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Reference Standard Polyethylene Resins and Piping Materials

Final Report
(October 1, 1985 - September 30, 1986)

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National Bureau of Standards
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REFERENCE STANDARD POLYETHYLENE RESINS AND PIPING MATERIALS

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(October 1, 1985 - September 30, 1986)

Prepared by

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For

GAS RESEARCH INSTITUTE

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GRI Project Manager
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Physical Sciences

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16. Abstract (Limit: 200 words)

Polyethylene piping is currently in widespread use in gas distribution in the United States, and represents approximately 80% of new installation. Research that is currently being performed on gas pipes often employs many different polyethylenes selected from the large number of polyethylenes available for this use. This variation in materials makes it difficult to compare results from different research laboratories, or to compare measurements carried out in the same laboratory at different times. To avoid this difficulty Gas Research Institute and the National Bureau of Standards (NBS) have undertaken to provide a permanent store of one particular polyethylene resin as well as piping and fittings made from it which would provide a source of well characterized materials for research related to gas distribution systems. This report describes the choice of this resin and the types and quantities of the materials to be provided by NBS and the characterizations performed which include the determination of the branch content, melt flow rate, molecular weight and molecular weight distribution, density, and specific tensile properties.

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Contractor	National Bureau of Standards GRI Contract Number: 5084-260-1013
Principal Investigator	J. M. Crissman
Coinvestigators	F. W. Wang C. M. Guttman J. R. Maurey H. L. Wagner B. M. Fanconi D. L. VanderHart
Report Period	October 1, 1985 - September 30, 1986
Objectives:	(1) The procurement of sufficient piping resin and piping products to supply the needs of the gas industry for at least 5 years. (2) Conduct characterization of the PE in various forms to ensure uniformity throughout the batch of resin and products to be warehoused. (3) Establish a storage and distribution system to ensure that the materials will be available for at least 5 years.

Technical Perspective

Polyethylene pipe is currently in widespread use in gas distribution in the United States, and represents approximately 80% of new installation. It has been found to be a reliable and cost effective alternative to the more traditional materials. At the same time there is a need to deepen our understanding of the long time behavior of the poyethylene material used in gas piping. The research that is currently being performed often employs many different polyethylenes selected from the large number of polyethylenes available. This variation in materials makes it difficult to compare results from different research laboratories, or even to compare measurements carried out in the same laboratory at different times. This difficulty would, to a large extent, be alleviated if there were a permanent store of one particular polyethylene resin as well as piping and fittings made from it which would provide a source of well characterized materials for research related to gas distribution systems.

Results

Recognizing the need to establish a supply of reference materials, a workshop, sponsored by GRI, was held at Northwestern University, Evanston, IL on September 7 and 8, 1983. A consensus was reached at the workshop as to the need for a sample bank of reference polyethylene. The attendees also reached a consensus that the medium density polyethylene resin TR418 from Phillips Petroleum Co., be the recommended polyethylene. The following inventory of reference materials was also recommended.

1.	Polyethylene resin (natural)	455 kg.
2.	Polyethylene resin (pigmented)	4550 kg.
3.	PE pipe (6.03 cm OD, 0.55 cm wall)	1.52 km in 0.76 M sections
4.	PE pipe (11.4 cm OD, 1.0 cm wall)	0.15 km in 0.76 M sections
5.	PE pipe (1.59 cm OD, 0.23 cm wall)	0.15 km in 0.76 M sections
6.	PE 5.1 cm socket T joint	500
7.	PE 5.1 cm butt T joint	500

As a result of the workshop, GRI entered into a contract with the National Bureau of Standards (NBS) to carry out the establishment of such a reference sample bank.

Technical Approach

NBS will perform the following tasks:

(1) Procure the resin, piping, and joint materials specified by the workshop.

(2) Characterize the resin and products for certain molecular and physical properties to ensure their uniformity, and thus to enhance calibration and inter-laboratory comparisons of data.

(3) Warehouse and distribute the resin and products through the NBS Standard Reference Materials Program.

Characterization of the materials will include determination of the melt index, viscosity number, molecular weight and molecular weight distribution, degree of branching, density, thermal properties, and load-extension data where appropriate.

Project Implications

It is common practice for polyethylene resin manufacturers to make changes from time to time in their resins. These changes are generally made for proprietary reasons and in a proprietary manner. While these changes may not affect the behavior of the pipe in the field, they do modify the behavior of the material enough under research conditions to make the intercomparisons of results among researchers and even among results obtained at the same laboratory at different times difficult. This results from the fact that these different experiments can be expected to have been performed on different material in a different laboratory and/or at different times. In order for different results to be intercompared, it is necessary that each researcher be able to calibrate his apparatus by means of a set of measurements carried out on a standard, well characterized polyethylene material of stable characteristics. It is the purpose of this project to make such material available over a period of time of five or more years. This is being done through the purchase, characterization and storage of a particular batch of material which will be available for sale to the research community. By making it possible for measurements at different laboratories at different times to be referred to the same basis, the utility of the limited research resources currently being applied toward developing a fundamental understanding of the field behavior of polyethylene pipe material is increased. This, in turn, makes it more likely that it will become possible to design such material to satisfy criteria for behavior in the field in a predictable fashion.

In addition to certified values of certain properties, NBS will supply each purchaser of the material with a copy of this report to ensure that the procedures used in the characterization are understood.

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7. Mechanical Properties

1. Introduction

This final report describes work done under GRI Contract Number 5084-260-1013 during the period from October 1, 1985 through September 30, 1986 [1][1]. The project entailed the procurement, characterization, and warehousing of standard reference polyethylene gas pipe resins, as well as piping and joint materials made from them. The contract between the Gas Research Institute (GRI) and the National Bureau of Standards (NBS) is the result of a workshop held at Northwestern University, Evanston, IL, on September 7 and 8, 1983. A final report describing the presentations, deliberations, and recommendations of the workshop was issued on May 14, 1984 [2].

Polyethylene (PE) has rapidly become the material of choice for gas distribution piping in the United States and currently accounts for about 80% of total new piping installation and accounts for essentially all new piping installation which is non-metallic. It has proven itself to be a reliable and cost effective alternative to the more traditional materials. At the same time, the gas industry has evolved a variety of standards governing the materials, production, and utilization of plastic materials, in general, and polyethylene, in particular, for gas distribution. In spite of the high degree of success achieved with polyethylene piping materials, there remains a need to better understand the long time behavior of both the PE materials being used and of the final products made from it in the form in which it is made and placed in actual service. As

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[1] Numbers in square brackets indicate references found at the end of this report.

a result, research is currently being performed in the laboratories of many of the companies involved in PE resin and pipe manufacture, much of it proprietary. There is also underway unrestricted research, primarily in universities and not-for-profit laboratories. Much of this non-proprietary research is sponsored by GRI.

In the research currently being done, the materials used must be selected from the large number of different polyethylenes available. This can lead to uncertainty in comparing results from different laboratories which might have selected different material. Moreover, the manner in which specimens are prepared from a given material can influence significantly the final properties, and therefore their performance. This can lead to considerable additional uncertainty in comparing or correlating data generated in different laboratories. The situation is made worse by the practice which the polyethylene resin manufacturers have of occasionally changing their manufacturing processes so that the same material may not always be available. This can make it difficult even to compare measurements carried out in the same laboratory at different times.

Much of this confusion would disappear if there were a permanent store of a particular polyethylene resin as well as piping and fittings manufactured from it. Researchers could then purchase supplies from this store at any time and repeat their measurements on the materials obtained, knowing that the material is from the same batch as that used by others, or even used in their own laboratories at an earlier time. Researchers would, of course, remain completely unrestricted with regard to design of experiments, and they would, therefore, remain free to choose the scientific questions motivating their research. They could, in fact, carry out most of their measurements on any material of their choice. They would, however, have available a reference polyethylene which could be included in each experimental design and which would provide a means for internal calibration of the data that a given research effort is producing. Future workers could thereby successfully build new knowledge by combining their results in a meaningful and unambiguous manner with what has already been published. The benefit would be that the reference polyethylene would provide a means for placing all such research on a common basis.

The workshop attendees recognized the need to establish such a supply of reference materials, and came to the consensus that the inventory of polyethylene needed to be housed in one repository where it would be readily accessible to workers throughout the world. The National Bureau of Standards (NBS) was cited as being especially well suited to serve as the repository because of its experience with reference materials and, in particular, "standard reference materials" for many other substances of commercial importance. Furthermore, it was considered highly important that the resin and piping to be placed in the repository receive competent and thorough characterization of all basic properties. Again, the National Bureau of Standards was cited for its fine reputation for carrying out such characterizations.

The workshop stipulated the following types and quantities of material to be characterized and warehoused for distribution:

	Item	Quantity
1.	Polyethylene resin (natural)	455 kg.
2.	Polyethylene resin (pigmented)	4550 kg.
3.	Polyethylene pipe (6.03 cm OD, 0.55 cm wall)	1.52 km in 0.76 m sections
4.	Polyethylene pipe (11.4 cm OD, 1.0 cm wall)	0.15 km in 0.76 m sections
5.	Polyethylene pipe (1.59 cm OD, 123 cm wall)	0.15 km in 0.76 m sections
6.	Polyethylene 5.1 cm socket T joint	500
7.	Polyethylene 5.1 cm butt T joint	500

In addition, it was decided to include one 0.15 km roll of the 1.59 cm OD, 0.23 cm wall pipe.

It was further agreed upon by the attendees at the workshop that the reference polyethylene would be the medium density polyethylene resin, TR418, from the Phillips Petroleum Co.[2]

The principal activities described in this final report are the characterization of the melt flow index of the pigmented and unpigmented resins, determination of the density of the as-received pellets, piping, and joint materials, and mechanical property studies to determine the yield behavior of the piping materials under tension. In addition, the butyl branch content was determined both by Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance (NMR).

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[2] Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

During part of this period, the project leader was assisted in carrying out the mechanical properties study by Dr. Peter Stockmayer from the Polymer Testing and Polymer Science Institute (IKP) at the University of Stuttgart in West Germany. Dr. Stockmayer was a guest scientist at NBS from October 7, 1985 through November 22, 1985. From March 16, 1986 until June 15, 1986 the NBS principal investigator (J. M. Crissman) was engaged in collaborative research at IKP, Stuttgart. During this time, the tensile properties of the pigmented TR 418 resin were compared with those of three different commercial gas pipe resins currently in use in Europe. The results of this effort are summarized in this report.

2.1. FT-IR Studies of Gas Pipe Polyethylene Resins

Infrared studies were conducted on pipe resin materials to determine:

1) the number of methyl groups per 100 carbon atoms
2) the concentration of terminal vinyl groups
3) crystallinity
4) spectral differences among the various specimens.

The polyethylene resins investigated were:

1) unpigmented resin in the form of molded sheets prepared from pellets
2) pigmented resin molded in sheets from pellets
3) pigmented resin shaved from the 6.03 cm OD pipe.

Spectral differences between the first two of these (i.e. the unpigmented and pigmented molded samples) were observed. To determine the source of these differences the infrared spectrum of the pigment was also obtained to see if these differenes were due to the pigment.

RESULTS:

1) Methyl Group Concentration

A wealth of literature is available on the use of infrared spectroscopy to determine the number of methyl groups per unit mass of polyethylene. We used the method of Rueda et al [3] which relates the peak extinction coefficient at 1378 cm^{-1} to sample thickness and methyl group concentration expressed as number of groups per 100 carbon atoms. The results, summarized in Table 1, indicated that the unpigmented resin contained approximately 0.5 methyl groups per 100 carbon atoms and the pigmented resins contained 0.55 methyl groups per 100 carbon atoms. The uncertainty in the concentration of these groups obtained by this method is about 10% owing to the precision of the absorption coefficient. This systematic error applies equally to the calculated concentration of methyl groups for both the pigmented and unpigmented resins so that the difference between them appears to be real. However, as discussed under item 4 below, other spectral differences indicate the presence of additional chemical species in the pigmented resin which may account for the increased absorption in the 1375 cm^{-1} region.

2. End Vinyl Group Concentration

The infrared spectrum of polyethylene containing vinyl end groups has two well-resolved peaks which are assigned to vibrations localized in terminal vinyl groups. Extinction coefficients were obtained from studies on alpha-olefins [4] and both infrared bands were used in the analysis. The results, given in Table 2, show little variation in the concentration of terminal vinyl groups, 5×10^{-4} per CC bond, among the various specimens.

3) Crystallinity

A number of infrared bands are assignable to vibrations of atoms in the crystalline regions. The band at 1896 cm^{-1} was selected for crystallinity determination since it is well-resolved from other bands. It was analyzed by the method of Okada and Mandelkern [5]. The results are given in Table 3. The only significant difference between the infrared spectra of samples taken from the pigmented resin and those taken from the pipe and from the unpigmented resin resulted from differences in the crystallinity.

4) Other Spectral Differences

Difference spectra were obtained for the pairs unpigmented pellets/pigmented pellets and pigmented pellets/pipe specimen. The difference spectrum for the unpigmented/pigmented pair, shown in Figure 1, has significant features in the 1750 cm^{-1} region, as well as bands at 1568, 1532, 1373, and 810 cm^{-1}. Aldehyde, ketones, and acids contribute to the infrared spectrum in the 1750 cm^{-1} region, and the positive/negative feature in the difference spectrum may be due to a slight higher degree in oxidation in the unpigmented sample (perhaps due to molding the sheets from the pellets) and the presence of an organic acid in the pigmented sample. The presence of an organic acid is also consistent with the appearance of bands at 1568 and 1532 cm^{-1}. No attempt was made to further identify the origins of the difference bands in this pair with the exception that the infrared spectrum of the pigment was obtained for comparison. No spectral bands of the pigment spectrum are present in the difference spectrum indicating that the pigment concentration is too low in the pigmented resin to be detected at the sample thicknesses used.

The difference spectrum between the pair pigmented pellets/pipe specimen is shown in Figure 2. The bands in this difference spectrum can be assigned to a difference in crystallinity (and amorphous content) between the two samples with the molded sheets having higher crystallinity (see Table 3).

5) Branch Content

It was reported under 2) that the concentration of vinyl groups per carbon-carbon bond was approximately $5x10^{-4}$ for the resin containing no pigment. This result yields a degree of polymerization of 2000, if it is assumed that each molecule contains one vinyl group which is located at a chain end. There are then 0.5 methyl groups per 1000 carbon atoms associated with chain ends. Under 1) it was determined that, in total, there were approximately 5.0 methyl groups per 1000 carbon atoms. Therefore the number of branch-terminated methyl groups is 4.5 per 1000 carbon atoms. This number is in very good agreement with the results for butyl groups from the NMR study reported in the following section.

2.2. NMR Study

The branch content of both the pigmented and unpigmented PE resins was analyzed by solution-state NMR. Solutions, 15% by weight in trichlorobenzene, were run at 120°C using a WM400 Bruker NMR spectrometer operated at 9.4T. The principal analytical result sought using NMR spectra was the number of butyl branches per 1000 backbone carbon atoms. The numbers determined were 4.27⊙0.25 for the unpigmented PE and 4.56⊙0.25 for the pigmented PE. A determination of the molecular weight was not attempted because of an insufficient signal to noise ratio. However, a rough estimate for M_n of 10,000-15,000 could be made.

3. Melt Flow Rate

Melt flow rate is widely used in polymer technology as a product specification since this value, including a statement of the load and temperature under which it is obtained, gives an indication of the processing properties of the polymer. The melt flow rate is defined as the mass of polymer melt pushed from the heated cylinder of the extrusion plastometer through its precision bore orifice by a piston in a specified period of time, the standard units being grams per ten minutes (g/10 min).

The melt flow rates were determined by Procedure A described in Section 8 of ASTM Method D-1238-82 [6]. The standard test conditions 190/2.16 were used for the unpigmented PE resin (SRM 1496) while conditions 190/2.16, 190/5.0 and 190/21.6 were used for the pigmented resin (SRM 1497). The flow rate was determined at 190.0 +/- 0.1°C at all three loads. The flow rate of the melt was measured by a manually operated extrusion plastometer obtained from the Tinius Olsen Testing Machine Co.

3.1.1. Instrument Calibration and Alignment

3.1.1a Temperature Indication

The temperature was indicated by a mercury column thermometer of the form described in paragraph 4.7 of ASTM Method D 1238-82 [6]. Calibration of the temperature indication is traceable to the NBS Temperature and Pressure Division. An iron-constantan thermocouple was calibrated by correlating its emf with the scale readings of an ASTM 68C thermometer at 22 points from 183° C to 195° C, in a constant temperature oil bath. The ASTM 68C thermometer had been calibrated at the ice point and at 190° C in the NBS Temperature and Pressure Division. The thermometer located in the cylinder of the extrusion plastometer was calibrated by correlating its scale readings with the temperature indicated by the emf from the thermocouple when the hot junction of the latter was replaced in a column of polyethylene melt in the bore of the plastometer, as described in paragraph 4.5.2 of the ASTM method. The conduction of heat between cylinder and thermometer, and between cylinder and the temperature control sensing probe, was enhanced by adding silicone oil to the wells in the cylinder for the thermometer and sensing probe.

The uncertainty in the final temperature indication may be regarded as equal to the nominal limit of resolution on the scales of the ASTM 68C thermometer, and of the thermometer in the extrusion plastometer. This was 0.1°C. A determination of melt flow rate dependence on temperature, for SRM 1496, resulted in a change of 0.00043 g per 10 min in melt flow rate for a 0.1° C change in temperature under the 2.16 kg load. This result affords an estimate of 0.17% change in the melt index per 0.1° C change in temperature.

3.1.1b <u>Metering of Plastometer Components</u>

The geometric dimensions of the cylinder, piston assemblies, and dies were found to comply with the specifications described in the ASTM method.

The diameter of the cylinder bore was determined by an inner diameter (ID) micrometer in the NBS Shops Division. The ID of the bore was measured at three locations at approximately 1 inch intervals from each end toward the middle. All six of the ID measurements between the ends of the bore were either 0.3759 in. or 0.3760 in., in compliance with the tolerance of this specification described in paragraph 4.2 of ASTM D 1238-82.

The apparent mass of the nominal 2.16 kg load was determined in the NBS Length and Mass Division. The apparent mass of the nominal 2.16 kg load was found to be 2.1599 kg, well within the + 0.5% tolerance described in paragraph 4.4.4 of the ASTM method.

3.1.1c Alignment of Plastometer

The cylindrical axis of the bore was aligned with the gravity vector by the following plumb-line procedure.

First, a die was selected as the "target" die and stationed on the structural baseplate of the extrusion plastometer directly below the cylinder. Its position on the plane of the baseplate was adjusted to have the axis of its orifice coincide with the projection from the axis of the cylinder bore onto that plane. This was accomplished by viewing the target die through the orifices of two "sighting" dies, one stationed at its operational position in the bottom end of the bore and the other stationed at the top end of the bore. The position of the target die on the plane of the baseplate was adjusted until it appeared centered in the view from above the cylinder through the sighting dies in the bore.

Next a plumb-bob was suspended by a plumb-line from the axis of a die supported in the top end of the bore, with the bob almost touching the top surface of the target die. The leveling screws were adjusted until the pointer of the plumb-bob appeared to be centered above the orifice of the target die.

3.1.1d Effect of Piston Diameter on Melt Flow Rate

A brief study of the variation of melt index with piston land diameter was conducted in order to estimate the dependence of the determined melt index value on clearance between the piston and the bore of the cylinder. Mr. Fred Reckner of Tinius-Olsen generously provided two piston feet with land diameters at the opposite extremes of tolerance described in paragraph 4.4.1 of the ASTM method, namely

0.3730 +/- 0.0003 in. Metering with a micrometer confirmed that the smaller piston had a land diameter = 0.3727 in., and the larger piston had a land diameter = 0.3733 in. A homogeneous supply of the polymer was collected by transferring approximately 40 grams of pellets from each of several sample bags of pigmented resin into a mixing jar, and then propelling the jar on a roll mill for 1 hour. The predetermined sequence in which the narrow and broad piston feet were to be applied was randomized by first assigning ordinal numbers from 1 to 8 to the piston feet identified in perfectly alternating sequence, and then randomizing the ordinal numbers.

The melt index determinations were performed on eight charges from the homogeneous polymer supply, in the manner described in Section 3. The results from these determinations are listed in Table 4.

Inspection of results in each line of Table 4 reveals that the standard deviation of each mean is greater than the difference between corresponding means, and the standard deviation of a single measurement within each mean is also greater than the difference between corresponding means. Also observe that, in three of the lines, the mean melt flow rate determined with the broad piston is greater than the mean value determined with the narrow piston, while in the other line, the mean value determined with the narrow piston is greater than those determined with the broad piston. In particular, observe in the line for the data overall that the difference between the mean values of the two groups is trivial, and that the standard deviations of the two group means are more than ten times as great as the difference between the two group means. Consequently, it appears that the mean index values resulting from application of the two pistons at opposite extremes of the diameter tolerance described by the ASTM method are statistically indistinguishable within the limits of this study.

3.2 Melt Flow Rate

3.2.1. Unpigmented Resin (SRM 1496)

3.2.1a Sampling and Randomization of Charge Sequence of SRM 1496

Material of the SRM 1496 came in one 455 kg container. Samples were collected from ten different sites in the container and put into screw cap jars. Of these sites eight were near each of the corners of the container, one was at the cubic center of the container and one was at the center of the container's top face. In preparation for the melt flow rate experiments two charges were taken from each sample. Charges to be extruded were identified by an ordinal number, each associated with an identified sample. The sequence of charges to be extruded was randomized according to a procedure described by Natrella [7].

3.2.1b Melt Flow Rate on SRM 1496

The melt flow rates on SRM 1496 were determined by procedure A described in Section 8 of ASTM Method D-1238-82. Standard test condition 190/2.16 was used. Thus the flow rate was determined at 190.0 + 0.1°C using a load of 2.16 kg. The flow rate of the melt was measured by a manually operated extrusion plastometer obtained from the Tinius Olsen Testing Machine Co.

A 2.7 g charge of pellets was used for extrusions under the 2.16 kg load. With such a charge, the 4 mm start section of the descending piston would enter the top of the guide collar partially at the end of the 6 min preheat interval without the necessity of any manipulative adjustment. The end of the 6 min preheat interval was marked as the beginning of timed extrusion. This was done by making the initial extrudate cut and discarding the preheat segment. Three timed extrudate segments were cut at 6 min intervals thereafter. After the third timed extrudate segment had been cut, the remaining melt in the cylinder was purged and discarded. The piston, bore, and die were cleaned free of the polymer at the end of each extrusion run.

3.2.1c Data Analysis on the Melt Flow Rate of SRM 1496

Data from 20 charges were analyzed for the 2.16 kg load. The data from a single charge run generally showed a flow rate decrease in going from the first timed extrudate to the third timed extrudate. Such a drift is reflected in the data shown in Table 5.

The 20 charges were made up by taking two from each of the 10 jars sampled. The jar to jar variation was less than the standard deviation of each point. Thus the sample was viewed as homogeneous with respect to melt flow rate.

Eight to 10 melt flow rate experiments could be done in a single day. The plastometer was then used on a different material or shut down for a few days before the next set of unpigmented resins were run. With this procedure, we hoped to show the effects of day-to-day variability on the equipment and have that reflected in our standard deviation. However the day to day variability was small compared to the charge-to-charge variability.

3.2.1d Error Analysis on the Melt Index of SRM 1496

Obtaining an error analysis of the melt index is difficult since it is not a fundamental property of the material and no simple relationship exists which describes its estimation. Nonetheless, in this section we shall make an effort to estimate the possible causes of error and their contribution to the overall actual error in the measurement made.

One estimate of error comes from the ASTM method on which melt flow rate is based (ASTM D 1238-82). Table 3 in that document suggests an expected reproducibility for polyethylene of ± 0.04 for a melt flow range of 0.25 g/10 min and ± 0.48 in the range of 7.0 g/10 min. (These are 95% confidence limits). Since this error estimate includes inter-laboratory as well as intra-laboratory error one would expect our error to fall within the ASTM prescribed range, which it does.

The source of uncertainty described in Table 3 of ASTM D 1238-82 is not clear. As we have pointed out, melt flow is not a fundamental physical property. As we have seen from our own measurements, its value may depend on where one chooses to make the cuts in the material (first extrudate or second extrudate). We may then ascribe part, if not all, of the ASTM error tolerance as described in Table 3 in D 1238-82 to operator-to-operator variability or to instrument to instrument variability which we are unable to estimate in our own work. Their estimate yields a possible systematic error of about 15% on the flow rate for SRM 1496. This is noted in our Table 6 as instrument variability.

Estimates of our own repeatability are presented in Table 6. These reflect the repeatability of our own experiments and do not contain any instrument-to-instrument or operator-to-operator variation since we had only one instrument and one operator. We did make our runs on various days and the day-to-day variability of the overall average of the first timed extrudate is reported in Table 6. In Table 6 the sample to sample variability is also reported on the first timed extrudate. Neither of these was significantly different from the overall error.

Finally, we shall try to estimate the intrinsic error in the measurement. We do this by considering the errors in the measured quantities (mass and time) as well as the errors in the controlled quantities (temperature and the specifications on the instrument). The melt flow rate, Mfr, is given by

$$Mfr = Mass/Time$$

Thus any error in the melt flow rate is then

$$dMfr/Mfr = dM/M + dt/t + dMfr/dT^{*}\ dT/T$$

dM/M is the fractional error in the weight of the samples. This is taken to include not only the possible error in the weighing due to balance error and moisture pickup but also to errors in the mass of the extrudate incurred due to the cutting of the material. dt/t is the fractional error in the timing of the extrudate and therefore includes only the timing error. The dT/T term arises from the inaccuracy of the temperature controller as well as temperature inhomogeneity of the instrument. The cause of the errors are discussed in the next few paragraphs. These, as well as the other errors, are given in Table 6 along with an estimate of the overall error resulting from all sources.

Mass Error

The extrudate segments were weighed on a balance with 0.01 mg resolution in mass indication. Replicate weighing of the segments agreed to within ± 0.01 mg. in general and never went beyond ± 0.02 mg at the extreme. Paragraph 8.8 of ASTM Method D1238-82 instructs the experimenter to "weigh the extrudate to the nearest 1 mg when cool." It should be noted that 1 mg of this polymer occupies very nearly 1 microliter of volume which is probably a valid estimate of the uncertainty in the cut considering the technique of cutting the extrudate. Consequently, the uncertainty in extrudate mass resulting from the process of cutting the segment is estimated to be dm = ± 1 mg. The overall average apparent mass m = 152 for SRM 1496 was calculated for all the extrudate segments in the characterization of this polymer. Consequently, the relative error in weight (dm/m) entering into the melt index characterization is

$$dm/m = \pm 1 \text{ mg}/151 \text{ mg} = 0.7\% \text{ for SRM 1496}$$

The extrudate segments were routinely weighed within 1/2 - 1 hour after having been cut, which is certainly in compliance with the instruction in paragraph 8.8 of the ASTM method. Considering the hydrophobic character of polyethylene it would not be anticipated that the extrudate would accumulate moisture beyond the initial cooling stage prior to being weighed. On a few occasions extrudate segments, which had been weighed at the end of a day, were weighed again on the following day without detecting any statistically valid change of weight within the groups. All individual changes, either positive or negative, were much smaller than 1 mg. Consequently, it may be assumed that there was no detectable error in weight attributable to moisture adsorption, and that the error in extrudate weight is dominated overwhelmingly by the volume uncertainty attending the process of cutting the extrudate.

Time Error

The 6 min. interval (t) between extrudate cuts for SRM 1496 was measured with a battery powered stopwatch having a 0.01 s resolution in time indication. The extrudate cut was timed to within 0.1 s. Consequently, the timing error may be equated with 0.1 s as a practical estimate. Hence, the relative error in time interval may be expressed

$$dt/t = \pm 0.1 \text{ s}/360 \text{ s.} = 0.03\%$$

Thermal Error

The thermal profile of an undisturbed column of polyethylene melt was scanned along the cylindrical axis of the cylinder bore. This experiment was conducted in another extrusion plastometer during an earlier determination of the melt flow rate of NBS SRM 1475 (whole polymer polyethylene) and NBS SRM 1476 (linear polyethylene). The temperature in the stationary melt column was measured with a thermocouple hot junction stationed at different heights above the top surface of the die, along the cylindrical axis of the bore. Throughout the experiment, the indicated cylinder temperature remained at 190.0° C in all observations of the mercury column thermometer which was used to indicate cylinder temperature. The results are listed in Table 7.

Inspection of the tabulated results indicates that the departure of melt temperature from the indicated cylinder temperature is less than ± 0.1° C, at any location in the melt column from 12 mm above the die upward. It may be observed that the 0.7 - 0.8° C drop in temperature, between the 12 mm and 1 mm levels above the die, occurred in the undisturbed melt column. This temperature drop is probably reduced by the downward flow of melt during an extrusion. It is also possible that the apparent smaller variation of temperature with height from 12 mm upward may simply be the variation of the temperature with the time at which the temperature was determined at the different levels. Because its heat capacity and volume displacement are considerably greater than those of a thermocouple junction, the mercury column thermometer is a very effective temperature averaging device and is far less responsive to brief and small changes in temperature than a thermocouple would be. Regardless of whether the temperature is changing with time or with height, or with both time and height, the maximum temperature error (ST) may be estimated as ± 1.0° C.

The greater significance of the temperature error is in its effect on the melt flow rate of the polymer. The variation of melt flow rate with temperature in the vicinity of 190° C was determined to be 1.65%/°C, as reported in paragraph 2.1.1. This is equivalent to a 1.7% per degree Celcius error corresponding to the 1.0° C maximum error in the melt temperature.

3.2.2 Pigmented Resin (SRM 1497)

Except where otherwise noted, all apparatus and procedures for determining the melt flow rate of the pigmented resin were the same as those described in Section 3.1.1 of this report.

3.2.2a Sampling and Randomization of Charge Sequence of SRM 1497

Samples of the orange pigmented polyethylene pipe resin were collected from each of the ten 455 kg containers of pellets. Two samples, each weighing approximately 1 to 1 1/2 kg, were collected from opposite sides of each container near the top. Two charges were taken from each sample bag for determining the average melt flow rate. Charges to be extruded were identified by an ordinal number, each associated with an identified sample. The sequence of charges to be extruded was randomized according to a procedure described by Natrella [7].

3.2.2b Melt Flow Rate of SRM 1497

The melt flow rates were determined by Procedure A described in Section 8 of ASTM Method D 1238-82. Standard test conditions 190/2.16, 190/5.0 and 190/21.6 were used. Thus the flow rate was determined at 190.0 ± 0.1° C using loads of 2.16, 5.0 and 21.6 kg. The flow rate of the melt was measured by the same manually operated extrusion plastometer described in Section 3.1.1a.

A 2.60 g charge of pellets was used for extrusions under the

2.16 kg load. With such a charge, the 4 mm start section of the descending piston would enter the top of the guide collar partially at the end of the 6 min preheat interval without the need for any adjustment. The end of the 6 min preheat interval was marked as the beginning of timed extrusion by making the initial extrudate cut and discarding this preheat segment. Three timed extrudate segments were cut at 6 min intervals thereafter. After the third timed extrudate segment had been cut, the remaining melt in the cylinder was purged and discarded. The piston bore and die were cleaned free of the polymer at the end of each extrusion run.

Essentially the same procedure was used during extrusions under the 5.0 kg load. However, for the 5.0 kg load an initial charge of 3.0 g was used.

Extrusions under the 21.6 kg load were initiated by a special procedure described in paragraphs 8.5 and 8.5.1 of ASTM method D 1238-82 for flow rates greater than 10 to 50 g/10 min. An initial charge of 5.40 g was used. After the extrusion was initiated, the descending piston came to rest, for the remainder of the first 6 min., on two removable sections of bakelite which supported the piston with the lower scribe mark of its start section 25 1/2 mm above the top of the guide collar. During this initial descent onto the temporary supports, the piston extruded 1.3 g polymer through the die, in compliance with the minimum 1 g extrudate specified by the ASTM method. At the end of the sixth minute of the preheat interval, the temporary piston supports were removed and the loaded piston was allowed to resume its descent. It was observed that the start section of the piston had always entered the top of the guide collar partially at the end of the seventh minute of preheat. Consequently, the preheat interval was recorded as 7 min. in this procedure under the 21.6 kg load. After discarding the preheat extrudate, the following extrudate was cut into three timed segments. The first two of such segments were cut at 30 s. intervals after preheat, and the third segment was cut after an interval of only 20 s. in order to obtain a third segment before all the polymer melt had been extruded from the cylinder. These time intervals are within the recommended limits listed in Table 5 of the ASTM method.

The certified value using ASTM condition 190/2.16 for assignment to the SRM was determined by analysis of the data obtained from extrusions of 56 charges. Condition 190/2.16 is the traditional melt index condition for polyethylene. [Ref: paragraph 13.1.1, ASTM D 1238-82 [6]] Three extrudates were cut from each charge run. Already mentioned, under the 2.16 kg load, the data from a single charge run generally showed a flow rate decrease as one went from the first timed extrudate to the third timed extrudate. Such a drift is reflected in the data shown in Table 4. In accordance with ASTM procedure [Ref:paragraphs 8.6 and 8.7, ASTM D 1238-82] the first timed extrudate was chosen as the certified value.

The 56 charges were made up by taking from 2 to 3 samples from different positions within each of the ten original bags of resin. The position-to-position variation was less than the standard deviation of the point. Thus the sample was viewed as homogeneous with respect to melt flow rate. The range of the position-to-position variability is given in Table 8 (see also Table 11).

Eight to ten melt flow rate experiments could be done in a single day. The plastometer was then used on a different material or shut down for a few days before the next set of pigmented resins were run. With this procedure, we hoped to show the effects of day-to-day variability on the equipment and have that reflected in our standard deviation. However the day-to-day variability was small compared to the charge-to-charge variability. The range of the day-to-day variability is given in Table 11.

Data for condition 190/5.0 is given in Table 9. For these data, there is little drift in the melt index from the first timed extrudate to the third.

Ten extrusions were also done using the higher load of 21.6 kg. In this case, the drift in the flow rate with time was opposite to that observed at the 2.16 kg load, i.e., the melt flow rate from the first timed extrudate being smaller than that of the later ones. The results are shown in Table 10.

3.2.2c Drift in Melt Flow Rate from the First Extrudate to the Third Extrudate

As mentioned in the earlier sections, we found that under condition 190/2.16 the first extrudate had a higher melt flow rate than the third extrudate while, under condition 190/5.0 and under condition 190/21.6, the third extrudate had a melt flow rate greater than the first. These results were found consistently and the trends were beyond the error of the measurement. It is often reported that the later extrudates have higher melt flow rates than the earlier ones. Such phenomena have been observed and reported in the literature. Rudin and Schrieber [8] have explained these phenomena by suggesting that the change in the decreasing melt flow rate as a function of time is a result of the elastic effect of the polymer. The increasing melt flow rate arises from a variety of causes one of which is the non-Newtonian behavior of these materials. We have made one measurement where we have seen both a decrease and a rise in melt flow rate in the same data. These data are shown in Figure 3. Stockmayer [9] has observed similar drifts as a function of time which even appear after the polymer has been degraded.

3.2.2d <u>Error Analysis on the Melt Index of SRM 1497</u>

It was noted in Section 3.2.1d of this report that obtaining an error analysis of the melt flow rate is a difficult matter since it is not a fundamental property of the material and there is no simple relationship describing its estimation. In this section the same error analysis has been used to make an estimate of the possible causes of error and their contribution to the overall actual error in the measurements mode on the pigmented resin.

As in the case of SRM 1496, one estimate of error comes from the ASTM method on which the melt flow rate is based (ASTM D 1238). We have seen from our own measurements that its value may depend on where one chooses to make the cuts in the material, for example first extrudate or second extrudate. We may here too ascribe part, if not all, of the ASTM error in Table 3 in D 1238-82 to operator-to-operator variability or to instrument-to-instrument variability which we are unable to estimate in our own case. This estimate yields a possible systematic error of 16% on the flow rate for Condition 190/2.16 and a possible systematic error of about 7% for the higher flow rates. In Table 11 this error is represented as instrument-to-instrument variability

Estimates of our own repeatability are also shown in Table 11. These reflect the repeatability of our own experiments and do not reflect any instrument-to-instrument or operator-to-operator variation. We did make our runs on various days and the day-to-day variability of the overall average of the first timed extrudate is also reported in Table 11. In Table 11, the sample-to-sample variability is also reported on the first timed extrudate. Neither of these was significantly different from the overall error. Finally we tried to estimate the intrinsic error in the measurement. We did this by considering the errors in the measured quantities (mass and time) as well as the errors in the controlled quantities (temperature and the specifications on the instrument). The cause of these errors are discussed in the next few paragraphs. These, along with the other errors, are given in Table 11 along with an estimate of the overall error resulting from all sources.

Mass Error

The extrudate segments were weighed on a balance with a 0.01 mg resolution in mass indication. Replicate weighing of the segments agreed to within ± 0.01 mg. in general and never varied beyond ± 0.02 mg at the extreme. Paragraph 8.8 of ASTM method D 1238-82 instructs the experimenter to "weigh the extrudate to the nearest 1 mg when cool." It should be noted that 1 mg of this polymer occupies very nearly 1 microliter of volume which is probably a valid estimate of the uncertainty in the cut considering the technique of cutting the extrudate. Consequently, the uncertainty in extrudate mass resulting from the process of cutting the segment is estimated as dm = ± 1 mg. The overall average apparent mass m = 107 mg was calculated for all the extrudate segments in the characterization of this polymer. Consequently, the relative error in mass (dm/m) entering into the melt index characterization is

$$dm/m = \pm 1\ \text{mg}/107\ \text{mg} = 0.0093458 = 0.9\% \text{ or } 1\%$$

The extrudate segments were routinely weighed within 1/2 to 1 hr after having been cut, in compliance with the instruction in paragraph 8.8 of the ASTM method. Considering the hydrophobic character of polyethylene, it would not be anticipated that the extrudate would accumulate moisture beyond the initial cooling stage prior to being weighed. On a few occasions, extrudate segments, which had been weighed at the end of a day, were weighed again on the following day without detecting any statistically valid change of weight within the groups. All individual changes, either positive or negative, were much smaller than 1 mg. Consequently, it may be assumed that there was no detectable error in weight attributable to moisture absorption, and that the error in extrudate weight is overwhelmingly dominated by the volume uncertainty attending the process of cutting the extrudate.

Time Error

The 6 min. interval (t) between extrudate cuts was measured with a battery powered stopwatch having a 0.01 s resolution in time indication. The extrudate cut was timed to with in 0.1 s. Consequently, the time error may be equated with 0.1 s. Hence, the relative error in time interval may be expressed

$$dt/t = \pm 0.1 \text{ s}/360 \text{ s.} = 1/3600 = 0.0002778 = 0.03\%$$

Temperature Error

The thermal profile of an undisturbed column of polyethylene melt was scanned along the cylindrical axis of the cylinder bore. This experiment was conducted in another extrusion plastometer during an earlier determination of the melt flow rate of NBS SRM 1475 (polyethylene whole polymer) and NBS SRM 1476 (linear polyethylene). The temperature in the stationary melt column was measured with a thermocouple hot junction stationed at different heights above the top surface of the die, along the cylindrical axis of the bore. Throughout the experiment the indicated cylinder temperature remained at 190° C. The results are listed in Table 7.

Inspection of the tabulated results indicates that the departure of melt temperature from the indicated cylinder temperature is less than ± 0.1° C, at any location in the melt column from 12 mm above the die upward. It may be observed that the 0.7 - 0.8° C drop in temperature, between the 12 mm and 1 mm levels above the die, occurred in the undisturbed melt column. This temperature drop is probably at least partially erased by the downward flow of melt during an extrusion. It is also possible that the apparent smaller variation of temperature with height from 12 mm upward may be a variation of temperature with time at which the temperature was determined at different levels. Because its heat capacity and volume displacement are considerably greater, the mercury column thermometer is a very effective temperature averaging device and is far less responsive to brief and small changes in temperature than is a very small thermocouple junction. Regardless of whether the temperature is changing with time or with height, or with both time and height, the maximum temperature error (ST) may be estimated as ± 0.2° C.

The greater significance of temperature error is its effect on the melt index of this polymer. The variation of melt flow rate of this polymer with temperature in the vicinity of 190° C was determined to be 1.65% per °C, as reported in paragraph 2.1.1. This is equivalent to 0.17% per 0.1° C corresponding to the 0.1° C nominal error in the melt temperature.

3.2.3. Melt Flow Rate of Material Taken from the Piping and Joints

Piping and joints were made of the same resin used for polyethylene SRM 1497. These pipes and joints, and their designation for future discussions, are

1.59 cm OD pipe	(P.5)
6.03 cm OD pipe	(P2)
11.4 cm OD pipe	(P4)
butt joint	(BJ)
socket joint	(SJ)

The melt flow rates of these materials were determined at points deemed to be significantly affected by the processing conditions. The samples obtained from various positions were

cross section of P.5
Inside part of P2
outside part of P2
inside part of P4
outside part of P4

Positions of cuts used to make charges from the joints are shown in Figure 4.

3.2.3a Sampling Procedure and Cutting of the Piping and Joints

After an unsuccessful attempt to obtain samples of the pipe by cryogenic fracture at liquid nitrogen temperatures, samples were cut from the pipes and joints with a sharp knife blade at ambient temperature.

In the initial effort to obtain samples by cryogenic fracture, a section of 1.59 cm OD pipe was scored with a file in the same manner that one scores a glass tube in preparation for a controlled break. The pipe was repeatedly immersed in liquid nitrogen for 1/2 hour. After each 1/2 hour immersion the pipe was subjected to a bending stress manually applied while the experimenter was wearing asbestos gloves. In all attempts the pipe would bend under the stress but did not fracture.

At ambient temperature, the 1.59cm OD and 6.03 cm OD pipes were cut with a sharp blade without observable surface deformation. A fine-toothed, low speed, band saw was used to cut rough samples from the 11.4 cm OD pipe and the joints. This slow sawing apparently did not heat the resin significantly above ambient temperature since the sample felt only warm to the touch after cutting. As a further precaution, the sawed surfaces of these samples were removed by slicing them off with a knife blade to a depth of a few millimeters. It was presumed that this procedure removed any resin modified as a result of the heat and tearing from the saw.

Charges to be extruded were obtained by cutting the samples, with the knife blade, into pieces which would fit down inside the bore of the plastometer.

3.2.3b Melt Flow Rate of the Piping and Joints

The melt viscosity of some of the samples was so great (melt flow rate so small) that the use of ASTM Condition 190/2.16 was found to yield data outside of the acceptable range for that condition as prescribed by the ASTM method. The melt flow rate under condition 190/5.0 using ASTM Method D 1238-82 was found to be adequate for these measurements. The technique used for the melt flow rate measurement and the calibration of the equipment has been discussed earlier in Section 3.1. The measurements were as described earlier, except that the charge weight was varied among the different samples. This was necessary because of the wide variation of melt flow rate among these samples. The charge weight of each of the samples had to be calculated in advance to order to achieve a conformity with both the uniform 6 minute preheat condition and the piston start position as required by the method. Nonetheless, the mass of all the initial charges remained within 5% of the 3 gm specified in the earlier discussion. This minor variation in initial charge was considered to have no effect on the measured flow rate.

As before, three timed extrudates were measured for each charge. Although there were the same drifts in these measurements with extrudate number, as reported in the discussion of the melt flow rate measurement on the resins, the drifts are not reported here because the differences between the melt flow rate from charge to charge was much greater than the differences among extrudates for a given charge. Thus we report the overall average from all three measured timed extrudates.

Data for the melt flow rates obtained for samples from the various pipes and joints are given in Table 12. For this preliminary report, only one melt flow rate for each position chosen and for only one pipe and joint of a particular type were measured except for the 4 inch pipe where measurements were made on two different pipes. Thus, except for this last measurement, which shows little pipe-to-pipe variation there is nothing that can be inferred from the data about pipe-to-pipe or joint-to-joint variation. This will need to be studied more in the future.

It is clear from Table 12 that there are significant differences among the various measurements of melt flow rate. What is clear from the data in Table 12 is that the joints show variations in the melt flow rate, it being both greater and smaller than the melt flow rate of the resin. These values are well outside the range of data observed for the resin data. Thus, the processing of the resin to make the pipe has changed the melt flow rate. Even the pipes show a significant effect of their processing, well beyond what is expected from just measurement variation.

At this point, we shall not speculate on the cause of the large variations in the melt flow rate. More experiments need be done to determine the pipe-to-pipe or joint-to-joint variation, as well as variations within the pipe or joint in order to establish bounds on the magnitude of the effect.

4. Density

4.1 As-Received Pellets

Density measurements were carried out on the as-received pellets of both the natural, or unpigmented, resin and the pigmented resin. In the case of the unpigmented resin one pellet was chosen from ten different locations within the 455 kg container, whereas for the pigmented resin one pellet was taken from each of the ten 455 kg containers. The measurements were done using a density gradient column which consisted of a mixture of ethyl alcohol and distilled water. For the particular column arrangement used, the error in each individual measurement is estimated to be ±0.0003 g/cm^3. Initially, the pellets were degassed by placing them under vacuum overnight in an alcohol-distilled water mixture.

The results are presented in Table 13. It can be seen that, on average, the density of each lot of resin was very nearly the same. By inspection, it would appear that the majority of the pigmented pellets have a higher density than the majority of the unpigmented pellets. However, the average values differ by only 0.0006 g/cm^3, a value which is only about twice the estimated error in each measurement.

4.2 Piping Materials

Density measurements were also carried out on the three piping materials. From the 1.59 cm OD pipe ten specimens were prepared by cutting rings, ranging in width from 0.5 to 0.75 cm, from five different locations along one 25 cm long section. Each ring was then cut in half to give two crescents. The same procedure was used to obtain ten specimens from the 6.03 cm OD pipe, except that all ten pieces were cut from only two rings taken from opposite ends of a 25 cm long section. In the case of the 11.4 cm OD pipe, five specimens were cut from one ring section. In all cases each specimen contained material from both the inner and outer surface (complete thickness of the wall).

The density was determined using the displacement method in distilled water. The water was degassed by boiling it for twenty minutes. It was then cooled to 22° C prior to use. A value of 0.99777 g/cm^3 was used as the density of water at 22° C and no other corrections were applied. Based on an analysis of the measurement technique the experimental error is estimated to be no greater than ±0.001 g/cm^3.

The results for all twenty five specimens are presented in Table 14. A comparison of the average values indicates that there is very little difference in density among the three pipe sizes.

4.3 Tee Joints

One butt tee joint and one socket joint were also examined for uniformity in density. Six specimens were taken at different locations from one butt tee joint, and six from one socket tee joint. For the six piece from the butt tee joint, the density ranged from 0.928 to 0.939g/cm^3, whereas for the socket tee joint, the range was from 0.921 to 0.940 g/cm^3. In both cases, the lowest densities recorded were for the pieces taken nearest the point of injection and the highest values were obtained for the pieces taken from a point on the inside wall well away from the point of injection.

5. Uniformity of Pipe Dimensions of the 1.27 cm Diameter Pipe

One 50 cm long section of the 1.27 cm diameter pipe was examined for uniformity of dimensions over its length. The pipe was marked at one centimeter intervals and the maximum and minimum values of the outside diameter was determined using a micrometer at each of the 50 locations along the length of the pipe. The pipe was then cut into short sections and the maximum and minimum values of the wall thickness were determined at 13 different locations using a tubing micrometer.

The average values for the various dimensions measured, along with their standard deviations, are shown in Table 15. The maximum out-of-roundness found among the 50 measurements was 0.024 cm (0.009 in) and the minimum wall thickness among the 13 measurements was 0.232 cm (0.913 in). The average outside diameter as a function of position along the length of the pipe is shown graphically in Figure

6. Size Exclusion Chromatography of the Pigmented and Unpigmented Resins

Both samples of resin (SRM 1496 and SRM 1497) were studied by size exclusion chromatography in order to examine their molecular weight and molecular weight distribution.

6.1 Experimental Procedures

A set of two Shodex mixed bed (AT-80M/S) columns were used in a Waters GPC150 Size Exclusion Chromatograph. These columns have 10 micrometer particles. Column #5J704 had 8500 theoretical plates per 25 cm, Column #4H729 had 9200 plates per 25 cm. The columns were operated at 145° C, at a flow rate of 1.0 ml/min., except where noted. The carrier solvent was 1,2,4 trichlorobenzene, 99% pure, (Aldrich Chemical Co.), which had been passed through a 5 μm Teflon (Millipore's Mitex) filter. No antioxidant was added to the eluent, but sample solutions were made up from trichlorobenzene, taken directly from the instrument, to which was added 0.2% of the antioxidant Santonox.

The columns were calibrated with three types of standards: narrow molecular weight distribution polystyrenes and polyethylenes, and SRM 1475, the NBS whole polymer polyethylene standard with known molecular weight distribution. The polystyrenes were obtained from several sources (Table 16), whereas the polyethylene fractions were SRM's from NBS.

The polystyrene calibrating solutions were made up at the concentrations shown in Table 16. Although the lower molecular weight standards were filtered at 60 C through a 10 μm Teflon filter, the standards above 1 million were not, in order to reduce the possibility of shear degradation. The high molecular weight standards were dissolved without using a shaker but were occasionally tumbled over a period of from several hours to as much as 5 days. Nevertheless, as shown below, there is still evidence of degradation in the case of the highest molecular weight standards.

To obtain representative samples of each of the GRI reference polyethylene resins, solutions were made up by cutting a small piece from 10 different pellets. In the case of the unpigmented material, each of the 10 pellets was taken from 10 different positions in the original container. The 10 pigmented pellets were taken from the bottle which had been previously mixed by rolling. The total weight of each sample was of the order of 30 mg, to which sufficient solvent was added to give a concentration of 0.125% by weight.

All the polyethylenes, standards as well as the reference pipe resin samples, were dissolved by heating in a 165 C oven for 1 hour with brief, gentle shaking about every 15 minutes. When dissolved, the pigmented samples as well as some of the unpigmented samples were filtered through a 10 μm Teflon filter.

Samples were run one at a time rather than in batches to minimize exposure of the polymers to the 145° C temperature for a long period of time. The polystyrene samples which were made up at room temperature or at 60° C were kept in the heated injector compartment for 30 minutes before injection. The polyethylene samples were transferred directly from the 165° C oven and were injected after being kept for 10-15 minutes in this compartment.

The injection volume for the narrow molecular weight standards were 300 $\mu\ell$, whereas for the whole polymer standard, SRM 1475, it was 200 $\mu\ell$. The reference PE samples were run at 200 $\mu\ell$ at a refractometer sensitivity of 256 and a scale of 99, the maximum possible.

The computer was set to acquire data rapidly after the first 5 minutes and to continue doing so for the next 25 minutes.

6.2 Universal Calibration

Calibration of the columns was obtained by measuring the peak elution volume of 18 narrow molecular weight distribution standards and the whole polymer, SRM 1475. The data are shown in Table 16. The higher molecular weight polystyrenes, with molecular weights above 13 million, eluted later than the 13 million standard, suggesting that degradation of the former had taken place. This might have occurred either in the solution process or during passage through the column at 145° C.

It was necessary to use the Mark-Houwink relations that had been determined at 135° C [10,11] in order to use the universal calibration method since no data are available at 145° C., the temperature of the experiment. These relations are:

For polystyrene - $[\eta] = 14.6 \times 10^{-3}\ M^{.689}$ mℓ/g

polyethylene - $[\eta] = 52.6 \times 10^{-3}\ M^{.70}$ mℓ/g,

where $[\eta]$ is the intrinsic viscosity.

The calibration curve of hydrodynamic volume vs elution volume (EV) consisted of 3 straight line segments:

Elution Volume Range	Calibration
10-10.5	22.7-1.23 (EV)
10.45-17.43	18.03-0.782 (EV)
17.43-18.94	55.11-2.91 (EV)

6.3 Comparison of Pigmented and Unpigmented Resins

To determine whether or not there was a difference between the pigmented and unpigmented resins, a series of runs was made in which two pigmented resins and two unpigmented resins were run alternately under the same conditions. The chromatograms, after being normalized, are superimposable as shown in Figure 6. Hence size exclusion chromatography does not show any significant difference between the two resins.

6.4 Molecular Weight Calculations

The calculation of molecular weight for these materials presents some problems because of the presence of both very high molecular weight species and very low molecular weight species.

The exclusion limit of the chromatographic columns occurs at about 10 ml which corresponds to a polystyrene molecular weight of over 20 million or a polyethylene molecular weight of over 5.6 million. The chromatogram indicates that there is material present at this molecular weight, and perhaps at higher molecular weights, which cannot be separated but passes through the column at the exclusion limit. As a result, these higher molecular weight species cannot be counted in the calculation of molecular weight. If differences exist in this higher molecular weight region between the pigmented and unpigmented samples, they will not be observed by this procedure.

At the lower molecular weights, a sharp drop occurs at the end of the polymer peak because of adjacent "peaks" due to other components in the solvent such as antioxidant or impurities. It was necessary to cut off the polymer peak arbitrarily at the elution volume at which this peak intersects the base line. The elution volume limits chosen for the molecular weight calculation were in the range 10.03 to 10.06 ml at the high molecular weight end and 18.77 or 18.78ml at the low molecular weight end.

6.5 Conclusions

No significant difference in the molecular weight or molecular weight distribution of the pigmented and unpigmented resins was observed by size exclusion chromatography, although the melt flow rate indicated the two resins were somewhat different (see Section 3). The weight average molecular weight M_w is 170,400 with a standard deviation of 4.5%, and the number average molecular weight Mn is 5500, with a standard deviation of 10.3%.

7. Mechanical Properties

7.1 Tensile Properties in Uniaxial Extension

Two tensile properties, the yield stress and the strain at yield, were examined as a function of strain rate for two of the three sizes of pipe. The largest diameter pipe was not included due to the inadequte load capacity of our test machines. Six pieces of the 1.27 cm (0.5 in) diameter pipe and four pieces of the 5.08 cm diameter pipe were selected at random from the two lots of pipe. From these pieces, 16 specimens were cut from the 1.27 cm pipe and 12 specimens from the 5.08 cm pipe. Each specimen was 25.4 cm (10 in) long. The specimens were mounted in grips such that the exposed length, or gage section, was 20.32 cm (8 in). The grips consisted of three parts, (1) a knurled central post which fitted tightly inside the end of the pipe, (2) a four section tapered split ring, and (3) an outer tapered compression ring which could be tightened down over the split ring by means of four Allen head bolts. The experiments were done in a servo-controlled hydraulic test machine operated in stroke control, and all of the tests were conducted using a constant rate of clamp separation. The experiment was stopped once a strain greater than the strain at yield was achieved. In the present work, the yield point was taken to be the point at which the stress-strain curve reached its initial maximum.

In order to obtain a measure of the specimen-to-specimen variability within the two lots of pipe, 10 specimens of the 1.27 cm diameter pipe and 6 specimens of the 5.08 cm diameter pipe were tested at one strain rate (81% per min). The results are presented in Table 17. The average yield stress for specimens 1 through 10 was 16.4 MPa with a standard deviation of 0.15 MPa. The strain at yield was found to be very nearly the same for all ten specimens (σ=0.125). For the larger diameter pipe, specimens 17 through 22, the average yield stress was 17.4 MPa, while the strain at yield was the same for all the samples tested (ϵ=0.127) and was only slightly higher than for the smaller diameter pipe.

Also shown in Table 17 are values of yield stress and strain at yield obtained at three other strain rates ranging from 0.82 to 810 percent per minute. At each of the three different strain rates, only two specimens were tested. The data presented in Table 17 is summarized in graphical form in Figures 7 and 8, where the points shown represent the average values obtained from Table 17. On the semilog plot it can be seen that both properties vary linearly with changing strain rate, at least over the three decade range examined. In both cases, the larger diameter pipe exhibits somewhat large values over the entire range of strain rates. Since both sizes of pipe were found to have very nearly the same density, it would not appear that differences in crystallinity would account for the differences in tensile behavior. Differences in the extent of crystal orientation between the two sizes of pipe could, however, result in the observed behavior.

For a strain rate corresponding to the condition designated as speed B in ASTM D 638 [6] and the geometry specified as Type I, II, or III (100% per minute), the yield stress is 16.8 MPa for the 1.27 cm diameter pipe and 17.4 MPa for the 5.08 cm diameter pipe.

7.2 Uniaxial Creep of Material Molded from the Pigmented Pipe Resin

The unaxial creep behavior of specimens prepared from the pigmented pipe resin has been studied. Tensile specimens were compression molded according to the following procedure. A mold consisting of a frame having an opening of 15 cm by 5 cm was placed between two 1.27 cm thick Teflon coated platens. The frame was filled with sufficient polymer to produce a sheet approximately 0.1 cm thick. The frame was placed in a press preheated to 150°C and was held at that temperature under only light contact pressure for a period of ten minutes. At that time the heat was turned off and the pressure increased to 15 MPa (2175 psi). The press was then cooled under ambient conditions (~1°C per minute) to a temperature below

80°C before the mold was removed from the press. From each sheet three specimens were cut using a dumbbell shaped die which had a width in its narrow straight portion of 0.30 cm.

In order to determine the creep strain, fiducial marks were placed approximately 3 cm a part on the narrow straight portion of the specimen. The separation between marks was monitored as a function of time under load. Loading of the specimen was accomplished by hanging a bucket containing lead shot from the lower clamp.

Results for six specimens subjected to applied stresses ranging from 10 to 20 MPa are shown in Figure 9. At the two highest stresses, the creep was sufficiently rapid to cause significant heating of the specimens and as a consequence failure during the cold drawing stage after neck formation. The specimen under an applied stress of 10 MPa required approximately 70 days to form a neck. In the range of intermediate stresses the specimens exhibit neck formation followed by a stage of rapid cold drawing until the neck has propagated through the entire gage section of the specimen. The one feature which distinguishes this particular polyethylene from other polyethylenes is the almost complete cessation of creep once the neck has propagated the length of the gage section. Most polyethylenes, continue to exhibit creep even in the highly extended state. The creep rate at high extensions is greatly reduced from that at the earliest stages, however creep continues until fracture occurs. In the present case, it would appear that the ethylene-hexene copolymer will remain at essentially a constant length out to very long times before fracture will occur. The maximum extension attained does depend upon the level of applied stress. For example, the specimen subjected to a stress of 16.25 MPa reached an extension of 8 times its original gage length, whereas at 10 MPa a specimen extended only about 5 times its original length. In order to determine the maximum tensile stress that the pigmented resin can sustain under creep, the specimen which initially was under a stress of 15 MPa was subjected to higher and higher stresses until failure occurred. The stress was increased in steps from 15 MPa to 35 MPa. In each case, the extension was measured after 2 minutes at the new stress, and then again after one hour. At each stress level up to 30 MPa there was little, if any, increase in the extension between 2 minutes and one hour. At 35 MPa the specimen failed after 5 minutes. The maximum extension is shown plotted versus the log of the applied stress in Figure 10. For the specimens prepared according to the procedure described above, the maximum extension attainable under creep was approximately 9.5 times its original length at a stress of 35 MPa.

Two specimens prepared from the unpigmented resin were also tested at stress levels of 12.5 and 15 MPa. The maximum extension for these two specimens was essentially the same as that found for the pigmented polymer at the same two levels of stress.

8. Comparison Between the Reference Polyethylene (Pigmented Resin) and Three Commercial Gas Pipe Resins in use in Europe: Short Term Tensile Properties

During the collaborative research carried out at IKP, University of Stuttgart, a comparison was made between the GRI reference polyethylene (pigmented resin) and three different gas pipe resins currently in use in Europe, one from Germany, one from Sweden, and one from Belgium. Each of the European resins was initially in the form of pellets, and all three contained yellow pigment.

Sheets were prepared from all four materials using the following procedures. A predetermined weight of pellets was placed in a mold which consisted of a 25 cm x 25 cm frame held between two ferrotype plates. The mold was placed in a press and heated under only light contact pressure to 175 C. The press was maintained at 175° C for 15 minutes at which time a pressure of 5 MPa was applied and the heat turned off. The mold was then cooled overnight to room temperature. The nominal thickness of the molded sheets was between 0.14 and 0.15 cm.

From each sheet, a 1 cm x 2 cm piece of material was cut and its density determined using the displacement technique in isopropyl alcohol at 23° C. The results are tabulated at the bottom of Table 18, where the error in each individual measurement is estimated to be no greater than ±0.001 g/cm^3.

Tensile specimens were then cut from each sheet using a die which conformed to the geometry specified in DIN 53504, Specimen 53A [12]. Three tensile properties were determined at 23° C for each specimen, the yield stress, the stress at break (tensile strength), and the strain at break. For the initial set of tests, six specimens from each of the four sheets were elongated to failure at one constant rate of clamp separation which corresponded to a strain rate (initial strain rate) of approximately 73% per minute. The strain at failure was determined by measuring the elongation of an initially 1.5 cm long gage section within the straight portion of the specimen. The results from the set of tests are presented in Table 18, where each value shown represents an average for six specimens. Also given in Table 18 are the drawing stress and ratio of the yield stress to drawing stress. The drawing stress is defined here to be simply the stress in that portion of the stress-strain curve beyond the yield point where the stress remains essentially constant while the "neck" propagates through the straight portion of the specimen.

In addition to the tests just described, tests were also done at three other rates of strain (initial strain rates) 873, 7.3, and 1.04% per minute. In this case, only two specimens of each material were tested at each strain rate. The dependence of all three tensile properties on strain rate is presented in Figures 11, 12, and 13. The yield stress increases linearly with the logarithm of the strain rate (Figure 11), except for the one set of tests at the highest strain rate for the material from Belgium. All four materials exhibit a maximum in the stress at break (Figure 12) at a strain rate of 73% per minute. The material from Belgium shows a much greater decrease in tensile strength at the highest strain rate than do the other three. The strain at break decreases monotonically with the logarithm of the strain rate (Figure 13) for all four materials.

Viewed overall, it is evident that all four materials show the same general trends in behavior and that there is not a great deal of difference among them. The material from Sweden shows consistently the highest values of yield stress and strain at break. These two observations along with the observation that it has the highest density suggest that, under the same molding conditions, it will have the highest crystallinity of the four materials. It is also evident that, at high strain rates, the tensile properties deteriorate most rapidly for the material from Belgium.

9. Summary

This report describes work done under GRI Contract Number 5084-260-1013 during the period from October 1, 1985 through September 30, 1986. The project entails the procurement, characterization, and warehousing of standard reference polyethylene gas pipe resins, as well as piping and joint materials made from them. The contract between the Gas Research Institute (GRI) and the National Bureau of Standards (NBS) was recommended at a workshop held at Northwestern University, Evanston, IL on September 7 and 8, 1983. A final report describing the presentations, deliberations, and recommendations of the workshop was issued by GRI (Report No. 84/0107) on May 14, 1984.

The workshop stipulated the following types and quantities of material to be characterized and warehoused for distribution:

Item	Quantity
1. Polyethylene resin (natural)	455 kg.
2. Polyethylene resin (pigmented)	4550 kg.
3. Polyethylene pipe (6.03 cm OD, 0.55 cm wall)	1.59 km in 0.76 m sections
4. Polyethylene pipe (11.4 cm OD, 1.0 cm wall)	0.15 km in 0.76 m sections
5, Polyethylene pipe (1.59 cm OD, 123 cm wall)	0.25 km in 0.76 m sections
6. Polyethylene 5.1 cm socket T joint	500
7. Polyethylene 5.1 cm butt T joint	500

In addition, it was decided to include one 0.15 km roll of the 1.59 cm OD, 0.23 cm wall pipe. It was further agreed upon by the attendees at the workshop that the reference polyethylene would be the medium density polyethylene resin, TR418, from the Phillips Petroleum Co.

All of the materials were on site at NBS by October, 1985, when the characterization work commenced. A detailed description of the equipment and procedures used in each phase of the characterization work is contained in this report. The principal areas of investigation were as follows:

(1) The number of methyl groups, butyl branches, and terminal vinyl groups was determined for the two polyethylene resins using FT-IR and NMR. One piece of the 6.03 cm (OD) pipe was also examined.

(2) The melt flow rate was determined for the two polyethylene resins. At least ten random samples were tested from each lot of material. In addition, the melt flow rate of material cut from various locations within the piping and joint materials was examined.

(3) The density was determined for all of the reference materials.

(4) Both lots of resin were examined by size exclusion chromatography in order to determine their molecular weight and molecular weight distribution.

(5) The yield stress and strain at yield were determined for two of the three sizes of pipe. In addition, the creep behavior of material molded from the pigmented resin was studied.

Several of the principal findings of this work are summarized below.

(1) Branching Characteristics

	FT-IR		NMR
Sample	Methyl Groups per 100 Carbon Atoms	Vinyl Groups per C-C Bond	butyl groups per 1000 carbon atoms
unpigmented resin	0.50	$5X10^{-4}$	4.27
pigmented resin	0.56	$5X10^{-4}$	4.56
pigmented pipe	0.55	$5X10^{-4}$	

(2) Melt Flow Rate(a)

Resin(b)

Sample	Mean	Standard Deviation	95% Confidence Interval of Mean
Unpigmented	0.253(c)	0.007	0.241 to 0.272
Pigmented	0.179(d)	0.010	0.177 to 0.180
	0.796(e)	0.025	0.789 to 0.802

Piping and Joint Materials(e)

1.59 cm OD	0.851
6.03 cm OD	
Inside	0.577
Outside	0.618
11.4 cm OD	
Inside	0.625
Outside	0.674
butt joint	0.996
socket joint	0.508

(a) gm/10min.
(b) Condition 190°C/2.16 kg.
(c) mean value for 20 charges
(d) mean value for 56 charges
(e) Condition 190°C/5.0 kg

(3) Density

Sample	Mean (gm/cm³)	Standard Deviation (gm/cm³)
Unpigmented resin	0.9322(a)	0.0040
Pigmented resin	0.9328(a)	0.0009
1.59 cm OD pipe	0.938(a)	0.001
6.03 cm OD pipe	0.937(a)	0.001
11.4 cm OD pipe	0.938(b)	0.001

(a) mean value for 10 samples
(b) mean value for 5 samples

(4) Size Exclusion Chromatography

Sample		M_w	Standard Deviation	M_n	Standard Deviation
Unpigmented Pigmented	(a)	17040	7670	5500	565

(a) No difference was observed between the two resins

(5) Tensile Properties (a)(b)

Pipe Size	Yield Stress	Standard Deviation	Strain at Yield	Standard Deviation
1.59 cm OD	16.40	0.15	0.125	0.001
6.03 cm OD	17.35	0.19	0.127	0.000

(a) MPa
(b) Strain rate = 81% per minute

Finally, it should be noted that the values of melt flow rate for the two joints differ by a factor of about two (0.996 for the butt joint versus 0.508 for the socket joint), and that both values are different from that of the base resin (0.796) by an amount well outside the standard deviation for the twenty charges of the base resin examined. We conclude that these differences are a consequence of changes in molecular parameters which occur during the processing. It is recommended, therefore, that additional work be done to determine which molecular parameters are affected and to what extent these changes may influence long term performance.

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[12] DIN 53504, DIN Deutsches Institut fur Normung e.V., Deutsches Informationzentrum fur Technische Regeln (DITR) und Beuth Velag GmbH, Burggrafenstrasse 6, D-1000 Berlin 30.

List of Tables

Table 1

Methyl Group Concentration
No./100 Carbon Atoms

Sample	Methyl Group Concentration
unpigmented resin	0.50 ± .05
pigmented resin	0.56 ± .05
pigmented (pipe)	0.55 ± .05

Table 2

Terminal Vinyl Group Concentration
No. per Carbon-Carbon Bond

Sample	Vinyl Group Concentration
unpigmented resin	$5 \pm 0.2 \times 10^{-4}$
pigmented resin	$5 \pm 0.2 \times 10^{-4}$
pigmented (pipe)	$5 \pm 0.2 \times 10^{-4}$

Table 3

Degree of Crystallinity
Weight Fraction x Density

Sample	Crystallinity
unpigmented resin	0.66 - 0.71[+]
pigmented resin	0.74 ± .03
pigmented (pipe)	0.67 ± .03

[+] variation among several molded sheets

Table 4

Variation of Melt Flow Rate with Piston Diameter: Pigmented Resin

	NARROW PISTON FOOT			BROAD PISTON FOOT		
	Mean	Std. Dev. of Mean	Std. Dev. of Sing. Meas.	Mean	Std. Dev. of Mean	Std. Dev. of Sing. Meas.
1st Time Extrudate	0.191	0.012	0.014	0.189	0.006	0.007
2nd Time Extrudate	0.179	0.008	0.009	0.182	0.003	0.004
3rd Time Extrudate	0.176	0.010	0.012	0.177	0.004	0.004
Data Overall	0.182	0.012	0.013	0.183	0.007	0.007

All data in g/10 minutes

Table 5

Melt Flow Rate of SRM 1496 at a Load of 2.16 kg

	Mean (a)(b)	95% Confidence Internal of Mean	Standard Deviation of a Single Measurement
1st Timed Extrudate	0.259	0.256 to 0.262	0.007
2nd Timed Extrudate	0.252	0.250 to 0.254	0.005
3rd Timed Extrudate	0.248	0.246 to 0.250	0.004
Overall Mean	0.253	0.251 to 0.255	0.007
Overall Data Range		0.241 to 0.272	

(a) g/10 min
(b) mean value for 20 charges

Table 6

Estimates of Errors in Melt Flow Rate
of SRM 1496 Polyethylene
under Condition 190/2.16

1.	Overall Estimated Repeatability of Experiment (see Table 1 of ASTM D 1238-82)	2.6%
2.	dM/M*100	0.7%
3.	dt/t*100	0.03%
4.	dMfr/dT*dT/T*100	1.7%
5.	Instrument Variability (estimated from ASTM D 1238-82 Table 3)	15
6.	Range of day-to-day variation overall mean	0.250 to 0.253
7.	Range of position-to-position variability	0.241 to 0.272
8.	Overall estimated error in melt flow rate (contributions are from 1-5. 6-7 are included in 1.)	15.2%

Table 7

Variation of Temperature with Height in Undisturbed Melt in Cylinder Bore

Height Above Die, mm	Melt Temp. Degrees C
48	190.09
36	189.93
24	189.97
12	189.94
1	189.23

Table 8

Melt Flow Rate of the Pigmented Gas Pipe Resin, SRM 1497, at a Load of 2.16 kg

	Mean (a)(b)	95% Confidence Interval of Mean	Standard Deviation of a Single Measurement
1st Timed Extrudate	0.186	0.182 to 0.189	0.011
2nd Timed Extrudate	0.177	0.175 to 0.180	0.009
3rd Timed Extrudate	0.173	0.170 to 0.175	0.008
Overall Mean	0.179	0.177 to 0.180	0.010
Overall Data Range		0.160 to 0.209	

(a) g/10 min
(b) mean value for 56 charges

Table 9

Melt Flow Rate of the Pigmented Gas Pipe Resin, SRM 1497, at a Load of 5.0 kg

	Mean (a)(b)	95% Confidence Interval of Mean	Standard Deviation of a Single Measurement
1st Timed Extrudate	0.788	0.778 to 0.798	0.023
2nd Timed Extrudate	0.797	0.785 to 0.809	0.025
3rd Timed Extrudate	0.805	0.790 to 0.815	0.026
Overall mean	0.796	0.789 to 0.802	0.025
Overall Data Range		0.758 to 0.878	

(a) gm/10 min
(b) mean value for 20 charges

Table 10

Melt Flow Rate of the Pigmented Gas Pipe Resin, SRM 1497, at a Load of 21.6 kg

	Mean (a)(b)	95% Confidence Interval of Mean	Standard Deviation of a Single Measurement
1st Timed Extrudate	15.1	14.8 to 15.4	0.4
2nd Timed Extrudate	16.4	16.0 to 16.8	0.5
3rd Timed Extrudate	17.9	17.4 to 18.4	0.6
Overall Mean	16.5	16.0 to 16.9	
Overall Data Range		14.6 to 19.5	

(a) g/10 min
(b) mean value for 10 charges

Table 11

Estimates of Errors in Melt Flow Rate of the Pigmented PE Resin (SRM 1497) under Condition 190/2.16

		%
1.	Overall estimated repeatablility of experiment (see Table 2 of ASTM D 1238-82)	5.9
2.	dM/M*100	1.0
3.	dt/t*100	.03
4.	dMfr/dT * dT/T*100	.2
5.	Instrument Variability (estimated from ASTM D 1238-82 Table 3)	16 for Mfr = 0.25 7 for Mfr = 7.0
6.	Range of day-to-day variation of overall mean	0.176 to 0.186 g/10 min
7.	Range of sample-to-sample variation of overall mean	0.171 to 0.188 g/10 min
Overall estimated error from 1-4		6
Overall estimated error from 1-5		17

Table 12

Melt Flow Rate of Parts Cut from Pipes and Joints Using ASTM Method D1238-82 Condition 190/5.0

		Flow Rate (g/10 min)	Standard Deviation
1.59 cm O.D.	pipe cross section	0.851	0.020
6.03 cm O.D.	pipe inside	0.577	0.008
	outside	0.618	0.014
11.4 cm O.D.	pipe inside (pipe 1)	0.633	0.004
	inside (pipe 2)	0.617	0.020
	outside (pipe 1)	0.683	0.020
	outside (pipe 2)	0.665	0.014
butt joint	injection port	1.103	0.023
	end	0.988	0.053
socket joint	injection port	0.605	0.026
	end	0.411	0.026
For comparison from our Table 9			
Resin		0.796	

Overall Range of Resin Data 0.758 to 0.878

Table 13

Density of the As-Received Pellets at 23° C Determined Using A Density Gradient Column

Pellet Number	Pigment	Density (g/cm^3)	Average Density (g/cm^3)	Standard Deviation (g/cm^3)
1	None	0.9330		
2		0.9322		
3		0.9320		
4		0.9320		
5		0.9320		
6		0.9320	0.9322	0.004
7		0.9320		
8		0.9320		
9		0.9330		
10		0.9320		
11	Orange	0.9320		
12		0.9330		
13		0.9330		
14		0.9320		
15		0.9335		
16		0.9335	0.9328	0.0009
17		0.9310		
18		0.9335		
19		0.9330		
20		0.9335		

Table 14

Density of the Piping Materials at 22° C Determined Using the Displacement Method

Pipe Outside Diameter cm (in)	Specimen Number	Density (g/cm^3)	Average Density and Standard Deviation (g/cm^3)
1.59 (0.5)	1	0.936	
	2	0.937	
	3	0.938	
	4	0.939	
	5	0.939	0.938
	6	0.938	0.001
	7	0.939	
	8	0.940	
	9	0.939	
	10	0.939	
6.03 (2.0)	11	0.938	
	12	0.937	
	13	0.936	
	14	0.937	0.937
	15	0.937	0.0005
	16	0.937	
	17	0.937	
	18	0.937	
	19	0.937	
	20	0.937	
11.4 (4.0)	21	0.937	
	22	0.939	0.938
	23	0.937	0.001
	24	0.938	
	25	0.937	

Table 15

Average Value of the Outside Diameter and Wall Thickness of One Section of the 1.27 cm Diameter Pipe

Dimension	Value (cm)	Standard Deviation (cm)
Average Minimum Outside Diameter (a)	1.586	0.027
Average Maximum Outside Diameter (b)	1.601	0.013
Average Outside Diameter (a)	1.594	0.016
Average Minimum Wall Thickness (b)	0.233	0.0005
Average Maximum Wall Thickness (b)	0.242	0.001
Average Wall Thickness (b)	0.237	0.0005

(a) Average for 50 measurements
(b) Average for 13 measurements

Table 16

Calibration Data

Standard	Run	M.W.	Type(a)	Con. mg/ml	Peak Elution Volume	Log Hydrodynamic Volume
SPP 541	388	519	P.S.	1	18.63	1.084
SPP 577	389	1811	P.S.	1	17.99	2.564
TSK A2500	387	2800	P.S.	1.1	17.85	3.987
P.C.61110	383	4000	P.S.	1	17.42	4.248
P.C.8b	382	10000	P.S.	1	16.69	4.920
SRM 1478	366	36590	P.S.	1	15.50	5.072
SRM 1482	372	12500	P.E.	1	15.82	5.686
SRM 1483	373	30500	P.E.	1	14.96	6.344
TSK F20	363	1.86e5	P.S.	1	14.11	7.065
SRM 1484	374	1.09e5	P.E.	0.5	13.89	7.285
P.C.5a	364	4.98e5	P.S.	0.5	13.13	7.787
SRM 1479	365	1.05e6	P.S.	0.5	12.27	8.334
TSK F288	367	2.87e6	P.S.	0.1	11.19	9.072
TSK F720	368	7.5e6	P.S.	0.23	10.55	9.776
TSK F1300	369	1.34e7	P.S.	0.21	10.20	10.202
TSK F1300	384	1.34e7	P.S.	0.19	10.11	10.202
BK2500	399	1.8e7	P.S.	0.33	10.54	10.419
TSK F2000	370	2.06e7	P.S.	0.28	10.55	10.517
TSK F2000	386	2.06e7	P.S.	0.28	10.33	10.517
BK3000	398	2.8e7	P.S.	0.3	10.44	10.743
SRM 1475	375		P.E.(broad)	0.5		
SRM1475	376		P.E.(broad)	0.5		

Polymer Standard Sources: SPP - Scientific Polymer Products; TSK - Toyo Soda; P.C. - Pressure Chemical Co.; BK - Japanese Synthetic Rubber Co.; SRM - Standard Reference Materials, NBS

(a) P.S. - polystyrene
P.E. - polyethylene

Table 17

Yield Stress and Strain at Yield as a Function of Strain Rate for Gas Pipe Tested in Uniaxial Extension

Pipe Size cm (in)	Specimen Number	Strain Rate (% Per Min)	Yield Stress (MPa)	Strain at Yield (%)
1.27 (0.5)	1	81	16.4	12.1
	2	81	16.3	12.5
	3	81	16.3	12.5
	4	81	16.3	12.5
	5	81	16.7	12.5
	6	81	16.6	12.5
	7	81	16.4	12.5
	8	81	16.4	12.5
	9	81	16.2	12.5
	10	81	16.4	12.5
	11	810	19.0	11.7
	12	810	19.0	11.7
	13	8.3	14.1	13.5
	14	8.3	14.2	13.5
	15	0.82	11.9	14.3
	16	0.82	11.9	14.3
5.08 (2.0)	17	81	17.6	12.7
	18	81	17.5	12.7
	19	81	17.1	12.7
	20	81	17.2	12.7
	21	81	17.3	12.7
	22	81	17.4	12.7
	23	810	19.6	11.9
	24	810	19.6	11.9
	25	8.1	14.5	13.9
	26	8.1	14.6	13.9
	27	0.80	12.1	14.9
	28	0.80	12.8	14.8

Table 18

Comparison of Tensile Properties of Four Commercial Gas Pipe Resins(1)

	Material			
Property(3)	U.S.A.	Germany	Belgium	Sweden
Yield Stress (MPa)	20.6	21.8	21.6	22.1
(Std. Dev.)	(0.2)	(0.5)	(0.6)	(0.5)
Stress at Break (MPa)	33.8	35.5	31.1	33.9
(Std. Dev.)	(1.45)	(0.8)	(3.5)	(2.3)
Strain at Break (%)	850	900	840	990
(Std. Dev.)	(30)	(23)	(50)	(50)
Drawing Stress (MPa)	14.1	15.5	14.6	1.45
Ratio of Yield Stress to Drawing Stress	1.45	1.41	1.48	2.52
Density (g/cm³)(2)	0.944	0.945	0.945	0.949

(1) Initial Strain Rate - 73%/min

(2) 23°C in Isopropyl Alcohol, Estimated Error ±0.001 g/cm³

(3) The values shown for the tensile properties represent the averages for 6 specimens

Captions for Figures

Figure 1. Difference spectrum for the unpigmented/pigmented pair.

Figure 2. Difference spectrum for the pigmented pellets/pipe specimen pair.

Figure 3. Drift of the Melt Flow Rate as a function of time. Measurements were taken at about every 2 min waiting for the 6 minute preheat.

Figure 4. Location of samples taken from the "T" joints for the determination of the melt flow rate.

Figure 5. Average value of the outside diameter as a function of position along the length of one 50 cm long section of the 1.27 cm diameter pipe.

Figure 6. Size exclusion chromatography of pigmented and unpigmented resins. Pigmented shown with (+). Unpigmented shown with (▢). Notice there is no measurable difference in the SEC of the two resins although their Melt Flow Rates show a 30% difference.

Figure 7. Yield stress versus log (strain rate) for specimens of the 1.27 cm and 5.08 cm diameter pipe tested in uniaxial extension at four different strain rates.

Figure 8. Strain at yield versus log (strain rate) for specimens of the 1.27 cm and 5.08 cm diameter pipe tested in uniaxial extension at four different strain rates.

Figure 9. Log (creep strain) versus log time for specimens prepared from the pigmented polyethylene resin. The numbers present the applied stress (MPa) and the arrows indicate fracture.

Figure 10. Maximum extension in creep versus log applied stress for one specimen prepared from the pigmented resin.

Figure 11. Yield stress versus strain rate (initial) in uniaxial extension for specimens prepared from four different commercial pipe resins. ○ - TR418, U.S.A.; △ - Germany; ▽ - Sweden; ▢ - Belgium.

Figure 12. Stress at failure versus strain rate (initial) in uniaxial extension for specimens prepared from four different commercial pipe resins. ○ - TR418, U.S.A.; △ - Germany; ▽ - Sweden; ▢ - Belgium.

Figure 13. Strain at failure versus strain rate (initial) in uniaxial extension for specimens prepared from four different commercial pipe resins. ○ - TR418, U.S.A., △ - Germany; ▽ - Sweden; □ - Belgium.

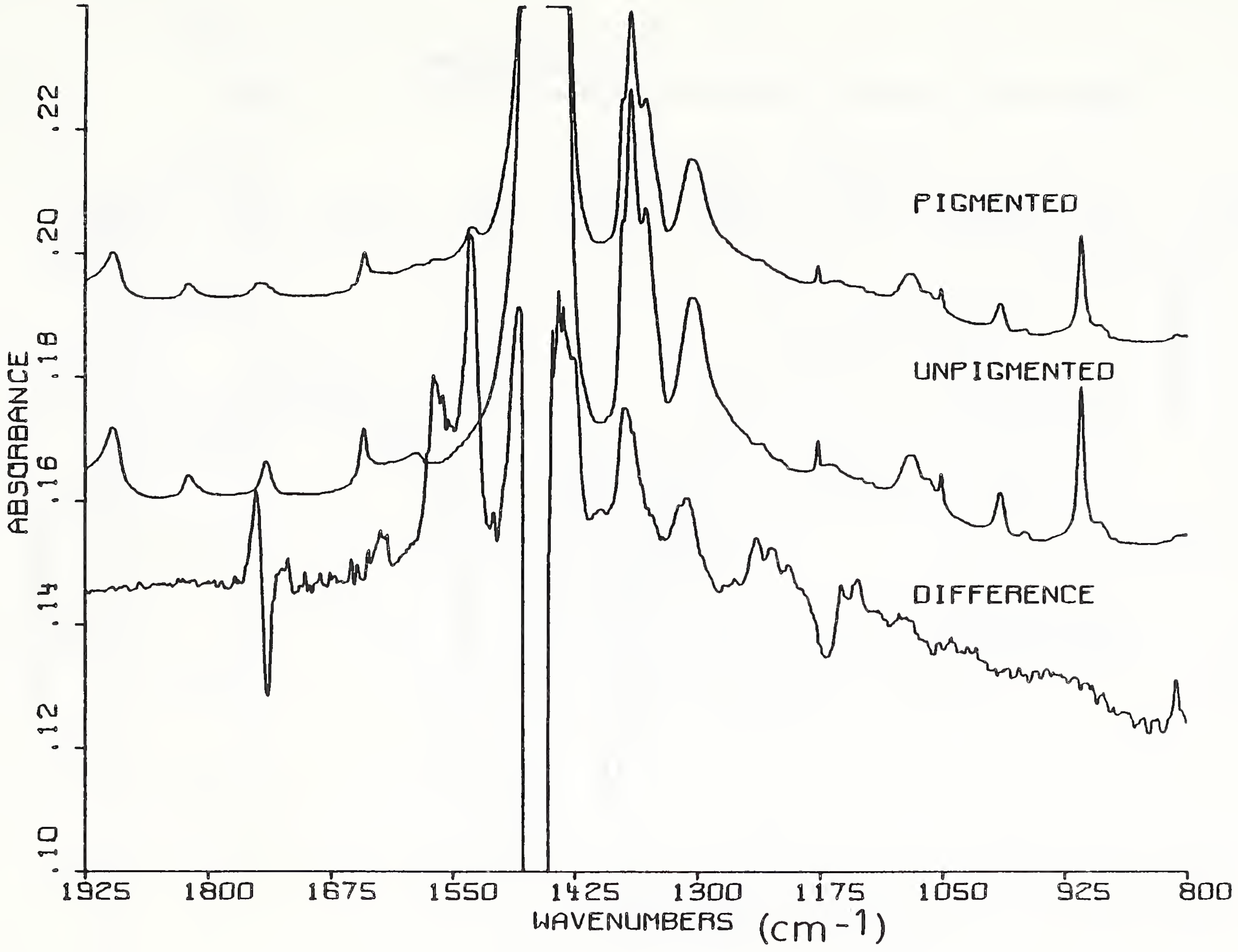


Figure 1. Difference spectrum for the unpigmented/pigmented pair.

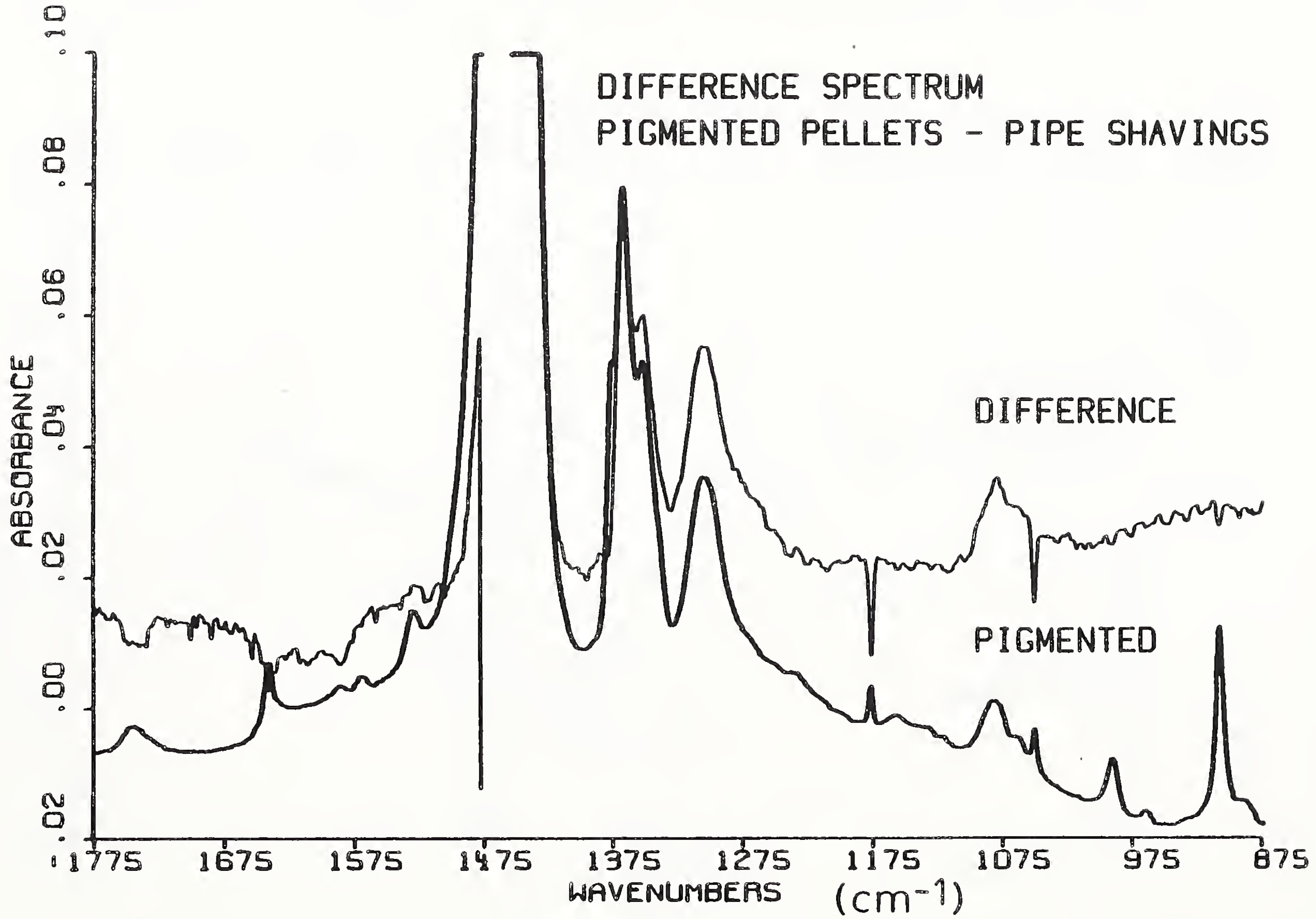


Figure 2. Difference spectrum for the pigmented pellets/pipe specimen pair.

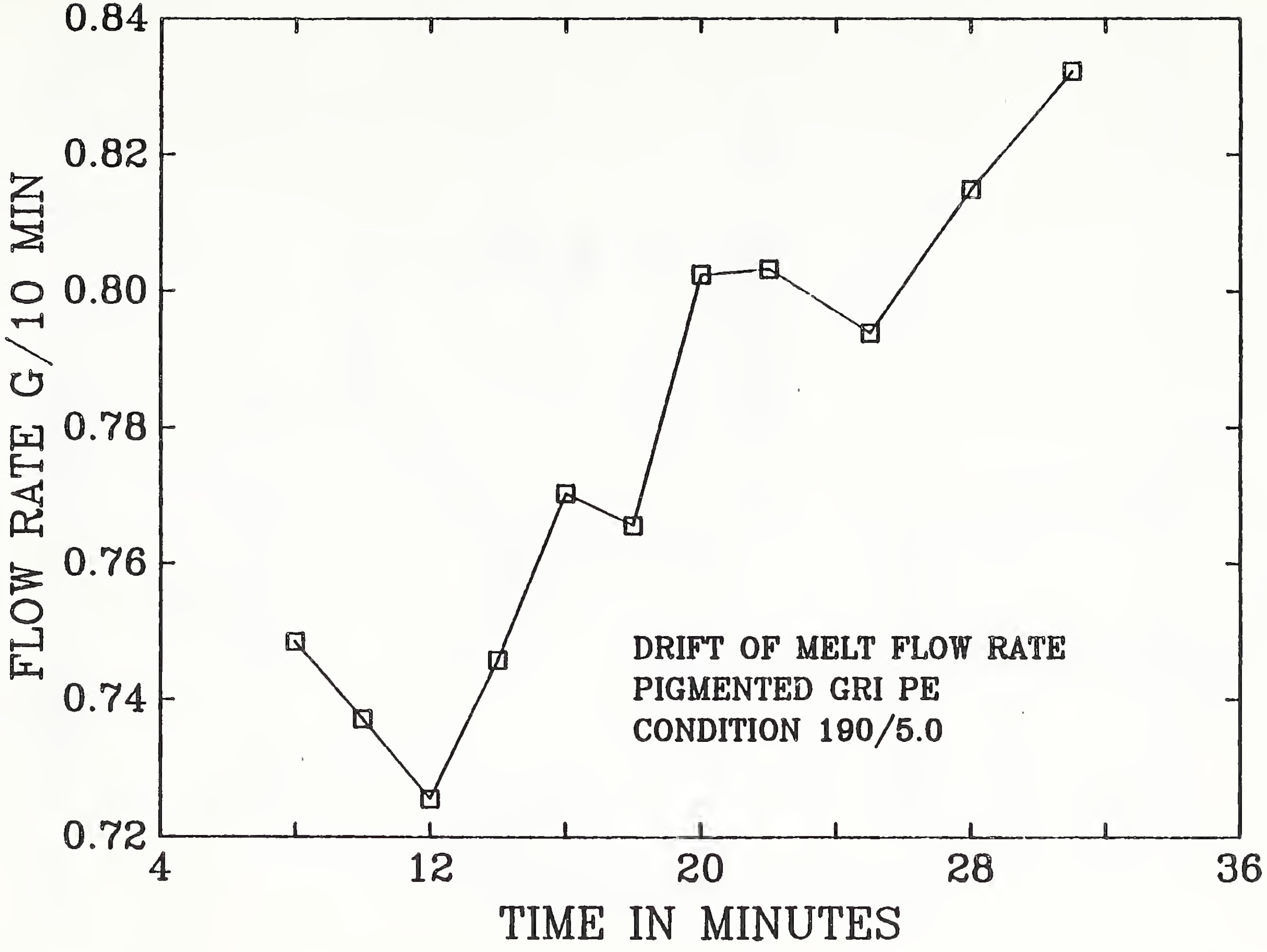
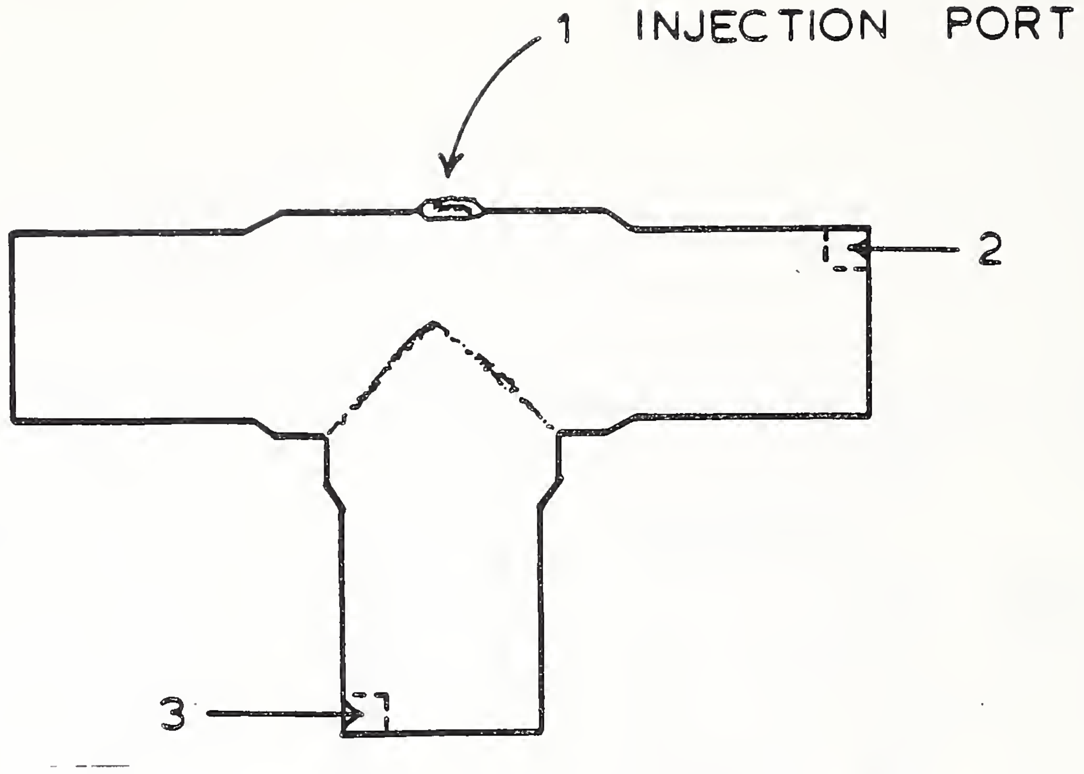
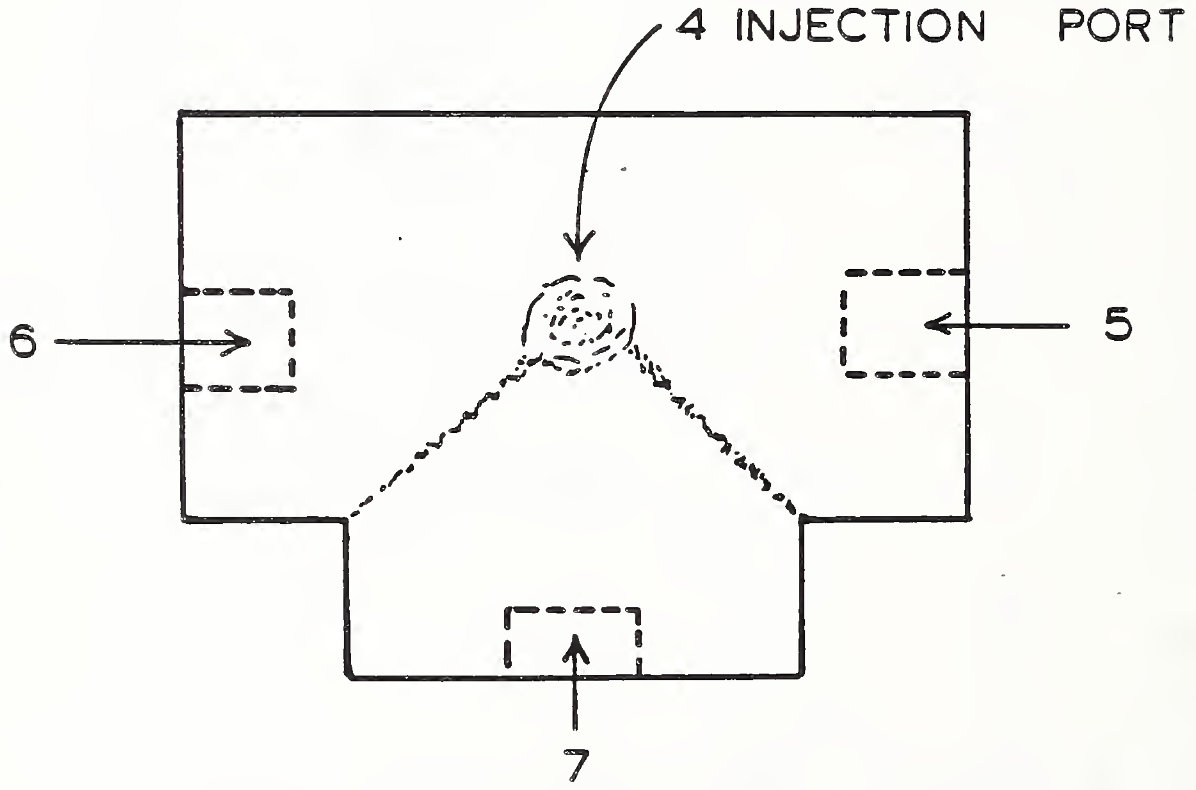


Figure 3. Drift of the Melt Flow Rate as a function of time. Measurements were taken at about every 2 min waiting for the 6 minute preheat.



(a) BUTT FUSION "T" JOINT



(b) SOCKET "T" JOINT

Figure 4. Location of samples taken from the "T" joints for the determination of the melt flow rate.

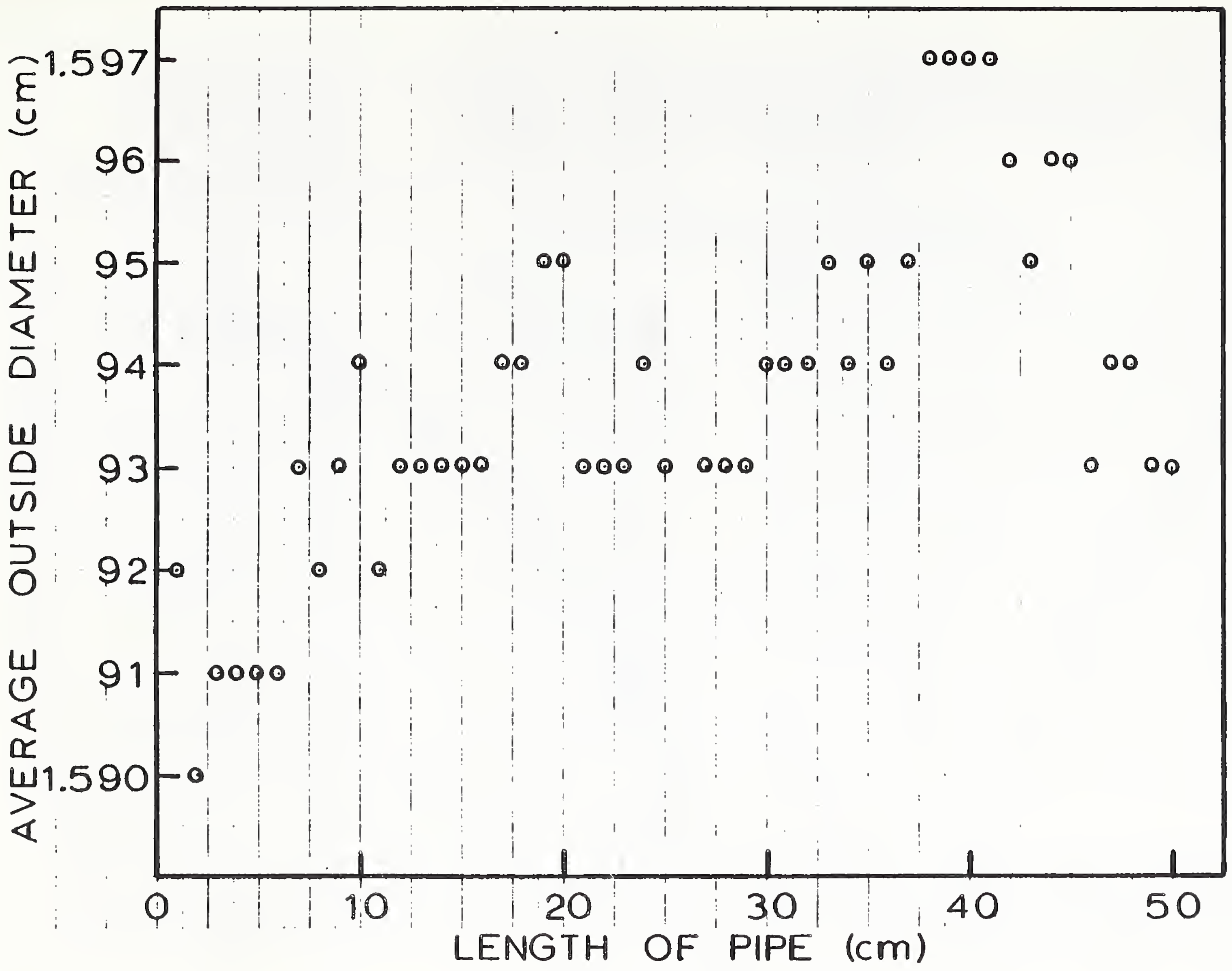


Figure 5. Average value of the outside diameter as a function of position along the length of one 50 cm long section of the 1.27 cm diameter pipe.

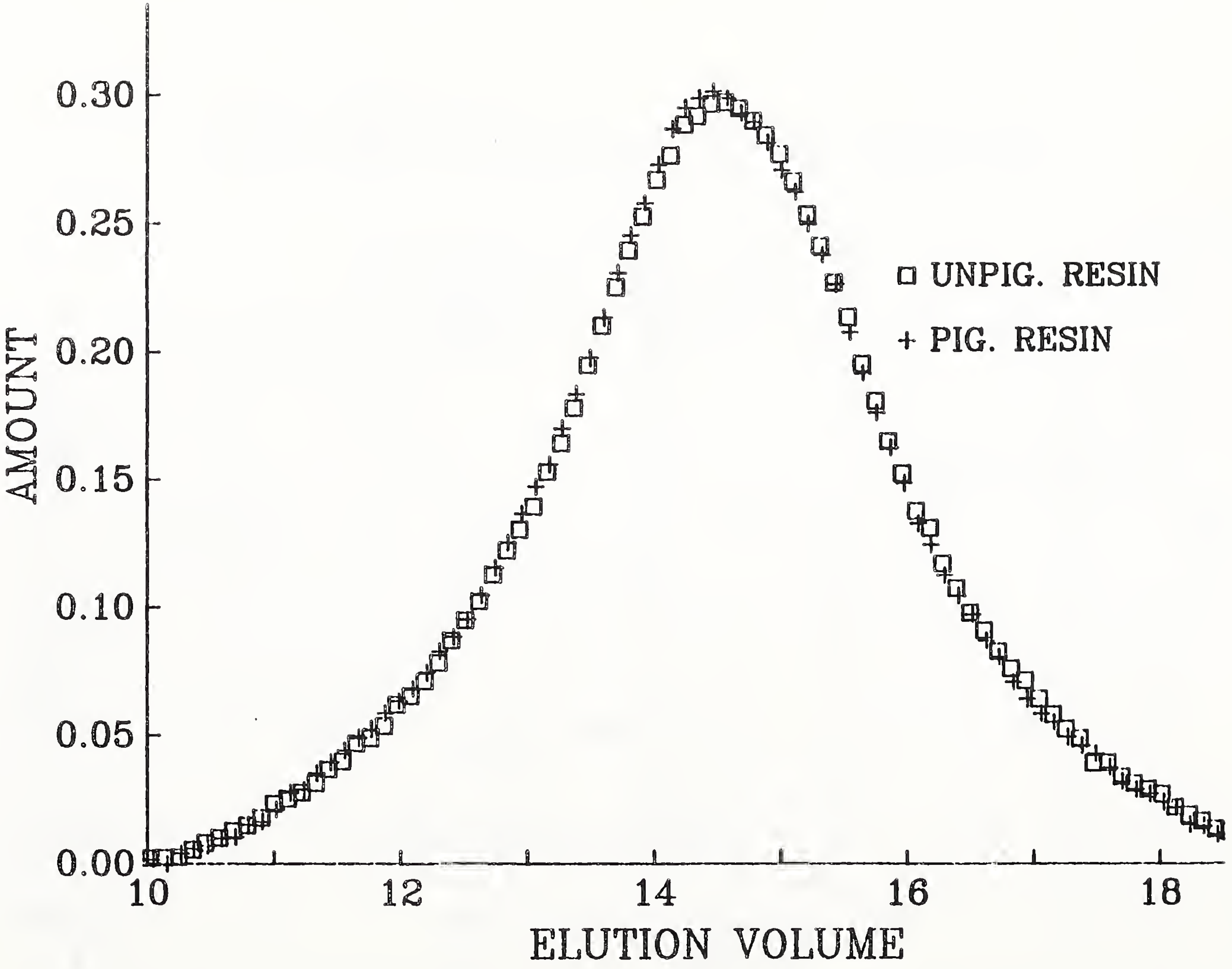


Figure 6. Size exclusion chromatography of pigmented and unpigmented resins. Pigmented shown with (+). Unpigmented shown with (□). Notice there is no measurable difference in the SEC of the two resins although their Melt Flow Rates show a 30% difference.

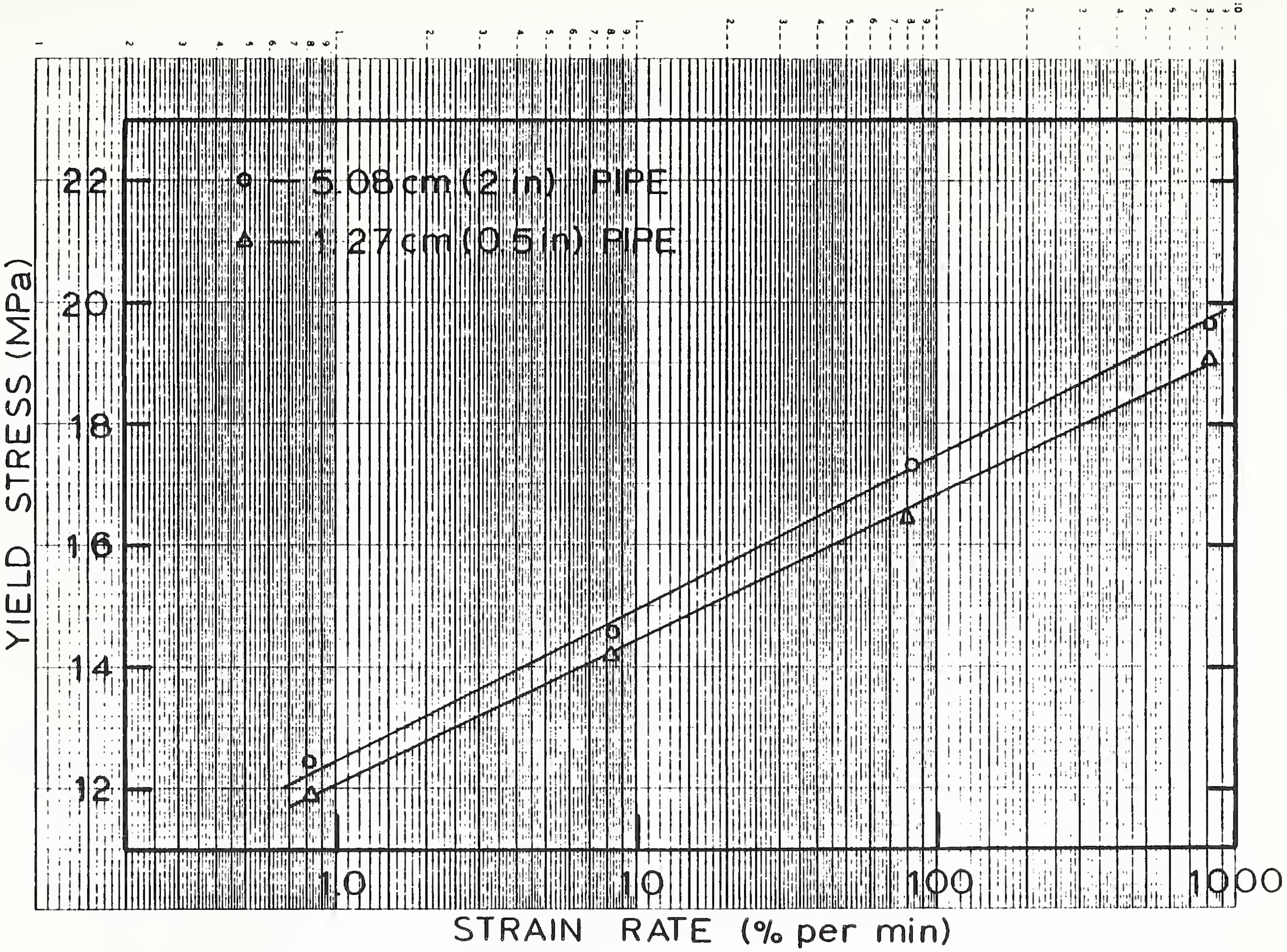


Figure 7. Yield stress versus log (strain rate) for specimens of the 1.27 cm and 5.08 cm diameter pipe tested in uniaxial extension at four different strain rates.

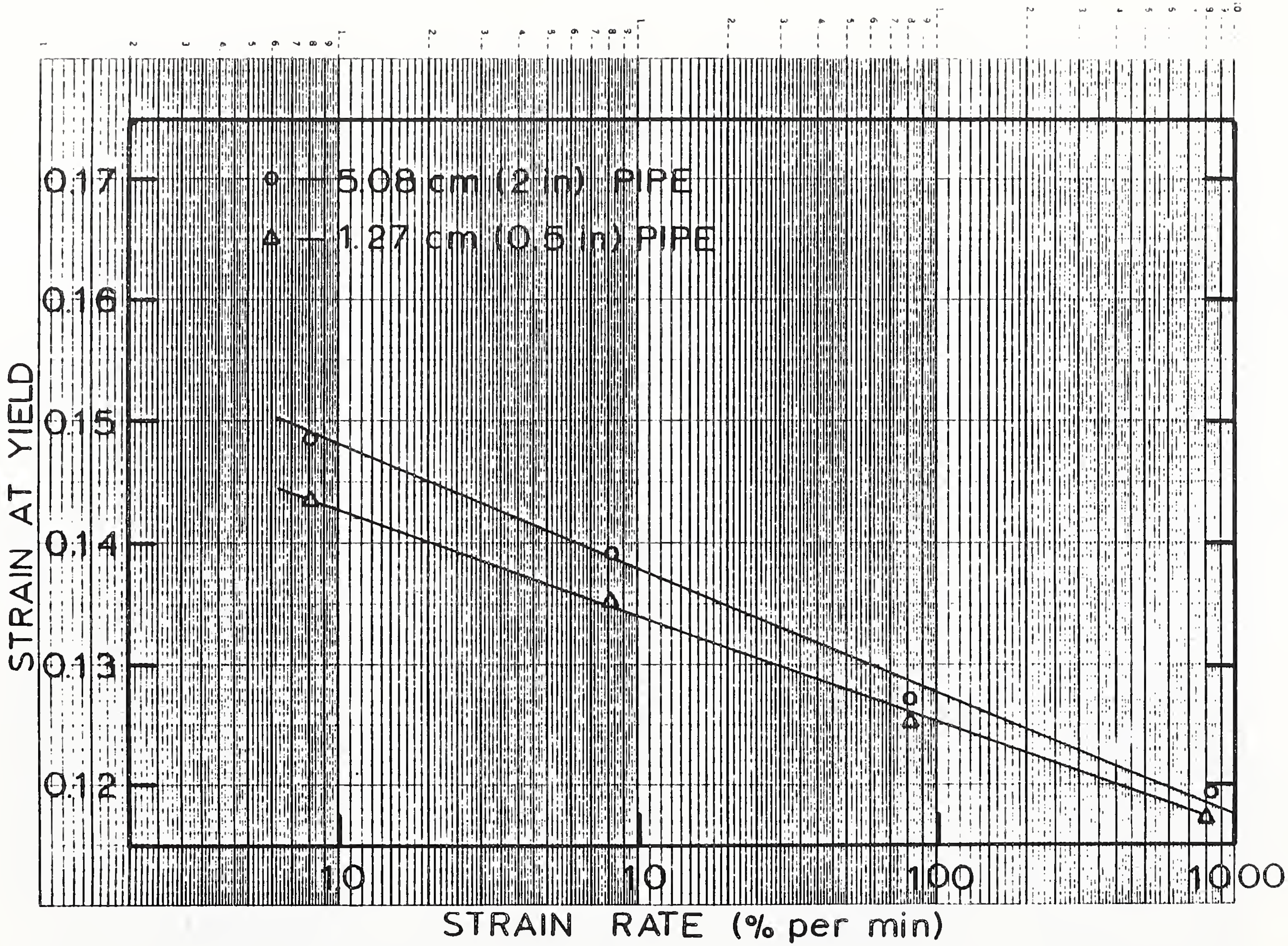


Figure 8. Strain at yield versus log (strain rate) for specimens of the 1.27 cm and 5.08 cm diameter pipe tested in uniaxial extension at four different strain rates.

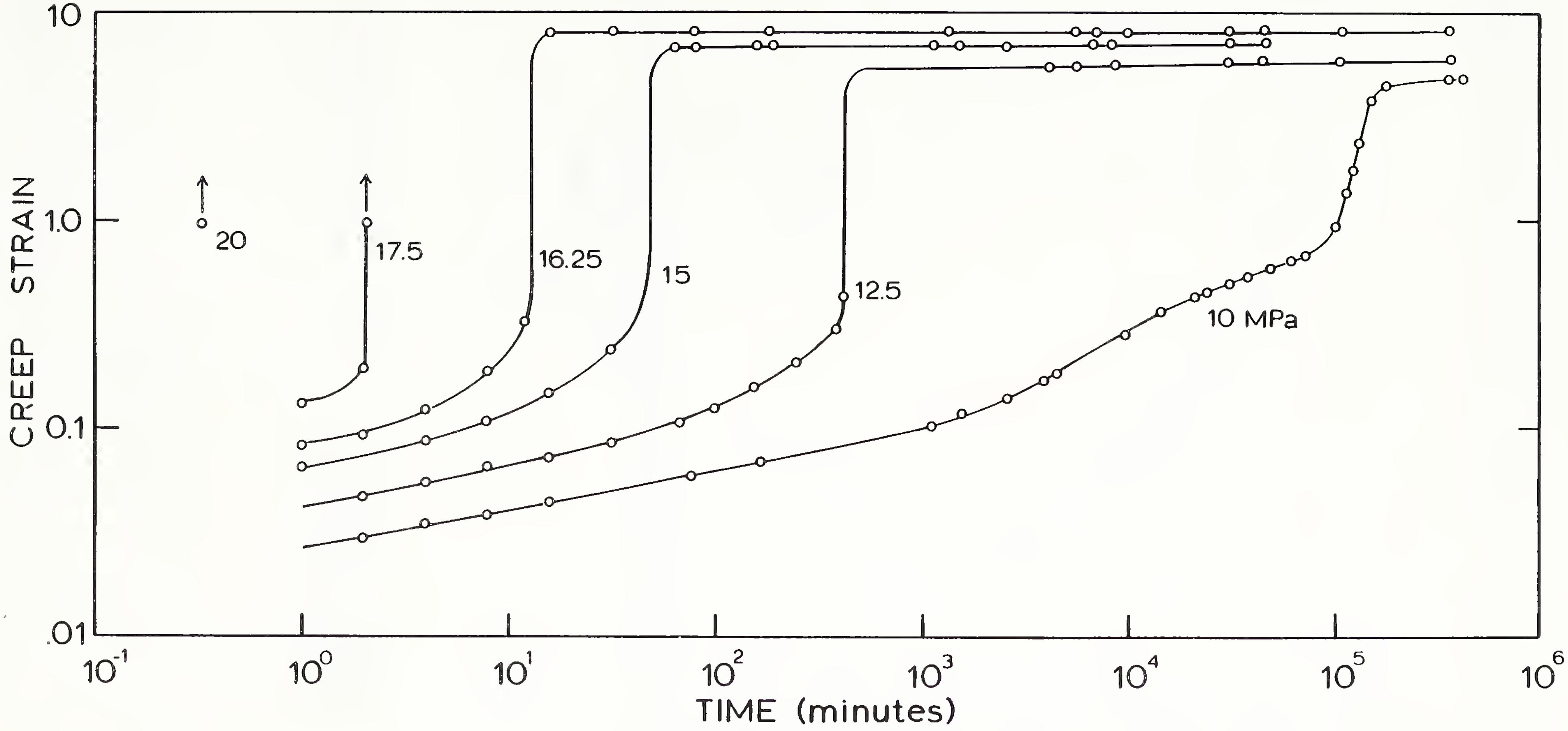


Figure 9. Log (creep strain) versus log time for specimens prepared from the pigmented polyethylene resin. The numbers present the applied stress (MPa) and the arrows indicate fracture.

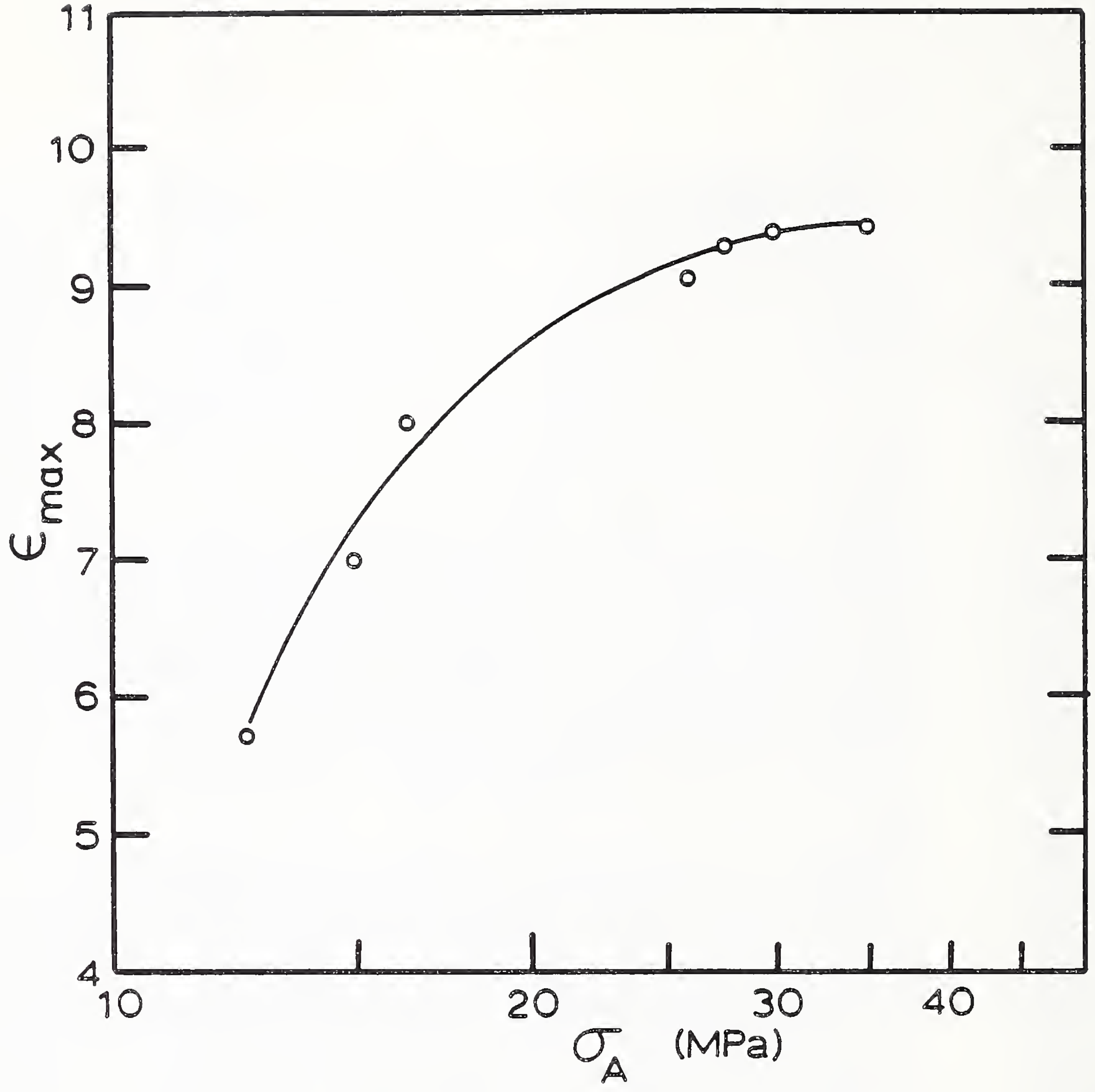


Figure 10. Maximum extension in creep versus log (applied stress) (engineering stress) for one specimen prepared from the pigmented resin.

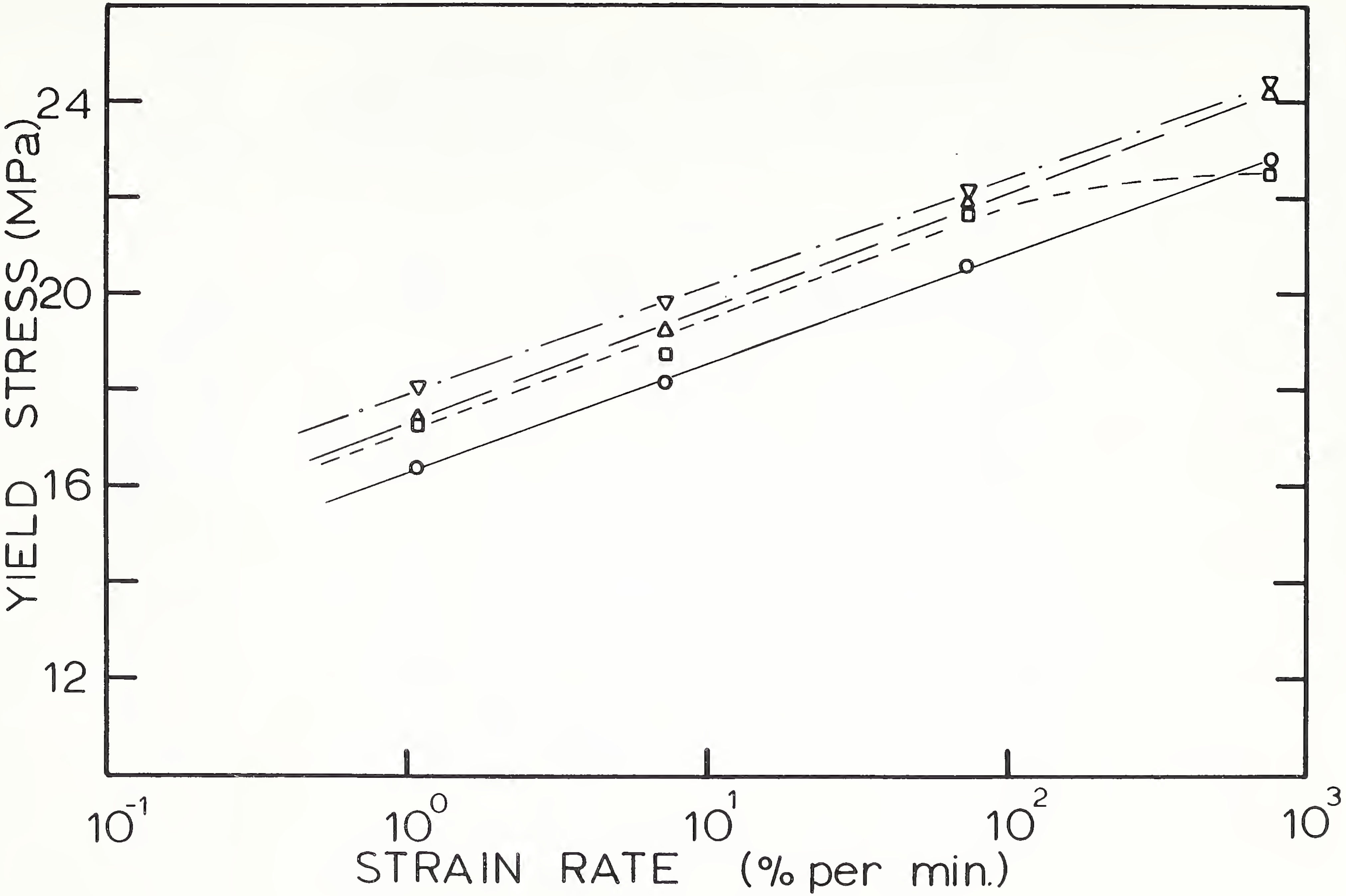


Figure 11. Yield stress versus strain rate (initial) in uniaxial extension for specimens prepared from four different commercial pipe resins. ○ - TR418, U.S.A.; △ - Germany; ▽ - Sweden; □ - Belgium.

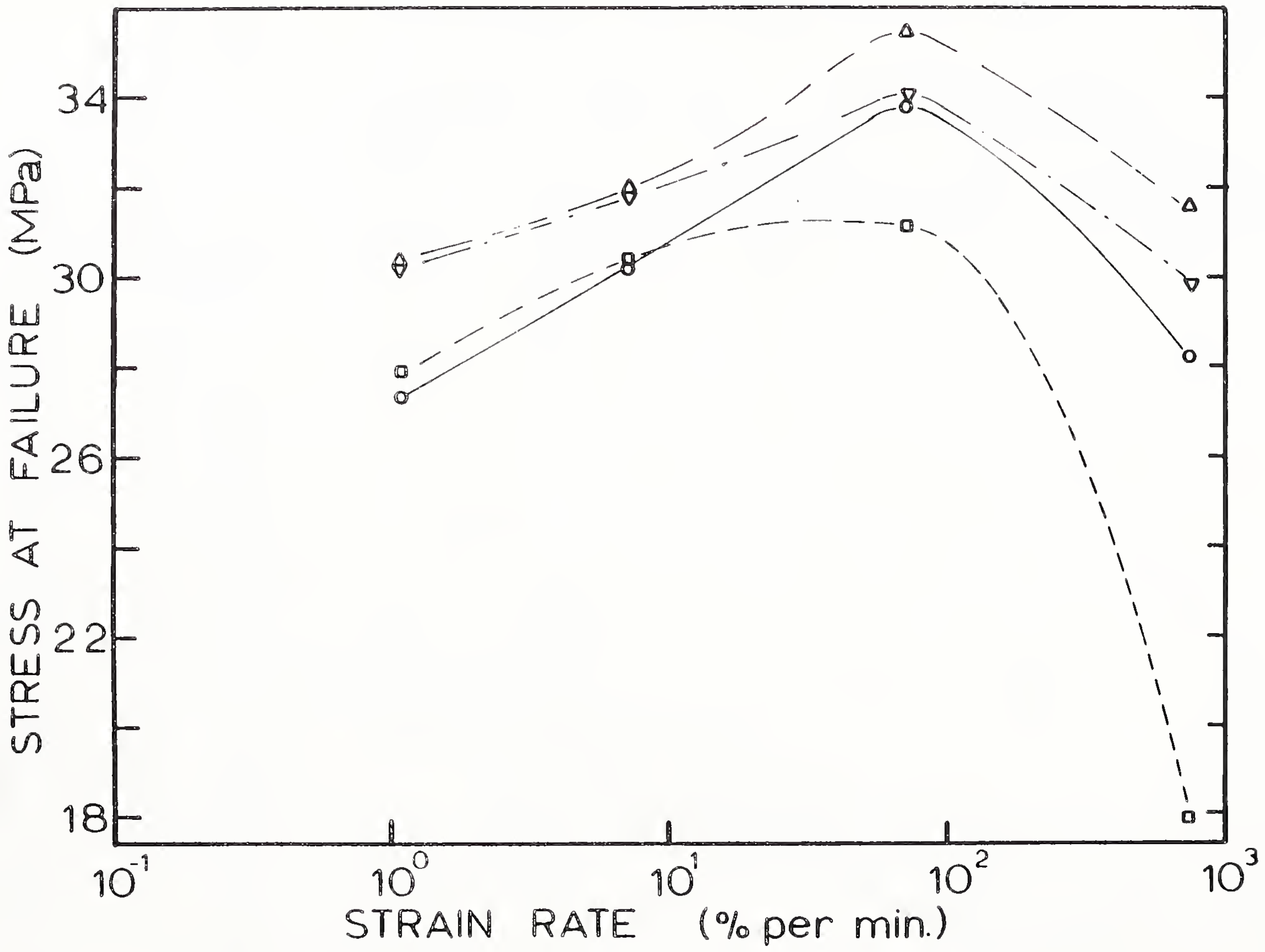


Figure 12. Stress at failure versus strain rate (initial) in uniaxial extension for specimens prepared from four different commercial pipe resins. ○ ~ TR418, U.S.A.; △ ~ Germany; ▽ ~ Sweden; □ ~ Belgium.

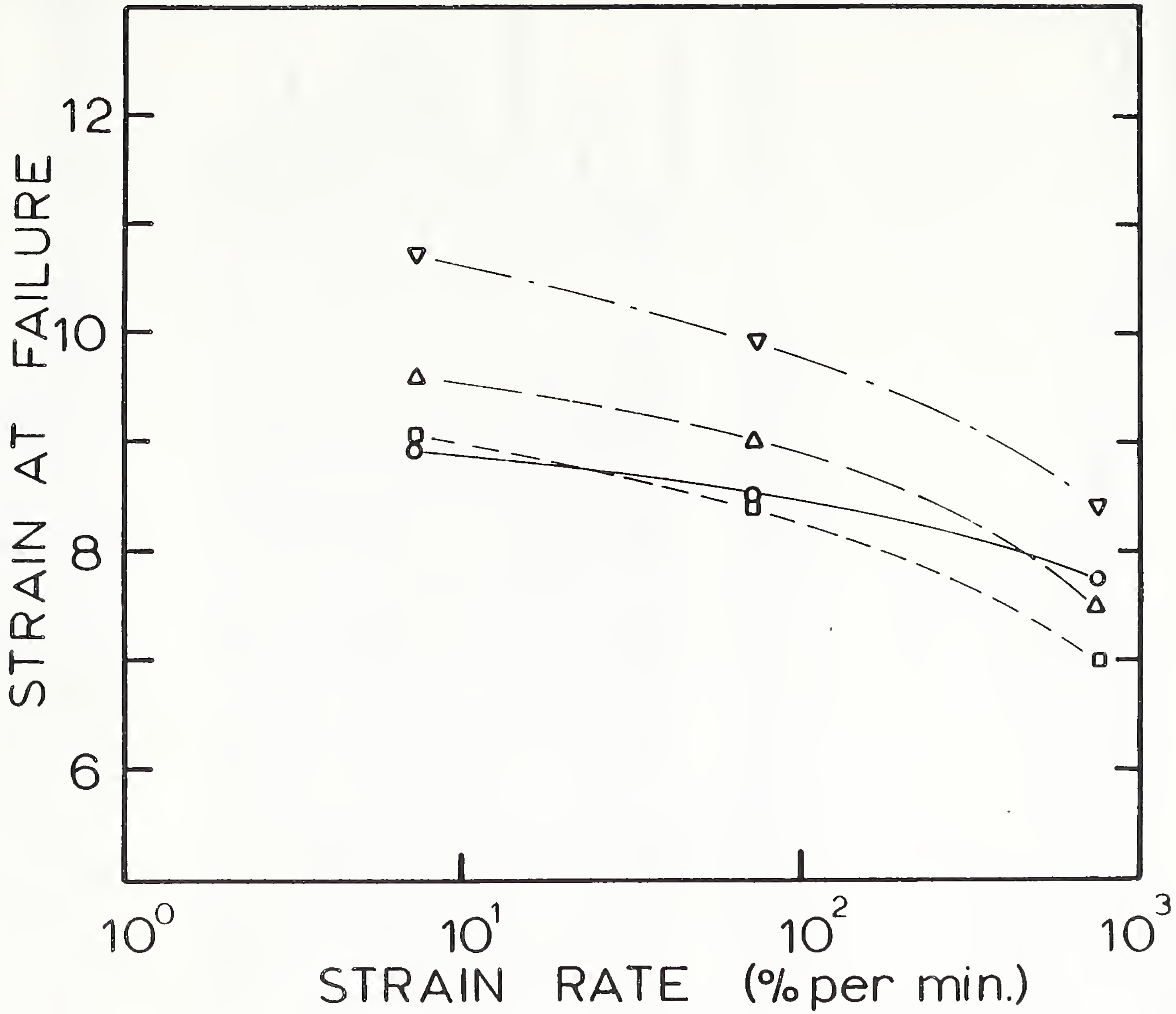


Figure 13. Strain at failure versus strain rate (initial) in uniaxial extension for specimens prepared from four different commercial pipe resins. ○ - TR418, U.S.A.; △ - Germany; ▽ - Sweden; □ - Belgium.

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Polyethylene piping is currently in widespread use in gas distribution in the United States, and represents approximately 80% of new installation. Research that is currently being performed on gas pipes often employs many different polyethylenes selected from the large number of polyethylenes available for this use. This variation in materials makes it difficult to compare results from different research laboratories, or to compare measurements carried out in the same laboratory at different times. To avoid this difficulty Gas Research Institute and the National Bureau of Standards (NBS) have undertaken to provide a permanent store of one particular polyethylene resin as well as piping and fittings made from it which would provde a source of well characterized materials for research related to gas distribution systems. This report describes the choice of this resin and the types and quantities of the materials to be provided by NBS and the characterizations performed which include the determination of the branch content, melt flow rate, molecular weight and molecular weight distribution, density, and specific tensile properties.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Branching; FT-IR; gas pipe; melt index; molecular weight distribution; NMR; polyethylene size exclusion chromatography; tensile tests.

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