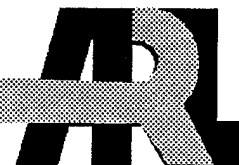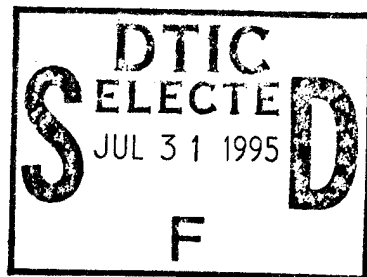*ARMY RESEARCH LABORATORY*

A Statistical Approach for the Evaluation and Selection of Medium Density Polyethylenes for Chemical Storage Canisters

David M. Spagnuolo, Peter G. Dehmer, David Dunn, and Stephen P. Petrie

ARL-TR-756

June 1995

DTIC
SELECTED
JUL 3 1 1995
F

19950728 007

DTI℗ QUALITY INSPECTED 5

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE June 1995	3. REPORT TYPE AND DATES COVERED Final

4. TITLE AND SUBTITLE A Statistical Approach for the Evaluation and Selection of Medium Density Polyethylenes for Chemical Storage Canisters

5. FUNDING NUMBERS

6. AUTHOR(S)

David M. Spagnuolo, Peter G. Dehmer, David Dunn, and Stephen P. Petrie

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Army Research Laboratory
Watertown, MA 02172-0001
ATTN: AMSRL-MA-PA

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-TR-756

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT Several specially compounded and commercially available olefinic materials were investigated in the presence of an organic liquid, Igepal CO-630, to test their environmental stress-crack (ESC) resistance (ASTM D1693). Chemical and physical characterization techniques were used to evaluate the proposed alternate medium density polyethylenes (MDPE) and antioxidants. Molecular weight, amount of antioxidant consumed during processing, and oxidation induction times were determined using size exclusion chromatography (SEC), reverse phase high performance liquid chromatography (RPHPLC), and differential scanning calorimetry (DSC), respectively. In addition, mechanical properties and strengths (ASTM D638) were determined in an attempt to obtain a quicker, more reproducible test. These properties were compared to a baseline material. Results showed that the commercial polyethylene, the baseline material, had the higher resistance to ESC.

14. SUBJECT TERMS

Extrusion, Antioxidants, Stress-Cracking, Polyethylene

15. NUMBER OF PAGES 70

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

ACKNOWLEDGMENTS

Accesion For		
NTIS CRA&I	☑	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and / or Special	
A-1		

TABLE OF CONTENTS

NOMENCLATURE

AO1   = Monsanto's Santonox R (bisphenol)
AO2   = American Cyanamid's Cyanox 1790 (hindered phenol)
AO3   = Ciba-Geigy's Irganox 1010 (phenolic)
PE1   = Soltex Fortiflex K4424-122 Flake (Density=0.944, MFI=0.32 g/10 min.)
PE2   = Chevron Hi-D 9326 Flake (Density=0.945, MFI=0.2 g/10 min.)
PE3   = Hoechst Hostalen GM5010TN Flake (Density=0.944, MFI=0.14 g/10 min.)
A   = Low Level of Antioxidant
B   = High Level of Antioxidant
1   = Low Processing Temperature (380°F)
2   = High Processing Temperature (460°F)
P   = Pellets
S   = Sheet Material
SCOMP = Soltex Fortiflex K4424-122 Commercially Compounded MDPE
CCOMP = Chevron Hi-D 9326 Commercially Compounded MDPE
HCOMP = Hoechst Hostalen GM5010TN Commercially Compounded MDPE
SCOMS = Soltex Fortiflex K4424-122 Commercial MDPE Sheet
CCOMS = Chevron Hi-D 9326 Commercial MDPE Sheet
HCOMS = Hoechst Hostalen GM5010TN Commercial MDPE Sheet

I. INTRODUCTION

A. Origin of the Study

Historically, the United States Army has had to deal with the handling, storage and transportation of chemicals. In many cases, steel and other metals are not suitable for these applications due to the corrosive nature of the chemicals involved. Due to their chemical resistance, lightweight, low cost and ease of fabrication, polyolefins are often selected as alternate materials.

In the past, the United States Army Research Laboratory (ARL), Watertown site and its predecessor organizations (AMMRC and MTL) have been tasked with the characterization and fabrication of these polyolefinics. At the beginning of this study, ARL received a contract from the U.S. Army Chemical Research Development and Engineering Center in Aberdeen, Maryland, to do some investigative research in this area.

Three characterization studies of polyethylenes have been described in technical reports (1-3). In these studies, C.R. Desper characterized several materials along with a given MDPE (Marlex M445, a copolymer of ethylene and hexene-1 with a melt flow index of 1.5g/10 min.) which was known to provide satisfactory resistance to stress-cracking. Stress-cracking can cause failure of a container through the development of a multitude of very small crazes and cracks which can lead to leakage of the container. This unwanted phenomenon can occur in a polymeric material in the presence of an organic liquid or its vapor (a hostile environment), with or without the addition of mechanical stress (4). The three studies performed by Desper identified molecular weight (MW), molecular weight distribution (MWD), crystallinity and short chain branching content as important parameters.

Another study performed to evaluate the effect of processing variables on the environmental stress-crack resistance (ESCR) of polyethylenes was done through MTL as a thesis at the University of Massachusetts Lowell (formerly the University of Lowell) by S.D. Kohlman (5). In this investigation, rotational molding was used to fabricate the test specimens in order to minimize the residual stresses in the test coupons. Ten commercial polyethylenes, which included linear low density polyethylene (LLDPE), MDPE, and a cross-linkable polyethylene, were evaluated to determine their ESCR. The materials were characterized to determine the chain branching by nuclear magnetic resonance spectroscopy (NMR), melt behavior by differential scanning calorimetry (DSC), and flow properties by capillary rheometry. A statistically designed experiment was used to evaluate the effect of processing parameters on the ESCR of selected resins which were

1

shown to have different characteristics. The results showed that LLDPE had the worst overall ESCR and the cross-linkable polyethylene had the best ESCR. In terms of the processing conditions, a combination of a long fusion and a slow cool had the worst ESCR and a short fusion and quench had the best ESCR (6).

The failure of polyethylenes is also of great commercial importance due to their wide spread usage in the fabrication of gas transmission lines (7). Failures have been noted since the early 1950's and as a result this problem has been studied extensively. In addition to the analyses performed on pipe that has failed in service, several experimental studies have been undertaken to determine the ESCR of olefinic materials. The material found most suitable for this application was medium density polyethylene (MDPE).

MDPE is polymerized by the addition of a small amount of an alpha-olefin which introduces short chain branches. The addition of side chain branching reduces crystallinity without lowering the molecular weight. This controlled amount of side chain branches increases the ESCR of the material. For instance, the MDPE previously found to be acceptable was Marlex M445, which is a copolymer of ethylene and hexene-1.

As previously cited, differences in the ESCR of a given class of polymers can be influenced by the MW and MWD whose values can be determined using size exclusion chromatography (SEC). In the previous studies, commercially available materials were evaluated and the effect of type or level of antioxidant were not investigated. Most polymers are susceptible to oxidative degradation which can occur during polymerization, processing, or end use. Antioxidants are used with polyolefins to inhibit the auto-oxidation of the polymer during processing at elevated temperatures, as well as during the service life of the material. Oxidative degradation occurs primarily by a free radical chain reaction process which ultimately results in polymer chain scission (8,9). This auto-oxidation process will lead to a reduction in the MW and a change in the physical and mechanical properties of the material.

Further information concerning the presence and amount of antioxidants can be obtained by the use of an additional analytical technique. Reverse phase high performance liquid chromatography (RPHPLC) can be used to determine the presence of small organic molecules such as inhibitors, stabilizers, and antioxidants. By using this chromatographic technique, materials such as antioxidants can be separated from other low molecular weight species, identified and analyzed to determine the type and amount present. This technique might prove to be useful in determining, for example, the amount of antioxidant consumed during fabrication of containers.

2

Although DSC had previously been used by Kolhman (5) to determine the thermal properties of the olefinic resins, this technique could also be extended to study oxidation induction times.

From the previously cited work in the literature, it appeared that several areas were worthy of further exploration. For example, if it appeared necessary to custom blend a given antioxidant with the polymer, the effect of processing variables during compounding might also be of importance. It should be noted that no reference to this type of study could be found in the literature.

Lastly, further investigation should be done to find MDPE's suitable for these applications since Marlex M445 is no longer available.

B. Design of Experiment

Since a statistically designed experiment yields the greatest amount of information with the least amount of effort, it was decided to cast this study within that type of framework.

As previously discussed, the variables of interest included: the type and level of antioxidant, the processing temperature used during compounding, and the type of MDPE. This investigation seemed quite well suited to a nested factorial design. By using three olefinic materials, one could nest the factors of antioxidant, level of antioxidant, and extrusion temperature during compounding under each of the materials. For example, if three antioxidants at three levels were used for each material, this would require twenty-seven experiments. To include three levels of temperature would further increase the number of experiments to eighty-one. Since this amount of work was in excess of the resources allocated to the study, it was decided to cut back on the number of levels from three to two. This design required thirty-six experiments.

The plan of the study was to use the previously discussed experimental design to compound the candidate resins. These formulations would be extruded into sheet at the same processing conditions (as closely as possible). The resultant sheet would be die cut into coupons and tested to determine which variables had the greatest effect on the ESCR. It is expected that these results would be able to rank each of the variables in order of increasing effect and also provide information as to any interactions which may be present.

3

C. Characterization of Materials

Since ARL has the capability of doing all of the chemical analyses previously discussed, it was decided to extensively characterize the polyolefinic materials both before, during and after the study to determine if any of the variables correlated with the ESCR results of the statistically designed experiment.

It is hoped that the results of this investigation will produce further knowledge in this important area.

4

II. EXPERIMENTAL MATERIALS AND PROCESSING METHODOLOGY

A. Polymer Materials and Characterization

The three medium density, pipe grade polyethylenes used in this study were Chevron's Hi-D 9326, Soltex's Fortiflex K4424-122, and Hoechst's Hostalen GM5010TN. These medium density polyethylenes had specific gravities approximately equal to 0.94.

The criteria for the selection of the resins were as follows: the materials should have similar physical and mechanical properties to Phillips' Marlex M445 material; the resins should have superior stress-crack resistance properties; and a fractional melt index (0.1-0.3g/10 min.).

All three of the resins are commercially available as compounded pellets. The manufacturers were contacted and agreed to supply the materials in the uncompounded flake form in sufficient quantities to perform this study. Both the commercially available materials and those compounded from their feedstocks (virgin flake) were evaluated in this study.

In order to characterize the polymeric materials, the samples first had to be milled to reduce the physical size to enhance solvation prior to chemical analysis. All pellet and sheet samples were passed through a Wiley Mill fitted with a 20 mesh screen. Approximately 80 grams of milled material were prepared for each sample, and all analyses for a given sample were performed from the single milling.

The molecular weight (MW) and molecular weight distribution (MWD) were determined by high temperature size exclusion chromatography (SEC) using a refractive index detector. SEC is a separation method for high polymers to determine the molecular weight distribution. Spheres of a rigid porous gel are used in a chromatography column. The separation of the molecules in solution takes place due to a difference in size. Smaller molecules can enter the pores and have a longer retention time in the column than larger molecules which are excluded from the pores and hence pass through the column quicker. This allows the molecular species to be separated according to their molecular size in solution.

A Waters 150C instrument, operating at 284°F (140°C), was used with a set of Waters Linear and 10^6 Ultrastyregal SEC columns. The sample solution concentrations were 0.15% in 1,2,4 trichlorobenzene. The solutions were heated to 320°F (160°C) for one hour, and allowed to cool to 293°F (145°C). After three hours at 293°F (145°C) the solutions were filtered through a preheated

5.0 micron membrane filter. The system was calibrated for MW analysis with narrow distribution polystyrene standards. The polystyrene MW values were converted to polyethylene MW values using the universal calibration technique (10).

The Mark-Houwink constants used for establishing the calibration curve are;

Polystyrene: (1,2,4 trichlorobenzene, 140°C);
                k=0.000117, a=0.706

Polyethylene: (1,2,4 trichlorobenzene, 140°C);
                k=0.000395, a=0.726

B. Antioxidants: Materials and Characterization

The three antioxidants chosen for this study were Monsanto's Santonox R (a bisphenol), American Cyanamid's Cyanox 1790 (a hindered phenol), and Ciba-Geigy's Irganox 1010 (a phenolic). All of the antioxidants used in this work are multifunctional. They contain two, three or four sterically hindered phenol groups per molecule. Table 1 lists some of the physical properties of the antioxidants and the loading levels used in this work. The average number of reactive functional groups per molecule is called the "functionality".

In order to analyze for the amount of antioxidant, reverse phase high performance liquid chromatography (RPHPLC) methods were developed. The determination of unreacted antioxidant remaining after melt processing required extracting the antioxidant from the milled samples. This was accomplished by refluxing preweighed samples (3 grams) of the milled material in 25ml of tetrahydrofuran. To account for any potential change in final solution concentration due to solvent loss during refluxing, an internal standard (0.01% terphenyl) was added to the solvent. The samples were refluxed for 2 hours, allowed to cool and then filtered through a 0.45 micron filter prior to quantitative analysis. An acetonitrile/water gradient was used to separate the antioxidant on a Waters Resolve C18 column. An ultraviolet detector with a setting of 214nm was used for detection and determination of the antioxidant present.

6

TABLE 1

Physical Properties and Loading Levels
for Antioxidants

ANTIOXIDANTS

	Functionality	MW	MP (DSC)	Wt% Compounded low	high
AO1	2	358 g/mole	332.6°F (167°C)	0.500%	2.000%
AO2	3	663 g/mole	321.8°F (161°C)	0.025%	0.100%
AO3	4	1176 g/mole	244.4°F (118°C)	0.050%	0.200%

(AO1=Santonox; AO2=Cyanox; AO3=Irganox)

Thermal analysis techniques can be used to determine the relative amount of protection from oxidative degradation both before and after processing. The oxidation induction times were determined using differential scanning calorimetry (DSC), which is an apparatus used for determining specific heats or for measuring quantities of absorbed or evolved heat. During operation, the sample and reference pans are heated at a programmed heating rate and the temperature is plotted on one axis of the graph. The sample cell is maintained at the same temperature as the reference cell by a proportionating heater. When the sample undergoes a thermal transition, the power to the sample cell heater is adjusted to maintain the programmed temperature relative to the reference cell. A signal proportional to the power difference is plotted on the second axis of the graph. The area under the resulting curve is a direct measure of the change in enthalpy within the specimen. A DuPont 912 DSC cell base with dual sample cell was used for the analyses. Open aluminum pans containing 10 mg of material were heated to 428°F (220°C) at a rate of 392 F°/min. (200 C°/min.), and held at that temperature through the auto-oxidation exotherm. During the analysis, the cell was purged with dry air at a constant flow rate of 100cc/min. All of the oxidation induction times determined in this study were obtained by measuring the time to the onset of the auto-oxidation stage of the degradation process.

The SEC method was also used to evaluate the effect of oxidative degradation on the MW and MWD of the material. Milled samples of the pelletized Soltex PE with 0.1% Cyanox 1790 processed at 460°F (238°C) and the pelletized Hoechst PE with 0.1%

Cyanox 1790 processed at 380°F (193°C), were heated in the DSC using the same conditions established for determining the oxidation induction times. Samples were removed from the DSC at various time intervals before and after the onset of the auto-oxidation exotherm.

C. Processing Overview

Some preliminary steps were required prior to the production of the sheet. The steps involved the dry blending of polyethylene and antioxidant. This powder mixture is not normally used in production, a more normal form is to use pellets, which are easier to handle than powder. Thus, the powder must be extruded through a "strand" die and subsequently through a chopper to produce pellets of 1/8" O.D. by 1/4" long. The pellets were then extruded into sheet form at a commercial operation.

D. Dry Blending

The dry blending of flake material and antioxidant was performed in-house utilizing fiberboard drums on a tumbling device. Figure 1 shows the tumbler/mixer used in this operation. The drum tumbler device consisted of a spring loaded stand with a clamping jaw at one end, driven by a three horsepower variable speed controlled motor. The drums were filled to the half way point with PE/antioxidant charge (approximately 50 lbs.) and mixed for two hours at 20 revolutions/minute. This resulted in the most uniform mixing measured by RPHPLC methods. The RPHPLC methods were initially used to verify the efficiency of the barrel mixing method developed for dry blending the antioxidant with the polyethylene flake.

The method of calculating the amounts of antioxidants used in this study was as follows. The recommended level supplied by the manufacturer of the antioxidant was multiplied by 2 to obtain the high level and divided by 2 to get the low level for all the antioxidants used in this study. For example, American Cyanamid suggests a concentration for its Cyanox 1790 of 0.05%. Therefore, the two concentrations of Cyanox 1790 were 0.1% on the high end, and 0.025% for the low. The other manufacturers' recommended concentrations were 0.1% Irganox, and 1.0% Santonox (11). After blending, samples were taken and assayed to determine both the level and uniformity of the inclusion of antioxidant.
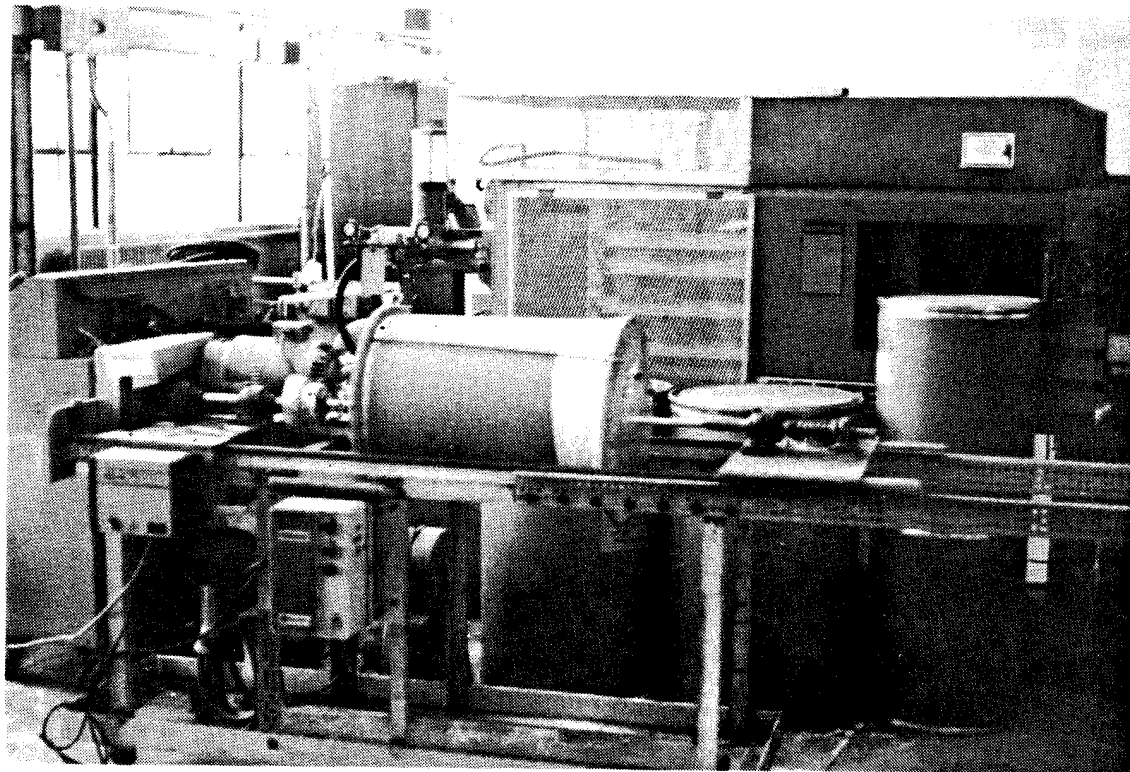
TUMBLER/MIXER USED FOR DRY BLENDING

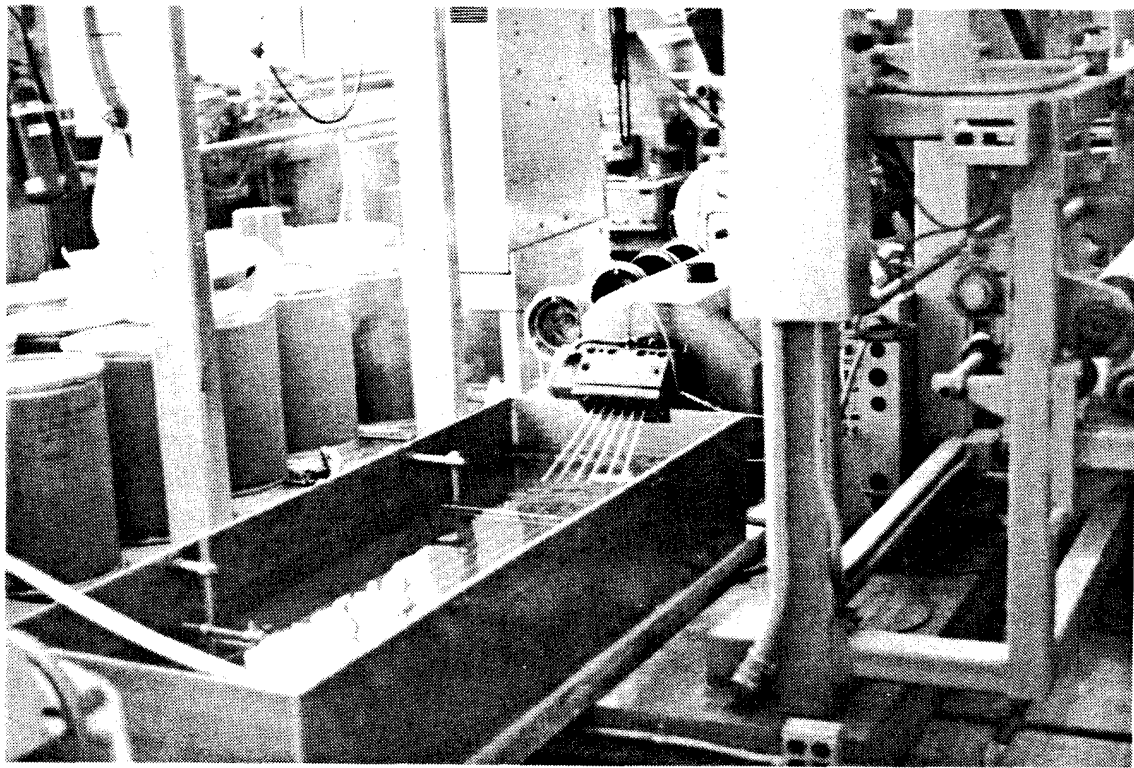FIGURE 1

E. <u>Pelletizing</u>

The next operation was to convert the blended powders into pellets, a more typical material used to feed an extrusion system. The compounding was performed at ARL using a Sterling Davis 2" diameter extruder with an L/D ratio of 24:1. Some modifications had to be made to the hopper to prevent bridging at the feed throat. Bridging is the build-up of material which forms an arch (or bridge) at the hopper throat preventing flow. To prevent bridging an air actuated vibrator was installed to the side of the hopper. A flow control valve was used to regulate the frequency of vibration of the hopper thus maintaining uniform material flow to the screw of the extruder. The production line consisted of a 2" vented and plugged extruder, air cooled, with four electrically heated zones. The screw used for this study was a 2" diameter polyethylene screw. The screen pack used throughout the experiment was as follows: 40/100/100/100/40 configuration, providing a back pressure of approximately 2300 psi. The extrusion set-up is shown in Figures 2 and 3.

A method similar to that previously described for the antioxidants was used to calculate the two levels (high and low) of temperature used in extrusion. Taking the manufacturers' recommended temperature in degrees Fahrenheit for polyethylene as a baseline, 40°F was added and subtracted to obtain the two processing temperatures. For example, Chevron recommended a processing temperature of 420°F, which resulted in temperatures of 460°F and 380°F being used in this study.

The operation started off with one material and one level of antioxidant extruded at the lower processing temperature of 380°F (193°C). This same material and concentration was then processed at the higher temperature, 460°F (230°C), and this procedure was followed for the remaining materials. To achieve the processing temperature, all heating zones and die were set to the desired temperature of 380°F (193°C) or 460°F (230°C). The screw rpm was 80 for all materials, which resulted in a throughput of 45 pounds per hour, with a residence time of 2 minutes and 13 seconds.

The extrudate was pelletized using the equipment supplied by Sterling Davis with the extruder. The resultant pellets were characterized as previously discussed.

The system consists of a heated barrel section with a multi-strand die. The extruded strands must be chilled in a water bath prior to being chopped to length. A calculation was done to determine the length of the water bath. The theoretical design length of 10 feet was not practical. A continuous concurrent flow of cold water supplied at the front of the water bath was increased to compensate for the shorter (6 foot) length bath. Temperature measurements were taken on the material before entering the pelletizer.

10

FRONT VIEW OF EXTRUDER (PELLETIZATION PROCESS)

FIGURE 2
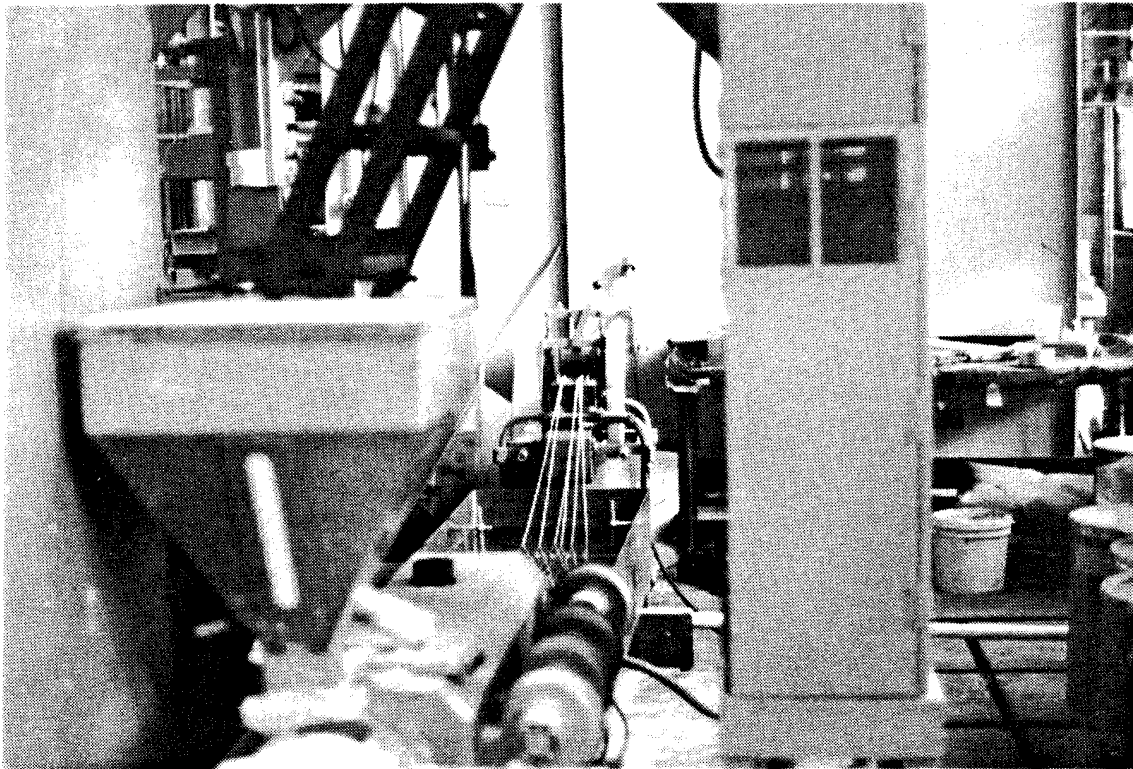
REAR VIEW OF EXTRUDER (PELLETIZATION PROCESS)

FIGURE 3

F. Sheet Extrusion

    Sheet extrusion was done by Springborn Laboratories, Inc. in Enfield, Connecticut. This operation was done using a 2.5" Hartig extruder equipped with a polyethylene screw. The die used was a 12" T-type. The screen pack consisted of 20/80/20 mesh configuration. The take-up equipment consisted of a roll stack and a pulling device for the removal of the extrudate from the die orifice at a rate of 5 feet per minute. The rolls were used to size and cool the material. Sheet thickness was controlled by pulling speed and a dimension-setting device on the roll nips. The specially compounded and commercial pellet materials were extruded into 12" wide by 0.060" thick sheets.

    The main criteria was to obtain commercial quality sheet and keep the process parameters in the same range. A typical profile used in the sheet process is shown in Table 2.

TABLE 2

Typical Profile for Sheet Extrusion Process

Sheet Extrusion Run Data

SPEED Ex. Set		SETTINGS TEMP ($^{\circ}$F) Extruder							
		Z1	Z2	Z3	Z4	Z6	Z7	Z9	Z10
17									
		315	340	385	445	430	427	425	430

	ROLL TEMP		
1	2	3	4
205	200	208	208

Mast Speed (set pt.): 15
Feet/Min. (Web): 5.0
Gage Thickness: 0.060"

G. Environmental Stress-Crack Resistance (ESCR)

    A stress-crazing test was performed on the polyethylene samples according to ASTM D1693. This method tests the susceptibility of ethylene plastics under certain environmental stress-cracking (ESC) conditions. The test is carried out by putting a controlled imperfection of 0.015" in depth in each specimen, which is parallel to the long edges and centered on one side of the specimen. The specimens were then bent and placed inside the specimen holders, which is a brass U-channel, and placed inside the test tubes. The test tubes were filled with a known stress-cracking agent, corked, and put in a constant

13

temperature bath. ESC is a property highly dependent on stresses and the thermal history of the specimen. Cracks develop at the controlled imperfection and will grow to the outer edge of the specimen at right angles. Any crack visible by normal eyesight was construed as a failure for the entire specimen.

The materials that would be the most susceptible to ESC were chosen for this study. To establish the most severe processing conditions, the polyethylenes mixed with the 0.025% Cyanox processed at 460°F were chosen. These samples would have the least amount of antioxidant remaining after processing. The Chevron commercial PE and the Marlex M445 materials were also tested for comparison. The samples for this study were cut to the dimensions stated in condition C, Table 3.

TABLE 3

Standard Test Conditions

Condition		Length	Width	Thickness	Notch Depth (in.)	Bath Temp., °C
A	min.	1.4	0.47	0.120	0.020	50
	max.	1.6	0.53	0.130	0.025	
B	min.	1.4	0.47	0.070	0.012	50
	max.	1.6	0.53	0.080	0.015	
C	min.	1.4	0.47	0.070	0.012	100
	max.	1.6	0.53	0.080	0.015	

Samples were then conditioned for 48 hours at 73°F (23°C) and a relative humidity of 50%. Once conditioned, the samples were placed into the specimen holders and put into test tubes. The test tubes were filled with Igepal CO-630, corked, and placed into the constant-temperature bath at 212°F (100°C). A visual inspection of the samples was performed at the following intervals: 0.1, 0.25, 0.5, 1.0, 1.5, 2, 3, 4, 5, 8, 16, 24, 32, 40, and 48 hours, according to the standard. When it became apparent that the materials were highly resistant to stress-cracking, inspections were made at six day intervals. According to the ASTM standard, any crack visible to the observer with normal eyesight shall be construed as a failure of the entire specimen. Due to the high stress-crack resistance of the commercial Chevron PE obtained from the ESC test, this material was chosen as the baseline.
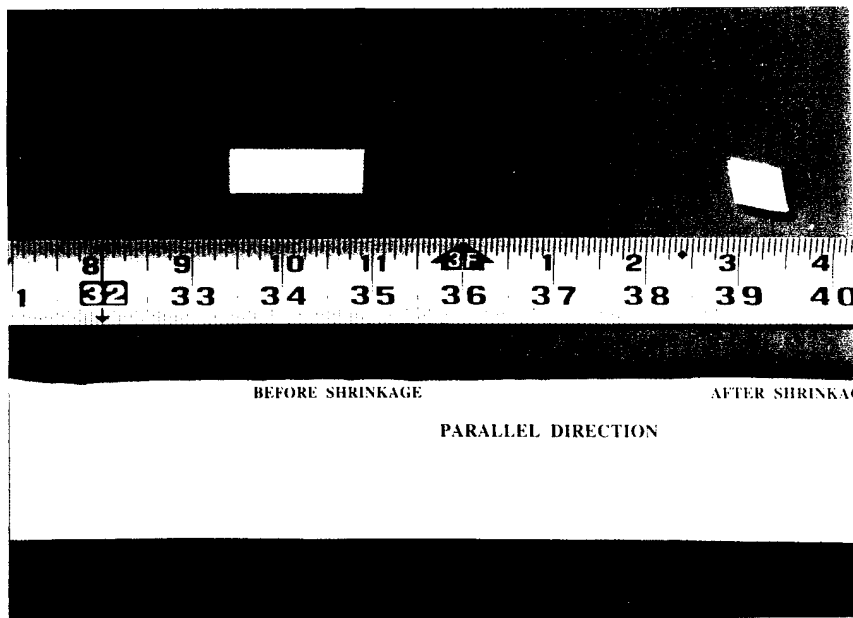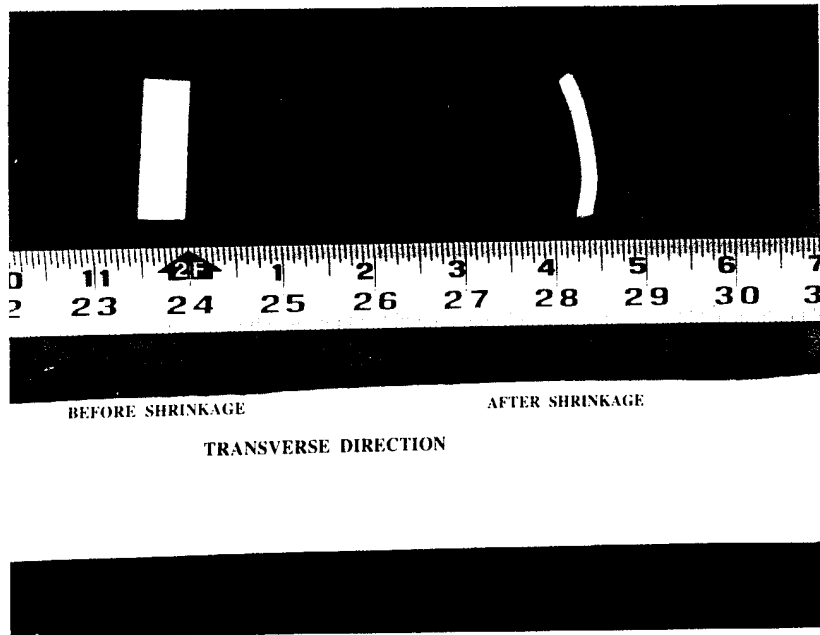
III.   EXPERIMENTAL RESULTS

A.   Preliminary Findings

In order to gain some experience with the stress-cracking test (ASTM D 1693), it was decided to do some preliminary tests with the Chevron Hi-D 9326 commercial polyethylene. The extruded sheet was examined for internal stresses using the procedure described in the ASTM standard. This task was accomplished by die cutting 0.5" x 1.5" samples from the sheet material in both the parallel and transverse directions to extrusion. Briefly, specimens of a known geometry were heated in a Petri dish containing talc at a temp of 302°F (150°C) for 30 minutes. After the specimens were allowed to cool, the change in dimensions were calculated as percentages. The values obtained are listed in Table 4. (A visual comparison of the effect can be seen in Figure 4 which shows a coupon of Chevron Hi-D 9326 before and after heat treatment.)

As can be seen in Table 4, the shrinkages for sample 1 in the machine direction averaged to 66.7% and in the transverse direction averaged to 10.2%. Sample 2, which was cut 90° perpendicular to sample 1, yielded average values of 59.3% in the machine direction and 9.69% in the transverse direction. A comparison of the results given in Table 4, shows that the residual shrinkage (stress) is highly dependent on orientation.

In order to get a better look at the orientation present in the extruded sheet, photographs were taken using wide angle X-ray scattering (WAXS). Figure 5 is a photograph of commercial Chevron material. As can be seen from the relative intensity of the two rings in the photograph, there is a strong orientation effect. Since the orientation of the sheet was parallel to the two white arcs in the photograph, it appears that the orientation was along this direction. Referring back to the shrinkage measurements discussed in the previous section, this result is in agreement with the previous findings. Because of the agreement of the sharp diffractions with the shrinkage results, it was decided to do more work with the X-ray method.

BEFORE SHRINKAGE   AFTER SHRINKAGE

TRANSVERSE DIRECTION

BEFORE SHRINKAGE   AFTER SHRINKAGE

PARALLEL DIRECTION

Before and After Shrinkage of Chevron PE

FIGURE 4
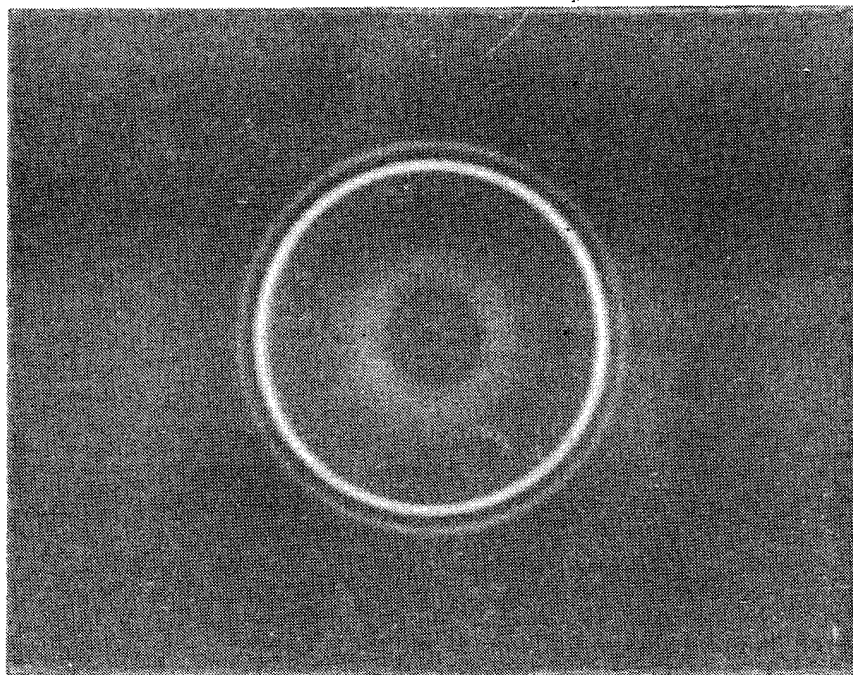
ORIENTATION OF CHEVRON PE BY WAXS METHOD

FIGURE 5

TABLE 4

Average Shrinkages in Percent

Chevron Hi-D 9326

Sample	Machine Direction	Transverse Direction
1	66.7	10.2
2	59.3	9.69

* Average Shrinkage of Compression
Molded Material = 4.28%

The commercial Chevron material was further characterized to determine crystallinity values in both the parallel and perpendicular directions. The results are shown in Table 5. As can be seen from the results, the percent crystallinity appears to be higher in the direction perpendicular to flow. These results agree with those reported in the literature (12). The numerical values again indicate that extrusion produces a material that is anisotropic. The results also show that the percent crystallinity is also dependent on the direction in which the specimen is oriented. Further research into this topic revealed the unusual intensities for the two crystal peaks at 2Q = 21.4 and 23.6 degrees. These intensities are nearly equal in the flow direction pattern while showing a ratio of around 2:1 in the perpendicular pattern (13-15).

In order to gain further information and show the generality of the effect, it was decided to look at another material, Marlex PE. Similar results can also be seen in Table 5, where the crystallinities were measured both perpendicular and parallel to flow. Again, it can be seen that the crystallinity measured in the perpendicular to flow direction was much higher (42.3 vs. 33.7%).

In order to remove the orientation effect, samples of Marlex were shrunk at 150°C according to the procedure previously discussed (ASTM 1693). From the results in the table, it can be seen that the crystallinity of the sample perpendicular to flow was essentially the same as the crystallinity parallel to flow after the samples had been shrunk (54.0% vs. 55.2%). Figure 6 and Figure 7 on the following pages show WAXS photographs of the Marlex PE before and after shrinkage. A comparison of the two figures reveals that the sharp diffractions (white arcs) have been removed by heating. Figure 7 shows that after heat shrinking the

Marlex sample at 302°F (150°C), there was no indication of orientation or stresses in the material. This is shown by the uniform ring completely around the circumference, which means that all of the stresses were allowed to relax and return to an isotropic state.

Since the purpose of this thesis is to compare the environmental stress crack resistance of the polyethylenes and correlate the values to the physical properties of the materials, this raises the question of how to determine the percent crystallinity of the polyethylenes. Since the orientation is obviously a major factor, it was decided to run another type of analysis in which the orientation is randomized by moving the sample through a quadrant while measuring the diffraction pattern. The result of this determination for Marlex can also be seen in Table 5.

TABLE 5

Crystallinity Values Determined by WAX

SAMPLE	CRYSTALLINITY
Chevron PE, Diffraction Perp. to Flow	0.440
Chevron PE, Diffraction In Flow Dir.	0.398
Marlex PE, Diffraction Perp. to Flow	0.423
Marlex PE, Diffraction In Flow Dir.	0.337
Marlex PE, 150°C shrink, Perp. to Flow	0.540
Marlex PE, 150°C shrink, In Flow Dir.	0.552
Marlex PE, Diffraction Randomized In The Instrument	0.467

Since it would be desirable to have a single value for the crystallinity for each of the three polyethylenes investigated in this study, it was decided to use the randomized technique. This was due to the additional step of shrinking the material and the variability introduced by doing so into the experimental results. The results of the analyses are given in Table 6.

19
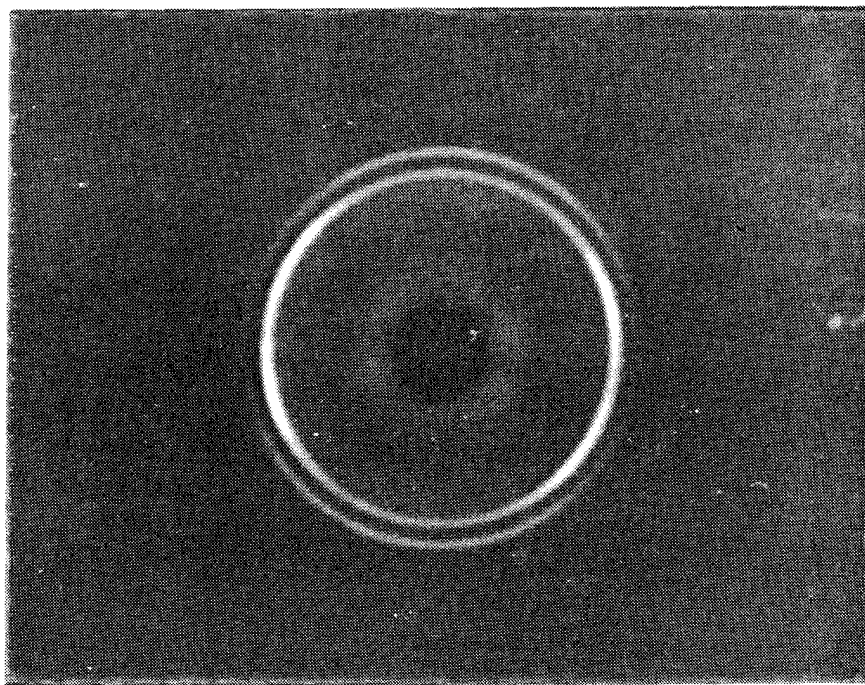
HIGHLY ORIENTED MARLEX M445 PE BY WAXS METHOD

FIGURE 6
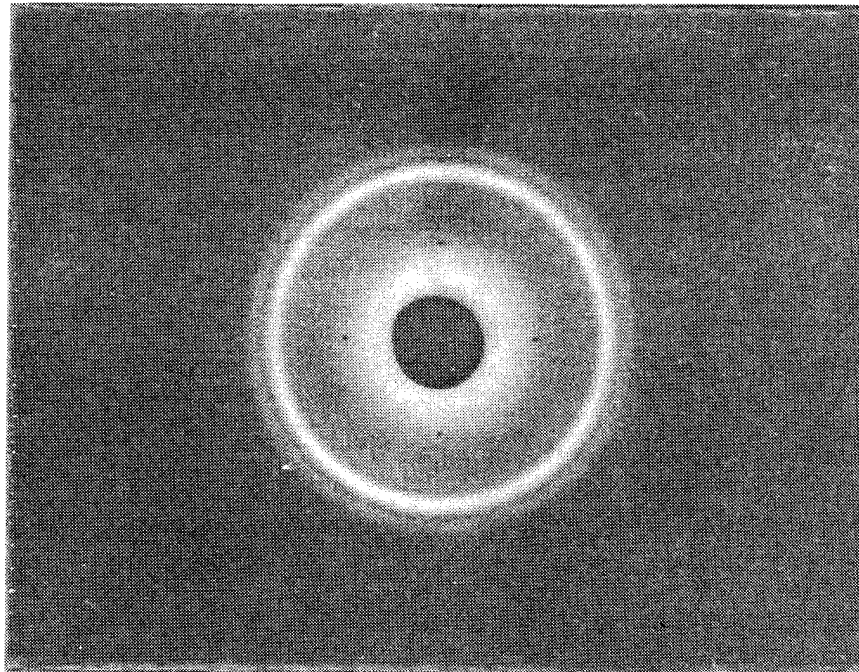
MARLEX M445 PE AFTER SHRINKAGE TEST

FIGURE 7

TABLE 6
Crystallinity Values For PE1, PE2, and PE3

	CRYSTALLINITY, X_C (X-RAY)
PE1 (Soltex Fortiflex K4424-122)	0.405
PE2 (Chevron Hi-D 9326)	0.389
PE3 (Hoechst Hostalen GM5010TN)	0.414

As can be seen from the values above, the crystallinities of all of the materials appear to be quite similar (within the precision of the experiment - 5%).

Another physical parameter of interest that can be determined by X-ray analysis is short chain branching. Instead of having regular chain folding as is typical with high density polyethylene, a small amount of another olefin such as 1-butene is incorporated into the polymerization reaction to deliberately produce side chain branches. These branch points break up the regularity of the folds of the chain and allow the polymer molecule to extend beyond the lamellar structure and enter into another crystallite, thus producing an entanglement. It should be obvious that these entanglements would make it more difficult to pull the material apart and thus result in a tougher plastic.

In order to determine the amount of chain branching, samples of the three polyethylenes were first heated to remove the residual stresses and the anisotropy. The specimens were heated to temperatures of 300 to 310°F. This temperature was found to remove the crystallites as evidenced by the optical transparency of the specimens. The samples were slowly cooled to room temperature and then sprayed with a coating of lacquer onto which was dusted a coating of graphite (diffraction standard). X-ray diffraction patterns were taken in a reflection mode to determine the raw 2Q data. A specimen of Chemplex 6109 resin, which is a linear polyethylene (zero branch content) was also run as a standard. The raw 2Q data were corrected for thickness and used to calculate the d spacing for the polyethylene crystallites. These values can be seen in Table A of the appendix. The d values in turn were used to calculate the chain branching values shown in Table 7. The chain branching is expressed as the number of methyl groups (CH_3) per 100 carbon (C) atoms.

22

TABLE 7
Chain Branching Results for PE1, PE2, and PE3

Sample	CH$_3$/100C
PE1 (Soltex)	1.9
PE2 (Chevron)	1.8
PE3 (Hoechst)	1.9

Again, these results are similar to those found for the degree of crystallinity. However, these will be discussed in more detail in a later section of the thesis.

Returning to the subject of the environmental stress-crack resistance test, the orientation effects have to be addressed further. As specified in the test method, "if the shrinkage of the specimens is less than 10% in the lengthwise direction, the molded sheet can be considered satisfactory" for internal stresses. Obviously, from the shrinkage results in Table 4 and the X-ray determinations, this is not the case. In order to verify that this condition could be met with the Chevron commercial material, sheets were compression molded in a platen press set at 420°F and 1000 psi using a window pane mold. The shrinkage values obtained using the same method are also given in Table 4. These results (4.28% shrinkage) are well within the ASTM specification. However, the desired process for fabricating the storage containers is extrusion which presents a bit of a problem.

From these experimental findings, the effect of residual stress induced by extruding the material was significant and it was decided to incorporate the effect of orientation (machine direction) into the experimental thesis.

By including another experimental variable into the nested factorial design, the number of experiments would be increased from 36 to 72 which would be unmanageable given the constraints placed upon this work. For this reason it was decided to do a set of experiments which would indicate the worse case scenario.

In order to create the worst possible case, the polyethylenes were processed at the highest temperature with the lowest concentration of antioxidant. Due to a limitation in the size of the constant temperature bath used to test the samples, only one antioxidant could be evaluated. Cyanox 1790 was chosen. The Chevron Hi-D 9326 commercial polyethylene was also tested for comparison.

B. Stress-Cracking Results

Since the resistance of the material was of primary interest, the ESCR results will be discussed first.

Samples were extruded and tested in accordance with condition C of ASTM D 1693, as described in the experimental section. Briefly, the procedure can be outlined as follows. Preconditioned, nicked specimens were placed in the Igepal CO-630 and examined periodically for any evidence of cracking. Since no visual sign of failure was noticed, the samples were examined weekly. The results of the first set of tests can be seen in Table 8.

TABLE 8

Results from Environmental Stress-Cracking Test

	No. of Failure	Time/Hrs.
Soltex Fortiflex K4424-122 Par. Dir., w/0.025% Cyanox 1790	No Failures	5136
Soltex Fortiflex K4424-122 Tran. Dir.w/0.025% Cyanox 1790	7 of 10 First Failure	5136 1944
Hoechst Hostalen GM5010TN Par. Dir., w/0.025% Cyanox 1790	1 of 10 First Failure	5136 3192
Hoechst Hostalen GM5010TN Tran. Dir., w/0.025% Cyanox 1790	3 of 10 First Failure	5136 2304
Chevron Hi-D 9326 Par. Dir., w/0.025% Cyanox 1790	6 of 10 First Failure	5136 3888
Chevron Hi-D 9326 Tran. Dir., w/0.025% Cyanox 1790	10 of 10 First Failure	1738 1176
Chevron Hi-D 9326 Par. Dir., Commercial Material	No Failures	5136
Chevron Hi-D 9326 Tran. Dir., Commercial Material	No Failures	5136

As can be seen in the table, the maximum time, in hours, for the test was 5136 (214 days). Five thousand hours is generally taken as a run-out or maximum time for the test. Several references were found where the ESCR for specific polyethylenes was listed as being >5000 hours. It should be noted that this test leaves much to be desired since it requires greater than a 1/2 year to run.

The polyethylenes which were specially compounded for this study are listed in the table in decreasing order in terms of their ability to resist ESC. As can be seen in the table, the Soltex cut in the parallel direction showed no failures after 5136

24

hours. It should also be restated that all of the specimens contained the same amount of antioxidant and were compounded at the same temperature. In other words, antioxidant and temperature are not variables.

Looking at the Soltex cut in the transverse direction, it can be seen that seven out of ten specimens failed during the same time. For reference, it can be seen that the first sample failed at 1944 hours (81 days).

From the difference in the results between the parallel and transverse orientation, it appears the processing has an important effect. This can be shown visually as in the following figure. As can be seen, the molecular orientation would be in the direction of extrusion. If the sample is cut perpendicular to the extrusion direction and nicked, the cracks will grow parallel to the molecular orientation. On the other hand, if the specimens are cut parallel to the extrusion direction, the cracks will run perpendicular to the molecular orientation which would be more difficult. This type of effect has been reported in regard to the crazing and cracking of polymers (16).

Also, from a design standpoint, it would be of practical importance to orient the flow perpendicular to any molded in defects such as notches or contours in the part. This could be accomplished in an injection molded part through proper gating.

The material which had the second best ESCR was the Hoechst polyethylene. Again, it can be seen in the table that the resistance to cracking was better in the parallel than in the transverse direction, which would be expected from the previous discussion.

Again, looking at the table it can be seen that the first failure for the Hoechst material occurred at 2304 hours (96 days). Comparing this to the result obtained for the Soltex material, there is only a difference of two time intervals (two weeks).

25
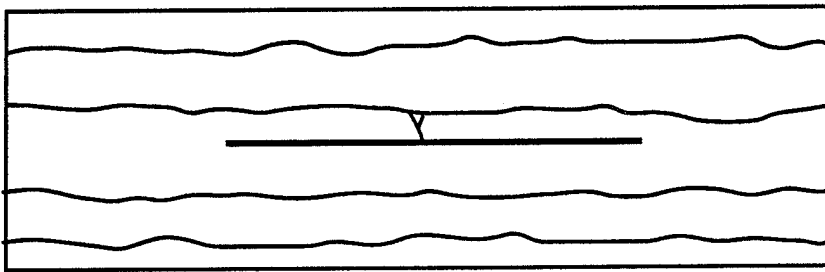
Flow Direction
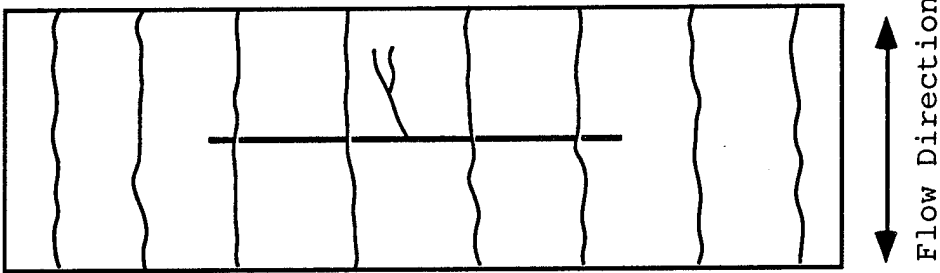
Flow Direction

Crack Propagation with Molecular Orientation
Figure 8

The material which showed the poorest ESCR was the Chevron polyethylene. In the case of the samples cut in the parallel direction to extrusion, six out of ten specimens failed during the allotted time. The first failure occurred at 3888 hours (162 days). Comparing this to the Hoechst material in the same direction, the Chevron material took longer to show the first failure but failed at a much quicker rate. In other words, the two materials would have much different failure distribution curves.

For the case of the Chevron samples cut transverse to the extrusion direction, all of the samples failed in 1738 hours (72 days). The first failure was observed at 1176 hours (49 days). From an experimental standpoint, the Chevron polyethylene in the transverse direction appeared to be the ideal material – all of the samples failed within the allotted time. At this point it was decided to look at the effects of antioxidant and temperature with this material and orientation.

The results of the previous test were plotted according to the ASTM standard procedure to obtain more information about the failure distribution in the material. Log normal probability paper was used to plot the log time versus the cumulative percentage failures for the Chevron material cut in the perpendicular direction. As can be seen in the following figure, the plot was linear. This type of plot is often used to determine the time at which a given percentage of failures would occur (e.g. 50%). This "good behavior" of the material further reinforced our choice of Chevron polyethylene in the perpendicular direction for this study.

As previously stated, all of the Chevron specimens failed in 1738 hours. In order to get some idea about the reproducibility of the test procedure, another set of specimens were tested along with the remaining samples listed in Table 8. The first failure was observed at 2544 hours which should be noted as being longer than the time required for all ten of the previous set to fail. After 3384 hours only two of the samples had failed which caused doubts as to the repeatability of the test procedure. For this reason, it was decided to do a repeat set of tests.

For comparison, the tests which were just discussed were those done on materials compounded specifically for this study. Chevron commercial material was also tested for ESCR in both directions during the first part of this study. As can be seen in the previous table, no failures were obtained. The difference in the results obtained with the two materials (commercial versus custom compounded) could be due to either the antioxidant or to the processing temperature.
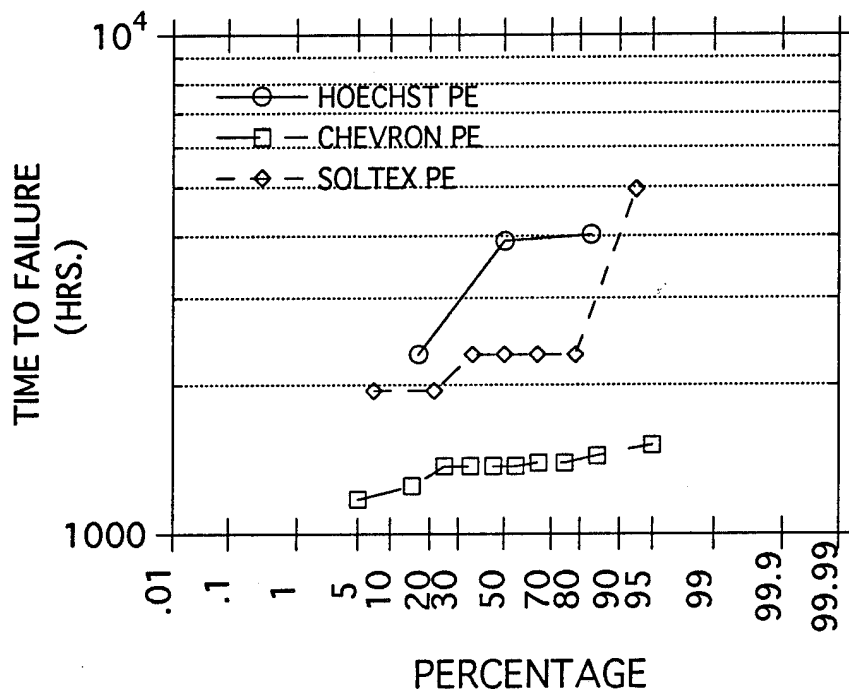
FAILURE POINTS FOR CHEVRON, HOECHST
AND SOLTEX POLYETHYLENES

Figure 9

28

In the case of the material compounded for this study, it is known that the level of antioxidant was 1/2 that recommended by the supplier. In the case of the commercial material, neither the type nor level of antioxidant was known. Therefore, the difference in the material's ability to resist stress-cracking could have been due to either the type of antioxidant, the level of antioxidant, or both.

Similarly, since the temperature at which the Chevron material was processed was not known, the difference in the material's ability to resist stress-cracking could also be due to processing.

From these observations, it was decided to conduct further tests with the Chevron material in the perpendicular direction. Due to a space limitation in the testing tanks, it was decided to vary the level rather than the type of antioxidant. The effect of temperature was varied as well.

In addition, in order to compare the remaining commercial materials, the Hoechst and Soltex polyethylenes would also be run.

Since only five of the available eight test cells were being used, it was decided to again repeat the test of the Chevron material in the perpendicular direction with 0.025% Cyanox and a processing temperature of 460°F. In this way, we would obtain an additional measure of the reproducibility of the standard test. The block of four experiments with the specially compounded Chevron materials along with the commercial Hoechst and Soltex polyethylenes can be seen in the following list.

            Chevron PE - With 0.1% Cyanox, Proc.Temp.:460°F
            Chevron PE - With 0.1% Cyanox, Proc.Temp.:380°F
            Chevron PE - With 0.025% Cyanox, Proc.Temp.:380°F
            Chevron PE - With 0.025% Cyanox, Proc. Temp.:460°F
            Soltex PE - Commercial Material
            Hoechst PE - Commercial Material

The second set of samples was conditioned and tested in the same manner. The test lasted the full 5,000 hours with no detected failures. This raises two interesting questions. Firstly, did the Chevron polyethylene processed at the higher temperature with the lower antioxidant concentration change between the times when the three sets of tests were run or secondly, is the test reproducible?

In order to address these questions, the manufacturers' data sheets were consulted. Most of the materials recommended for gas pipe applications have run out times greater than 5000 hours. The test results obtained for the commercial grades of the Chevron, Hoechst, and Soltex met these specifications. These results do not lead one to suspect non-reproducibility of the test method.

On the other hand, the Chevron material with the higher processing temperature and lower antioxidant level was processed in a single lot. It was quite surprising to have one set of samples completely fail in 1738 hours while a second set cut with the same nicker, tested in Igepal CO-630 taken from the same drum, and exposed to an elevated temperature in the same test equipment, had only two failures in 3384 hours. A third set had no failures at all in 5000 hours. It should also be noted that the three sets of specimens were taken from adjacent sections along the length of extruded sheet and that the samples were cut with the same sampling pattern across the sheet. This led to a suspicion that the material had somehow changed with time (214 days).

Since the parameter that had shown the greatest difference was the orientation of the samples, it was decided to try a simple test to evaluate the hypothesis that the material had relaxed during this time period.

At the outset of the experimentation, samples were tested to determine the level of residual stress. As previously discussed shrinkage values far in excess of recommended values were obtained. In order to test the hypothesis that the custom compounded Chevron material had relaxed over the time period between tests, the previous results were again checked. Unfortunately, no tests were performed on this material. However, the trial with the commercial Chevron material was repeated. The results showed shrinkage values similar to those previously obtained. From these results, it was not possible to conclude that time was a factor in obtaining the erratic results.

In order to gain more insight into the differences obtained in the previous tests, a comparison of the results from the chemical analyses will be made.

C. Chemical Test Results

    1. DSC Results

The relative amount of protection from oxidative degradation that a given antioxidant or loading level can provide has been evaluated using isothermal differential scanning calorimetry (DSC). A typical thermogram obtained from this analysis is shown in Figure 10.

30
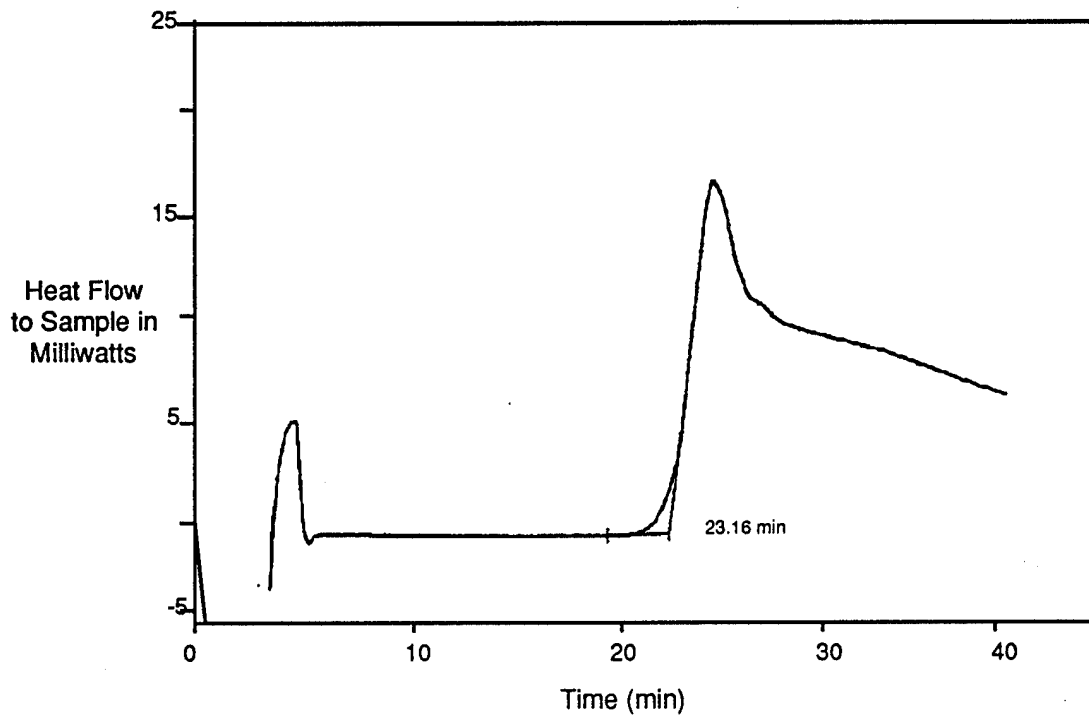
**OXIDATION INDUCTION TIME BY ISOTHERMAL
DSC FOR PE1/A03/B1P**

Figure 10

In the figure, the change in enthalpy is plotted as a function of time for the Soltex PE and the Irganox at the higher level, processed at the lower temperature. Briefly, the experiment consists of placing a known amount of the compounded plastic into a sample pan and heating it to a given temperature (220°C). The difference in the amount of energy required to keep the sample pan at the same temperature as the reference pan is plotted on the ordinate. This difference in energy represents the amount of heat either taken up (endothermic) or given off (exothermic) by the plastic. As can be seen from the beginning portion of the plot, heat has been taken up by the polymer to the point where there is an apparent overshoot in the curve. Beyond a time of approximately five minutes, the change in enthalpy with time is constant (zero). At about twenty minutes, the change in enthalpy becomes extreme. If the slope of both portions of the curve are extrapolated, as shown in the figure, to the point where they intersect, an oxidation induction time can be determined.

The oxidation induction time is the time from when the sample heating begins to the time of the exotherm. The times determined for the commercial polyethylenes and the materials custom compounded in this study are listed in Table 9.

Looking first at the level of antioxidant, a comparison of the effect of antioxidant level will be made using the Soltex material, shown in Figure 10. The oxidative induction time for this material was found to be 23.1 minutes as can be seen in Table 9. The oxidative induction time for the lower concentration of antioxidant in the same polymer processed at the same temperature, was found to be 7.2 minutes. The results show that the oxidation induction time is strongly dependent on the level of antioxidant used. In this case, it can be seen that the level of protection has been decreased roughly by a factor of two-thirds by decreasing the level of antioxidant. In order to give some perspective to these times, it should be remembered that the residence time for the extruder used in compounding is roughly two minutes.

In general, it can be seen from all of the results in the table for the low processing temperature in compounding the pellets, that the protection has been increased between two and three times. This was true for all of the polymers using any of the antioxidants for which results were obtained. The lowest oxidative induction time determined from the pelletized resin processed at the lower temperature was found to be four minutes, which is twice the residence time.

Looking at the effect of temperature, similar comparisons can be made. Again, using the previous material (PE1/AO3/B1P) as a basis of comparison, it can be seen that the oxidative induction time increased from 23.1 minutes to 28.1 minutes when the material was pelletized at the higher temperature (2P). This is not what was expected. Looking at the other results in the table, one can find examples which would make more physical sense - the oxidative

32

TABLE 9
Oxidative Induction Times (Min.) Isothermal DSC, 220°C, 100cc/min. Air

MATERIALS COMPOUNDED :

	/A1P	/A1S	/A2P	/A2S	/B1P	/B1S	/B2P	/B2S
PE1/AO1	138.5	103.2	113.2					
PE1/AO2	6.6	5.7	6.7	6.0	11.4	11.0	14.8	14.4
PE1/AO3	7.2	6.7	8.2	6.3	23.1	22.8	28.1	27.6
PE2/AO1	93.0	87.3	93.0	88.4				
PE2/AO2	7.1	6.5	9.6	8.6	16.2	16.4	18.2	16.7
PE2/AO3	8.1	7.8	9.0	8.1	31.4	27.9	25.0	25.2
PE3/AO1	76.7	58.6	80.2	64.4				
PE3/AO2	4.0	4.0	4.1	3.0	11.7	10.6	13.4	10.7
PE3/AO3	4.0	5.5	4.3	4.2	15.1	19.2	16.5	14.6

COMMERCIAL MATERIAL

SCOMP	37.5	SCOMS	39.3
CCOMP	17.8	CCOMS	15.4
HCOMP	23.8	HCOMS	19.6

where,
    PE1: Soltex PE
    PE2: Chevron PE
    PE3: Hoechst PE
    AO1: Santonox R
    AO2: Cyanox 1790
    AO3: Irganox 1010

    A: Low concentration of Antioxidant
    B: High Concentration of Antioxidant
    1: Low Processing Temperature (380°F)
    2: High Processing Temperature (460°F)

33

induction time decreases with increasing processing temperature, as for example in the case of PE2/AO3/BP1 and BP2. Perusing the table, in the case of PE2/AO1/A1P and A2P, the oxidative induction times are exactly the same (93.0 minutes). These results can be explained by variations in either the material or the precision of the test method. Due to limitations in resources, only one assay was done in each case. This precluded the determination of the variance in each lot of material or the reproducibility of the experiment.

Next, the issue of an additional processing step will be evaluated. Samples were analyzed after extrusion which allows a comparison to be made to the previously discussed results. The difference in oxidative induction times can easily be seen in the table since they are in adjacent columns (P and S). In most cases the effect of the additional processing step was found to decrease the oxidative induction time. However, in a few cases, the opposite or no effect was found.

While the previous results show that the oxidative induction time is highly dependent on the concentration of antioxidants, similar effects were not found for an increase in temperature or the addition of a processing step. From the magnitude of the changes produced by the three variables, it appears that the level of antioxidant was the most significant.
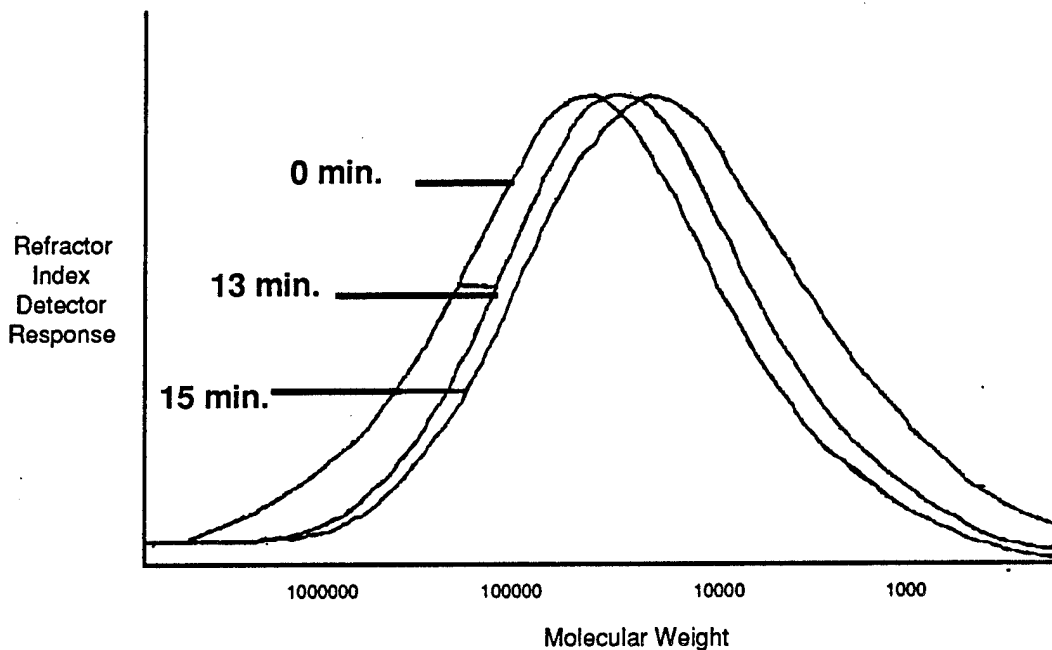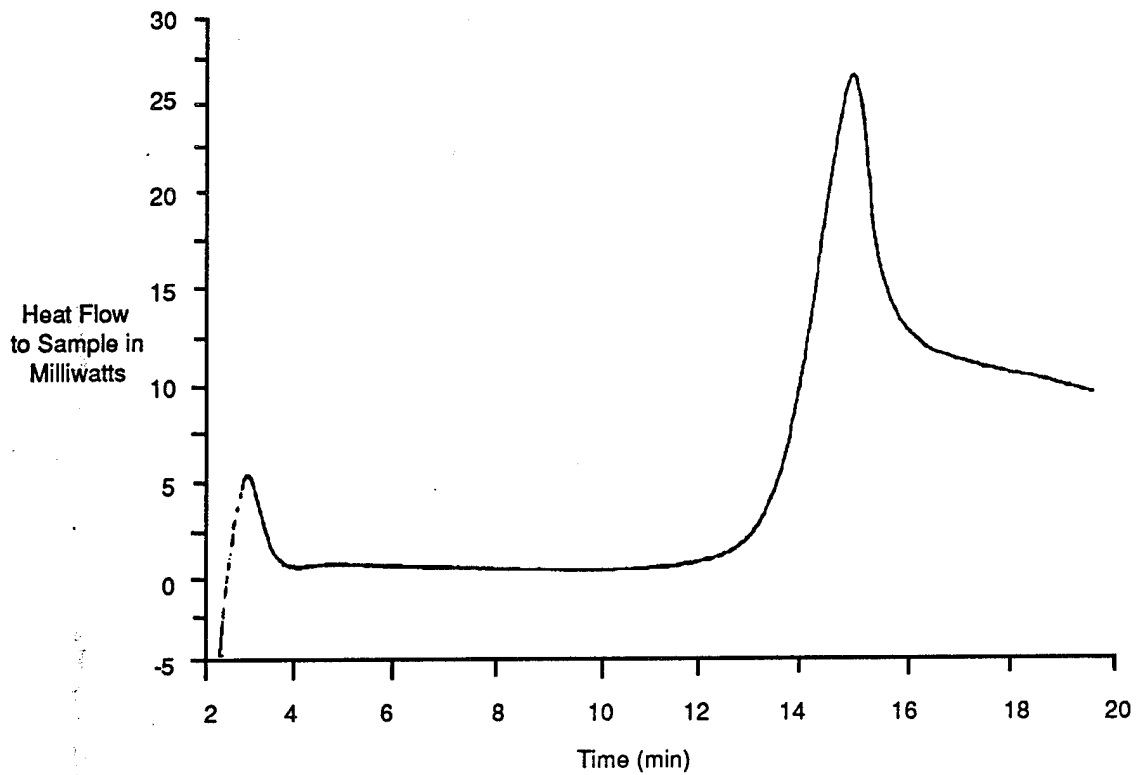
Oxidative induction times were also determined for the commercial materials (in pelletized and sheet form) and can be seen in the same table. In general, the oxidative induction times obtained at the high loading levels, are similar to those obtained for the commercially compounded materials. As can be seen from the results, the oxidative induction times range from 15.4 minutes to 39.3 minutes.

Rather than using a single antioxidant, as was the case in this compounding study, commercial materials will generally use an "additive package" that consists of different types of antioxidants (primary, secondary) that can act synergistically, as well as inhibit discoloration. The large amount of Santonox antioxidant in the polymer samples resulted in significantly longer induction times, however the samples became noticeably discolored long before the oxidation exotherm. Typically, most of the samples did not show a significant discoloration until the oxidation exotherm. At the low antioxidant loading levels, the presence of Vanox 1290 in the Chevron PE may account for the general increase in induction times compared to Soltex PE samples. The significantly shorter times obtained for the Hoechst PE samples may be attributed to the difference in the polymerization method used to produce this material. A polymer more susceptible to oxidation would be expected to have shorter induction times. Processing at temperatures greater than those used in this study might result in some degradation appearing in the Hoechst materials before the Soltex and Chevron materials.

34

Ancillary experiments were conducted to determine the effect of the oxidative degradation on the polymer. Samples of compounded resin were heated isothermally in a DSC to determine the oxidation induction time and the time at which the peak occurred in the exotherm. As can be seen in Figure 11, the induction time and peak time occurred at 13 and 15 minutes, respectively. To determine the effect on the physical properties, the molecular weight distribution was determined by SEC at these times and zero time for a reference. The results of the SEC determinations can be seen in the lower part of Figure 11 where the detector response is plotted as a function of decreasing molecular weight. As can be seen from the figure, the shape of the MWD curve does not appear to change. The effect of time in the DSC at the elevated temperature appears to shift the entire curve to the right (lower molecular weights). From the two plots in Figure 11, it appears that the auto-oxidation process is readily detected by the appearance of an exotherm in the isothermal DSC experiments. This exotherm, in turn, relates well to the decrease in the molecular weight distribution shown by the SEC chromatograms. These chromatograms indicate the onset of the polymer chain scission process prior to the auto-oxidation phase.
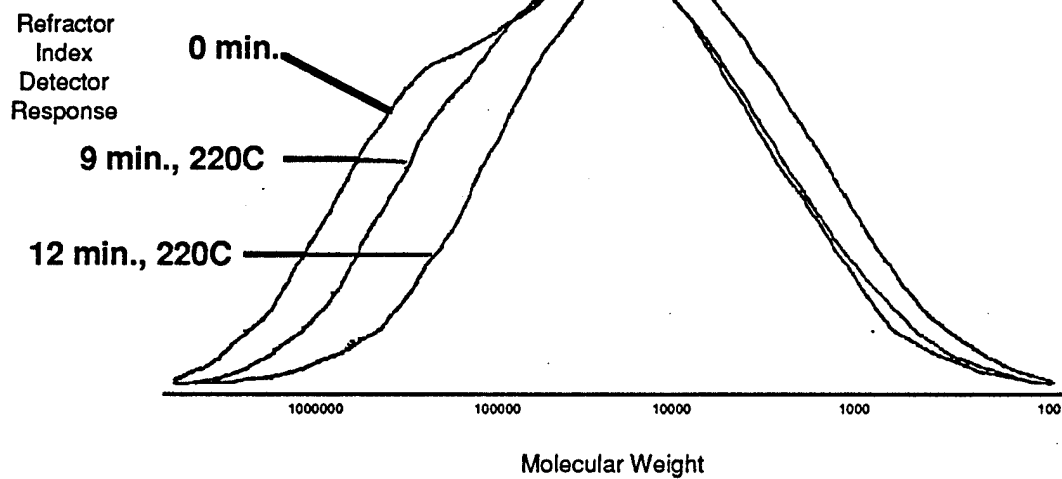
Figure 12 shows a similar set of curves obtained for the Hoechst material. The upper curve shows the oxidative induction time and auto-oxidation peak time obtained for this material during isothermal heating in the DSC. The two times were taken as 9 and 12 minutes respectively. Similarly, SEC curves were determined at 0, 9, and 12 minutes and can be seen in the lower part of Figure 12. As with the Soltex material, the curves shift to lower molecular weights, again indicating chain scission. As can be seen from the curves, a greater decrease in the high MW end of the distribution is evident for this polymer in the earlier stage of degradation. A high MW shoulder is evident in the SEC curve at 0 minutes, reduced at 9 minutes, and is no longer evident at 12 minutes. In this case, the degradation of the material appears to be at the expense of the high molecular weight end rather than across the board.

These DSC results show at long times, 9 to 15 minutes, the polymer oxidizes as evidenced by the change in color and suffers a loss in molecular weight which is detectable by SEC. However, it remains to be seen whether these changes are in effect a practical consequence in the extrusion of the material and subsequent stress-cracking tests.

35

SEC CHROMATOGRAMS OF PE1/A02/B2P SAMPLES
HEATED ISOTHERMALLY BY DSC

Figure 11

Heat Flow to Sample in Milliwatts

Time (min)

Refractor Index Detector Response

0 min.

9 min., 220C

12 min., 220C

Molecular Weight
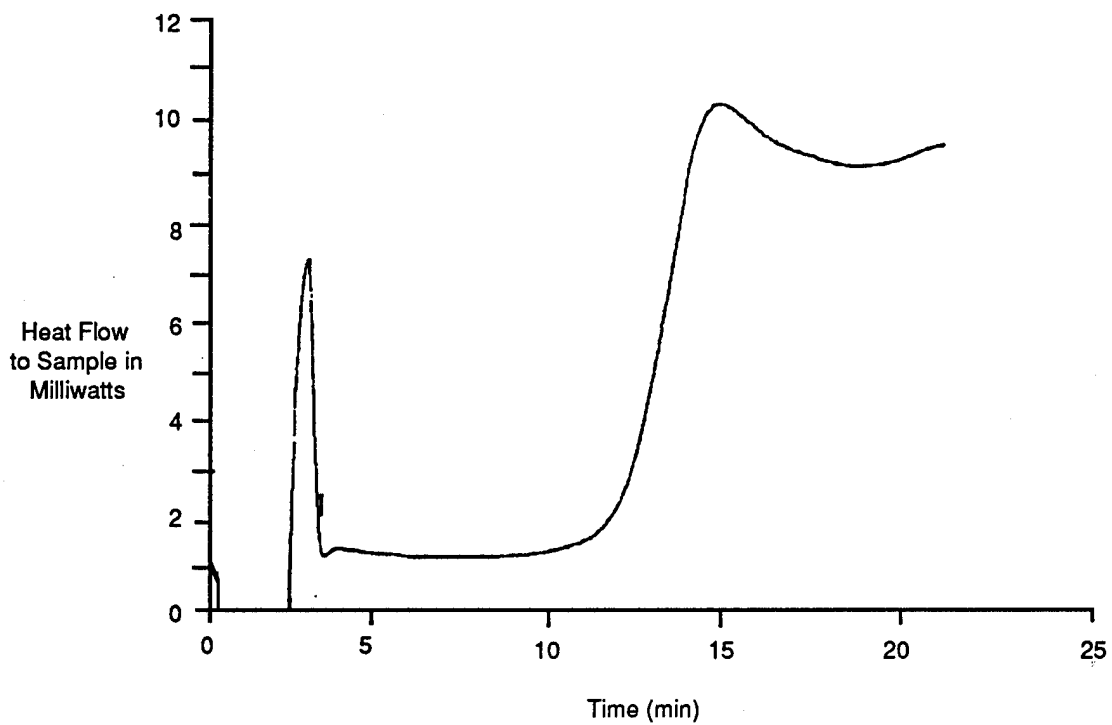
SEC CHROMATOGRAMS OF PE3/A02/B1P SAMPLES HEATED ISOTHERMALLY BY DSC

Figure 12

2. RPHPLC Results

In order to determine the amount of antioxidant consumed during processing, reverse phase high performance liquid chromatography (RPHPLC) was used. This technique involves passing a solution of the antioxidant through a chromatographic column in order to separate the antioxidant from the other chemical species which may be present. When the solution leaves the column, it passes a detector to determine the amount of antioxidant present. The amount is determined from a calibration plot.

In order to obtain calibration plots, solutions were made from each of the antioxidants and measured spectrophotometrically. The area under each peak was determined instrumentally. Plots of peak area versus concentration for each of the antioxidants are shown in Figure 13. For reference, A01 is the Santonox, A02 is the Cyanox, and A03 is the Irganox in the graphs on the following page. From the linearity of the plots, it appears that there is good agreement with Beer's law and that this is a good technique for analysis of concentration.

The same batch of antioxidant used for compounding was used as the chromatographic standard. Quantitation was based on the primary peak in the chromatograms, although minor impurities were evident in the antioxidant standards and reaction products were evident in the chromatograms of extracts from the milled samples.

To ensure the ability of the material to obtain its desired morphology, as well as its characteristic mechanical/physical properties, the polyolefin needs to be protected from oxidative degradation during processing. The additives evaluated in this study were commercially available primary antioxidants that are recommended for use in polyolefins. Not only should the antioxidant be at the proper level, it also should be uniformly distributed throughout the material. In order to check whether this was indeed the case, representative specimens were selected from three areas each of two dry-blended lots. The specimens were extracted and analyzed using the chromatographic technique previously described. The results are presented in Table 10.

TABLE 10
Antioxidant Compounding Efficiency

	WT% COMPOUNDED	WT% EXP. DETERMINED
PE1/A01/A	0.500	0.531, 0.512, 0.535
PE1/A03/A	0.050	0.051, 0.053, 0.053
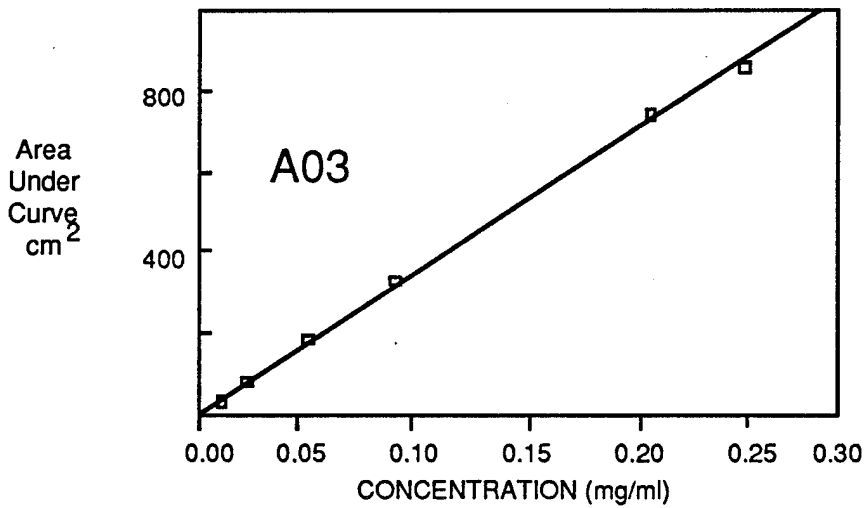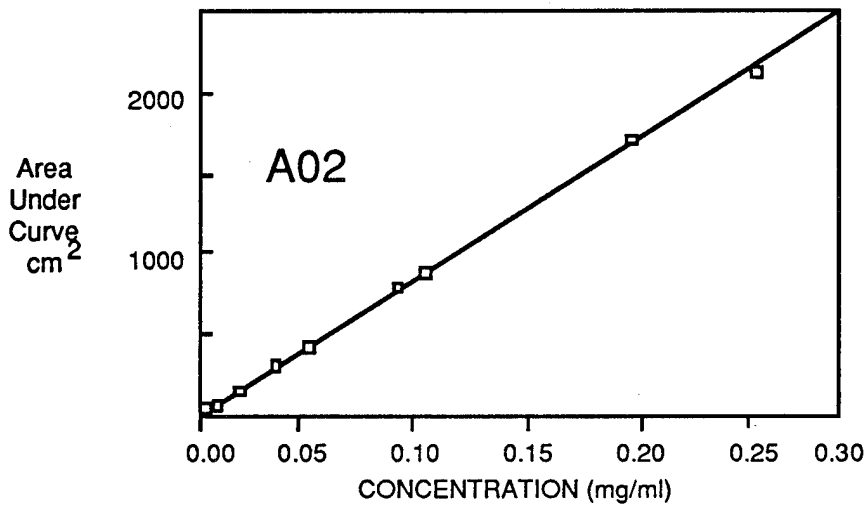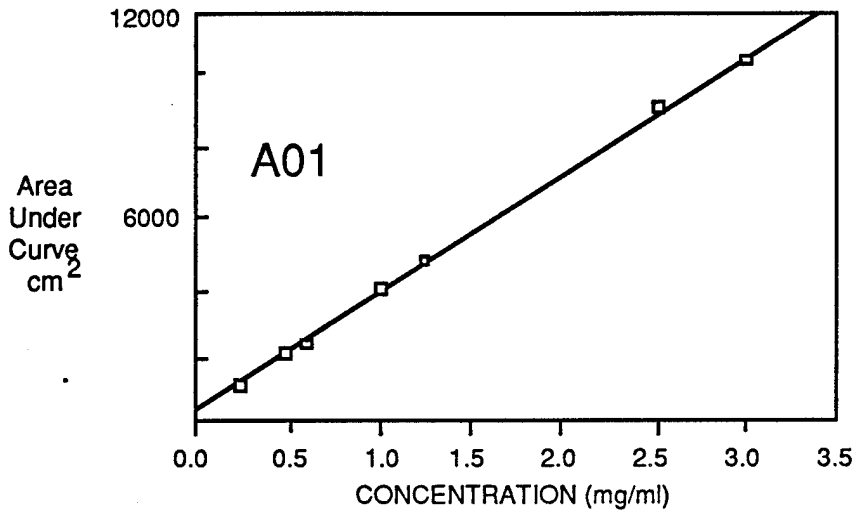
ANTIOXIDANT SOLUTION CONCENTRATION vs. CHROMATOGRAPHIC PEAK AREA FOR A01, A02 AND A03

Figure 13

As can be seen from the results, the Santonox (AO1) was compounded at the 0.5% level and the Irganox (AO3) was compounded at the 0.05% level. The percentages experimentally determined by this method not only were in the proper range, but also indicated that a thorough distribution of the antioxidant was achieved by the dry blending method.

As also can be seen in the table, the loading levels chosen for the Santonox antioxidant are significantly higher than those used for the Irganox. These high levels were due to the recommendations made by the manufacturer of the antioxidant. For this reason, a comparison of antioxidant efficiency can only be reasonably made between the Cyanox and Irganox antioxidants.

After it was ensured that the samples were dry-blended properly, they were extruded into pellets and then processed into sheet. In order to determine the decrease of antioxidant in each one of the two steps, specimens were milled and extracted. These extracts were analyzed and the results can be seen in Table 11.

As can be seen in the table, using the Soltex polyethylene with the Santonox at the half percent level (PE1/AO1) as an example, the concentration changes at the low antioxidant level and the low processing temperature (A1) from 0.434% in the pellets to 0.394% in the extruded sheet. In general, the results of the analyses for the milled samples, presented in Table 11, reflect this trend. However, some of the analyses such as that for the Chevron processed at the higher level of Irganox, show a reversal where the concentration appears to increase from 0.097% in the pellets to 0.118% in the sheet at the lower processing temperature, and correspondingly from 0.090% to 0.112% at the higher processing temperature.

The chromatograms shown in Figure 14 are of the antioxidants and extracts from the milled sheet samples.

The chromatogram for the sheet Chevron PE with 0.2% Irganox 1010 processed at 380°F (193°C) and the sheet Chevron PE with 0.2% Irganox 1010 processed at 460°F (230°C) samples show an additional major peak at 11 minutes. This component was present in all of the Chevron PE milled samples as well as the flake. The component was extracted from the Chevron PE flake and identified by mass spectroscopy as 2,2'-ethylidene bis (4,6-di-t-butyl phenol), which is an antioxidant available under the tradename Vanox 1290. This material was apparently dry mixed with the Chevron PE flake prior to shipping. The presence of the Vanox 1290 may have caused these unexpected results.

TABLE 11

Weight Percent of Unreacted Antioxidant in Pellets (P) and Sheet (S)

	/A1P	/A1S	/A2P	/A2S	/B1P	/B1S	/B2P	/B2S
PE1/A01	0.434	0.394	0.359	0.385	1.510	1.450	1.790	1.590
PE1/A02	0.008	0.006	0.010	0.008	0.024	0.026	0.032	0.029
PE1/A03	0.005	0.009	0.007	0.008	0.058	0.041	0.037	0.056
PE2/A01	0.428	0.253	0.367	0.347	1.860	1.512	1.760	1.407
PE2/A02	0.016	0.009	0.016	0.008	0.065	0.041	0.076	0.035
PE2/A03	0.019	0.016	0.017	0.014	0.097	0.118	0.090	0.112
PE3/A01	0.361	0.357	0.326	0.336	1.755	1.027	1.805	1.136
PE3/A02	0.006	0.001	0.004	0.001	0.031	0.013	0.031	0.015
PE3/A03	0.006	0.004	0.005	0.005	0.039	0.032	0.042	0.038

PE1: Soltex PE

PE2: Chevron PE

PE3: Hoechst PE

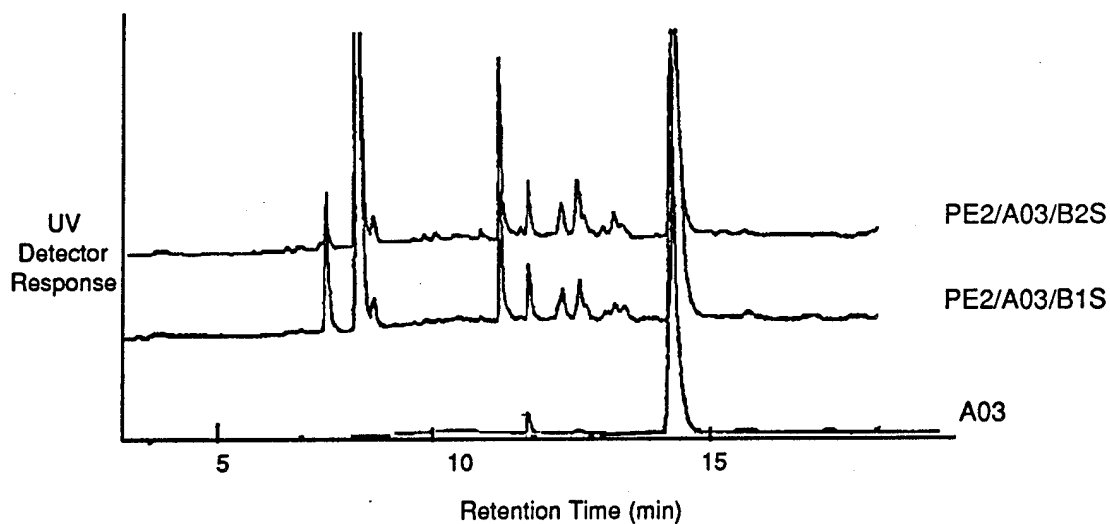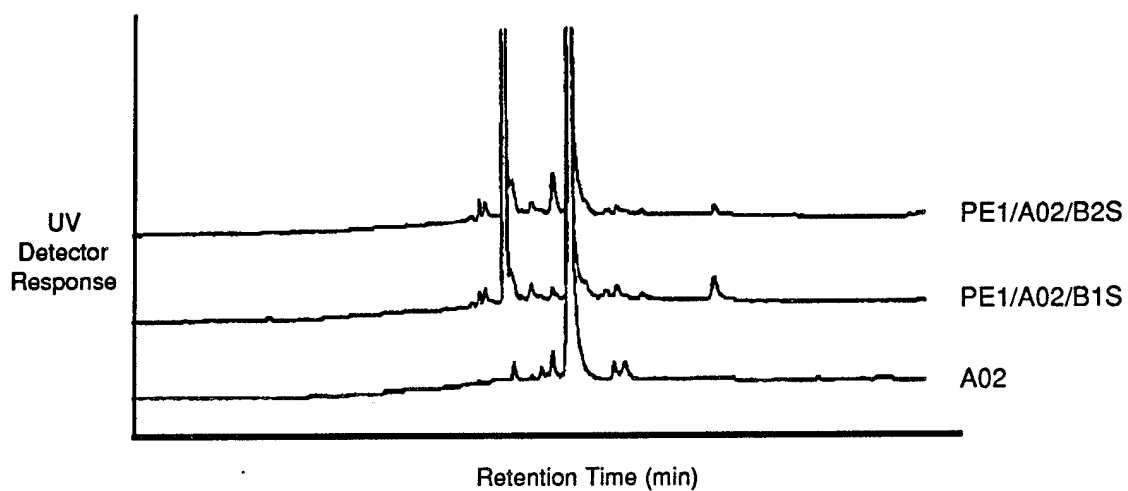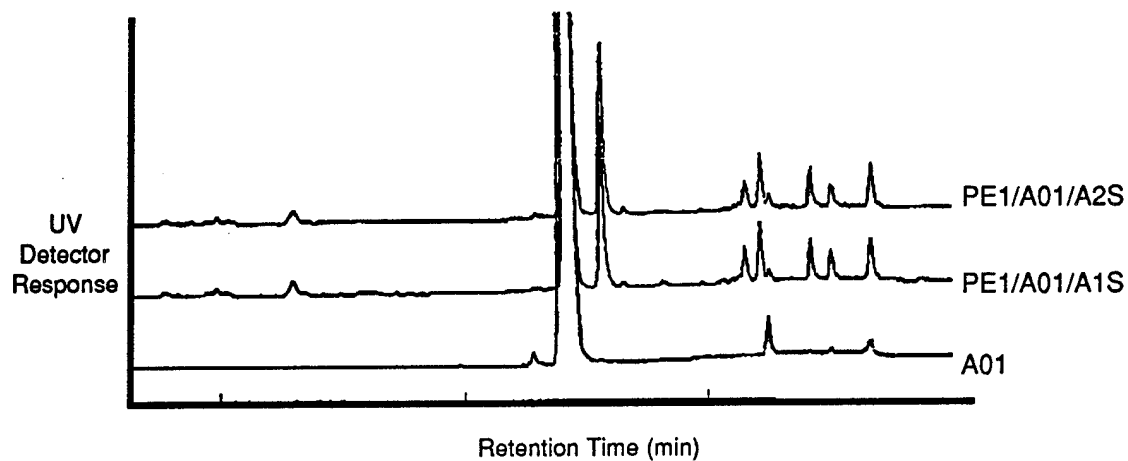AO1: Santonox R

AO2: Cyanox 1790

AO3: Irganox 1010

A: Low Level of Antioxidant

B: High Level of Antioxidant

1: Low Processing Temperature (380°F)

2: High Processing Temperature (460°F)

RPHPLC CHROMATOGRAMS OF ANTIOXIDANTS AND EXTRACTS
FROM MILLED SHEET SAMPLES
Figure 14

The material of greatest interest in the study was the Chevron PE dry-blended with the Cyanox antioxidant (PE2/AO2). As the data in Table 11 indicates for this material, an increase in processing temperature or an additional processing step resulted in a decrease in the amount of unreacted antioxidant in the material. These results reinforce the findings previously discussed, that the Chevron material processed at the higher extrusion temperature with the lower antioxidant concentration had poorer stress-crack resistance than the other Chevron materials.

To further investigate the effect of the change in antioxidant concentration, the results of the ESCR tests in Table 11 were compared. In order to remove the confusion of a large table, the pertinent results were taken from the previous results and grouped in Table 12.

TABLE 12

Residual Antioxidant Determined After Blending, Pelletizing, and Extruding the Three Polyethylenes Along With the Number of Failures Obtained in the ESCR Test

Percent Cyanox (by weight)

PE	Blend	Pellets	Sheet	Failures
Chevron	0.025	0.016	0.008	10
Soltex	0.025	0.010	0.008	7
Hoechst	0.025	0.004	0.001	3

The polyethylenes are ranked in increasing order with regard to stress-crack resistance in the table where the Chevron was worst with ten failures and the Hoechst was best with three. The percentages of Cyanox in the dry-blended, pelletized, and sheet specimens are presented as percentages in the table. Although, the level of antioxidant can be seen to decrease with each processing step, the results do not indicate a correlation between ESCR and residual antioxidant in the materials.

The Soltex and Chevron polyethylenes appeared to be produced by the same polymerization process and would be expected to have similar levels of unreacted antioxidant after processing under the same conditions. However, the data in the previous table shows that a larger amount of unreacted antioxidant is present in the Chevron samples after processing. This also may be due to the presence of an additional antioxidant, Vanox 1290, which was apparently dry mixed with the Chevron flake. The Hoechst polyethylene samples generally have less available antioxidant when compared to both the Soltex and Chevron materials. The

43

Hoechst material is produced by a different polymerization method that may produce a polymer more susceptible to oxidation. An increase in the relative amount of tertiary hydrogens, present at polymer branch points, or the presence of metallic impurities from the polymerization catalyst can increase the rate of oxidation (8).

Generally, the reactivity of an antioxidant during melt processing will be dependent upon temperature, time in the melt and the concentration of oxygen available. An insufficient amount of antioxidant during processing can result in polymer degradation, typically observed as a change in the polymer MW and/or MWD. Polymer degradation of polyolefins typically involves chain scission or cross linking reactions. In the presence of oxygen, primarily peroxy radicals are formed at elevated temperatures and the reaction of these radicals results in chain scission as the dominant mode of polymer degradation. Polyolefins tend to degrade by a random chain scission process which leads to a decrease in the MW values and a corresponding shift in the MWD. In the absence of oxygen, an increase in polymer radical formation can occur thermally and by shear. The reaction of polymer free radicals can also lead to cross linking, which will tend to increase the MW values and broaden the MWD of the polymer.

3. SEC Results

In order to see whether there were any changes produced in either the MW or MWD by processing, size exclusion chromatography (SEC) was used. Briefly, the material is dissolved in a solvent, passed through a column which separates the molecules by size, and eluted from the column at which point a detector determines the amount present. The result is a plot of amount of material as a function of elution time. Using the "universal calibration" technique to determine molecular weight as a function of elution time, various parameters (molecular weights) can be calculated.

The number, weight and Z average MW values ($\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$) obtained from the analysis of the polyethylene samples are listed in Table 13.

$\overline{M}_n$ represents the number-average molecular weight, which is the weight of the sample divided by (or averaged by) the total number of molecules

$$\overline{M}_n = \frac{\sum\limits_{i=1}^{\infty} M_i N_i}{\sum\limits_{i=1}^{\infty} N_i} \tag{1}$$

where M_i is the molecular weight of the i species and N_i is the number of the i species.

The next higher molecular weight (next moment of the distribution curve) that can be measured by absolute methods is the weight-average molecular weight $\overline{M}_w$.

$$\overline{M}_w = \frac{\sum\limits_{i=1}^{\infty} N_i M_i^2}{\sum\limits_{i=1}^{\infty} N_i M_i} \tag{2}$$

As can be seen from the equation, the numerator is divided or averaged by the weight of the specimen - hence the name weight average molecular weight.

$\overline{M}_z$ represents the Z-average molecular weight and is the next higher moment of the molecular weight distribution curve. This has the formula

$$\overline{M}_z = \frac{\sum\limits_{i=1}^{\infty} N_i M_i^3}{\sum\limits_{i=1}^{\infty} N_i M_i^2} \tag{3}$$

Another parameter that is used to measure changes in the molecular weight distribution curve is the polydispersity index, which is the ratio of the weight average to number average molecular weights. $\overline{M}_w / \overline{M}_n$ is a measure of the breadth of the distribution curve.
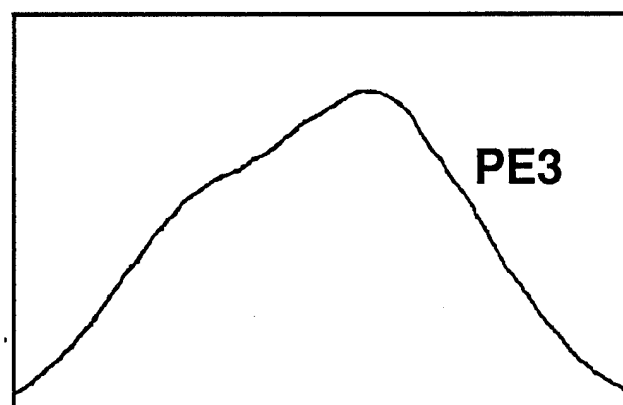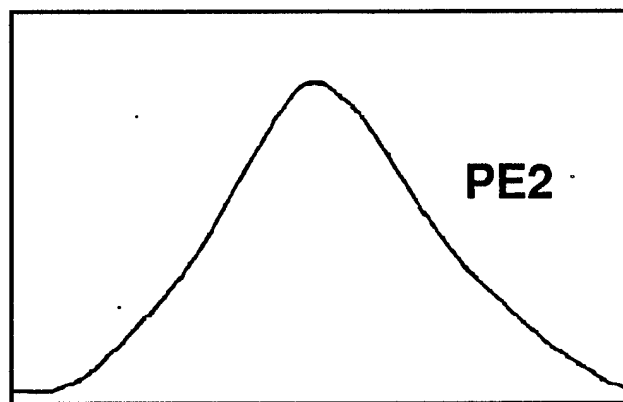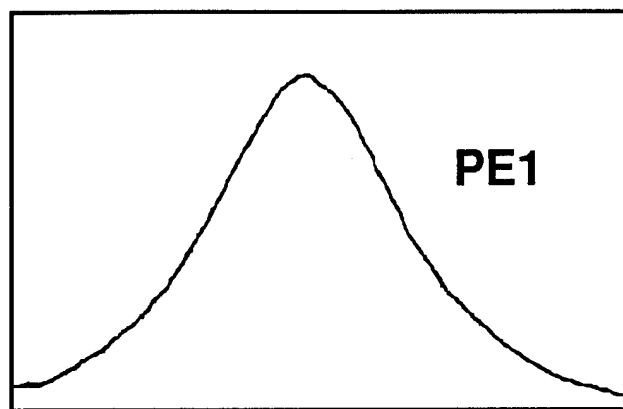
TABLE 13

Number, Weight and Z Average MW Values

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w / \overline{M}_n$
PE1/FLAKE	14,900	149,900	638,500	10.1
SCOM	14,200	153,200	645,000	10.6
PE2/FLAKE	9,600	139,900	637,700	14.5
CCOM	12,300	154,700	691,900	12.6
P3/FLAKE	7,900	210,600	950,300	26.7
HCOM	8,400	194,000	827,400	23.1
M445	16,200	208,700	791,500	12.9

Before looking directly at the values in the previous table, it may be useful to look at the chromatograms for each of the three polyethylenes investigated in this study. Representative chromatograms are shown as Figure 15 on the following page. As can be seen from the three plots, PE3, the Hoechst PE, appears to differ from the other two. Instead of having what appears to be a normal distribution, the Hoechst material appears to have a higher molecular weight shoulder in its chromatogram. The MWD for the Soltex (PE1) and Chevron (PE2) polyethylenes are similar. Remembering that the three polyethylenes had different ESCR properties as obtained from the first set of tests, the superior stress-crack resistance of the Hoechst material may be due to the presence of the higher molecular weight shoulder. For polyethylenes, the environmental stress-crack resistance is generally increased by an increase in molecular weight (17). On the other hand, the difference observed between the Chevron which had the poorest ESCR and the Soltex cannot be explained by differences in the molecular weight distributions.

During an earlier part of this work, several physical parameters were determined by X-ray analysis. The one of interest here is chain branching. Referring back to Table 7 on page 33, values are given for all three polyethylenes. The issue here is whether or not there is any difference between the Soltex and Chevron materials. As can be seen from the table, the difference in the methyl content per hundred carbon atoms is only 0.1 between the Chevron and Soltex materials. While this difference (about 1 in 20) is not overwhelming, the results qualitatively indicate a larger extent of intercrystalline entanglement with the Soltex material. Again, these results agree well with the theories dealing with the effect of molecular structure on ESCR.

SEC CHROMATOGRAMS OF PE1, PE2, PE3
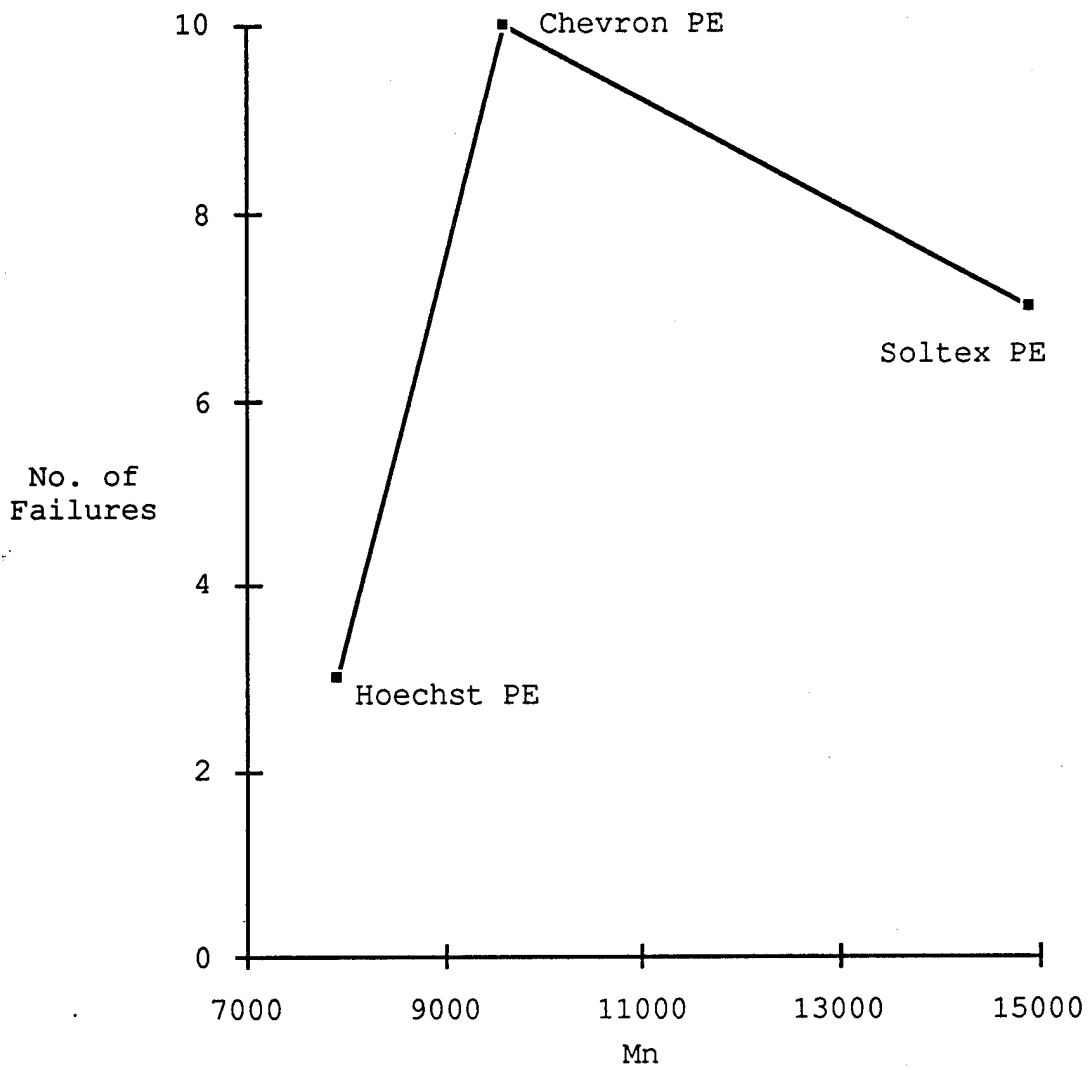
Figure 15

47

Referring back to the values in Table 13, the number average molecular weight for the Soltex flake (14,900), appeared to be about 50% greater than that for the Chevron flake (9600). Similarly, this is in agreement with the theory that the higher molecular weight produces better ESCR properties.

However, if one looks at the number average molecular weight, Figure 16, for the Hoechst material (7900), it appears that the material with the best ESCR had the lowest molecular weight. Therefore, it appears that number average molecular weight alone does not explain the change in properties.

Looking at the values for weight average molecular weight shown in Figure 17, the best material (Hoechst) had a value of 210,600; the second best material (Soltex) had a value of 149,900; and the worst material (Chevron) had a value of 139,900. From these results it appears that the ESCR of the polyethylenes correlate well with the weight average molecular weights. In other words, the ESCR increases with increasing weight average molecular weight.

The z-average molecular weights were also plotted to show how they correlate to the number of failures. These results are shown in Figure 18.

Processing was not found to produce any significant difference in either the MW or MWD for all three polyethylenes compounded in this investigation. Even at the low antioxidant loading levels, the SEC analysis method did not detect any changes in MW or MWD when compared to the unprocessed polymer flake. Specifically, the differences found in the ESCR results for the Chevron compounded with the low concentration of Cyanox at the two processing temperatures could therefore not be explained by changes in either the molecular weight or molecular weight distribution.

Number Average Molecular Weight for
Chevron, Hoechst, and Soltex PE's

FIGURE 16
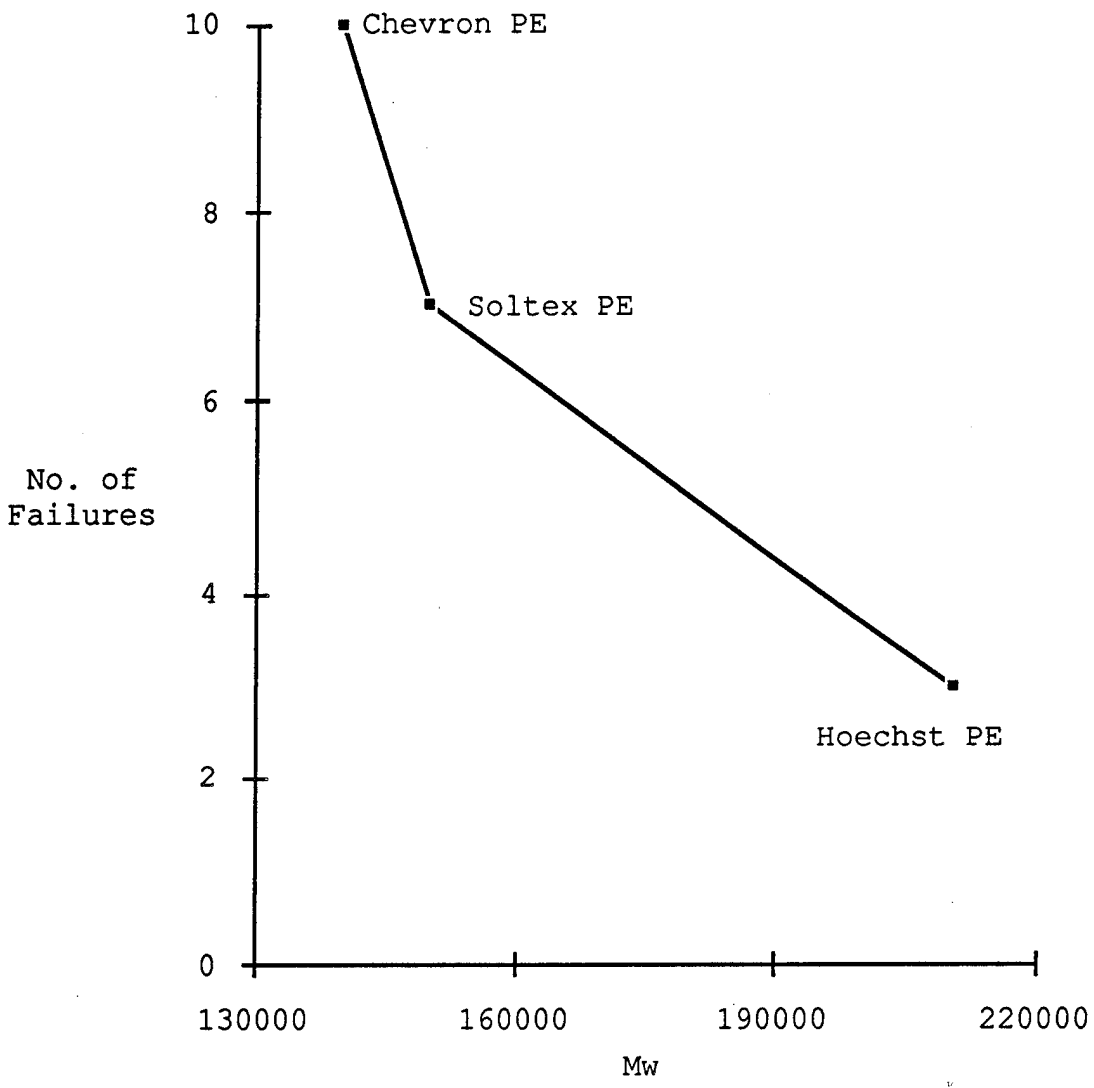
Weight Average Molecular Weight for Chevron,
Hoechst, and Soltex PE's

FIGURE 17
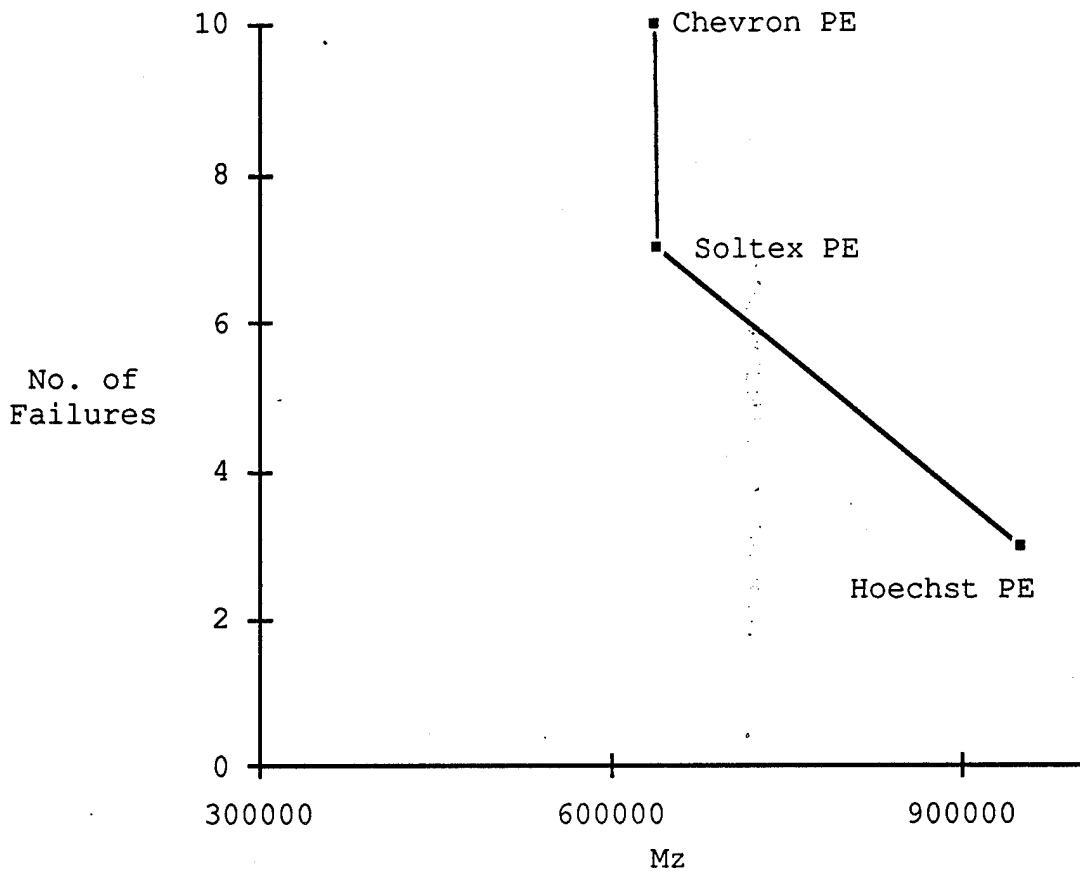
Z-Average Molecular Weight for Chevron,
Hoechst, and Soltex PE's

FIGURE 18

D. Other Mechanical Testing

The two biggest difficulties encountered in this thesis were with the ESCR tests. Firstly, the results from replicates did not appear to be consistent, and secondly the test took too long to do (5000 hours).

The lack of consistency in the case of the Chevron PE compounded in this study appeared to be a problem. A closer examination of the results revealed that the number of failures in the test decreased with the amount of time that had elapsed since the material had been extruded. The first set of ESCR tests showed ten failures; the second set two; and the last set zero. There are several possible explanations for this type of behavior.

A search of the literature revealed similar results to those obtained in this thesis. In determining the longevity of polyethylene, Scholten, Pisters, and Venema (18) observed that solutions of nonionic exthoxylated nonyl phenols such as Igepal, Anthrox, and Arkopal showed a pronounced brown discoloration after extended use.

The workers tested specimens punched out from butt welded pipes under constant load at 80°C using 2% Arkopal N100 solutions of different ages. Their results showed, for example, that the average time to fail for a freshly prepared solution increased from 38 hours to 81.5 hours when the solution was 1557 hours old at the outset of the experiment. It should also be noted that more than the twofold increase in the average failure time was accompanied by more than an order of magnitude increase in the standard deviation from a value of 3.1 to 40. From their experiments, the authors concluded that the average failure times of the pipes became progressively longer as the age of the solution increased.

Measurements made on the discolored solutions revealed pH values of between 3 and 5. Further experiments with 2% solutions of Arkopal held at 80°C revealed two important effects that are relevant to this investigation.

Firstly, when the detergent solution was allowed contact with air, the pH value was observed to drop quickly with time from about 9 to about 3. In contrast, measurements of the pH of the Igepal CO-630 used in these experiments showed little if any change between the beginning and end of the test (5000 hours).

Secondly, in an elegant experiment, the workers showed that the change in the nonionic detergent was due to oxidation. By blanketing the Arkopal solution with nitrogen and thus preventing contact with oxygen, the pH was observed to increase slightly and then remain constant with time. The presence of oxidation was

52

further reinforced by infrared spectroscopy. Again it should be noted that the stoppered test tubes used in this work were filled with Igepal CO-630, which would preclude contact with air.

Although these other workers in the field have reported changes in the fluid medium and the average time to fail, this is apparently a result of using the solutions too long at an elevated temperature in contact with air. In the present work, fresh Igepal was used in each of the successive tests which were performed to determine the ESCR of the Chevron material, processed at the higher temperature and the lower concentration of antioxidant.

Another cause of the change in material behavior could have been due to the production of defects in the extrusion process and their subsequent removal with time. It is well known that exit effects for viscoelastic fluids can cause instabilities resulting in a broken extrudate. Tordella (19) coined the term "melt fracture" to describe this phenomenon. It is interesting to note that the pictorial example used in the text by McKelvey (20) (as supplied by Tordella (19)) to show this behavior was that of a polyethylene. The photograph of extrudates shows a worsening of the effect with increasing volumetric flow rate. The cracks and discontinuities produced in the surface of the extrudate would elevate the level of stress in that area and increase the probability of having the sample fail. It should be noted that no gross instabilities were observed in the extrudate when it was processed, but on the other hand, since no problem was expected, a microscopic examination was not made of the surface. Unfortunately, more than one year had elapsed since the materials had been extruded and it was impossible to test additional material.

Another possible mechanism for this effect could have been the relaxation of stresses produced by the process with time. Since the polyethylene is well above its glass transition temperature, $-110^{\circ}C$ (21), the residual stresses could relax with time, thus reducing the tendency of the material to crack under strain in a hostile environment.

Again, looking at the ESCR test, one takes a specimen containing a crack and deforms it to a given strain. The material is then immersed in a hostile environment until it cracks. Although the strain may be considered to be constant during the test, this assumption may not be made of the stress since polyethylene is viscoelastic. Furthermore, the elevation of temperature is also well known to hasten relaxation processes, which in turn further reduces the possibility that the stress remains constant during the test. Allowing this scenario to continue with time, it might be expected that at a given time the stress would relax to a level at which no cracking would occur

53

even in the presence of a chemical agent. Evidence of this type of behavior was obtained when the specimens were removed from the ESCR test fixture. The bent polyethylene samples showed little if any tendency to recover to a flat condition.

In order to test the hypothesis that the residual processing stresses had relaxed with time, repeat shrinkage determinations were made. These measurements were made on the Chevron samples, which were found to crack in the ESCR test. However, no significant difference was determined in the shrinkage results. These findings indicated that, if relaxation caused the change in material behavior, it was on a microscopic level.

The other difficulty experienced in the experimental work was that the ESCR test took too long to complete (5000 hours). Previous experience with other polyethylenes, e.g. HDPE's, has shown that this test can be quite productive - failure occurs in less than eight hours. In this case, most of the materials did not fail at 5000 hours and the test was terminated. In order to find a better test method, one would want a procedure which would break the specimens quickly.

After some thought, it was decided that a tensile test would be the solution to both of the problems. Firstly, even at the slowest strain rate possible on the machine, it was expected that the test would take no longer than a couple of days (rather than the 5000 hours required in the ESCR test). Secondly, the stress in the tensile test was envisioned as increasing with time (rather than decreasing with time as in the ESCR test).

Since it was anticipated that the tensile test would be much faster, it would also eliminate the long time periods, of about 6 months, between lots of ESCR tests. In addition, it would also permit the testing of more samples, which in turn would produce more precise results.
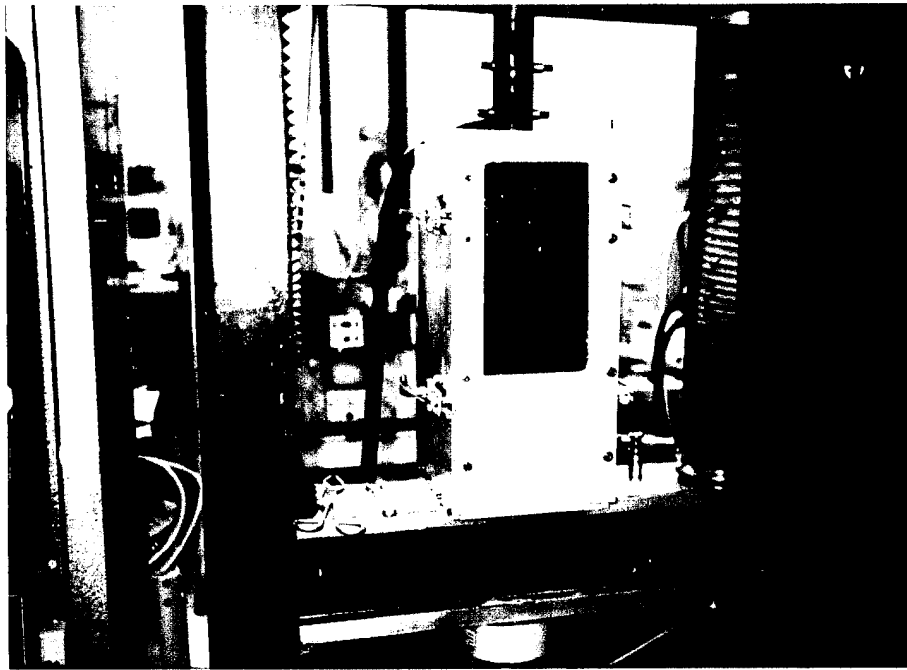
Immersion Tank Mounted on Instron

Figure 19

The first task was to make a tank which could be mounted on the Instron, which would house the grips and the stress-crazing agent. A previous attempt at making such a tank with polycarbonate at MTL failed since the tank cracked where the edges were mechanically fastened together with screws. A more suitable material was found to be aluminum. Aluminum however had one serious drawback. Since aluminum is not transparent, glass windows were installed in the tank to allow viewing of the specimen during the test. A picture of the tank can be seen on the previous page.

Two other important aspects of the tank design are as follows. In order to obtain the maximum working distance, it was decided to bolt the tank onto the movable crosshead. This eliminated the need for the male/female coupling which is normally used to attach the grip to the crossarm which takes up working distance.

The second aspect was a unique removable door. This door was utilized as a cover for part of the front of the tank. By having a false bottom, the front of the tank was designed so that the crazing agent did not have to be completely emptied after each test. From previous experience, it was found that if the entire front of the tank was removed there was an appreciable spillage of liquid. In addition, with a partial front, less time was required to empty the tank and still allow adequate room to reach the grips. A groove was machined along the front of the tank for a rubber gasket to assure a good seal. The door was held tightly in place by four latches, which could be easily opened and closed for removal and placement of specimens.

This immersion tank was found to work quite well by a previous graduate student. Charbonneau (22) investigated the effect of weld lines on the mechanical properties of several polymers in different media. The previous worker found significant decreases in the tensile strength with polycarbonate and nylon. However, when polyethylene was tested in Igepal, no significant difference in properties was detected. It should be stated that the polyethylene was tested at 72°F and not at the elevated temperature used in the ESCR test. Therefore, it was anticipated that the test might have to be run at an elevated temperature which in turn might require a heated tank.

Since orientation had previously been shown to be an important factor in the ESCR results, it was decided to look at this effect first. It was thought that, by injection molding the polyethylene, the orientation effect could be increased further than that obtained by extrusion. It was also anticipated that the production of these "fresh specimens" would give samples with high residual processing stresses (and without the melt fracture surface flaws) which were theorized to cause the stress-cracking.

56

Unfortunately, when the Chevron polyethylene was injected into the standard test mold, it was found that the material would not flow and pack the mold. This was due to the low (fractional) melt index of the Chevron PE.

Since the previous approach to the problem did not work, it was decided to look at the effect of orientation with the extruded specimens.

In order to obtain a benchmark for comparison, samples of polyethylene were first tested at room temperature. All mechanical testing was done on a Universal Testing Machine, mechanical screw type, (Model #TT-01, Serial #31) manufactured by Instron Engineering Corp., Canton, MA. The first set of tests for this experiment was performed at a crosshead rate of 2"/min. using a standard ASTM D638 tensile bar. A Microcon I from Instron (Model #4100, Serial #70695) data analysis system was utilized to reduce the data. Unfortunately, the specimens would not break in the test - the machine traverse was not long enough. For this reason it was decided to try a shorter ASTM D1708 specimen.

Similar tests with the sub-sized specimen showed that failure occurred within the traverse length of the tensile tester. This result also reduced the concern of the sample extending beyond the surface of the liquid in the immersion test. For this reason, it was decided to use the microtensile specimen as described in ASTM D1708.

Tensile tests were performed on the sheet materials according to ASTM D638 with the microtensile specimens to obtain mechanical properties in both the parallel and transverse directions. It was desired to obtain the parameter which was the most sensitive in order for comparison of the various effects. For example, as the stiffness of the material increases, the toughness decreases. Rather than make a repetitious analysis of several properties which in effect show the same thing, it was decided to pick the one property which had the largest amount of change normalized by the variability. The sensitivity was calculated using the following equation:

$$q = (X1 - X2) / S.D. \tag{4}$$

where   q: sensitivity
      X1: average of data set 1
      X2: average of data set 2
    S.D.: largest standard deviation between the two sets.

For example, one can see the values listed in the table on the following page. The properties measured or calculated from the load-deformation curve were the yield load in pounds, yield energy in inch-pounds, yield elongation in inches, the yield

stress in psi, the yield strain in percent, the breaking load in pounds, the breaking energy in inch-pounds, the breaking elongation in inches, the breaking stress in psi, and the breaking strain in percent.

TABLE 14
Sensitivity Measurements for Chevron Commercial PE

Property	A	B	$\Delta M/S_{n-1}$
Yield Load (Lb.)	40.28	38.94	0.8246
S_{n-1}	1.2138	1.6251	
Yield Energy (in-lb)	6.808	6.4319	0.3225
S_{n-1}	1.0301	1.1663	
Yield Elong. (in)	.2341	.2281	0.2239
S_{n-1}	.0268	.0265	
Yield Stress (psi)	2701.3	2651.6	0.8506
S_{n-1}	43.29	58.43	
Yield Strain (%)	23.41	22.81	0.2236
S_{n-1}	2.683	2.646	
Break Load (lb)	61.70	75.02	3.7638
S_{n-1}	3.207	3.539	
Break Energy (in-lb)	528.0	756.5	6.4933
S_{n-1}	35.15	35.19	
Break Elong. (in)	13.46	18.32	9.896
S_{n-1}	.4911	.3351	
Break Stress (psi)	4137.1	5107.9	5.730
S_{n-1}	169.44	122.22	
Break Strain (%)	1346.2	1831.6	9.884
S_{n-1}	49.11	33.51	

A: With Flow

B: Transverse Flow

Looking at the individual values, it can be seen that the yield load with flow is 40.28 pounds versus a value transverse the flow of 38.94 pounds. The absolute difference in the values was calculated as the absolute difference between the numbers in

58

column A and column B, this result, ΔM, was divided by the larger of the two standard deviations (1.6251) to obtain a sensitivity of 0.8246. Similar calculations were made for all the parameters.

For the case of the breaking elongation in inches, a value of 13.46 was obtained with the flow. When the orientation of the specimens was changed to the transverse direction, the elongation was found to increase to 18.32 inches.

Again, looking at the change produced by orientation, the results appear to be consistent with theory. Since there were no apparent problems, a decision was made at this point to determine the most sensitive parameter.

Looking at the results in Table 14 in the right hand column, one can see the sensitivities calculated for all the parameters. From these results, it appears that the breaking strain and breaking elongation had similar values for the sensitivity at 9.9. Comparing these values to the next most sensitive parameter, the energy at break, it can be seen that the sensitivity of either elongation or strain was about 50% more than that of the load at break (6.4). From the results it was decided to use the strain at break because this is the more common value used in engineering applications. (It should be noted that this calculation to determine the most sensitive parameter was repeated at several later stages in the investigation. The results showed consistently that the strain at break was the most sensitive parameter.)

When the issue of sensitivity had been resolved, the next task was to find a method to show whether the effect of orientation, the type and/or level of antioxidant, or processing temperature was significant. From the variability of the test results shown in the previous table, it was decided to use a statistical test. Since the average value was of more interest than the scatter of the values, a t-test was chosen. Because the difference of the results could be either positive or negative, a two-sided test was used. The same method of analysis was used for all of the test results and can be seen summarized briefly below.

Using the results of the strain at break values used in the sensitivity calculations, the method is as follows. Since the null hypothesis is that the means come from the same population, all of the individual values are combined to calculate a pooled variance.

$$S_p = \sqrt{\frac{(n_A-1)S^2_A + (n_B-1)S^2_B}{n_A+n_B-2}} \qquad (5)$$

Using the values for the standard deviations (ten tests were performed in all cases) a pooled variance of 42.21 was obtained.

The next step involves the calculation of a confidence band from the pooled variance. In order to do this a value of t must be obtained from a table. In this case, it was decided to accept a chance of 5% of being wrong or in other words a confidence of 95% of being right. For 18 degrees of freedom at a 95% confidence level, the value of t was found to be 2.101 (23). The confidence interval is calculated as follows.

$$U = t_{1-\alpha/2} S_p \sqrt{\frac{n_A + n_B}{n_A n_B}} \qquad (6)$$

Substituting the values into the above equation, one obtains a confidence interval of 39.66.

The last step involves calculating the absolute difference between the two experimental means. If this difference is less than or equal to the confidence level previously calculated, the null hypothesis is accepted. The means came from the same population. Calculating this difference it can be seen that the difference is greater than the confidence interval. For this reason the null hypothesis was rejected or in other words, the means are different. From these results one can conclude with a 95% degree of certainty, that testing the material at a 90 degree off axis angle changes the strain at break.

Numerous tensile tests were performed in a variety of situations to try and find significant differences produced by the main effects. These tests were conducted in both air and Igepal.

The strains at break were then compared using a statistical method, namely the Student's two sided t-test. This method was also used at MTL earlier, where weld lines in polycarbonate, nylon, and polyethylene were investigated in a variety of solvents. The stress-crazing agents used were ethanol, heptane, and Igepal CO-630. Micro tensile specimens were used for the tests in order to keep the specimen fully submerged.

In order to most closely mimic the state of stress in the ESCR test, it was decided to use a standard tensile bar (ASTM D256) with the inclusion of a notch.

Using the same gage length specimen and the same material, leaves three remaining variables. These are: the test speed; the orientation of the material; and the testing medium. Rather than complete the entire set of experiments, it was decided to do a few preliminary tests to see if any significant differences were obtained. The results of this first set of tests can be seen in Table 15.

TABLE 15
Chevron Commercial Material With Notch
at Room Temperature

SET	ORIENTATION	SPEED (in./min.)	MEDIUM	BREAK STRAIN
1	Parallel	0.5	Igepal	47.29±0.9575
2	Transverse	0.5	Air	46.13±0.8843
3	Parallel	0.05	Igepal	50.27±2.341
4	Transverse	0.05	Air	50.12±0.6697

Looking at the results for sets 1 and 2 in the previous table, one can see there was very little if any difference produced by changing the orientation and test medium. In fact when the two sets of results were compared statistically by calculating the confidence interval as discussed previously, it was concluded that the two sets came from the same population or in other words; there was no difference. Similarly, in looking at sets 3 and 4 the same statistical conclusion was obtained.

From the previous set of results, it became apparent that the Igepal was not significantly reducing the strain to break. It was theorized that the Igepal did not have sufficient time to attack the polyethylene. For this reason it was decided to test the MDPE at lower speeds. From the previous discussion it was apparent that a shorter specimen would be required to prevent the material from extending beyond the fluid medium during the test. The next set of tests was done to compare reducing the gage length from 2.5 to 1 inch. In both tests, commercial Chevron PE was used in the flow direction, at the same speed. The results can be seen in the following table.

TABLE 16

Comparison of Gage Lengths

Sample	Parallel Flow Break Strain
G.L.=2.5"	1350±31.70%
G.L.=1.0"	1346±49.11%

An analysis of the results showed that there was no statistical difference between the tests. Further testing was done using speeds of 0.05, 0.005, and 0.002 inches per minute.

Contrary to that expected, if the Igepal had more time to attack the material, the strain to break increased rather than showing a decrease. In order to further test this hypothesis, the Chevron processed at the highest temperature with the lowest level of Cyanox, was also tested perpendicular to flow. The strains to break were higher than those obtained with the commercial material. These results are totally opposite to those obtained in the ESCR test.

The next step in the investigation was to increase the temperature of the Igepal during the test. At first thought, it was decided to use an immersion heater in the tank. When this was done, it was found that the available immersion heater was not able to heat the system to a high enough temperature. Another problem that was immediately obvious was that the immersion heater took an extremely long time to elevate the temperature of the medium. For this reason, an alternate method was tried.

It was decided to use a large capacity constant temperature bath (whose heater could not be removed) and pump the liquid into the tank just prior to testing. By measuring the temperature of the fluid during the tensile test, it was found that there was no appreciable change in temperature. Therefore, this new set-up was utilized where the Igepal was constantly heated in a water bath, and pumped in and out of the tank for testing. This new method provided a faster means of testing samples in a controlled environment.

When the polyethylene was tested at an elevated temperature of 60°C in Igepal, the strain at break showed a significant decrease. Numerous sets of tests using polyethylenes processed at different conditions with varying amounts of antioxidant, showed this generality in behavior. From these results, the next question became immediately apparent. Did the decrease in the strain to break result from the increased chemical attack of the Igepal, or just from the increase in temperature? To answer this question, a set of samples were tested at 60°C in water.

When the commercial Chevron specimens, having a gage length of 1" were tested in the flow direction at a crosshead speed of 2"/min. at 60°C in water, the average strain to the break was statistically the same as that obtained in Igepal at the same temperature.

IV. CONCLUSIONS

Of the three polyethylenes investigated in this study, the Hoechst Hostalen GM5010TN material had the best inherent resistance to environmental stress-cracking, the Soltex Fortiflex K4424-122 material had the second best resistance, and the Chevron Hi-D 9326 material had the least resistance. These differences were attributed to differences in the molecular weight, molecular weight distribution, and chain branching.

In addition to the differences in the polymers, a change in the ESCR was also produced by changing the chemistry of the antioxidant. For example, ten failures were obtained with the Chevron Hi-D 9326 PE containing the low level of Cyanox 1790, whereas no failures were obtained with the commercial material containing an "antioxidant package" processed at the same temperature.

Although changes in the ESCR of the material could be produced by changes in the chemistry, no direct evidence was found by changing the processing temperature. Replicate experiments, albeit conducted at time intervals up to seven months, showed an increase in crack resistance with time. It is thought that this effect masked the effect of using a higher processing temperature.

An indirect effect of processing was the orientation produced in the extruded sheet as evidenced by x-ray and shrinkage measurements. The orientation effect appeared to be far greater than that produced by changes in the chemistry. The orientation effect was shown dramatically by the fact that the samples were far more prone to cracking when tested in a direction transverse to extrusion.

The standard test to determine the ESCR properties of polyethylenes leaves much to be desired. By raising the processing temperature and lowering the antioxidant concentration, failures were produced with all three materials which were advertised to have ESCR times greater than 5000 hours. Unfortunately, large enough reductions in failure times could not be produced by reasonable changes in temperature or additive concentrations. An alternate method of testing using a constantly increasing level of strain rather than a constant strain, was not successful.

63

V. RECOMMENDATIONS

It is recommended that the three commercial materials used in this study undergo further evaluation, and should be tested in a more hostile environment. There are also a number of other commercially available medium density, pipe grade materials which could be investigated. Further research should be conducted in the area of expediting the stress-crazing test. Preliminary results of testing at an elevated temperature in a stress-crazing agent show promise of a more rapid ESC test.

VI. LITERATURE CITED

1. Desper, C. R., "Characterization and Selection of Polymer Materials for Binary Munitions Storage", AMMRC TR 83-45, 1983.

2. Desper, C. R., "Characterization and Selection of Polymer Materials for Binary Munitions Storage, Part 2: Characterization of LLDPE Resins", AMMRC TR 84-28, 1984.

3. Desper, C. R., "Characterization and Selection of Polymer Materials for Binary Munitions Storage, Part 3: Branch Content Determination", MTL TR 87-47, 1987.

4. Billmeyer, F. W., Jr., Textbook of Polymer Science, 3rd Edition, p.252, John Wiley & Sons, New York, 1984.

5. Kohlman, S.D., "The Effect of Processing Variables on the Environmental Stress Crack Resistance of Rotationally Molded Polyethylenes", University of Lowell, Master of Science Thesis, 1990

6. Kolhman, S.D., Petrie, S.P., Desper, C.R., "The Effects of Processing Variables on the Environmental Stress Cracking of Rotation Molded Polyethylenes", SPE Technical Papers (ANTEC), 32, 472-474 (1987).

7. Brostow, W., Corneliussen, R.D., Failure of Plastics, Hanser Publishers, New York, 1986

8. Kamiya, Y., Niki, E., "Oxidative Degradation", Chap.3 in, "Aspects of Degradation and Stabilization of Polymers", Jellinek, H. H. G ed., Elsevier Scientific Publishing Co., New York, NY, 1978.

9. Horng, P., Klemchuk, P. P., "Investigation of Thermal Oxidation and Stabilization of HDPE", Polymer Preprints, 25, p.76, 1984.

10. ASTM Standard Test Method D3539, "Molecular Weight Averages and Molecular Weight Distribution of Certain Polymers by Liquid Size Exclusion Chromatography Using Universal Calibration", ASTM, Philadelphia, PA.

11. Allbee, N., "A Review of Antioxidants", Plastics Compounding, (May/June 1984), pp.70-82.

12. A. Keller and M.J. Machin, J. Macromol. Sci. B1, pp.41-91, 1967

13. Desper, C. R., "Characterization and Selection of Polymer Materials for Binary Munitions Storage, Part 3: Branch Content Determination", MTL TR 87-47.

14. Doherty, R. D., Strutt, T. R., "Crystallite Orientation in Heat Shrinkable Polytetraflouroethylene Tubing", J. Materials Sci. 11, (1976), p.2173.

15. Wunderlich, B., Macromolecular Physics, Academic Press, New York, Volumes 1 and 2, 1973.

16. I.L. Hay and A. Keller, Kolloid Z. 204, 43, 1965

17. I.L. Hay and A. Keller, J. Mat. Sci. 1, 41, 1966

18. F.L. Scholten, J. Peters, and B. Venema, "A More Reliable Detergent for Constant Load Experiments on Polyethylene", pp. 385-405, 1989

19. J.P. Tordella, J. Appl. Phys., 27, p.454 (1956)

20. James McKelvey, Polymer Processing, Chemical Engineering, Washington University, John Wiley and Sons, Inc., New York, 1962

21. "Engineering Properties of Polyethylene", The Plastics Pipe Institute of the Society of the Plastics Industry, Inc., pp. 3-38, 1993

22. M. Charbonneau, "The Effect of Weld Lines on the Mechanical Properties of Nylon, Polycarbonate, and Polyethylene, University of Lowell, Master of Science Thesis, 1989

23. "Engineering Design Handbook - Experimental Statistics", AMC Pamphlet No. 706-110, (1969), p.3-34.

APPENDIX A: Dimensional Stability

Polyethylene Peak Position Correction Using Graphite Standard

Raw 2Θ	True 2Θ	D, Angstroms	Chemplex
26.8	26.576	3.353986	
21.75	21.526	4.128046	
24.19	23.966	3.713007	

Raw 2Θ	True 2Θ	D, Angstroms	Chevron
27.34	26.576	3.353986	
22.13	21.366	4.158596	
24.55	23.786	3.740696	

Raw 2Θ	True 2Θ	D, Angstroms	Soltex
27.4	26.576	3.353986	
22.17	21.346	4.162447	
24.6	23.776	3.742247	

Raw 2Θ	True 2Θ	D, Angstroms	Hoechst
27.47	26.576	3.353986	
22.24	21.346	4.162447	
24.67	23.776	3.742247	

Polyethylene Branch Content From D200 Value
Using Slope 33.03 [A (zero)] 7.426

D200	A	[CH3/100C]	Sample
3.7407	7.4818	1.829858	Chevron
3.74225	7.4845	1.932249	Soltex
3.74225	7.4845	1.932249	Hoechst

67

DISTRIBUTION LIST

No. of Copies	To

1   Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301

Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1   ATTN: AMSRL-OP-SD-TP, Technical Publishing Branch
1   AMSRL-OP-SD-TA, Records Management
1   AMSRL-OP-SD-TL, Technical Library

Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 23304-6145
2   ATTN: DTIC-FDAC

1   MIA/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905

Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211
1   ATTN: Information Processing Office

Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1   ATTN: AMCSCI
1   AMCMI-IS-A

Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1   ATTN: AMXSY-MP, H. Cohen

Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35809
1   ATTN: AMSMI-RD-CS-R/Doc

Commander, U.S. Army - ARDEC, Information Research Center, Picatinny Arsenal, NJ 07806-5000
1   ATTN: AMSTA-AR-IMC, Bldg. 59

Commander, U.S. Army Natick Research, Development and Engineering Center Natick, MA 01760-5010
1   ATTN: SATNC-MI, Technical Library
1   SATNC-AI

Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1   ATTN: Technical Document Center

Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1   ATTN: AMSTA-ZSK
1   AMSTA-TSL, Technical Library
1   AMSTA-SF

President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307
1   ATTN: Library

No. of Copies	To

Director, U.S. Army Research Laboratory, Weapons Technology, Aberdeen Proving Ground, MD 21005-5066
1   ATTN: AMSRL-WT
2   Technical Library

Commander, Dugway Proving Ground, UT 84022
1   ATTN: Technical Library, Technical Information Division

Commander, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783
1   ATTN: AMSRL-SS

Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1   ATTN: AMSMC-LCB-TL
1   AMSMC-LCB-R
1   AMSMC-LCB-RM
1   AMSMC-LCB-RP

Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901-5396
3   ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger

Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1   ATTN: Technical Library

U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1   ATTN: Building 5906-5907

Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 3636
1   ATTN: Technical Library

Commander, Clarke Engineer School Library, 3202 Nebraska Ave., N., Fort Leonard Wood, MO 65473-5000
1   ATTN: Library

Commander, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39180
1   ATTN: Research Center Library

Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1   ATTN: Quartermaster School Library

Naval Research Laboratory, Washington, DC 20375
1   ATTN: Code 6384

Chief of Naval Research, Arlington, VA 22217
1   ATTN: Code 471

Commander, U.S. Air Force Wright Research and Development Center, Wright-Patterson Air Force Base, OH 45433-6523
1   ATTN: WRDC/MLLP, M. Forney, Jr.
1   WRDC/MLBC, Mr. Stanley Schulman

No. of Copies	To

U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899
1 ATTN: Stephen M. Hsu, Chief, Ceramics Division, Institute for Materials Science and Engineering

1 Committee on Marine Structures, Marine Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418

1 Materials Sciences Corporation, Suite 250, 500 Office Center Drive, Fort Washington, PA 19034

1 Charles Stark Draper Laboratory, 555 Technology Square, Cambridge, MA 02139

General Dynamics, Convair Aerospace Division, P.O. Box 748, Fort Worth, TX 76101
1 ATTN: Mfg. Engineering Technical Library

Plastics Technical Evaluation Center, PLASTEC, ARDEC, Bldg. 355N, Picatinny Arsenal, NJ 07806-5000
1 ATTN: Harry Pebly

1 Department of the Army, Aerostructures Directorate, MS-266, U.S. Army Aviation R&T Activity - AVSCOM, Langley Research Center, Hampton, VA 23665-5225

1 NASA - Langley Research Center, Hampton, VA 23665-5255

U.S. Army Vehicle Propulsion Directorate, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
1 ATTN: AMSRL-VP

Director, Defense Intelligence Agency, Washington, DC 20340-6053
1 ATTN: PAQ-4B (Dr. Kenneth Crelling)

U.S. Army Communications and Electronics Command, Fort Monmouth, NJ 07703
1 ATTN: Technical Library

U.S. Army Research Laboratory, Electronic Power Sources Directorate, Fort Monmouth, NJ 07703
1 ATTN: Technical Library

Director, U.S. Army Research Laboratory, Watertown, MA 02172-0001
2 ATTN: AMSRL-OP-WT-IS, Technical Library
5 Author

70