(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 372 622 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89203017.2**

(22) Date of filing: **28.11.89**

(51) Int. Cl.5: **D01F 6/18, D01D 5/06, D01F 6/38**

(30) Priority: **02.12.88 IT 2283688**

(43) Date of publication of application: **13.06.90 Bulletin 90/24**

(84) Designated Contracting States: **AT BE CH DE ES FR GB GR LI LU NL SE**

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(54) Acrylic precursor for carbon fibres and method for its preparation.

(57) A method for preparing acrylic precursors with improved characteristics suitable for transformation into carbon fibres of superior mechanical characteristics comprises wet-spinning an acrylic polymer dissolved in dimethylacetamide followed by coagulation in a solvent-non solvent binary mixture bath of rigorously controlled composition and temperature, and a series of controlled-condition stretching operations with interposed washing stages, followed by yarn drying before its final collection.

The method is characterised essentially by its coagulation stage, which is conducted under such rigorously controlled bath temperature and composition conditions as to obtain at the end of the process an acrylic yarn which has a perfectly compact structure practically free of flaws (voids), a perfectly circular cross-section and mechanical characteristics which are distinctly better than those of acrylic yarns of identical composition obtained by spinning processes of the known art.

The specific destination of the acrylic yarn is the production of high-performance carbon fibres.

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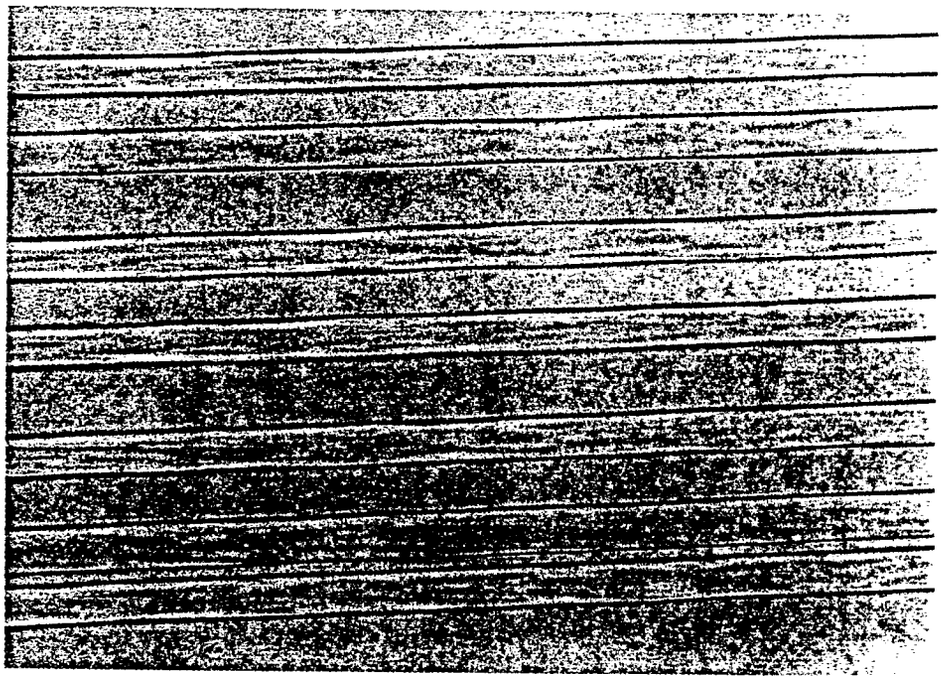
Fig.1



ACRYLIC PRECURSOR FOR CARBON FIBRES AND A METHOD FOR ITS PREPARATION

This invention relates to a wet spinning process for acrylonitrile copolymers in a polar solvent solution, in particular dimethylacetamide, for producing an acrylic yarn of high mechanical characteristics suitable for conversion into carbon fibres (C. F.)

The production of acrylic yarns suitable for conversion into carbon fibres is known and widely described in the patent and scientific literature. Such yarns are generally known as "acrylic precursors for carbon fibres" because of their specific use. The methods mostly used for producing acrylic precursors are mainly the wet spinning of solutions of suitable acrylic polymers in organic or inorganic solvents. The organic solvents mostly used include polar compounds of high solvent power towards acrylic polymers, such as dimethylformamide, dimethylacetamide, dimethyl sulphoxide, ethylene carbonate etc.

Widely used inorganic solvents include aqueous sodium thiocyanate solutions, aqueous zinc chloride solutions and concentrated aqueous nitric acid solutions.

In all cases of the known art, these solutions are spun by passage through multi-orifice spinnerets with a orifice diameter of between 50 and 200 microns, the filaments then being coagulated by passage through a bath of suitable non-solvent liquid. The acrylic precursor production process is completed by stretching the yarns generally at high temperature (80-120 ° C) by their passage about rollers rotating at constant speed, after which they are washed, dried and finally collected. Known acrylic precursor production processes which have proved particularly interesting are those described in US patents 3,993,719 and 4,154,807, which use the wet-dry spinning method. This consists of maintaining the spinneret not in immediate contact with the coagulating bath, so that the dope leaving the spinneret has to pass a few millimetres through the air before being immersed in the bath. This process enables a high spinneret stretch to be obtained.

The patent literature also describes methods for increasing the orientation of the yarn and thus the mechanical characteristics of the acrylic precursor obtained.

These methods are based on further considerable stretch applied to the fibre after the consolidation and drying stage, and thus following the coagulation and initial stretching stages.

The polymers most widely used for forming the solutions used in those spinning processes of the known art for the preparation of carbon fibre acrylic precursors are those which contain one or more monomer units of the following list: methyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, itaconic acid etc., copolymerized with the acrylonitrile.

With the spinning processes of the known art and using acrylic copolymer solutions of the aforesaid type, acrylic precursors are generally obtained having a maximum tenacity of 50-55 cN/tex and generally containing defects, this having a certain importance with regard to the characteristics of the carbon fibres deriving from them.

The defects depend on the type of spinning process used.

In spinning processes in inorganic solvents, metal residues (such as sodium and zinc) always remain on the fibre, and are deleterious when the acrylic fibre is used in the production of carbon fibre, this as stated being the specific product obtainable from this type of fibre. In this respect, the metal residues contained in the acrylic precursor prejudice the proper progress of the acrylic fibre carbonization stage and lessen the oxidation resistance of the carbon fibre obtained thereby.

In addition the solvent recovery process is very complicated and costly. An inorganic solvent also leads to frequent corrosion problems for the spinning plant.

The maximum tenacity attainable in fibres produced by spinning processes in inorganic solvents is 50-55 cN/tex even when air stretching at the exit from the spinneret is used as described in the aforesaid USA patents plus extra stretching after the fibre consolidation as stated.

The technique of stretching at the spinneret exit is not easily applicable to the production of tows containing a large number of filaments (obtainable by suitable spinnerets) because of the danger of the individual filaments adhering together, in that on leaving the spinneret orifices they are still in a non-consolidated gelled solution stage.

The spinning processes for acrylic polymer solutions in organic solvents generally produce acrylic precursors in which the structural characteristic are generally worse that for the same precursors obtained from solutions in an inorganic solvent because of the presence of possibly large cavities (macrovoids).

Moreover, these latter generally have an irregular cross-section in the shape of a bean or kidney instead of a circular cross-section which would provide better mechanical properties for the fibre, and would therefore allow more uniform progress of the oxidation process which precedes the carbonization stage in the production of carbon fibres.

The drawbacks of the said known art are well obviated by the spinning method for acrylic polymer solutions according to the present invention, which enables an acrylic precursor yarn to be obtained with very good mechanical characteristics, a perfectly circular filament cross-section free of voids, and a metal impurity content of less than 220 ppm (parts per million).

The acrylic precursor of the present invention is further characterised by a compact fibre structure free of flaws, a regular filament count, a constant count of the various filaments and good separation between them.

The present invention also relates to the acrylic fibres produced by the method and the carbon fibres deriving from them by oxidation and subsequent carbonization, in accordance with the well known processes of the state of the art.

The spinning process is of the wet type comprising the use of solutions of an acrylic polymer of the type described hereinafter in a suitable polar solvent.

According to this process, the acrylic polymer solutions are carefully purified of any impurities which may be present by filtration through two or three napped cotton cloths or metal meshes having mesh apertures of 5-10 microns, and are then fed to the spinning section.

Spinning is carried out by spinnerets containing between 3000 and 40000 orifices, with a capillary diameter variable between 120 and 180 microns, and immersed in the coagulating bath.

The process is characterised essentially by the coagulation stage, which is conducted under such bath temperature, time and composition conditions as to obtain at the end of the process an acrylic yarn having the aforesaid characteristics and tenacity values which have never been encountered in acrylic fibres forming part of the known art.

In accordance with the aforesaid, the yarns leaving the spinneret are passed into a coagulating bath maintained at a temperature of between 15 and 35 °C and consisting of a binary solvent-non solvent mixture in which the solvent is that of the acrylic polymer solution and the non-solvent is water.

The binary solvent-non solvent mixture has a rigorously controlled composition with a solvent content of between 78 and 82% by weight, and preferably a solvent content which is a fixed value within this range and strays from this value by not more than ± 0.5%. The stretch in the spinneret during coagulation is 1.5-5 times the solution extrusion rate through the spinneret orifices.

After coagulation, the yarn passes about a roller rotating at a peripheral speed of 4-10 m/minute and is stretched in air by passage about a second roller rotating at a peripheral speed of between 1.5 and 3.5 times that of the preceding roller.

The yarn is then washed in countercurrent with demineralized water at a temperature of between 20 °C and 50 °C and is again stretched in a water bath maintained at a temperature of between 95 and 99 °C.

The subsequent stages in the wet spinning process according to the present invention comprise lubrication, consisting of passing the yarn through a bath containing a lubricant and an antistatic agent, drying by passage over rollers heated to a temperature of between 120 and 150 °C and preferably between 130 and 140 °C, and further stretching to the extent of 1.2-1.5 times and thermal stabilization by contact with hot rollers or heating elements heated to 140-180 °C.

The yarn collection rate on the bobbins is between 50 and 80 m/minute.

The aforesaid sequence of operations plus a proper choice of process parameters such as the solution concentrations, the temperatures of the various process stages, the stretch in the spinneret, the coagulation conditions and the total stretch conditions enable acrylic fibres to be obtained having a tenacity of between 60 and 75 cN/tex, these being values with which the corresponding tenacity values obtained by spinning the same polymer solutions in the known processes of the state of the art in no way compare.

Furthermore, the fibres obtained by the spinning process according to the present invention have perfectly round cross-sections and an extremely compact structure free of flaws.

Those acrylic polymers which are most widely used in preparing polymer solutions for feeding to the spinnerets are acrylonitrile copolymers (ACN) with one or more acrylic monomers such as acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, acrylates and methacrylates in general, itaconic acid and other ethylenically unsaturated monomers able to copolymerize with acrylonitrile.

The preferred copolymers are those of high acrylonitrile content (acrylonitrile content exceeding 90%).

Other preferred copolymers are those of high ACN content containing some percentage (1-10 % by weight) of monomers containing the carboxyl function, such as acrylic acid, methacrylic acid, itaconic acid etc.

The most suitable polymers include acrylonitrile-acrylic acid copolymers containing 94-98% of acrylonitrile, and acrylonitrile-methylacrylate-acrylic acid terpolymers containing from 94-97% of acrylonitrile, 1-3% of acrylic acid and 1-5% of methylacrylate.

These copolymers are prepared by the usual radical polymerization methods well known to the expert

of the art.

The acrylic solutions of the said copolymers are formed by dissolving them in a polar solvent of high solvent power. Those particularly preferred are dimethylformamide, dimethylacetamide and dimethylsulphoxide.

The polymer concentration in the spinning solution is a function of its molecular weight.

Preferred polymers are those having a molecular weight corresponding to an MD of 1500-2000 where MD = ηspec.1000/C (ηspec is the specific viscosity in dimethylformamide measured at 35° C and C the concentration in g/100 c.c.).

As stated heretofore, the specific application of the "acrylic precursors" produced by the method according to the present invention is the production of carbon fibres by carbonization methods well known in the state of the art.

The use of acrylic precursors produced by the method of the present invention enables carbon fibres having excellent mechanical characteristics to be obtained, while using thermal oxidation temperatures for the acrylic fibres (this being a well known stage in the carbonization process) which are relatively low and for shorter times.

For example, an acrylic precursor consisting of an acrylonitrile (ACN) - methylacrylate (MA) - acrylic acid (AA) terpolymer containing 94% of ACN, 2% of AA and 4% of MA, processed in a carbon fibre production plant by way of a first oxidation stage in air at a temperature of 220-240° C and two carbonization stages in an inert environment (nitrogen) with a maximum temperature of 1500° C, resulted in carbon fibres with the following characteristics:

Tenacity	≥ 3.5 GPa
Modulus	220-270 Pa
Elongation	1-1.7%
Density	1.75-1.78
Carbon percentage	95-96%

The following examples illustrate the invention but must in no way be considered as limitative of its scope.

EXAMPLE 1

a) Polymer preparation

The following reactants were continuously fed to a continuous aqueous suspension polymerization plant comprising three reactors in cascade:

a - acrylonitrile
b - methyl acrylate
c - aqueous solution of acrylic acid
d - aqueous solution of H_2SO_4
e- aqueous solution of sodium hydroxylamine sulphonate
f - aqueous solution of sodium bisulphite.

The feed rates were such as to satisfy the following ratios: Monomer composition: 94.5% ACN, 3.5% MA, 2% AA; Catalysts: 0.6% of sodium hydroxylamine sulphonate and 1.5% of sodium bisulphite on the monomers; Aqueous H_2SO_4 solution such as to maintain the reaction pH at 2.5; Ratio H_2O/monomers: 5.5/1; Total reaction time 9 hours; Reaction temperature 55° C; Conversion 92%; MD 1800.

The polymer, obtained in the form of a slurry, was filtered through a rotary filter, washed with deionized water until the salts (catalyst residues) had completely disappeared, and dried in a fluidized bed drier.

b) Solution preparation

The polymer was dispersed in DMAc at -7° C; the polymer slurry was then transformed into a solution by heating in a plate heat exchanger at 88° C.

The polymer solution obtained, containing 23% of solids, was carefully filtered in a filter press through suitable filter cloths consisting of cotton linters (1st stage), 20 micron aperture metal cloth (2nd stage), and 10 micron aperture metal cloth (3rd stage).

c) Spinning

The polymer solution from the filtration stage was then spun in a wet spinning plant under the following spinning conditions:

- Temperature of polymer solution at spinneret inlet 50 ° C.
- Circular spinneret 80 mm diameter with 6000 orifices of 150 microns in diameter.
- Coagulating bath consisting of an aqueous 80% solution of dimethylacetamide maintained at 24 ° C.
- Collection rate after coagulation 5 metres/minute.
- Stretch in spinneret 2.4
- Stretch in air through two pairs of rollers, stretching 2.5 times.
- Countercurrent washing in 4 stages with deionized water at 45-50 ° C.
- Stretch in water at 98 ° C, stretching 4 times.
- Lubrication with aqueous solution of Span 60 + Tween 60 + G 265 of Atlas in ratio 3:1:1.
- Yarn drying under tension over steam heated rollers at maximum temperature of 130 ° C.
- Further stretching under dry conditions over rollers heated to 140 ° C with stretching 1.4 times.
- Stabilization over hot rollers at 140 ° C.
- Yarn collection under constant tension at a rate of about 70 metres/minute.

The characteristics of the obtained fibre were as follows:

Overall count	7,200 dtex
Filament count	1.2 dtex
Tenacity	70 cN/tex
Elongation	13%
H_2O regain 100 ° C	10%
Finish percentage	0.3%
Sodium	100 ppm
Filament cross-section	circular
Voids after coagulation	0
Flaws in finished fibre	0 (see photographs, enclosures 1 and 2: cross-sections through final fibre).

EXAMPLE 2

The polymer solution of Example 1 was spun under the following spinning conditions:

- Spinneret 6000 orifices, orifice diameter 52 microns.
- Coagulating bath: aqueous 50% solution of dimethylacetamide maintained at 45 ° C.
- Collection rate after coagulation 7 metres/minute.
- Stretch in spinneret 0.67
- Stretch in air, not possible.
- Countercurrent washing as in Example 1.
- Stretch in water at 98 ° C, 7 times (the maximum possible).
- Lubrication, drying, extra stretching and collection as in Example 1.

The fibre characteristics were as follows:

Overall count	7,200 dtex
Filament count	1.2 dtex
Tenacity	55 cN/tex
Elongation	14%
H_2O regain 100° C	11%
Finish percentage	0.3%
Sodium	110 ppm
Filament cross-section	kidney shaped
Voids after coagulation, number/mm	10-30
Flaws in finished fibre, number/mm	5-10 (see photographs, enclosures 3 and 4: cross-sections through final fibre).

The given examples clearly show that the best fibre characteristics are obtained under the spinning conditions suggested by our invention.

EXAMPLE 3

The fibres produced in Examples 1 and 2 are both converted into carbon fibres in an industrial plant operating under the following conditions:
Feed 200 bobbins
Oxidation in two furnaces operating in 4 stages, ie 220, 230, 235, 240° C
Stretch under oxidation 5%
1st carbonization stage in N_2 at 900° C
2nd carbonization stage in N_2 at 1400° C
Surface treatment by electrolysis with an ammonium bicarbonate solution.
Lubrication by aqueous epoxy resin dispersion
Drying at 150° C.
The carbon fibre characteristics were as follows:

	Precursor Ex. 1	Precursor Ex. 2
Count dtex	3,600	3,600
Tenacity	3.6 GPa	3.0 GPa
Modulus	230 GPa	235 GPa
Elongation	1.5%	1.3%

Claims

1. An acrylic precursor for carbon fibres characterised by:
   a) a fibre structure of the individual filaments which is compact and completely free of flaws;
   b) a perfectly circular filament cross-section;
   c) a maximum metal impurity content of 220 parts per million, expressed as metal in the elemental state;
   d) a tenacity greater than or equal to 60 cN/tex;
   e) an elongation exceeding 10%;
   f) a total yarn count of between 3000 and 500,000 dtex;

g) count of each individual filament between 1 and 1.6 dtex.

2. Carbon fibres obtained from the precursors claimed in the preceding claim, characterised by a tenacity greater than or equal to 3.5 GPa and a modulus greater than or equal to 200 GPa.

3. A method for preparing the carbon fibre acrylic precursors claimed in claim 1, comprising the following stages:

a) wet-spinning a solution of an acrylic copolymer in a polar organic solvent through 120-180 micron diameter orifices of a spinneret immersed in a coagulating bath at a temperature of 15-35 °C which contains said solvent in binary mixture with water, the mixture composition being rigorously controlled and having an organic solvent content of 78-82% by weight, said content being preferably maintained within said range at a value from which it strays by not more than ± 0.5%, with simultaneous stretching in the spinneret of between 1.5 and 5; said stretching in the spinneret being the ratio of the collection speed after coagulation to the speed with which the polymer solution passes through the spinneret orifices.

b) stretching in air at ambient temperature to the extent of between 2 and 3 times;

c) washing the resultant fibre with countercurrent water;

d) stretching from 3 to 6 times at a temperature of between 98 and 105 °C;

e) lubrication;

f) drying under tension at a temperature of between 100 and 150 °C;

g) stretching from 1.2 to 1.5 times at a temperature of between 120 and 150 °C;

h) stabilization under tension at a temperature of between 120 and 170 °C;

i) final collection.

4. A method as claimed in the claim 3, wherein the polar organic solvent is chosen from dimethylformamide, dimethylacetamide and dimethylsulphoxide.

5. A method as claimed in claims 3 and 4, wherein the polar solvent is dimethylacetamide.

6. A method as claimed in claim 3, wherein the acrylic polymer is a copolymer of acrylonitrile with one or more monomers chosen from the group comprising acrylates, methacrylates, acrylic acid, methacrylic acid and itaconic acid.

7. A method as claimed in claims 3 and 6, wherein the acrylic polymer is a terpolymer of acrylonitrile with methyl acrylate and acrylic acid, and contains at least 94% of acrylonitrile.

8. A method as claimed in claim 3, wherein the coagulating bath of point a) consists preferably of a water/dimethylacetamide binary mixture.

9. A method as claimed in claim 8, wherein the dimethylacetamide content of the binary mixture is preferably 80% by weight.

Fig.1

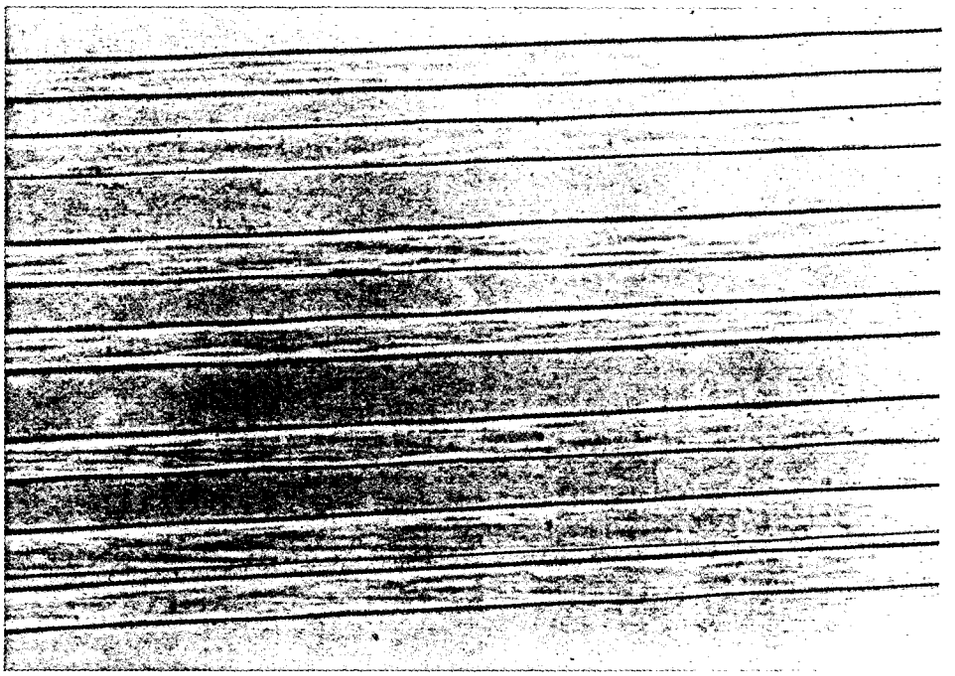


Fig.2

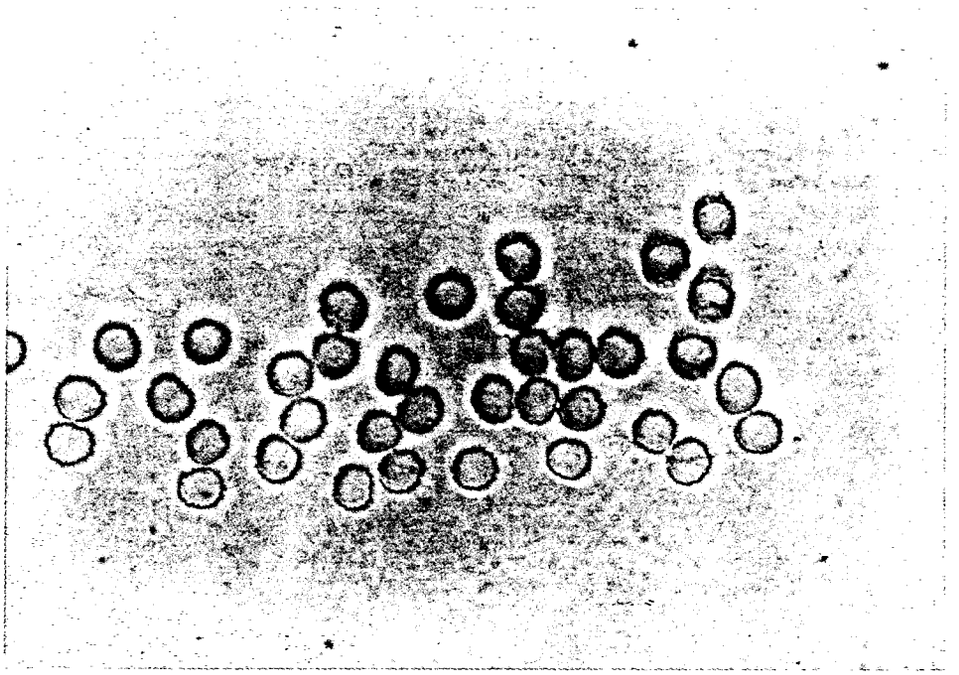


Fig.3

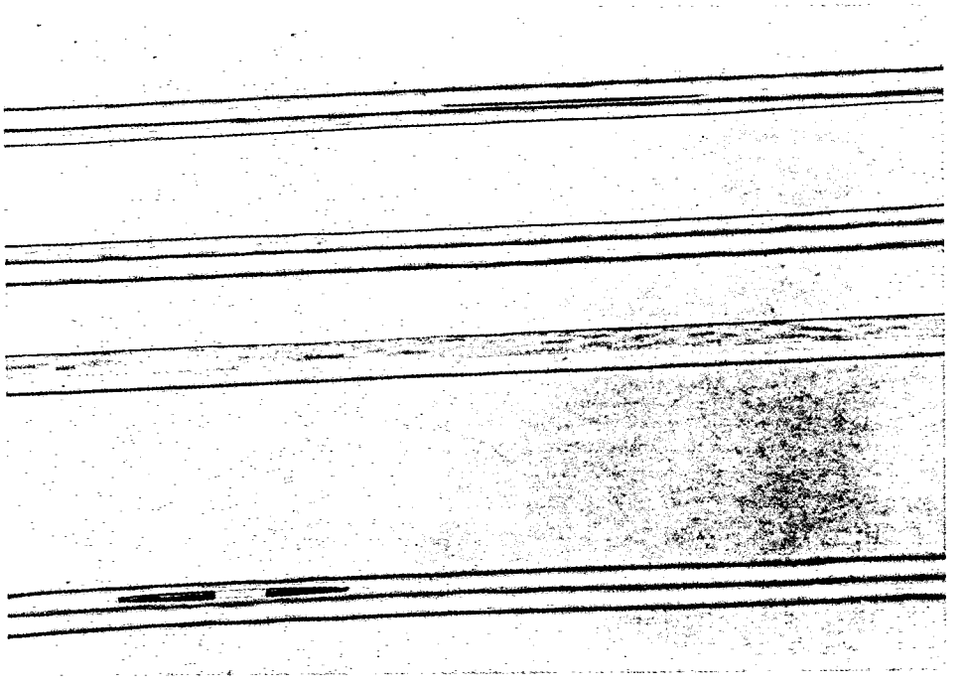


Fig.4