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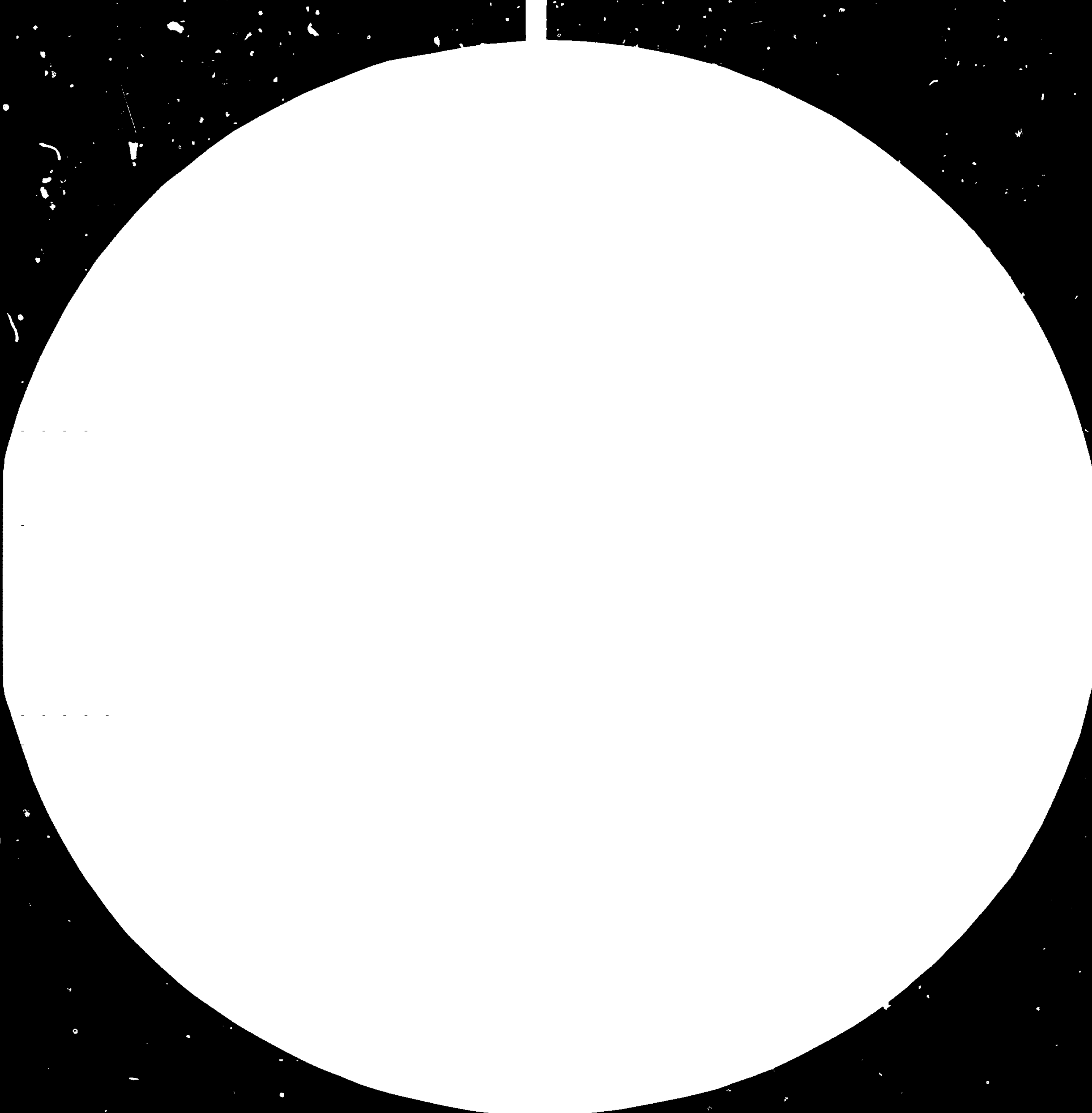

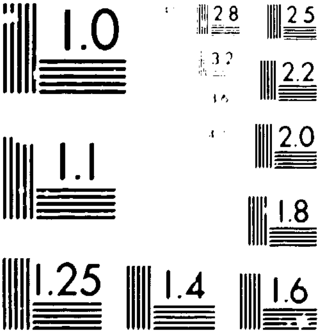
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PRODUCTION OF POLYAMIDE FILAMENTS

by Dr.rer.nat.Dipl-Chem.Hartmut Steffens

(Lecture hold during the Unido Training Programme on Synthetic Fi
in Vienna, 1978)

Summary

Following a short survey of the economic development and the present position of the polyamides on the world market this paper describes the production of polyamide filaments for textile and industrial purposes. Practical uses are dominated by nylon 6 and nylon 6.6 while other variations of this fibre family play a very secondary role. Main emphasis is laid on the practical side of nylon technology. Physical and chemical theories are only included in as far as they are necessary for the general understanding of the production technique.

The starting material ε-caprolactam, a monomer, is generally polymerised in a continuous process to give polyamide 6 while the AH or nylon salt for nylon 6.6 production is polycondensated by discontinuous methods. Addition of stabilisers, dulling agents and other substances has a marked influence on the physical and chemical properties. The polymer chips are flash dried under a protective gas (in the case of polyamide 6 drying is preceded by extraction).

The melt spinning process uses a grid or extruder for the formation of the filaments. This melt may also be enriched with additives such as permanent antistatics. The quality of the final filaments is very much influenced by uniform melting, uniform temperatures from spinneret to spinneret and the shortest possible duration of the molten condition. Further influential factors are cooling conditions for the freshly-spu filaments, constant winding conditions, uniform finish application and moistening, and the proper finish mixture.

The polyamide filaments obtain their well-known strength properties only by a drawing process in which they are - either cold or hot - stretched to about three times their original length. Depending on further processing the filaments are then wound onto pirns or draw-win bobbins. Working techniques and painstaking attention during this operation are decisive for the running properties of the yarns during subsequent processing.

Drawing may be combined with other treatments such as preshrinking, crimping, texturing or the like.

Modern processes combine spinning and drawing in one single operati i.e. by spin-draw-winding or high-speed spinning.

Waste may be depolymerised and re-used similar to reclaimed and reconcentrated monomer by renewed polymerisation and spinning, so that polyamide operations scarcely are a burden on the environment.

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1. Introduction

The production of natural textile fibres requires the use of agricultural acreages, also in the case of wool and silk. In the face of a growing world population acreage available for such agricultural purposes gets ever smaller while at the same time the demand for textile fibres increases. The development of semi-synthetic fibres on the basis of cellulose, initiated early in this century, was the first step towards the solution of a problem emerging at the horizon but this still requires natural resources as a starting material. A true breakthrough was achieved by the invention of the synthetics, of which the polyamides were ones the first to be made and used. The textile filament on the basis of nylon 6.6 was produced in the United States in 1935. The polymerisation and spinning of nylon 6 happened [illegible] the first time in Germany in 1939. Fig. 1 illustrates the increase in textile filament world production since 1900. While production of wool could be increased only by a marginal amount, cotton production shows quite impressive gains. In 1910 we have the first man-made fibres in any mentionable quantities. Production of fully synthetic materials got on stream only after the Second World War and was since then increased by leaps and bounds, and in our days the synthetics almost rival cotton production. But it is not only the world population which shows increases, also per capita consumption has increased enormously as shown by our next illustration (fig.2). The circles re[illegible] per capita demand for textiles. The white area gives the share of synthetics. Today almost half of the textile fibres are synthetic. Fig. 3 gives a breakdown of the synthetics and their share in total textile fibre supplies. In 1962 the cellulosics still provided the lion's share of some 70 per cent, but since then production of viscose yarns was not markedly increased. Meanwhile the amount of polyamide fibres has increased four times and itself has been overtaken by polyester.

Where are these synthetic fibres made? The answer is provided by fig. 4: approximately one third of synthetic fibre production is situated in the United States, a further third in Western Europe, one fifth in Japan while the rest of the world contributes only 13 per cent.

In a previous paper by Dr. Krässig you learned about the chemical composition and nomenclature of the polyamides. Practical use is only being made of polyamides 6 and 6.6, to some limited extent also polyamides 11 and 12 known under the name Rilsan. So we may restrict our considerations to types 6 and 6.6 (fig. 5).

2. Polymerisation

2.1 General

Basically the polyamides are all made according to the same method. assume we have the monomeric starting material. Fig. 6 is an illu of the production stages. The starting material is polymerised or condensated at temperatures between 260 and 290 °C. This may be done either continuously or discontinuously, i.e. in separate batches. resulting polymerisate is extruded in tape or noodle form and quench with cold water, chopped into chips and then ready for the spinning operation proper. The chips are molten again and transported via too gear pumps through the spinnerets. The 260 °C hot melt is exposed stream of cold air, hardened into filament form and is wound on a To distinct it from production methods using a spinning solution method is called melt-spinning. This may look rather simple but there are a number of problems which must be considered. First the molten polyamide is very sensitive to oxygen. All operations must, therefor be carried out in a protective medium. This is generally pure nitro (with an oxigen content of less than 0.003 %), or steam (free of oxy of course). Nylon 6 has certain advantages over nylon 6.6. Its melti point is lower (approx. 220 °C) and it is less sensitive to therm influences so that it may be transported through a piping system in the molten condition. Nylon 6.6, on the other hand, starts melting at 265 °C, is rather sensitive against temperature influences and would form deposits of cracked substances on the walls of the pipe which in the course of time grow in thickness and start releasing small particles which contaminate the melt. These differences and others resulted in quite different production and processing equi and methods.

2.2 Polymerisation of nylon 6

2.21 Handling ε-caprolactam

Let us first look at the production of nylon 6. The starting materi is ε-caprolactam, supplied in bags or drums as white cristals which melt at 68 °C. In melting vessels heated with hot water or steam these cristals are melted under constant stirring at the lo possible temperature of 70 - 80 °C and under a blanket of protecti gas. This process requires 29 kcal of melting heat per kg caprolact The same amount of energy was beforehand extracted by the producer cause the material to change into the solid condition. It is of co much cheaper to cut out solidification altogether and ship the lac as a liquid. The leading lactam producers have therefore switch to heated tanker vehicles which transport the material at a te of about 100°C under a nitrogen blanket by rail or road. They ships for the purpose. At the customer's plant these vessels emptied with the required caution, preferably into a special recei tank (fig. 7). At this stage samples are drawn from the li tested at the laboratory. As the liquid runs out of the tank the volume must be refilled with nitrogen. If testing at the laboratory proves the liquid to comply with the standards it is pumped over to the customer's storage tanks which, like all subsequent vessels, are steam-heated to 90 - 100 °C. Polymerisation of the caprolactam into nylon 6 today is carried out in modern equipment by continuous operation in a so-called VK-column. This method was developed in Germany in 1940.

2.22 Polymerisation kinetics

Before we can look at the technical side of the process we must go back to its chemistry. Caprolactam can be polymerised into polyamide 6 by different methods. We must distinguish between hydrolytic polymerisation, polyaddition, cationic polymerisation and alkaline polymerisation. These different processes show, of course, widely varying kinetics. Their common feature is the production of a certain degree of equilibrium in molecular weight distribution, i.e. the production of a substance not made up of one uniform molecular weight but a wide range of molecules of different sizes. The actual form of distribution depends on quite a number of influential factors. Be it only said that the technical side in this case is a mixture of hydrolytic polymerisation and polyaddition. In the presence of a small amount of water some of the lactam rings are cracked which results in an ε-amino capronic acid. Two of these molecules are able to react with each other so that the amino groups together with the carboxylic groups of another molecule combine into an acid amine. The chain so formed can add on and on. Thus we get a chemical equilibrium between caprolactam, ε-amino capronic acid and water (fig. 10). This is the reaction which cracks up the ring. There is a further equilibrium possible obtained via polycondensation, i.e. the equilibrium between the water content, the acid amide groups, the amino end groups and the carboxylic end groups in the melt. Parallel to this reaction we have polyaddition and this contributes the major share of the chemical reaction. The caprolactam ring fixes itself by its acid amide group to one of the carboxylic end groups and the result is a kind of reamidation. This gives rise to a third equilibrium, namely equilibrium between the free caprolactam and the caprolactam bound by polymerisation. In principle all the amino end groups and all the carboxylic end groups are capable of further reaction. In order to control this process, to limit average molecular weight and to stabilise the melt a stabiliser is added in the form of an acid whose carboxylic groups react with some of the amino groups to produce an acid amide and thus block further growth of the chain. The most common stabilisers are acetic acid and benzoic acid.

Reaction speed and position of the equilibrium depend on temperature (fig. 11). Tables 1 and 2 (fig. 12) show the order of the equilibrium constants and their dependence on temperature; the position of the equilibrium is controlled by the amount of water present during the first stages (fig. 13).

The acid serves not only as a stabiliser but also by dissociation as a catalyst which helps to open the rings and allow the formation of chains. In this way it serves a double function. Fig. 14 illustrates the influence of catalyst concentration on the average degree of polymerisation. The less catalyst we add, the slower is the reaction and the higher the average degree of polymerisation at equilibrium. The amount of catalyst depends on the intended use of the polyamide. A higher degree of polymerisation at a given temperature gives markedly increased melt viscosity and hence worse pumpability, flow and filter processing. For textile purposes the medium ranges of molecular weights are preferred while industrial uses require a higher molecular weight. The equilibria show that apart from the polymer there is also a certain residue of monomer and oligomer present which have lower molecular weights. Their incidence is, of course, also dependent on the working temperatures. At the normal level of 260 °C a monomeric content of 10 - 11 per cent may be expected at equilibrium. This is a serious disadvantage of nylon 6 compared with nylon 6.6, which otherwise shows similar kinetics but has a different position of the equilibrium, and with nylon 6.6 the content of low molecular substance is negligible.

2.23 Practical polymerisation

Let us revert to nylon 6 polymerisation. Before polymerisation a predetermined amount of benzoic or acetic acid is dissolved in the caprolactam (fig. 7). The common ratio is 0.1 - 0.2 mol acid/100 mol caprolactam.

The overriding consideration in all operations is painstaking cleanness. A single alien molecule may cause the reacting chain to crack. In polyamide operations we control polymerisation at a relatively low degree. On the average a molecule chain will be made up of some 200 monomer units. If there were 1 hostile molecule per 200 which causes a chain to break, i.e. 0.5 mol-% of contamination, this would reduce the average molecular weight to 100. Contamination may be caused by volatile bases which mask the carboxylic groups. They can be generated by thermal degradation of the caprolactam and their presence must be closely observed to keep it under 2×10^{-4} mol/mol caprolactam.

The caprolactam plus the stabilising additive is continuously fed to a filter device and the column (fig. 8). These columns may be different in size but they generally measure some 14 m in length to ensure sufficient contact time. Column diameters range between 1 and 1.5 m and their capacities between 5 and 15 tons. Treatment time in the column may be varied in wide limits and depends on temperatures so that one type of column may put through quite different amounts ranging from 5 to some 20 tons per day. The column head is equipped with a heat exchanger which transfers heat rapidly to the caprolactam to increase its temperature to ca. 260 °C. The column must be heated over its entire length with careful temperature control at the different levels. The heating medium is generally diphyl, the azeotropic boiling mixture of diphenyl and diphenyl ether. As a protective medium nitrogen or steam is injected at the head of the column. Together with the benzoic acid and other substances which may be added to the melt for simultaneous polymerisation a certain amount of water is injected. This water helps initiate the formation of chains, but later it must again be removed to allow the predetermined molecular weight to be obtained. The heat transferred from the outside and that generated by chemical reaction cause the mixture in the column head which consists of caprolactam, low molecular weight polymer, water etc. to boil. A distillation device collects and precipitates evaporating caprolactam and redirects it to the melt, thus eliminating most of the water added previously.

At the bottom of the column the nylon 6 polymer is drawn off continuously by pumps and pressed in tape or noodle form through nozzles into a bath of water in order to avoid degradation by the oxygen in the air. Then the material is fed to a cutting machine which chops it into chips or granules. The quality of this cutting operation is governed by uniform size of the granules as the distribution of grain sizes in turn governs the flowing properties of the granules. Improper cutting may produce uneven surfaces which rub together so that dust may be chafed off which deposits during subsequent operations, contaminates the material and disturbs the process, particularly during spinning.

2.24 Extraction of low molecular matter

Following the cutting operation the granules must be freed from monomers and oligomers. This operation may be carried out either in batches or in a continuous process. The chips are filled into an extractor where a counterstream of hot water washes out low molecular matter. Afterwards the chips are dried, also continuously or discontinuously.

It stands to reason that the extract is concentrated up to 60 - 70 per cent by evaporation of the water and later on recycled.

2.25 Additives

Before we turn to the further steps of polyamide filament production we should consider the problem of additives. Caprolactam filaments are highly brilliant and transparent. Textiles, on the other hand, are preferred to have good coverage - also in thin layers - and a brilliant sheen is allowed only in special cases. This means: the polymer must be enriched with a dulling agent. Titanium dioxide is the additive. It gives good coverage and a fine degree of white, it is highly reflective, chemically neutral, will not wash out and is fast to light. The chemical industry offers titanium dioxide in many different types. For the manufacture of textile filaments the material must be chemically pure, have uniform particle size in the lower size ranges and be readily dispersable. TiO_2 is offered in two modified versions: Anatas and Rutil. Rutil is prone to yellowing but softer than Anatas whose hardness may cause the filaments to cut into guides and pins. The amount of dulling agent added to the melt depends on the intended end-use and we have semidull, dull and deep-dull yarns with a TiO_2 content of between 0 and 2 per cent.

Other yarn properties, too, may be influenced and controlled by additives. These include light stability and thermal stability. The action of light causes damage to the polyamide filaments, particularly in the presence of TiO_2. Their strength is reduced, they become brittle and yellow. Stabilisers are selected among inorganic and organic compounds. The most popular agent contains mangan ions, sometimes copper is also used. Since ions may wash out in the course of time, further additives are used to prevent loss of ions during washing. All these auxiliaries are added to the caprolactam before polymerisation either by injection into the column head or during preparing batches.

The amount added of each substance depends on the intended end-use of the yarn. Carpet or upholstery yarns for instance must have much better light stability than clothing textiles. There are, moreover, still other additives such as dyes. Another possibility is to dye the chips after extraction, and this process is often used. The prime requirement is the use of dyes which resist temperature degradation encountered during spinning.

2.26 Drying of the chips

Before the granules are used for spinning they require careful drying. In our earlier consideration of chemical equilibria we learned that water acts as a catalyst. When the chips are melted during the subsequent spinning operation the equilibrium reached at an earlier stage might be disturbed. Although this cannot be prevented altogether it can be controlled within narrow limits by elimination of residual moisture from the chips. This can again be achieved by continuous or discontinuous methods. Modern plants use continuous processes (fig. 9). Emerging from the extraction column the chips are continuously fed to a drier where residual water is removed; when they leave the drier the moisture content is much below 1 per cent and in most cases below 0.1 per cent. Drying temperature varies between 120 and 160 °C and is coupled with a certain extent of post-polymerisation. The drying medium may be a neutral gas, preferably nitrogen, but also superheated steam. The drying medium is recirculated and freed from dust and water and re-heated to the required temperature. Finally the chips are cooled to room temperature and filled into a storage tank.

2.3 Polycondensation of nylon 6.6

Polycondensation of nylon 6.6 is a very similar process. The chemical equilibrium is governed by similar considerations. The starting material in this case is nylon salt, the salt of adipic acid and hexamethylene diamine. Unlike nylon 6 nylon 6.6 is always made by discontinuous condensation in autoclaves. The nylon salt is melted, enriched with the required amounts of water and stabiliser or catalyst and heated in the autoclave under a protective gas blanket for 1 1/2 hours to 220 °C; this results in a steam pressure of some 23 - 25 atmospheres. Over the next two hours the temperature is slowly raised to 275 °C and held at this point while steam is drawn off. Then pressure inside the vessel is slowly reduced to 1 atmosphere gauge and maintained at this level for a further half hour

while most of the water is removed from the melt. The autoclave is emptied by creating nitrogen overpressure and pumping off of the melt. Again the melt is formed into tapes or noodles by pressing through nozzles into a water bath and cut or broken into small pieces. And again the nitrogen must be of high purity as discussed earlier in connection with nylon 6.
As the monomer content of polyamide 6.6 is very low the extraction process can be eliminated. Drying is then carried out much as described for nylon 6.

3. Spinning

The invention of the polyamides was coupled with the invention of a spinning process not known before, the melt spinning method. A number of spinning machines was devised, all based on a common principle. First we need means to melt the granules under as mild conditions as possible (fig. 15), followed by spinning pumps and spinnerets which shape the filaments. Then comes a range where the freshly spun filaments are cooled and finally means to wind them up on spools.

3.1 Grid spinning

Among the many melting devices developed in the course of time the grid and the extruder have gained a prominent position. The grid is formed by a row of parallel hollow rods heated from the inside by a fluid medium, generally diphyl. The polymer granules are poured onto the grid and the melt drops off and flows in the direction of the pumps (fig. 16). As with the viscose spinning process the paramount condition for uniform yarn formation is uniform dosing of the melt. The melt being a very highly viscous substance with a viscosity of between 1500 to 2000 poise, dosing is achieved via tooth-wheel pumps (fig. 17). Dosing should be uniform from point to point and precision of the pumps is a prime requirement (fig. 18). To ensure constant working conditions at the pump pressure just before that point must be held at a sufficient and uniform level. This is done by arranging a pressure pump before the metering pump which works after the same principle.

3.2 Extruder spinning

Grid spinning is progressively being replaced by extruder spinning (fig. 19). There are different systems but the general principle is the single screw extruder in which the screw is situated either horizontally or vertically (fig. 20). The chips are drawn from a storage bunker where they are stored under a protective gas blanket and enter the feeder zone of the extruder. At this point begins the process of melting and consolidation of the mass into a melt free from gas bubbles. The greater part of the melting heat is obtained by friction in the second section of the extruder screw (fig. 21).

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It goes without saying that the extruder is also heated from the outside, as ordinarily used in injection moulding. However the amount of heat introduced in this way is only a fraction of the total amount of heat needed. The third and final section of the extruder screw called metering zone works as forwarding organ. In extruder spinning the pressure pump may therefore be eliminated. The screw supplies the melt at a pressure of some 50 - 150 atmospheres gauge to the dosing pump, this one, metering by each revolution of the tooth-wheels, presses exactly the same amount of melt into the spinneret against a pressure of between 150 and 250 atmospheres. Maximum tolerances in the amount of melt dosed and forwarded by the pump are limited to less than 0.5 per cent. This can only be safeguarded if not only the spinning pumps are highly precise but also the driving gear and the turning speed of the motor drive. Another important condition is a constant temperature level. In the case of nylon 6 spinning temperatures range around 260 °C, in the case of nylon 6.6 around 280 °C. Pipes, pumps and spinnerets must all be held at this temperature level (fig. 22). Moreover temperatures must be uniform from pump to pump and spinneret to spinneret. If several extruders are used to spin yarns of the same titre and if the yarn is to be combined in later operations into one fabric, then all the spinning points supplied by these extruders must be held at the same temperature. Variations should not be larger than 1 - 2 °C, and this condition is not easily fulfilled. Larger variations result in visible differences in dyestuff affinity and are only detected while finishing after the yarn having been processed into knitted fabrics. But even if the temperature is held constant differences may still develop inside the pipes between the inner and outer regions of the stream, that can lead to unevenness in dyestuff affinity. And finally such unevenness may result from different speed of the melt. It is therefore necessary that the path of the melt be of equal length. The changes in dyestuff affinity are caused by post-polymerisation of the polyamide in the molten condition which cannot be totally suppressed. The molecules react with each other, the average degree of polymerisation increases and in the case of polyamide 6 we find newly created monomeric caprolactam. The extract, in a previous stage of production diminished to about 1 per cent increases to 2 - 4 per cent in the time taken by the melt to flow to the spinneret (fig. 23). Everything should therefore be done to keep post-polymerisation as low as possible and on equal levels. This is one of the main advantages of extruder spinning equipment.

3.3 Melt filtration and spinneret

Before the melt is pressed through the spinneret it is filtered once more. Most careful filtration is one of the basic conditions to get a sufficient yarn cleanness, i.e. the avoidance of single filament breaks during subsequent processing. As the single filaments are very fine indeed the slightest contamination may give rise to breaks. Such contaminations need not necessarily be foreign matter but also gel particles, small particles of unmolten matter or particles damaged by oxygen or heat. These particles will cause little neps in the filament calles spin flexes, followed by a neck in the filament

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cross-section. At this point the filament breaks under processing loads. Filtration therefore requires utmost care and many different apparatus were devised for the purpose. Some producers press the polyamide melt through sand filters, consisting in shifts of different granular size, others use wire screens with 10 - 20,000 meshes/cm^2. Latest developments include sinter metal filters.

The spinneret plate has as many holes as the yarn has single filaments. The holes have diameters of between 200 and 500 µm.

3.4 Formation and winding-up of the filaments

As it passes the holes of the spinneret and is formed into thin streams the freshly spun yarn is cooled down in an airstream. Again care should be taken to have uniform conditions at all spinning points. The airstream should show as few disturbances as possible, cause as little movement in the yarn as possible and move in an uniform stream along the filament. Room temperature is reached during the last part of the blowbox where the yarn is allowed to fall freely to the point where it is wound onto spools. During this part of the yarn path the filaments should be guarded against contact with other bodies to avoid premature damage. Before the yarn is allowed to touch upon another surface it receives a protective finish. It then passes over godets and reaches the take-up spool.

Modern winding speeds range between 1,000 and 1,500 m/min for nylon 6 while nylon 6.6 is generally wound up at speeds of less than 1,000 m. Extrusion of the melt through the spinneret is only a fraction of the winding speed. On its way from the spinneret to the take-up roll the filament undergoes drastic changes which have a deepreaching influence on its final processing properties and physical characteristics.

The difference between extrusion speed at the spinneret and the winding speed at the spool governs the titre of the resulting yarn. It is therefore necessary to carry out spooling and drawing-off via the godets with at least the same amount of precision as the forwarding of the melt through the spinning pumps (fig. 24).

As the winding-up speed is about 30 - 50 times higher than the exit speed of the melt, the yarn as it coagulates is subjected to high tension loads. These forces act especially at those places where the yarn is still relatively plastic and exert decisive influences on the orientation of the molecules parallel to the filament axis which increases cristallisation. Close control of this process is instrumental in obtaining good drawing properties.

Winding devices have been developed in many types and shapes. In [illegible] the yarn passes one or two godets which apply a spin finish, then [illegible] a pair of take-up godets which forward the yarn to the winding [illegible]. Uniform taking-up speed is obtained by friction-driving of the [illegible]. One winding arrangement may take up as many as 4 spinning spools and wind up 4 threads in one operation (fig. 25 and 26). The yarn package is built up by a traverse motion of thread guides or grooved rollers at a traverse speed of 200 - [illegible] cycles/min.

Each spool receives up to 10 or more kg of yarn.

3.5 Spin-finish

The spin-finish applied to the yarn at this stage serves several purposes. It protects the yarn against damage by yarn guides, godets a.s.o., at the same time protecting these devices against damage by the yarn. It is easily understood that a yarn containing such hard particles as TiO_2 is liable to cut into a surface over which it is drawn at high speed over long periods of time. Therefore the yarn requires smoothing, and this is generally achieved by application of a mineral oil. Textile yarns being poor electric conducters they tend to generate static charges through friction against other bodies. and that may severely disturb later operations. For this reason an antistatic is added to the spin-finish. On the other hand this finish must be easily removable in subsequent operations. This requires addition of a wetting agent which facilitates emulsifying of the oil in the securing treatment. And all these various substances must be compatible with each other and must be easily applied. The mixture must have low viscosity to reduce yarn friction, it must also be of low volatility in order not to evaporate too quickly from the large surface. These are requirements many of which are contradictory and difficult to harmonise.

Up to a general degree polyamide is a hygroscopic substance which tends to establish equilibrium with the moisture content of its ambient medium. Water imbibition results in a certain swelling of the yarn, and moreover the water acts as a cristallisation catalyst on the molecules which form the material. As these are mainly arranged in a parallel direction to the fibre axis and as cristallisation further promotes this parallel orientation, water imbibition results in some lengthening of the yarn. This in turn may weaken package stability. In order to wind large yarn packages such yarn growth must be avoided. For this purpose two ways are used. A certain amount of water is applied to the yarn to allow absorption and growth before the yarn is taken up on the spool. Moistening of the yarn can be carried out with the help of a wetting godet or, as is the general practice now, by applying the spin-finish in form of an aqueous emulsion. Care should however be taken to remove excess water from the yarn surface before the outer wrap on the package is covered by the next yarn layer. This may be achieved by keeping relative humidity in the spooling area so low that rapid evaporation takes place. The atmospheric conditions in the spooling area are one of the limiting factors on spinning speed.

3.6 Spin-breaks

It sometimes may happen that the thread breaks while it is spun. Frequency of this incident is a pointer to quality. Spin-breaks may occur for many reasons and in each case the causes must be carefully traced.

First we distinguish between true breaks occurring near the spinneret, and so-called winding breaks. Spin-breaks may occur if the interfacial relationship between polyamide melt and spinneret surface is disturbed, i.e. when the polyamide tends to wet the spinneret surface.

A corrective measure is the treatment of the spinneret surface with a hydrophobic agent such as spray-on silicone. This protective layer must be renewed from time to time, and with great care. Residual melt and soil must be carefully removed from the spinneret surface before the new silicone film is applied. Winding breaks may be caused by damaged yarn guides, insufficient finish application, spin-flexes in the freshly spun yarn etc.

It should also be emphasised that the processing properties of the yarn in subsequent stages are very much dependent on the careful handling of the spin-spools during doffing.

4. Draw-twisting

4.1 General

As it comes from the spinning machine the yarn is not yet ready for textile purposes. It requires drawing to obtain its desirable textile properties. Depending on the end-use the yarn is stretched to 2.5 - 5 times its initial length whereby yarn thickness is proportionally reduced. Such reduction in yarn thickness is no gradual process but results from the rather sudden formation of a neck in the yarn at a certain point which moves over the length of the yarn. At this point heat is generated which allows greater mobility of the molecules to arrange themselves parallel to the fibre axis (fig. 23) which results in a marked increase in fibre strength. In terms of textile characteristics this gives an increase in breaking strength while elongation at break is reduced. Proper selection of the drawing ratio is a decisive factor for the quality of the finished article. For textile uses a drawing ration of about 1 : 3 is preferred as further textile processing applies loads which require a certain degree of elasticity in the yarn. For industrial uses a higher ratio of 1 : 5 is generally used as strength in this case is a more important consideration than elongation.

4.2 Ambient conditions and running properties

In the spinning room the yarn packages must be relatively hard to give sufficient stability for high-speed winding. Feeding to the drawing machine, however, requires easy unwinding properties and hence a soft package. This is obtained by exploiting the hygroscopicity of the polyamide, i.e. by exposing the spools before drawing to an atmosphere of higher humidity. While spooling was done at 30 - 40 per cent rel. humidity, conditioning is carried out at 60 - 70 per cent rel. hum. for several hours. During this period the yarn absorbs moisture which causes swelling, more cristallisation and hence some lengthening of the yarn, resulting in a softer yarn package. The yarn is then unwound overhead from the package and fed via tensioning device to the feeder arrangement of the drawing machine. Textile yarns are generally treated on machines equipped with a supply roll/pressure roll arrangement, while aprons and other systems may also be used.

4.3 Drawing

At the feeder arrangement the yarn is fixed by being wrapped 3 - 6 [illegible] around the pressure roll (fig. 28). Then it is led to the drawing [illegible] where another 3 - 6 wraps serve as a second fixing point. The g[illegible] turns at a higher circumferential speed than the feed rolls and [illegible] takes place between these two fixed points. Additional devices [illegible] must help in the process, e.g. by arranging drawing pins beneath [illegible] feed rolls to control the point of stretching (fig. 29). Sometimes it is necessary to heat these pins, especially in the case of de[illegible] of thick capillaries and for high drawing ratios. Drawing speed [illegible] has an influence as higher speeds facilitate the process, probably [illegible] the greater heat which is generated in the yarn. Textile yarns are generally drawn at speeds between 800 and 1300 m/min.

4.4 Taking-up

4.41 Drawing pirns

Most of the draw-twisting machines being offered to the trade are based on the principle of the ring twisting machine where the yarn is wound onto pirns with the help of ring twisting spindles. In the course of time the size of these pirns has increased and now reaches up to 40 - 50 cm for textile yarns, holding packages of 3 kg and [illegible]. From the drawing zone the yarn is passed through the traveller and deposited on the pirn (fig. 28) which is placed on a spindle turning at 7,000 to 10,000 rpm. The traveller is a freely movable attachment to the ring fixed to the rail which moves up and down while depositing the yarn on the package (figs. 30, 31 and 32). It is not easy to describe the winding process in a few simple words. The revolutions of the spindle cause the winding up of the yarn. A balloon is formed during the process which carries the traveller with it. The number of wraps added per minute is a function of the difference between spindle revolutions and traveller revolutions. The traveller reaches quite impressive speeds which depend on the ratio between 10 and [illegible] (fig. 33). Such high speeds cause the traveller to wear off rapidly, and of course the rings too. This places an upper limit on machine speed. Higher traveller speed means higher yarn tension in the balloon. For the first few wraps tension is adjusted to 1 - 2 g and increases with growing package diameter to 10, 12 and more grams. Higher winding tensions on the outer yarn layers as compared with the inner layers [illegible] a serious disadvantage and damage the yarn. In recent times efforts are therefore being made to devise a spindle programming system which reduces the number of spindle revolutions in tune with growing pirn diameter and thus holds yarn tension constant (fig. 34). At the same time traveller speed is also held more or less constant. All these improvements add to the cost of the machine.

Deposition of the thread on the package surface can be varied via changes in the main and side traverse motion of the rail. The speed of the rail may also be varied and there is the possibility of introducing reversed acceleration. In this way a number of different k[illegible] of pirn packages can be wound (figs. 35, 36 and 37). The type of package chosen in each individual case depends on a number of considerations such as unwinding in subsequent warping, texturing etc.

4.42 Draw bobbins

In an effort to achieve higher drawing speeds and larger yarn packages new machines were devised which are very similar in their feeding and drawing parts to the conventional draw-twisting machine. After drawing the yarn is gathered on spools somewhat similar to spinning spools and arranged for friction driving. In this way an X-wound bobbin is produced onto which the yarn is deposited via a slotted drum (fig. 38). This arrangement allows winding of packages between 5 and 12 kg. Drawing speeds range from 1,200 to 2,000 m/min, but in this case the yarn is only wound up and not given any twist.

4.5 Additional processing

Drawing may be combined with other yarn treatments inserted between the drawing zone and the yarn take-up. The yarn may e.g. be heat-set or pre-shrunk by leading it over a heated plate or godet (figs. 39 and 40). The treatment may also include crimping by suitable attachments such as tooth-gears. The filaments may moreover be tangled in a stream of air which gives better adhesion of the single filaments. Adjusting the spindle revolutions and the running speed of the yarn it is possible on the draw-twisting machine to vary the number of turns per metre.

4.6 Yarn breaks during drawing

Drawing can be interrupted by yarn breaks. Their frequency is a decisive pointer to yarn quality. Many faults which arise during warping, knitting and texturing show a direct relationship with the number of breaks during drawing. It is therefore very important that the causes for breaks during drawing be carefully traced and corrected in order to reduce their number. Such causes may be found way back during polymerisation or spinning, e.g. thermal or oxygen degradation of the polymer, contamination, irregular particle size of the dulling agent, improper temperatures during spinning, poor spinning spool build-up, insufficient control of spinning and drawing conditions etc. And there are purely technical shortcomings such as damaged yarn guides on the spinning and drawing machines, wrong type of surface finish on godets and guides etc. Texture and finish of surfaces, the thread runs over, and of the thread itself, both regarded in microscopic scale are very important factors in polyamide yarn production. Quality results depend on a well-chosen balance between grain depth, carrying surface, hardness etc. These must be adjusted to the type of spin-finish which forms an intermediate layer between the surface of the machine element and the yarn.

Attention to the frequency of drawing breaks, their distribution over the feeding, drawing and taking-up sections of the machine cannot be overemphasized. More often than breaking altogether the multifilament yarns suffer single filament breaks, and this happens about 10 times more often than total yarn breaks. In subsequent processes such as warping these lose single filament ends are pushed up the yarn axis when the yarn passes reeds and tension devices and cause yarn breaks at once or later on the knitting machine. The further advanced the treatment during which breaks occur, the more expensive the [illegible] becomes.

When the yarn breaks on the drawing machine the lose end wraps around the machine element immediately before the place of breaking. These wraps led easily to fibre fly which may be caught by other running threads, forming fibre fly-fluffs.This type forms a good [illegible] of the total fluff number. Fly is a very common cause of processing difficulties in subsequent operations. Utmost care and painstaking cleanness are the only remedies against this hazard.

5. Latest developments

The question will arise whether it is not possible to combine various stages of yarn production into one operation in order to get more continuity into the process. Efforts have been and are being made.

5.1 Vacuum extruders

It would be an advantage to be able to spin the polyamide right after polymerisation without the necessity to cool, cut, extract, dry and remelt it. Efforts have repeatedly been made but the main difficulty is the fact that polymerisation in order to give good polymer quality must be carried out continuously over long periods of time under maintained conditions of throughput. Frequent changes in production following changes in demand - o.g. different titres, tonnages etc. - are a big obstacle for the introduction of this principle and it is good practice to build up a buffer amount of chips between the stages of polymerisation and spinning. Where staple fibres are produced things are somewhat different and it is in fact possible to directly spin the polymer. In the case of nylon 6 we still have the problem of extraction. For this purpose machine builders devised the so - called vacuum extruder which is equipped in the melting zone with facilities to expose the polymer to so much underpressure that volatile substances such as monomeric caprolactam and water are removed from the melt. These machines would indeed allow filament yarns to be spun directly without intermediate extracting and drying of the chips. So far, however, this method is only rarely used.

5.2 High-speed spinning and spin-drawing

Another question raised in connection with rationalization efforts was, whether it would be possible to combine the spinning and drawing on one machine thus saving much manuel work. The problem is aggravated by the fact that very high winding-up speeds would be necessary. If the present spinning speed of 1ooo or 12oo is to be maintained, the take-up speed for the stretched yarn would have to be raised to 3 or 4ooo m/min. Several manufacturers are offering take-up devices which are capable of such high-speed operation. The spinning part of the machine, i.e. extruder, spinneret etc.. would remain unchanged. Massive acceleration of the yarn, which leaves the spinneret at a speed of 2o-3o m/min. exerts very high tensional forces which initiate progressive orientation of the molecules at a time when setting of the material has progressed to a high degree of viscosity and elasticity is accordingly reduced. At that point the filament is, however, not yet fully drawn. Post-stretching at a rate of 1:1.5 becomes necessary. This type of high-speed spinning at "medium high speeds"was originally developed for polyester and only later transferred to polyamide because conditions with polyamide are much complicated by the tendency of this material to absorb moisture. A balance must be found between lengthening of the filament due to moisture absortion by the yarn while wound on the spool (whose degree depends on pre-orientation on the one hand) and the shrinking forces in the tensely wound yarn.The [illegible] forces [illegible] influenced by spinning speed, titer, air friction, moisture [illegible]

The take-up devices supply x-wound bobbins with a package weight of up to 3o kg. Filaments from several spinning points can be simultaneously wound and an automatic tail can be provided which allows continuous operations in subsequent processing steps. The latest machine developments even provide for automatic bobbin replacement. Investment requirements are rather high.

In addition to the complicated winding mechanismus the process requires stop motion devices which would automatically cut a broken filament and suck off the free end. Finishes can no longer be applied by rollers but must be precisely dosed by dosing pumps.

The new process not only offers the advantage of doing away with subsequent work (and wage) absorbing separate drawing, it also results in higher spinning output of the machines whose extrusion rate per point and minute would be higher than with regular spinning; and finally power consumption can be cut by some 2o %.

The additional spinning output is, of course, not 4oo % as might be assumed at first glance, but only 25 % depending on the degree of forced pre-orientation. The resulting filament, on the other hand, is more sensitive, the tendency to spinning breaks will increase and still higher demands must be put to the quality of the polymer while the build-up of stable packages with easy unwinding properties will become more difficult.

In view of their relatively high residual elongation these filaments are not suitable for textile processing as flat yarns, e.g. on knitting machines. They would, on the other hand,be well suited for texturing,where the drawing-texturing method allows post-drawing and texturing in one operation. In this area the high-speed spinning method is already beeing widely used.

Regular yarns, however, require to be fully drawn and to get them post-drawing must be effected before winding. This operation must be entrusted to take-off godets which would to be arranged as fixed points, similar to the drawing godets on drawing machines,revolving at a speed differential adjusted to the required drawing ratio.

In view of the very high yarn speed the drawing process is advantageously facilitated by the supply of heat,possibly via heated godets. Being another addition to the equipment this makes the process even more complicated and expensive, reducing profitability virtually to nil. This would be one of the reasons why the polyamide yarns for the knitting trade are practically without exception made after the conventional spinning method.

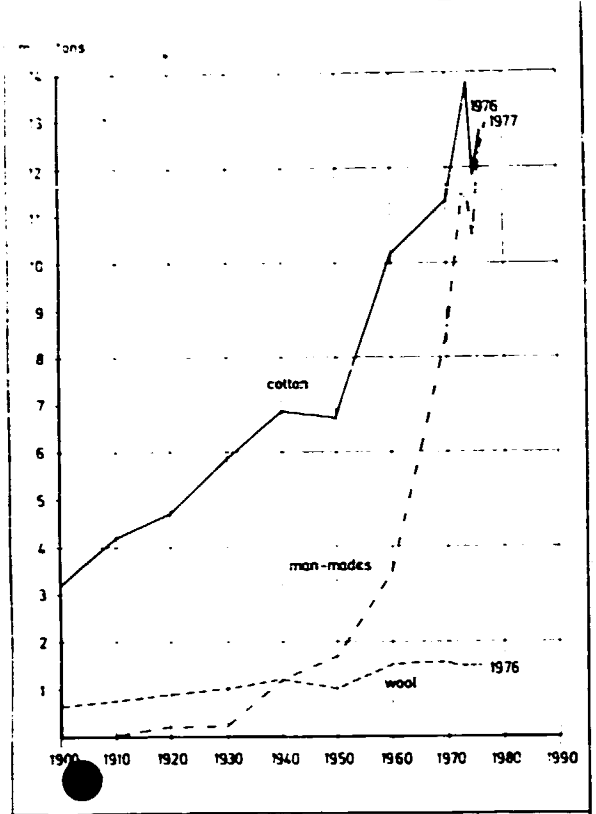
It is thinkable that further increases in spinning speed might result in a yarn which requires no more post-drawing.Machines for this purpose have already been built - at least for experimental purposes - to run at speed as high as 8ooo m/min.(Fig.41-45) The yarns so produced, however, still posess a sizeable amount of residual elongation and cannot yet be regarded as fully stretched filaments.

5.3 Permanently antistatic yarns

The polyamides nylon 6 and nylon 6.6 have proved to be highly valuable textile materials which offer many advantages. But there are also some disadvantages such as flammability, poor moisture dissipation or the tendency to build up electrostatic charges. To take the latter, it may cause some difficulties in the clothing field. Clinging and riding up could perhaps be tolerated in the light of other advantages. But in the case of carpets and upholsteries matters are more serious. For instance walking over a larger distance on polyamide carpeting may result in electric shocks when metal doorhandles are touched, and these shocks may be quite painful. It is high time that new ways be explored to eliminate these adverse properties in synthetic textiles. The search for suitable antistatics has made good progress during recent times and various yarn producers, of which Enka Glanzstoff was the first - are now offering textile and carpet yarns with a durable antistatic finish. In clothing textiles this is even coupled with improved moisture absorption. The new generation of polyamid textiles gives much improved wearing comfort. The yarns are made antistatic by adding small amounts of certain substances to the polyamide which increase its electric conductivity and thereby reduce static generation. Suitable additives are already being offered by a number of manufacturers.

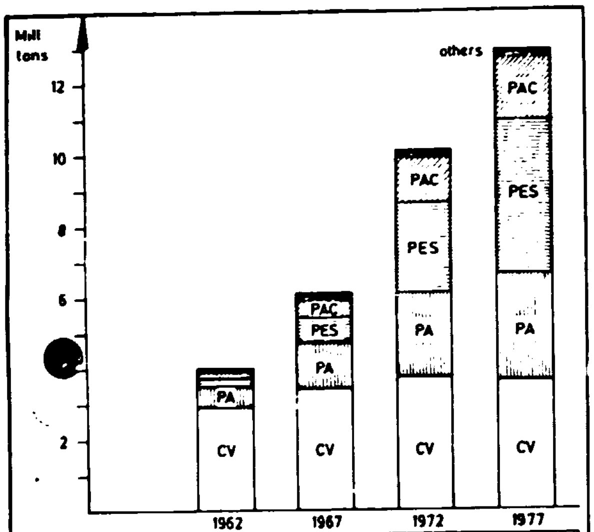
6. Raw material recycling - Protection of the environment

In all technical processes it is now necessary to consider possible pollution and how to avoid it. In the case of polyamide production conditions are rather favourable.Being a melt spinning process we need no solutions and therfore need not dispose of polluted waste water.Larger amounts of water are required for extraction of the polymide 6 chips, but this water is recirculated to evaporating plants, cleaned and reused. All vessels containing caprolactam or nylon salt are tightly closed to avoid contamination with foreign substances, particularly oxygen, and none of these substances ever gets into the waste water. The one exception is the water used for cleaning the vessels,the cooling water for the head of the column and water for quenching the polymide noodles or tapes. Both caprolactam and nylon salt are easily degraded by biological processes and any small amount slipping into the waste is easily degraded. Moreover they are readily soluble in water and scarcely affect the water surface tension. Yarn waste is always reclaimed and reused. Hydrolysis in an acid medium is used to crack the macromolecules and to reclaim the monomer. It may therefore be rightly said that the production of polyamides is a loo per cent safe process as far as pollution of the convironment is concerned.



Enka TTI World produktion of textile fibres in mill. tons

Fig. 1

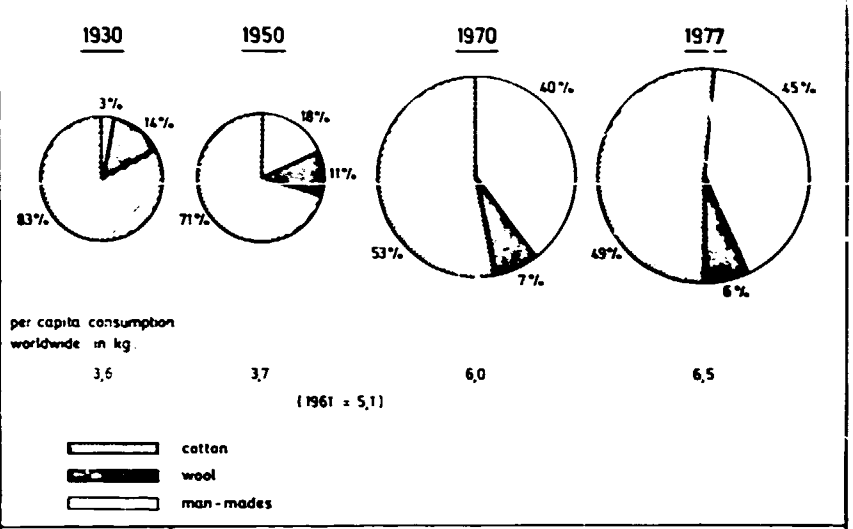


	1962	1967	1972	1977
Filament	1,8 = 45 %	2,8 = 46 %	4,5 = 45 %	5,7 = 44 %
Staple	2,2 = 55 %	3,3 = 54 %	5,6 = 55 %	7,2 = 56 %

		1962		1967		1972		1977	
CV	Filament	1,2	10^6 t	1,3	10^6 t	1,3	10^6 t	1,2	10^6 t
	Staple	1,7		2,1		2,6		2,6	
PA	Filament	0,5		1,2		2,0		3,0	
	Staple	0,1		0,1		0,4			
PES	Filament	0,1		0,2		1,1		4,3	
	Staple	0,1		0,5		1,6			
PAC	Filament	[illegible]		0		0		1,8	
	Staple	0,2		0,5		1,3			
others	Filament	0		0,1		0,1		0,2	
	Staple	0,1		0,1		0,1			

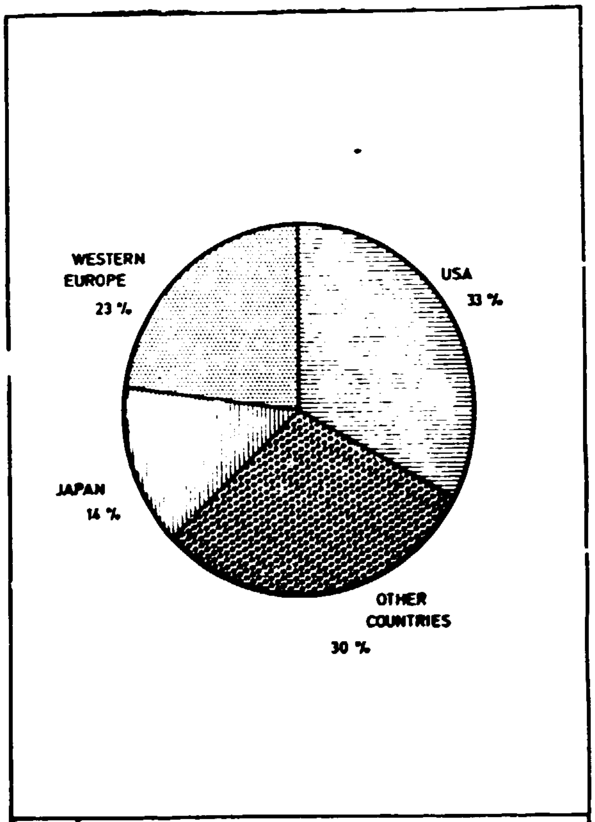
Enka TTI World man-made fibre production 1962 - 1977

Fig. 3



Enka Glanzstoff TTI "World textile cake" and per capita consumption

Fig. 2



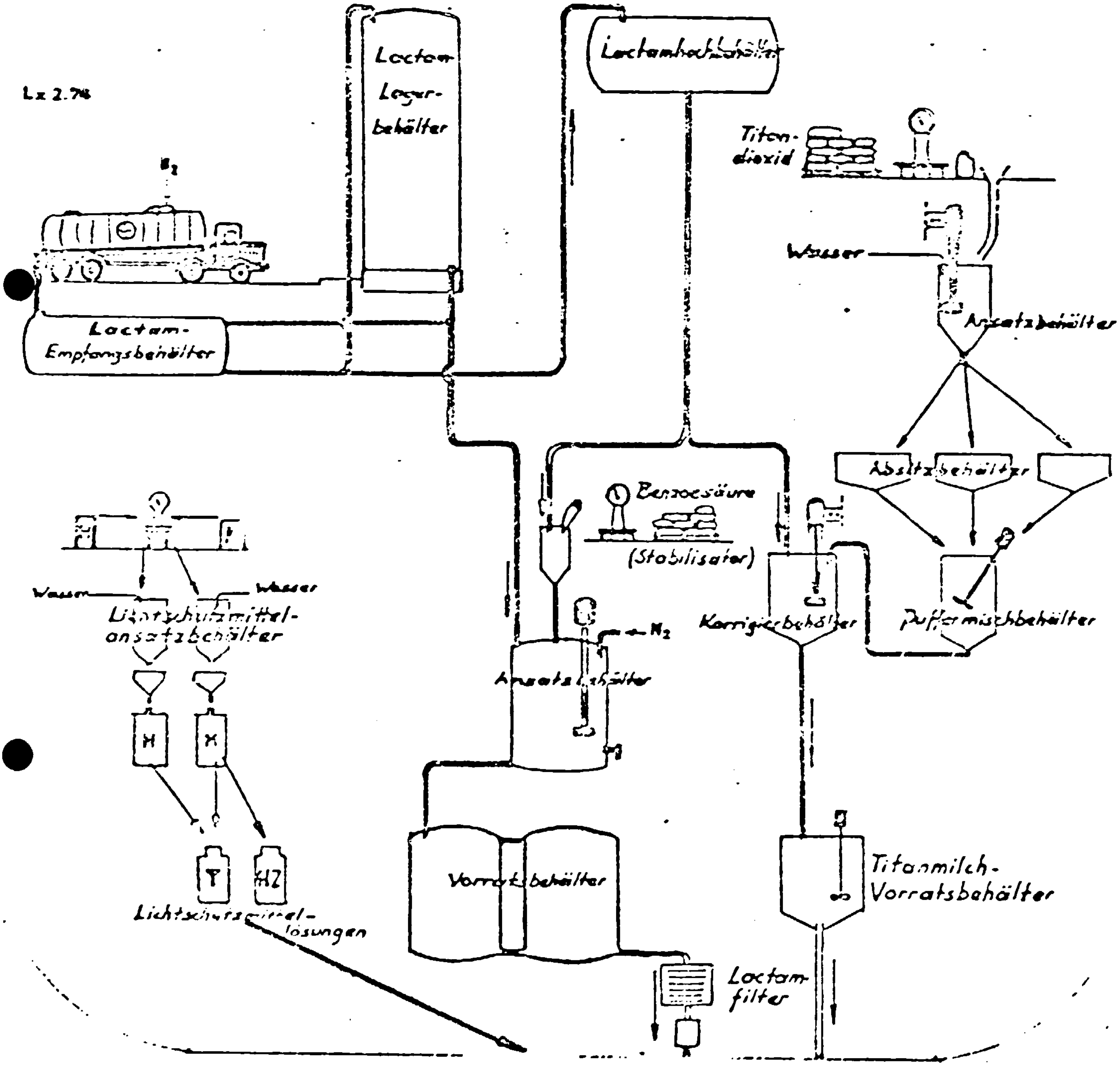
Enka TTI World production of synthetics - 1977 regionale breakdown

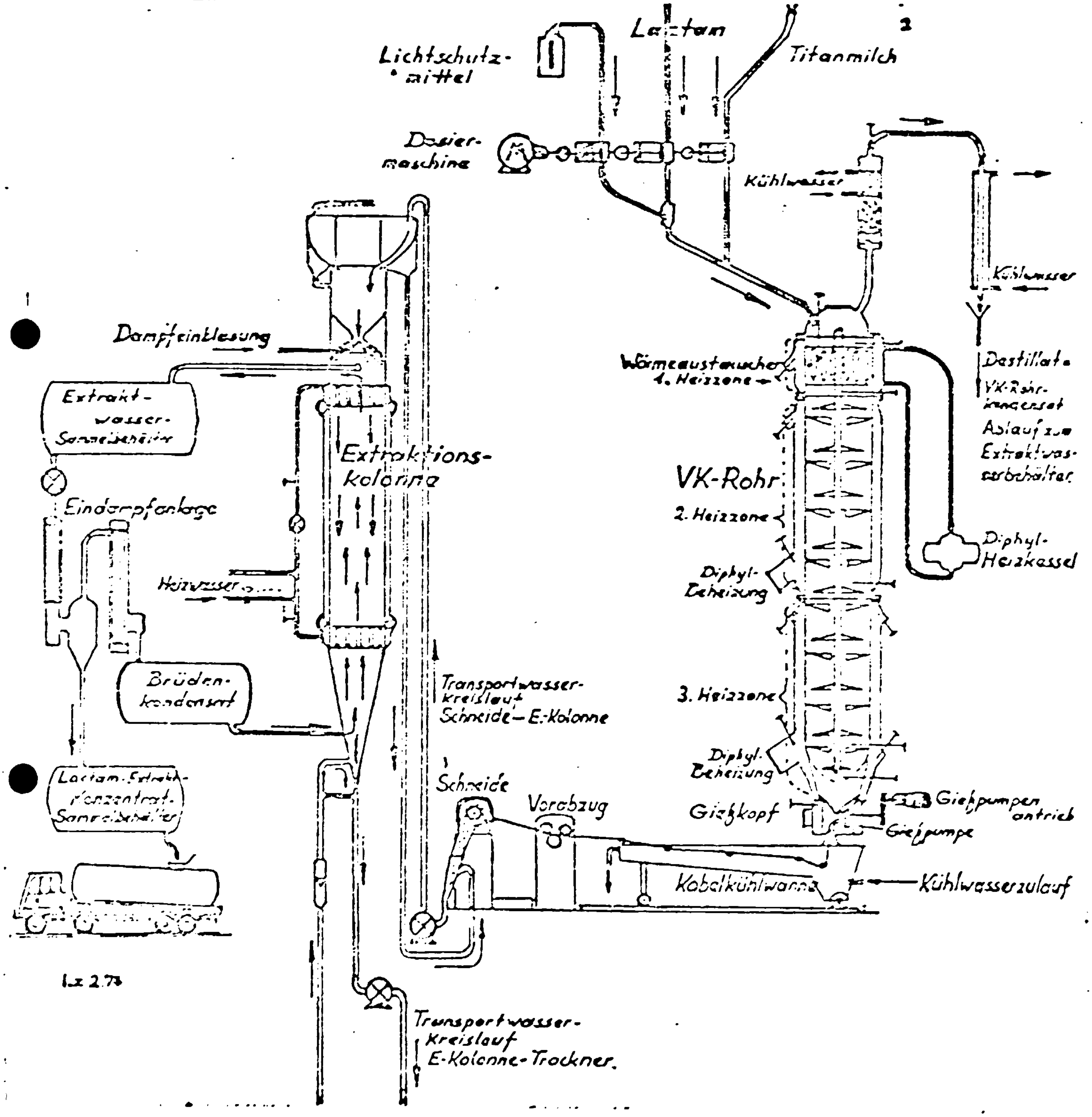
Fig. 4

	raw material production	raw material processing	melting point °C	spec gravity
Polyamide 3	possible	critical	340	1 33
Polyamide 4	possible	critical	266	1 26
Polyamide 5	possible	critical	260	1 13
Polyamide 6	easy	simple	215	1 12
Polyamide 6 6	easy	simple	265	1 13
Polyamide 6 10	satisfactory	simple	193	1 10
Polyamide 7	possible	simple	228	1 10
Polyamide 8	possible	simple	200	1 08
Polyamide 9	possible	simple	210	1 08
. amide 11	possible	simple	190	1 08
Polyamide 12	possible	simple	180	1 08
aromatic polyamides	difficult	difficult	(chars at 420 °C)	1 38

DECIVISE CONDITIONS FOR POLYAMIDE PRODUCTION

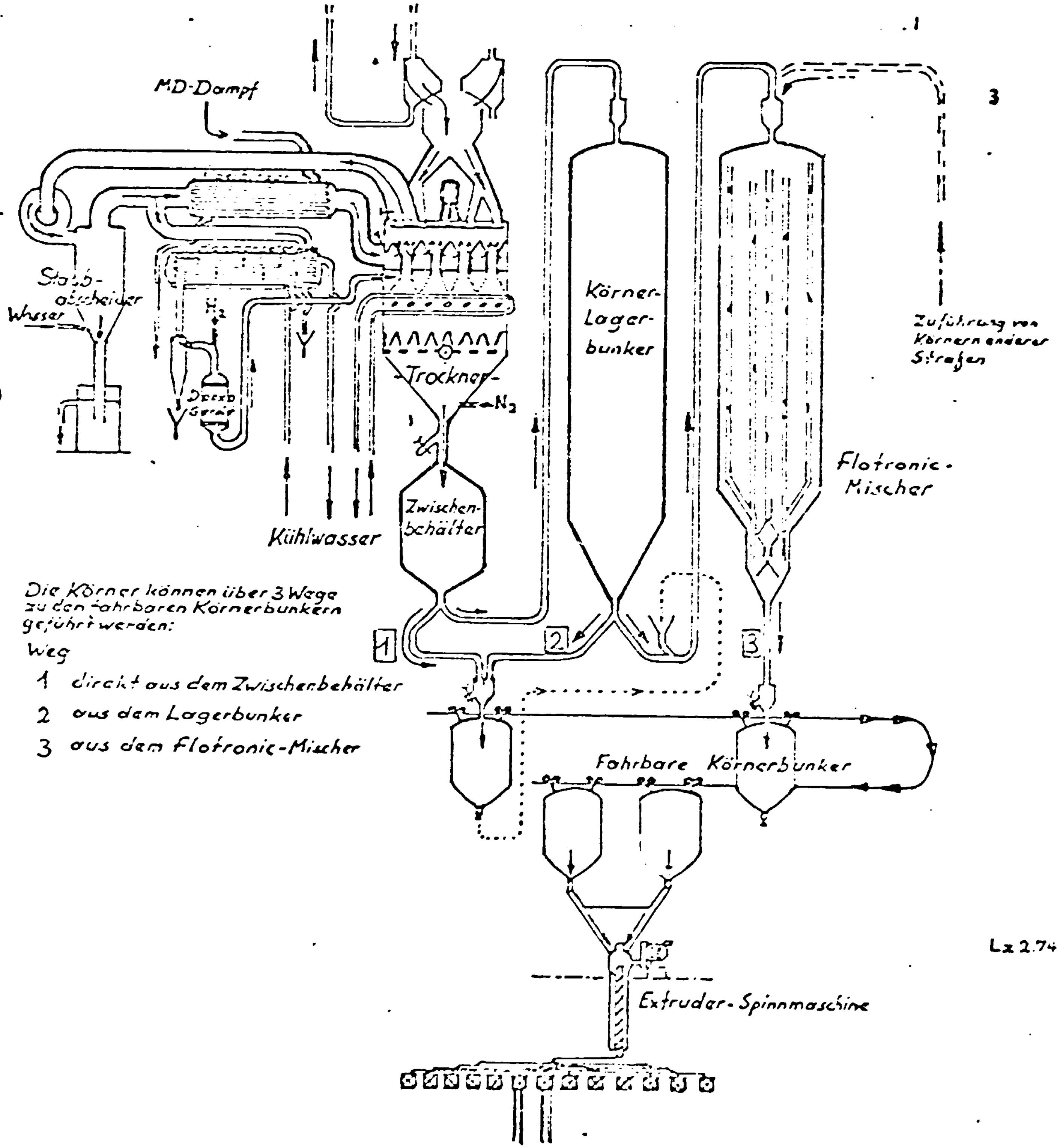
Lx 2.74


Lactam-Lagerbehälter
Lactamhochbehälter
N_2
Lactam-Empfangsbehälter
Titandioxid
Wasser
Ansatzbehälter
Absitzbehälter
Benzoesäure (Stabilisator)
Korrigierbehälter
Puffermischbehälter
Wasser
Wasser
Lichtschutzmittel-ansatzbehälter
H
X
T
HZ
Lichtschutzmittel-lösungen
N_2
Ansatzbehälter
Vorratsbehälter
Titanmilch-Vorratsbehälter
Lactamfilter


2
Lactam
Lichtschutzmittel
Titanmilch
Dosiermaschine
Kühlwasser
Kühlwasser
1
Dampfeinblasung
Extraktwasser-Sammelbehälter
Extraktionskolonne
Eindampfanlage
Heizwasser
Brüdenkondensat
Lactam-Extrakt-Konzentrat-Sammelbehälter
Wärmeaustauscher
1. Heizzone
VK-Rohr
2. Heizzone
Diphyl-Beheizung
3. Heizzone
Diphyl-Beheizung
Destillat
VK-Rohr-innenset
Ablauf zum Extraktwasserbehälter
Diphyl-Heizkessel
Transportwasser-Kreislauf Schneide–E-Kolonne
Schneide
Vorabzug
Gießkopf
Gießpumpenantrieb
Gießpumpe
Kabelkühlwanne
Kühlwasserzulauf
Transportwasser-Kreislauf E-Kolonne-Trockner.

Lx 2.73

F. 4



Die Körner können über 3 Wege zu den fahrbaren Körnerbunkern geführt werden:

Weg

1 direkt aus dem Zwischenbehälter

2 aus dem Lagerbunker

3 aus dem Flotronic-Mischer

Lx 2.74

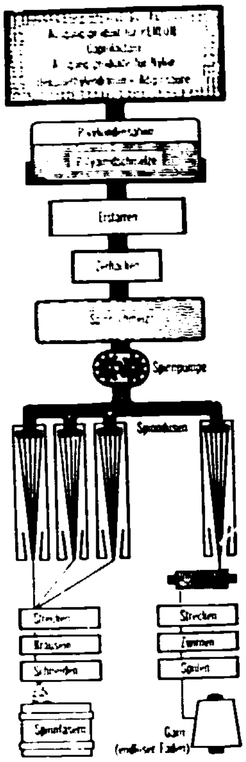


Fig. 6

I die Ringöffnungsreaktion:

$$CL + H_2O \rightleftharpoons ACS_1 \qquad + \Delta H_1$$

$$K_1 = \frac{(ASC_1)}{(CL)\cdot(H_2O)}$$

II die Polykondensation:

$$\left.\begin{array}{l} ACS_1 + ACS_n \rightleftharpoons ACS_{n+1} + H_2O \\ \text{oder} \\ ACS_n + ACS_m \rightleftharpoons ACS_{n+m} + H_2O \\ \text{oder} \\ -NH_2 + -COOH \rightleftharpoons -CO\cdot NH- + H_2O \end{array}\right\} + \Delta H_2$$

$$K_i = \frac{(ACS_{n+1})\cdot(H_2O)}{(ACS_1)\cdot(ACS_n)} = \frac{(ACS_{n+m})\cdot(H_2O)}{(ACS_n)\cdot(ACS_m)} = \frac{(-CO\cdot NH-)\cdot(H_2O)}{(-NH_2)\cdot(-COOH)}$$

III die Polyaddition:

$$CL + ACS_n \rightleftharpoons ACS_{n+1} \qquad + \Delta H_3$$

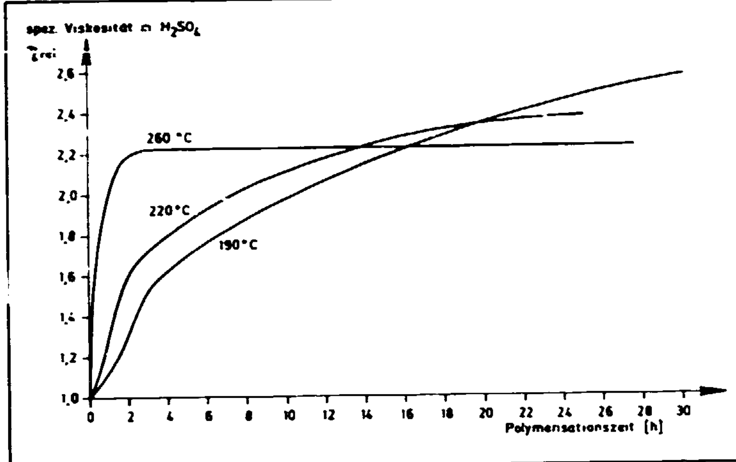
$$K_3 = \frac{(ACS_{n+1})}{(CL)\cdot(ACS_n)}$$

für $\bar{P} > 100$ gilt näherungsweise:

$$K_3' = \frac{1}{(CL)}$$

Enka Glanzstoff AG Textil - Techn. Institut	Nylon 6 Polymerisationsgleichgewichte	

Fig. 10



Enka Glanzstoff AG Textil - Techn. Institut	Polymerisationsverlauf Abhängigkeit von Temperatur und Zeit	

Fig. 11

Tabelle 1 Die Konstanten der Caprolactamgleichgewichte (Mol/kg)

Autor	$K_1 \cdot 10^3$	K_2	K_3	t °C
Wiloth [1]	2,5	800	2,0	220
van Velden u. Mitarbeiter [2]	2,6	740	1,9	221,5

1) Wiloth, Z. Physik. Chem., n. F. 5 (1955), S. 66

2) Van Velden u. Mitarbeiter, Rec. trav. Chim. 74 (1955), S. 1376

Tabelle 2 Temperaturabhängigkeit der Konstanten der Caprolactamgleichgewichte

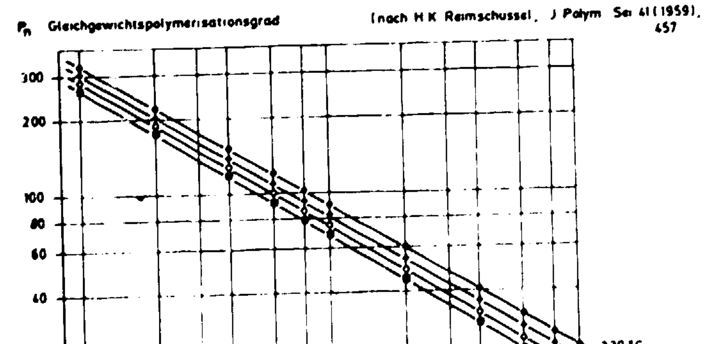
t °C	220	230	240	250	260	265
$K_1 \cdot 10^3$ *)	2,54	2,66	2,79	2,91	3,04	-
K_2	775 (770)	672	603	507 (510)	447	(415)
K_3 *)	1,97	1,79	1,63	1,49	1,36	-

Werte nach A. V. Tobolsky u. A. Eisenberg, J. Amer. Chem. Soc. 81 (1959), S. 2302

Werte in Klammern nach H. K. Reimschussel, J. Polym. Sci. 41 (1959), S. 457

Enka Glanzstoff AG Textil - Techn. Institut	Gleichgewichtskonstanten der Caprolactampolymerisation	

Fig. 12



Enka Glanzstoff AG Textil - Techn. Institut	Gleichgewichtspolymerisationsgrad Abhängigkeit vom Anfangswassergehalt	

Fig. 13

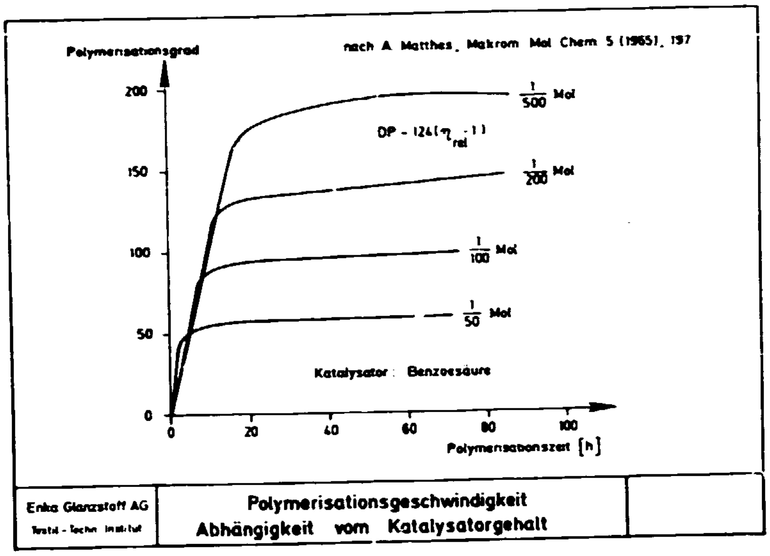


Fig. 14

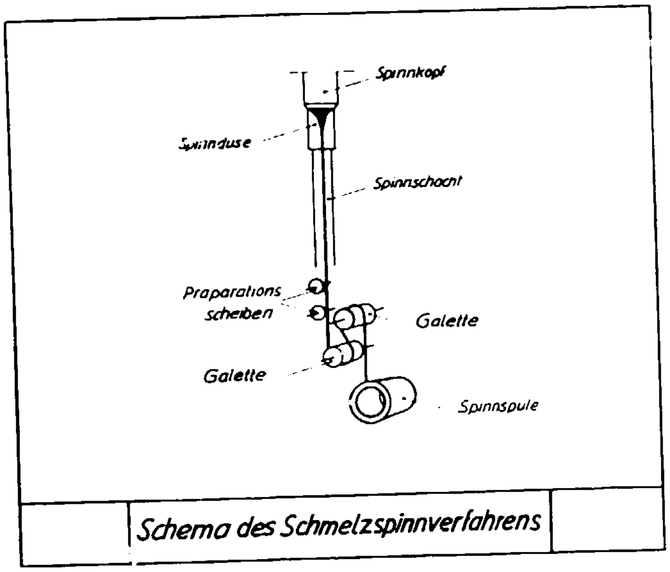


Fig. 15

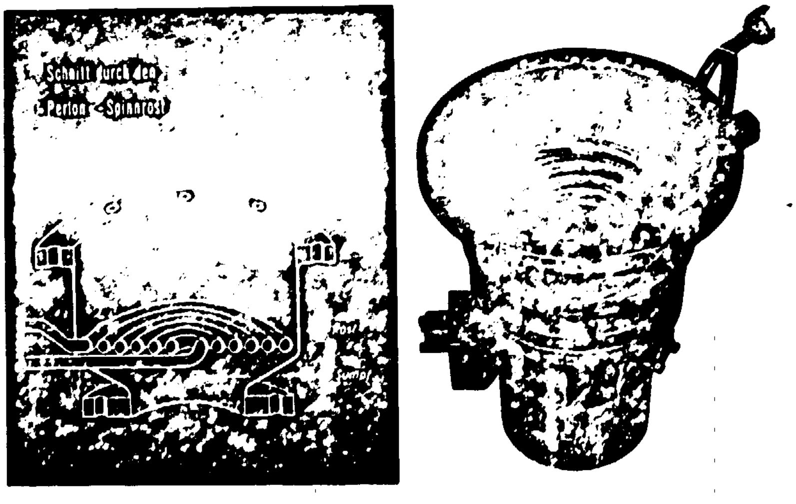


Fig. 16

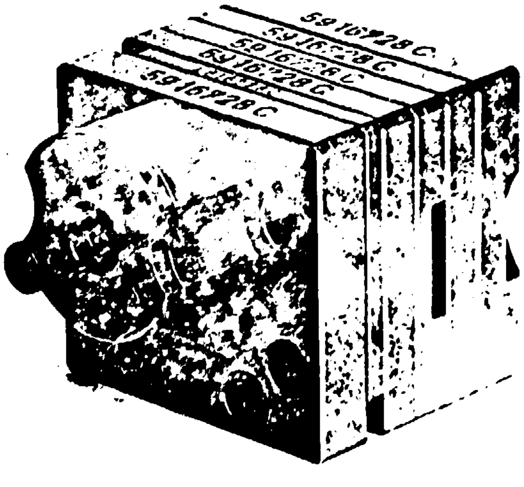


Fig. 17

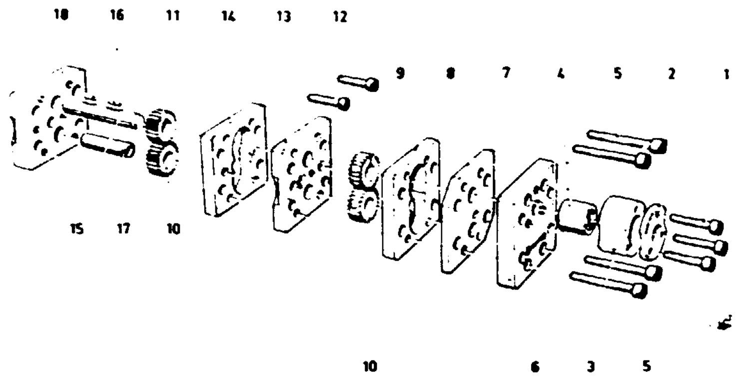


Fig. 18

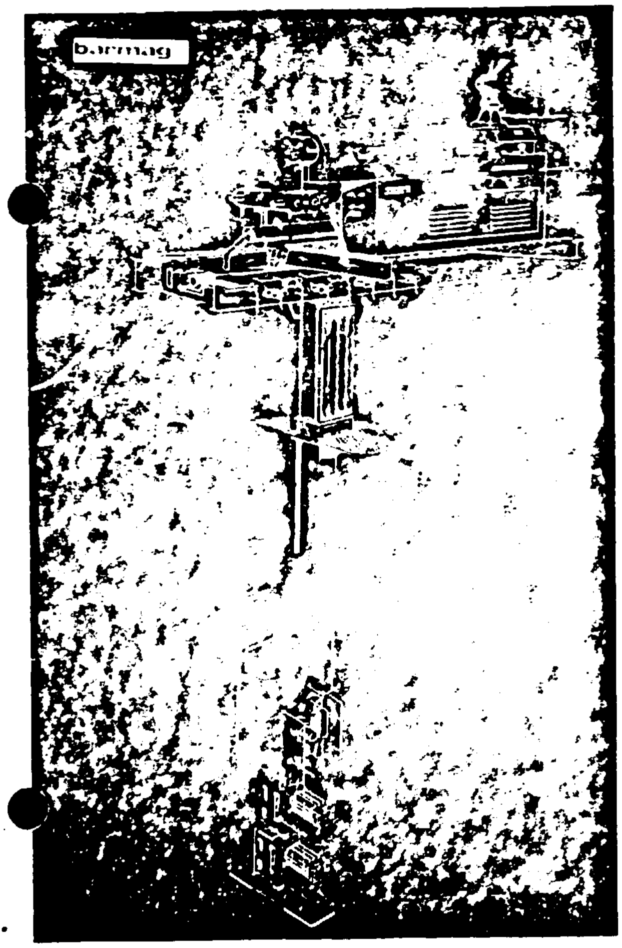


Fig. 19

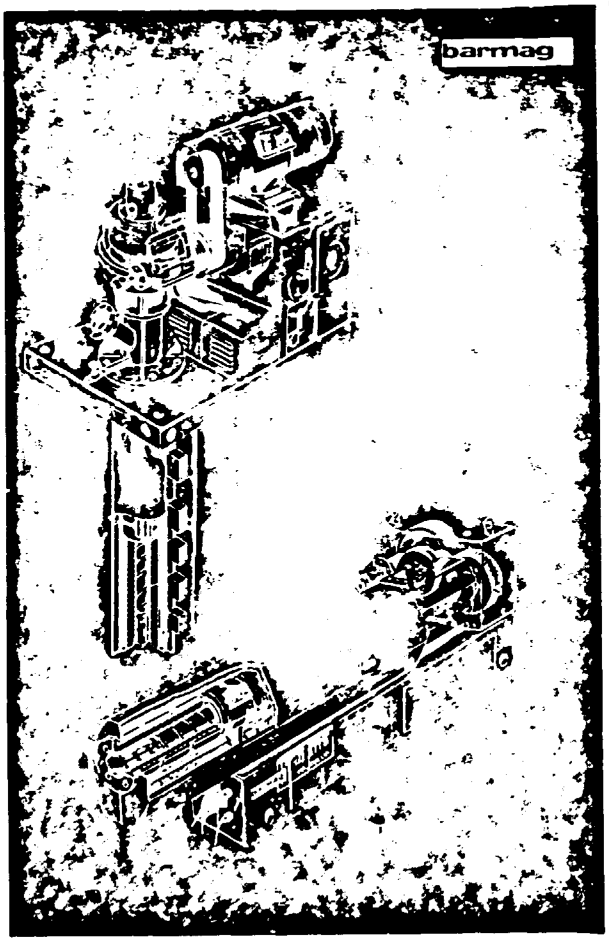
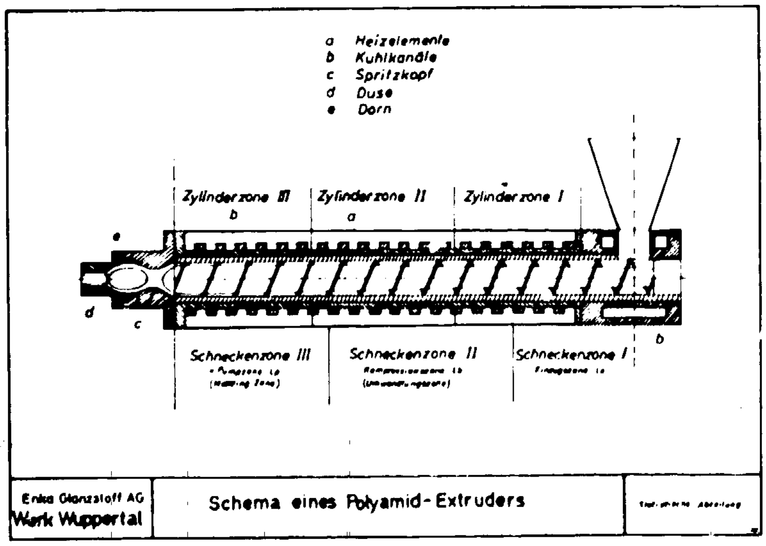


Fig. 20



Schema eines Polyamid-Extruders

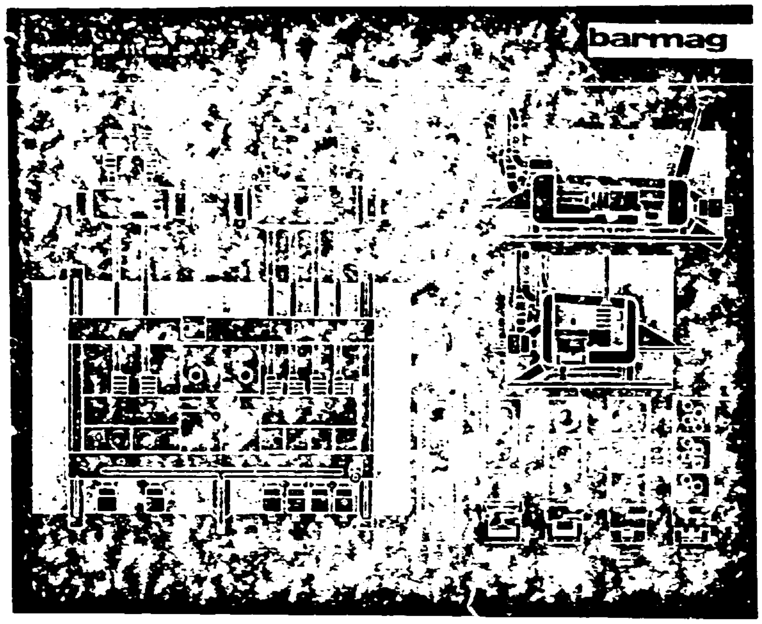
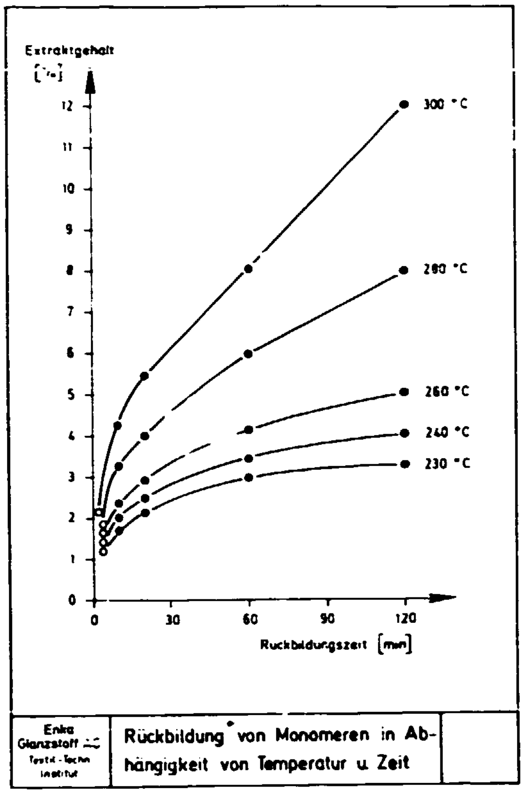


Fig. 22



Rückbildung von Monomeren in Abhängigkeit von Temperatur u. Zeit

Fig. 23

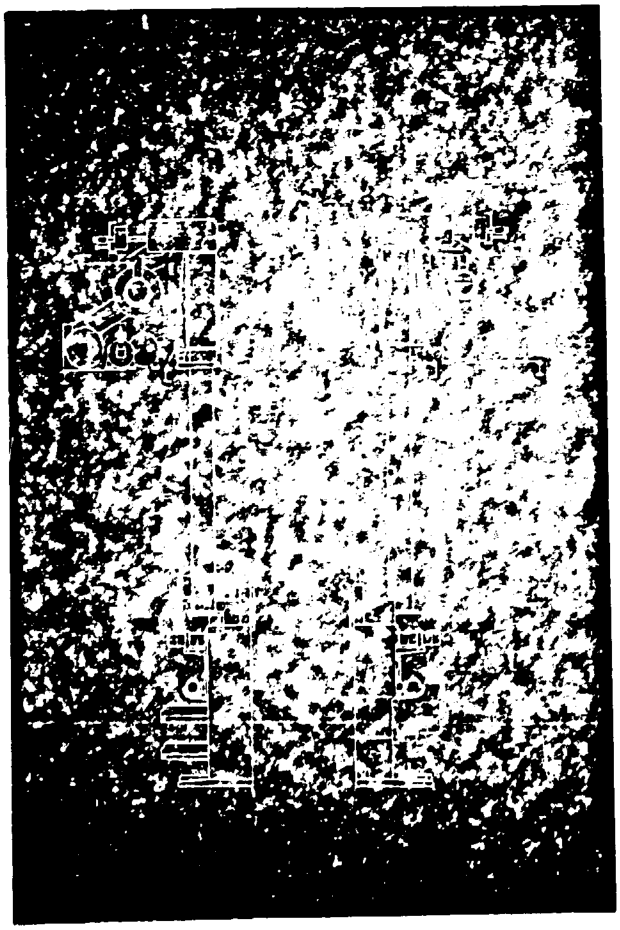


Fig. 25

Fig. 24

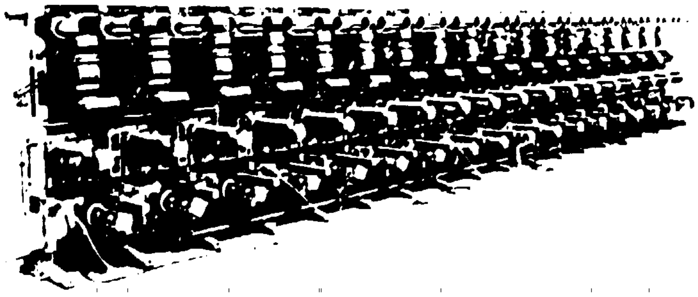


Fig. 26

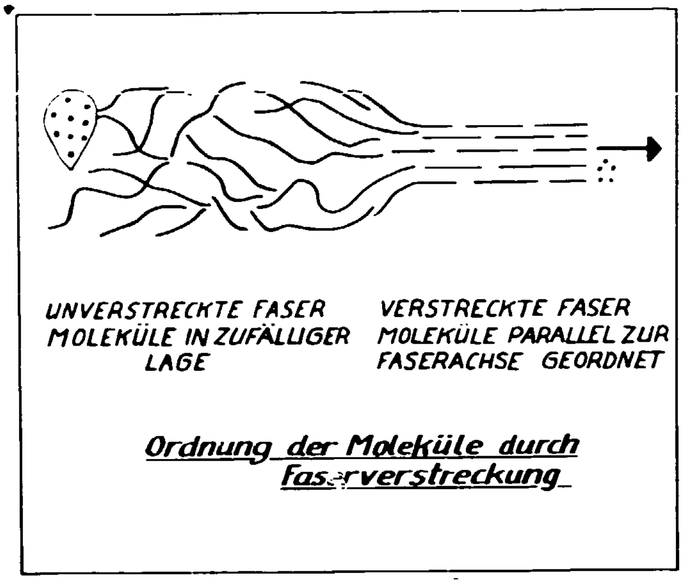


Fig. 27

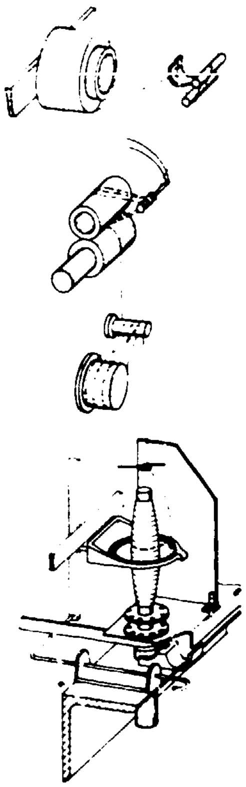


Fig. 28

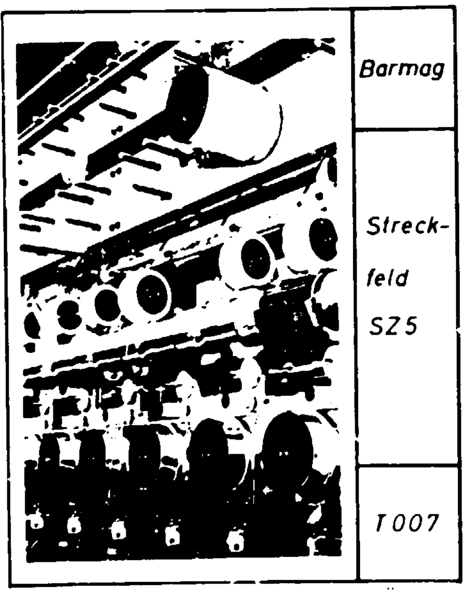


Fig. 29

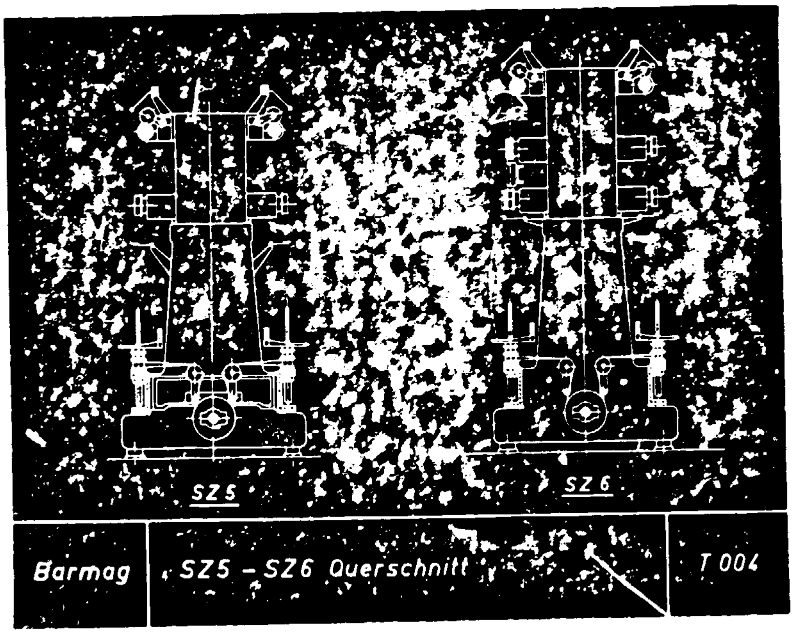


Fig. 30

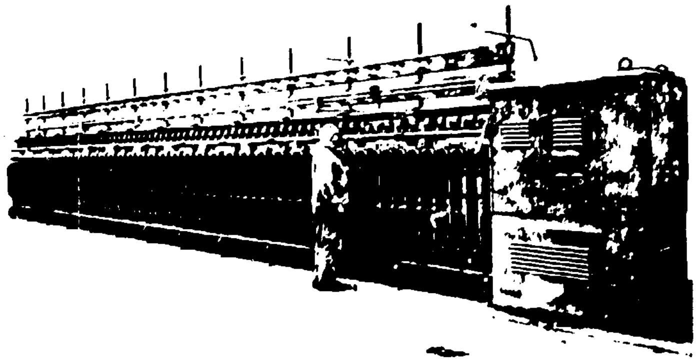


Fig. 31

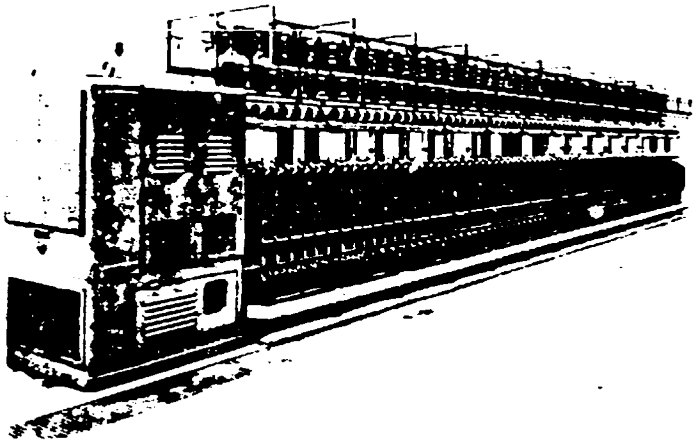


Fig. 32

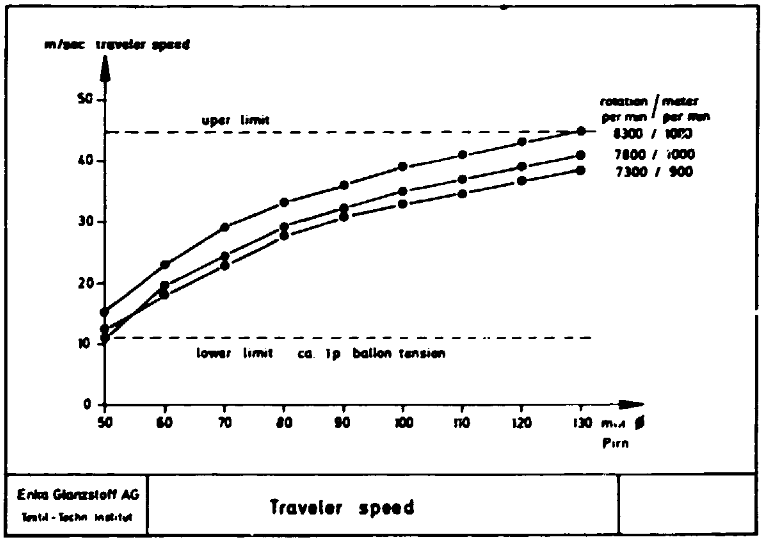


Fig. 33

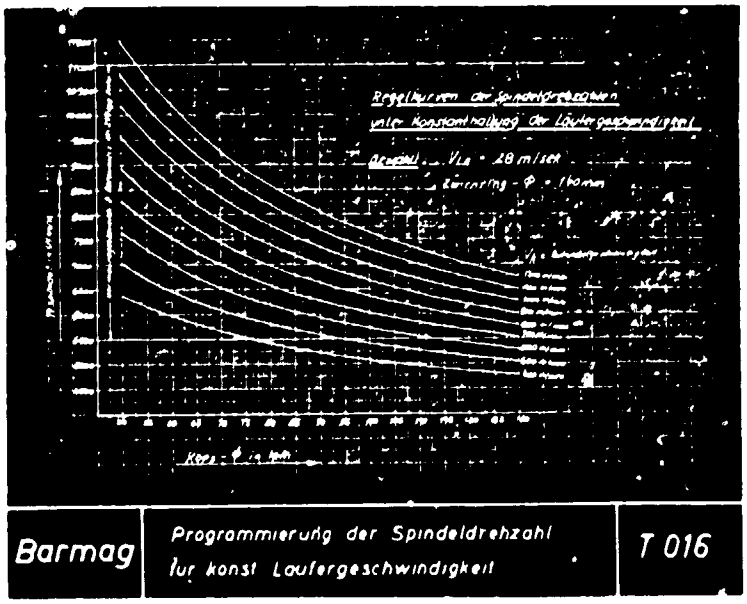


Fig. 34

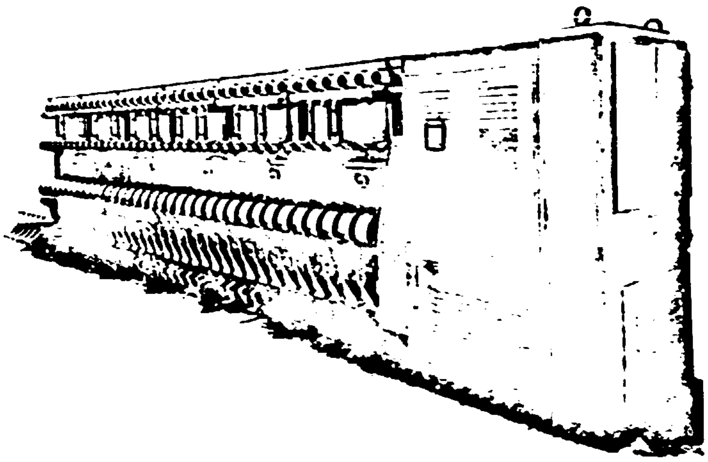


Fig. 38

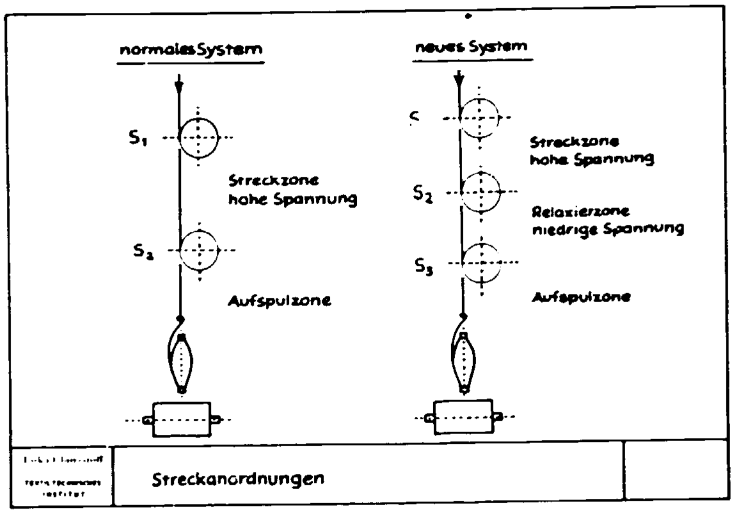


Fig. 39

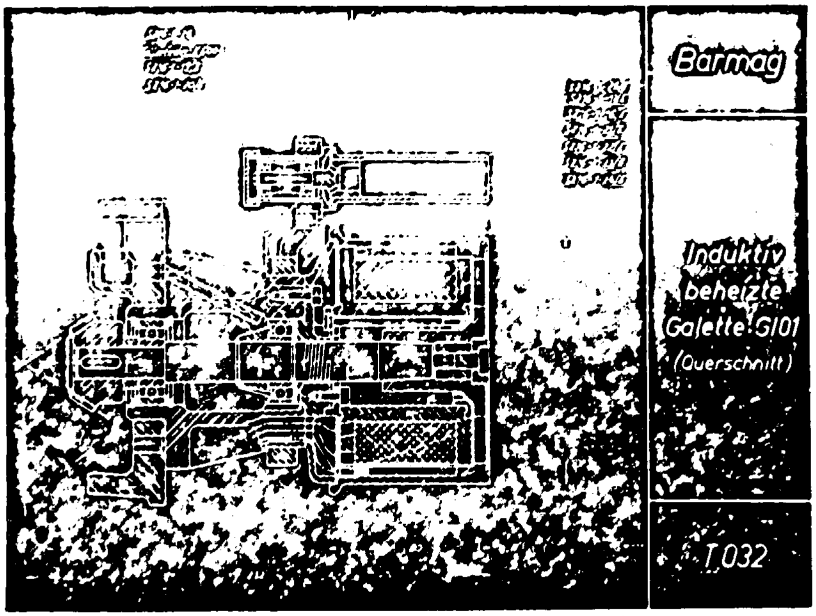


Fig. 40

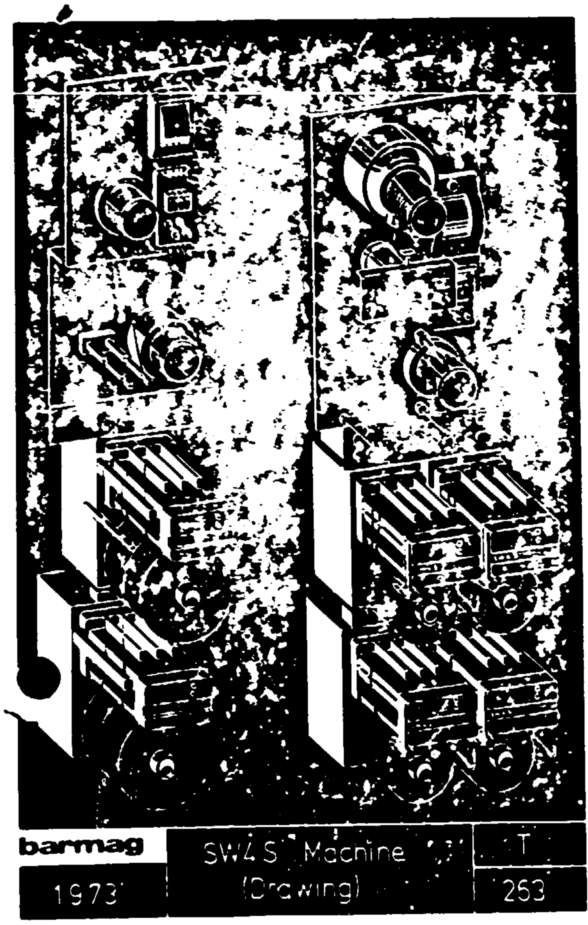


Fig. 41

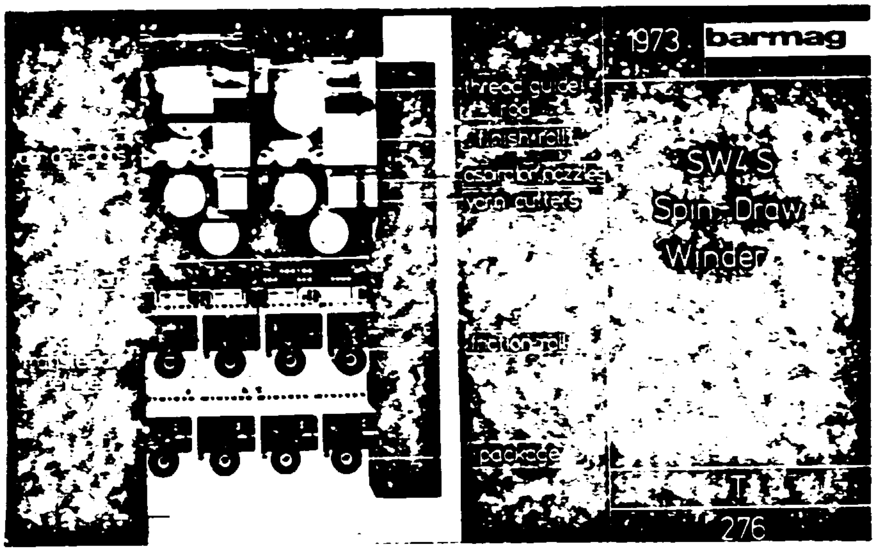


Fig. 42

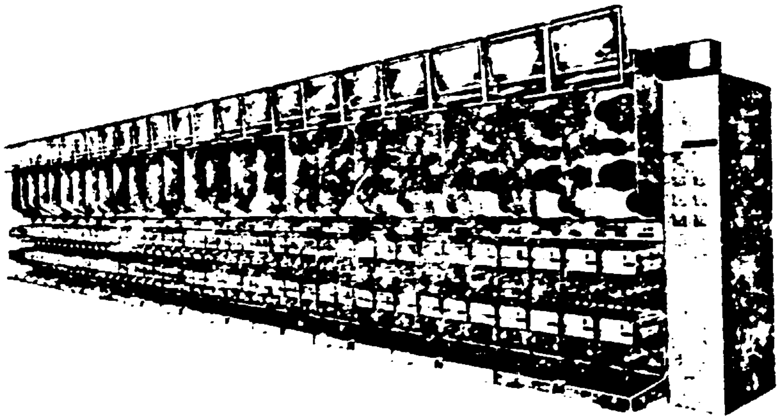


Fig. 44

Fig. 43