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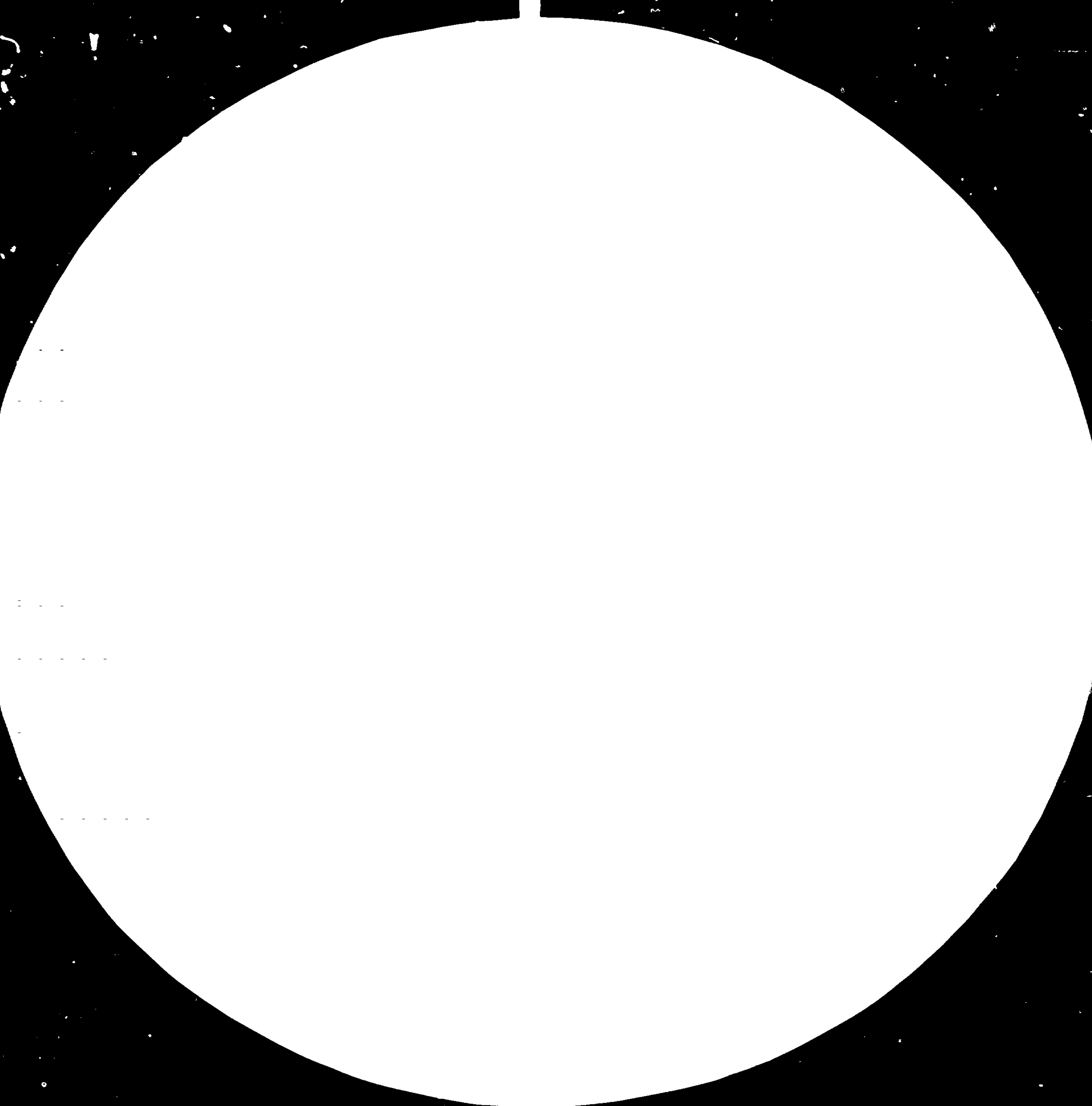
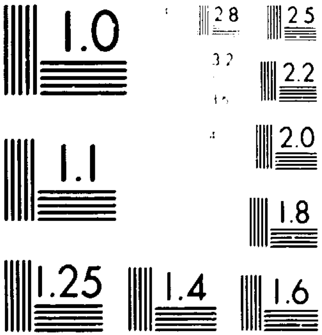
UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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Chemistry and Technology of Cellulosic Staple Fibres and Filaments

Dipl.Ing. Faerbar

Erste Österreichische Glanzstoff-Fabrik AG

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Chemistry and Technology of Cellulosic Staple Fibers and Filaments

The discovery of man-made fibres has made a deep impact on many spheres of human activities and habits. It has significantly changed the material conditions of life. Therefore I may say there is not only the research and the technology we have to discuss but also the raw materials we need now and in the future for this production just as the links which connect the fiber industry with the producers of clothing and even with the ultimate consumer.

The increasing population and the steady improvement in the standards of living have greatly increased the demand for clothing and for better clothing at that.

In the past we can observe four distinct phases in the development of man-made fibres.

The early years of this century saw the discovery and the technical development of the regenerated cellulosic fibres, of which the most important become viscose, acetate and cuprammonium. The most amazing aspect of this development is that it took place in the absence of any exact knowledge of the structure of the cellulose. In spite of this, the growing acceptance of rayon fibres by the textile industry and by the consumer assumed considerable economic importance.

The second phase, the great leap forward was initiated like so many other technical advances by a pure fundamental research. In the 192o's X-ray analysis unravelled the chain-molecular concept of fibres structure. Up to that time it had not even been accepted the cellulose was a chain-molecule; much less how it was put together to form fibres.

Once it was established that the science of fibres was part of polymers, research into the posibility of building chain-molecules begans. It soon achieved its first spectacular success. The synthesis of polyamids, and the development of fibres from caprolactam, showed that it was possible to produce entirely synthetic fibres.

The third phase began in the 194o's with the application of the newly gained knowledge to the industrial production of nylon, quickly followed by the discovery of many other fibre forming polymers, such as polyesters, acrylics and polyvinyls. Within a few years large factories shot up for the production of the new fibres.

Usually there is a gap of 25 years between the fundamental scientific discovery and its industrial application just as the enjoyment of its results by the consumer. In the case of man-made fibres this gap has been shortened considerably.

In the fourth phase tremendous efforts have been made on perfecting every stage of the fibre forming process. Discoverie of new technique and new applications followed each other in a continous stream.

Some of the discoveries have not only given birth to a wide range of new fibres and yarns. They have profoundly influenced research and technical development in many associated industries.

It is as if science had released a source of great force, which in its way has fertilised many fields and totaly changed our ideas of how fibres can be used and the performance of which they are capable.

In the first place, the chemical industry has been stimulated to search for better ways of producing the wide range of raw materials required. This search has also given considerable stimulus to the petro-chemical industry. Research has led to a better understanding of mechanics of polymerization and easier methods have been disvovered for producing high polymers.

Competition from the newer fibres has induced the producers of the regenerated fibres to improve the quality of their products. The most important result has probably been the progressive improvement in the properties of viscose, but there have been other developments also of great significance.

Regenerated cellulosic fibres, because of their low cost, still account for one third of the worlds total man-made fibre production. The development of polynosics, with their higher modulus when wet and of crosslinked viscose with improved resilience, will help to maintain their high share of fibre consumption. The development of triacetate, a relatively cheap fibre which combines thermoplatic characteristics and drip-dry-easy care properties with silkiness and handle, has led to an amasing revival in the demand for acetate fibres.

Even the producers of the natural fibres have been stimulated by the competition of the man-made fibres to improve the properties of their products. Much of their effort is concentrated with the help of new finishing techniques on producing fabrics which are quick drying and do not crease easily, which do not burn, perish or lose shape, and which require the minimum of attention in weare and after care.

As the experience of the last years shows the political and ecconomical situation can change very quickly. The prices of base materials can rise as high, that the industry cannot afford them or only in diminished quantities. Considering the statment of the Club of Rome the situation will certainly come, that some resoures will cease to exist.

On the contrary the raw material for the cellulosics grows on any place of our surrounding day by day and there will be always places where no other crops but trees can be grown. The planting of trees must be done systematicaly so that a wood of high quality can be harwested for a production of a pulp of uniform quality.

Cellulose is the most abundant naturally occuring polymer in the world. It is composed of β 1,4-D-glucose units and is the chief structural element and major constituent of the cell-walls of trees and other higher plants. Wood and cotton are the major sources of cellulose. It is fount to a lesser degree in bast fibres, straws, grasses and various agricultural residues. Cellulose is the only renewable raw material for man-made fibres. It is biodegradable, in sharp contrast to synthetics which are derived from nonrenewable, non-biodegradable petroleum raw materials.

Cellulosic fibres have a unique moisture absorbing characteristics needed for comfort in textiles; synthetics have not developed to this stage yet.

FIG 2

In the past, cotton represented a substantial portion of the world's total fibre consumption. In recent years, however, this usage has significanthy decreased. At present cotton represents less than 40% of the total fibre consum. Increasing pressure is brought upon cotton-growing land for planting food crops, whereas wood, as I said before, can be grown on land unsuitable for other agricultural crops.

The polymeric polysaccharide fraction of wood accounts for approximately 65-70% and cellulose represents 40-45% . Lignine, an aromatic network polymer, is present in wood in amounts ranging from 25-30%. Pulp yields vary depending on the degree of refining performed in cooking and bleaching. The ultimate objective is to produce chemical cellulose with specific purity containing 90-98% α-cellulose polymer. Native cellulose cannot be separated as is from wood due to at least some depolymerisation which takes place in pulping.

Molecular weight distribution in the final product is controled during cooking and bleaching.

FIG 2

In the case of paper pulps, there are more lower DP components as evidenced by the double peak. The more higher refined tire cord pulp has a single peak indicating more uniform and narrower DP distribution, characteristics which are required for rayon tire yarn manufacture.

Wood fibres usually range from 1-5 mm in length, depending upon wood sources; those from hardwoods are shorter than those from softwoods. Wood fibres can be converted to longer fibres or filaments for instance by the viscose or acetate process.

Rayon is suitable for a broad range of demanding applications, both in 100 % construction or in combination with other fibres. In the textile area, cellulose acetate fibres are used primarily for apparal with an appearance of apparent luxury. A major end use for cellulose acetate fibre is in cigarette filters.

Conversion of cellulose to viscose rayon was first discovered by Cross, Bevan and Beadle in 1892. While a large number of refinements have taken place in the process since its discovery the basic sequence is illustrated in Fig. 3 Pulp, in sheets or slury form, is steeped in sodium hydroxide of 18-19% concentration for a fixed length of time, the liquer drained the resulting alkali-cellulose is set free from the surplin of bye and shredded to permit uniform eccess af air during aging or controled depolymerization, to reduce cellulose chain length. Aged alkali cellulose is reacted with carbonbisulfide to form cellulose xanthogenate which is subsequently dissolved in dilute caustic to make viscose. Unreacted fibres, fibre gels or particles which interfere with the spinning are removed by filtration . The solution is deaerated and held to ripen prior spinning.
In spinning, viscose is extruded through spinnerettes with holes of 40-100 micron in diameter into a bath containing sulfuric acid sodium sulfate and, frequently, zincsulfate or $MgSO_4$ or both. While the viscose process was originally a batch process, it has been streamlined and manufacturing steps are being consolidated so that a continous closed-loop process is now emerging. For instance the SINI-Process invented by Sihtola.

Depending on the spinning conditions employed, rayon fibres with all skin, that is, highly oriented, or all core, with lower orientation can be obtained. Regular rayon fibre has a low degree of molekular orientation and there is evidence of a fibre with low skin to core ratio. In spinning regular rayon, speeds of approximately 100m/min are used, regeneration of the cellulose is rapid, only one spinbath is employed, performing both coagulation and regeneration.

Fig 4 a

Chemical regulation of the rate of regeneration can be obtained by utilising regeneration retardants in the viscose or in the first bath. Organic modifiers such as amines, polyethylene glycols and inorganic salts such as zinksulfate are widely used for this purpose. Formaldehyde can also be added to the viscose or to the spinbath. Organic modifiers delay regeneration by providing an alkaline reserve function. Zink forms a cross link between neighboring xanthate groups. Formaldehyde acts in a dual manner: it reacts with the xanthate groups to form thiomethylene linkages and also thorgh glycosidic hydroxyl group to form methylene cross-links which are much more stable than those formed between two xanthate groups. Thiomethylene bonds are eventualy destroyed during regeneration wheras methylene cross-links become an enherent part of the fibre structure and lead to strength improvement.

In all cases, chemical regeneration retardants permit the use of higher stretch to be applied to the spinning tow while in a plastic gel state. This applied strech represents a combination of jet and godet strech. The former case occurs as a consequence of the higher speed of the godet in relation to the jetting rate. Godet strech occurs between two godets. The stretch coupled with a slow rate of regeneration permits molecular orientation which results in development of strength. Fibre strength properties vary with orientation.

High wet modulus and polynosic rayon fibres are made from high purity pulps at slower spiiningspeed and lower temperatures (30-40°C) in the bath. Regeneration retardants and stretch levels of 100-300 % are employed during the wet spinning. The cumulative effect of these factors gives a quality with high strength due to a high skin/core ratio formed during the regeneration process resulting from crystaline aliguement.

High wet modulus fibres are usually prepared with an initial pulp DP of 900-1000. A typical viscose solution used for spinning such fibres contains 8% Cell., 6% NaOH and 34% CS_2. A stained cross-sectional micrograph of these fibres have a much higher skin/core ratio than regular fibres. The fibres prepared under these conditions have a circular cross-section in contrast to the crenulated surface of regular rayon fibres.

Fig 4 b

In polynosic rayon production, a high initial DP but somewhat lower purity of pulp is generaly used than for HWM rayon. Viscose prepared in this process has a high viscosity of 100-200 bfs. A typical polynosic viscose contains 6% Cell., 3-4% NaOH and 40-55% CS_2. The excess of CS_2 acts as a modifier, slowing down the rate of regeneration and allowing stretch levels as high as 300%. Sometimes small amounts of modifiers are added to the viscose and about 0,1% zink is employed in the coagulation bath. The result is a strong fibre with relatively low elongation which is essentially all skin.

Fig 4 c

Fibre physical properties are shown in the fig.5 Stress-strain curves are significanthy different for each type of fibre. Increasing tenarity generally results in fibres with lower elongation. The area under the stress-strain curve represents fibre toughness. Highest strength properties can be achieved with formaldehyde-cross-linking. This is due, in part, to the exceptionally high stretch levels which can be applied to the fibre during spinning, resulting in a highly oriented, cross-linked fibre with a high skin/core ratio.

Fig 4d

Specialized rayon can be formed by screen extrusion of hydroxyethyl cellulose (HEC) solution into a bath of high activity, HEC production is comparable to viscose manufacturing. The caustic solution of HEC is staple while viscose is not and the product has a higher moisture affinity than rayon. The process for the formation of this fibre is similar to viscose up to and including alkali cellulose formation. At this point, ethylen-oxide is reacted with alkali cellulose which is aged to the required degree of polymerisation and HEC is dissolved in sodium hydroxide. A typical solution contains 9% HEC and 6% NaOH. Fibres produced by the screen extrusion have adequate physical properties and a cross-sectional structure desirable for high water retention. This fibre is less crenulated than regular rayon. Filaments produced by this manner may be converted directly into nonwoven structure. They are free of sulfur, do not require bleaching and have an excellent whitenes. Waste fibres can be reclaimed since they are staple and soluble in dilute alkali. One of the unique properties of these fibres is their high moisture absorbency. Never dried HEC fibres retain 350% water based on fibre weight.

Coming to an end I will introduce to you the Austrian fibre industry, which has at present two man-made fibres enterprises: Chemiefaser Lenzing, producing rayon and acrylic/staple is one of the largest in Europa and Erste Österreichische Glanzstoff producing rayon filament and tyre cord is one of the oldest in Europe.

Austria has always taken an activa part in the development af man-made fibres and in txtile research. The austrian engieer Urban started the austrian rayon industry in 1904 with the foundation of the 1.Österreichische Glanzstoff in St.Pölten.

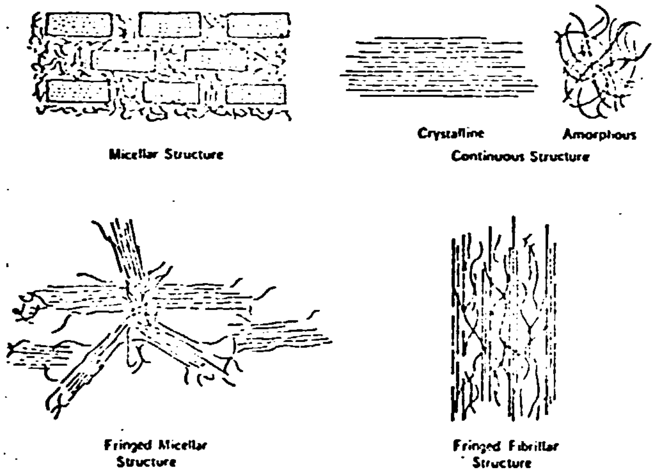
Under the leadership of Mr.Urban and Mr.Fremery at first copperoxide-ammonia-process wa installed and allready 1911 the young company swithed its entire capacity to the new viscose process, 19 years after Cross and Bevan found the posibility to disolve cellulose in combination of Alkali and CS_2.

In the thirties Chemiefaser Lenzing was foundet. Its capacity now is approximately 150 tons of staple fibre daily. Being the only concern of its kin in Austria it is obliged to produce all the types required by the market in all marketable staple lengths and standards. A part of the output is produced as spun dyed fibre which is gaining still increasing importance in the production programms. Two thirds of the production are for export and one third for the home market. Bearing in mind that the domestic textile industry also exports yarn and finished textiles of staple fibre, the total export reach about 85% of the whole output.

It is notworthy that the Lenzing works produce no less than 3,5% of the world output in staple fibre and that Austria ranks nineth among the producing countries of the world.

To resume I think that in spite of the difficulties of the last years the indutries of man-made fibres with its past achievements should still feel justified in loocking forward to the challenge of the future with confidence.

Fig. 1.



Micellar Structure

Crystalline Amorphous

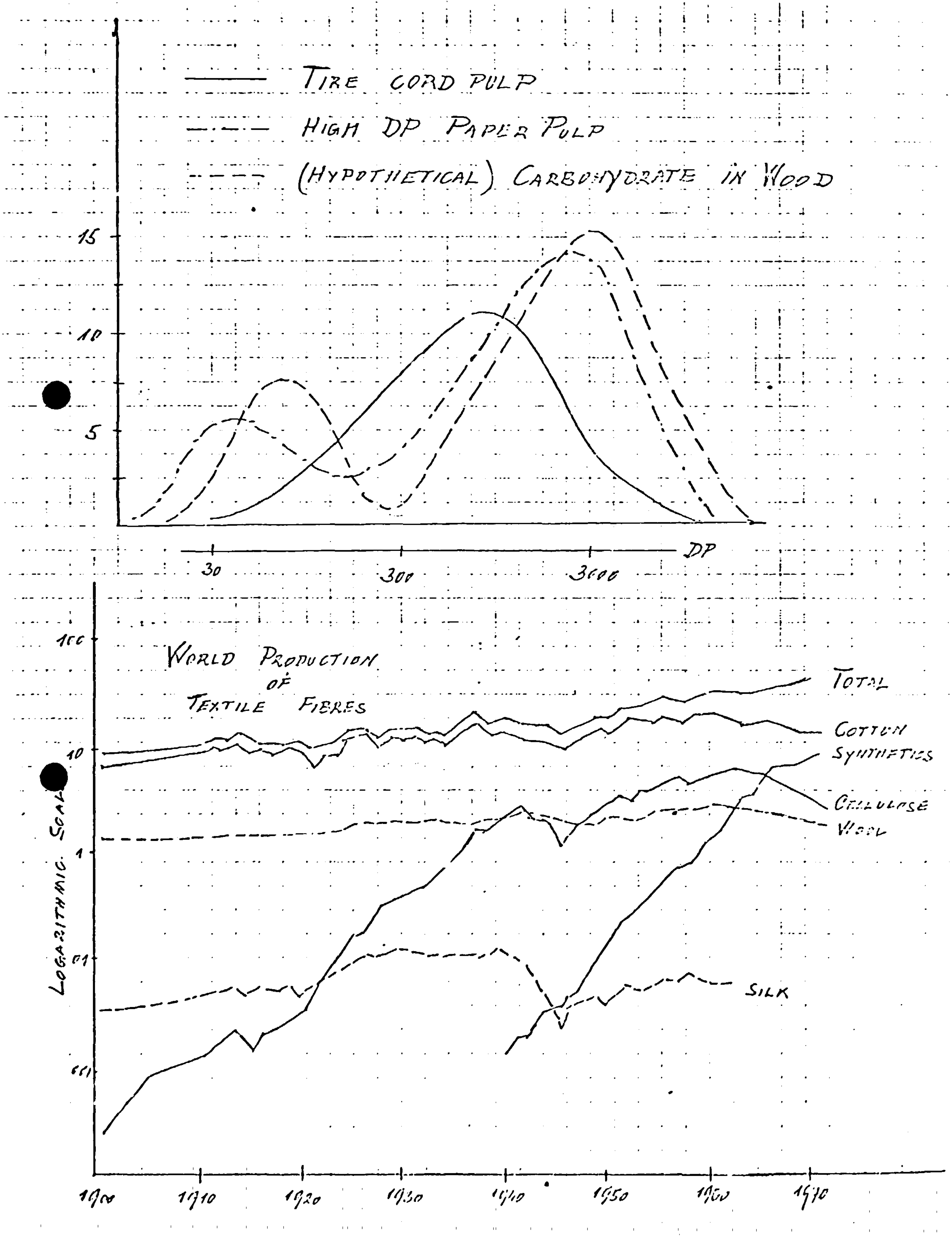
Continuous Structure

Fringed Micellar Structure

Fringed Fibrillar Structure

Abb. 1: Schematische Darstellung verschiedener Theorien von Faserstrukturen

Fig. 2.



TIRE CORD PULP
HIGH DP PAPER PULP
(HYPOTHETICAL) CARBOHYDRATE IN WOOD
15
10
5
30
300
3000
DP
WORLD PRODUCTION OF TEXTILE FIBRES
100
10
1
0.1
0.01
LOGARITHMIC SCALE
TOTAL
COTTON
SYNTHETICS
CELLULOSE
WOOL
SILK
1900
1910
1920
1930
1940
1950
1960
1970

Fig 3

Werdegang des Reyons

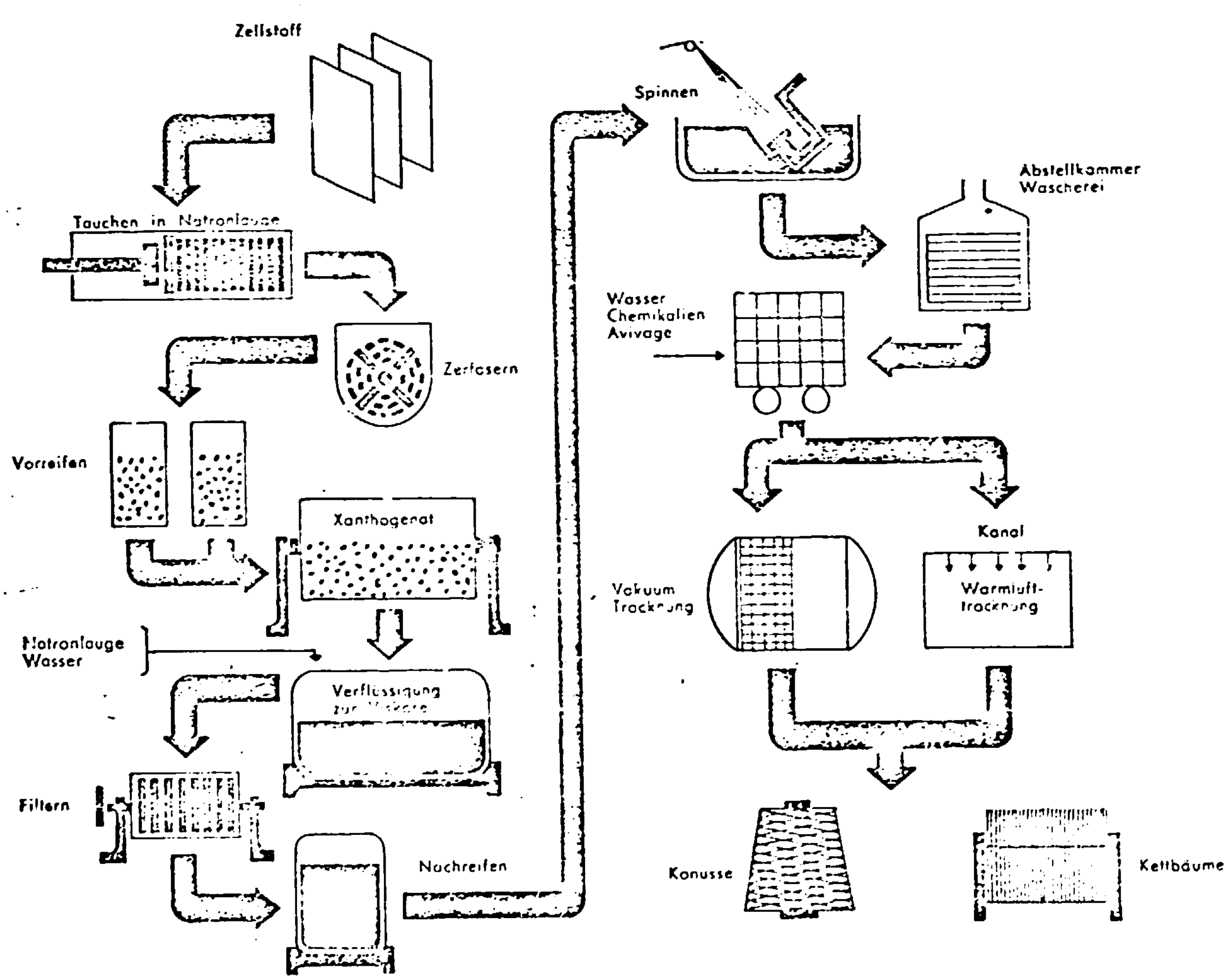
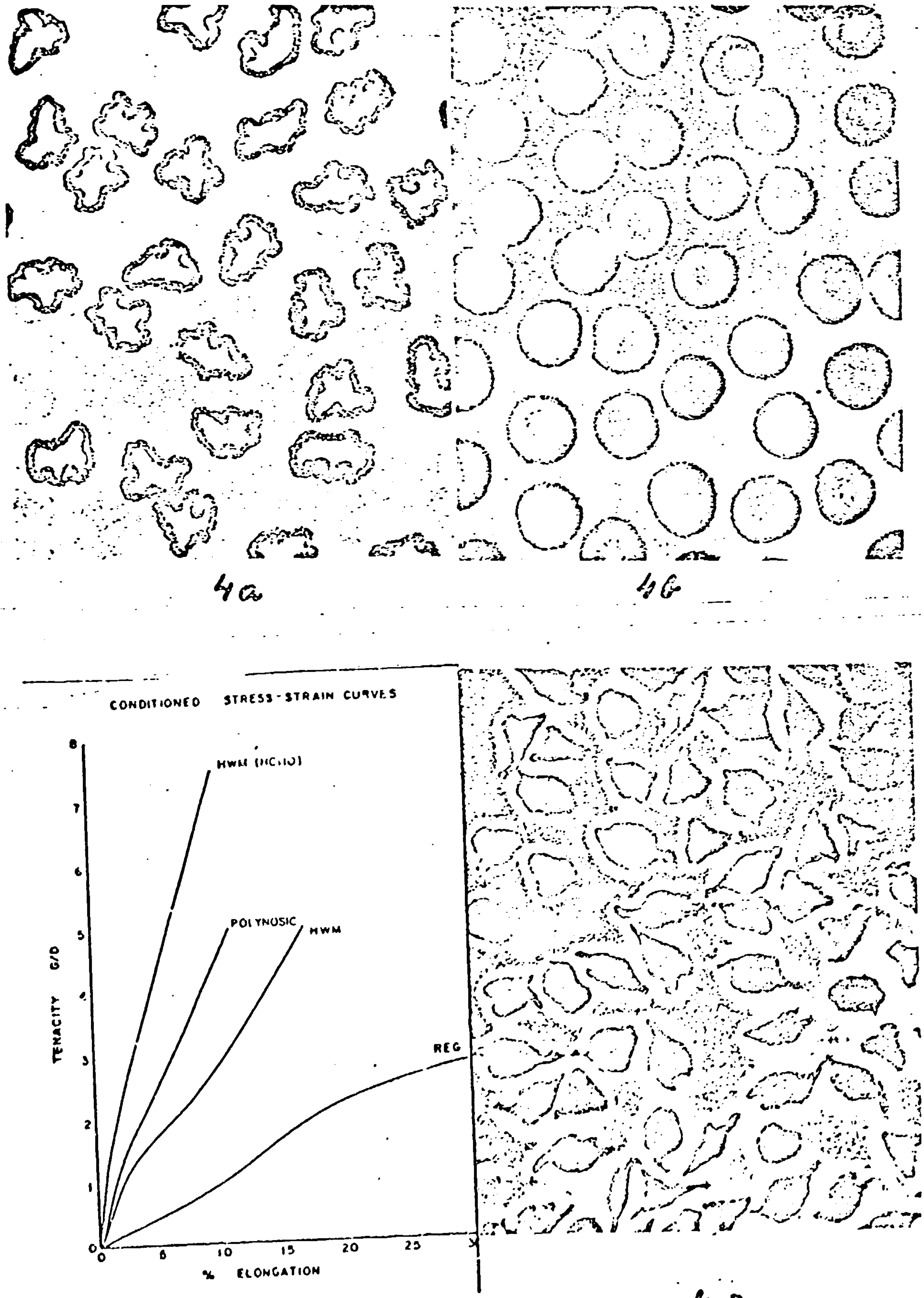


Fig. 4.



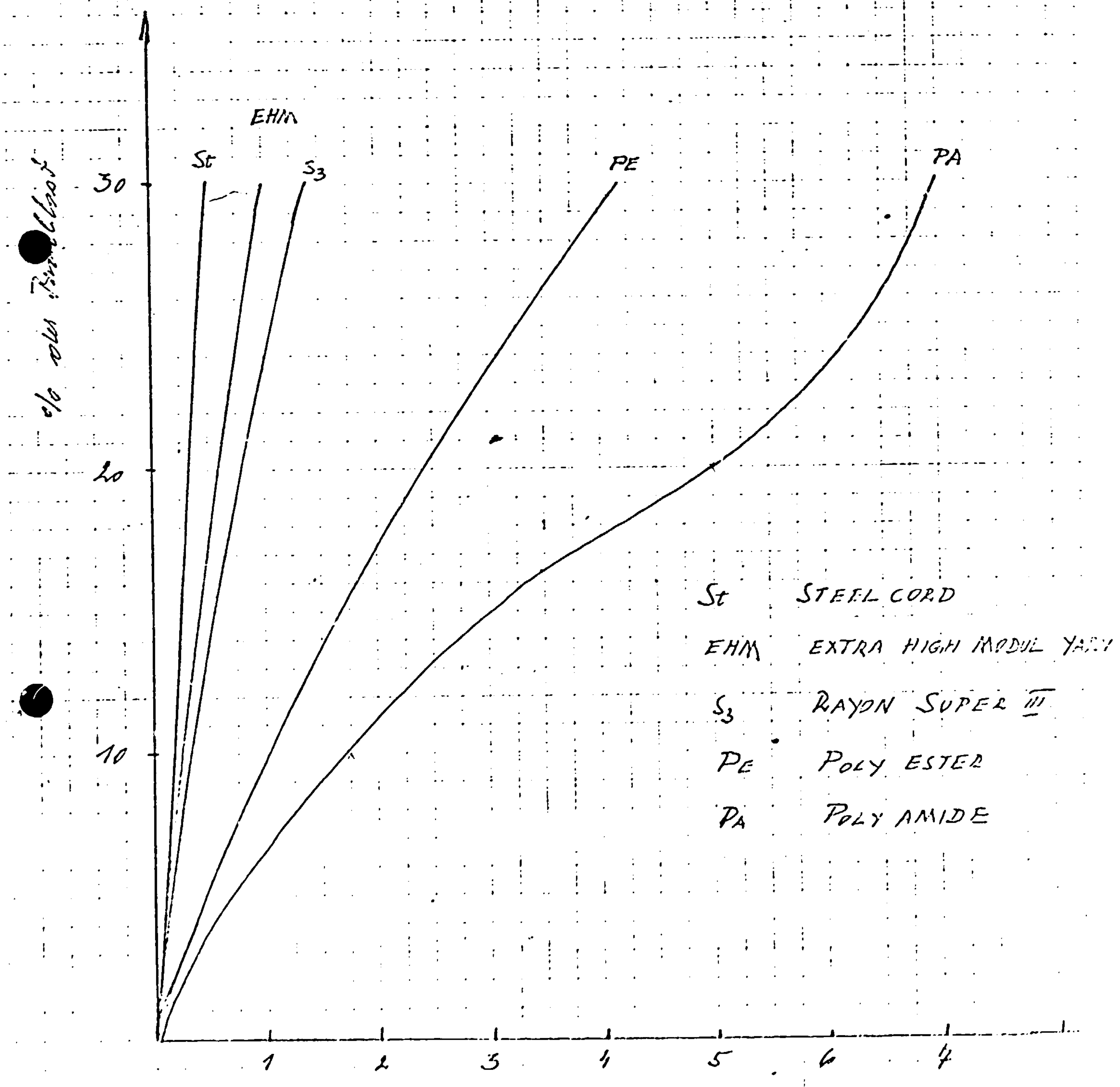
4a

4b

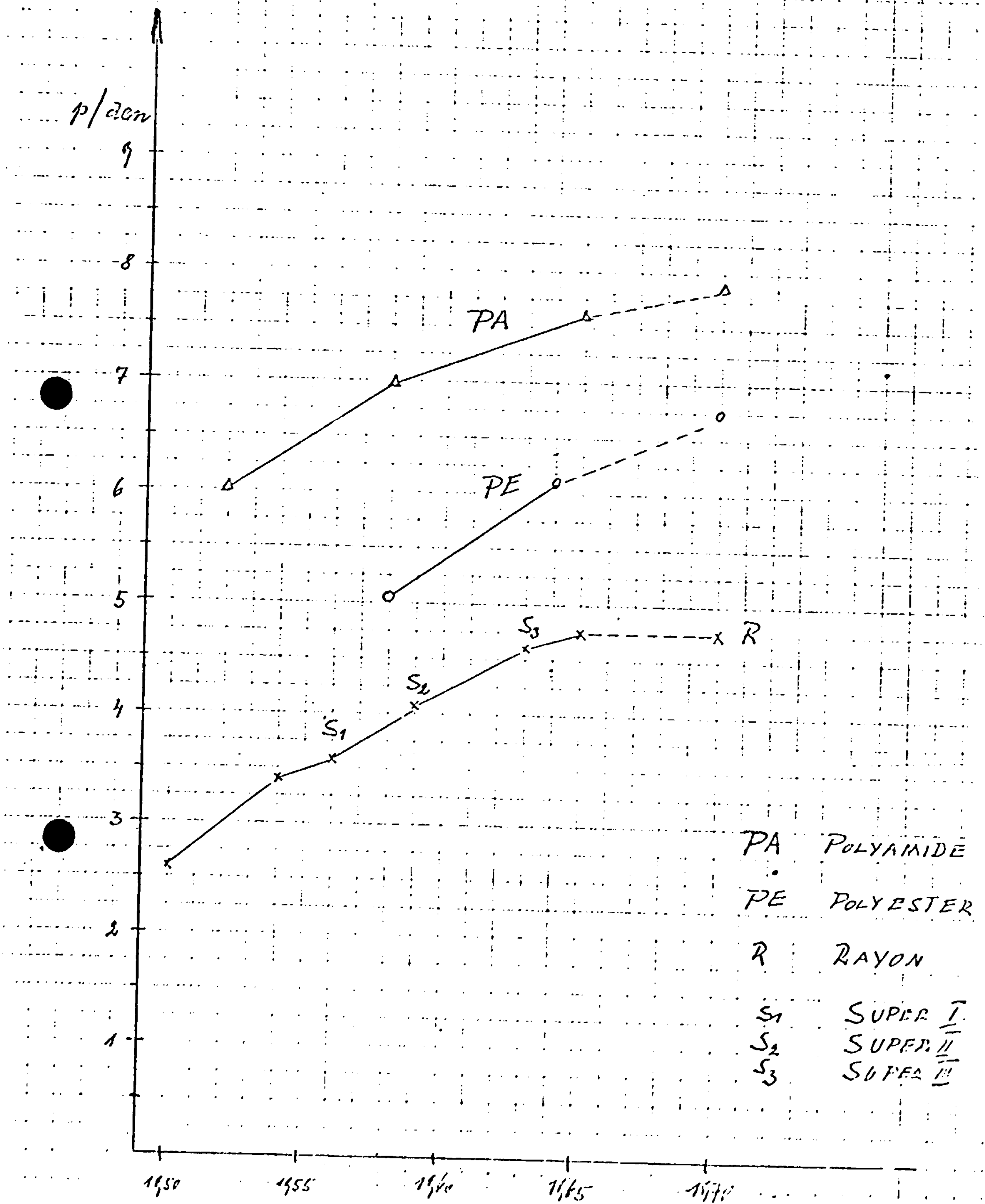
4c

4d

Fig. 3

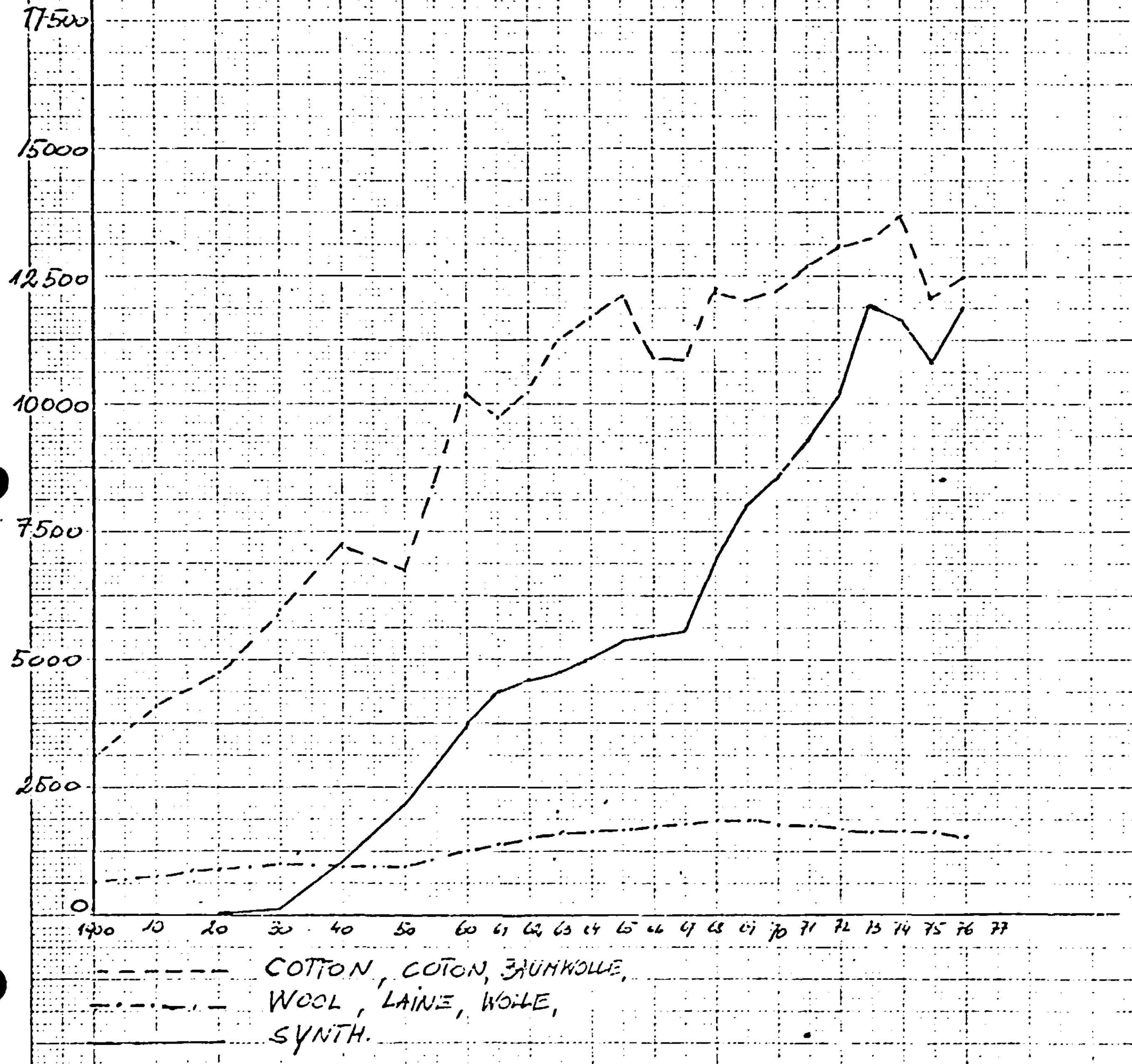


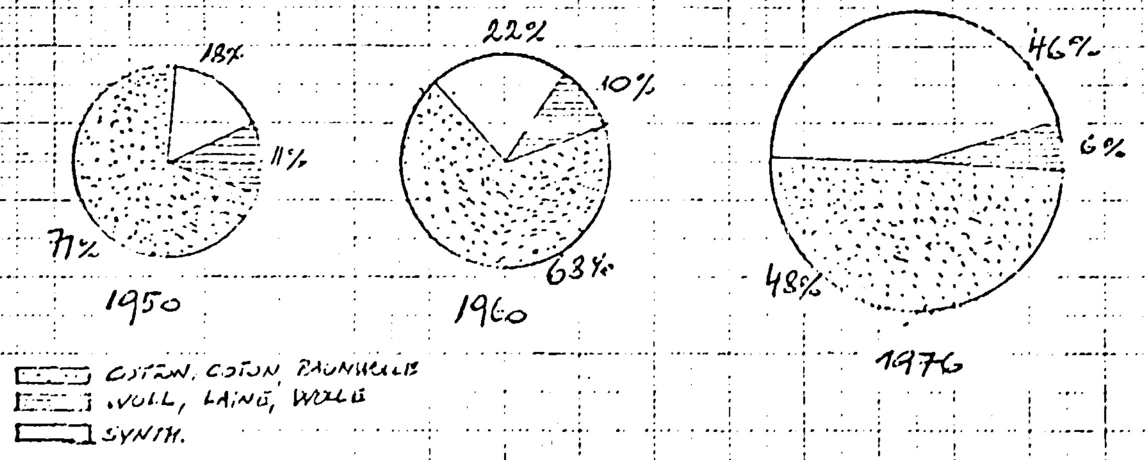
STESS-STRAIN-CURVES
OF CORDMATERIAL USED IN RADIAL TIRES



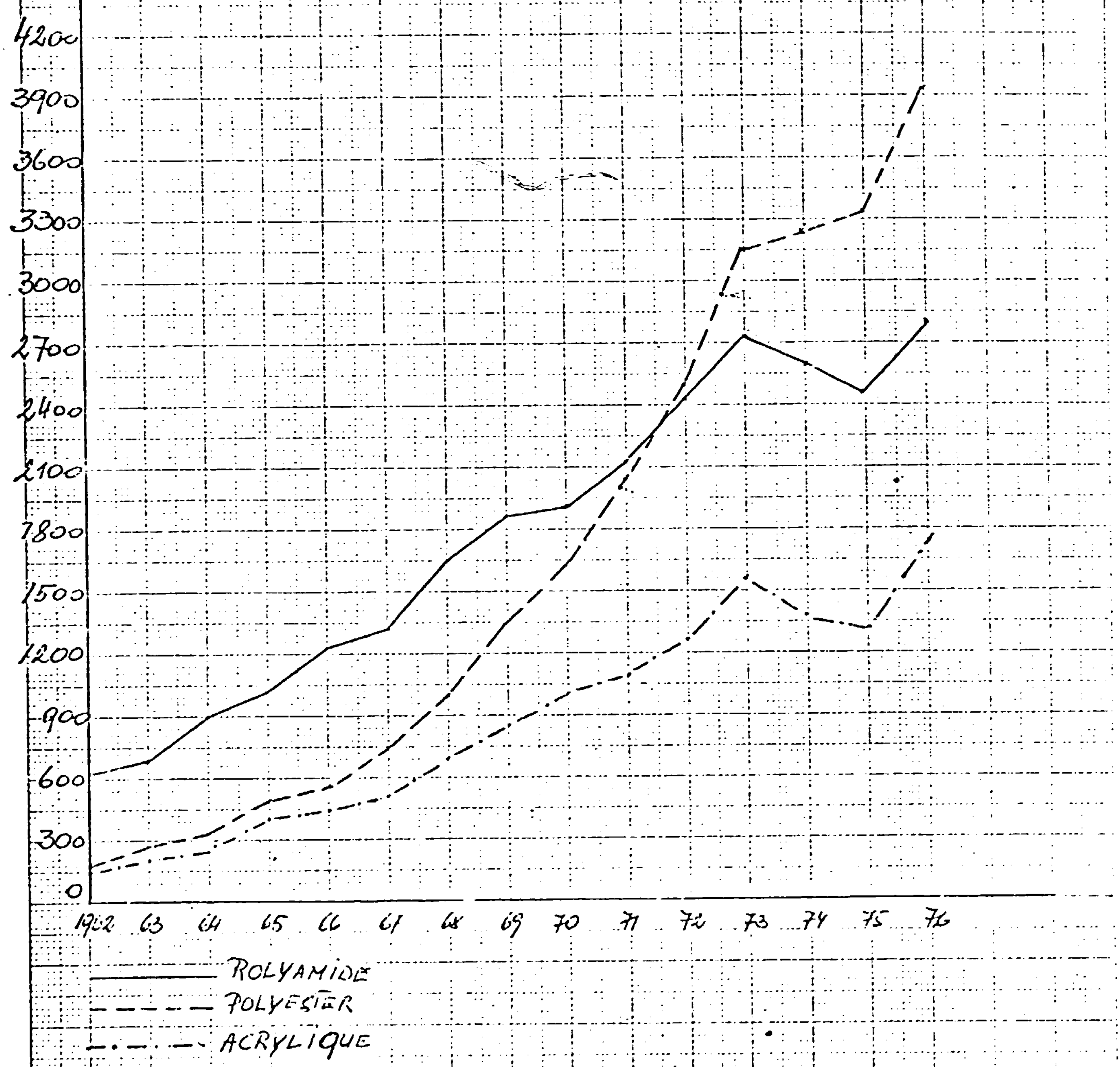
DEVELOPEMENT OF TENACITY OF CORDMATERIALS
IN THE PERIOD FROM 1950 TILL 1970

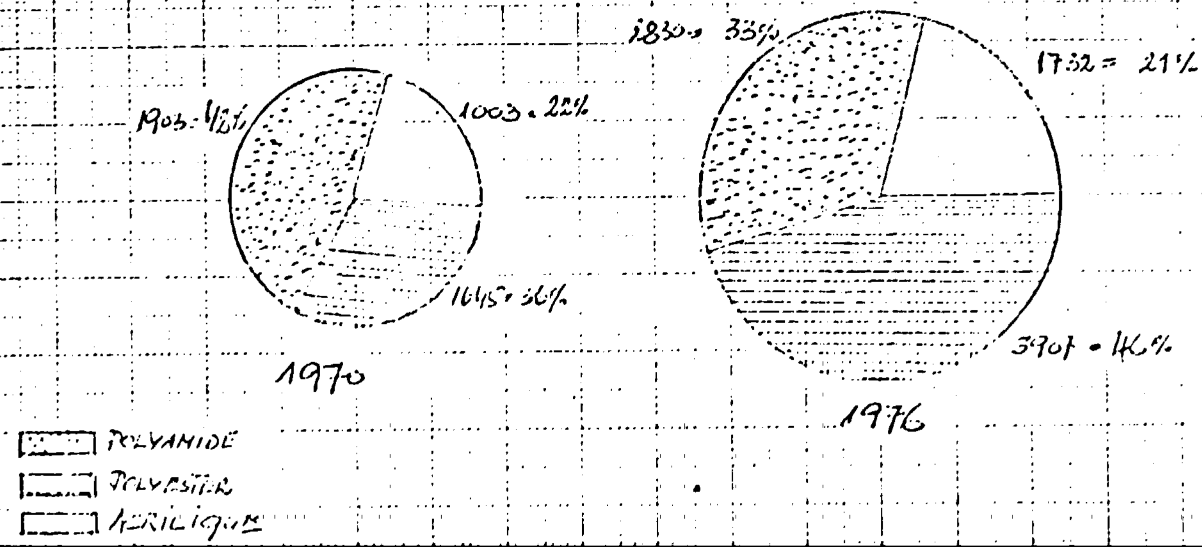
WORLD PRODUCTION OF COTTON, WOOL AND MAN-MADE FIBRES





WORLD PRODUCTION OF SYNTHETIC YARN AND STAPLE





WORLD PRODUCTION OF MAN-MADE FIBRES