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ID/WG.137/4
18 September 1972

Original: ENGLISH

United Nations Industrial Development Organization

Symposium on the Development of the Plastics Fabrication Industry in Latin America

Bogotà, Colombia, 20 November - 1 December 1972

DEVELOPMENT AND PROSPECTS IN MANUFACTURING METHODS FOR LOW DENSITY POLYETHYLENE [1]

by

Pierre Durand
Ethylene Plastique
Lillebonne France

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SUMMARY

DEVELOPMENT AND PROSPECTS IN MANUFACTURING METHODS FOR LOW DENSITY POLYETHYLENE [1]

by

Pierre Durand
Ethylène Plastiques
Lillebonne France

In a modern manufacturing process for low density polyethylene the polymerization procedure can be adjusted to obtain the most suitable resin for each application, such as coating paper or aluminium, wire insulation, heavy duty bags, general purpose film or moulding. Such a wide range of grades is obtained by varying melt-index (between 0.2 and 100), density (0.913 to 0.937 at $23^{\circ}C$) and also molecular weight distribution ($\frac{MW}{Mn}$ between 2 and 15 for melt index 2).

The adjustment of molecular weight distribution is obtained by variation of the polymerization temperature curve in the reactor. The shape of temperature profile can be changed from the steady temperature profile of the autoclave ideally homogeneous to the sharp slope profile of the tubular reactor. Ethylene Plastique solved this problem by using a reactor of low ratio $\frac{\text{length-}}{\text{diameter}}$ (below 20) including a special stirring device.

Another target of improvment in manufacturing process forlow density polyethylene is to obtain a low cost price for "standard" uses, whatever may be the technical performance - For example a grade suitable for packaging fertilizers must be able to resist to stress-cracking action of the anti-caking agents included in the fertilizer; for such use the cost price must be very low. Thisis achieved by increasing the size

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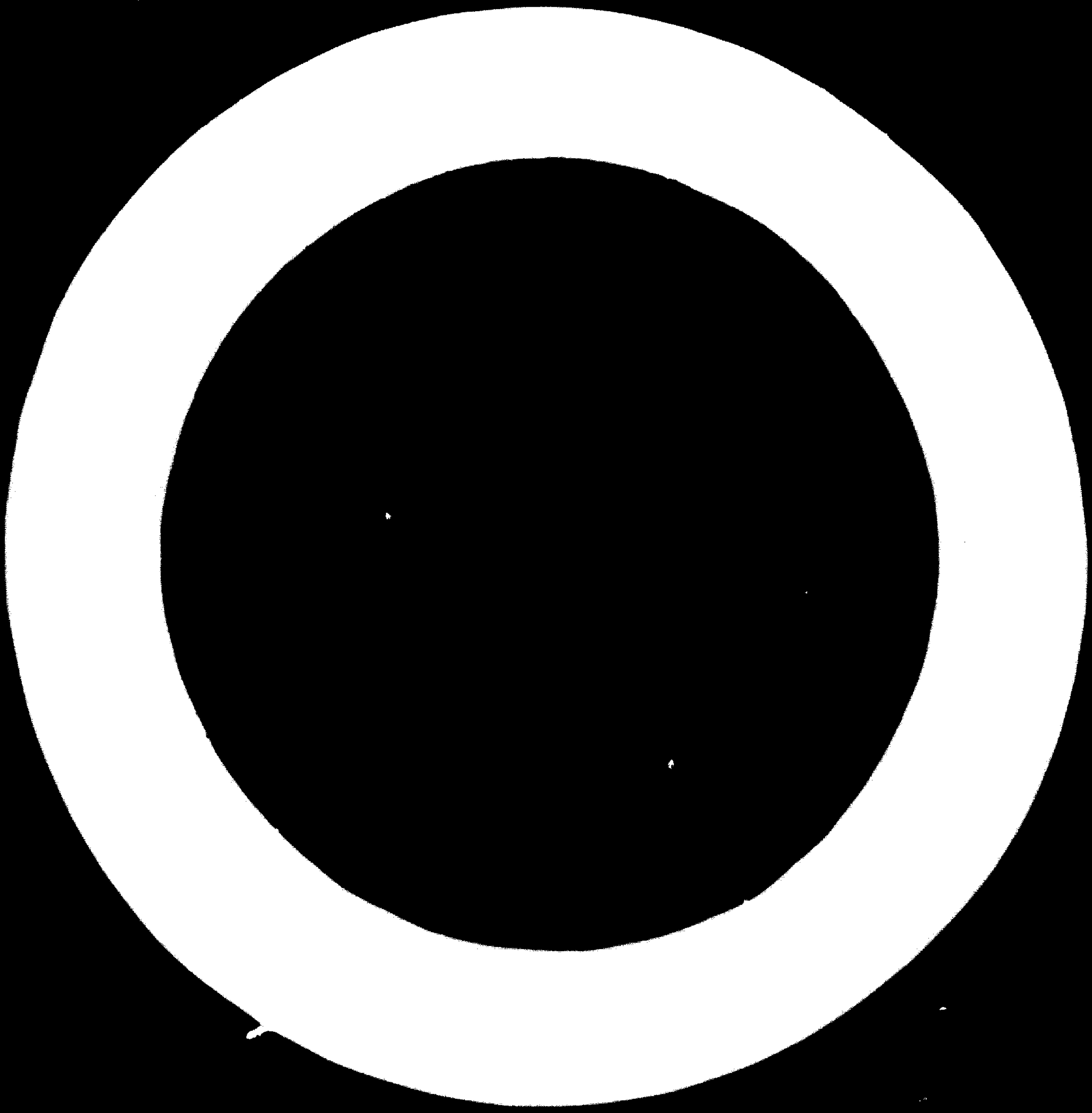
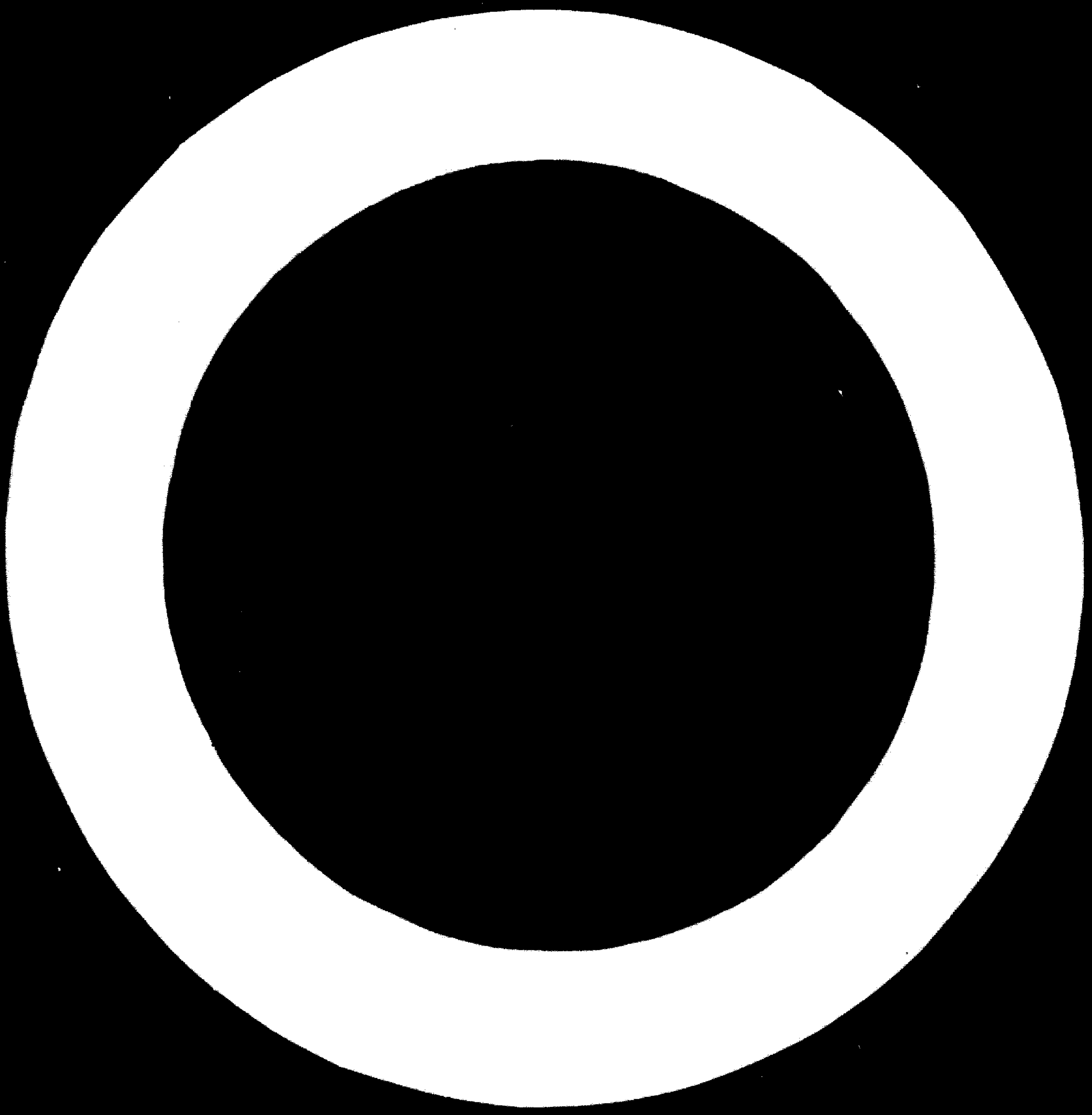


of the unit (50,000 to 100,000 tons per year); capital cost and production cost per kilo of polyethylene are thus much lower - We shall present a detailed study of the influence of unit size on the cost price.

Another very important advantage of Ethylene Plastique process is the use of rather low polymerization pressures - Tubular processes are for example obliged to use very high pressures (2,500 to 3,000 bars) formany reasons (decrease of the initiation temperature by oxygen, increase of density, reduction of the plugging of the tube and so on). The process allows to produce all grades at pressure below 2,000 bars. Thus the investment cost is reduced and also the power consumption. The reliability of the equipment is increased and the safety too.

These improvements of the high pressure polymerization of ethylene process have been achieved by a good knowledge of two kinds of correlations: on the one hand correlation between polymerization conditions structure and rheological behaviour, on the other hand correlation between structure rheological behaviour and application properties. These technical aspects are elaborated.



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I - INTRODUCTION

To understand the evolution of low density polyethylene manufacturing techniques, it is necessary to appreciate the market for this plastic material. There are two types of applications :

- First, what we might call the "noble" uses, in which the polyethylene is used as supplementary material on a given support, owing to its special properties ; the main feature of this application lies in the fact that the polyethylene cost is only a small percentage of the cost price of the end item, but it has a determining influence on the quality of the latter. This is the case, for instance, in cable sheathing or coating. In this market, quality will be the main test for the choice of the polyethylene, a better price being obtained for a first quality product.

- Second, "standard" uses in which the low density polyethylene is the basic material, often the only one, and thus forms the greater part of the cost price of the end item. This is the case in the moulding and film markets, both of these remaining by far the most important for this plastic material. In these fields it is impossible to sell polyethylene at a higher price than competitors, whatever may be technical performance. Owing to the evolution of manufacturing equipment, technical requirements become from day to day more severe, whereas the selling price of the polyethylene itself falls steadily.

Research for the best quality at lowest cost price is therefore, as anywhere else, the basic target for those in charge of a low density polyethylene project. But they have to keep in mind that, if technical performance is profitable in the "noble" application field, it is compulsory to keep, on the contrary, at the lowest possible level the cost price of polyethylene intended for "standard" uses whatever may be the technical performance.

Before entering into technical considerations to show how Ethylene Plastique solved this problem, we shall first briefly describe this Company.

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II - THE ETHYLENE PLASTIQUE COMPANY

Ethylene Plastique is a subsidiary of two large French chemical companies :

- Société Chimique des Charbonnages de France
- Société l'Air Liquide.

This company has been specialised in the low density polyethylene process since 1954. It is the most important French producer of high pressure polyethylene ; in France, its yearly production will reach 350 000 tonnes per year by the end of this year. Its recent achievements in France are as follows :

- Start up of two 60,000 tonnes per year production lines at Carling (Saint-Avold) in 1970 ; the first one in January 1970, the second one in July 1970 ;
- start up of 90,000 tonnes per year line at Lillebonne, this year in September.

In both cases, at the time they came on stream, they were the biggest units in the world.

Abroad, the Ethylene Plastique process has already been licensed to three foreign companies :

- Showa Denko in Japan, which has been using it since 1969 in Tsurusaki, through its joint venture with Phillips Petroleum, the Company Japan Olefin Chemicals.
- Montecatini Edison, in Italy, which has been using it since 1969 in its Brindisi complex.
- More recently, Polimeros del Lago, in Venezuela, subsidiary of the Venezuelan Institute for Petrochemicals, which will be using it from 1974 in El Tablazo.

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More details about the Ethylene Plastique Company are available in the process booklet. This booklet also gives the outline of the process flow sheet. Now let us see in more detail some characteristics of this process.

In the evolution of any process, there are two over riding considerations : the cost price has to be reduced and the quality has to be improved.

Below are given some details about these two points.

III - COST PRICE

Among the elements of the cost price, some are independant on the capacity of the line, others, on the contrary, depend upon it.

Among the first, let us quote :

- The annual hours on stream
- Polymerization pressure.

Among the second :

- The conversion rate
- The investment cost
- The operating cost.

Let us first examine the factors independant of size :

1. Annual hours on stream

This is a main factor ; in our process, it is more than 95 % of the

.../...

total time. This result has been obtained by limiting the number of decompositions (we have less than one per year and per line) and by improving the reliability of the equipments (compressors, catalyst pumps, etc.).

2. Polymerization pressure

As is well known, the tubular reactors operate at very high pressures (2,500 to 3,000 bar) for many reasons (such as decrease of the initiation temperature by oxygen, increase of density, reduction of the plugging of the tube and so on). None of these reasons concerns the autoclave processes.

However, some companies with the autoclave process operated at high pressure, expecting to improve the thin film optical properties. Ethylene Plastique had been following this way for a short while but is quickly appeared that pressure was not the most effective agent for improving optical properties and draw down of thin film. As we shall see later, the most effective way to improve them is to reduce the width of molecular weight distribution mainly dependent on the temperature profile ; the target was to control the temperature profile, thereby controlling the molecular weight distribution, instead of increasing the operating pressure. This pressure reduction has widely contributed to improve the above mentionned number of operating hours per year. The economical advantages are important :

- First, reduction of investment cost :
  For the same purchase price, the nominal output of a compressor may be multiplied roughly by 1.5. when the maximum service pressure is reduced from 3,000 to 2,200 bar.

- The ratio of high pressure tube prices for a difference in service pressure of 600 bar is 1.5.

- Second, reduction of the operating cost.
  Maintenance cost is noticeably reduced and on the other hand, electricity consumption, for 20 % conversion rate for instance, falls by 0.30 kWh per kg polyethylene when polymerization pressure is reduced by 1,000 bar.

.../...

Finally, this reduction of pressure is an obvious improvement of equipment safety.

To turn now to the factors depending upon the size of the unit.

3. Conversion rate

The increase in the conversion rate with the size of the unit is remarkabke and may seem surprising at first. It is owing to the fact that the autoclave process is adiabatic. As there is not heat exchange with the outside, all the polymerisation heat is absorbed by the fresh ethylene entering the reactor. The conversion rate is thus given by a simple enthalpic balance :

$$t\ \% = \frac{\int_{te}^{ts} Cp\ dt}{Q} \times 100$$

Cp = ethylene specific heat
Q = polyethylene heat of formation
te = ethylene temperature at inlet of reactor
ts = outlet temperature of reaction mixture.

Thus the conversion rate can only be modified by increasing ts or reducing te. The increase of capacity allows, for the same quality, to increase appreciably the difference ts - te.

Another advantage lies also in the fact that these conversion rates are but little different from one polymer to another.

It is often said that the main advantage of the tubular process compared with the autoclave one lies in the fact that the former allows the removal of heat from the reaction area which increases the conversion rate.

.../...

This is a little rough analysis for it does not consider the fact that it is necessary to pre-heat all or part of the ethylene at the inlet to the reactor to the initiation temperature which is about 165°C when oxygen is used. In fact, in the tubular processes, the conversion rate can exceed 20 per cent only by using side entries which leads to a decrease of quality. The true average conversion rates obtained on big units (50,000 tonnes per year and more) do not differ more than 10 per cent from tubular to autoclave. Now, the benefit of increasing the conversion rate is to reduce the size of the recycling compressor for a given production rate, which consequently decreases the cost of this equipment and the power consumption. But as said above, these costs are also greatly dependent on the operating pressure, and if the tubular processes have an advantage of 10 per cent for the conversion rate, they have at the same time a disadvantage of 50 % due to the use of an operating pressure 800 bar higher.

4. Investments and sizes

a) Ethylene plastique has carried out special surveys about the influence of the size of the lines upon investment costs, and it seems that the so-called "two thirds" law is confirmed :

$$I_1 = Io \left(\frac{C1}{Co}\right) \text{exp. } \frac{2}{3}$$

In fact, the coefficient was found to be 0.603. It is only an average coefficient and in table I, for instance, the coefficients found when passing from 30,000 tonnes per year line to a 60,000 one with a similar technology are given.

Nevertheless, thanks to a change of technology and particularly by the suppression of the separate finishing plant, Ethylene Plastique has succeeded, when building its Saint-Avold plant, in reducing the coefficient from 0.603 to 0.520. This technological progress can be applied to any size of line, and under such conditions, the 0.603 coefficient is again found, which allows comparison with other plants of similar technology.

.../...

Graph 3 shows the fall of investment cost "i" in francs per kilo of product, according to the increase of line capacity (unit value 1 being given to a 20,000 tonnes per year line).

$$I = a\ C^{0.603} \qquad \text{but } i = \frac{I}{C}$$

$$\therefore\ i = a\ C^{0.603\ -\ 1}$$

$$\text{i.e. } i = a\ C^{-0.397}$$

If coefficient <u>a</u> is given such as a value that $i = 1$ franc per kilo, for $C = 25$ k t/year, or $a = 3.6$, the formula becomes :

$$i = 3.6.\ C^{-0.397}$$

Fig. 3 gives representative curve of this function i (C) which passes by the following points :

$i = 1.00$	for	$C = 25$ k t/year
$i = 0.76$	for	$C = 50$ k t/year
$i = 0.64$	for	$C = 75$ k t/year
$i = 0.58$	for	$C = 100$ k t/year

b) If investments are plotted against the number of lines for a given plant capacity the bunch of curves on fig. 4 is obtained with :

- on the x-axis : the number of lines
- on the y-axis : the investment taken equal to 100 in the case of a plant of 100,00 tonnes per year with four lines of 25,000 t.

Each curve corresponds to a plant capacity of 50 to 150 k t/year (the smallest line capacity has been assumed to be 25 k t/year).

These curves have been drawn according to the line investments within battery limits (without the utilities) including the before tax cost of the equipment, custom duties, transport, transit and erection costs.

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Thus, each unit includes :

- a compressor house
- a polymerization section
- a remote control room
- a cold blending and technical storage section
- a transformating plant HT/LT
- open spaces and basements for all interconnections, etc.

5. Production cost and sizes

The production cost is usually broken down into fixed and variable costs. Obviously, for the so-called fixed costs, the increase of the unit's size reduces the cost corresponding to a tonne of product. In fact, these expenses are fixed only for a certain range of capacity, but thanks to technical improvement, the level of this range can be raised.

For instance, the operating labour has been kept unchanged when passing from a 30,000 tonnes per year to a 60,000, then to a 80,000 tonnes per year unit. An 80,000 tonnes per year unit is operated with the following labour :

- 4 men for polymerization (3 shifts)
- 1 man for cold blending (3 shifts)
- 3 men for bagging (2 shifts).

If a second 80,000 t/year line. is coupled with the first one, a single man is to be added for polymerisation and bagging will need 3 shifts.

The maintenance expenses, considered as proportional to investment, are themselves reduced by the cut in investment. So are the plant overhead expenses which usually reach 60 % of the total maintenance and production labour costs.

Variable expenses usually fall when the line capacity is increased ; the ethylene specific consumption passes from 1.04 to 1.035 kg/kg, that of

.../...

electric power falls by 10 %.

These few figures show the advantage of increasing the production line capacity.

In the present state of technical knowledge, Ethylene Plastique considers that the above increase of unitary capacity is favourable up to about 100,000 tonnesper year. Beyond this figure, important technological changes will have to be made (in the compressor field, for instance).

Here are some slides taken at our Saint-Avold plant, which show you a unit with two, 60,000 t/year lines.

IV - QUALITY

Here is the second part of the evolution of a manufacturing process - that of seeking for quality improvement. Successively will be examined :

- the influence of polymerisation conditions on the polymer structure and its rheological behaviour,
- the application properties of some Ethylene Plastique grades compared with competing products.

1. Relationship between polymerisation conditions and structure

Without coming back to the theory of polymerisation by free radicals (an idea of which is given in tables II and III), let us simply keep in mind that the ethylene polymerisation high pressure processes make use of free radical generators or initiators, which are, according to requirements, oxygen, peroxydes or organic peresters.

.../...

All the autoclave processes make use of peroxydes or organic peresters nowadays. These have, if compared to oxygen, numerous advantages :

- Safety in use : the use of oxygen is dangerous in the secondary compressor area, the oxygen being usually injected at this compressor. Any defective operation of the valve, leading to a temperature rise in the compressed ethylene becomes more dangerous when this ethylene contains the initiator.

- Flexibility of use.

- Better control of reaction steadiness (considerable reduction of the number of decompositions).

- Possibility of adjusting the temperature profile inside the reactor, to obtain the required structure.

The great variety in the half-life of these initiators (wrongly called "catalyst") allows the most satisfactory polymerisation temperature (between 140 and 300° C) to be chosen.

The use of these various initiators in a reactor fitted with appropriate stirring devices ensures any temperature profile inside the reactor from a uniform temperature (inlet - outlet) profile, to a multiple temperature profile.

This possibility of choosing with great accuracy the best temperature profile is a big advantage of the Ethylene Plastique process.

The temperature profile, the polymerisation pressure, the nature of the transfer agents (telogene) used, are the factors that control the structure of the polymers. Before giving more details about the relationship between polymerisation conditions, structure and application properties, a brief account of the means of analysis must be given.

.../...

a) Structure analysis

The analysis usually gives values to a certain number of characteristic parameters such as :

η : "intrinsic viscosity" obtained by measuring the viscosity of a polymer solution at a given concentration, in decalin at 135° and by extrapolating for concentration zero.

b : long chain branching (intermolecular transfer) (special parameter of Ethylene Plastique).

Mn : average molecular weight (by number)

$$Mn = \frac{\Sigma\ N\ (M)\ x\ M}{\Sigma\ N\ (M)}$$

Mw : average molecular weight (by weight)

$$Mw = \frac{\Sigma\ N\ (M)\ x\ M^2}{\Sigma\ N\ (M)\ x\ M}$$

$\frac{Mw}{Mn}$ = ratio featuring the width of molecular weight distribution.

These are the most characteristic parameters. Parameter "b" is particularly important. The realisation of a quantity to represent this long chain branching is tricky. Meanwhile, it is still under active investigation.

The values of b, Mn, Mw and $\frac{Mw}{Mn}$ are obtained by gel permeation chromatographe which allows the separation of the macromolecules according to their hydrodynamic volume (calibration by a standard polyethylene, the mass distribution of which is known). A molecular distribution characteristic curve is thus obtained, giving the percentage of moles of molecular weight M, against molecular weight (M varying from 10^3 to 10^6, the peak of the maximum frequency peak being between 10^4 and 5.10^4).

.../...

Other interesting information is given by infrared spectroscopic analysis allowing the determination of the number of methyl groups and of double linkings for 1,000 carbon atoms, as well as the nature of these double linkings (vinylene, vinyl, vinylidene). These figures are related to the polymerization conditions (temperatures, pressures, nature of the transfer agent).

b) Measuring viscosities under molten conditions

A first analysis method consists in determining by means of the high pressure grader (capillary extrusion) the following curves :

Shearing tension as a function of the shearing rate, by measuring pressure P and outflow Q.

Shearing tension : $\sigma = \frac{PR}{2L}$ in dynes per cm2

Shearing rate : $\varepsilon = D = \frac{4\,Q}{\pi R^3}$ in s^{-1}

From these experimental curves, the true curves will be found by application of the so-called "entrance" or "couette" and "non-Newtonian" corrections.

After these two corrections have been made, the so-called "true curves" $\sigma v \varepsilon$ are obtained with which can be traced the viscosity/shearing curves, as, by definition the viscosity $\eta = \frac{\sigma}{\varepsilon}$

A second method of analysis consists in making tests under dynamic conditions The "balance rheometer" (two concentric hemispheres rotating at the same angular velocity ω and with a small angle α between their axes) are used : this device, discovered by the Research and Development Manager of Ethylene Plastique Company, M. Kepes, has been submitted to the Fifth International Congress of Rheology (1968). But its use, the reaction of a viscoelastic medium, periodically distorted, can be calculated.

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c) Measuring viscoelastic behaviour

Besides the measure of the "entrance correction" above mentioned, which is related to the elastic behaviour, we should mention the measurement of the swelling of the extrudate from the capillary tube :

The ratio is measured, of the diameter of the extruded strand to that of the throat of the die.

d) Interpretation of the analytical results

The Ethylene Plastique engineers have been busy for several years in connecting these structural and rheologic behaviour characters to the various application properties on one hand, and to the polymerization conditions on the other. The Ethylene Plastique process allows the modification of these structural and rheological characteristics quite a lot, and thus ensures the manufacture of the most suitable resin for each special application.

Structure

Fig. 2 shows the various types of distribution curves which may be obtained :

Curve 1 : resin for heavy duty bags with high stress-cracking resistance (plastylene FB 3010)

Curve 2 : resin for high clarity film with very good draw-down : plastylene FX 341 and FA 0240 X (this curve will again be found for film grades manufactured in tubular reactors).

Curve 3 : resin for general purpose thin film with very good mechanical properties (general purpose film) : plastylene FA 0240

Curve 4 : products with similar structure to those of polymers obtained in a typical autoclave reactor : resin for coating, resin for injection moulding.

.../...

Curve 5 : resin for telephonic wire insulation which may be extruded at high line speed (1,200 to 1,500 m/mn) "plastylene CB 3528".

To quote a few figures, we may say that for the same melt index (2 for instance), Mw can vary from 50,000 to 250,000, b can vary from 1.1 to 2.

$\frac{Mw}{Mn}$ can vary from 2.5 to 14.

η (intrinsic viscosity) can vary from 1 to 1.4.

Rheology

As regards the non-Newtonian behaviour N, fig. 6 shows that it is all the more strongly marked as D or $\frac{PR}{2\ L}$ are higher. This means that polyethylenes come nearer to true Newtonian behaviour at low shearing rates, and deviate progressively at high shearing rates. On the other hand, for given melt-flow conditions, N rises progressively as the melt-index of the polymer falls (as its molecular weight rises).

Examining now the rheologic behaviour differences, for a given melt-index, and molecular distribution, it can roughly be said that the resins with narrow molecular distribution ($\frac{Mw}{Mn}$ low, Mn low, b low) are characterized by :

- A lower viscosity limit.

- A more extended Newtonian behaviour (viscosity is maintained to a higher shearing value).

- For higher gradients, a steeper slope of viscosity fall as a function of shear rate (non-Newtonian behaviour).

(These three characters are shown on fig. 5)

.../...

- A weaker swelling of the extruded strand.

- A lower "entrance correction" (drop in pressure owing to convergency at the entrance of a capillary tube).

2. Application properties

The statistical surveys of consumption of low density polyethylene in France in 1971 give the following figures according to applications :

film : 59 % out of which heavy duty bags 15 %
general purpose thin film 26 %
agricultural film 6 %

injection and blow moulding : 23 %

coating : 4 %

wire and cable : 6 %

piping : 6 %

The outstanding importance of the so-called "standard" applications is obvious ; the "noble" applications represent a rather small tonnage but this market is more profitable. It is thus necessary that a polyethylene process should permit production of suitable resins for each of the applications. Ethylene Plastique is able to do so, as is shown by table n° IV giving the main commercial choices, thanks to the possibility of controlling the molecular distribution of the polymer.

As an example, let us look into the details of the choices offered for three characteristic applications :

- thin film
- heavy duty bags
- coating.

.../...

a) Grades for thin film

Until about 1965, it was generally believed that the grades manufactured in tubular reactors were better for film than those manufactured in a standard autoclave reactor.

Fully aware of the problem, Ethylene Plastique studied thoroughly the reasons for this difference of behaviour and established that the application properties considered important, these being the draw-down and the optical features, were mainly related to high molecular weights and long branchings (intermolecular transfer) of the molecules. Now, these structural properties mainly depend upon the polymerization temperature profile used. The transformation of the usual autoclave process into an autoclave process allowing deliberate adjustment of the temperature profile was to lead Ethylene Plastique to answer this problem. The grades now offered for these applications are by no means inferior to the best tubular grades as can be seen from the tables comparing the structural and applications properties. In these tables, the thin film group has been broken down into three distinct subgroups.

- Grades for high clarity (or "crystal") films

The required properties are mainly clarity, gloss and draw-down. The mechanical resistance properties are less important. For this reason, the grades offered for this application usually have a rather high density : 0,927 to 0,930 (all indicated densities are corrected to 20°C). For this application we offer FX 341, melt index 3, density 0,927.

Table V gives the values of the structural parameters for resin FX 341 compared to the best competing resins.

Table VII compares the application properties of FX 341 with those of five competing resins in the extrusion conditions of table VI.

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- Grades for general purpose thin film

Clear films - FA 0240 X - FD 0328 - FD 0330

Contrarily to FX 341, these grades are intended for a wide variety of uses, we enter the field of the "general purpose" film. They are very good comprises of the qualities required for this application : draw-down, clarity, mechanical strength.

The structural characteristics are given in table V, the application tests in table VIII (extrusion conditions of table VI) in comparison with those of 7 competing grades. Note the particularly high value for gloss of FA 0240 X and its excellent draw-down. These high standards have been attained, while keeping a very high level for mechanical properties (impact strength particularly).

Standard films - FA 0238 and FA 0240 - GA 0238 and GA 0240

This is the field of medium thickness extrusion (30 to 50 microns).

The optical properties are of minor importance, the main feature is ease of extrusion, flexibility to very various and often badly controlled extrusion rates.

The application results are also given in table IX, compared with those of six competing resins (extrusion conditions of table VI).

Another grade in this category is also worth mentionning although it is intended for a very exacting and special application, which is the extrusion of very wide films (used in building and agriculture). Ethylene Plastique offers for this application FA 0121. This is a resin of melt index 1 and 20°C density of 0,922 (see table X).

- Grades for heavy duty bags

These grades are used to make shopping bags, shrink films and heavy duty bags. For simplicity, we will examine only one of these grades - FB 3010 intended for large capacity bags (for fertilizer bagging, particularly).

This is in fact a very tricky problem because the polyethylene used has to resist the stress-cracking provoked by the anti-caking agents incorporated in the fertilizers. The welding of the standard polvethylene bags are destroyed by these anti-caking agents. FB 3010 on the contrary resists perfectly well. This stress-cracking strength can be obtained with EVA copolymers but the bags are deficient in stiffness and cannot be used on the self-acting bag-machines of the European market. In this field FB 3010 has an outstanding position, and no tubular resin can match it at the present time.

FB 3010 is a striking sample of technically sophisticated grade used for what we have called a "standard" application. For a polyethylene manufacture, this is the most difficult problem to solve, because this sophisitication has to be obtained at a very low cost-price.

- Coating grade

We now enter the field of these resins, referred to as "noble" on account of their critical uses. We have chosen, to associate in this paper this application with other grades, in order to show the great flexibility of the Ethylene Plastique process which permits the manufacture of resins or thin films comparable to tubular resins as well as resins for coating more usually considered as a prerogative of the autoclaves. These are technically sophisticated resins which are also compromises between a certain number of requirements (great lamination speed, reliability of the neck-in, good adhesion, good water impermiability, weak emission of smoke and smell) with more or less influence of one or another of these factors according to the desired type of coating. The following types can be noted, for instance.

.../...

- High speed lamination (above 300 m/mn) of kraft paper, cardboard and other backing-materials for which are required : good resistance to water vapour, good mechanical properties but with a medium welding rate of the laminate.

  Lamination thickness : 12 to 20 microns.

  The grade offered is then LX 350 (melt index 3, density 0.926).

- Medium speed lamination (between 100 and 280 m/mn) of papers, cardboard, aluminium sheets, needing very satisfactory thermowelding (high welding rate of the composite).

  Lamination thickness : 12 to 60 microns.

  The grade offered is LA 0703 (melt index 7, density 0,920).

  Structural parameters are then very different from those of the film grades (see table XI giving the values of these parameters for LX 350, LA 0703 and three competing autoclave resins).

V - CONCLUSIONS

In this paper, we hope we have pointed out the trends in the evolution of low density polyethylene manufacture in the years to come. The necessity of reducing the cost price of polyethylene demands :

- The erection of units of capacity equal to or above 50,000 tonnes per year capacity in a very short delay (in 1972, Ethylene Plastique puts into operation the first 80,000 tonnes per year unit).

.../...

- To reduce continually the construction cost of these units by limiting as far as possible the operating pressure, which will at the same time increase the reliability and safety of the equipment.

The process of the future has thus to be a synthesis of the old autoclave and tubular processes, which means that it must permit the polymerization temperature profile to have any intermediate shape between the sharp slope of the tubular and the steady temperature profile of the autoclave ideally homogeneous. The use of a polymerization reactor of low ratio $\frac{\text{length}}{\text{diameter}}$ (below 20) including a special stirring device allows us to solve this problem which in our view is well-nigh insoluble with the tubular reactor.

Figure 1

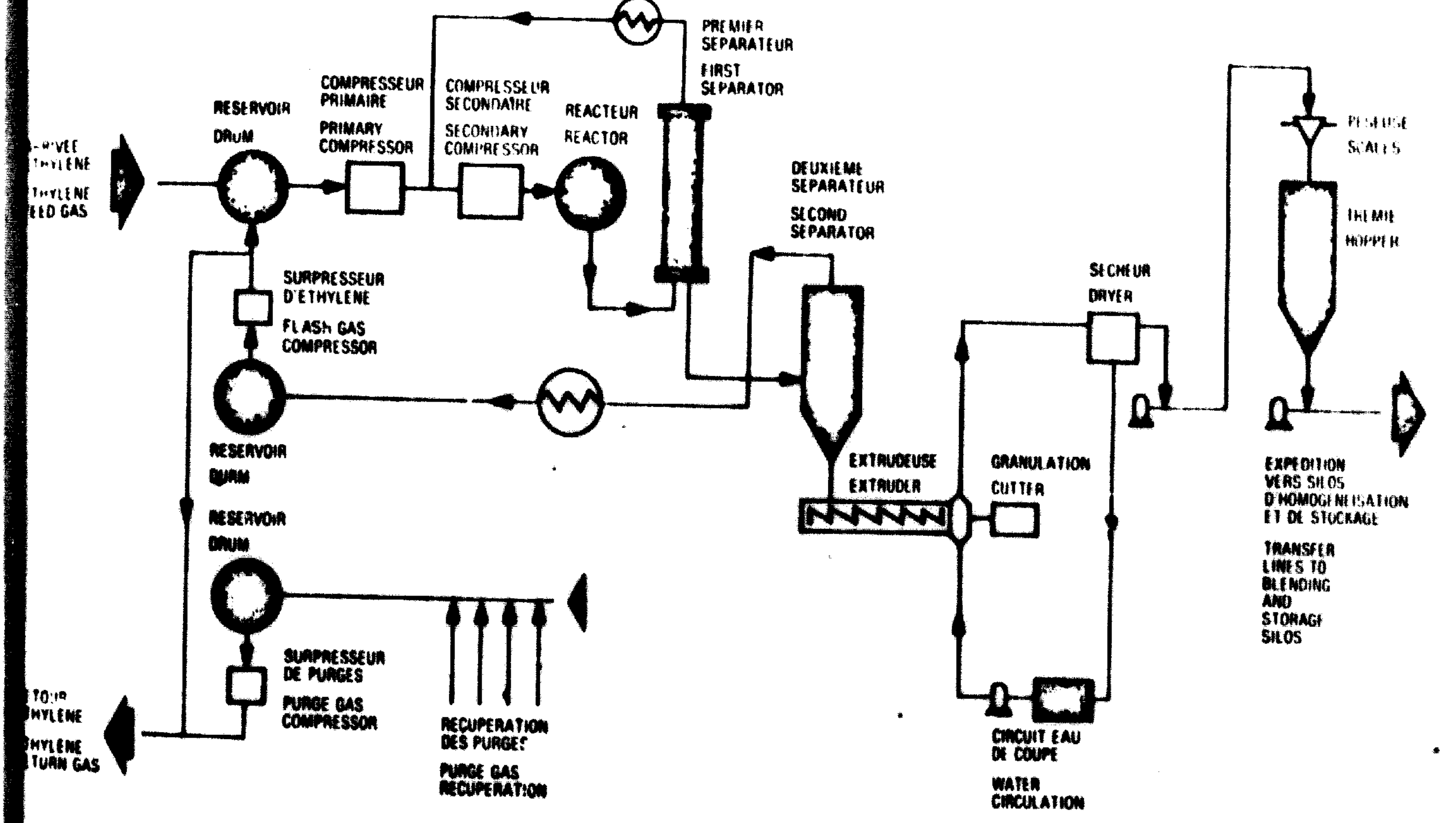
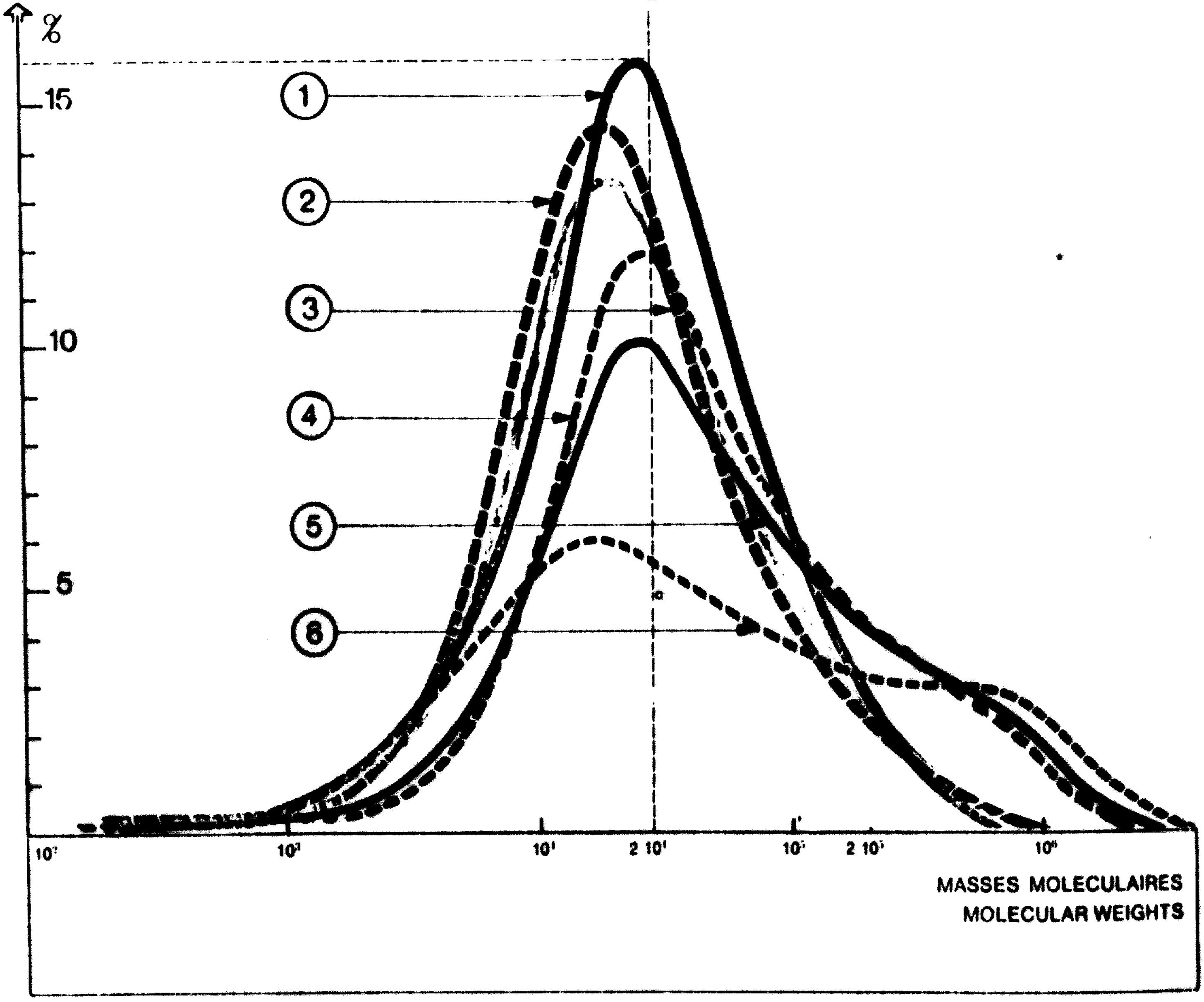
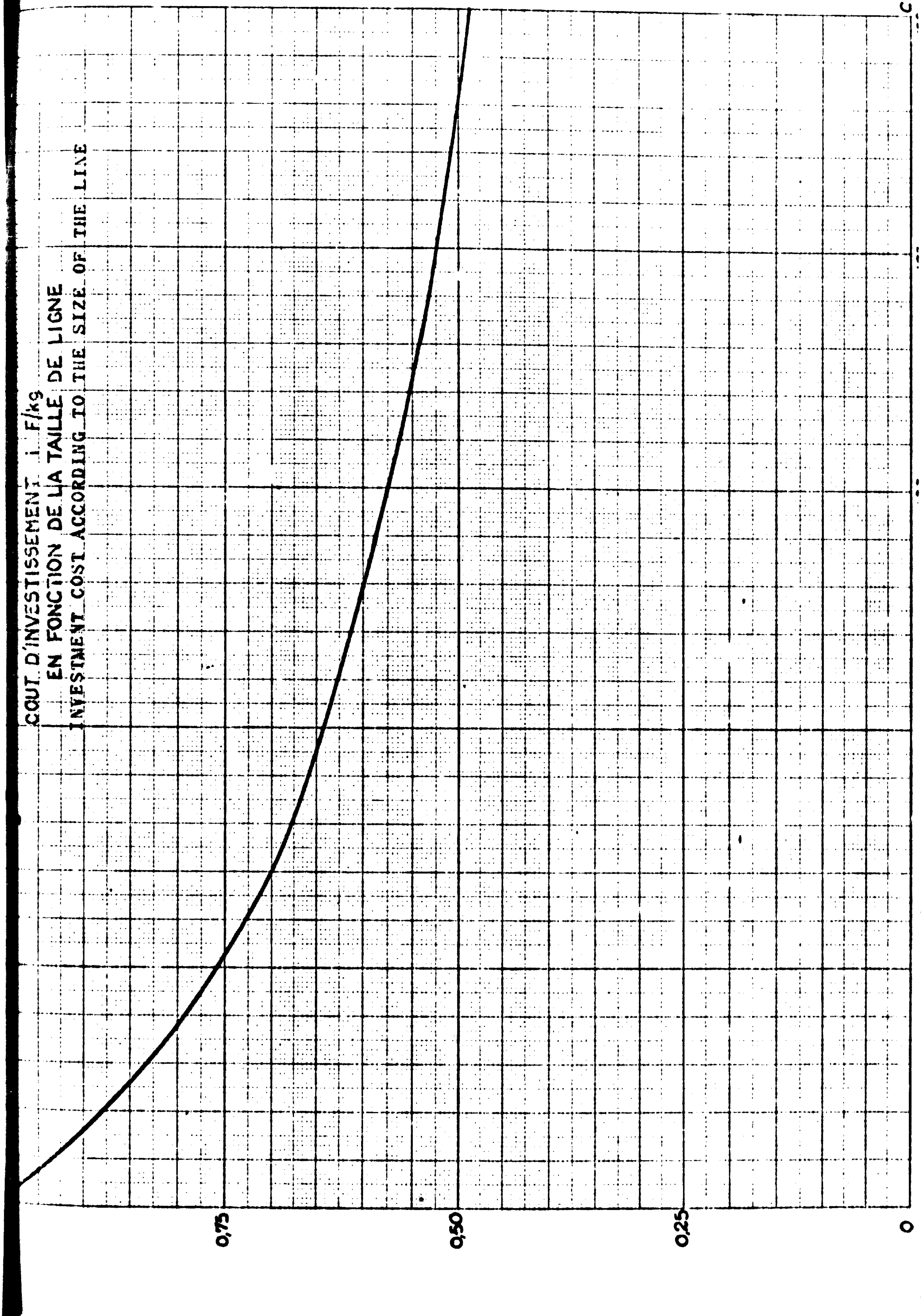

RIVEE
THYLENE
THYLENE
EED GAS
RESERVOIR
DRUM
COMPRESSEUR PRIMAIRE
PRIMARY COMPRESSOR
COMPRESSEUR SECONDAIRE
SECONDARY COMPRESSOR
REACTEUR
REACTOR
PREMIER SEPARATEUR
FIRST SEPARATOR
DEUXIEME SEPARATEUR
SECOND SEPARATOR
SURPRESSEUR D'ETHYLENE
FLASH GAS COMPRESSOR
RESERVOIR
DURM
RESERVOIR
DRUM
SURPRESSEUR DE PURGES
PURGE GAS COMPRESSOR
TOUR
HYLENE
HYLENE
TURN GAS
RECUPERATION DES PURGES
PURGE GAS RECUPERATION
EXTRUDEUSE
EXTRUDER
GRANULATION
CUTTER
CIRCUIT EAU DE COUPE
WATER CIRCULATION
SECHEUR
DRYER
PESEUSE
SCALES
TREMIE
HOPPER
EXPEDITION VERS SILOS D'HOMOGENEISATION ET DE STOCKAGE
TRANSFER LINES TO BLENDING AND STORAGE SILOS

Figure 2

REPARTITIONS MOLECULAIRES
DE QUELQUES
POLYETHYLENES HAUTE PRESSION
ETHYLENE PLASTIQUE

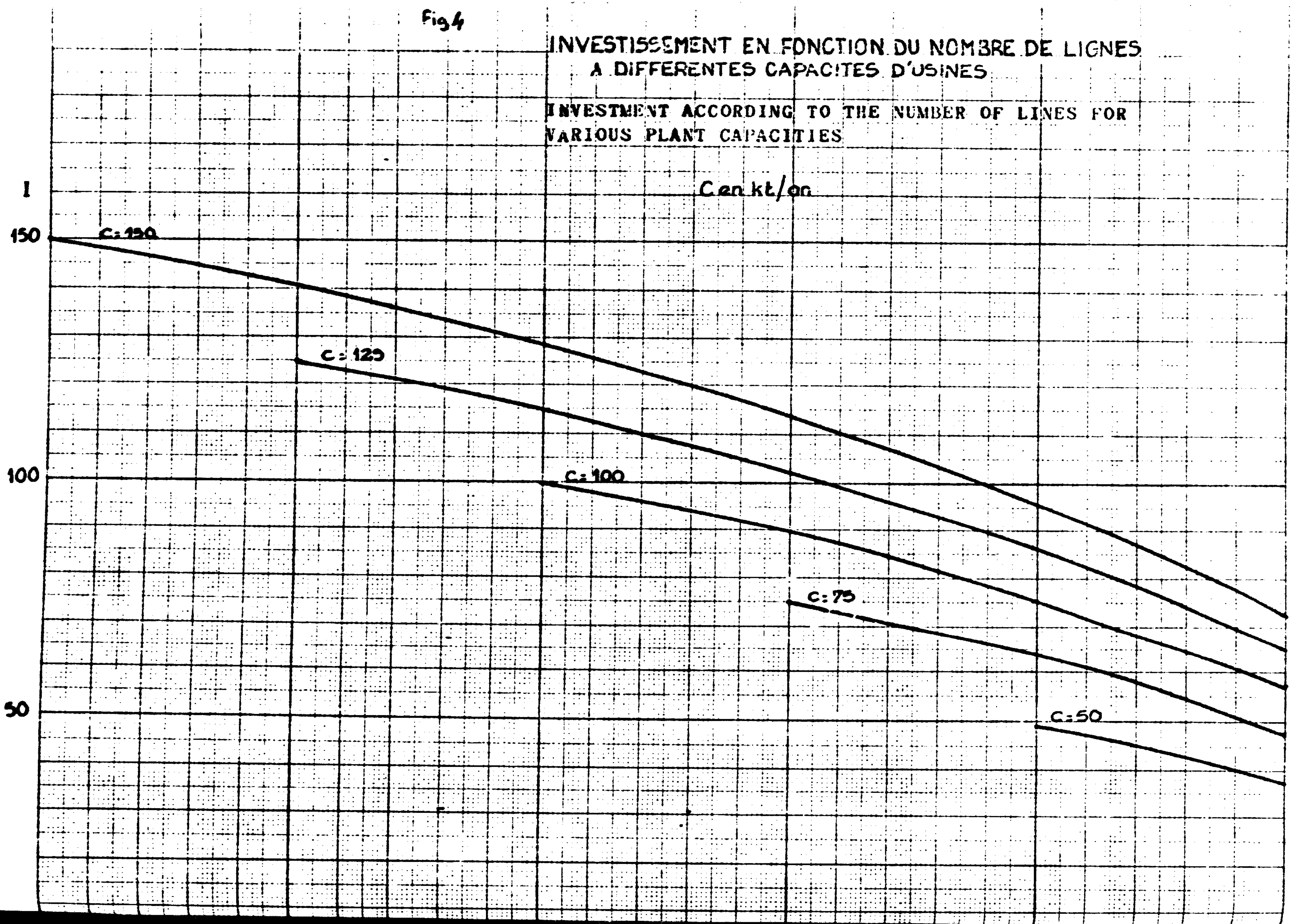
MOLECULAR WEIGHT
DISTRIBUTIONS OF SOME
HIGH PRESSURE POLYETHYLENES
FROM
ETHYLENE PLASTIQUE





COUT D'INVESTISSEMENT i F/kg
EN FONCTION DE LA TAILLE DE LIGNE
INVESTMENT COST ACCORDING TO THE SIZE OF THE LINE

Fig 4



INVESTISSEMENT EN FONCTION DU NOMBRE DE LIGNES
A DIFFERENTES CAPACITES D'USINES

INVESTMENT ACCORDING TO THE NUMBER OF LINES FOR
VARIOUS PLANT CAPACITIES

Figure 5

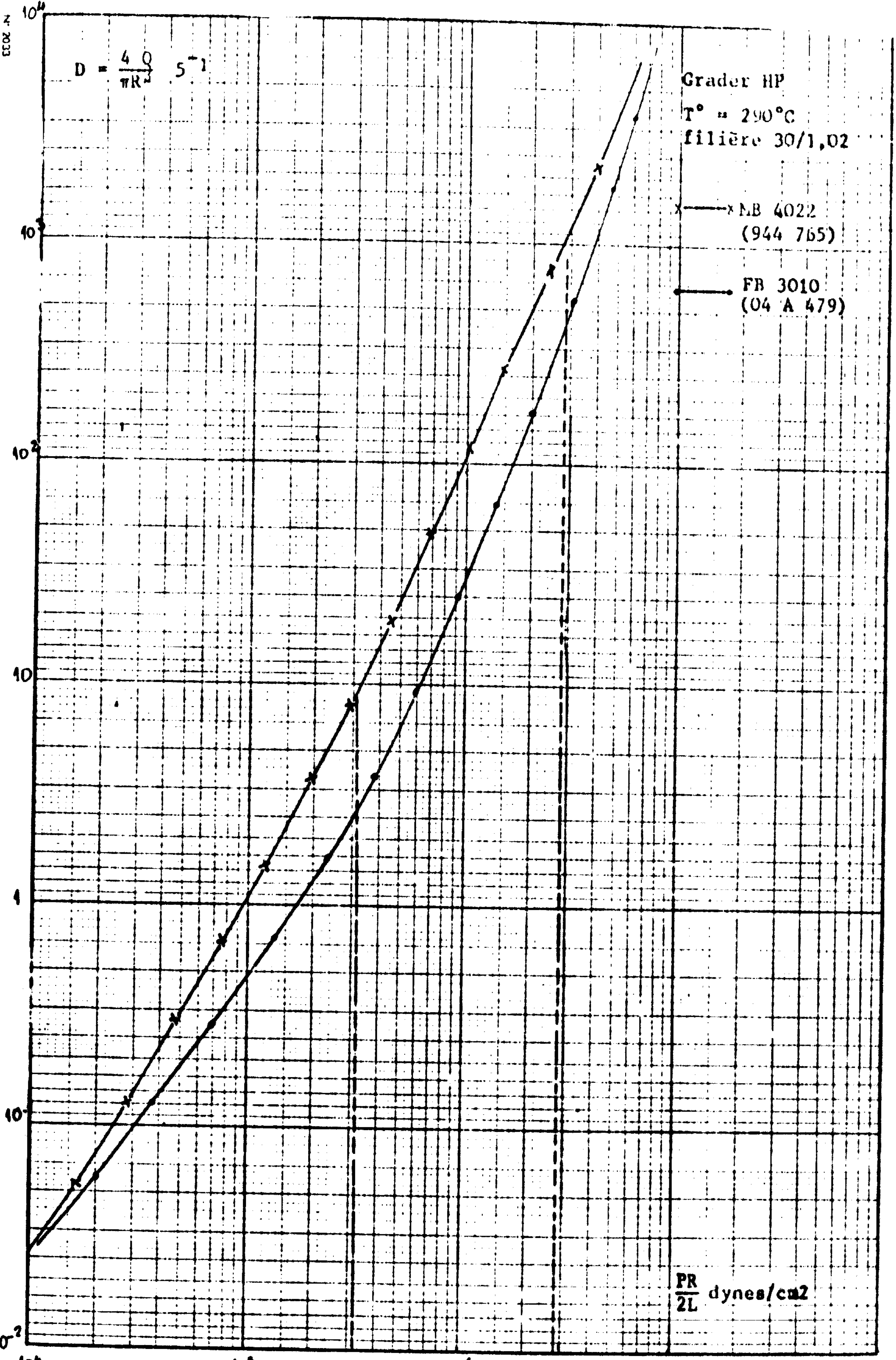

$D = \frac{4Q}{\pi R^3}$ s^{-1}
Grader HP
T° = 290°C
filière 30/1,02
x——x MB 4022 (944 765)
●——● FB 3010 (04 A 479)
10^4
10^3
10^2
10
1
10^{-1}
10^{-2}
10^4
10^5
10^6
10^7
$\frac{PR}{2L}$ dynes/cm2

Figure 6

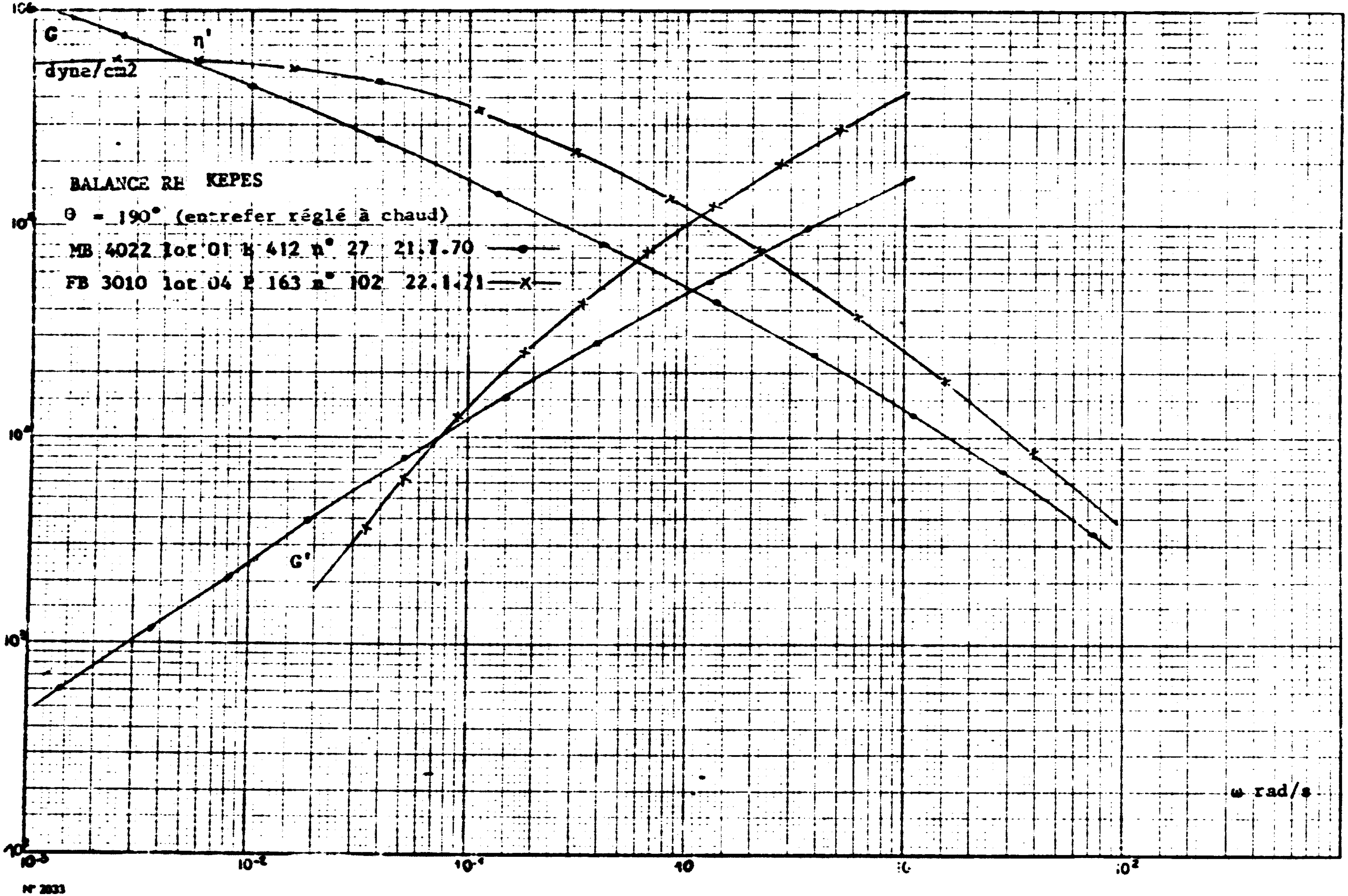

G
dyne/cm2
η'
BALANCE RE KEPES
θ = 190° (entrefer réglé à chaud)
MB 4022 lot 01 E 412 n° 27 21.7.70 —●—
FB 3010 lot 04 P 163 n° 102 22.1.71 —x—
G'
ω rad/s
10⁶
10⁵
10⁴
10³
10²
10⁻³
10⁻²
10⁻¹
1
10
10²
N° 2033

TABLEAU I

ITEM	COEFFICIENT
COMPRESSION	0,294
POLYMERISATION	0,834
GRANULATION COMPOUNDS........................	0,488
STORAGE – HOMOGENISATION	0,569
SET OF HEAVY EQUIPMENT	0,474
THERMAL EQUIPMENT	0,717
CENTRAL HEATING	0,515
CHILLED WATER SUPPLY	0,489
UTILITIES	0,603
INSTRUMENTATION	0,634
CIVIL WORK	0,659
ELECTRIC DEVICES	0,362
PIPING PAINTING INSULATION	0,660
TOTAL INVESTMENT	0,603

INITIATION

Tableau II

$$I \longrightarrow R^* + R'^*$$

Exemple : $(CH_3)_3C-OO-C(CH_3)_3 \longrightarrow 2(CH_3)_3-C-O^*$

Puis $(CH_3)_3-C-O^* \longrightarrow CH_3-CO-CH_3 + CH_3^*$

PROPAGATION

1ère $R^* + CH_2 = CH_2 \longrightarrow R-CH_2-CH_2^*$

nème $R-(CH_2-CH_2)^*_{n-1} + CH_2 = CH_2 \longrightarrow R-(CH_2-CH_2)^*_n$

TERMINAISON

Addition $R-(CH_2-CH_2)^*_n + R'^* \longrightarrow R-(CH_2-CH_2)_n-R'$

Dismutation $R-(CH_2-CH_2)^*_n + R'^* \longrightarrow R-(CH_2-CH_2)_{n-1}-CH=CH_2 + H-R'$

TRANSFERTS

Tableau III

PAR LE MONOMERE

$$R-(CH_2-CH_2)_n^* + CH_2=CH_2 \longrightarrow R-(CH_2-CH_2)_{n-1}-CH=CH_2 + CH_3-CH_2^*$$

PAR UN "AGENT" (Télogène)

$$R-(CH_2-CH_2)_n^* + AH \longrightarrow R-(CH_2-CH_2)_{n-1}-CH_2-CH_3 + A^*$$

$$A^* + CH_2=CH_2 \longrightarrow A-CH_2-CH_2^*$$

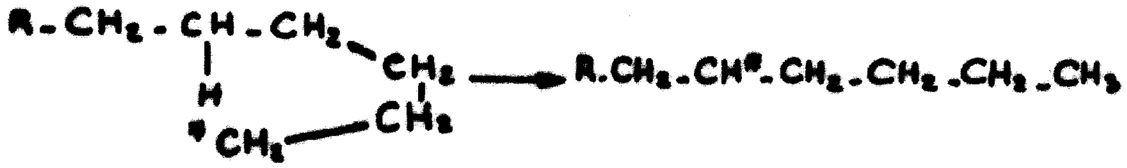
PAR LE POLYMERE

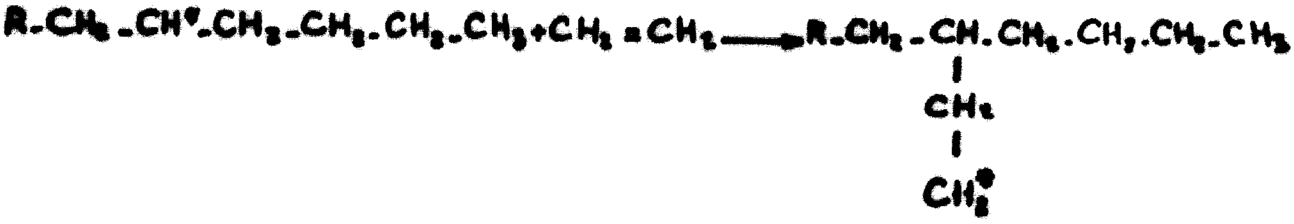
- INTERMOLECULAIRE

$$R-(CH_2-CH_2)^* + R'-CH_2-CH_2-R'' \longrightarrow R.CH_2.CH_3 + R_2-CH^*-CH_2-R_3$$

$$R_3-\overset{R_1}{\underset{CH_2}{}}\!>CH^* + CH_2=CH_2 \longrightarrow R_3-\overset{R_1}{\underset{CH_2}{}}\!>CH-CH_2-CH_2^*$$

- INTRAMOLECULAIRE





$$R-CH_2-CH^*-CH_2-CH_2-CH_2-CH_3 + CH_2=CH_2 \longrightarrow R-CH_2-\underset{\underset{\underset{CH_2^*}{|}}{\underset{CH_2}{|}}}{CH}-CH_2-CH_2-CH_2-CH_3$$

Tableau IV

LISTE DES PRINCIPALES QUALITES **ETHYLENE PLASTIQUE**

LIST OF THE MAIN **ETHYLENE PLASTIQUE** GRADES

EXTRUSION DE FILM
FILM EXTRUSION

FILM A USAGE GENERAL
GENERAL PURPOSE FILM

FA 0422 FD 0326 FA 0238
FA 0433 FD 0328 FA 0239
FX 284 (EVA) FX 353 FA 0240

FILM DE HAUTE CLARTE
HIGH CLARITY FILM

FD 0330 FA 0238 X FD 0726
FD 0331 FA 0240 X FX 341

SACS DE HAUTE RESISTANCE
HEAVY DUTY BAGS

MB 4022 FB 3010 FB 5005
MB 7025 FX 286 (EVA) FB 5021

FILM AGRICOLE
AGRICULTURAL FILM

FB 5036 FA 0227 FD 0336
FA 0226 FA 0230 FX 444

ENDUCTION
COATING

FA 0401 LA 0703 LX 350

CABLES
WIRE AND CABLE

CB 3528 CA 0226 CA 0228
CB 3529 CB 3526 CD 0302

CD 0161 - Auto-extinguible
self extinguishing

EA 0224 - Expansible
Cellular

CX 407 - Réticulable
Cross linkable

TUBE ET TUYAU
TUBE AND PIPE

MB 4022 T TE 4025
FA 0235 TE 7024

EXTRUSION-SOUFFLAGE
BLOW MOULDING

MA 0701 MD 0303 MV 2001 (EVA)
MA 2004 MD 0707 MV 0201 (EVA)
MA 4005 MD 2002

POUDRES
POWDERS

PA 0780 PA 4031 PV 0231 (EVA)
PA 2080 PA 7032 PV 2030 (EVA)

TABLEAU V : COMPARAISON des PARAMETRES de STRUCTURE

Echantillons	(n)	G	d	b	B	Mw	Mn	$\frac{Mw}{Mn}$	CH_3/1 000 C	Nombre de =/1 000 C		
										Trans	Vinyle	Vinylidène
FILMS de HAUTE CLARTE												
FX 341	1,08	2,6	0,9270	1,3	4,8	72 000	17 000	4,2	20,8	0,055	0,205	0,157
T 1	0,92	3,6	0,9266	1,5	6	72 000	18 000	4	19,5	0,045	0,037	0,200
T 2	0,92	4	0,9270	1,3	7,6	67 000	15 500	4,4	18,4	0.031	0,033	0,173
FILMS CLAIRS												
FA 0240 X	1,02	1,8	0,9253	1,3	5,35	65 500	18 200	3,6	18,4	0,033	0,033	0,217
FB 0330	1	2,9	0,9264	1,7	3,8	92 300	21 800	4,2	22,2	0,048	0,204	0,138
FD 0328	1,05	2,9	0,9258	1,8	4,0	115 000	21 800	5,3	20,8	0,050	0,202	0,124
9	0,84	2,05	0,9272	1,9	3,2	83 500	24 200	3,5	17,2	0,022	0,118	0,098
T 20	1,08	1,65	0,9255	1,85	5,3	101 000	19 800	5,1	18,9	0,036	0,039	0,198
A 19	0,93	4,3	0,9270	1,75	4,3	84 500	19 000	4,4	21,8	0,092	0,035	0,283
T 21	1	3,3	0,9272	1,2	6,8	65 500	18 200	3,5	18,8	0,050	0,037	0,169
FILMS STANDARDS												
FA 0240	1,11	1,8	0,9236	1,7	4,6	109 000	21 900	5	21	0,045	0,034	0,217
FA 0121	1,20	1	0,9241	1,4	5	92 950	20 150	4,6	20,8	0,042	0,034	0,270
T 30	1,08	1,08	0,9247	1,7	5,2	105 000	20 000	5,3	21	0,041	0,035	0,222
T 26	0,98	1,8	0,9271	1,8	7,75	129 300	15 800	8,2	23,4	0,047	0,081	0,282

T A B L E A U VI

EXTRUSION CONDITIONS	OPTICAL AND MECHANICAL PROPERTIES	DRAW-DOWN
EXTRUSION PRESS	Samafor	"
Type	45 x 20 D	"
Compression ratio of the screw	3,3	"
DIE		
Type	Lateral feeding	
Die-gap	75/100 mm	"
Diameter	165 mm	"
EXTRUSION TEMPERATURE		
CE	140°C	"
CC 1	140°C	"
CC 2	145°C	"
CS	145°C	"
T 1	150°C	"
T 2	150°C	"
T 3	150°C	"
F	150°C	"
RESIN TEMPERATURE	175°C	"
ROTATING SPEED OF THE SCREW	60 tr/mn	90 tr/mn
BLOW UP RATIO	2	1,2
WINDING UP SPEED	10 m/mn	
THICKNESS OF THE FILM	25 microns	

T A B L E A U VII

FILMS HAUTE CLARTE HIGH CLARITY FILM

APPLICATION PROPERTIES			PRODUCTS					
Properties	Standard or method	Unit	FX 341	T 1	T 2	A 4	T 5	T 7
Melt index	Afnor NPT 51-016	g/10 mn	2.80	3.7	3.6	4.2	2.4	4.7
Density	BNMP 3 733/2	g/cm3	0.9270	0.9244	0.9260	0.9260	0.9255	0.9295
Optical characteristics of blown film								
Clarity Gardner								
Thickness	E 2.4.1.2. (1) (ASTM D 1746-62 T)	micron	25	25	25	25	25	25
Clarity		%	65	59.4	60	55	50	65
Haze Gardner								
Thickness	E 2.4.2.1. (1) (ASTM D 1003-61)	micron	25	25	25	25	25	25
Haze		%	9	6	8.4	9	9.4	8.7.
Gloss Gardner								
Thickness	E 2.4.3.1. (1) (ASTM D 2457-65 T)	micron	25	25	25	25	25	25
Gloss		%	9.6	9.5	9.6	9.3	9	9.3
Draw-down of blown film								
Minimum thickness		micron	23	30	25	30	26	18
Winding up speed	-	m/mn	32.5	17.5	25	20	27.5	29.5

(1) E.P. method

TABLEAU VIII

FILMS CLAIRS CLEAR FILMS

APPLICATION PROPERTIES			PRODUCTS								
Properties	Standard or method	Unit	FD0328	FA0240X	T 9	T 14	T 15	A 15	A 17	A 18	T 2
Melt index	Afnor NPT 51-016	g/10 mn	3	1.9	2.2	1.55	2	1.7	1.9	1.95	2
Density	BNMP 3 733/2	g/cm3	0,9245	0.9235	0.9254	0.9263	0.9263	0.9255	0.9250	0.9236	0.92
Optical characteristic of blown film											
Haze Gardner											
Thickness	E 2.4.2.1. (1) (ASTM D 1003-61)	micron	25	25	25	25	25	25	25	25	25
Haze		%	10	6	11	12.4	9.1	6.8	9.3	7.7	12.
Gloss Gardner											
Thickness	E 2.4.3.1. (1) (ASTM D 2457-65 T)	micron	25	25	25	25	25	25	25	25	25
Gloss		%	7.6	10	6.2	6.6	8.1	9.7	7.9	9.8	7.1
Draw-down of blown Film											
Minimum thickness		micron	27	23	26	40	40	55	36	32	44
Winding up speed		m/mn	26	32	27.5	16.5	16.5	12.5	18.5	20	10.
Mechanical properties of blown film 50 microns											
Yield point stress		daN/mm2									
Longitudinal	ASTM D 882-67 T (20°C ; 65 % HR ; 500%/mn)		1.2	1.2	1.5	1.3	1.35	1.3	1.2	1.2	1.1
Transversal			1.2	1.2	1.7	1.45	1.4	1.3	1.25	1.2	1.1
Tensile strength		daN/mm2									
Longitudinal			1.85	2.3	2.3	1.85	2.4	2.4	2	2.2	1.8
Transversal			1.7	2.1	1.8	1.95	2.1	1.95	1.5	2	1.6
Elongation		%									
Longitudinal			500	450	320	260	420	400	360	400	420
Transversal			630	730	660	620	780	720	600	790	680
Impact (T.G. = 2)	ASTM D 1709-67	kgm/mn	1.1	1.55	1.15	1.3	1.1	1.3	1.2	1.1	1.2

(1) E.P. method

TABLEAU IX

FILMS STANDARD STANDARD FILM

APPLICATION PROPERTIES			PRODUCTS							
Properties	Standard or method	Unit	FA0238 FA0240	T 23	T 24	T 25	GA0238	T 28	A 29	T 30
Melt index	Afnor NPT 51-016	g/10mn	1.85	1.53	1.54	1.66	1.70	1.15	1.64	1.58
Density	BNMP 3 733/2	g/cm3	0.9220	0.9217	0.9195	0.9218	0.9220	0.9216	0.9206	0.9235
Optical characteristics of blown film										
Haze Gardner										
Thickness	E 2.4.2.1. (1) (ASTM D 1003-61)	micron	25	25	25	25	25	25	25	25
Haze		%	13	14.2	14.4	11.2		24.4	24.1	17.8
Gloss Gardner										
Thickness	E 2.4.3.1. (1) (ASTM D 2457-65 T)	micron	25	25	25	25	25	25	25	25
Gloss		%	5.8	5	5.7	6.6	4.75	3.2	2.8	4.6
Draw-down of blown film										
Minimum thickness		micron	37	80	35	40	45	56	58	48
Mechanical properties of blown film 50 microns										
Yield point strength		daN/mm2								
Longitudinal			1	1.04	0.9	1	1	0.7	0.9	1.14
Transversal			1.15	1	1	1.8	1.25	1.1	0.8	1.11
Tensile strength		daN/mm2								
Longitudinal	ASTM D 882-67 T (20°C ; 65 % HR ; 500%/mn)		1.8	1.6	1.8	1.8	1.8	1.25	1.9	1.96
Transversal			1.8	1.8	1.6	1.5	1.6	1.6	1.7	1.65
Elongation		%								
Longitudinal			300	260	250	410	285	280	370	425
Transversal			600	710	560	640	580	630	730	660
Impact strength			- 1.5	1.05	2	1.1	1.5	1.4	2.4	1.3

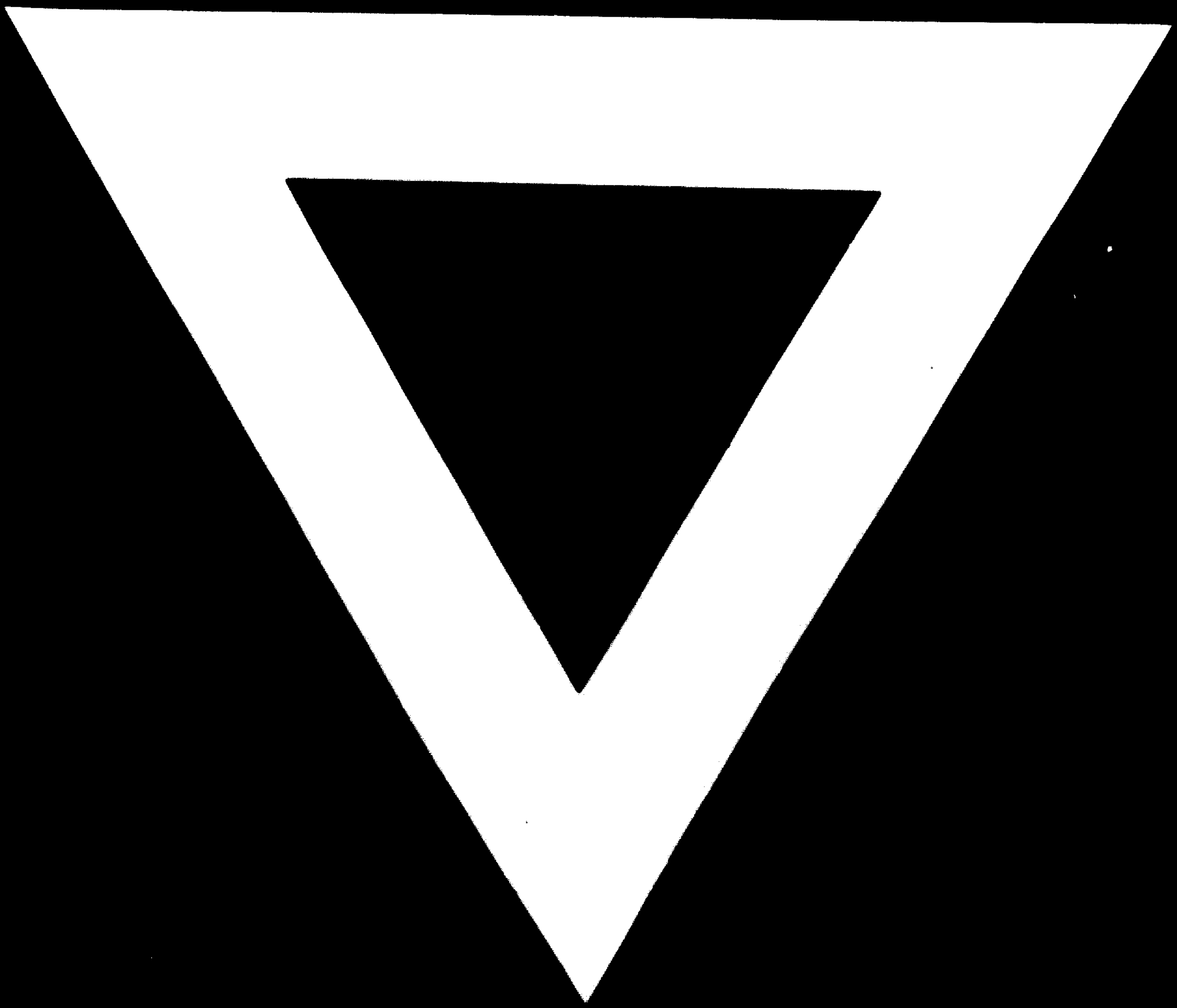
(1) E.P. method

T A B L E A U X

PROPERTIES		UNIT	FA 0121-122	32	23
Melt index		g/10 m	1	0,89	1,15
Density		g/cm3	0,9225	0,9217	0.9216
Output (a ~ 155 - 168°C and G 110 s^{-1})		kg/h	15.6	15.2	15,6
Draw-down		micron	45 - 50	90	56
Yield point strength	L	daN/mm2	1.1	1.2	0.7
(50 microns)	T		1.1	1.2	1.1
Tensile strength	L	daN/mm2	1.9	2	1.95
(50 microns)	T		1.9	2	1.6
Elongation	L	%	400	330	280
(50 microns)	T		600	600	630
Impact strength (50 microns)		kgm/mm	1,6 - 1,7	2,1	1,4
Gloss 25 microns		%	5,6		3,2
50 microns			8,5	3,8	4
Clarity 25 microns		%	8		1,5
50 microns			4	0,9	1,1
Haze 25 microns		%	18		24,4
50 microns			14	25,7	16,3

Tableau XI

Echentillons	(η)	G	d	b	B	Mw	Mn	$\frac{Mw}{Mn}$	CH_3/ 1 000 C	Nombre de = / 1 000 C		
										Trene	Vinyle	vinylidène
LA 0703	1,07	7,0	0,9230	2,15	5,0	158 500	20 400	7,8	23,5	0,046	0,040	0,310
LX 350 A	1,17	3,5	0,9266	1,6	6,0	111 400	17 600	6,3	16,9	0,026	0,027	0,158
A 33	1,16	3,3	0,9270	1,65	4,6	118 000	20 200	5,9	1,70	0,030	0,027	0,142
A 34	1,05	3,7	0,9270	1,7	5,0	107 000	18 400	5,8	16,6	0,020	0,020	0,164
A 35	1,01	4,6	0,9269	2,0	4,5	117 600	21 000	5,6	17,7	0,029	0,028	0,158



23.7.74