

## Mechanism of Environmental Stress Cracking in Linear Polyethylene\*

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### INTRODUCTION

Environmental stress cracking can be defined as the accelerated failure of a stressed polymeric member resulting from specific environmental activity. This phenomenon occurs in linear and branched polyethylene, and is by now well known. Extensive studies of stress cracking have been carried out with the Bell Telephone Laboratories bent strip test<sup>1</sup> in which a notched strip of polyethylene is bent nearly double and immersed in a detergent. Under the influence of complex stresses and the active environment, rupture occurs. However, the results of this test are strongly dependent on the elastic modulus of the test specimen. Carey<sup>2</sup> has shown that more meaningful data can be obtained from a test which imparts a constant uniaxial tension to the specimen. With this test, Carey has studied the stress and temperature dependence of the time to failure; and, utilizing a similar test, Lander<sup>3</sup> has explored the effect of melt index and density on the time required for rupture for both linear and branched polyethylene. The mechanism of environmental stress cracking, however, has received comparatively little attention. Hopkins and Baker<sup>4</sup> have postulated a mechanism involving the spreading pressure of liquids adsorbed onto surface cracks. The recent studies of Keith and Padden<sup>5</sup> and Ullman<sup>6</sup> of the morphology of stressed polyethylene films are noteworthy. The purpose of the present work has been to obtain as complete as possible a description of the stress-cracking process on both a macro and micro scale with a view toward understanding the mechanism of environmental attack and ultimate failure. In addition, the effect of low molecular weight species on the stress-crack resistance of linear polyethylene has been examined in quantitative fashion. Stress cracking in various liquid media has also been studied together with related tests to learn whether some specific property of an environment determines its ability to cause stress cracking.

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## EXPERIMENTAL

The construction and operation of the Carey-type stress-cracking device has been described<sup>2</sup> previously. The original design has been modified to accommodate smaller samples (3.5 in.  $\times$  0.25 in.  $\times$  0.010 in.) and to facilitate visual observation (see Fig. 1). For microscopic observation, a spring-loaded device was employed which consisted of a stationary and movable jaw of such size that it could be placed on microscope stage. Very thin (0.002–0.0005 in.) samples were used. For the majority of this

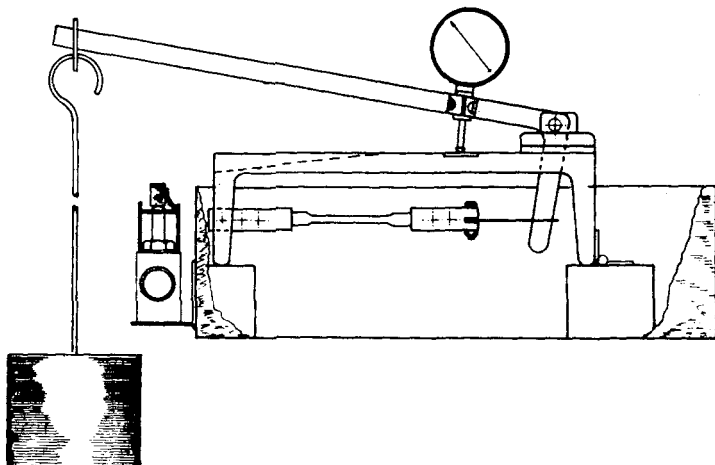


Fig. 1. Modified Carey-type stress-cracking apparatus.

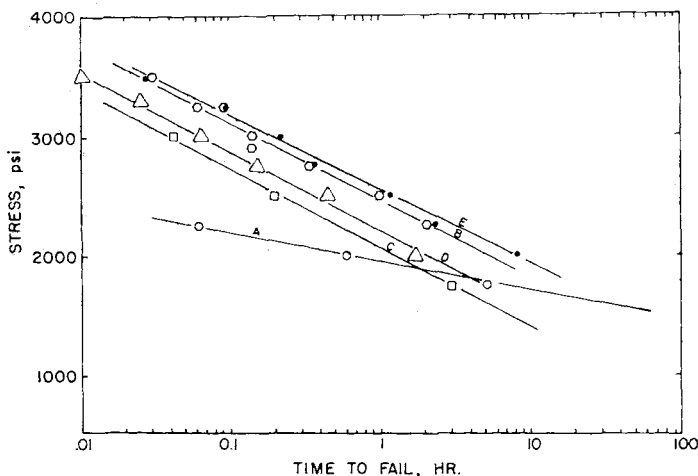


Fig. 2. Effect of crystallinity on environmental stress-crack resistance: (A) quenched, density 0.9431 g./cm.<sup>3</sup>; (B) annealed at 112°C., 0.9564 g./cm.<sup>3</sup>; (C) annealed at 98°C., 0.9495 g./cm.<sup>3</sup>; (D) annealed at 105°C., 0.9529 g./cm.<sup>3</sup>; (E) slow-cooled in press, 0.9549 g./cm.<sup>3</sup>.

work, isopropyl alcohol was chosen as the active environment because of its chemical simplicity and stability relative to the commonly used detergents. In all cases, films were compression-molded at 350°F. and allowed to cool over a period of 2-3 hr. in a laboratory press except when stated otherwise. Polyethylene of 0.960 g./cm.<sup>3</sup> density and of melt index 40 was used along with a moderately sharp fraction prepared by solution precipitation from the same whole polymer.

The advantages of the Carey-type stress-cracking test have been described in detail by Lander.<sup>3</sup> This test is carried out by applying a pre-determined stress to a test piece and recording time to failure. In an active environment at loads approaching the yield stress, rather ductile failure with much cold-drawing is observed. At lower stresses, the failure is more and more brittle in nature. Although the gross nature of the failure changes in this fashion, the relationship between stress and log time to failure is linear over at least five decades of time. The data in Figure 2 show the increase in stress-crack resistance that accompanies an increase in crystallinity. This relationship has been previously observed.<sup>3</sup>

## DISCUSSION

### Microscopic Examination of the Stress-Cracking Process

Optical examination of thin films of the whole polymer under tensile stress have been made in the following manner: films of 0.002-0.0005 in. thickness were first annealed at 120°C. for 4 hr. The resultant structure was a monolayer of spherulites volume filling in some areas. A film strip was mounted in the micro stress apparatus, and a constant load applied to produce an initial stress of 2000 p.s.i. A razor cut was made in the edge of the specimen to localize the phenomenon for microscopic observation, and the sample immersed in distilled water, a nonactive environment.

Figure 3 shows a series of microphotographs taken at 140 diameters as a function of time. One can see the development of "fissures" or elliptical shaped microzones of cold drawing which develop in advance of the razor cut. These fissures are seen to form both in spherulite diameters and at interspherulite boundaries with no apparent preference for either. Gradually, the razor-cut edges spread apart, with cold-drawn material forming at the cut tip. This drawn area grows by means of the development and interconnection of the fissures, but the drawn material remains largely unbroken. Since this drawn material reinforces the cut edges, growth is slow, and large-scale cold drawing eventually results.

In the presence of an active environment, the development of a field of fissures in advance of the razor cut occurs in the same fashion. However, as the parabolic region of drawn material forms at the cut tip, it is seen to suffer rupture and ultimately complete failure (see Fig. 4). Careful study of the distribution of drawn material led to the conclusion that the location of the beginning of ultimate failure was at the zone between drawn and undrawn material at the crack tip. Since the drawn material

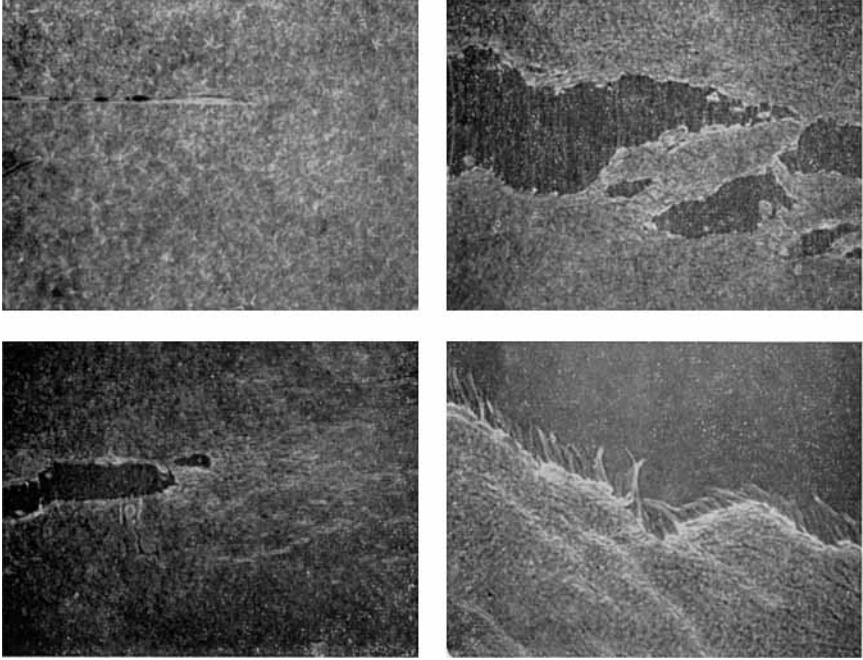


Fig. 3. Response of a notched polyethylene specimen to stress in water. Phase contrast, 70 $\times$ .

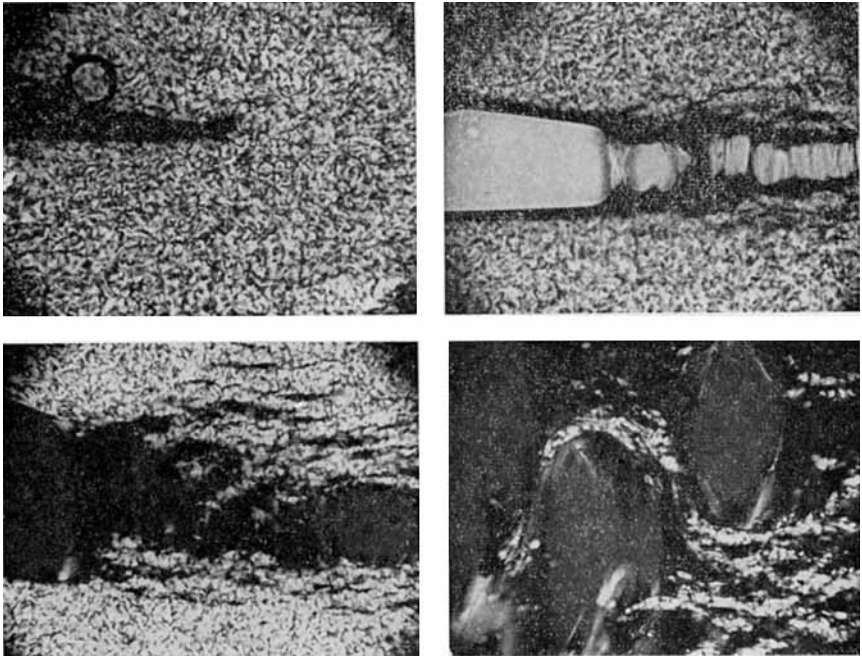


Fig. 4. Response of a notched polyethylene specimen to stress in igepal. Crossed polaroids, 70 $\times$ .

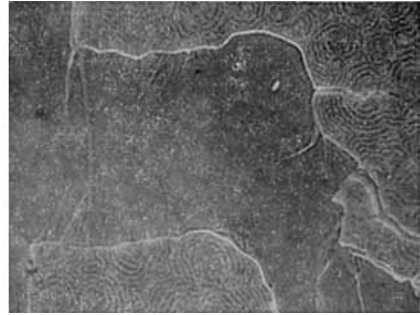
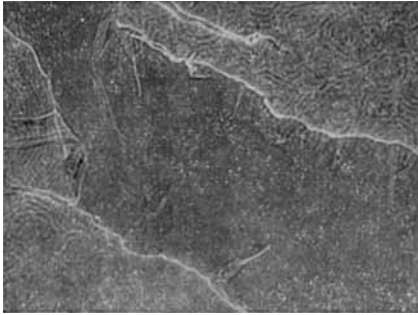
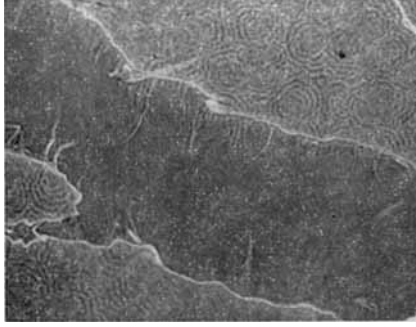


Fig. 5. Fracture edge of an unnotched sample stressed in igepal. Phase contrast, 70X.

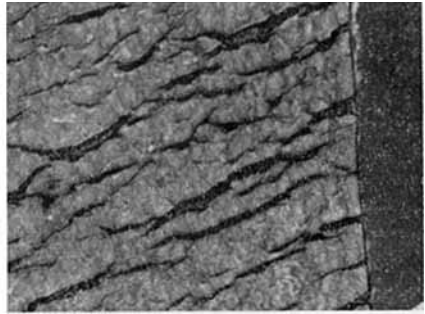
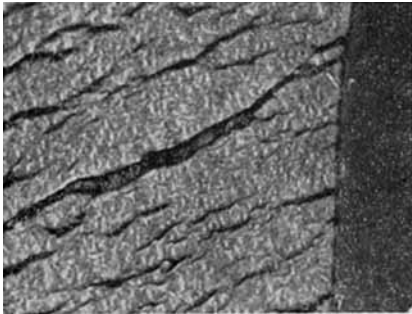
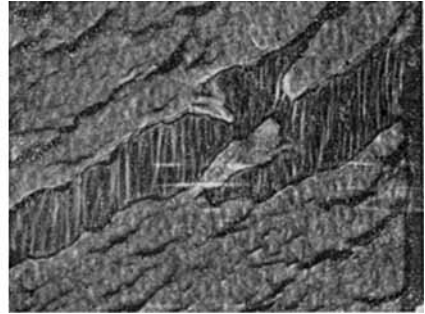


Fig. 6. Response of an unnotched polyethylene specimen to stress in water. Phase contrast, 70X.

ruptures as it develops in an active environment, little support is given the crack edges and crack growth is very much more rapid.

In order to confirm the view that the region of environmental attack was indeed the zone between drawn and undrawn material, a tensile dumbbell sample of whole polymer was stretched in air until a cold-drawn region, ca.  $\frac{1}{2}$  in. long, had developed. The sample was then transferred to a Carey device and cold drawing allowed to continue for 10 min., at which time an active environment, isopropanol, was added. Almost immediately macro cracks parallel to the applied stress were observed to form at the drawing shoulder and to proceed out into the drawn material. Thus, in agreement with microscopic observations, the active environment causes *fracture specifically at the drawing boundaries*.

Figure 5 shows the fracture edge of a sample broken in an active environment. The main crack is seen to have proceeded both through the centers and through boundaries between spherulites. However, significant amounts of drawn material are seen only when the crack traversed the diameter of a spherulite, with little drawing being observed at boundaries.

The development of a field of fissures in a sample immersed in water is shown in Figure 6. These fissures are seen to interconnect, forming a large-scale drawing zone, and ultimately to fail with the broken edge exhibiting much cold-drawing. The development of areas of partial failure ahead of the main crack as observed in linear polyethylene is, of course, well known. Zinc foil, for example, exhibits fracture origins beyond the main crack which grow, join together and result in rapid crack extension.<sup>7</sup> This ductility of the fracture process in polyethylene accounts for the lack of notch sensitivity which has been observed. Notched specimens do not fail more quickly than those that are not notched at the same stress. Ultimate failure and rapid propagation of a crack across the entire specimen follows a general weakening of the specimen by the development of a system of localized small scale failures as described in the preceding paragraphs. A notch localizes the process by concentrating the stress field but does not otherwise appreciably accelerate the rate-determining weakening process ahead of the crack. In the absence of an artificial notch, weakening first occurs throughout the specimen to the point where rapid fracture may occur from a flaw or crack which may develop at an edge. Thus, the influence of small surface cracks as proposed by Hopkins and Baker<sup>4</sup> is not felt to be significant.

### Effect of Molecular Weight

It had been reported<sup>4</sup> that very low molecular weight species in polyethylene have a deleterious effect on strength properties and cause embrittlement under biaxial stress. In order to evaluate quantitatively the effect of a low molecular weight component on the stress-cracking behavior of linear polyethylene under uniaxial tension, mixtures were made of fraction 2 and linear hydrocarbons by coprecipitation. Three low molecular weight, linear hydrocarbons ( $\bar{M} \cong 500, 1500, \text{ and } 2000$ ) were added and the

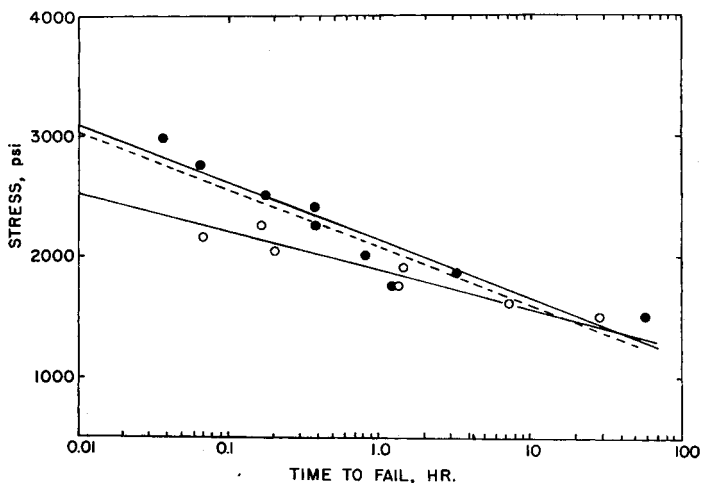


Fig. 7. Effect of the addition of a hydrocarbon  $M \sim 500$  on the stress-cracking resistance of Marlex 50 in isopropanol: (○) 90% Marlex 50, Type 40, Fraction 2 + 10% *n*-hexatriacontane; (●) 95% Marlex 50, Type 40, Fraction 2 + 5% *n*-hexatriacontane; (—) Marlex 50, Type 40, Fraction 2 control.

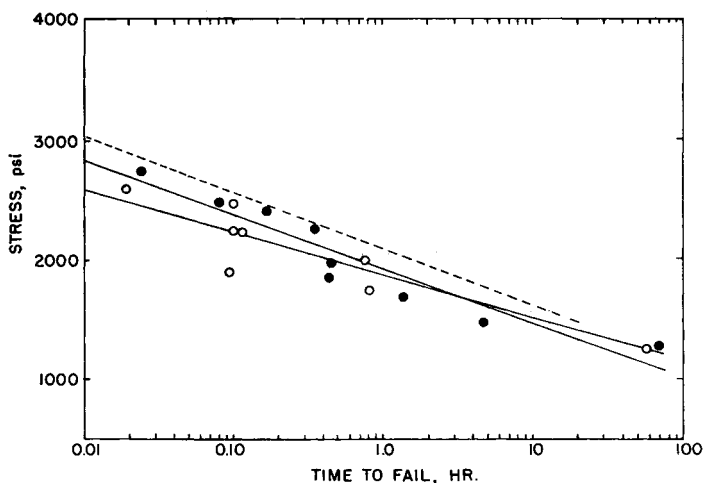


Fig. 8. Effect of the addition of a hydrocarbon  $M = 1500$  on the stress-cracking resistance of Marlex 50 in isopropanol: (○) 90% Marlex 50, Type 40, Fraction 2 + 10% PE 617 ( $M = 1500$ ); (●) 95% Marlex 50, Type 40, Fraction 2 + 5% PE 617 ( $M = 1500$ ); (—) Marlex 50, Type 40, Fraction 2, control.

mixtures tested to determine the effect of amount and molecular size of the addend on stress crack resistance. The data obtained are shown in Figures 7-9.

In the case of the mixtures containing the hydrocarbon of  $\bar{M} = 500$  and 1500, the plots relating stress and time to failure are found to converge at long times. This indicates that the presence of the addends has little

TABLE I  
Tensile and Related Data on Polyethylene-Low Molecular Weight Hydrocarbon Mixtures

Samples	Density, g./cm. <sup>3</sup>	Young's modulus, psi $\times 10^3$	Elongation at fail, %	Stress at fail, psi	Stress-cracking parameters <sup>a</sup>		$\bar{M}_n$ calc.	$\bar{M}_v$ calc.
					A, psi	B, psi		
Fraction 2	0.955 $\pm$ 0.001	140 $\pm$ 20	7 $\pm$ 0.5	3400 $\pm$ 100	2100	470	20,000 <sup>b</sup>	33,000 <sup>c</sup>
Fr. 2 + 5% (500)	0.954 $\pm$ 0.001	82 $\pm$ 10	11 $\pm$ 2	3180 $\pm$ 10	2050	600	6,800	29,000
Fr. 2 + 10% (400)	0.954 $\pm$ 0.001	80 $\pm$ 4	10 $\pm$ 1	3100 $\pm$ 100	1880	320	4,100	27,000
Fr. 2 + 5% (1500)	0.952 $\pm$ 0.001	72 $\pm$ 4	11 $\pm$ 1	2690 $\pm$ 10	1900	550	11,000	29,000
Fr. 2 + 10% (1500)	0.951 $\pm$ 0.001	81 $\pm$ 6	10 $\pm$ 3	2700 $\pm$ 100	1880	350	9,000	27,000
Fr. 2 + 1% (2000)	0.952 $\pm$ 0.001	—	—	—	1750	700	19,000	32,000
Fr. 2 + 3% (2000)	0.951 $\pm$ 0.001	—	—	—	2050	550	18,000	30,000
Fr. 2 + 5% (2000)	0.951 $\pm$ 0.001	Too weak and brittle to test	—	—	—	—	19,000	29,000

<sup>a</sup> Constants of the equation: stress =  $A - B \log$  (time-to-fail, hours).

<sup>b</sup>  $\bar{M}_n$  measured by osmotic pressure.

<sup>c</sup>  $\bar{M}_v$  obtained from intrinsic viscosity.



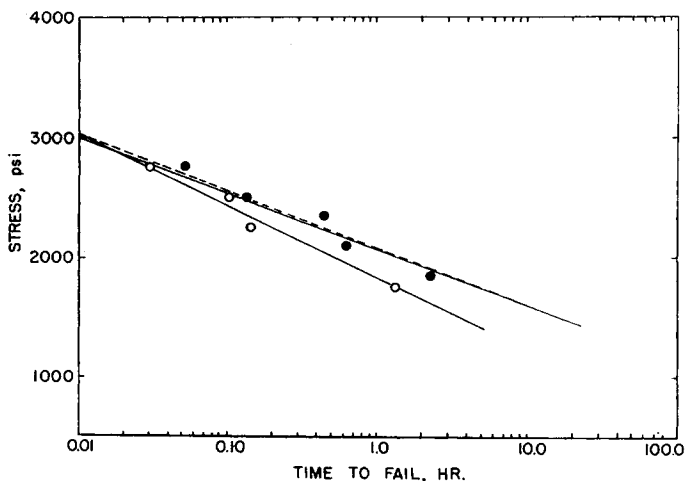


Fig. 9. Effect of the addition of a hydrocarbon  $M \approx 2000$  on the stress-cracking resistance of Marlex 50 in isopropanol: (○) 97% Marlex 50, Type 40, Fraction 2 + 3% PE 2000; (●) 99% Marlex 50, Type 40, Fraction 2, +1% Pe 2000; (---) Marlex 50, Type 40, Fraction 2, control.

effect on the long-term brittle type of failure. The shorter times to failure at higher stresses are probably related to the reduction of tensile properties resulting from the presence of the addend, as shown in Table I.

The flexural strength of all of the mixtures was very much less than that of pure fraction 2; none could be bent double without breaking. When linear polyethylene was blended with 5% of the hydrocarbon with  $\bar{M} = 2000$ , the resultant film was too brittle to test. Thus smaller quantities of this addend were used. All hydrocarbon mixtures exhibited very little cold drawing on tensile testing. The inability of these specimens to absorb energy by cold drawing probably causes the shorter times to failure at high stresses. This effect may be balanced at lower stresses, however, because fewer sites of environmental attack may be available in samples which do not cold-draw readily.

An investigation of the disposition of the hydrocarbon in the polyethylene was carried out (see Appendix). Through x-ray and dilatometric measurements it was concluded that the hydrocarbon is finely distributed as a discrete phase in the polyethylene disordered regions. The weakening of these areas which would result probably contributes to the inability of these samples to cold-draw.

### Role of Crystallinity

As has already been pointed out by Lander,<sup>3</sup> more highly crystalline polyethylene specimens are more resistant to stress cracking, when compared on an equivalent stress basis. In the bent strip test, the opposite result is obtained because strain rather than stress is constant, at least

initially. Figure 2 shows the results obtained on samples of whole polymer the density of which was varied by thermal treatment. At any given stress, more crystalline samples require a longer time to fail. The behavior of the quenched samples is not understood.

Attempts were made to determine the effect on stress crack resistance of reducing spherulite size while maintaining constant the degree of crystallinity. This was done in comparison to slow cooled films by quenching from the melt in ice water and subsequently annealing at 120°C. The average spherulite size was about half that of slow-cooled films (20 as opposed to 10  $\mu$  diameter). The crystallinity as measured by density was very nearly the same (0.954 and 0.955 g./cm.<sup>3</sup>, respectively). A very slight improvement was observed in the stress-cracking resistance of the film with smaller spherulites, but this was not sufficient to be considered significant.

### Environment Study

A further area of interest is the specific mechanism by which the environment weakens drawing shoulders and causes rupture. As a first attempt to determine the mechanism of environmental attack, two solvent properties, wettability and absorption, were measured as well as time to failure in the Carey test.

TABLE II  
Wettability and Stress Cracking Activity of Solvents

Solvent	Wettability <sup>a</sup>	Time to failure, hr. <sup>b</sup>
<i>n</i> -Amyl alcohol	4.5	2.5
<i>n</i> -Propanol	3.8	1.7
Acetone	3.8	Stretches
Ethanol	3.1	8.7
Dodecyl alcohol	2.6	3.4
Isopropanol	2.5	6.5
Toluene	2.1	Stretches
Methanol	2.0	50
Hexane	1.5	Stretches
Benzene	1.1	Stretches
Triresyl phosphate	0.3	14.6
Diethylene glycol	0.2	28.5

<sup>a</sup> Equilibrium area to which a 0.2-ml. drop spreads on a fresh polyethylene surface in cm.<sup>2</sup>

<sup>b</sup> Under 2000 psi stress.

The criterion of wettability has been advanced as the property which governs the stress cracking activity of an environment. The wettability of a series of solvents was determined as well as time to failure at a standard load. The data obtained are shown in Table II.

There appears to be no correlation between wettability and stress cracking. A further possible criterion is the quantity of liquid absorbed by the polymer. The results are shown in Table III.

TABLE III  
Equilibrium Absorption of Solvents in Polyethylene and Stress Cracking Activity

Solvent	Absorption, mmole-% <sup>a</sup>	Time to failure, hr. <sup>b</sup>
Benzene	74.5	0.77 <sup>c</sup>
Xylene	60.4	1.1 <sup>c</sup>
Hexane	53.2	0.3 <sup>c</sup>
Acetone	50.0	10.4 <sup>d</sup>
Toluene	43.0	0.85 <sup>c</sup>
Butyl acetate	22.0	1.0 <sup>c</sup>
Acetic acid	11.3	3.7
<i>n</i> -Amyl alcohol	9.8	2.5
Ethanol	8.7	13.2
<i>n</i> -Propanol	8.5	1.7
Isopropanol	5.7	6.5
Dodecyl alcohol	4.6	3.4
Diethylene glycol	8.5	28.5
Tricresyl phosphate	0.6	14.6
Water	0.2	55.0 <sup>d</sup>

<sup>a</sup> Absorption as wt. of solvent  $\times 10^5$ /wt. of sample  $\times M$  of solvent.

<sup>b</sup> Under 2000 psi.

<sup>c</sup> Stretches.

<sup>d</sup> Cold draw.

Inspection of Figure 10 will show that a reasonable correlation is obtained, the data falling into three more or less distinct zones. This suggests that for a given solvent it may be possible to alter the response of polyethylene to stress from homogeneous stretching (high absorption) to stress

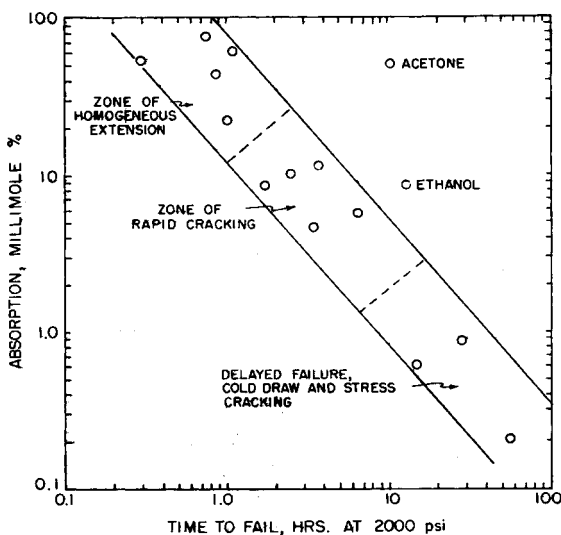


Fig. 10. Relationship of solvent absorption to time to failure of Marlex 50 in the Carey test.

cracking (intermediate absorption) to cold drawing (low absorption) by varying the solvent takeup. It was felt that vapor-phase experiments would be the best method of varying the extent of absorption and of testing this view.

In order to determine whether cracking occurs in a vapor environment, initial stress crack tests were run in isopropanol vapor in a sealed chamber. Cracking was observed, and time to failure at 2000 psi was found to be increased to 16 hr. from 6.5 hr. in the liquid phase. It was then decided to reduce the equilibrium absorption of benzene by decreasing its activity with dimethyl phthalate. It was desired to learn if benzene could cause cracking when its absorption was reduced to the "critical" range. Absorption experiments in the vapor phase gave the results shown in Table IV.

TABLE IV  
Vapor-Phase Absorption by Polyethylene of Benzene in  
Mixture with Dimethyl Phthalate

Benzene in mixture, %	Benzene absorbed, wt.-% <sup>a</sup>		
	17 hr.	41 hr.	113 hr.
0	0.10	0.12	0.14
5	0.24	0.48	0.42
10	0.47	0.70	0.70
20	0.44	0.90	0.90
50	0.94	1.39	1.26
100	5.40	5.53	5.64

<sup>a</sup> Error estimated to be  $\pm 8\%$ .

Corollary vapor-phase stress-cracking experiments were run with the use of 5, 10, 20, and 50% benzene mixtures. In every case, homogeneous extension resulted, as was the case with the pure solvent. It does not, therefore, appear possible to change the nature of the failure by changing the level of absorption. It must be concluded that the specific chemical nature of the solvent is important in the stress cracking process and not the level of absorption per se. For reasons not understood at this time, those solvents with high stress-cracking efficiency (Zone 2) simultaneously possess a chemical structure which results in limited solubility in the polymer.

It has been advanced in the literature<sup>7</sup> that oxidation of strained amorphous chains is a primary environmental effect. Carey tests run in an oxygen atmosphere, however, resulted exclusively in cold-drawing behavior. In addition, aqueous solutions of strong oxidizing agents such as  $\text{KMNO}_4$  have no stress-cracking activity, while solutions of salts such as  $\text{Na}_2\text{CO}_3$  do have such activity.<sup>8</sup> It is felt, therefore, that oxidation is not a primary environmental influence at room temperature.

The zone of reorganization is one of great disorder and stress concentration. Spherulitic structure is being destroyed and crystallites are being

sheared and redirected into a more ordered state. The resultant drawn material is white and opaque due to the large number of minute voids present. It is hypothesized that molecules of the active environment are strongly adsorbed onto newly formed internal surfaces in this highly activated zone. These partially polar molecules (most active environments consist of polar and nonpolar segments) could exert an internal or spreading pressure on this already weakened structure and in addition, could inhibit crystal alignment and reformation. As a result, the structure of the shoulder is no longer sufficiently strong to pass over the energy barrier between the drawn and undrawn states. Internal pressure is observed when hydrogen diffuses into steel.<sup>9</sup> In addition, the surface tension of steel is diminished by the absorption of hydrogen. This may also occur in polyethylene and, as a consequence of the Griffith criterion,<sup>10</sup> reduce the energy required for the formation of new surfaces (rupture). We hope to pursue these hypotheses in future publications.

We wish to acknowledge the assistance and cooperation given us by C. M. Crofoot with sample preparation and testing, W. Golba with photography, R. L. Miller for x-ray analysis, and Q. A. Trementozzi for his strong support of the program.

## APPENDIX

### Disposition of the Hydrocarbon Component in Mixture with Linear Polyethylene

A sample of fraction 2 prepared by coprecipitation containing 20 wt.-% of  $C_{36}H_{74}$  was compression-molded and allowed to cool slowly in the press. Examination of the resultant film by x-ray diffraction gave no evidence of a  $C_{36}H_{74}$  crystal phase. When a similar mixture was prepared by dry blending and cold pressing of coarse powder, a distinct x-ray diffraction pattern indicative of  $C_{36}H_{74}$  was obtained. When this cold-pressed slab was repeatedly heated at 100°C. for 10 min. intervals, the  $C_{36}H_{74}$  x-ray pattern became less and less distinct and finally vanished, indicating dispersion of the  $C_{36}H_{74}$  throughout the polyethylene. Volume measurements were then carried out on a 20%  $C_{36}H_{74}$  mixture (prepared by coprecipitation) to determine whether cocrystallization had occurred.

Dilatometers were calibrated and filled in accordance with techniques developed by Kovacs<sup>11</sup> and modified by Newman.<sup>12</sup> The data obtained on the mixture and on a sample of pure fraction 2 along with the liquid and crystal lines given by Swan<sup>13</sup> are shown in Figure 11. Inspection of the specific volume-temperature relationship of the mixture shows a volume change at 76°C. indicating melting of  $C_{36}H_{74}$  ( $T_m = 75.5^\circ\text{C}.$ ). This interpretation is however, in apparent contradiction to x-ray evidence, indicating the absence of a  $C_{36}H_{74}$  crystal phase.

If the following assumptions are made, it is possible to compute the weight fraction of the  $C_{36}H_{74}$  hydrocarbon in the crystalline state as a function of temperature: (1) volume of the various crystalline and amor-

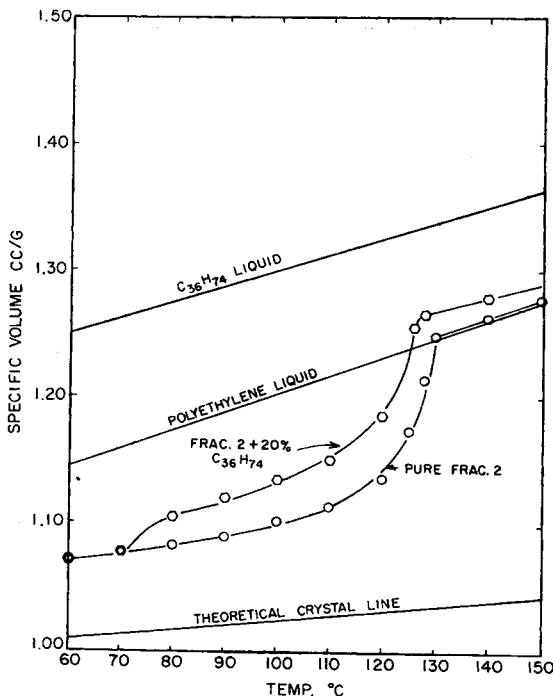


Fig. 11. Specific volume-temperature data for Marlex 50 alone and containing 20%  $C_{36}H_{74}$

phous phases are additive and independent of the degree of crystallinity; (2) there is no interaction of any kind between any of the phases.

The equation for the specific volume,  $\bar{V}$  of the mixture which follows from these assumptions is:

$$V = X_{pc}(\bar{V}_c - \bar{V}_{pa}) + X_{hc}(\bar{V}_c - \bar{V}_{ha}) + X_p(\bar{V}_{pa} - \bar{V}_{ha}) + \bar{V}_{ha}$$

where  $\bar{V}$  = specific volume of mixture;  $X_{pc}$  = weight fraction of mixture which is polyethylene in crystal form (obtained by multiplying the weight fraction of polyethylene in the mixture by the crystallinity of pure, unmixed polyethylene at that temperature);  $\bar{V}_c$  = theoretical crystal specific volume of both polyethylene and  $C_{36}H_{74}$ , which are very nearly the same;  $\bar{V}_{pa}$  = specific volume of amorphous polyethylene;  $X_{hc}$  = weight fraction of the mixture which is  $C_{36}H_{74}$  in crystalline form;  $\bar{V}_{ha}$  = specific volume of amorphous  $C_{36}H_{74}$ ;  $X_p$  = weight fraction of the mixture which is polyethylene.

Using this equation,  $X_{pc}$  and  $X_{hc}$  were computed for a range of temperatures as shown in Figure 12. The  $X_{hc}$  relationship indicates that a  $C_{36}H_{74}$  crystal phase exists far above its own melting point. Obviously, phase interaction must have occurred. Alternate explanations of the data are possible: (a)  $C_{36}H_{74}$  crystallites are finely distributed throughout the polyethylene amorphous phase so as to be undetectable by x-ray and act

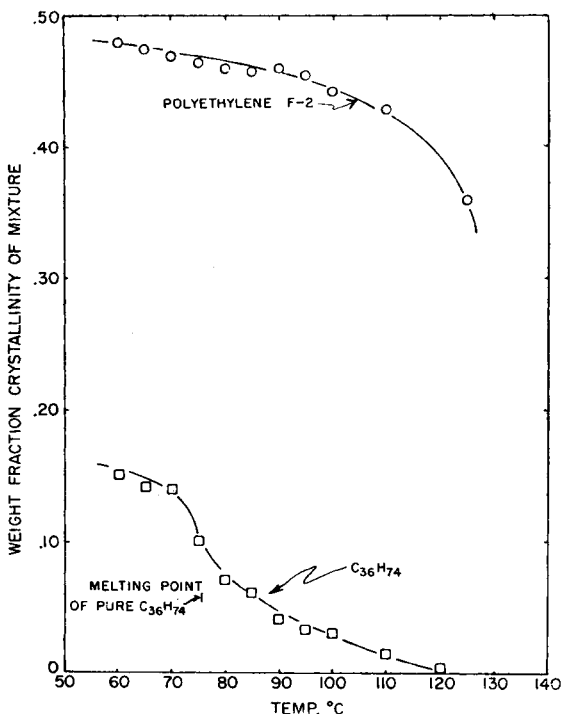


Fig. 12. Calculated weight fraction crystallinity for components of the Marlex 50- $C_{36}H_{74}$  mixture.

as a plasticizer above  $76^{\circ}C$ . or (b) there is cocrystallization with polyethylene. Under slow cooling conditions, the former explanation seems more reasonable; cocrystallization, if it occurs at all, takes place only to a small extent.

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### Synopsis

By means of a constant stress test, the environmental stress-cracking behavior of linear polyethylene has been studied on a macro and micro scale in an effort to determine

the mechanism of the process. Upon the application of stress, linear polyethylene develops a network of very fine, elliptical fissures, the edges of which are connected by cold-drawn material. In the absence of an active environment, these fissures slowly grow and interconnect, resulting ultimately in the formation of a "neck." When exposed to an active environment, however, the cold-drawn material ruptures as it is formed at the tips of the fissures. Unsupported, these fissures grow rapidly and interconnect resulting in sample failure. Fissures form both around and through the centers of spherulites with less cold drawing occurring at the interspherulite boundaries. Macroscopic studies confirmed the observation that active environments attack stressed polyethylene specifically at microzones of cold drawing. The effect of low molecular weight hydrocarbon species on the stress-crack resistance of linear polyethylene was evaluated. The role of flaws in the process is also discussed. Attempts have been made to establish a criterion of environmental activity. All of the active stress-cracking agents studied were found to reach similar levels of absorption in polyethylene; however, the specific chemical nature of the environment and not merely its level of absorption determines its ability to cause stress cracking.

### Résumé

En utilisant un test à tension constante on a étudié à l'échelle macro et micro le comportement de l'entourage sur la rupture par tension du polyéthylène linéaire, ceci en vue de déterminer le mécanisme du processus. Sous l'application de la tension, le polyéthylène linéaire développe un réseau de très petites fissures de forme elliptique, dont les bords sont connectés par du matériel étiré à froid. En absence d'un entourage actif, ces fissures croissent lentement et s'interconnectent ce qui conduit finalement à la formation d'un "col." Cependant exposé à un entourage actif le matériel étiré à froid se rompt par suite de la formation aux extrémités des fissures. Non supportées, ces fissures croissent rapidement et interconnectent conduisant à une cassure de l'échantillon. Des fissures se forment à la fois autour et au travers des centres des sphérulites lorsqu'on effectue l'étirement, moins à froid, aux limites des sphérulites. Des études macroscopiques ont confirmé l'observation que des entourages actifs attaquent le polyéthylène sous tension spécifiquement dans des microzones d'étirement à froid. On a évalué l'effet des espèces hydrocarbonées de bas poids moléculaire par tension du polyéthylène linéaire. Le rôle des défauts dans le processus est aussi discuté. On a essayé d'établir un critère d'activité d'entourage. On a trouvé que tous les agents actifs de rupture par tension étudiés atteignent des niveaux similaires d'absorption dans le polyéthylène; cependant, la nature chimique spécifique de l'entourage, et non pas simplement son niveau d'absorption, déterminent son aptitude à causer la rupture par tension.

### Zusammenfassung

Mit einem Test bei konstanter Spannung wurde die milieubedingte Spannungsrissebildung bei linearem Polyäthylen im Makro- und Mikromasstab zur Ermittlung des Mechanismus des Prozesses untersucht. Bei Einwirkung einer Spannung entwickelt lineares Polyäthylen ein Netzwerk von sehr feinen, ellipsenförmigen Spalten, deren Kanten durch kalt verformtes Material verbunden werden. Bei Abwesenheit eines aktiven Milieus wachsen diese Spalten langsam und vereinigen sich, was schliesslich zur "Hals"-bildung führt. Bei Einwirkung eines aktiven Milieus hingegen reiss das kalt verformte Material unmittelbar nach seiner Bildung an den Spitzen der Spalten. Ohne diesen Halt wachsen die Spalten rasch und vereinigen sich, was zum Bruch der Probe führt. Spalten bilden sich sowohl um die Sphärolithe als auch durch die Sphärolithzentren, wobei an den Sphärolithgrenzflächen geringe Kaltverformung stattfindet. Makroskopische Untersuchungen bestätigen die Beobachtung, dass ein aktives Milieu spannungsbeanspruchtes Polyäthylen spezifisch an Mikrozononen der kalten Verformung angreift. Der Einfluss niedermolekularer Kohlenwasserstoffe auf die Spannungsrissebeständigkeit von linearem Polyäthylen wurde bestimmt. Die Rolle von Fehl-



stellen bei dem Vorgang wird ebenfalls diskutiert. Es wurde versucht ein Kriterium für die Aktivität des Milieus aufzustellen. Alle untersuchten, bei der Spannungsrissbildung aktiven Substanzen zeigten in Polyäthylen ähnliche Absorptionsverhältnisse. Die Fähigkeit zur Spannungsrissbildung hängt jedoch nicht nur vom Ausmass der Absorption, sondern auch von der spezifischen chemischen Natur des Milieus ab.

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