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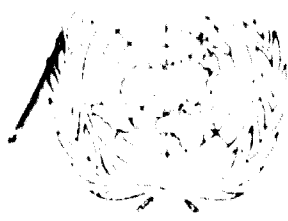
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D00432



United Nations Industrial Development Organization

Distribution
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ID/IG.34/62
23 July 1969

ORIGINAL: ENGLISH

PET SYMF D/11

United Nations Industrial Development Organization
Development of the Petrochemical Industries in
Developing Countries

Tskva, USSR, 21 - 31 October 1969
21

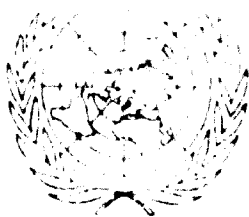
CONTINUOUS PROCESS OF PRODUCING SYNTHETIC FIBRES

FROM D-C-PROLACTAM^{1/}

by

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Distribution
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ID/WG.3/62 SUMMARY
23 July 1969
ORIGINAL - RUSSIAN

Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries
in Developing Countries

Doc. IDP. 5/11

Baku, USSR, 20 - 31 October 1969

SUMMARY

CONTINUOUS PROGRESS OF PRODUCING
SYNTHETIC FIBRES FROM P-CARBOLACTAM 1/

by

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At present the leading position among synthetic fibres is held by polyamide fibres accounting for 43% of the world production. Of all commercially produced polyamide fibres Nylon-6 and Nylon-66 have found the most extensive application. In spite of the fact that the commercial production of Nylon-66 was started much earlier than that of Nylon-6, the trend today is towards reducing the gap in the volume of production of the said fibres. Thus, in 1965 the production of Nylon-6 and Nylon-66 amounted to 42% and 58% respectively, in 1970 it is expected to become 46% and 54%.

At the present time in some countries, including the USSR, investigations are being carried out with the view of shortening the

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technological process of Nylon-6 production containing 2.5 - 3 % of low molecular constituents (LMC) after spinning. Despite of the known variations of methods for the production of such fibres, the principal flow sheet of the process remains unchanged. Namely:

1. melting of ϵ -caprolactam;
2. polyamidation of ϵ -caprolactam;
3. denomerization of the polymer;
4. melt spinning;
5. textile processing.

Experience gained in operating units for Nylon-6 continuous production as well as the investigations carried out in the USSR have resulted in the development of an efficient continuous process in this country.

ϵ - Caprolactam polyamidation

To obtain high-performance capron filament yarn it is necessary that the polymer should have not only an adequate molecular weight but also maximum uniformity in its macromolecules along their length. To a certain degree this depends on the design of the polymerization apparatus. Equipment for continuous polyamidation (AMP-3, VNIISV design) has been developed in the USSR. This equipment meets the above requirements and advantageously differs from the existing equipment in its technical and economic indices.

Denomerization of the melted poly- ϵ -caproamide

To obtain high-performance capron filament yarn through denomerization it is necessary to solve at least two problems:

1. to obtain a melted polymer uniform in its properties, which would not substantially change its physical and chemical characteristics with time
2. to remove maximum of the low molecular constituents from the melted polymer.

Denomerization under vacuum has proved to be the best method to solve these problems.

System for LMC condensation

A system for LMC condensation has been developed providing for preliminary splitting of caprolactam oligomers to a monomer thus, establishing stable conditions for the operation of the unit as a whole. In some cases it is possible to return the condensate into the technological cycle.

Spinning and textile processing of a filament yarn.

Spinning of a filament yarn and its textile processing are conventional.

Chain-breaking regulating agent

The chain-breaking regulating agent commonly used possesses a number of specific properties determined by the technology requirements.

Heat stabilizer

Stabilin - 10 is used as a heat stabilizer, it ensures good retaining tenacity of polyamide filament yarns at temperatures in the range of 150-200°C. At the same time Stabilin - 10 is an effective light stabilizer. The stabilizer is injected at the stage of ε-caprolactam polyamidation.

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The 20th century is characterized by rapid progress in the field of man-made fibres. In 1962 the world production of man-made fibres amounted to 7,257,000 tons including 3,757,000 tons of synthetic fibres. The leading position among synthetic fibres is held by polyamide fibres accounting for 33% of the world production of synthetic fibres. Of all commercially produced polyamide fibres Nylon-6 and Nylon-66 have found the most extensive application.

In spite of the fact that the industrial production of Nylon-66 was started considerably earlier than that of Nylon-6, the trend today is towards reducing the difference in the volume of production of these two fibres. Thus, in 1955 the production of Nylon-6 and Nylon-66 was divided 42% and 58% respectively, in 1970 it is expected to come to 45% and 55%.

One of the major reasons for rapid rate of growth of Nylon-6 production is the expansion of its end uses, the development of new advanced processes of production, characterized by high productive capacity and automation, and the improvement in service properties of the filament product.

This paper deals with one of the major methods of improving the production of filament from poly- ϵ -caprolacton.

Continuous process for ϵ -caprolacton polymerization with the Direct Spinning of Filaments from the Deacetymerized Melted Polymer

Almost since the time of the first commercial manufacture of Capron (Nylon 6) yarn, research work on the improvement of the process has been started.

The research has been aimed at solving the problem of producing filaments by a continuous process which included ϵ -caprolacton polymerization and direct melt spinning. Thus, in 1950 the possibility of producing filaments from ϵ -caprolacton by a continuous process was demonstrated. The yarns produced by the above process contained about 1% of low molecular water-soluble constituents, compared to the classical process (the production of filaments from polymer chip) the above process had the advantage of

combining the continuous process of polyamidation with the direct spinning of filaments from the melted polymer. Taking into account that the above process has been carried out strictly under conditions which resulted in establishing a kinetic equilibrium between the polymer and the monomer, the conditions for production of yarn with steady stable quality characteristics have been determined. In spite of its advantages the above process has had a number of serious shortcomings:

1. The presence of 10% of the monomer and its oligomers in the spun filament has necessitated provision of a washing stage in the flow sheet. This operation has thus required the inclusion of an expensive stage of caprolactam recovery from low-concentration oil-containing washings.
2. The washing stage has made the flow sheet for textile processing of the yarn unduly complicated.

At the present time in some countries including the USSR, research is being carried out with the aim of shortening the technological process of Nylon-6 production. The key to the solution of this problem is in manufacturing filaments which would contain (after spinning) not over 2.5% - 3.0% of low-molecular constituents. The presence of such small quantities of caprolactam and its oligomers in the yarn makes it possible to exclude from the flow sheet the operations of washing, drying and rewinding. In spite of the fact that different processes of producing such fibres are known, the principal flow diagram remains practically the same. The process includes, mainly, the following operations:

1. Melting of ϵ -caprolactam.
2. Polyamidation of ϵ -caprolactam.
3. Demonomerization of the polymer.
4. Melt spinning.
5. Textile processing.

Experience gained in operating plants for Nylon-6 continuous production as well as the results of research carried out in the USSR have given rise to the development of an efficient flow sheet for continuous production of filaments based on poly- ϵ -caproamide.

A brief outline of the basic stages of producing filaments by the continuous process is given below.

II - Caprolactam Polyamidation

It is well known that for producing Capron filament yarn having good mechanical properties it is necessary that the polymer should have not only a high molecular weight but also a uniformity of its macromolecules along their length, i.e., in other words, the polyamide molecular weight distribution (presented as a differential curve) should be narrow. As shown by research, this may be achieved by establishing conditions for polyamidation under which exchange reactions such as isomerolysis, hydrolysis, acidolysis, transamidation and others would proceed with a high conversion and would give a polymer with macromolecules showing maximum uniformity along their length. The destructive reactions such as hydrolysis, partial pyrolysis and similar processes also occur at the same time and contribute to levelling of polyamide macromolecules. However, for technological reasons, the latter reactions should be cut down to a minimum. It is practically impossible to increase the polymer uniformity when carrying out polyamidation in the continuous apparatuses of a standard design; even prolongation of the process gives no useful results in practice.

Numerous investigations have shown that the construction of the equipment exerts a definite influence not only upon its production capacity, but also on the quality of the polymer produced and of the filaments made from it.

Experiments carried out in the laboratories, at the pilot plant and under industrial conditions have resulted in design for an apparatus for continuous polyamidation (MIF - 5, VNIISV design); to a certain degree the apparatus meets the above requirements and advantageously differs from the existing apparatus in its technical and economic performances (Table 1 figures 1 and 2).

Table 1

No	Name of indices	Units	MP - 5,5 V (commercial)	MP - 5 (UNITARY design)
1.	Daily polymer output per 1 cu.m. of the working volume of an apparatus	kg/cu.m.	804	917
		%	100	114.1
2.	Daily polymer output per 1 sq.m. of the total floor area.	kg/sqm.	15	23
		%	100	154.0
3.	Weight of the equip- ment per 1 ton of polymer	kg/t	2.91	1.14
		%	100	39.2
4.	Power consumption per 1 ton of polymer of the polymerization stage	kwh/t	573	306
		%	100	52.4

Demonomerization of Melted Poly - ϵ - caprolactam

In modern practice there is a number of methods for demonomerization of melted polymers: steam, gas, vacuum demonomerization and others. To develop an economical continuous process for production of a high-quality yarn it is necessary to solve, at least, 2 problems involved in demonomerization:

1. To obtain a polymer of uniform quality which in the molten state would be little affected in its physico-chemical properties.
2. To achieve maximum removal of low molecular weight constituents from the melted polymer.

These aims may be achieved most effectively by applying the vacuum demonomerization process. Experience has shown that under specific conditions of vacuum polymerization a high-quality polymer can be produced which having been dis-

charged from a vacuum apparatus forms low molecular weight constituents at only half the rate of the polymer obtained under conventional conditions. In this case the polymer molecular weight is little affected (fig.4). This is particularly important for producing filaments of uniform properties from the melted polymer.

System for Condensation of Low Molecular Weight Constituents

The system worked out for condensation of low molecular weight constituents provides for preliminary decomposition of a preformed oligomer to monomer, and this ensures more stable operating conditions for the plant as a whole. The equipment designed for the process ensures sufficiently complete trapping of low molecular weight constituents which are continuously removed from the system as 98% concentrate. The last-mentioned circumstances are of particular importance as the process for subsequent concentrating of low molecular weight constituents is excluded from the flow sheet. Apart from this, the high content of low-molecular constituents in the distillate allows (when producing filaments of a lower grade) the low molecular concentrate to be returned to the main technological cycle. This considerably increases the efficiency of the continuous process as a whole.

Spinning and Textile Processing of Filament Yarn

Spinning of a filament yarn and its textile processing are the traditional operations relating to Nylon-6 production, hence appropriate up-to-date equipment should be used for production of high quality industrial and textile yarns.

Chain-breaking (regulating) Agent

Chain-breaking agents commonly used in Nylon-6 production such as sebacic, adipic and stearic acids, but diamine sebacate for various technological reasons, do not comply with the requirements for production of a polymer with reproducible quality characteristics. This is particularly important for producing filaments from demonomerized polyamide by the continuous process.

The advantages of the chain-breaking agent used by us (in addition to complying with the above mentioned requirements) are as follows:

1. Sufficiently high reactivity.
2. Non-volatility.
3. Nonfunctionality.
4. Forms stable compounds with end functional groups of the polymer macromolecules.
5. Nontoxicity.
6. Does not form coloured products with polyamide.
7. Has a high solubility in caprolactam.

Polyamide Text Stabilizer

Stabilin-10 used as a text stabilizer for the above mentioned process ensures good tenacity retention of polyamide filament yarns at the temperature of $150^{\circ} - 200^{\circ}\text{C}$ (table 2, fig.5). At the same time Stabilin-10 is an effective light stabilizer (table 3, fig.6). The stabilizer is injected at the stage of ϵ -caprolactam salicidation which makes it possible to avoid the use of various devices commonly used for injecting the stabilizer directly into the melted polymer. In the melted polymer Stabilin-10 retains its properties for a long period due to its high heat stability. The stabilizer is not washed out by water treatments. Its light-blue shade imparts a pleasant appearance to the yarn.

Brief Outline of the Flow Sheet

The proposed continuous process can be used for production of Capron cord and textile yarns.

The process developed is based on the inventions protected by the Patent of the USSR (Nos. 149536; B - 2424; B - 24206; 234996; B - 1950; 176680; 131238; resolution for granting the Patent on application No.1214914/23-5).

The process proposed includes continuous ϵ -caprolactam salicidation at atmospheric pressure, one stage desensitization of the melted polymer and direct spinning of filament yarns.

The plant (fig.) for producing Capron cord yarns by the continuous process comprises:

1. Continuous polyaddition unit (melting tank /1/, mixing tank /2/, metering device /3/, continuous polyaddition apparatus /4/).
2. Demonomerization unit (evaporator /5/, splitter for conducting oligomers /6/, condenser for low molecular weight constituents /7/, holding tank for low molecular constituent concentrate /8/, screw pump /9/ for feeding the melted polymer to the spinning machine).
3. Spinning unit (pump units, self-spinning, spinning machine).

Also provision is made for producing, if required, granulated polymer of adequate quality immediately after polyaddition and demonomerization; to this end special equipment is used.

The continuous process is more efficient and economic compared to the non-existent batch (intermittent) process for Gopran yarn production.

Production of industrial yarn by the continuous process allows the number of technological operations to be reduced from 15 to 9.

It is present in the USSR in manufacturing plant in operation having a capacity of 4.5 tons per day of an industrial yarn (cord).

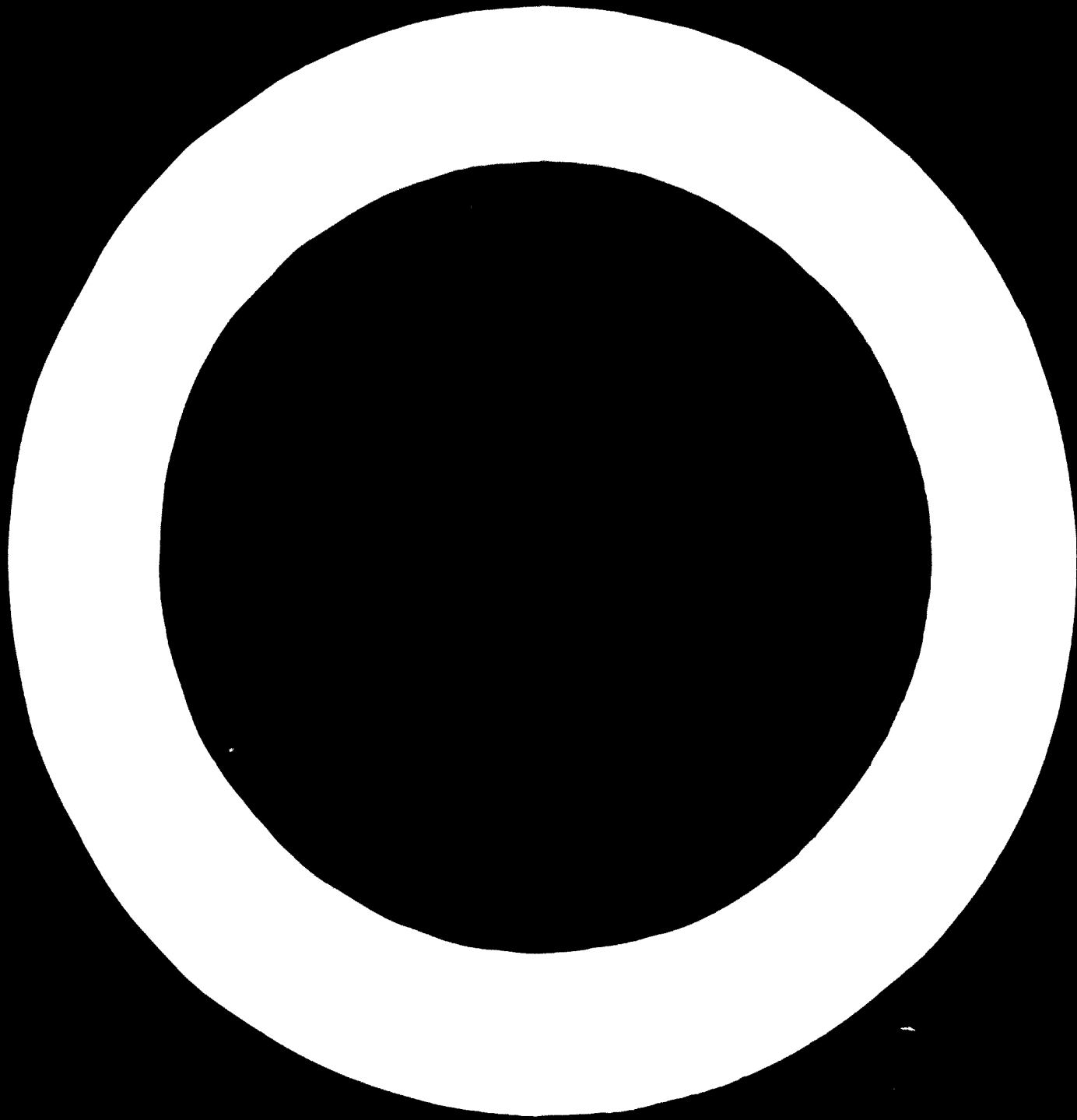
Mechanical properties of "Ilex" produced by the continuous process

The properties of non-twisted heat-stabilized industrial yarn with 60% sulfur ($\lambda_{\text{rel}} = 20.7$) produced by the continuous process are given in Tables 1, 2 and in figures 5, 6, 8-10.

Table 2

Mechanical properties of the filament yarn

No.	Det. designation	Unit	
1.	Actual thickness	tex	94.8
2.	Tensile strength	kg	7.23-7.5
	----- " -----	$\frac{g}{tex}$	75-80
3.	Breaking elongation	%	17
4.	Stress at 5% elongation	$\frac{g}{tex}$	22
5.	Hot tensile strength	kg	5.4-5.9
	----- " -----	$\frac{g}{tex}$	58-72
6.	Hot breaking elongation	%	25
7.	Residual Strength after exposure to Xenon lamp for 100 hours	%	96
8.	Residual Strength after thermal treatment in the air at 200°C for 2 hours	%	80-85
9.	Residual Strength after thermal treatment in the air at 175°C for 30 hours	%	80
10.	Residual strength after thermal treatment in the air at 100°C for 2 hours	%	100



Характеристики инициатора, инициатора
и температуры

- температура инициатора (100°C)
- температура инициатора (50°C)

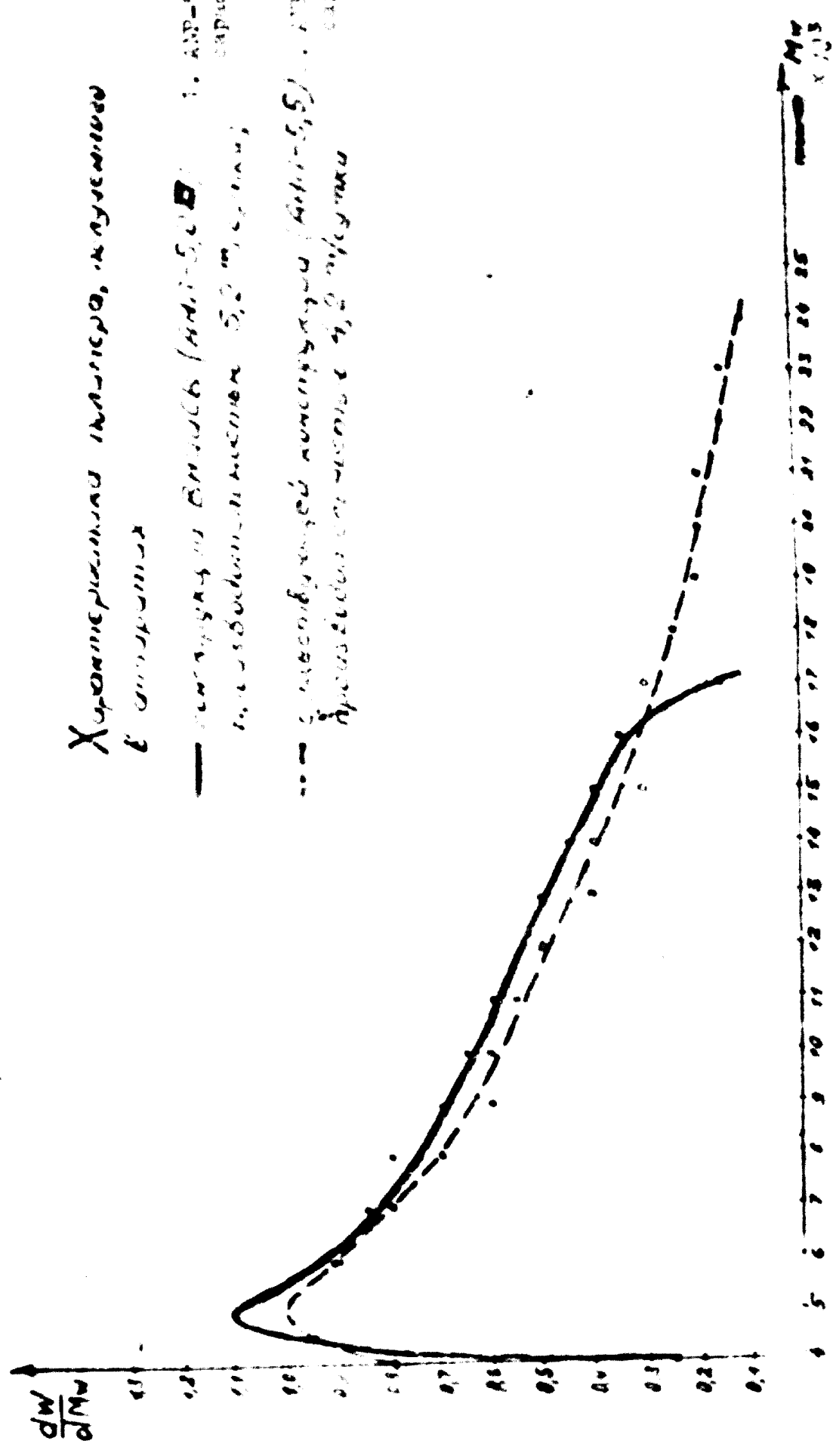
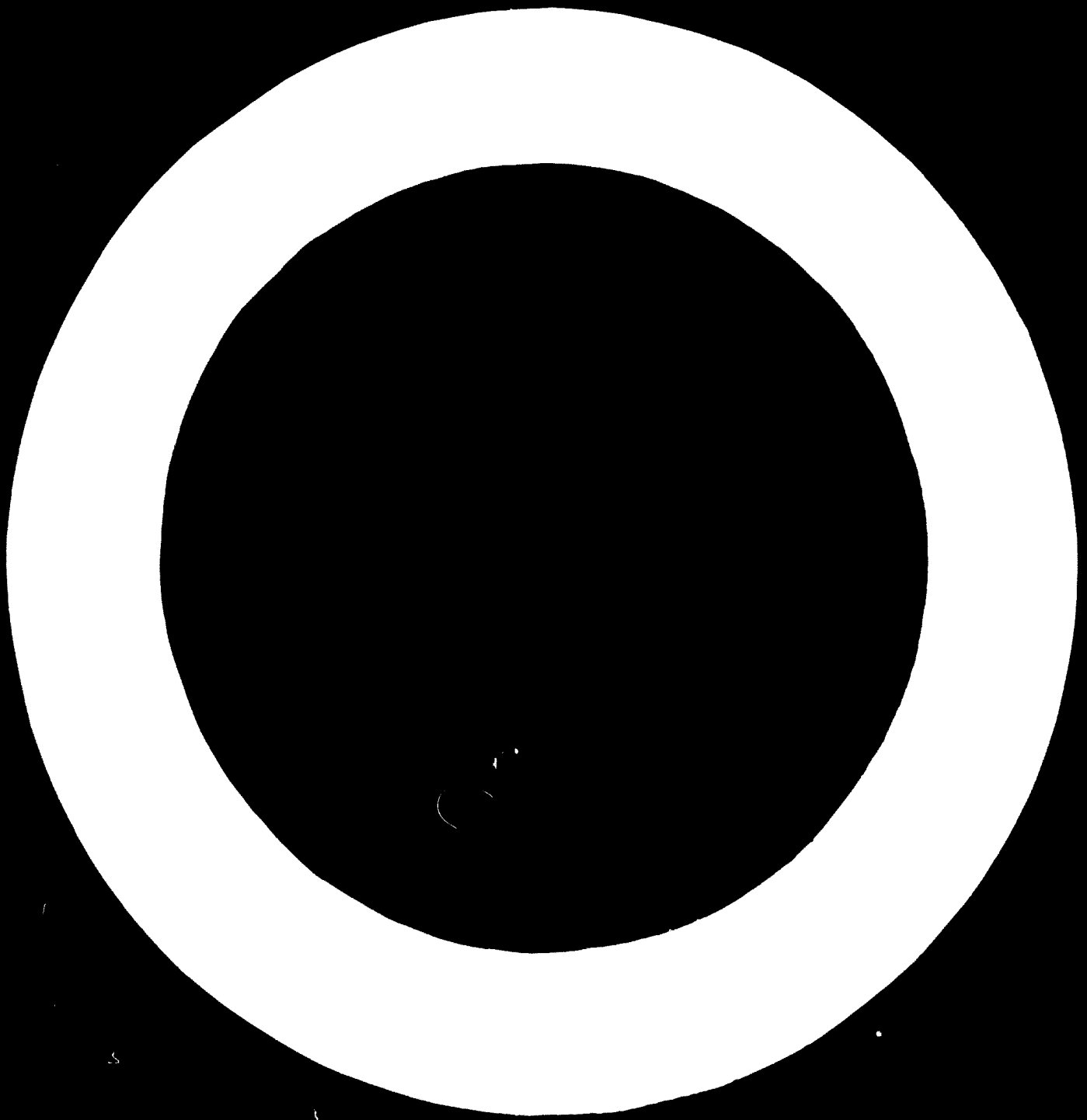
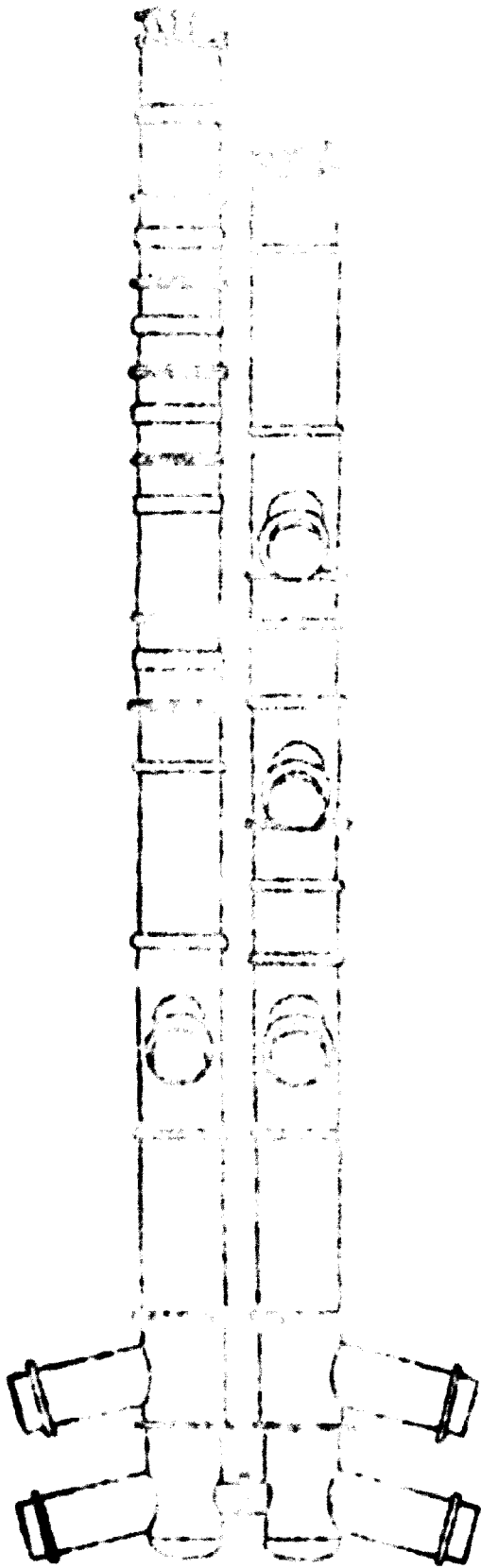


Fig. 1 Differential molecular-weight distribution of polymer



АНП-5.5
(серия 500)

АНП-5.5 У (портативный)



АНП-5.5
(вчипов) (вид)

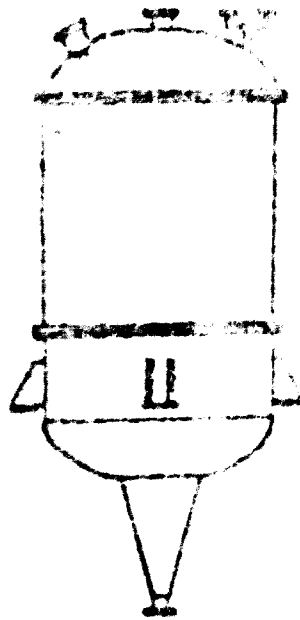
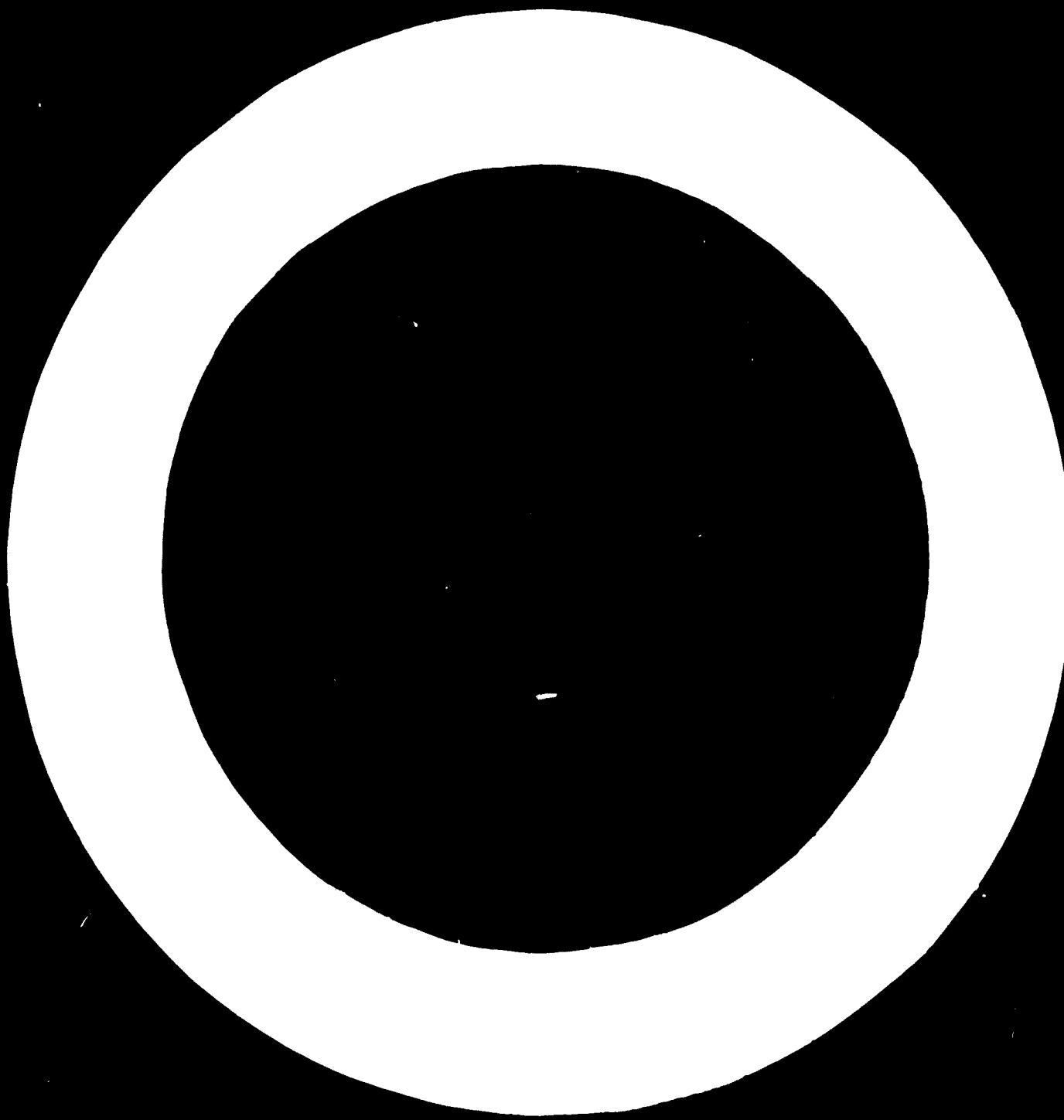


Рис. 2 Вид сзади аппарата непрерывного электролиза (при одинаковой массе)



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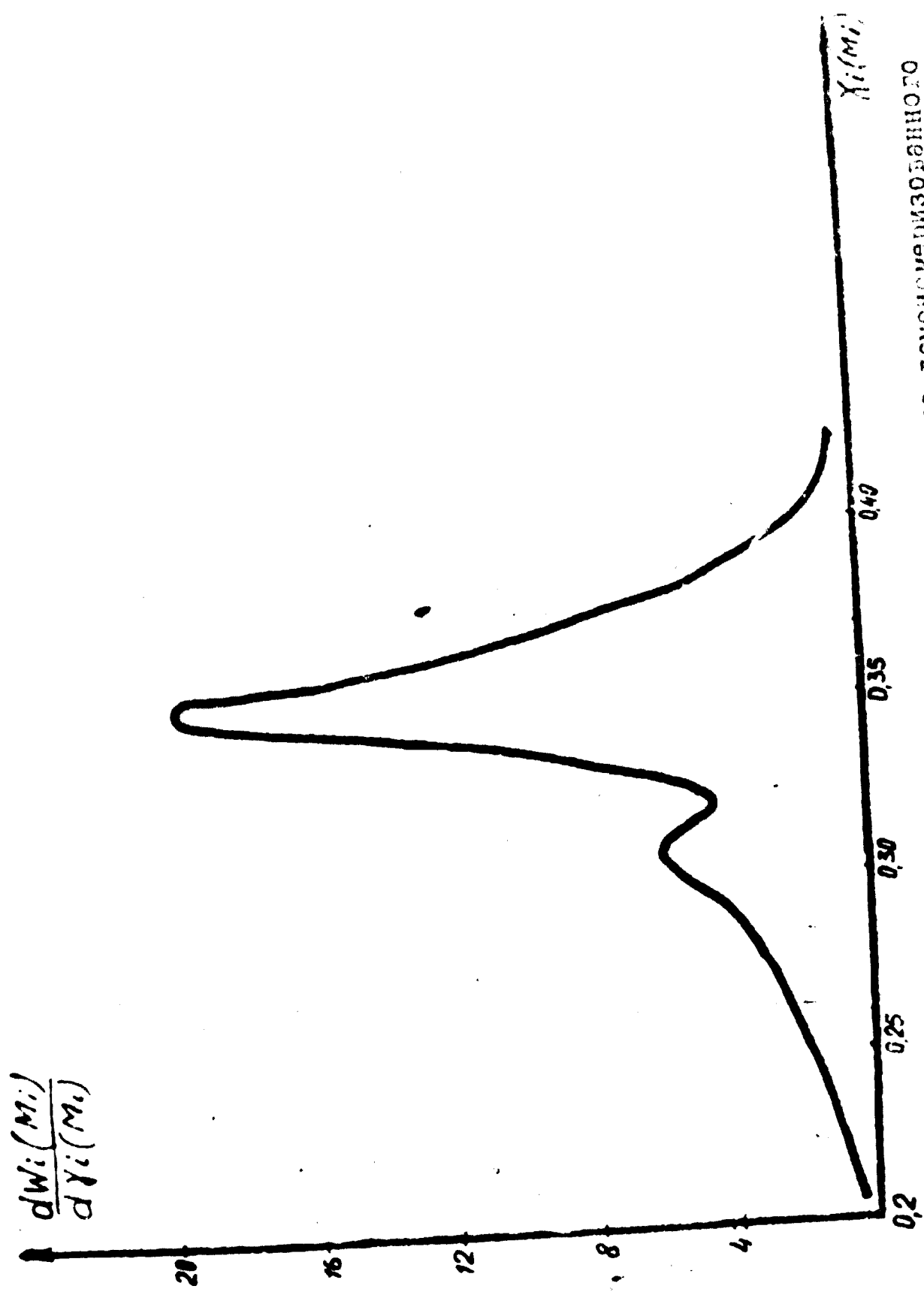
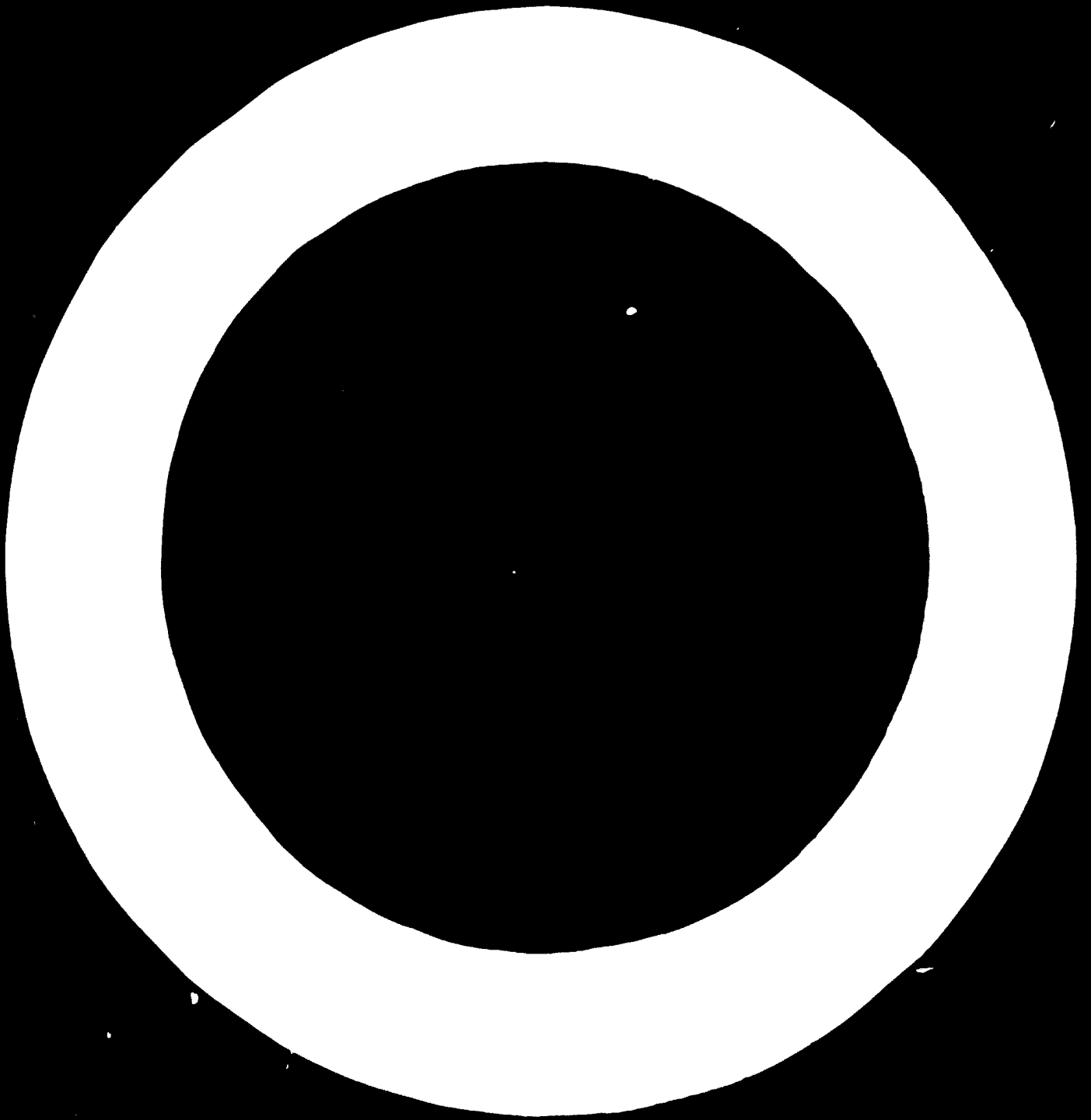


Рис. 3 Дифференциальное распределение деионизованного полимера по молекулярным весам.

Fig. 3 Differential molecular-weight distribution for the deionized polymer.



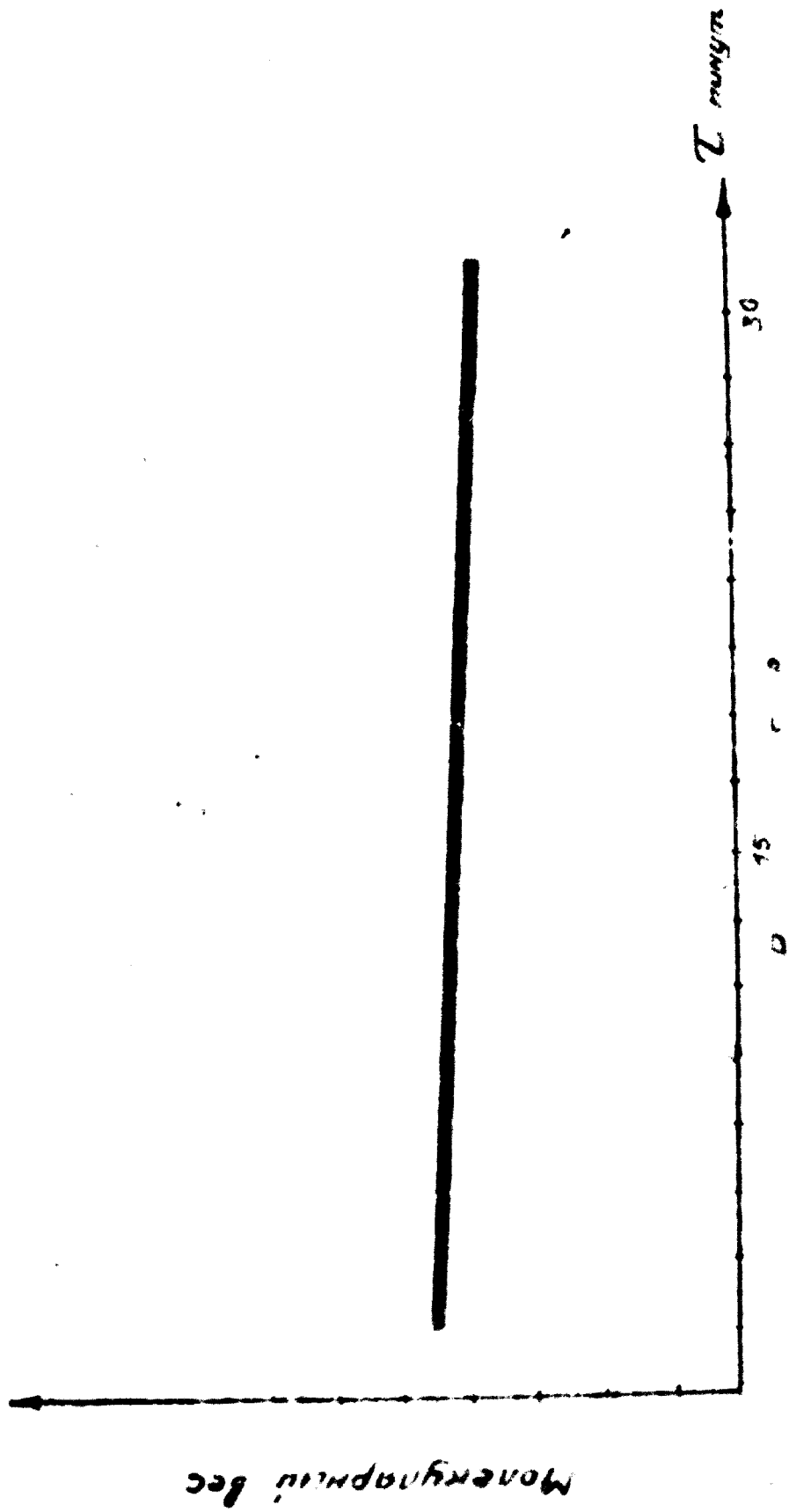
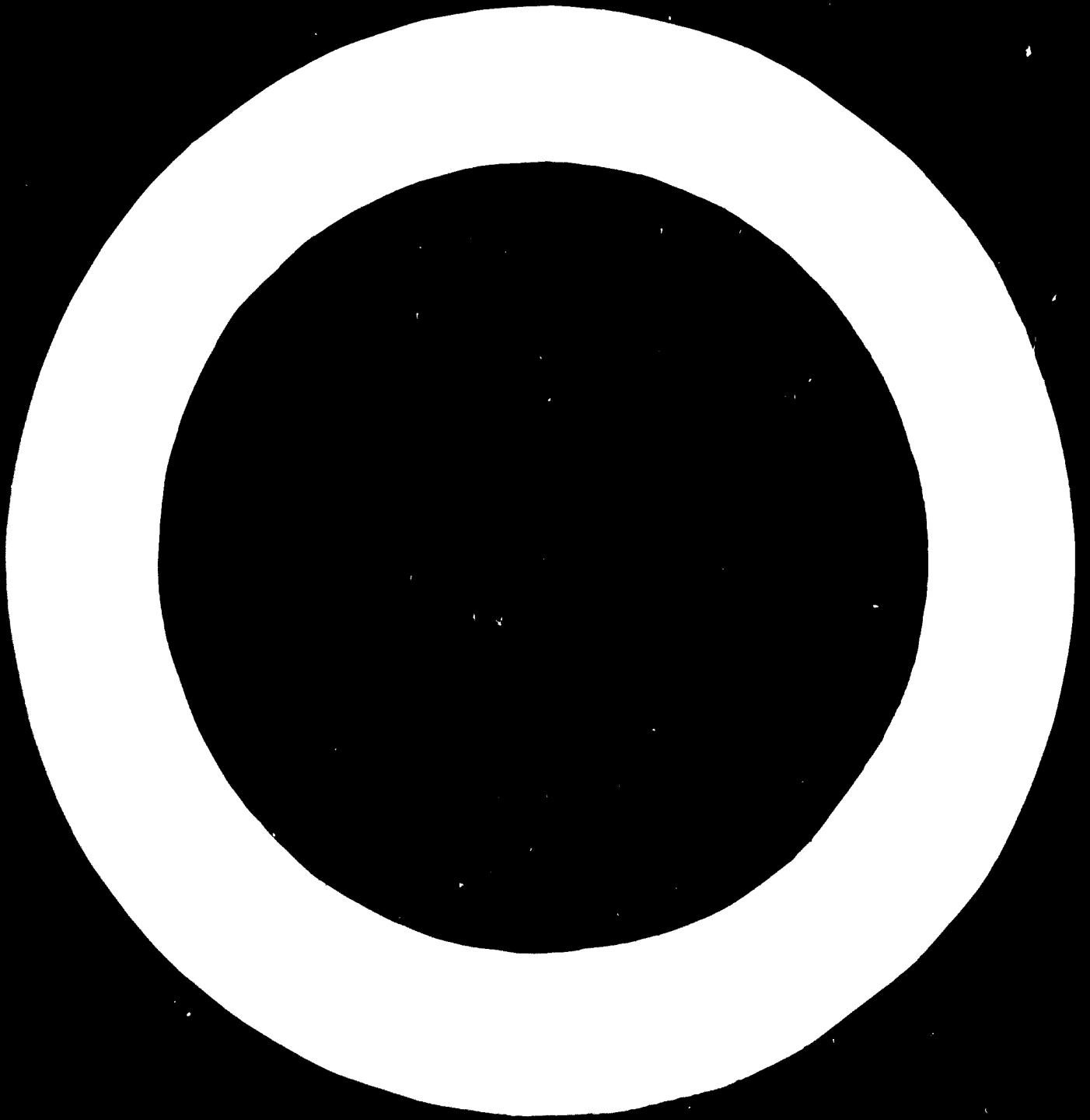


Рис. 4 Значения мониторингового веза пологоразношного
 вольера по времени по 2000 м.

1980 г. 10.10.1980



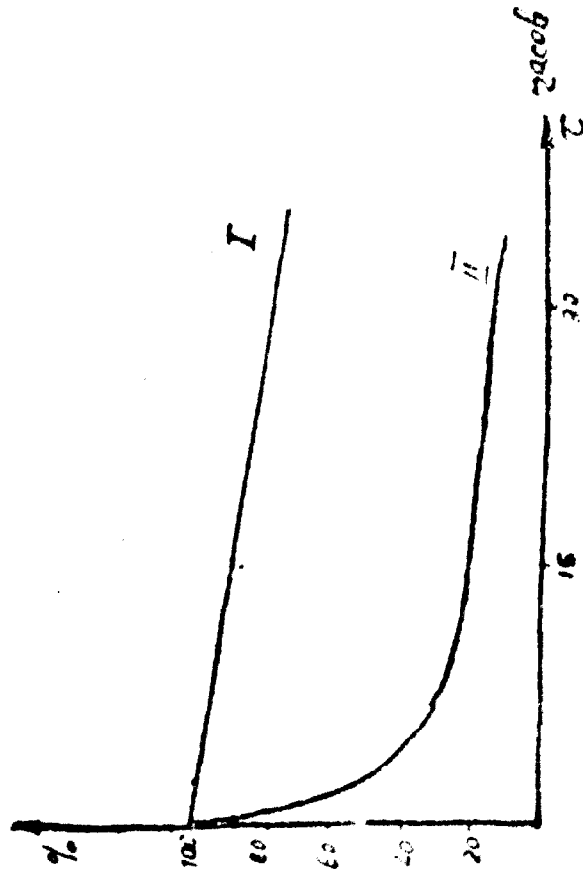


Рис. 5 Изменение разрывной прочности волокон в зависимости от времени пребывания его в атмосфере воздуха при температуре 175°C

I - волокно со стабилизатором Славонин-10,

II - нестационарный стабилизатор.

Fig. 5 The tensile strength of the filament yarn as a function of its exposure to a Xenon lamp at 175°C.

I. Yarn stabilized with Slatvin-10
II. Non-stabilized yarn

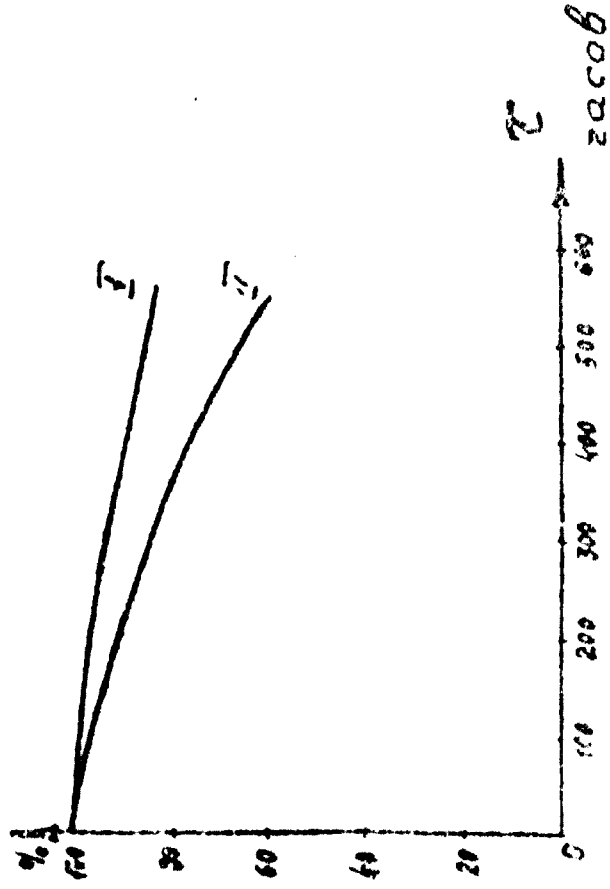
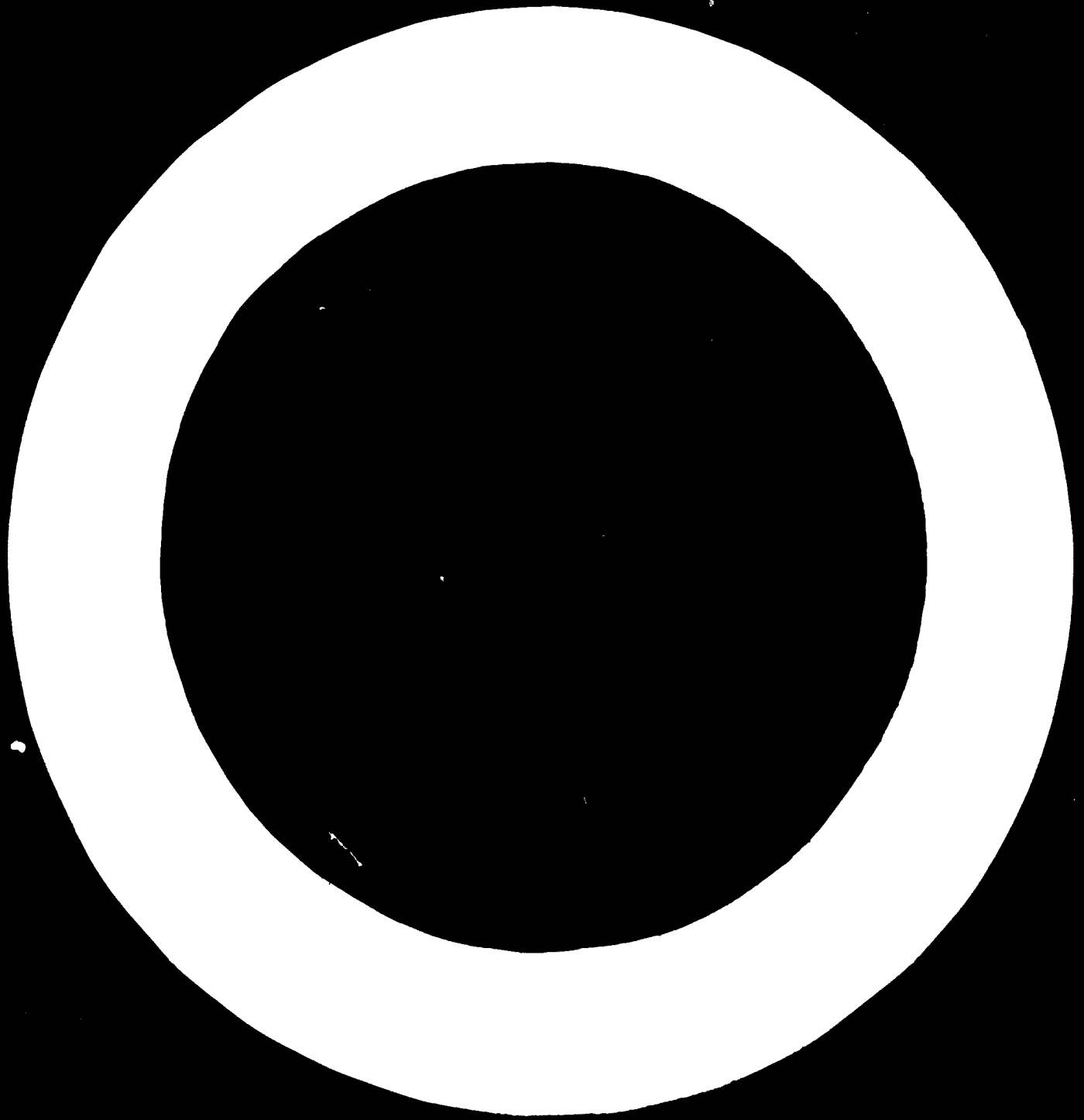


Рис. 6 Изменение разрывной прочности волокон в зависимости от времени облучения ксеноновой лампой

I - волокно со стабилизатором Славонин-10
II - нестационарный стабилизатор.

Fig. 6 The tensile strength of the filament yarn as a function of its exposure to a Xenon lamp.

I. Yarn stabilized with Slatvin-10
II. Non-stabilized yarn



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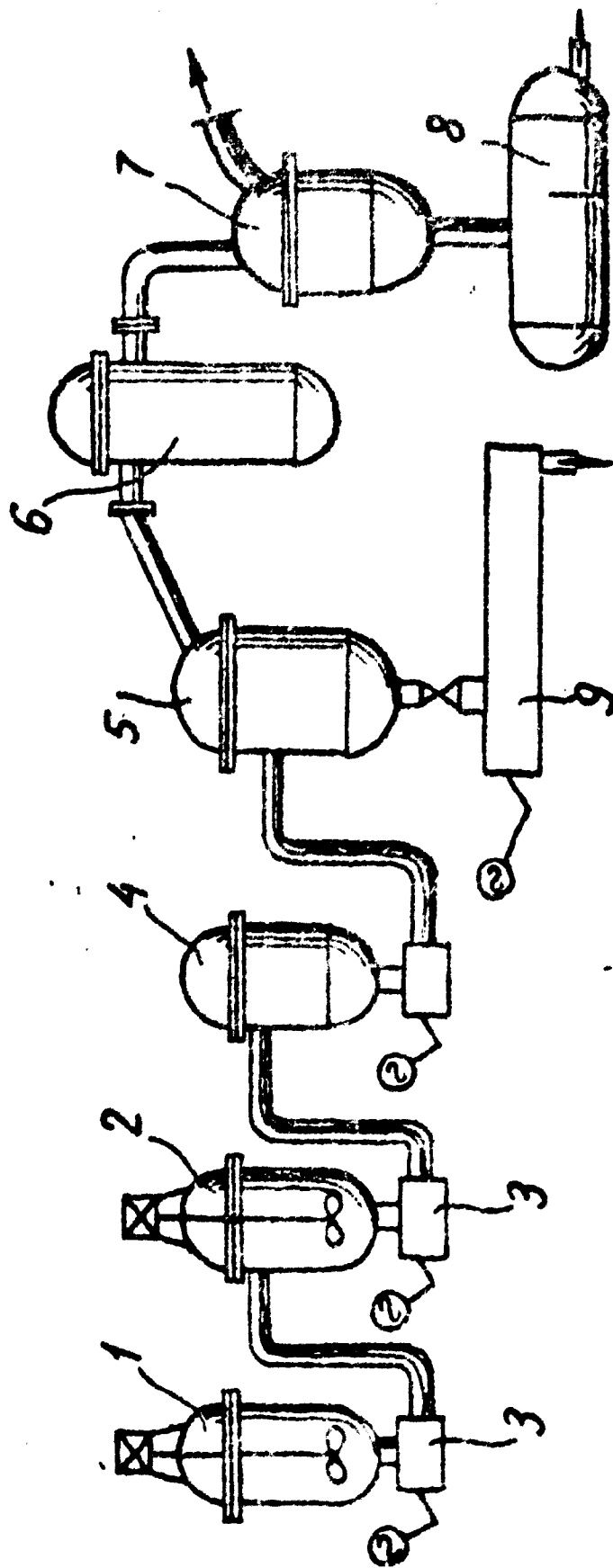
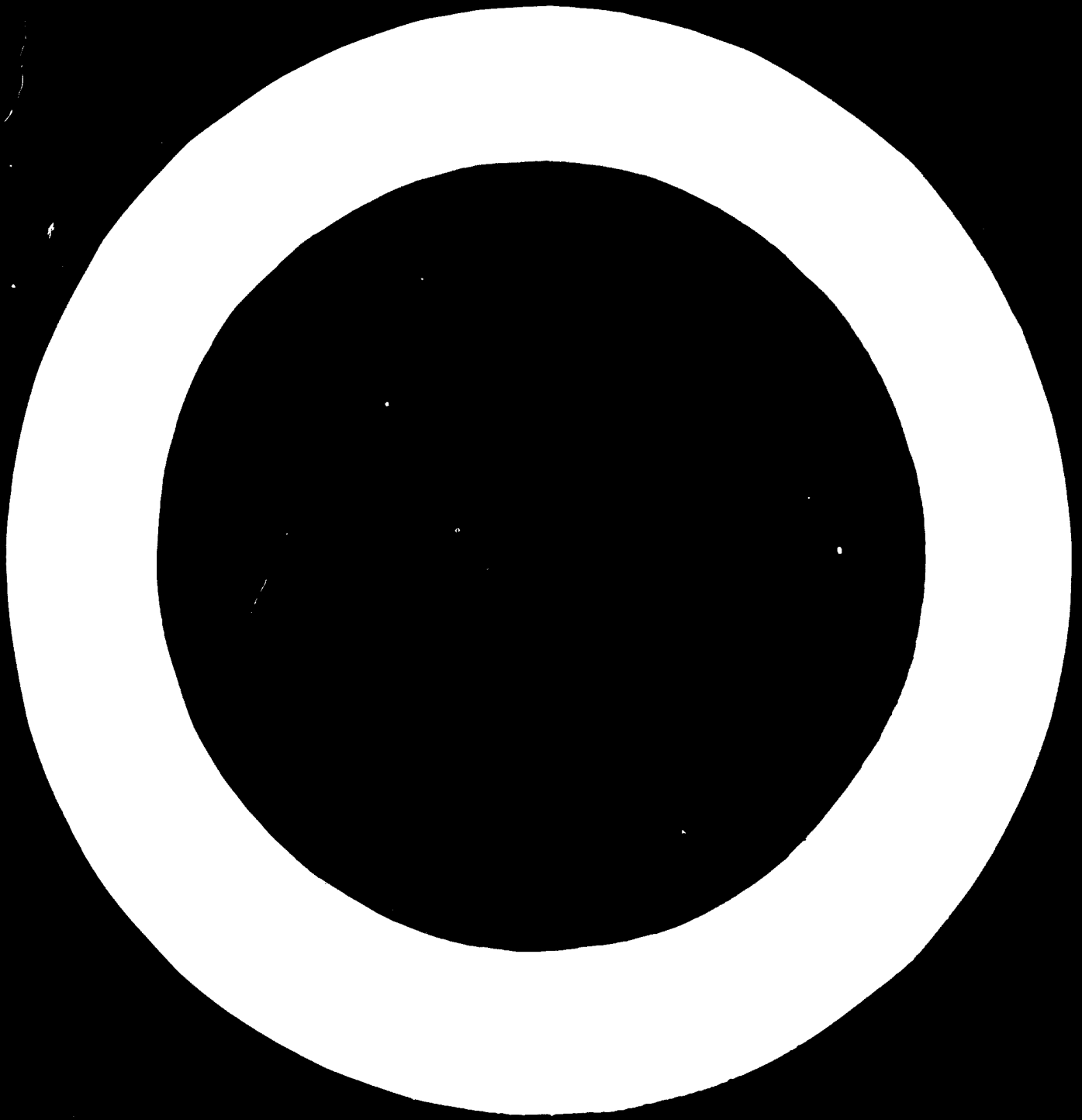


Рис. 7 Принципиальная схема получения

изобретения по заявке № 1000000

Fig. 7 The principle diagram for the continuous process



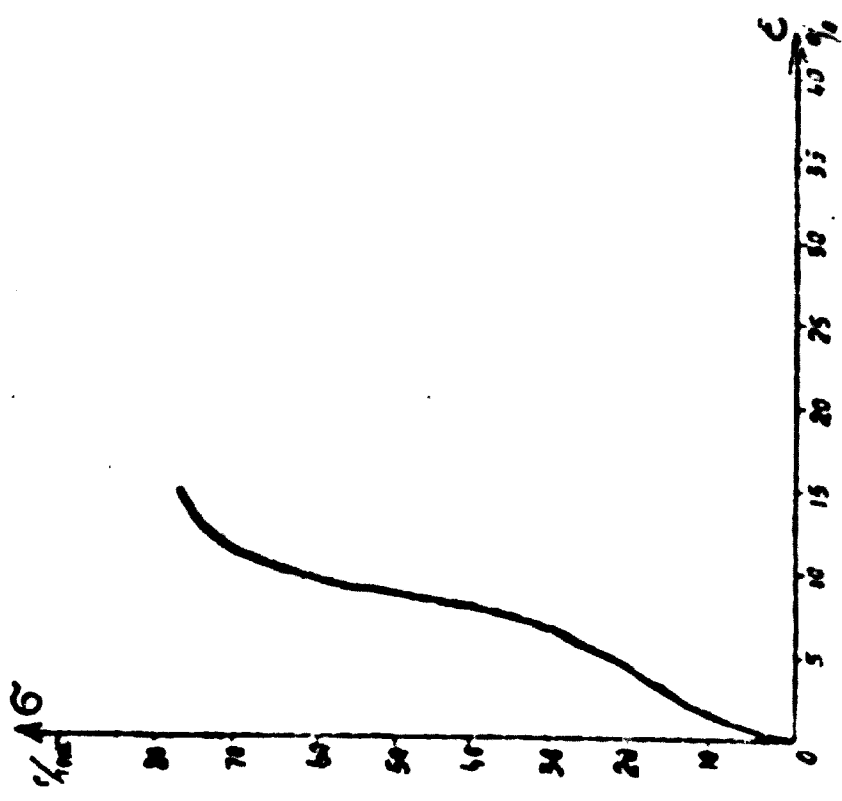


Fig. 8 Stress () - strain () curve for the conditioned filament yarn (temperature = 20°C, relative humidity = 65%)
 РИС. 8 Кривая напряжения (AG) - деформации (ε) для кондиционированной пряжи (температура 20°C, относительная влажность 65%)

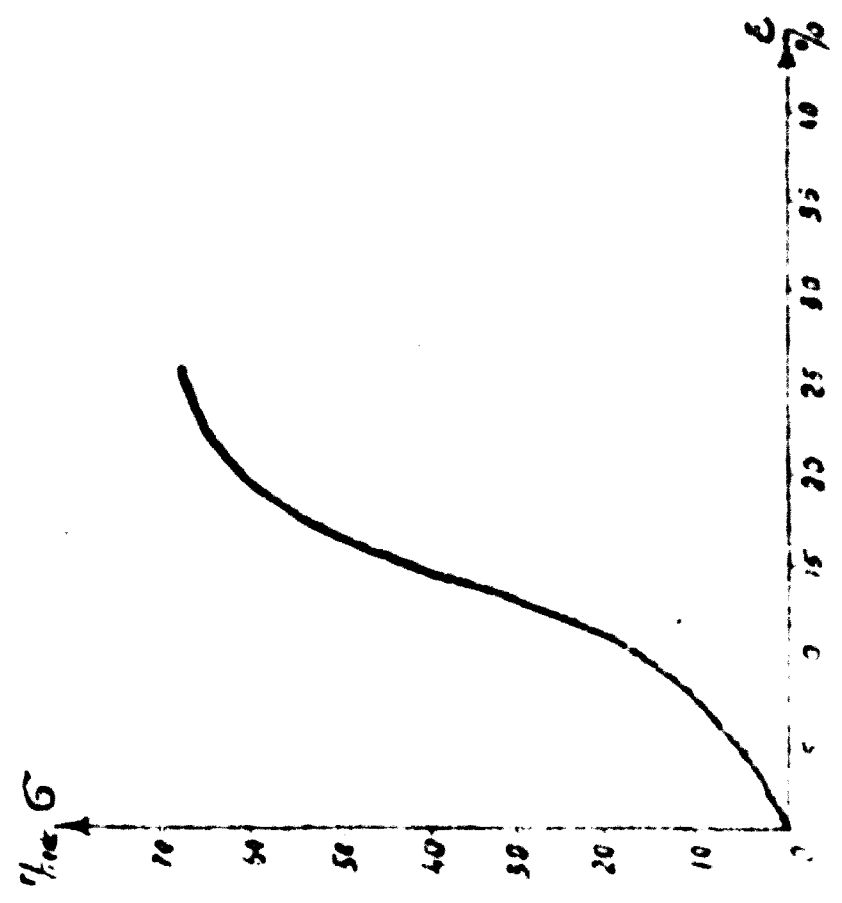
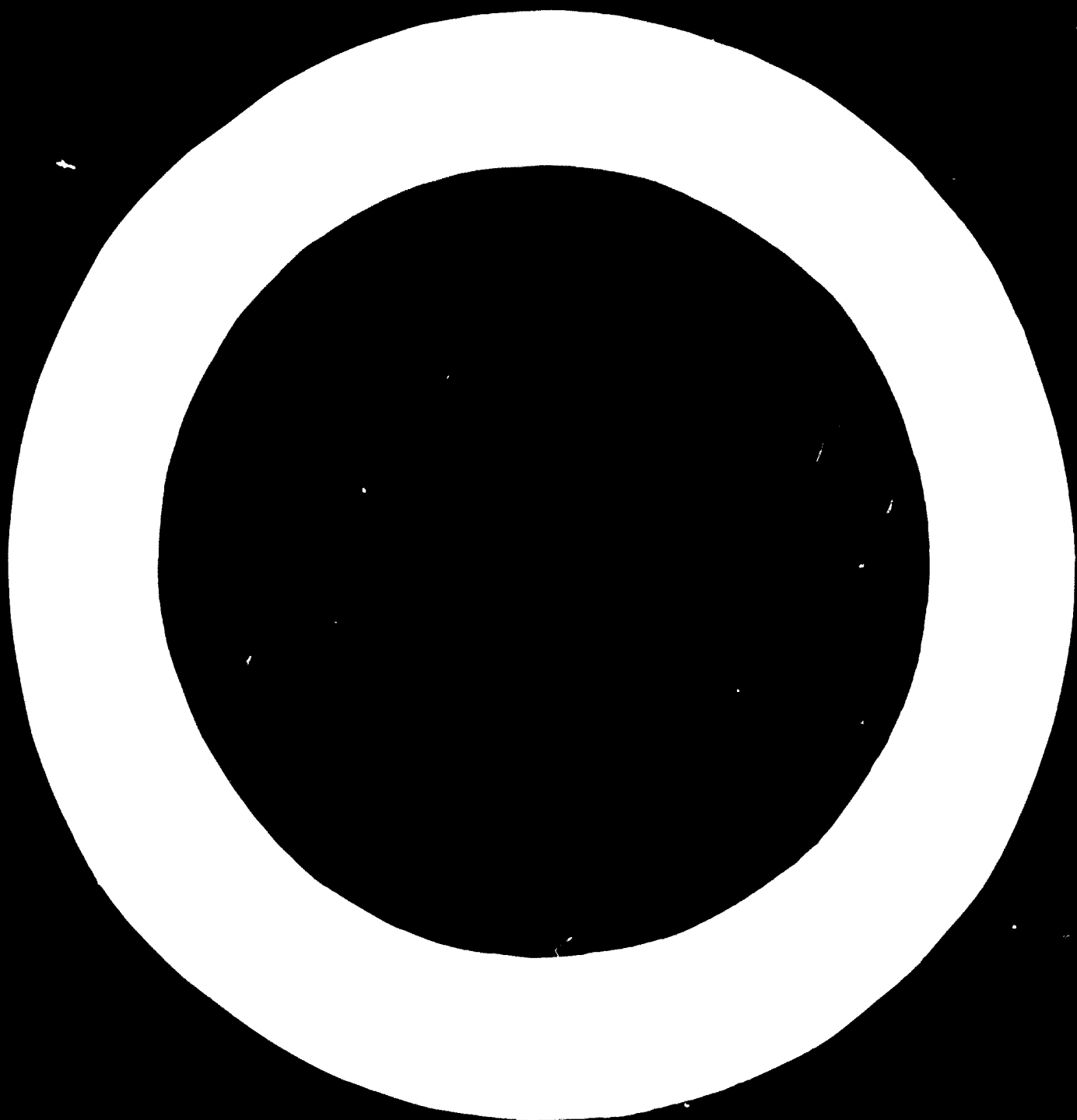


Fig. 9. Stress () - strain () curve for the wet filament yarn after its soaking in water for 10 minutes.
 РИС. 9 Кривая напряжения (AG) - деформации (ε) для влажной пряжи после ее вымачивания в воде в течение 10 минут.

Рис. 8

Рис. 9



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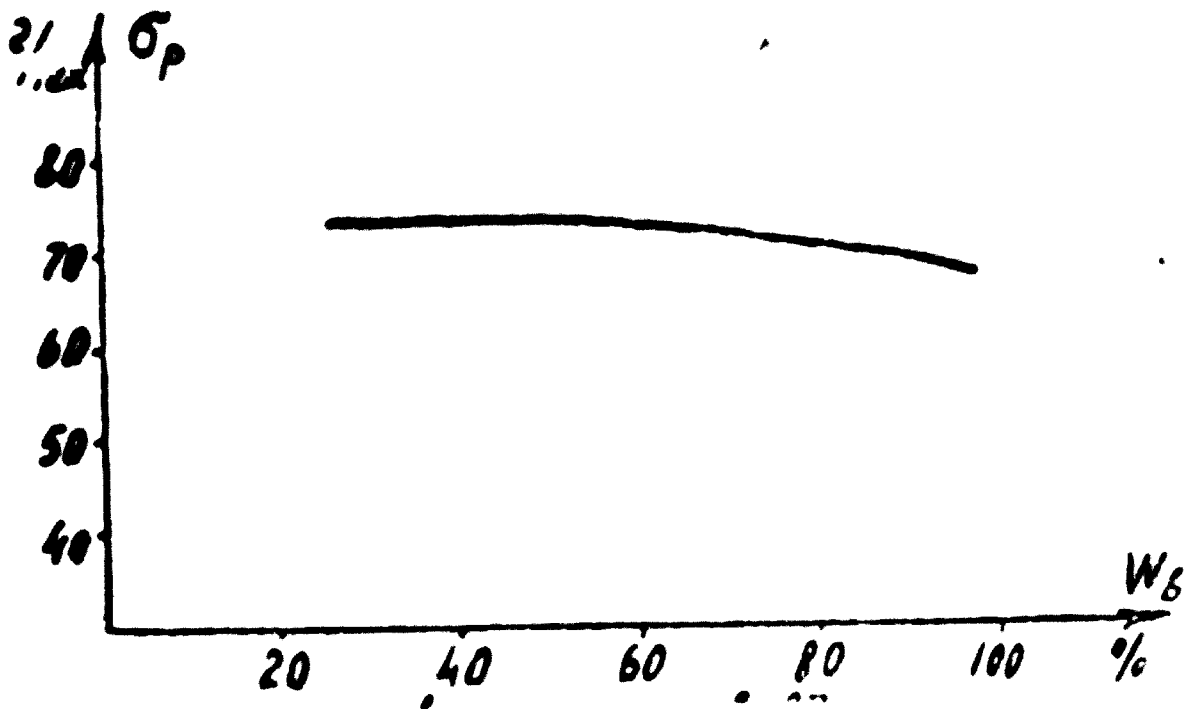


Рис. 10 Изменение разрывной прочности волокон (σ_p) в зависимости от относительной влажности окружающего воздуха (W_b)

Fig. 10 The tensile strength of the filament yarn (σ_p) as a function of the ambient air relative humidity (W_b)





15.

3.

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