or of a liquid, and that it is especially selected from the group consisting of

- silanes of the general formula I



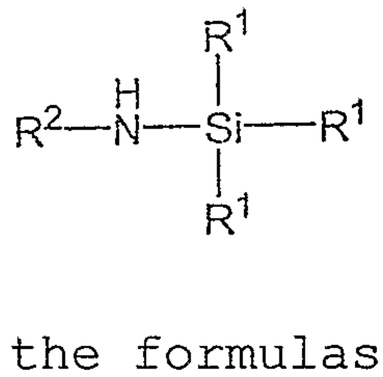
(I)

- disilazanes of the general formula II



(II)

- silazanes of the general formula III



(III)

wherein in the formulas I to III the residues R^1 und R^2 are, independent from each other, a C_1 to C_6 containing straight or branched alkyl group,

- silicone oils, especially oils on the basis of polyphenyl-methylsiloxane, polydimethylsiloxane, or a 1:1 mixture of polydimethylsiloxane and polydiphenylsiloxane,

- diphenylsilandiol,

- polymethylhydrosiloxane, and

- polyethylhydrosiloxane.

9. The process according to one of claims 6 to 8, characterized in that in the first step the melted PET is "virgin"-PET or waste-PET, post consumer PET waste, for example obtained from crushed, washed and dried PET bottles, including any mixtures of "virgin"-PET and post consumer PET waste, and has a temperature from about 260°C to about 300°C, especially about 260°C.

10. The process according to one of claims 6 to 9, characterized in that in the first step the modifying agent is added continuously into the melting zone of a twin screw extruder.

11. The process according to one of claims 6 to 10, characterized in that in the first step the reaction time between the melted PET and the modifying agent, in dependency of the temperature of the melted PET and in dependency of the length of the melting zone, is from about 3 to about 10 minutes.

12. The process according to one of claims 6 to 11, characterized in that in the second step the cooling of the extruded product is realized in water, especially either by an underwater pelletizing or by cooling of a continuous string in a water bath, followed by a pelletizing.

13. The process according to one of claims 6 to 12, characterized in that in the second step the extruded string has any cross section, for example a round, an angular, for example a 3- to 8-angular, or an elliptic cross section.

14. The process according to one of claims 6 to 13, characterized in that in the third step the tem-

perature treatment for the transformation of the amorphous product into a crystallized product is realized at a temperature from about 135°C to about 165°C during at least about 30 minutes, especially during about 1 hour to about 2 hours.

15. The process according to one of claims 6 to 14, characterized in that the crystallized polyethylene terephthalate has an average molecular weight of not less than about 40'000.

16. The process according to one of claims 6 to 13, characterized in that the process is stopped after the second step and that the amorphous polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, is obtained.

17. Crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, obtainable in that

- in a first step is added to melted PET not more than 4 % by weight, referred to the total of the mass, of at least one modifying agent, which contains silicon and which is able to connect together low molecular fragments of PET, is then mixed and allowed to react,

- in a second step the obtained product is extruded in the respective desired form, the extruded amorphous product, which contains silicon in a bounded and integrated into the molecular structure of PET form, is cooled for maintaining the amorphous form,

- in a third step the amorphous product is subjected for a controlled transformation into the crystallized form to a temperature treatment, and

- in a fourth step the formed crystallized product is obtained.

18. Crystallized polyethylene terephthalate according to claim 17, obtainable in that the process according to one of claims 7 to 15 is carried out.

19. Use of crystallized polyethylene terephthalate, PET, which contains silicon in a bounded and integrated into the molecular structure of PET form, as a substitute of polyethylene terephthalate, which contains no silicon, for example as

- row material for the preparation of a preform,

- row material for the preparation of fibers, wires, sheets.

20. Use according to claim 19, characterized in that the crystallized polyethylene terephthalate is a product according to one of claims 1 to 5, preferably prepared according to the process according to one of claims 6 to 15.

21. Use according to one of claims 19 to 20, characterized in that the crystallized polyethylene terephthalate is mixed in any mixing ratio with any polymeric material, for example with polypropylene, PP, polycarbonate, PC, or polyethylene terephthalate, which contains no silicon.

22. Use according to one of claims 19 to 21, characterized in that the crystallized polyethylene terephthalate is mixed in any mixing ratio with any material, which is suitable for the preparation of a preform, for example with polyethylene terephthalate, which contains no silicon.

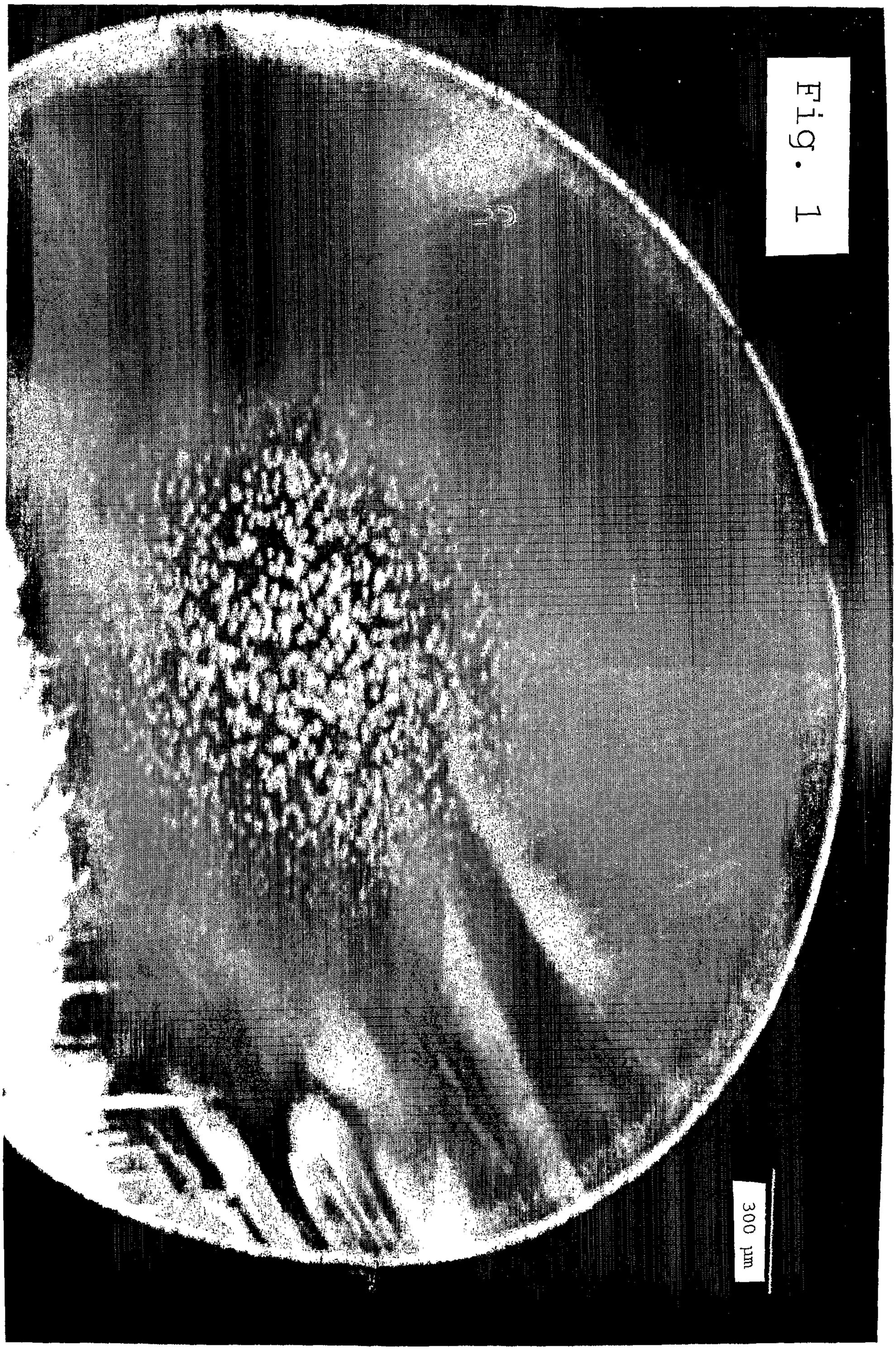


Fig. 1

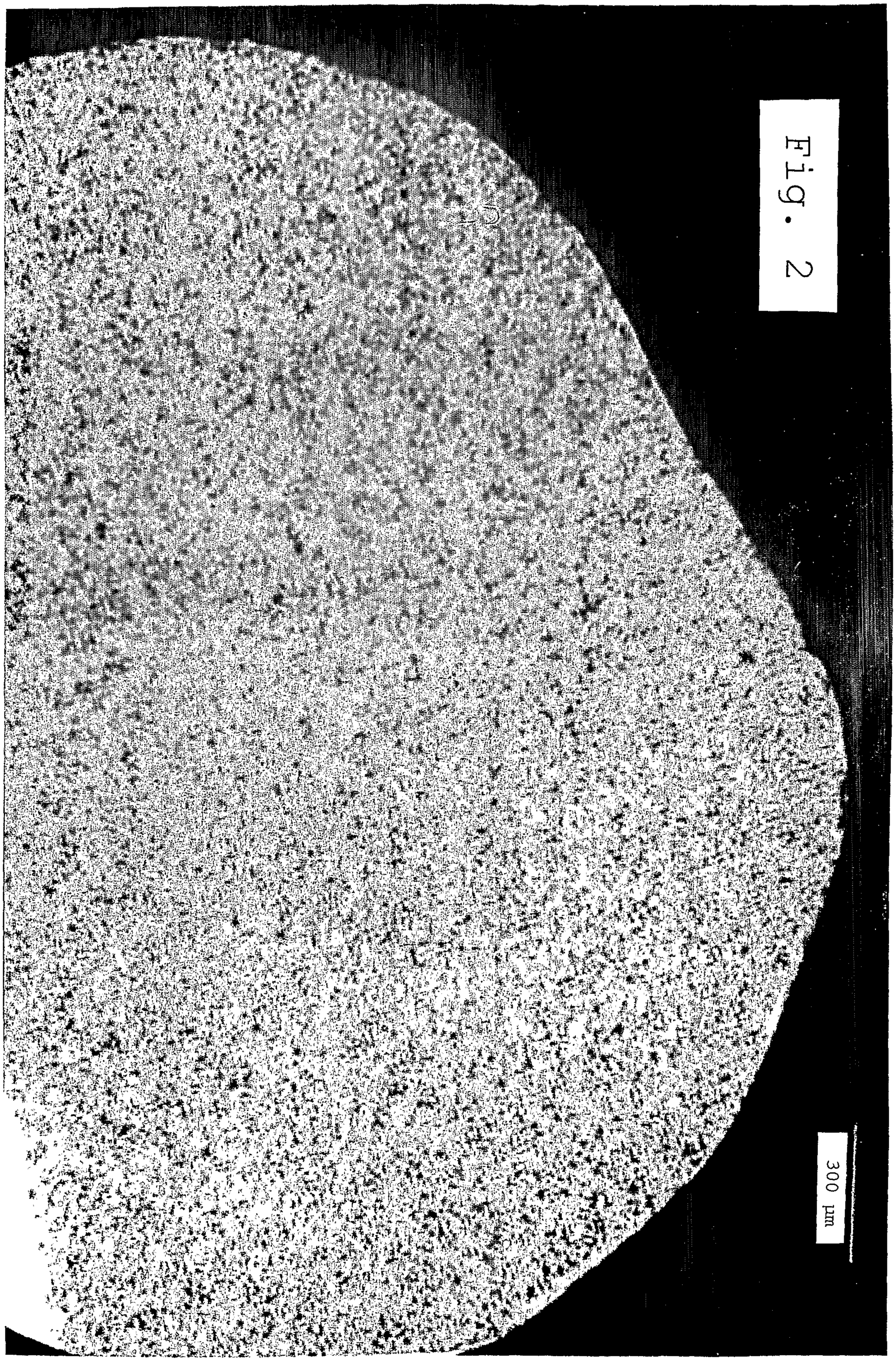


Fig. 2