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Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/S1474-6670(17)55589-5
IFAC Proceedings Volumes, 20, 13, pp. 223-228, 1987-10-01

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IGM86-403-257
CNRC 25090

AN AUTOMATIC MEASUREMENT OF DENSITY OF POLYETHYLENE

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Submitted to the:
6th International IFAC/IFIP/IMEKO
Conference on Instrumentation and Automation
in the Paper, Rubber, Plastics and
Polymerization Industries
October 27-29, 1986, Akron, Ohio/USA

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ABSTRACT

The value of density, ρ, is a very important parameter for the characterization of polyethylene (PE). Usually, ρ, is measured using a density gradient column, on a small piece taken from a plaque prepared according to ASTM standards. Here, we present a new technique of measuring the density of PE. The technique is based on the propagation of ultrasonic waves in the standard (ASTM) plaques of PE. While the acoustic method has an accuracy which is equivalent to that of the standard method, it also possesses a number of advantages: ease of use, foolproof, reliable, repetitive and nondestructive. Above all, the measurement is automatic and rapid (30 sec.). The basic principle of the measurement will be described and results shown. The theoretical foundation will be discussed on the grounds of a model for the elastic moduli in a multiphase medium.

I. INTRODUCTION

Polyethylene (PE) is probably the most important product of the polymer industry. This is due in great part to the fact that PE is relatively economical to make but with the important added feature that the fabrication cycle can be modified to yield a wide spectrum of products having different properties. In order to take advantage of this, it is of primary importance for the producer and also for the processor to have means and methods to characterize the material in a representative manner.

Polyethylene is a semi-crystalline material and the degree of crystallinity has a strong bearing on the end use properties, such as the elastic moduli, the impact strength, the melting point and others. On the other hand the degree of crystallinity reflects itself in the value of density (1), which explains why density (ρ) has always been the major criterion for the characterization of polyethylene.

The most commonly used method for the measurement of density is that of the Density Gradient Collumn (ASTM-1505). First a plaque is made by compression molding the material to be tested. Then a small piece is cut out of this plaque, conditioned and placed in a column of liquid that exhibits a known density gradient. After the small piece has reached its equilibrium level, its density is obtained by reading its position in the column. The basic principle of the method is sound and well established, but the technique is in fact quite involved and tedious. However, for the purpose of quality or process control, the main drawback comes from that the measurement is long and time consuming (anywhere from 45 mins to 2 hrs).

In a previous paper (2) we proposed that a technique based on the measurement of ultrasonic velocity would allow for an accurate, reliable, yet rapid determination of density. Here we shall describe more extended experimental results which bring us to reassert the usefulness of this new approach as a tool for quality control. Also, our measurements of sound velocity give access to the elastic modulus of PE. Using these measurements we shall discuss the possible origin for the behaviour of velocity using a model for the elastic moduli that takes into account the microstructural details of the material. This will help to establish the physical foundations for the ultrasonic determination of density in polyethylene.

II. METHODOLOGY

It is not common practice to use ultrasonic techniques for the study of polymers (3), however, the method is practical and well documented. Polyethylene has been studied by several authors (4 to 8) and the various measurements tend to indicate that there exists a correlation between the velocity of sound, v, and the density, ρ. However, no systematic study has been done in the range of ultrasonic frequencies (MHz) and the nature of the correlation is neither clear nor well defined (6).

In our previous work we established (2) that there was indeed a strong correlation between the velocity of compressional sound waves, v_c and the density, ρ, of PE. Here we shall extend our study and measure the velocity of shear waves, v_s. This additional measurement is of importance since the knowledge of both the compressional velocity, v_c, and the shear velocity, v_s, together with the value of density, ρ, allow to calculate the bulk modulus, B, and the shear modulus, G. Indeed, for an isotropic material these are given (9) by:

$$B = \rho\ (v_c{}^2 - 4v_s{}^2/3) \tag{1}$$

$$G = \rho\ v_s{}^2 \tag{2}$$

Alternately one obtains the elastic (Young) modulus E, and the Poisson ratio ν:

$$E = 9BG/(3B+G) \tag{3}$$

$$\nu = 1/2 - E/6B \tag{4}$$

In these techniques, the strain is very small ($\Delta\varepsilon/\varepsilon \simeq 10^{-5}$), so the problem of strain dependence or creep, which is important for polymers, is virtually eliminated. On the other hand, the presence of molecular relaxation processes causes the elastic properties of polymers to depend on the rate at which the strain is applied. For polyethylene, torsion pendulum measurements at a frequency of 1 Hz versus temperature (10) show the existence of two main relaxation processes: the γ process at a temperature of -120°C and the combined β and α processes centered near 20°C. However experience shows (7) that increasing the frequency to the MHz region corresponds to a temperature shift of -60°C. Therefore, ultrasonic measurements, performed at room temperature, are actually made in a dispersionless region, between the γ and β, σ peaks, where no relaxation occurs.

III. Experimental Procedure

A) Samples

Our measurements were made on a representative number of samples, which covered the whole range of commercial grades (11) of PE. These included VLDPE, LDPE, HDPE, VHDPE, LLDPE and VHMWPE with densities ranging from 0.91 to 0.97g/cm^3. The actual samples used in the measurements are the same of press-molded plaques (approximately 80 X 50 X 1.9 mm) that are normally prepared for density assessment. In most cases, the plaques were made by the resin manufacturer who also indicated the density he had obtained. The plaques were used "as is" with no further preparation; however, we repeated the measurement of density with our own density-gradient column in the standard manner. In this way, we were able to define the standard deviation for values of density obtained in different columns. We found $(\delta\rho/\rho)_{col.} = \mp 0.0007$ a value which accounts for all sources of uncertainty and gives a good idea of the reproducibility for this technique.

B) The ultrasonic techniques

In the present study, we have chosen to use a water immersion technique because of the ease with which the measurements can be made and repeated. The setup is depicted in Fig. (1). A fast pulser excites a highly damped transducer which produces a short (1 or 2 periods) burst of high frequency (f = 3.0 MHz) sound. In the absence of a sample, the sound pulse travels in the water as a pure compressional wave with a velocity V and arrives at the receiving transducer (identical to the first) at time t_o. The signal is first amplified then it is sent to an oscilloscope equipped with a dual time base that allows precise (± 2 ns) time delay measurements. In order to measure the compressional wave velocity v_c, the sample (in the form of a plate of thickness ℓ) is introduced with its parallel faces perpendiculat to the beam. Part of the sonic energy which arrives on the sample (face 1) is transmitted forward in the material. There it travels a time t_e before it meets the other face (2). At that point, part of the energy is transmitted in the liquid and picked up by the receiver at time tc:

$$\Delta t = (t_c - t_o) = \ell / v_c - \ell / V \qquad (5)$$

There (face 2) a reflexion also occurs which sends part of the signal back to face 1 ... and so on. This gives rise to the formation of echoes that are observed at equal time intervals 2 t_e:

$$2t_e = 2\ell / v_c \qquad (6)$$

The velocity is obtained from Eq. 5 and 6:

$$v_c = V\ (1 - \Delta t / t_e) \qquad (7)$$

The value of V can be found with great accuracy by changing the distance between transducers. The velocity v_c is thus obtained solely from the measurement of time delays which gives the technique a high degree of accuracy: $\Delta v_c \simeq 0.1\%$.

The procedure to obtain the shear velocity v_s is somewhat more involved. The sample is inclined so that the normal to its faces makes an angle δ with the direction of propagation in the water. Then according to the acoustical analogue of Snell's law:

$$\sin \delta / V = \sin \alpha / v_c = \sin \beta / v_s \tag{8}$$

the incident compressional wave from the water will be refracted in the sample with both a compressional component at an angle α and a shear component at an angle β. In practice, if $v_c > V$, which will be seen to verify in our case, β is chosen such that only the shear wave can propagate. The arrival time of the signal t_s is measured. From the difference in travel times $\Delta ts = (t_s - t_o)$ and Eq. 7 and with some geometrical considerations to account for the actual sound path in the sample, v_s is given by:

$$v_s = V \left[(\cos \delta + V \Delta t_s / \ell)^2 + \sin^2 \delta \right]^{-\frac{1}{2}} \tag{9}$$

The angle δ and the corresponding time delay Δt_s are measured, ℓ is deduced from Eq. 6 and Eq. 7 and v_s is computed. The accuracy in this case is $\Delta v_s / v_s \simeq 0.5\%$.

C. Experimental Results

The results obtained in the measurement of the compressional velocity, v_c, versus density, ρ, are shown in Fig. (2) and those of the shear velocity, in Fig. (3). The various curves that appear in the figures correspond to the theoretical modeling and will be referred to in the discussion.

The results illustrated in Figs. (2 and 3) were obtained at a frequency of 3 MHz. However, in order to investigate the possible influence of viscoelasticity, we performed measurements at other values of frequency: our observations show that, within 1 percent, there is no dispersion in the range of 1.0 to 50.0 MHz.

D. Ultrasonic determination of density

In reference to Figs. (2 and 3), it can be seen that to a very good approximation, both the compressional and the shear velocities are linearly correlated to the density. We performed a regression analysis of the data. Using linear models such as $v_c = Ac\ \rho + Bc$ and $v_s = As\ \rho + Bs$, we found: in units of $10^5 cm^4/g$ sec, $Ac = 10.32 \mp 0.06$, $As = 9.99 \mp 0.15$ and, in units of $10^5 cm^4/sec$, $Bc = - 7.42 \mp 0.08$ and $Bs = -8.53 \mp 0.14$. The correlation factors were $r_c = 0.998$ and $r_s = 0.997$ and the relative average values for the standard errors of estimate $(\delta v_c/v_c) = \mp 0.0020$ and $(\delta v_s/v_s) = \mp 0.0124$. From a statistics point of view, the linear model was considered as good and lead to the idea (2) that the measurement of sound velocity could be used for the determination of density in PE. From a practical point of view the measurement of v_c was preferred. Again, using a linear model, $\rho = a\ v_c + b$, we found $a = (0.0965 \mp 0.0010) \times 10^{-5}$ g sec/cm^4 and $b = (0.7218 \mp 0.0020)$ g/cm^3. The standard error of estimate was 0.00090 g/cm^3, yielding the relative average value $(\delta\rho/\rho) = \mp 0.00095$. This value integrates errors from all sources, and yet it compares quite well with what can be expected using a density-gradient column: $(\delta\rho/\rho)_{col.} = \mp 0.0007$. Given this result we are lead to believe that the ultrasonic approach should allow the determination of density in polyethylene with the accuracy required for quality control purposes.

IV. THEORETICAL FOUNDATIONS

In order to understand the behaviour of sound velocity with changing density, it is important to recall that fundamentally, the velocity is determined by the modulus of the material. Since it has been ascertained in the previous sections that the velocity was not influenced by viscoelasticiy, the data (v_c, v_s and ρ) can be used to compute the elastic moduli (Eq. 1 to 4).

On the other hand, as it was mentioned earlier, PE is a semi-crystalline material where crystalline regions coexist with what can be considered a disordered liquid-like phase. It has been established (1, 12) that the value of density, ρ, is to a good approximation linearly related to the degree of crystallinity, c, through:

$$\rho = (1-c)\rho_1 + c\rho_2 \qquad (10)$$

where ρ_1 is the density of the amorphous phase and ρ_2 that of the crystalline phase. At room temperature (20°C), $\rho_1 = 0.855$ g/cm^3 and $\rho_2 = 1.000$ g/cm^3 (1).

This brings about the idea that PE can be considered as a composite material, for which the effective modulus depends on the relative volume contents of each phase. With this in mind, we present our results for the bulk modulus, B, in Fig. (4) and those for the shear modulus, G, in Fig. (5) versus crystallinity, c. In these figures, the continuous curves represent theoretical predictions which we will now discuss.

In all that follows, the properties (density, compressional and shear velocities, bulk, shear moduli) of the amorphous matrix will be written as ρ_1, v_{c1}, v_{s1}, B_1, G_1, those of the crystalline inclusion as ρ_2, v_{c2}, v_{s2}, B_2, G_2, and those of the composite as ρ, v_s, v_c, B, G; c indicates the fractional volume content, i.e. crystallinity.

A great deal of attention has been devoted to the theoretical calculation of effective static moduli of multiphase materials. In all approaches, the composite material is defined as an homogeneous isotropic, infinite elastic medium (matrix) in which are embedded a number of independent inhomogeneities which are supposed to be distributed at random and bonded to the matrix. Here we shall distinguish those models which are based on global energy considereations from those which account for the local perturbation of the strain field at the level of the individual particle. Models of the first category are the better known and have been reviewed (13). The first is the Voigt average which is based on the assumption that the strain is uniformly distributed. Averaging yields the so-called rule of mixtures also referred to as the series model:

$$B = (1-c)B_1 + c\ B_2 \tag{11}$$

$$G = (1-c)G_1 + cG_2 \tag{12}$$

Proceeding in a similar way but, this time assuming that the stress is uniform, Reuss proposed the parallel model:

$$1/B = (1-c)/B_1 + c/B_2 \tag{13}$$

$$1/G = (1-c)/G_1 + cG_2 \tag{14}$$

Both approaches will yield extreme bounds for B and G. It has been suggested by several authors that both models could be combined into a series-parallel model (Takayanagi). However this implies the introduction of an additional unknown (13) and arbitrary parameter to describe the relative contribution of each phase. In this respect, using variational methods, Hashin and Shtrickman (14), were able to establish tighter bounds for the moduli, which are exact.

We applied these various models in an attempt to fit our data. The better results were obtained using the Reuss (parallel) model, but, in the whole, the quality of the fit was not satisfactory.

category are sensitive to the microscopic details of the composite. They are based on the calculation of the elastic field which surrounds the individual inclusion. The reference work is that of Eshelby (15) who, by using topological arguments produced an elegant solution to this complicated problem. The model is however limited to low concentrations. Therefore, various schemes, such as mean field approximations or self consistent approaches, have been proposed in order to describe the case of finite concentrations. In one of these, referred to as the differential scheme (DS), the composite is built up by adding a new particle to an existing effective media. In the model (16), it is assumed that the inclusions are isotropic in their elastic properties, that they are uniformly distributed and oriented at random. The geometry of the inclusions is specified in terms of the aspect ratio, p. For an ellipsoïd, p is given by the ratio of the lengths of the principal axes, such that $p > 1.0$ corresponds to a prolate speroïd (fiber like), $p < 1.0$ to an oblate speroïd (disk like) and $p = 1.0$ to a a sphere.

We used this model as an approach to describe our problem. The calculations require the knowledge of B_1, G_1, B_2, G_2 and the aspect ratio, p, as input parameters. Since they are not known, one must assume values and proceed by trial and error until the best fit is obtained. We performed the exercise and arrived at the results which are shown by the continuous curves in Fig. (4 and 5). The fits were obtained assuming the following values of the elastic constants (in GPa): $B_1 = 2.30$, $G_1 = 0.0050$, $B_2 = 6.10$ and $G_2 = 2.30$. The results are given for different values of the aspect ratio: $p = 1.0$ (curve label 1), $p = 0.040$ (curve label 2) and $p = 0.0020$ (curve label 3).

Even though a thorough discussion of these results requires further work, a certain number of comments can already be made. First, we note that the values found for the effective moduli of the crystalline phase, B_2 and G_2, are consistent with the results obtained by calculating from theoretical elastic constants (17), aggregate averaged Reuss bounds.

Concerning the values found for the amorphous phase, some caution must be exerted. Indeed it must be said that the amorphous material cannot be isolated as such: in a somewhat simplified manner, it can be viewed as an entaglement of molecular loops, tie-chains, dangling chain ends etc. (18) confined between the crystalline entities. Very little data exists concerning the modulus of the amorphous phase; values found in the litterature extend from $G_1 = 0.5$ GPa (19, 20, 21) down to $G_1 = 0.0035$ GPa (22). We will simply argue that the value we have found, $G_1 = 0.005$ GPa, compares well to what is expected for the relaxed modulus (9, 19) of PE and to theoretical predictions (18, 19); also it reflects the liquid-like state which is proposed to describe the amorphous phase.

Turning now to the question of the aspect ratio p, we see that for our choice of B_1, G_1, B_2, and G_2, all the data lies within the bounds set by $p = 0.040$ and 0.020. These values of the aspect ratio, whereby the crystalline entities are approximated as disk-like inclusions, reflect the well known fact (1) that PE crystallizes by forming lamellae. The values found here for the aspect ratio are very consistant with what can be expected for materials such as ours.

In the whole, this first approach appears satisfactory and sets us in a posibtion to calculate the velocities v_c and v_s. The results are shown in Figs. (2 and 3). As could be expected, the data points are nicely bounded by the curves corresponding to $p = 0.040$ (label 2) and $p = 0.020$ (label 3). From this, it can be said that the linear relationship between the velocity and the density finds its origins in the intimate microstructure of the material.

V. CONCLUSION

We have reported measurements of both the compressional and shear ultrasonic waves in polyethylenes of commercial origin which included all available grades. A linear relationship was shown to exist between the velocity of sound and density. In an approach to understand this behaviour, polyethylene was considered as a composite material, where crystalline regions are embedded in an amorphous matrix. Several existing models for the elastic modulus of composites were described and evaluated for their ability to represent our experimental data. It was found that models which take into account the microstructural details of the material offer a satisfactory description of the bulk properties. In view of this, it can be proposed that the behaviour observed for the velocity has its origin in the morphology of the material and in the growing habits for its structure.

Here, we will add that the idea of using the measurement of sound velocity to determine the density has actually been implemented in an instrument which is commercially available. The instrument (23), Fig. (6) performs the measurement on samples which are the size of a credit card, with any thickness in the range of 1 to 3 mm. The instrument is fully computorized and the measurement of density is performed automatically in about 30 sec. The accuracy is good, $(\delta\rho/\rho)_{meas} = \mp 0.0009$ and the measurement can be repeated to better than $(\delta\rho/\rho)_{repeat} = \mp 0.0004$. As added advantages, the system requires no special preparation or maintenance, it is insensitive to shock and vibrations and is temperature compensated. The operation is simple, requires no special skills or art and is virtually foolproof.

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23. Courtesy of Tecrad Inc., 775, ave St-Jean-Baptiste, suite 105, Québec, P.Q., Canada G2E 5G5, tél.: (418) 871-3505, télex: 051-31679.

FIGURE CAPTIONS

Fig. 1 Schematic of the experimental setup.

Fig. 2 Velocity of compressional ultrasonic waves, v_c, in polyethylenes of different densities, ρ. The symbols represent the data taken at 3 MHz; the curves were calculated from a model for composite materials at different values of p, the aspect ratio of the crystalline entities.

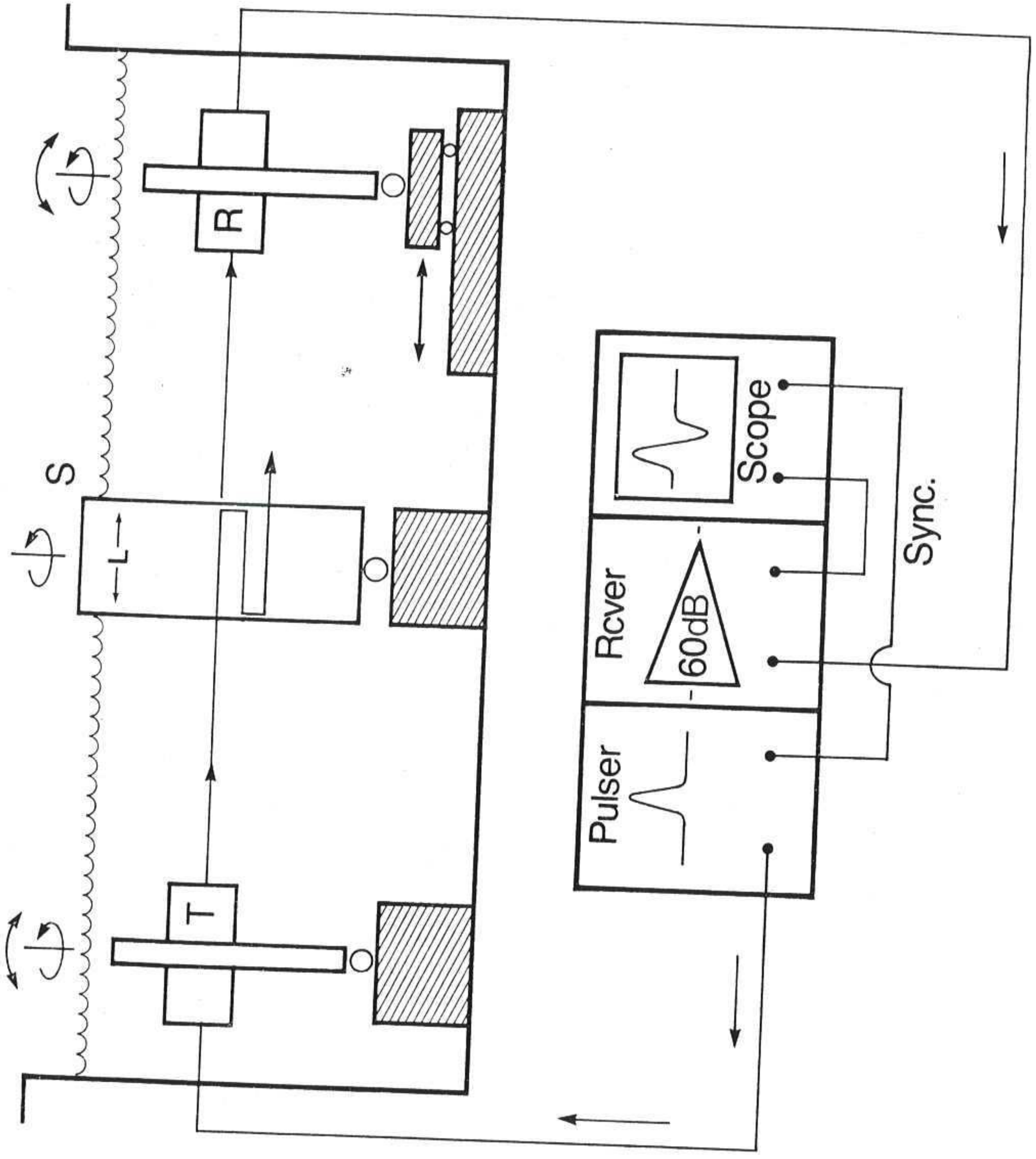
Fig. 3 Velocity of shear ultrasonic waves in polyethylenes of different densities, ρ. The symbols represent the data taken at 3 MHz; the curves were calculated from a model for composite materials at different values of p, the aspect ratio of the crystalline entities.

Fig. 4 Variation of the bulk modulus, B, versus the degree of crystallinity, c. The symbols are translated from the data in Figs. (2 and 3) using Eqs. (1, 2 and 10); the curves represent the best fit obtained from a model for composite materials and are given for different values of p, the aspect ratio of the crystalline entities.

Fig. 5 Variation of the shear modulus, G, versus the degree of crystallinity, c. The symbols are translated from the data in Fig.(3) using Eqs. (2 and 10); the curves represent the best fit obtained from a model for composite materials and are given for different values of p, the aspect ratio of the crystalline entities.

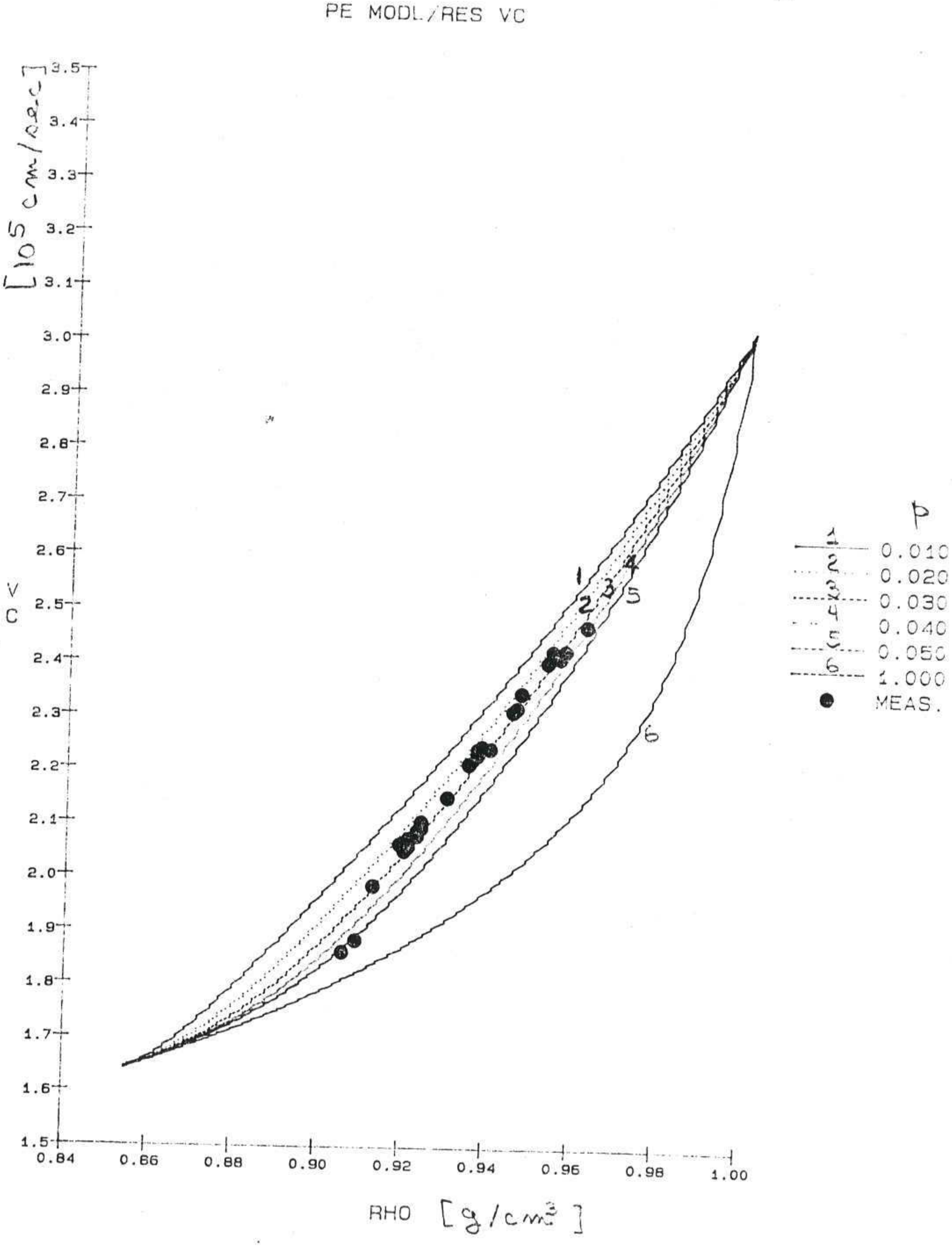
Fig. 6 Photograph of the commercial (23) instrument designed for the automatic measurement of polyethylene density.

PICHÉ
FIG 1



PE_VC

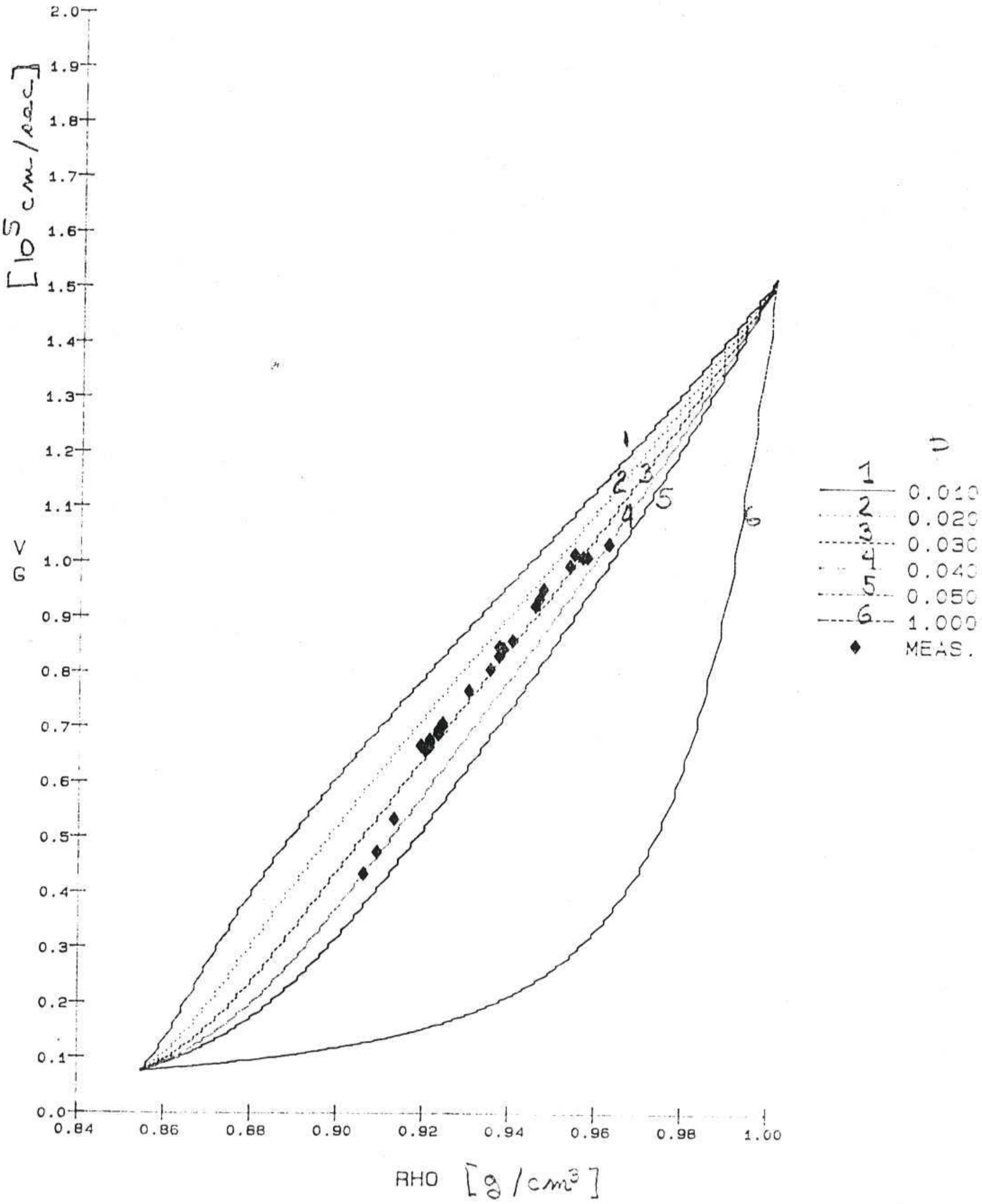
FICHE
FIG 2



PE_VG

FICHE
FIG. 3

PE MODL/RES VG

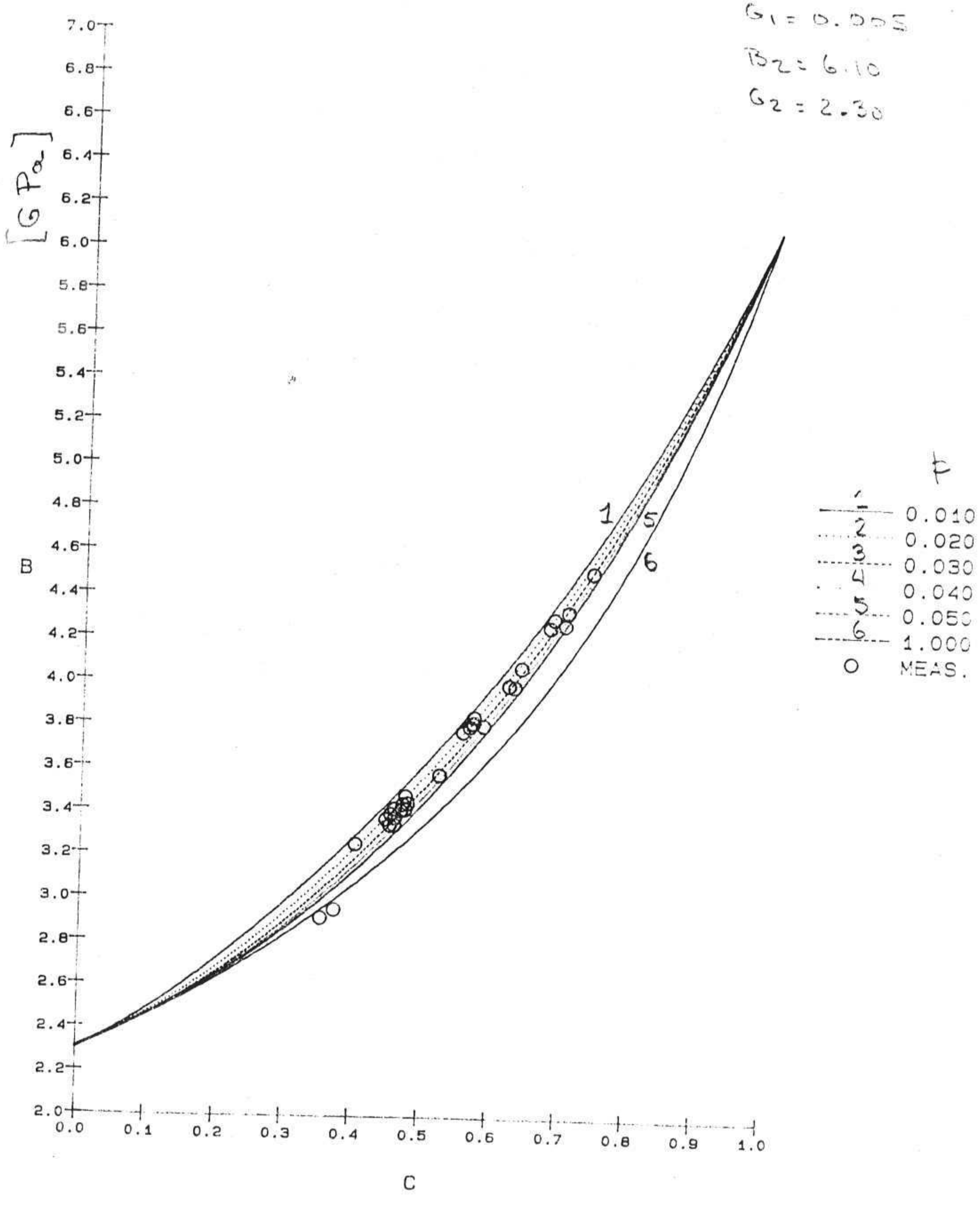


PE_B

FIG 1

PE MODL/RES B

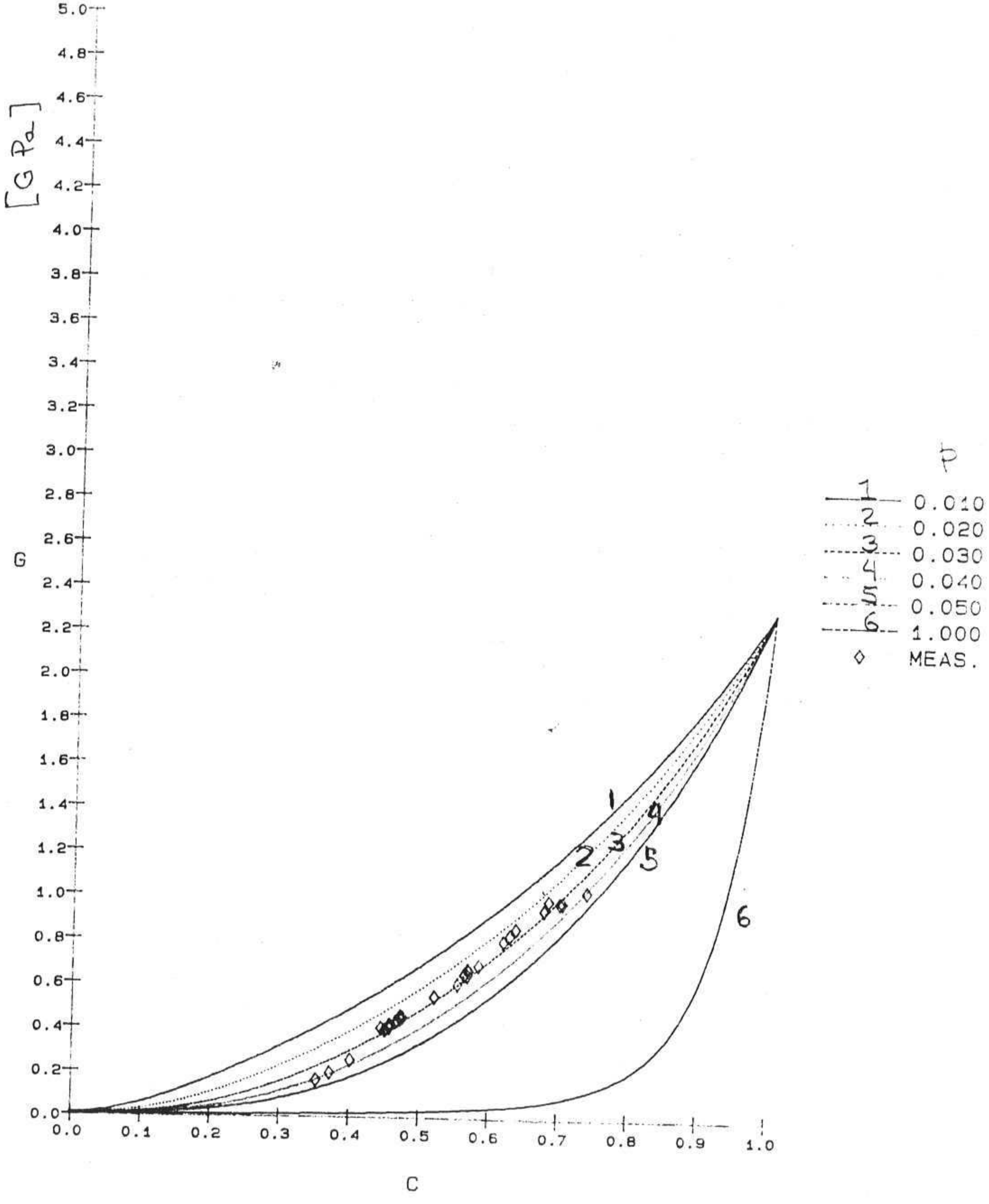
$B_1 = 2.30$
$G_1 = 0.005$
$B_2 = 6.10$
$G_2 = 2.30$

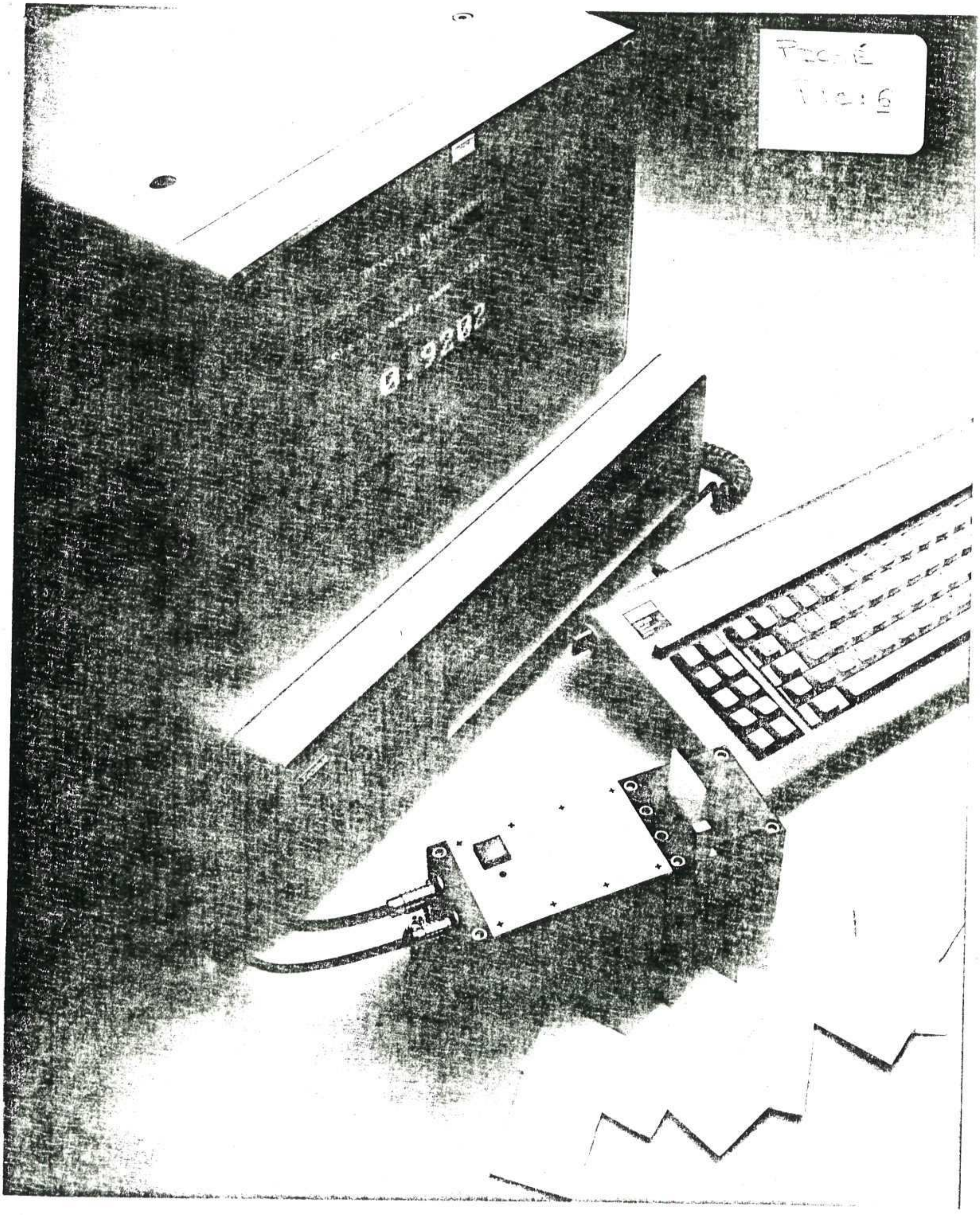


PE_G

FIGURE
FIG. 5

PE MODL/RES G





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